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EASY-CARE FINISHING OF SILK

By

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ABSTRACT.

Keywords: silk, easy-care, polycarboxylic acid, zero-formaldehyde, finishing, cross-linking, machine-washable, silicone, softener, swelling agent.

A zero-formaldehyde, easy-care finish for silk fabric has been developed using a polycarboxylic acid (PCA) finishing system. This thesis confirms that treatment of silk fabric with selected PCA finishing systems improves the stability of silk fabric. The treated fabric had improved stability to heat, reduced swelling in solvents, and improved elastic recovery in the dry and wet states.

A number of interesting mechanistic possibilities are proposed for improving the easy-care performance of silk fabrics with a PCA finishing system. It is postulated that the improvement in elastic and stability properties of the treated silk fabrics could be as a consequence of new fibre inter-chain cross-links and/or a new intra-fibre PCA polymer network being formed within the silk fibres. Three different types of possible bonds between the PCA and silk fibroin were proposed :

- Ester links formed via acid and/or base catalysis with hydroxyl containing amino acids, serine, threonine and tyrosine, in silk fibroin.
- Amide links may also be formed between the basic amino acids, arginine, lysine and histidine, in silk fibroin and acid anhydrides formed during curing.
- Hydrogen bonds formed with acid, basic and hydroxy side groups and with the silk fibroin backbone.

This thesis extends previous research with respect to PCA finishing. It proposes the use of a new analytical method to pre-determine the effectiveness of an acid/catalyst system as an easy-care finish. It recommends the use of combination acids to compete with 1,2,3,4-butanetetracarboxylic acid and proposes the use of monosodium citrate as an alternative catalyst to sodium hypophosphite when cured at 165°C.

Good easy-care performance was achieved with silk fabrics treated with selective PCA/catalyst finish in the presence of a swelling agent, such as formic acid or acrylic acid, followed by after-treatment with a silicone softener. The finish produced a super soft, minimum iron fabric with enhanced resistance to fabric abrasion. The treated fabric was machine-washable.

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LIST OF ABBREVIATIONS

AA	Acrylic acid
PAA	Polyacrylic acid
ATR	Attenuated total internal reflectance
BCME	bis(chloromethyl)ether
BTCA	1,2,3,4-Butane tetracarboxylic acid
C	Calvin unit of temperature
CA	Citric acid
CIE	CIE illuminant D65
CL	Ceranine L (Clariant)
-COOH	Carboxylic acid group
Cp	Chymotryptic precipitate
CPTA	1,2,3,4-cyclopentanetetracarboxylic acid
CRA	Crease Recovery Angle.
Cs	Soluble Cs fraction of chymotryptic precipitate
CSI	The CSI Wrinkle Rating System
CY	Cyanamide
DCRA	Dry Crease Recovery Angle
DMA	poly(N(n-butoxymethyl)methacrylamide)
DMDHEU	1,3-dimethylol-4,5-dihydroxy ethylene urea
DMeDHEU	1,3-dimethyl-4,5-dihydroxy ethylene urea
DMEU	1,3-dimethylol ethylene urea
DP	Durable press
DSC	Disodium citrate
DSC	Differential Scanning Calorimetry
DSM	Disodium maleate dihydrate
DSP	Disodium phosphate
DST	Disodium tartrate
EU	European Union
EDGE	Ethylene glycol diglycidyl ether
ETMA	Ethoxyethylmethacrylate
FA	Formic acid
FDNB	1-fluoro-2,4,-dinitobenzene

FEW	Ultratex FEW (Ciba)
FFDNB	1,3-difluoro-4,6-dinitrobenzene
FT-IR	Fourier transform Infra-red
GA	Glutaric acid
HCl	Hydrochloric Acid.
HEMA	2-hydroxy-ethyl methacrylate
IA	Itaconic acid
KBr	potassium bromide
KOH	Potassium hydroxide
LiCl	Lithium chloride
MA	Maleic acid
MAA	Methacrylamide
MAN	Methacrylonitrile
MEL	Permafresh Mel (Warwick)
MF	Melamine formaldehyde.
MgCl ₂	Magnesium chloride hexahydrate
MLA	DL-Malic acid
MMA	Methyl methacrylate
MSC	Monosodium citrate
MSP	Monosodium phosphate
MSM	Monosodium maleate
MST	Monosodium tartrate
NaI	Sodium iodide
NI	Sandozin NI (Clariant)
Newton	Unit of force
OH	Hydroxyl group
PA	Phthalic acid
PBC	pad-batch-cure
PBW	pad-batch-wash-off
PCA	Polycarboxylic acid
PDC	pad-dry-cure
PDLC	pad-dry-(leave 24h)-cure
PEG	Polyethylene glycol
PMA	Pyromellitic acid
RCOO ⁻	Carboxylate anion

RCOOR'	General formula of Esters
RCOY	Acyl derivative
RH	Relative humidity
SA	Succinic acid
SHP	Sodium hypophosphite monohydrate
SW	Ultratex SW (Ciba)
TCA	Tricarballic Acid
TEA	Triethanolamine
Tg	Glass Transition Temperature
TG	Thermogravimetric
TGA	Thermogravimetric analysis
TMM	Trimethylol melamine
TPA	Terephthalic acid
TSC	Trisodium citrate
TSP	Trisodium phosphate
UHF	Ultra High Frequency
UV	Ultra Violet
VSI	Video Shrinkage Inspector
Wa	Bone dry weight of finished sample
Wb	Bone dry weight of the sample prior to finishing
WCRA	Wet Crease Recovery Angle
WF	Weighting Factor
WR	Wrinkle recovery
YI	ASTM Yellowness Index
ZnCl ₂	Zinc chloride

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1. INTRODUCTION.

The aim of this thesis was to research chemical finishes for silk fabrics that would provide optimum easy-care performance while maintaining the luxurious handle and aesthetics that contribute to the characteristics associated with the fibre. The term 'easy-care' describes a garment that does not crease easily while being worn and one in which any creases inserted during washing can be easily removed by ironing (1).

1.1 THE STRUCTURE AND PROPERTIES OF SILK.

This thesis begins with a summary of the structure and properties of silk. It was thought important to update any previous literature studies and to review the structure and properties of silk from a chemical viewpoint that would form a useful background for any textile technologist researching silk.

1.1.1 Introduction.

1.1.1.1 The Importance of Silk as a Textile Fibre.

Silk, a natural protein, is a highly valued textile fibre, and is the only natural continuous filament used in the manufacture of textile fabrics. Silk filaments, reeled from the cocoon of the silkworm larvae, are fine, strong and durable. The fabrics woven from silk yarns are known for their qualities of strength, elasticity, drape, handle, lustre and absorbency (2).

Historical evidence from an archaeological find in Chekiang province in south-eastern China dating back nearly 5000 years shows that the Chinese were the first to develop silk textiles (3). Silk production was a closely guarded secret for nearly 3000 years, during which time the Chinese developed a highly lucrative trade in silk fabrics. Gradually the knowledge spread to Japan, America, India, Persia and Europe.

Attempts to imitate the structure of silk filaments led to the introduction of the first synthetic fibres. Over the years these have replaced many traditional uses for silk. Silk fabrics are more comfortable to wear than synthetics; they are moisture vapour-permeable and feel cool in summer and retain heat in winter (4). However, the easy-care properties of silk fabrics do not compare favourably with those of synthetic fabrics. Silk fabrics suffer from poor recovery from creasing in the wet state, low resistance to

abrasion, and poor resistance to photoyellowing in sunlight (5). These inferior textile properties need to be modified if silk consumption is to be expanded.

Silk represents the lowest fraction of the world's natural fibre production, approximately 0.2%, generating a multi-billion dollar turnover (6). World trade in silk products has experienced dramatic changes in size, structure, production location, and markets over the past decade. From 1988-1993 raw silk production grew by 60% to over 100,000 tons in 1994 (6).

There has been a significant geographical shift in the sources and processing of raw silk (6). Sericulture (the cultivation of silkworms for the production of cocoons from which silk is unwound to produce a textile thread) is a labour intensive industry that requires a great mass of land for mulberry cultivation and thus is best suited to countries where labour is cheap (3). China has now replaced Japan as the largest source of raw silk. Between 1988-1994 Chinese output of raw silk grew by almost 16% per annum; in contrast Japanese sericulture declined. Indian silk production has doubled since 1985 making India the second largest silk producer. The Indian silk industry currently caters mainly for its domestic market but it is likely to enter the export market in the future (6). Among the smaller suppliers of raw silk are Brazil, and Vietnam.

The most significant change in the last decade has been in the composition of Chinese exports to Western markets (7). China has shifted production downstream and now exports large quantities of finished silk goods at comparatively low prices generating for itself increased foreign exchange earnings. Previously trade in made-up silk goods had been dominated by high value, low volume haute couture manufactured by European producers (8). China dictates the price and quality of its silk products. Although China has invested heavily in downstream silk processing, the country has failed to invest sufficiently in research into breeding and rearing to improve the productivity and quality of its raw silk production, and has failed to reach the levels achieved by Japan (6). In 1994 both the USA and European Union (EU) imposed quota restrictions on certain finished silk goods from China partly as a strategy to bring the Chinese into discussions on the issues of silk trading policy, pricing and quality standards (6).

Chinese finished goods have created a new, lower price range for silk garments and

have introduced more consumers to wearing silk products than before (6). It is possible that two distinct markets for silk are developing: a market for relatively inexpensive silk goods and a market for high quality expensive silk products. Silk has become an acceptable fabric for the middle fashion market due to an increase in consumer interest for natural fabrics and the sandwashing process, see section 1.1.7.3.3, which introduced machine washable silk. Although the so-called “sandwashed” silk phase has passed, it is likely that a proportion of these new consumers will continue to buy and wear silk.

If demand for silk in the middle market is to be maintained new ideas and techniques are needed to make it competitive with the technically advanced man-made fibre products. This requires silk products of consistent quality with good easy-care properties having acceptable dimensional stability at a reasonable price.

1.1.1.2 Sources of silk.

The collective term ‘silk’ is applied to the protein-containing secretions from more than 30,000 known species of spider and by most of the 113,000 species of the insect order lepidoptera from the phylum arthropoda (2, 9). Silk filaments used in the textile industry are extruded by the domesticated moth *bombyx mori*, the wild Chinese tussah moth, *antheraea pernyi*, and the Indian tussah moth, *antheraea mylitta* (9).

Silk from the *bombyx mori*, also known as mulberry silk, dominates the world-wide silk cocoon market, occupying 80-85% in total. This silk has a long history as a textile fibre. Fabric woven from mulberry silk was used in the practical work associated with this thesis and is therefore the focus of the following discussion.

As a result of controlled rearing and breeding *bombyx mori* silkworms are completely domesticated and the moths depend entirely on humans for feeding and protection (9). In this respect they are unique amongst insects.

Mulberry silkworms can be divided into three groups:

- **Univoltine** - (one generation per year); usually found in Europe, due to the cold climate the eggs lie dormant in the winter.
- **Bivoltine** - (two generations per year) this is the most common variety and is normally found in China, Japan, and Korea.

- **Polyvoltine** - (up to eight generations per year) which are bred in the tropics (3, 10).

	Trait	Bivoltine Yield/Quality	Polyvoltine Yield/Quality
Silk	Cocoon shell	High	Low
	Fibre length	High	Low
	Reelability	High	Low
	Neatness	High	Low
	Lousiness	Low	High
Silkworm	Cocooning rate	Low	High
	Disease resistance	Low	High
	Heat tolerance	Low	High
	Life cycle	Long	Short

Table 1. 1. The differences between bivoltine and polyvoltine strains (3).

Breeding of genetically-improved silkworm strains, introduced by Toyama at the beginning of this century (3), have resulted in the production of hybrids. Varieties can differ in the number of generations they produce a year, larval growth rates, climate tolerance, disease resistance, silk yield and silk mechanical properties. From a geneticist's point of view, the bi- and polyvoltine stains, shown in Table 1. 1, represent a diversity of characteristics, which through crossbreeding and selection can produce new hybrids combining the best characteristics of both types. Goldsmith and Shi (3) are constructing a molecular linkage map that when completed will enable geneticists to engineer hybrids with predetermined combinations of beneficial characteristics.

1.1.1.3 Life cycle of the silkworm bombyx mori.

The life-cycle of the silkworm, Figure 1. 1, takes approximately 55-60 days to complete depending upon the rearing conditions and the type of eggs laid (2). The entire economy and profitability of sericulture are dependent on silkworm rearing and cocoon production. The silkworm eggs for rearing are carefully selected to help eliminate disease and subjected to cold storage until they are required for incubation. One gram of eggs contains 1500-2000 eggs, which take 10-12 days to hatch (11). Great care has to be taken in rearing silkworms because they are very susceptible to disease and sensitive to environmental conditions such as temperature and humidity (12).

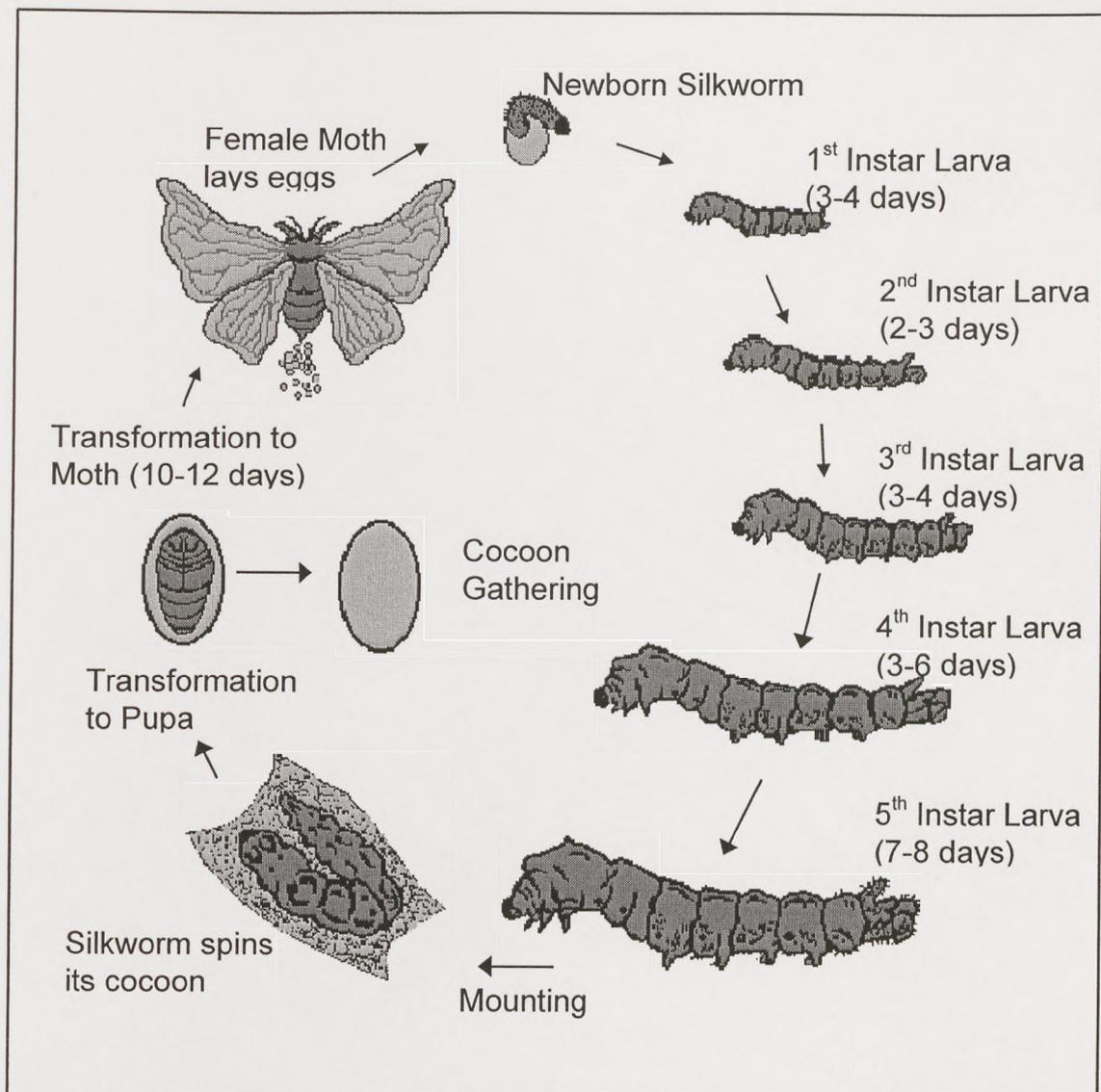


Figure 1.1 Life cycle of the silkworm *Bombyx mori*.

The domestic silkworm is fed on leaves from the white mulberry tree, it utilises approximately 65% of the amino acids from the leaves eaten to synthesise the silk proteins fibroin and sericin (13, 14). The silk filaments are composed of fibroin and coated with gum, sericin. The quality of the silk spun by the silkworm to make its cocoon depends on the quality of the mulberry leaf it eats. In contrast to silk proteins the mulberry leaf is rich in acidic amino acids that the silkworm transforms by biosynthesis into the amino acids that constitute the silk itself, see Table 1.3 (14). The larva feeds voraciously on chopped mulberry leaves for about 25-30 days, growing rapidly and changing its skin four times, every 3-6 days. These periods are known as instars.

The health of the silkworm is affected by the quality of leaf it eats, and its living conditions. It is important to keep high levels of general hygiene and to clean the

rearing bed prior to moulting. Environmental conditions affect the growth of silkworms. Under normal conditions the body weight of a silkworms increases 10,000 times from hatching to the spinning stage. Ideal conditions for instars 1-3, are 26-28°C and 90% relative humidity, and for instars 4-5, 25°C and 75% relative humidity. If the temperature is too high or too low the health of the larva may be affected.

On reaching maturity, the silkworm rests for 24 hours before seeking some support on which to spin its cocoon. The cocoon is gradually formed over a period of 3-6 days after which the larva undergoes metamorphosis before emerging as a moth 14 days later. The moth forces its way out of the cocoon by secreting an enzyme that softens the sericin (silk gum) through which it pushes a hole. The silk moth cannot fly and lives for only a few days, during which time female fertilisation takes place, resulting in 350-600 eggs. The life cycle then begins again.

Cocoons from which the silk filaments are reeled are collected undamaged, before the moth emerges. They are sorted, graded and the chrysalises destroyed either by steaming, hot air or boiling (2, 11, 15).

1.1.1.4 Fibre spinning.

The silk filament spun by the larva to make its cocoon consists of two proteins, fibroin and sericin. Two fibroin filaments, known as brins, are bound together by sericin gum to form a single thread or bave, see Figure 1. 2. This bave has an average diameter of 15-25 μ m and is 1-2 thousand metres in length (2, 16).

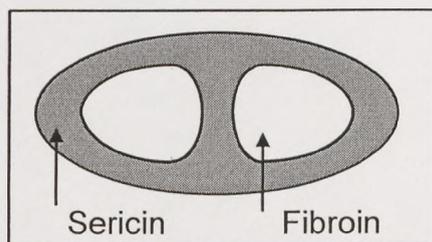


Figure 1. 2 Schematic diagram of the cross-sectional view of a raw silk filament (15).

The proteins, fibroin and sericin, are produced by the silk-producing glands, a pair of long tubes lying one on each side of the larva, see Figure 1. 3 (18). Each gland can be divided into three sections, posterior, middle and anterior divisions. The epithelial wall of the gland consists of large hexagonal cells where the silk proteins are synthesised.

Fibroin is synthesised in the posterior division, which is closed at one end and is narrow and very convoluted. The fibroin is stored as an aqueous gel in the massive reservoir of the middle division where the sericin is synthesised and accumulates as a separate layer around the fibroin. There are three types of sericin, namely sericin I, II, and III, which are synthesised in the anterior, middle and posterior parts of the middle gland respectively.

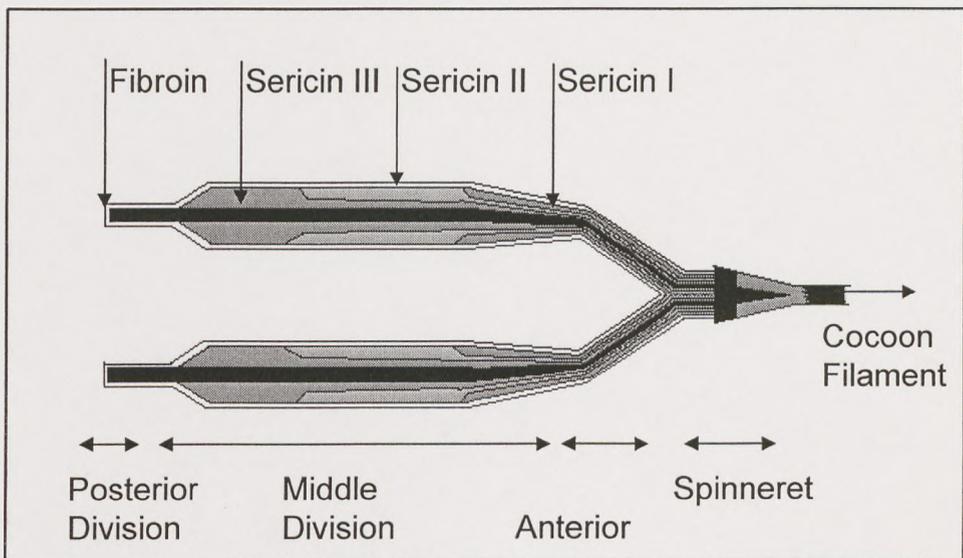


Figure 1. 3 Schematic Diagram of the Silk Glands of the Mature Larva (18).

When it is time for the silkworm to spin its cocoon, the proteins proceed forward without mixing into the anterior division; this becomes narrower and joins with the second gland to form a single duct leading into the spinneret. At the spinneret a layer of sericin surrounds two brins of fibroin.

Before spinning begins the fibroin is stored as an aqueous gel which on moving towards the spinneret slowly unfolds and realigns itself so that its molecular chains are orientated in the direction of flow (18). The aqueous gel assumes a liquid-crystal character prior to spinning, which is controlled by an increase in cation concentration, and a decrease in pH and viscosity. The larva extrudes a viscous-like fluid through its spinneret, which is situated above its mouth. The water content of the aqueous gel at the spinneret is 70%; this is lost from the spun filament on contact with the air causing many pores to be formed within the fibre. On extrusion into the air the water-soluble fibroin is converted, at room temperature, into an insoluble high-performance fibre, by

physical rather than chemical means. The fibroin is transformed from the mainly random coil silk I format to the well-ordered β -conformation of the spun silk filament, silk II (16).

The silkworm spins the silk at a rate of 360-480mm/min. It spins by the joint forces of continuous ejection of the aqueous silk from the silk gland and by drawing, the silkworm stretches back its head in a figure-of-8 motion, orientating the long fibrous chains in the direction of the fibre axis. The resultant fibre is super-drawn. It takes the silkworm 48 hours of continuous spinning to spin 1200-1500m of silk filament to make its cocoon.

The behaviour of silk as a textile fibre is affected by the nature of the individual chemical units that compose the long-chain molecules as well as by the degree of alignment or order of the molecules. The silkworm controls the molecular orientation of the fibre very accurately during spinning. The fibrous chains are very closely packed and have an ordered molecular structure obtained by the realignment and super-drawing of the silk molecules by the silkworm during spinning. The structure created here at the macromolecular level is directly related to the properties of the fibre.

1.1.2 The Structure Of Silk.

1.1.2.1 Morphological structure of silk fibroin.

Figure 1. 4 is a schematic diagram of the structure of a raw silk filament (15). Two fibroin filaments are surrounded by sericin gum. The fibroin chains are made up of amino acids arranged in crystalline and amorphous regions contained within the microfibrils. These are packed together in bundles, with several bundles forming a strand of fibroin. Chains with more than 50 amino acids are called proteins. Silk is a structural protein; the fibroin has a crystalline structure, whereas the gum, or sericin, is amorphous and has a different amino acid composition.

Sericin gum surrounding the silk fibroin makes the brins hard and stiff, hence the sericin is removed by a process known as degumming. Degummed silk filaments produce silk fabric that is soft, smooth and highly lustrous. Degummed silk was used in the practical work associated with this thesis and thus only the structure of fibroin is discussed.

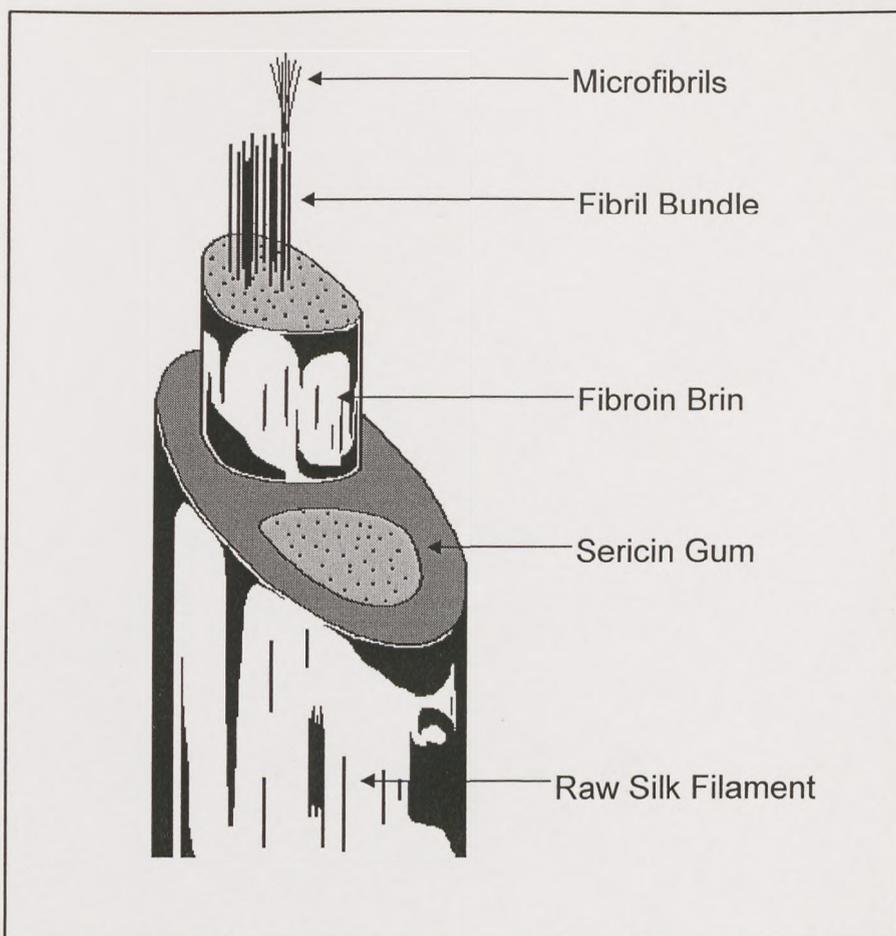


Figure 1. 4. Schematic diagram of the structure of raw silk (15).

1.1.2.2 The structure of silk fibroin.

A protein is so large in comparison with most organic compounds that when discussing its structure chemists separate a protein into four different levels (19):

1. **Primary structure**, the sequence of amino acid residues.
2. **Secondary structure**, the orientation of the peptide backbone into a regular pattern.
3. **Tertiary structure**, the overall three-dimensional shape of the protein molecule.
4. **Quaternary structure**, the way in which several protein molecules come together to yield large aggregate structures.

1.1.2.2.1 The primary structure of silk fibroin.

Proteins are made up of α -amino acids; i.e., the amino group is a substituent on the carbon atom next to the carbonyl group. All, except proline are primary amines, RNH_2 , and differ only in the nature of their side chain substituents. Proline is a secondary amine with both its nitrogen and α -carbon atoms being part of a pyrrolidine ring. The

α -carbon atom is asymmetrical and thus, with the exception of glycine, $\text{H}_2\text{NCH}_2\text{COOH}$, two different enantiomeric forms of each amino acid are possible. Natural proteins all have stereochemistry similar to that of L-sugars, and are thus often referred to as L-amino acids.

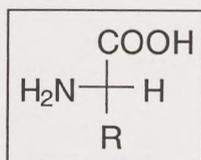


Figure 1.5 Fischer projection of a naturally occurring α -amino acid (20).

Fibroin consists of about 20 different amino acid residues of which glycine, alanine and serine make up 80-85% of the total, see Table 1. 2. These amino acids are linked together by amide bonds in long polypeptide chains.

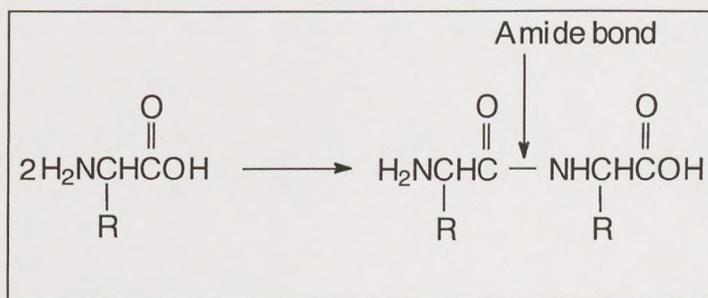


Figure 1.6 A dipeptide (one amide bond) (20).

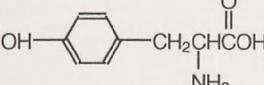
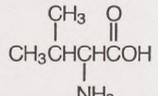
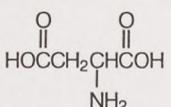
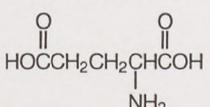
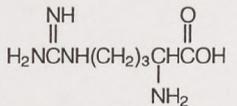
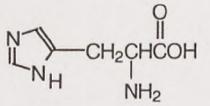
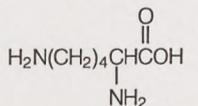
The total number of both basic and acidic side chains in silk fibroin is relatively small, subsequently the quantity of acid or alkali that the fibre can absorb is also small (Sandoz 37). However, the hydroxyl-containing amino acids, serine, threonine, and tyrosine supply the majority of the polar side groups in silk fibroin (29).

The amino acid sequence of silk fibroin has been studied after treatment in aqueous cupriethylenediamine with the enzyme chymotrypsin at pH 7.8, 40°C for 24h (21). Chymotrypsin only catalyses the hydrolysis of the carbonyl side chains of tyrosine, phenylalanine and tryptophan with the amino acid next in the polypeptide chain. The chymotryptic precipitate, the Cp fraction, remaining after digestion of the fibroin, is thought to correspond to the crystalline regions within the fibre. X-ray diffraction patterns of the Cp fraction compared with those of fibroin display sharper arcs indicative of a more crystalline structure (34).

Neutral amino acids	RMM	% in Fibroin	Structure	Isoelectric Point	pKa α -COOH	pKa α -NH ₃ ⁺
Alanine (Ala)	89	28.78		6.0	2.3	9.8
Asparagine (Asn)	132	-		5.4	2.0	8.8
Cysteine (Cys)	121	-		5.0	1.8	10.2
Glutamine (Gln)	146	-		5.7	2.2	9.1
Glycine (Gly)	75	43.74		6.0	2.3	9.8
Isoleucine (Ile)	131	0.65		6.0	2.3	9.7
Leucine (Leu)	131	0.52		6.0	2.3	9.7
Methionine (Met)	149	-		5.7	2.3	9.2
Phenylalanine (Phe)	165	0.62		5.5	2.6	9.2
Proline (Pro)	115	0.35		6.3	2.0	10.6
Serine (Ser)	105	11.88		5.7	2.2	9.2
Threonine (Thr)	119	0.89		5.6	2.1	9.1
Tryptophan (Trp)	204	0.33		5.9	2.4	9.4

RMM = Relative Molecular Mass.

Table 1.2 The twenty common amino acids found in proteins (continued on page 12)

Neutral amino acids	RMM	% in Fibroin	Structure	Isoelectric Point	pKa α -COOH	pKa α -NH ₃ ⁺
Tyrosine (Tyr)	181	5.07		5.7	2.2	9.1
Valine (Val)	117	2.16		6.0	2.3	9.7
Acidic amino acids						
Aspartic acid (Asp)	133	1.28		3.0	2.1	9.8
Glutamic acid (Glu)	147	1.00		3.2	2.1	9.5
Basic amino acids						
Arginine (Arg)	174	1.83		10.8	2.0	9.0
Histidine (His)	155	0.53		7.6	1.8	9.1
Lysine (Lys)	146	0.63		9.7	2.2	8.9

RMM = Relative Molecular Mass.

Table 1.2 The twenty common amino acids found in proteins (continued from page 11) (20).

Edman serial degradation has been used to determine the sequence of amino acids within this Cp fraction (34). It involves treating the precipitate with phenyl isocyanate, which attaches a marker to the N-terminal amino acid, followed by mild acid hydrolysis to cleave the end terminal residue from the chain. Unfortunately complete sequencing of large peptides is not possible because build-up of unwanted by-products limits the number of useful cycles. The Cp fraction is therefore broken down by partial hydrolysis into smaller fragments either chemically with aqueous acid or enzymatically prior to Edman degradation. These individual fragments have been pieced together to suggest the following sequence: -

Gly-Ala-Gly-Ala-Gly-Ser-Gly-Ala-Ala-Gly-(Ser-Gly-(Ala-Gly)_n)₈-Tyr

(where n has a mean value of 2) (21)

This hexapeptide first identified by Lucas et al. (2, 22) is believed to be the principal repeating sequence of the more crystalline portion of fibroin. It corresponds to approximately 60% of the total amino acid residues in silk fibroin.

The arrangement of the soluble Cs fraction of chymotryptic hydrolysis is less certain. It has been suggested that it is composed of octa- and tetra-peptides ending with tyrosine and phenylalanine, in which the Gly-x (x being Ala or Ser) alternating sequence is preserved (13).

By treating the fibroin with trypsin, an enzyme that catalyses the hydrolysis of the carbonyl side chains of the basic amino acids arginine and lysine, a new precipitate which constitutes 88% of the protein was isolated. This has then been treated with chymotrypsin and a new precipitate, 62%, and a soluble fraction, 25%, has been separated. This soluble fraction was found to contain the following sequence (23):

Gly-Ala-Gly-Ala-Gly-(Cys)_{1/2}-Asx-Ser-Ala-Val-(Cys)_{1/2}-Pro-Leu

This peptide was also isolated by Robson et al from fibroin in the glands of *Bombyx mori* silkworms fed on mulberry leaves coated with ³⁵S cysteine. It is expected to account for 75% of the cystine present. Earland and Robins (23) also managed to isolate a peptide containing cystine. Their octapeptide came from the chymotryptic digests of acid-washed silk, to which they assigned the following sequence that accounts for approximately a third of the total cystine present in fibroin.

Arg-Ala-Leu-Pro-Cys-Asn-Val-Cys

Bombyx mori silk fibroin contains approximately 0.23% cystine in total. The structural significance of this amino acid has yet to be uncovered. No evidence has been produced for the existence of interchain disulphide bridges. Hydrogen bonds, salt links and hydrophobic bonds stabilise the tertiary and quaternary structures of fibroin almost exclusively.

Analysis of studies of the amino acid sequence of silk fibroin led Shaw (2, 24) to postulate a three-phase structure for silk fibroin.

Phase 1, the Cp fraction, constituting approximately 60% of the protein.

Phase 2, approximately 30%, made up of octa- and tetrapeptides of glycine, alanine, valine, and tyrosine.

Phase 3, the truly amorphous part of fibroin, composed of the remaining amino acid residues, including those with bulkier side groups.

The combination of these three phases is uncertain; Shaw favours 1, 2, and 3 in series.

1.1.2.2.2 The secondary structure of silk fibroin.

The amino acids in silk fibroin are held together by amide bonds. This bond is stabilized by delocalization of the nitrogen lone-pair electrons through orbital overlap with the carbonyl group. This overlap restricts rotation about the amide C-N bond bestowing a certain amount of double-bond character to it.

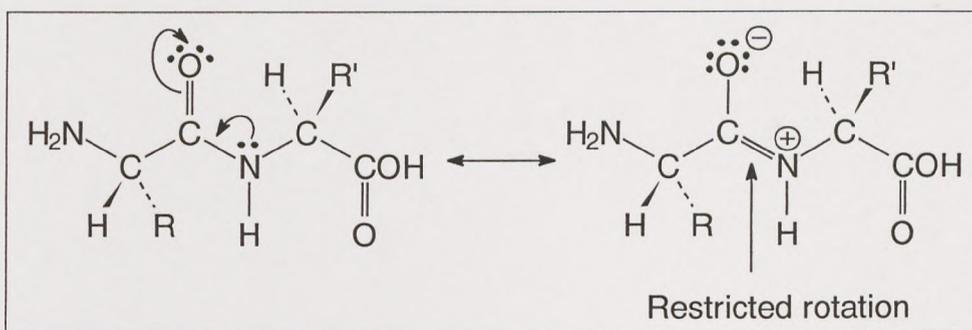


Figure 1.7 The two contributing forms to the amide bond resonance effect (20).

The prevalence of so many small amino acid residues, glycine, alanine, and serine, permits the regular arrangement of the protein chains in the crystalline regions of the fibre (2). The consequence of so many amino acids with hydrocarbon side-chains is that hydrogen bonding is the predominant force holding the fibroin chains together. There is no evidence to support the concept of covalent bonding of the peptide chains such as inter-chain cystine cross-links analogous to the structure of wool.

Using X-ray diffraction methods it has been shown that certain sections of amino acids in fibroin are arranged in the anti-parallel β -pleated sheet form, see Figure 1.8 (25, 26). This β -pleated sheet is analogous with the more ordered, or crystalline, regions of the fibre (27). Silk also possesses local regions of disorder associated with its more random

Fossey and Kaplan (26, 29) proposed a silk I model in which the alanyl residues adopt a right handed sheet-like conformation and the glycylyl residues a left handed sheet-like conformation, with an orthorhombic unit cell where $a = 0.894\text{nm}$, $b = 0.646\text{nm}$, and $c = 1.126\text{nm}$. This may represent the structure of silk in the nematic liquid crystal phase prior to fibre spinning. They pointed out that the transformation to form the anti-polar silk II form does not involve the breaking of any hydrogen bonds or chain rotations. The lower energy barrier required to form the anti-polar, as opposed to the polar, silk II model accounts for the validity of the proposal by Takahashi despite the fact that the polar form has a lower conformational energy.

1.1.2.2.4 The quaternary structure of silk fibroin.

Characterisation of the fundamental structure of silk fibroin has not been elucidated. The understood general picture is of a filament of silk fibroin consisting of aggregates of β -pleated sheets, arranged parallel to the fibre axis. These are held together by lateral forces with freedom and space in disordered regions, in which the amino acids with larger, bulkier side-chains are found (23). In the crystalline regions close packing of the chains permits van der Waals forces to act co-operatively. Extra cohesion between the molecular chains is provided by hydrogen bonds and salt links. The molecular chains within silk fibroin have evolved so that good close packing and therefore maximum hydrogen bonding is attained (30). Covalent cross-links between chains provide strong links and increase stability, however, there is no evidence to support this type of bonding in native silk.

1.1.3 The Physical Properties Of Silk.

1.1.3.1 Composition of raw, bombyx-mori silk.

Substance	Percent
Fibroin	70-80%
Sericin	20-30%
Waxy matter	0.4-0.8%
Carbohydrates	1.2-1.6%
Inorganic matter	0.7%
Pigment	0.2%

Table 1.3 Composition of raw, bombyx-mori silk (31).

1.1.3.2 Shape and appearance of silk.

Raw cultivated silk is off-white/yellow in colour and 1-2 thousand metres in length, with a rounded, triangular cross-section, see Figure 1. 2. Fine filaments are bound together in pairs by silk gum. The diameter of a bave of silk is approximately 15-25 μm , the brins being approximately half the diameter. A typical fibroin brin consists of about 1000 macrofibrils, each of which is composed of a bundle of microfibrils. Sawaji (14A) suggested that the fibre glossiness is a result of these microfibrils being arranged parallel to one another, absorbing and reflecting polarized light in specified directions, similar to a bar antenna of a UHF television set. In the raw state the silk filament is matt, but on degumming the fine twisting filaments with few external markings become soft and lustrous and have a characteristic scroopy handle (10).

1.1.3.3 Density of silk fibres.

Raw silk has a density of 1.33g/cm³, except if weighted during finishing, see section 1.1.7.3.2, when the density can be greater than 1.60g/cm³ (2).

1.1.3.4 Regain.

Silk is very hygroscopic; it can absorb up to 30% moisture from the air without feeling damp (32). At 65% relative humidity silk has a regain of between 9.9 and 10.65%. Commercial regain is set at 11% (B.S. 4784:1973).

1.1.4 Chemical Properties Of silk.

The properties of proteins depend primarily on the summation of the properties of the reactive groups of their constituent amino acids combined with the properties associated with the size of the protein.

1.1.4.1 Reactions of amino acids.

It can be seen from Table 1. 2 that 20 common amino acids can be classified as either neutral, acidic or basic, depending on the nature of their side chains. Acidic amino acids, e.g. aspartic acid and glutamic acid, both have an extra carboxylic acid function, and the basic acids, lysine, arginine, and histidine, have basic amino groups in their side chains.

As their name implies amino acids are difunctional; they contain both a basic amino group and an acidic carboxyl group. The combination of both acidic and basic groups in the same molecule, causes an intermolecular acid-base reaction to occur, and amino acids exist primarily as a dipolar ion, or zwitterion, see Figure 1. 9 (20). Amino acid zwitterions act as internal salts and consequently have large dipole moments; they are soluble in water but not in hydrocarbons, and are crystalline substances with high melting points (33).

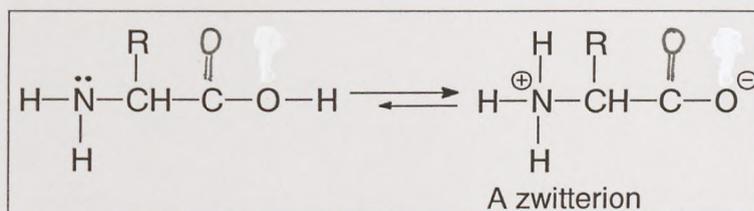


Figure 1. 9 Amino acid dipolar ion or zwitterion (20).

Amino acids are amphoteric, they can react either as acids or bases depending on the circumstances. A carboxylate anion, -COO^- , accepts a proton in acid solution to yield a cation, and an ammonium cation, RNH_3^+ , acts as the acidic site and donates a proton in base solution.

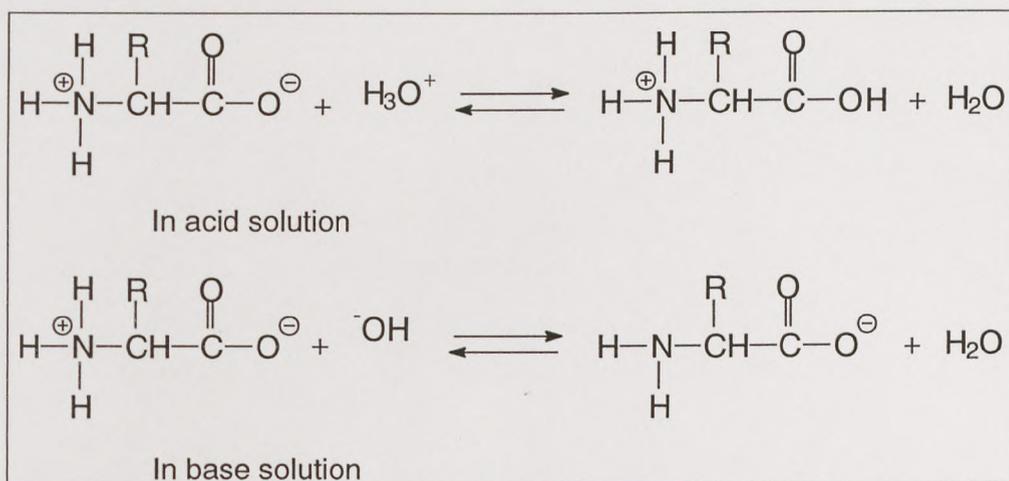


Figure 1. 10 Amino acid dipolar ion or zwitterion (20).

At low pH an amino acid is protonated and exists primarily as a cation, whereas at high pH it is deprotonated and exists primarily as an anion. There is a pH, known as the isoelectric point, at which the amino acid is exactly balanced between anionic and cationic forms, and exists as the dipolar zwitterion. The isoelectric point of an amino acid varies depending on its structure, and the values are listed in Table 1. 4 (20).

Neutral amino acids have isoelectric points in the pH range 5.0-6.5; these values are slightly acidic due to the fact that carboxyl groups are stronger acids in aqueous solution than amino groups are bases. Acidic amino acids have isoelectric points at lower pH values and thus suppress the dissociation of the extra carboxylic acid group, whereas, basic amino acids have isoelectric points at higher pH values and thus suppress protonation of the extra amino group.

Fibroin contains very few amino acids with either acidic or basic side chains and has an isoelectric point at around pH 5 (15). The main reactive side chains in silk fibroin are the hydroxyl-containing amino acids, serine, threonine and tyrosine. It has been reported (34) that 50% of the serine and threonine and 100% of the tyrosine residues exist in the accessible, amorphous regions of the fibre. Zahn and Wurz found that 79% of the lysine and 96-99% of the tyrosine residues reacted with the cross-linker 1-fluoro-2,4,-dinitrobenzene (33,35).

Table 1. 4 shows the amino acid residues with reactive side groups in silk fibroin and their percentage occurrence. The reactions of these substituent groups with external compounds are, as expected, all producing the normal reaction products (33).

- **Reactions of amino groups.** The two types of amino groups in silk fibroin; the α -amino groups of residues at the end of the peptide chains and the ϵ -amino groups of lysine side chains, undergo the typical reactions of amino groups.
- **Reactions of carboxylic acid groups.** Glutamic and Aspartic acid have an extra carboxylic acid group in their side chains that are capable of typical reactions of carboxylic acids. The extra carboxyl group contributes an acidic property to silk.
- **Reactions of hydroxyl groups.** The hydroxyl-containing amino acids; serine, threonine and tyrosine, are capable of forming esters or ethers. Serine and threonine contain aliphatic hydroxyl groups whereas the hydroxyl group in tyrosine is attached to a phenolic group. This phenolic hydroxyl group also imparts acidic properties to fibroin as the phenoxide anion is stabilised by delocalisation of the negative charge into the aromatic ring.
- **Reactions of other basic groups.** The imidazole ring of histidine and the guanidino group of arginine. The imidazole ring undergoes typical substitution reactions and the guanidino group, being highly basic, forms salts with acidic groups.

OH-containing amino acids	RMM	% in Fibroin	Structure	Isoelectric Point	pKa α -COOH	pKa α -NH ₃ ⁺
Serine (Ser)	105	11.88		5.7	2.2	9.2
Threonine (Thr)	119	0.89		5.6	2.1	9.1
Tyrosine (Tyr)	181	5.07		5.7	2.2	9.1
Acidic amino acids						
Aspartic acid (Asp)	133	1.28		3.0	2.1	9.8
Glutamic acid (Glu)	147	1.00		3.2	2.1	9.5
Basic amino acids						
Arginine (Arg)	174	1.83		10.8	2.0	9.0
Histidine (His)	155	0.53		7.6	1.8	9.1
Lysine (Lys)	146	0.63		9.7	2.2	8.9

RMM = Relative Molecular Mass.

Table 1. 4. Amino acids with reactive side groups in silk fibroin (20).

- **Reactions of benzenoid groups.** Reactions of the phenolic hydroxyl groups of tyrosine can either occur at the hydroxyl group or on the aromatic ring. The hydroxyl group strongly activates the aromatic ring toward electrophilic substitution reactions. This benzenoid group undergoes typical reactions of benzenoid compounds.
- **Reactions of the indole nucleus.** The indole group of tryptophan contains a reactive hydrogen which is believed to be involved in the condensation reaction of proteins with formaldehyde.

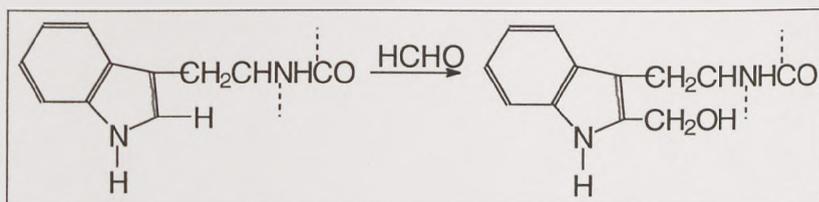


Figure 1. 11 Condensation Reaction of Tryptophan with Formaldehyde (33).

1.1.4.2 Reactivity with water.

Fibroin is practically insoluble in water. In boiling water or steam the fibroin polypeptide chains undergo degradation by hydrolysis.

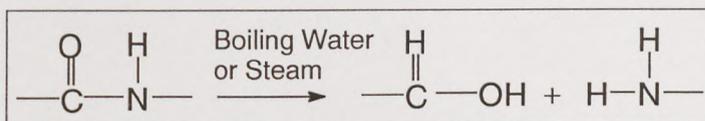


Figure 1. 12 Hydrolysis of Polypeptide Chains (23).

The extent of this hydrolysis is temperature-dependent but is thought to be relatively low at temperatures normally encountered during silk processing (2). The hydrolytic decomposition of fibroin results in fission of peptide bonds.

Hard water or dirty water both impair the lustre and handle of the silk fibre and must therefore be avoided (15).

1.1.4.3 Reactivity with acids.

Silk has a relatively high stability to acids, but concentrated acids and in particular hot mineral acids, attack the peptide bonds, leading to fibre damage (23). The degradation process, which leads to hydrolysis of the peptide links and subsequent loss in tensile strength and elasticity, is pH-dependent, the least degradation occurring between pH 4-8 (36, 37). An increase in temperature and liquor agitation increases degradation.

Dilute organic acids are used in silk finishing to produce a rustling effect known as scroop. At low concentrations, acetic, formic, tartaric and citric acids are used for this purpose in combination with oil emulsions with no harmful side effects (see section 1.1.7.3.5). However concentrated solutions of organic acids, or mineral acids, such as, sulphuric, nitric and hydrochloric acids, can cause fibre degradation and/or dissolution (2, 38).

1.1.4.4 Reactivity with alkalis.

Silk is more susceptible to hydrolysis in base solution than in acid solution. Dilute alkalis, especially at elevated temperatures, can degrade silk and impair its lustre. Alkalis degrade the chain ends of silk polypeptides and this degradation is determined by the pH of the solution and also by the alkali cation (23). The action of hot alkali causes the loss of one third of the residues of serine and threonine, liberating ammonia (2, 38). A 5% solution of sodium hydroxide at the boil dissolves silk completely (39). Silk should preferably not be treated in alkaline baths, and soap free from alkali is recommended for use in laundering silk fabrics (15).

1.1.4.5 Reactivity with proteolytic enzymes.

Proteolytic enzymes do not readily attack silk, probably because of the closely packed structure of the fibroins. The high degree of crystallinity prevents the large enzyme molecules from penetrating the silk fibre (2, 37, 38).

1.1.4.6 Reactivity with oxidising agents.

Fibroin is highly susceptible to oxidising agents so that considerable care is required especially in the bleaching of pigmented silks with hydrogen peroxide or peracids (see section 1.1.6.5.2). The reactions are very complex and degradation is considered to take place at the side chains of tyrosine, the amino-terminal residues of the main chain, and at the peptide bonds. The action of peracids causes more rapid scission of the peptide bonds and produces more acidic groups due to oxidation of the tyrosine side chains. Thus, hydrogen peroxide is generally the preferred bleaching agent (2, 37, 38).

1.1.4.7 Reactivity with reducing agents.

Fibroin is resistant to the main reducing agents (e.g. hydrosulphite (dithionite), sulphurous acids and its salts) normally used in textile applications, see section 1.1.6.5.1.

1.1.4.8 Reactivity with metal salts.

Silk has the ability to form a chemical bond with certain metal salts such as stannic chloride; this reaction has been used to weight silk in the past (see section 1.1.7.3.2.2) although synthetic weighting processes are now more common (15). Synthetic

weighting processes are more environmentally friendly treatments.

1.1.4.9 Effect of heat on silk.

Bombyx mori silk fibroin is thermally stable below 100°C (40). This can be attributed to the high degree of molecular orientation of silk fibroin. Silk yellowing begins to occur at 110°C after 15 min, thus ironing should be done quickly with an iron that is not too hot (41).

Nakamura et al. (41), using differential scanning calorimetry (DSC) curves, found silk to have an endothermic peak at 100°C which they attributed to the evaporation of water. Silk also exhibited an endothermic shift of the base line at 175°C, attributed to the glass transition temperature for silk fibroin, and a prominent endothermic peak at about 280°C due to the degradation of silk fibroin. Initial weight loss starts at about 250°C.

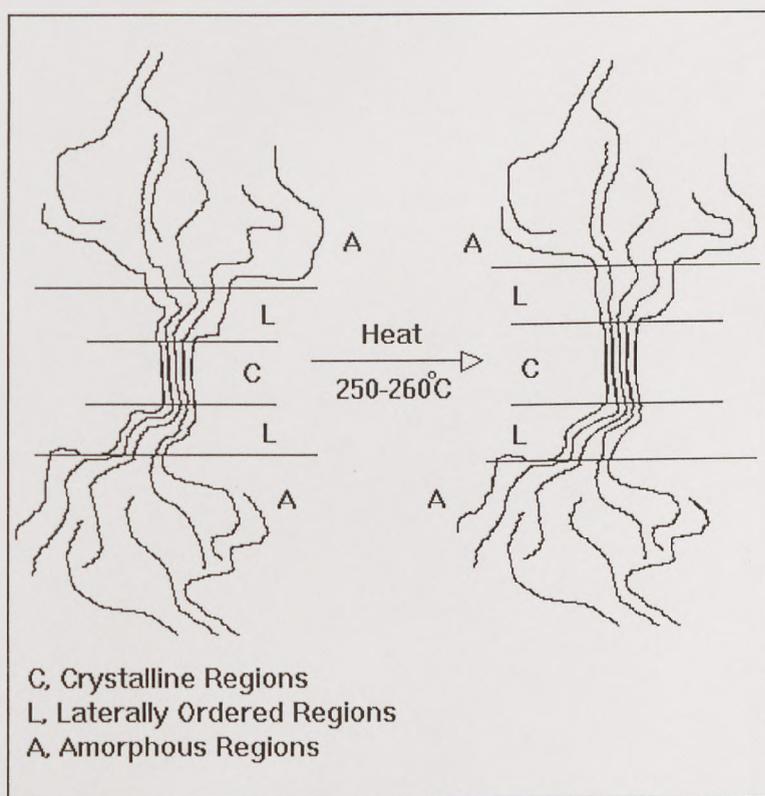


Figure 1. 13 Schematic Representation of the Structural Changes of Bombyx Mori Silk Fibres Induced by Heat Treatment (40).

Tsukada et al. (40) investigated the structural changes in both the amorphous and the crystalline regions induced by heat treatments at 250-260°C. Their results indicated that the amorphous regions play the major role in determining the behaviour of silk fibres subjected to heat treatments. Figure 1. 13, shows the fine structural changes induced by

thermal treatment, indicating an increase in the number and size of the crystalline regions (40).

The original crystalline structure of the silk showed no significant change. The amorphous regions are not completely free to move, being blocked firmly in position, and thus exhibit only a slight contraction (0.7% at 250-260°C) suggesting that there is a high degree of order and molecular orientation even in these sections of the fibre.

1.1.4.10 Effect of ultra-violet radiation on silk.

Silk is more susceptible to photochemical degradation caused by the action of light than any other natural fibre, resulting in fabric yellowing (2). Becker and Tuross (42) used biochemical techniques showing that amino acids with hydroxylated and ionisable side chains were degraded at a faster rate than the aliphatic amino acid side chains. Under the treatment conditions tyrosine showed the highest percentage weight loss and lysine, arginine, threonine, aspartic acid, serine and glutamic acid were lost at appreciable rates. Valine, leucine, isoleucine, glycine and alanine were relatively stable although they showed substantial weight loss under severe exposure. Under mild artificial ageing conditions it was shown that the amorphous regions were degraded first and then as the exposure and dose increased the whole fibroin matrix, including both crystalline and amorphous regions, were attacked.

Becker and Tuross (42) concluded that the biochemical degradative changes in fibroin were:

- a) appreciable loss of tyrosine,
- b) loss of acidic and ionisable amino acids,
- c) increase in quantity of ammonia gas released by photochemical reactions,
- d) cleavage of the peptide bond along the length of the silk molecule.

An initially selective deterioration of fibroin at the tyrosine side chains then becomes a more random chain breakage with increasing exposure.

1.1.5 Mechanical Properties Of silk.

1.1.5.1 Tensile strength.

Silk is one of the world's strongest fibres having mechanical properties more characteristic of synthetic fibres (43), see Table 1.5.

Degummed silk has a strength of 4-4.5g/dtex, equivalent to that of nylon; it exceeds 2.7g/dtex the strength of drawn wire made from soft steel (43). Silk combines strength with high elasticity, being the most nearly perfect elastic fibre for strains up to 5%. At 20% strain, which is near the breaking extension of silk and of nylon 6.6, the recovery of silk is poor in comparison with nylon, 33% versus 75% respectively. The elastic recovery decreases with increasing humidity in common with most other textile fibres (2). Bombyx mori fibres have a load extension curve that shows a characteristic steady curve convex to the load axis up to an extension at break of about 24% (44).

Fibre	Tenacity (N/tex)	Breaking Extension (%)	Work to Rupture (mN/tex)	Initial Modulus(N/tex)
Nylon 6.6 medium tenacity	0.48	20	63	3.0
Nylon 6 (Perlon)	0.29	46	77	0.6
Polyester medium tenacity (Terylene)	0.47	15	53	10.6
Silk	0.38	23.4	59.7	7.3
Cotton (Upper)	0.32	7.1	10.7	5.0
Wool (Botany 64s)	0.11	42.5	30.9	2.3

Table 1.5 Typical tensile properties of silk compared to other textile fibres (45).

Iizuka found that there was a direct linear relationship between fibre fineness and recovery from any given stress (46). The finer the fibre the better the recovery, which agrees with the conclusion that the thinner the thread spun by the silkworm, the more crystalline and more advanced its fibrous structure (14 ,47). Lucas et al. postulated that the difference in tensile properties of the silks could be directly attributed to differences in the side-chain spacings and indirectly to the amount of crystalline and amorphous regions in silk fibroin (44).

The behaviour of silk, as with any fibre, upon application of tensile forces can be accounted for by changes that occur at the molecular level (2, 44). When tension is applied, the initial deformation occurs in randomly orientated chains of amino acid residues found in the amorphous regions. The relatively high initial modulus of silk is determined by the high strength of the combined interacting forces between chains in the amorphous regions and between those interacting with the crystalline regions. Release of tension at this stage allows for almost complete elastic recovery (48).

If, however, increased forces of tension are applied, inter-chain bonds are broken allowing the randomly arranged chains to extend which may pass over each other resulting in a loss of energy of plastic flow. Broken bonds are reformed in new positions causing permanent deformation. The extent of the deformation depends on the amount of stress and the strain applied. As more chains are further extended, the load will begin to be taken up by the crystalline regions. The fibre finally ruptures when the load can no longer be accommodated and inter-chain hydrogen bonds and possibly even peptide bonds are broken (2).

Matsudaira and Kawabata (49, 50, 51), investigated the mechanical properties of degummed, woven silk fabrics under small loads and compared them with the handle and drape of the fabric. Silk fabrics exhibit extremely low shear stiffness and hysteresis of shear force in the region of relatively small strain. These properties become larger with an increase in shear strain. They associated this to an 'effective gap' at the warp and weft crossover points. They estimated the gap, using shear deformation theory, to be in the range of 6-7 μm . This gap was not visible under the microscope; this was attributed to fibre bulkiness and crimp, and it was suggested that only a very few fibres support the crossover point, stabilizing the woven structure, the majority of the fibres being out of contact.

The tensile behaviour of silk fabrics with an 'effective gap' happens in two stages. Firstly the warp or weft yarns or both that are bent by the weave crimp are stretched until the gap disappears. There are no mechanical restrictions to this stretching. The bending rigidity of silk yarns is small and the gap comparatively large, thus the tensile modulus is very low in the initial tensile region. When the gap becomes zero the tensile force of the fabric is dependent on the yarn tensile, bending and compression properties. The low modulus of silk fabrics at this stage was attributed to high yarn compressibility.

The 'effective gap' is said to contribute to the soft handle and smooth drapability characteristic of silk fabrics. The removal of sericin after weaving may contribute to decreasing the yarn contact force. Silk-like polyester fabrics have been developed using a weight-reducing technique to try to reduce the contact between the warp and weft threads at the crossover point.

1.1.5.2 Abrasion.

The high degree of crystallinity of silk fibroin gives rise to an extremely sensitive fibre surface (52). The surface of silk is easily damaged by abrasion especially when wet thus care must be taken to minimise chafing during processing (15). Faults that occur during pre-treatments such as degumming, bleaching or weighting may only become visible after dyeing, printing or finishing.

1.1.6 Raw Silk Processing.

1.1.6.1 Cocoon selection.

The cocoons obtained by the reeler are subjected to pre-reeling processes to improve the quality of the silk and assure the reeler higher profits. His success is dependent on his ability to determine the quality of the cocoons and to price the lot purchased (53).

The cocoons chosen for reeling are first subjected to high temperatures to kill the chrysalises and dried to remove the moisture contained in the cocoon shells and pupae so that they can be stored (53). Prior to reeling the cocoons are sorted and then placed in a steam heated water bath to soften the silk gum. The cocoons are turned regularly with brushes, allowing the outer layers to fall away and the outside ends of the filaments are collected for reeling. The outer and inner layers of the cocoon are reeled off as waste; these are used in the production of spun silk yarns, which are spun on the woollen system.

1.1.6.2 Cocoon reeling.

Reeling is the unravelling of the silk thread from the cocoon. A single filament is too thin and delicate to be woven or knitted by itself, thus several cocoons are reeled together to obtain a firm, strong yarn. The cocoons are placed in a constant temperature reeling basin from which 6-10 ends are reeled off together, depending on the fineness of the silk filaments and the denier required. Reeling is carried out in a diamond crossing formation; this controls the yarn tension, helps to avoid any hard gum spots and allows the tracing of any broken ends. In twisting the strands together some of the silk gum is forced out; this helps to stick the filaments together forming a cohesive single thread of silk (15, 11). The water in the reeling basin is frequently changed to remove any stains or sediment and to keep the silk reeled fresh and clean.

1.1.6.3 Throwing.

The throwster combines the required number of reeled threads and adds twist to produce a yarn suitable for weaving or knitting (53). Thrown silk is called by a variety of names dependent on the number of reeled threads used and the twist given.

- **Singles**, 3-8 silk filaments that may or may not be twisted.
- **Tram**, this is made by twisting two, three or more threads with a small amount of twist (3-6 per inch) used for hosiery and as weft yarn in weaving.
- **Crêpe**, high twist yarns (60-100 turns per inch).
- **Organzine**, this involves two stages, firstly 16-20 turns per inch are given to the left, then two or three of these threads are combined and 12-14 turns per inch to the right are inserted. This is called 2-fold organzine and is used as a warp yarn in weaving.
- **Georgette**, 2-3 reeled yarns with 70-75 turns per inch twist are used as weft yarns in weaving.

1.1.6.4 Degumming of silk.

Degumming, the removal of sericin from the silk fibroin was traditionally carried out predominantly in hank form, but in China 90-95% of degumming is now in fabric form (54). Sericin imparts a harsh stiff handle to the fibre but is useful in its action as a protective layer during processing; therefore the sericin is not removed until all the mechanical operations are completed. Degumming needs to be carefully controlled as any creases or defects inserted are permanent, and variations in the degumming process show up as defects in subsequent dyed and finished fabric.

Sericin is removed from silk by hydrolytically breaking it down into smaller water-soluble fractions by the actions of acids, alkalis, enzymes or water at high temperature and pressure (55). Two pH bands exist; pH9.5 - 10.5 and pH1.5 - 2, in which efficient degumming can take place. Sericin contains the same amino acid residues as fibroin but in different quantities, therefore the degumming process must be carefully controlled in order to prevent damage to the fibroin. It is important to use soft water, and control the pH, and the temperature (this should not exceed 95°C) and to minimise mechanical strain (56, 57).

Degumming is carried out to varying degrees to produce the required softness, subtleness and lustre and to make the fibre absorbent for level dyeing and printing (58).

Ecru (raw) silk, 2 - 5% gum removed.

Souple (supple) silk, 6 - 15% gum removed.

Cuite (completely degummed) silk, 21 - 26% gum removed (59, 60, 56).

Ecru silk is mainly used for warp threads and the gum is purposely left on to act as a natural size; it is quite hard and not very lustrous in nature. It is produced either by washing the raw silk in lukewarm or hot water or by treatment overnight in a weak 4-5% solution of formaldehyde at 20°C. Ecru silk is not widely used as the wet-fastness properties of dyed fabrics are poor.

Souple silk is used as a filling yarn where extra bulk is desired producing yarns with added strength and a dull finish (59, 57). This partial degumming takes place under acidic conditions.

There are several different methods used for completely degumming silk:

1.1.6.4.1 Degumming with water under pressure at 120°C .

This process needs large autoclaves and prolonged treatment times at high temperatures that can cause damage to the fibroin. This process is difficult to control and not very effective. The addition of soap or synthetic detergent is sometimes needed to obtain complete degumming (10, 55).

1.1.6.4.2 Traditional method using Marseilles soap.

Silk is degummed with Marseilles soap; a neutral soap made from olive oil. The pH is adjusted to between 10.2-10.5 and a sequestering agent is added to correct for the hardness of the water. Silk is treated for 2 - 4 hours at 92 - 98°C, and rinsed in warm water followed by cold water. This process has the advantage of giving a soft handle finish but is time-consuming and the process tends to attack both the sericin and the fibroin causing fibre damage (59, 56, 57).

1.1.6.4.3 Degumming with synthetic detergents.

Synthetic detergents are increasingly replacing soap because they permit shorter processing times, usually boil for 1-2h, and thus damage the fibre less. The pH must be carefully controlled to prevent alkaline hydrolysis of the fibroin, because degumming generally occurs under alkaline conditions between pH 11.2 - 11.5. Shukla et al. found synthetic detergents at pH 11.5 to be the most efficient method of degumming silk (61). If alkalis are used on their own they leave the silk dirty, yellowish, thin and harsh (58). The best compromise is achieved by using a mixture of soap and alkali (5).

In China 90-95% of degumming is carried out by the soap-soda method (54). In order to preserve the quality of the silk the process is a long and gentle one, involving several stages; wetting, first degumming, second degumming and washing. The majority of the sericin is removed in the first degumming which is carried out at 90°C for 120 min. The second degumming is gentler, the objective being to remove any residual sericin. The silk is washed first in ammonia at 85-90°C for 30 min, then given an acid wash to remove any traces of alkali, followed by a warm water wash.

1.1.6.4.4 Degumming with acids.

Degumming of silk with acids attacks the amino acid residues of aspartic and glutamic acid, these are much more abundant in sericin than in fibroin. Gulrajani et al (55) found succinic acid to give the best results. This process is not often used, as it is believed to have a more damaging effect on the fibroin (10).

1.1.6.4.5 Degumming with enzymes.

Trypsin and papain are the most common proteolytic enzymes used to hydrolyse the peptide bonds of the amino acid residues in sericin (10, 59, 56). The fibroin is not attacked due to its higher degree of crystallinity, lower polarity and lower content of lysine and arginine residues. For effective results a pre-treatment is used to swell the sericin, making this a two-step process. The addition of soap is often required for complete degumming. This method has the advantages of proceeding at lower temperatures, e.g. 40 - 45°C, causing less damage to the fibroin and is easier to control. Enzyme degumming has a mild, uniform action that produces whiter fabric, with a soft handle and reduced lousiness (58). It is more time-consuming than degumming using synthetic detergents and thought to be more expensive.

1.1.6.4.6 Measurement of the Efficiency of Degumming.

There are several methods for determining the efficiency of the silk degumming process (56). This is important for ensuring that the desired level of cleanliness has been reached with minimal damage to the fibroin. The two most common methods are:

Gravimetric method: This involves determining the weight loss by weighing the silk in the conditioned state before and after degumming. This method is time-consuming but exact (56).

Colouring test: Fibroin and sericin are coloured differently by some dyes and reagents such as Neocarmine W (Merck), CI Direct Red 80, Picocarminic acid or the Pauly reagent. If the Pauly reagent is used, fibre damage can be analysed as it shows up as darker patches than the degummed fibre. This method is easy and rapid to apply but not as accurate as the gravimetric method (56).

1.1.6.5 Bleaching of silk.

Silk is only bleached when very white fabrics are required or before dyeing pale shades or bright colours where the natural yellowish cast of the fibre will affect the dyeing. There are two different types of bleaching process (56, 62).

1.1.6.5.1 Reductive Bleaching.

In reductive bleaching sulphur dioxide or sulphurous acid, sodium hydrosulphite (dithionite) or sodium sulphonylates are used as the bleaching agent.

1.1.6.5.2 Oxidative Bleaching.

Potassium permanganate, sodium perborate or hydrogen peroxide are used as bleaching agents.

Hydrogen peroxide is the most popular reagent used (58). Bleaching is carried out at 80°C for 1 hour with the addition of a stabiliser, e.g. sodium silicate, in the bath to maintain the pH and to help prevent alkaline hydrolysis of the silk fibre (63). Sequestering agents are also added, to protect the fibre against traces of copper and iron in the bath, which can exert a catalytic effect on the peroxide bleaching causing fibre damage.

Efforts have been made to combine degumming and peroxide bleaching into a single step to decrease process time and to minimise silk damage (56).

For extra whiteness the fibre can be given a subsequent treatment in a separate bath with fluorescent brightening agents. These are colourless dyes that absorb invisible ultra-violet light and re-emit light at the blue end of the spectrum, which counteracts the reflection of excessive yellow light (59). Different fluorescent brightening agents are used, giving either a reddish or bluish fluorescence that can withstand steaming conditions in further processing such as printing (39).

1.1.7 The Dyeing, Printing And Finishing Of Silk.

Silk dyeing, printing and finishing treatments are very important processes in manufacturing the end result of the product. The exclusiveness of silk, especially in the 'haute couture' market, demands high quality dyeing and printing. In order to meet customer requirements the smooth finish and luxurious handle of silk must be maintained in combination with better wear and easy-care properties (64).

To maintain the lustre and handle of silk it is important to minimise damage during processing. Chafe marks may be exacerbated by the use of high temperatures, long treatment times, and extremes of pH, i.e., in excess of pH 10 or below pH 4 (65). Alkaline pH and mechanical stress easily damage silk. Alkalis cause a loss of strength which if combined with mechanical agitation can lead to a state termed lousiness caused by 'silk lice', protruding broken fibrils, on the surface of the fibre, giving rise to a hairy appearance (66). These 'silk lice' cause problems during dyeing as they dye much lighter than the rest of the fabric. Another problem in silk dyeing and finishing is unlevelness; unsuitable treatment conditions or inefficient degumming can cause this.

1.1.7.1 Silk Dyeing.

Silk fibroin contains neutral, acidic, and basic amino acid side chains which permit silk to be dyed by most dye classes (67). Silk is primarily dyed with anionic dyes, acid, metal complex and selected direct dyes, but, the presence of free carboxyl groups in fibroin means that cationic dyes can also form ionic bonds with the fibre. In recent years reactive dyestuffs have become more popular due to their improved wet fastness properties (65). The affinity of the fibre for dyes is dependent on the amount of yarn

twist, degree of degumming, and previous finishing treatments, such as weighting (66). Gulrajani et al. (30, 68, 69, 70) have studied the dyeing of silk with different dye classes developing a data bank of the dyeing characteristics, such as exhaustion, L^* , C^* , h values, and fastness properties, of different dye classes relating to specific colours.

There are two important properties of silk fibroin that determine its colouristic behaviour (52).

- Very fine fibre fibrils.
- High fibre orientation.

The very fine fibre fibrils lead to a high surface area to volume ratio. Thus more dye is required to achieve the same depth of colour in comparison with other textile fibres such as wool and polyamide. Consequently the wet fastness properties will be poorer due to the larger quantity of dyestuff on the substrate.

The large fibre surface area also leads to a high initial strike rate as a result of the rapid saturation of the freely accessible side chains at the fibre surface. Dependent on the dye class, its affinity and molecular size as much as 60-80% of dye from the dyebath may be exhausted at the beginning of dyeing. The high fibre orientation acts as a barrier to diffusion, thus after the initial surface saturation the remaining dye is absorbed relatively slowly.

1.1.7.1.1 Direct dyes.

This is the simplest method of dyeing silk; it is straightforward and cheap (52). The direct dyes are applied with a levelling agent in a slightly acidic dyebath to give deep, solid shades of low wet fastness. Deep shades can be difficult to achieve with other dye classes due to the lack of available dye sites; in direct dyeing the dye is bonded to the silk fibroin by van der Waals forces (52). The low wet fastness of these dyes means that they are only used in special circumstances, however, the wet fastness can be improved by selected after treatments (66).

1.1.7.1.2 Acid dyes.

Acid dyes have to be carefully selected with respect to dyeing kinetics and wet fastness properties. Acid dyes tend to have a high initial strike rate, due to the high fibre surface area of silk and a low colour yield, thus dyebath conditions must be carefully controlled

in terms of temperature, and pH to avoid unlevelness. Large molecular size dyes are preferred, such as Sandolan Milling N and Nylosan F dyes for bright shades, and Lanasyn S/SD and Lanasyn CF dyes (Clariant) for dull shades (52).

In acid solution the small protons diffuse into the swollen fibre and protonate the amino groups forming -NH_3^+ ions. In order to maintain the electrical neutrality of the fibre the anions present in the dyebath, i.e. those associated with the acid, with any salts present and with the dye, begin to diffuse inside the fibre to neutralize the charge on the -NH_3^+ groups. The larger dye anions diffuse more slowly, but due to a higher substantivity towards the fibre they slowly replace any smaller anions. The dye anions are bound to the fibre not only by ionic bonds but also by additional hydrogen bonds and van der Waals forces, see Figure 1. 14. Acid dyes also dye by hydrophobic bonding, the extent of ionic or hydrophobic bonding depending on the size and hydrophilic nature of the dye molecule. Large, sparingly soluble acid dyes tend to dye predominantly by van der Waals forces, either dye-dye, or dye-fibre bonds (71).

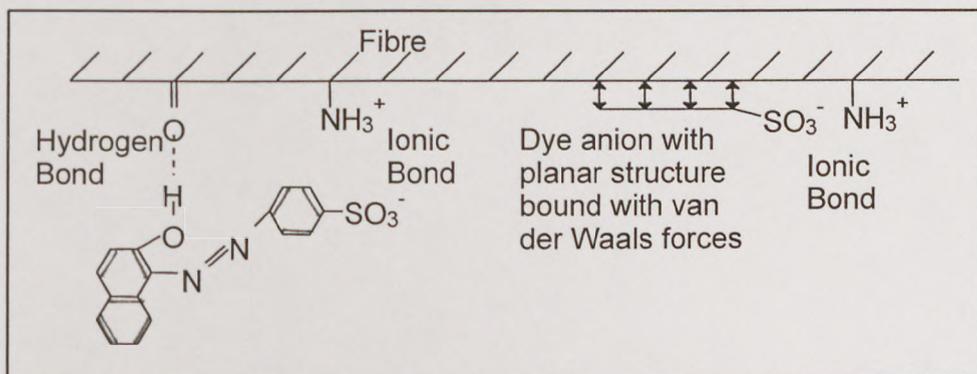


Figure 1. 14 Schematic diagram of the reaction of acid dyes with silk fibroin (65).

Due to the high strike rate of acid dyes on silk the temperature of the dyebath at the beginning of dyeing should be low, 20°C for 20 min, followed by a slow heating rate $1^\circ\text{C}/\text{min}$ to a temperature of $60\text{-}70^\circ\text{C}$. Good dyebath exhaustion is achieved after dyeing for 60 min.

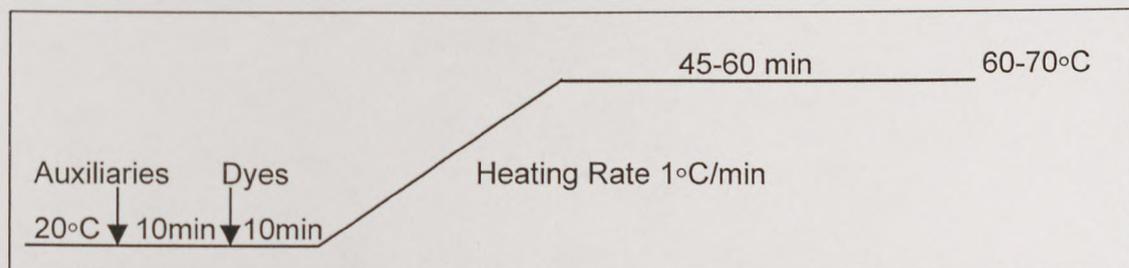


Figure 1. 15 General Procedure for Acid and Pre-metallised Dyes on Silk.

A low dyeing temperature is used to avoid acid hydrolysis of the peptide chain and reduce chafe marks. For deep shades a lower final pH is required, pH 4, this can be varied up to pH 7 for pale shades, while buffer systems are used during dyeing to keep the pH constant. Where level dyeings are required acid donors can be incorporated into the dye bath to reduce the initial dye strike. The wet fastness properties can be improved by an after-treatment with Sandofix WES Powder/ Sandofix WE Liquid (Clariant). Low temperature buffer (72) and redox (73) dyeing systems have been developed to improve the exhaustion and fixation of acid dyes on to silk fibroin.

1.1.7.1.3 Metal complex dyes.

Both 1:1, and 1:2, metal complex dyes, can be used to dye silk; the conditions being similar to those for acid dyes. Increasing the size of the metal complex contributes to the wet fastness properties of the dye.

1.1.7.1.4 Reactive dyes.

Reactive dyes form covalent bonds with silk fibroin producing dyeings with the highest wet fastness, and are thus the preferred dye class. However, for plain dyed goods reactive dyeings are not so popular as faulty dyeings are difficult to correct (52). High fixation ratios are achieved with dyes that have two reactive centres. Good yields are obtained with difluorochloropyrimidyl dyes, such as Drimalan F and Drimarene K dyes (Clariant), and α -bromoacrylamide reactive dyes because these form the most stable and colourfast bonds with silk fibroin (67).

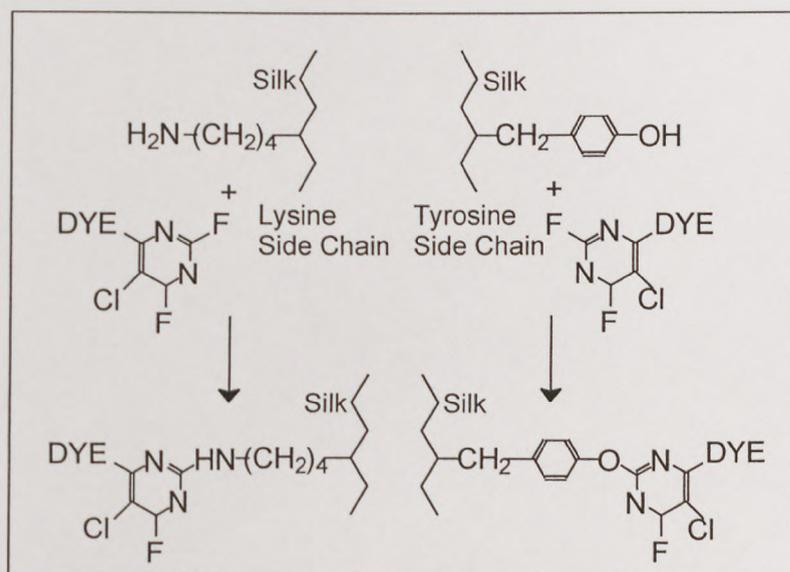


Figure 1. 16 Reaction between Silk Fibroin and a Difluorochloropyrimidine Reactive Dye (65).

The anions essential for the dye-fibre bond are generated by the addition of alkali and salt to the dyebath, this controls the internal pH of the silk fibre. With difluorochloropyrimidyl dyes the main reactive groups are the amino end-groups and the side chains of lysine if dyed in weakly acid to neutral conditions. If the pH is increased to pH 8-9 the hydroxyl groups of tyrosine also react increasing the uptake of the reactive dye.

The pH of dyeings is usually kept below pH 9 to minimise alkali hydrolysis of the silk fibroin. Reactive dyeing begins at low temperature, in neutral pH, and in the presence of 20-60g/l of electrolyte, dependent on the colour depth required. As the temperature is increased to an optimum 60-70°C, the Glaubers salt is added. Silk is dyed for 20-40 min at optimum temperature before adding sodium carbonate; it is then dyed for a further 30-40 min, cooled and rinsed. Due to the relatively small quantity of available functional groups in silk fibroin a strong alkali treatment is given towards the end of the dyeing process to improve the wet fastness properties of the reactive dyeing (52).

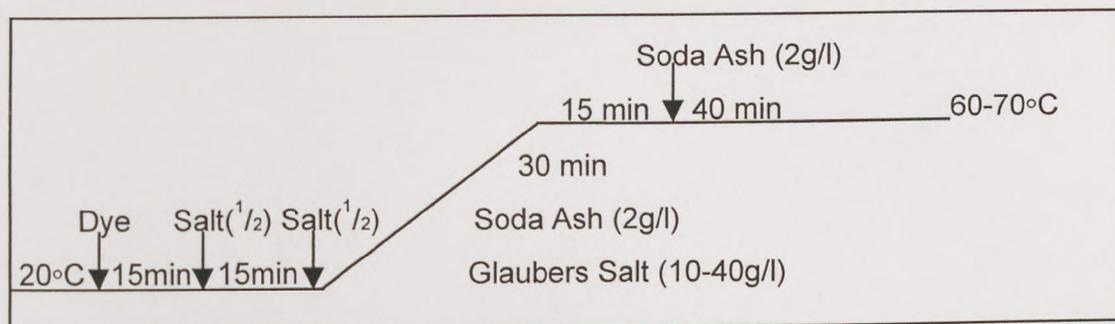


Figure 1.17 General Procedure for Reactive Dyes on Silk (74).

1.1.7.2 Silk Printing.

Traditionally, printed silk goods such as scarves, ties and 'haute couture' dresswear, formed a high proportion of the total output of the silk industry. The majority of silk printing is carried out using flat screens either by hand or machine. Rotary screen and roller printing are not generally used due to the short print lengths in silk printing. The high value of silk prints necessitates high quality printing, good sharpness and definition of motifs and levelness within the printed area. Many of these goods were marketed as 'dry clean only' and thus little regard was given to fastness properties, and this was particularly true with discharge styles (74). Pre-treatments such as weighting are rarely given to printed silk as they increase the risk of fibre damage during the steaming process.

1.1.7.2.1 Direct printing.

Direct printing is the printing of white or pale dyed silk with a printing paste containing dye. Traditionally direct printing was carried out using acid and/or metal complex dyes. Selected dyes are suitable for washable articles if given a cationic after-treatment, but they are unsuitable for very bright shades. Reactive dyes are increasingly replacing acid dyes due to their higher fastness properties and the shorter steaming times required for fixation.

1.1.7.2.2 Discharge printing.

Discharge printing involves printing dyed silk with a discharge paste that destroys the colour at the place where it is applied causing the white ground to reappear. Discharge-resistant dyes can be added to the discharge paste to produce coloured discharge prints (75). In discharge printing the fastness properties are generally poor especially if bright coloured discharges are required. The choice of dyestuff is important; in order to obtain level printing dyes must be chosen with the same dischargeability. Reducing agents such as sodium, zinc, or calcium formaldehyde sulfoxylate, thiourea dioxide, or stannous chloride are used to produce the discharge effect. The prints should be dried quickly and gently to avoid oxidation of the discharge paste.

1.1.7.2.3 Resist printing.

In resist printing the printing paste is printed prior to dyeing or overprinting. If no dyes are added to the resist paste the white ground is retained where the paste is applied, otherwise a coloured resist effect is produced (75). Since the 1980's the demands for higher fastness in printing have renewed interest in this method. In Japan, they have developed a resist paste Thiotan WS powder (Clariant); this can be used alone or in combination with selected acid dyes to produce prints with better fastness properties than discharge prints (75).

1.1.7.2.4 Sublimation transfer printing.

Sublimation transfer printing involves the heat transfer at high temperatures (180-230°C) of disperse dyes to the substrate. Silk naturally has little affinity for disperse dyes, so for this method to work silk has to be chemically modified to improve its substantivity towards disperse dyes. This has been done by grafting with vinyl

monomers, or acylation of silk with some compounds, see section 1.2.2. Good transfer printability can be obtained by these methods. However, due to the high temperatures involved in printing silk, yellowing is unavoidable. Chavan and Nalankilli (76) have imparted an affinity for disperse dyes using a synthesised resin precondensate of melamine, formaldehyde, and poly(ethylene glycol). This pad, dry, simultaneously cure and transfer print combines transfer printing with crease-resistant finishing.

1.1.7.3 Silk Finishing.

Silk finishing is used to adjust and modify certain fabric properties to meet the requirements of the end product. Properties such as dimensional stability, anti-soil, water/oil repellency, and wash and wear properties are becoming increasingly important. These finishes need to be fixed into or on to the fibre in such a way that they are durable to washing and customer care requirements.

1.1.7.3.1 Scroopy handle.

The classical feel of silk, which is termed, scroopy handle, is the peculiar crackling sound produced when silk fabric is rubbed together. This can be adjusted to be either hasher or softer depending on market trends. This process usually occurs prior to the actual finishing process by adding oil emulsions or Marseilles soap which are precipitated on the surface of the fibre with an inorganic acid such as tartaric, oxalic, formic or acetic acid in a fine dispersion. Investigations have shown that it is the acid alone that contributes to the fabric scroop by forming a fine skin on the fibre surface produced by the reorientation of fibroin molecules at the outermost layer of the fibre (64).

1.1.7.3.2 Weighting of silk.

Weighting replaces the weight lost during degumming; this can be up to 25% of the weight of the raw fibre. It improves the handle and drape of the material and with some polymer weighting systems flame retardant and easy-care properties can be introduced. The increase in fabric weight is measured in 'par', either 'below par' or 'above par' and can be as high as 300% above par based on the raw weight of the silk (77). Excessive weighting can be detrimental, as this diminishes the affinity of the fibre for dyestuffs and causes brittleness and a loss in fibre strength.

A variety of methods have been used over the years to weight silk, essentially these fall into three categories: (56, 78)

1.1.7.3.2.1 Vegetable weighting.

The use of tanning agents is a relatively simple operation causing improvements in hydrophobicity, but due to their inherent colour can cause problems with light dyeings or white fabrics. This method is now rarely used.

1.1.7.3.2.2 Mineral weighting.

Tin / phosphate / silicate is the most popular weighting process (64). This method involves several stages and careful monitoring to ensure minimum undesirable side effects. The silk is soaked in stannic chloride at room temperature for about 1.5 hours, excess solution is removed by centrifugal hydroextraction and the silk is washed in cold water. This removes any uncombined stannic chloride and allows the combined stannic chloride to hydrolyse to the insoluble metastannic acid. The silk is then treated at 60 - 70°C for 1 hour with a dilute solution of disodium phosphate, washed with soft water, and acidified to give an insoluble tin phosphate compound of molecular weight 249. The whole process is repeated; the number of treatments is continued until the percentage weight increase required is obtained. Finally an insoluble tin silicophosphate is formed of high molecular weight by treating the silk with dilute sodium silicate at 70°C for 1 hour. Deposition of the metallic salt takes place in the amorphous regions of the fibre with little alteration of fabric appearance.

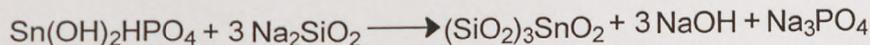
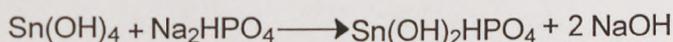
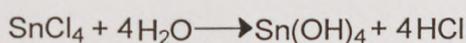


Figure 1. 18 A Summary of the Main Reactions in Mineral Weighting (58).

Fabric that has been given a mineral weighting treatment can be identified by a burning test. Untreated silk partly melts and forms little charred balls, whereas mineral weighted silk burns to leave an ash skeleton (66).

1.1.7.3.2.3 Polymer weighting.

Organic weighting by grafting has recently been introduced to try to decrease costs and the deleterious effects of metallic weighting. This method of weighting is based on a treatment of methacrylamide and ammonium persulphate (78). It is reported that polymer weighting of up to 50% can be achieved without impairing the fabric handle (79). The disadvantage of this method is that it alters the dyeing properties of the fibre, but it is preferred as it is less harmful to the environment than mineral weighting.

1.1.7.3.3 Sandwash finishing of silk.

The sandwash finish produces a machine washable fabric with a soft, velvet-like feel. The sandwashing process itself gives rise to a rough handle, but this is modified using softeners to produce the sandwash feel. The effect is produced by treating silk under harsh conditions, this roughens the fabric surface breaking the surface fibrils to create a peachskin-like texture. Depending on the method used the fabric also shrinks; this makes it dimensionally stable. The traditional handle of silk is lost along with as much as 50% of the initial fabric strength (54).

There are several ways in which this sandwash finish can be produced. Silk can be dyed on overflow machines under harsh conditions, e.g. longer time or higher temperatures, either directly during dyeing or as a pre-wash treatment. The process can be carried out in a washing machine sometimes with the addition of pumice stones or small pieces of expanded clay. The disadvantage of these methods is inadequate uniformity of the finish and the risk of chafe marks. Other methods include mechanical raising of the fibre surface using an emerizing machine, although with this method there is a risk that whole fibrils may be broken. Surface modification using a protein-active enzyme such as Bactosol SI (Clariant), is claimed to be capable of producing a uniform effect (52).

1.1.7.3.4 Flame retardant finishing of silk.

Flame retardant finishes are important where products have to meet statutory flammability requirements. Silk, along with other natural fibres, is rendered fire resistant and self-extinguishing by coating with a reaction product of polyhalogenated acids with a cyclic nucleus, such as chlorendic acid and thiourea. Titanium hexachloride, titanium tetrachloride and zirconyl chloride are found to give good flame retardant finishes for silk (78, 80); they lower the pyrolysis onset temperature and

increase char formation. A multifunctional finish that imparts flame resistance, dimensional stability, and easy-care properties has been reported based on N, N'-ethylene-bis (P, P-bis[aziridiny]-N-methyl phosphinamide).

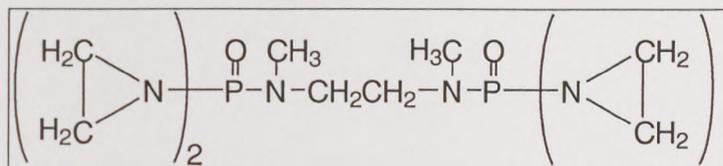


Figure 1. 19 N, N'-ethylene-bis P, P-bis[aziridiny]-N-methyl phosphinamide) (58).

1.1.7.3.5 Oil and water repellent finishing of silk.

Traditionally metallic acid salts or oxides, proteins, or nitrogenous compounds were used, however currently, the trend is for combined polymeric finishes that offer resistance to both oil and water, based on silicones, acrylamide, acrylic acid or fluorochemicals. A combined treatment with a fluorocarbon derivative, a reactive resin, and a water-repellent finish produces a versatile finish (58). Grafting with the vapour of hexafluoro propylene, vinyl fluoride, vinyl chloride and acrylonitrile produced an increase in water repellency, oil repellency, mineral acid resistance and photo-stability (78, 80).

1.1.7.3.6 Anti-static finishing of silk.

Silk has a fairly low static charge build-up but this can increase if silk is grafted with monomers used to improve certain fibre properties. Treatment with selected water-soluble vinyl monomers (e.g. N,N'-methylene bisacrylamide, triacryloyl polyethylene glycol methacrylate) etc., in acid produces an increase in antistatic and hygroscopic properties. The deposition of certain metallic particles has also been found to increase the antistatic and conductivity properties of the fibre (78, 80).

1.1.7.3.7 Anti-microbial finishing of silk.

Antimicrobial finishes protect the fibre from microbial attack and protect the owner against transfer of pathogenic germs. Silk is relatively resistant to attack by mildew, fungi and other bacteria, but if stored in moist conditions damage can occur. The fungal resistance can be improved by treatment with compounds like N-(2,2'-dichlorovinyl) salicyl amide and a 0.01 - 0.25% solution of benzalkonium chloride. This increases the resistance of silk to mildew during long storage (up to two years) even at high relative humidities (78, 80).

1.1.7.3.8 Ultra-violet-resistant finishing of silk.

One of the major problems with silk fibres is their susceptibility to photochemical degradation. UV-absorbers, organic compounds that absorb UV-radiation can impart some protection by dissipating the energy as heat. Screening agents, energy transfer agents and pigments can also be used to deactivate the fibre degradation process (80).

1.1.7.3.9 Softeners and lubricants.

Softeners and lubricants are used to improve handle, drape, cutting, sewing, etc. and to help retain the traditional feel of silk. Fabric softening is carried out during the final stages of wet processing, usually in the final wash bath. A wide variety of softeners can be applied to silk; recently the use of multifunctional silicone softeners has become popular, particularly amino-functional polysiloxanes in micro-emulsion form (58).

1.2 EASY-CARE FINISHING OF SILK.

Commercially an easy-care fabric or product is one that does not crease readily while in use, can be washed and requires no or minimum ironing to restore its original appearance. In addition the traditional comfort, handle, texture, drape and colour of the product should not be affected. Technically an easy-care finish enhances the fabric resistance to, and recovery from, creasing without any adverse affect on other intrinsic fabric properties. Resistance to creasing depends on rigidity, and recovery from creasing depends on elasticity (81). In today's market easy-care products are applicable to almost all clothing materials. In silk finishing there is a gap in the market for a product that can impart true easy-care characteristics. This section reviews the easy-care finishing methods that have been used to improve the properties of silk fabrics.

1.2.1 Introduction.

1.2.1.1 Properties of Silk as a Textile Fibre.

Fibres are defined by the Textile Institute as units of matter characterized by flexibility, fineness and a high ratio of length to thickness (45). If a fibre is to be of any use as a textile product it needs to have a sufficiently high temperature stability, a certain minimum strength and elasticity, resistance to abrasion, good moisture absorption and dyeability (45, 48).

Fibre properties such as strength, elasticity, stiffness, permeability and swelling are controlled largely by the stereochemistry of the polymer, and the arrangement and interactions of the atoms in the molecular chains (48). Silk is a highly tenacious fibre as a result of good close packing and hydrogen bonding between chains, but the high degree of crystallinity of silk means that it is easily damaged by abrasion. The polypeptide chains are pleated and it is the stretching and contracting of these folded chains that allows for the good extensibility and recovery properties of the fibre. Degummed silk is very hygroscopic and can absorb up to 30% of its weight in water before feeling wet. It is also easily dyed by most dye classes due to the incorporation of acidic, basic and neutral amino acid side chains within the amorphous regions of the fibre.

Natural silk fabrics are fine, strong and lustrous, they have a soft handle and good drape, but they have poor resistance to alkali, heat, and sunlight and are difficult fabrics to launder. As can be seen from Table 1.6 the fabric dry crease recovery angle (DCRA), for silk is relatively high, more akin to polyester than cotton, but the fabric wet crease recovery angle (WCRA) is low, approximately 60% of its DCRA, hence silk creases easily when wet or when laundered. DCRA is the angle that a small piece of conditioned fabric 40x15mm recovers to when folded in half and subjected to a force of 10N for five minutes, placed in a crease recovery test machine and allowed to recover for a further five minutes. The WCRA refers to fabric that has been wetted out and had the excess water removed prior to testing.

Fabric Type	Fabric Weight (g/m ²)	DCRA (degrees)	WCRA (degrees)
Cotton Lawn	109.3	183	157
Polyester Satin	65.3	286	300
Polyester Cotton (65/35) Print Cloth	111.4	266	283
Silk Habutae	41.3	258	152

Table 1.6 Comparison of wet and dry crease recovery angles (degrees) of silk, cotton, polyester and polyester cotton fabrics (82).

The ionic cross-linkages (hydrogen bonds and salt links) between silk chain molecules that give the fibre good dry stability are easily broken in water, giving silk low wet fibre stability. Because there are no covalent cross-links, such as the disulphide cross-

linkages that stabilise wool fibres, when a silk fibre absorbs water and the fibre swells the ionic linkages between the chain molecules are broken. This allows the fibroin chain molecules to slip and be deformed by any sufficient creasing force. Upon subsequent drying or with a decrease in moisture absorption the hydrogen bonding begins to reform fixing the crease under wet conditions, and thus the original position of hydrogen bonding is not retained, leading to a lower fabric WCRA. The low wet resiliency and severe laundry shrinkage of silk fabric limit the commercial usage and these properties need to be improved after silk fabric manufacture if silk fabric is to remain a viable commercial fabric.

The properties of silk as a textile fibre are a combination of the properties of the natural fibre as spun by the silkworm and additional properties that the fibre assumes after silk fibre processing. The final product relates to a material with a distinct processing history.

1.2.1.2 Chemical Modification of Fibres.

There are several ways of chemically modifying fibres to manufacture a specific end product. Below are the four main types of chemical reagents that can be used to modify fibres to improve their easy-care characteristics.

1.2.1.2.1 Self-Cross-Linking Agents.

In 1925 Foulds, Marsh and Wood invented a finishing process in the laboratories of Tootal, Broadhurst and Lee Co. Ltd., with the objective of improving the recovery from creasing of cotton and viscose rayon fabrics (81). This involved the polycondensation of methylol compounds within the fibre so that the product consisted of an interlocking and entangled system of the cellulose polycondensate and the resin polycondensate. They observed that the synthesis of suitable synthetic resins within the fibre improved the crease resistance of fabrics, made them easier to launder and reduced the amount of ironing required. The treated fabrics had a high degree of recovery from creasing in the dry and wet state, which they attributed largely to an increase in fibre elasticity, bringing about a return to the original shape of the fabric. A high degree of stabilisation within the fabric is necessary so that the relative positions of the fibres and yarns remain unchanged, and the original configuration of the fabric is restored.

Self-cross-linking agents are generally applied by padding in aqueous medium. The fibre swells through the diffusion and absorption of water molecules and the self-cross-linking agent diffuses within the fibre. In the presence of a catalyst and under high temperature it forms a three-dimensional network in the accessible regions within the fibre. It has not been proved if the lattice structure formed within the fibre is held in position purely by its size and hydrophobic character or whether it interacts with the fibre itself. The synthetic resins stabilise the fabric by restricting the movement of molecular chains in the non-crystalline regions of the fibre.

1.2.1.2.2 Fibre Cross-Linking Agents.

In 1949 a new class of crease-resist finish, based on bifunctional reactant resins was introduced from the USA; these were proposed to react with the fibre, rather than with themselves, to form fibre inter-chain cross-links. These were generally applied by padding in an aqueous medium and in the presence of an acid catalyst, drying, and curing at high temperature.

Fibre inter-molecular cross-links provide anchoring points for the chains that restrain excessive movement and maintain the position of the chain in the network. Strong covalent chemical bonds formed between polymer chains by a cross-linking agent tend to improve the dimensional stability, reduce the creep rate, improve stability to heat because the glass transition temperature of the fibre (T_g) is raised, increase the strength and elastic recovery of a polymer and reduce its swelling in contact with solvents (67). All these properties tend to increase as the cross-link density increases, and can be controlled by adjusting the quantity of cross-linking.

1.2.1.2.3 Fibre Grafting Agents.

Graft copolymers are homopolymer branches of one monomer unit that are 'grafted' on to another polymer. Grafting involves attaching polymeric side chains to suitable chemical groups on the main polymer backbone (67).

This technique modifies polymer surfaces because the additional grafted molecular chains at the fibre surface tend to align themselves so that the grafted polymer units point away from the fibre surface. The primary advantage of this technique is that some properties of the grafted polymer are imparted to the substrate. Properties such as

hydrophilicity or hydrophobicity, soil-release, wickability, handle, easy-care, dyeability, etc. can be altered (67).

1.2.1.2.4 Surface Elastomers.

Textile elastomers and fabric coatings are soft, extensible and highly flexible. These are properties characteristic of a predominantly disordered, rather than crystalline, chain configuration and one in which the monomer units are free to rotate about the chain linkages (67). Surface elastomers are often added in combination with resin finishes, of both the self- and fibre cross-linking agent types. These resins tend to impart stiffness and reduce the extensibility of the material. Surface elastomers may impart an increase in crease recovery associated with the rubber-like properties of the elastomers, and the coating may act as a rubbery cushion or mechanical buffer (81).

1.2.2 Literature Review: Easy-Care Finishing of Silk.

There are a variety of methods that have been investigated in the past to improve some of the inferior properties of silk fibroin. This section contains a review of the chemical modification techniques used with the aim of improving the easy-care properties of silk.

1.2.2.1 Initial Study of Cross-linking Silk Fibroin.

Zahn (1950, 1951) showed that fibroin reacts with 1-fluoro-2,4,-dinitrobenzene (FDNB) and 1,3-difluoro-4,6-dinitrobenzene (FFDNB) under mildly alkaline conditions to give products with enhanced resistance to hydrochloric acid and a decreased solubility. Zahn and Wurz (1952) investigated these reactions in great detail to determine the accessibility of tyrosine and lysine residues that led them to believe that extensive cross-linking of fibroin might be possible. Zahn and Zuber (1953) prepared a series of bifunctional fluoronitrobenzene derivatives in which the distance between the two reactive fluorine atoms varied from 3 to 14Å. When the distance was less than 10Å, the reaction was largely monofunctional and bifunctional reactions predominated at a distance of 10Å. The reagent 4,4-difluoro-3,3-dinitrodiphenylsulfone was found to be 100% bifunctional in its reaction with tyrosine residues (35, 83a).

1.2.2.2 Resin finishes based on formaldehyde, urea and melamine.

These can either be in the form of self cross-linking agents or fibre cross-linking agents.

The simplest reagent for fibre cross-linking is formaldehyde, which probably acts in the form of methylene glycol $\text{CH}_2(\text{OH})_2$, a bifunctional compound (81). The cross-linking mechanism of formaldehyde with proteins involves the formation of methylene cross-links between chains in the amorphous regions of the silk fibroin (2, 38). These inter-fibre cross-links between chains are very short, and they improve the fabric crease recovery angle but reduce fabric flexibility. Longer inter-fibre cross-links have been studied using 1,3-dimethylol ethylene urea, DMEU, and 1,3-dimethylol-4,5-dihydroxy ethylene urea, DMDHEU, (see Figure 1. 20) but these produce only a very slight improvement in fabric dry and wet crease recovery angle (84), see Table 1. 7.

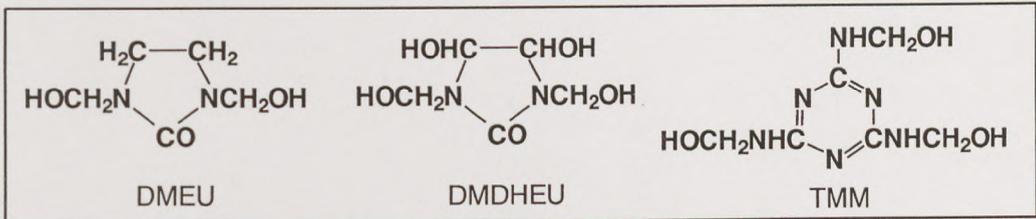


Figure 1. 20 Chemical structures of DMEU, DMDHEU and TMM

The most successful self cross-linking resin for improving the easy-care properties of silk based on methylol compounds is trimethylol melamine, TMM (see Figure 1. 20) (82).

Resin Type	Silk Crepe		Cotton		Polyester		Polyester/Cotton	
	DCRA	WCRA	DCRA	WCRA	DCRA	WCRA	DCRA	WCRA
Untreated	268	153	198	141	287	279	273	285
DMEU	262	186	282	216	314	276	304	292
DMDHEU	253	188	296	208	298	270	280	290
TMM	264	208	304	210	304	276	316	302

Table 1. 7 CRA measurement (degrees) of conventional Pad-Dry-Cure with amino-formaldehyde resins (82).

Lee and Sin, (1991), reported on the application of TMM with the addition of fibre swelling and hydrogen bond breaking agents (82). They suggested that the additives aid the penetration of the finish into the fibre, and thus increase the wet resiliency of silk. They claimed that conventional pad-dry-cure finishing of amino-formaldehyde resins only improved the DCRA of the fabric because the fibre is finished in the dry and collapsed state during the curing stage. In silk the accessible regions for resin permeation are limited and thus any fibre cross-linking in the dry and collapsed state is

also limited. A slight improvement in WCRA was found using a pad-batch-dry route, but they considered that insufficient fibre swelling prevented any further improvement in WCRA. By incorporating a fibre-swelling agent such as an organic acid and a hydrogen bond-breaker they attained higher values of WCRA which they attributed to finishing in a swollen state.

Yang and Li, (1992), followed up this work looking at the finishing of silk fabrics with TMM and formic acid (85). They concluded that it was possible to obtain an improvement in both DCRA and WCRA using a pad-batch-dry technique and the treated fabric retained its breaking strength and whiteness very well.

Padding Method	DCRA (degrees)	WCRA (degrees)	% Retention Tensile Strength	Stiffness mm.cm	CIE Whiteness
Control	265	217	100	67.72	75.7
Pad, dry, cure	293	256	96.9	83.56	69.7
Pad, batch, dry	283	261	112.8	148.78	71.4
Pad, batch	292	253	100.0	54.88	75.1

Table 1.8 Physical properties of silk finished with 6% w/w TMM, 8% w/w Formic Acid and 0.5% w/w Softener (a non-ionic aqueous emulsion of polyethylene) (85).

The melamine resin is a hard resin, due possibly to the close lattice structure formed or because of the rigidity of its ring structure (81). Yang and Li stated that the stiffness of the fabric varied depending on the finishing conditions and that it could be controlled by suitable techniques (85). In a separate paper (86), they indicated that there were no adverse effects produced by this finish on the dyeability of silk.

Since 1980 there has been increasing research in order to decrease and even eliminate formaldehyde from easy care finishes. This is because a toxicological study by the Chemical Institute of Toxicology suggested that rats exposed to a very high content of formaldehyde in the air developed a rare form of nasal cancer (87). No connection in humans has been found between formaldehyde exposure and cancer, possibly due to the fact that man cannot tolerate breathing air containing even 3ppm formaldehyde (88). It is claimed that if formaldehyde reacts with chloride ions from acid catalysts bis(chloromethyl) ether (BCME) could theoretically be formed, which is a very potent carcinogen (89). However, no evidence for BCME formation under practical finishing conditions has been reported. Nevertheless, formaldehyde is an established dermatitic

agent and a known irritant to the eyes and mucous membranes. It can cause allergic reactions in some people and thus suitable alternatives have been researched (90).

Finishers have moved towards using ultra-low formaldehyde-containing cross-linking agents, mostly based on 1,3-dimethylol-4,5-dihydroxy ethylene urea (DMDHEU) and its modified derivatives (91). Alternatively, zero-formaldehyde cross-linking agents have been researched (92). One of them is 1,3-dimethyl-4,5-dihydroxy ethylene urea (DMeDHEU), a dialkylurea-glyoxal-based product. This compound is not as effective as the DMDHEU finish on cellulosic fabrics and is more expensive because higher additions and higher curing temperatures are required (93).

1.2.2.3 Epoxides.

Shiozaki, Tanaka et al. introduced the use of epoxides to chemically modify silk in 1969. Since then, this technique has been developed, mainly in Japan, particularly with respect to ethylene glycol diglycidyl ether (EDGE). It is used to improve some of the inferior properties of silk fabrics, namely, crease recovery in both the dry and wet states, photoyellowing resistance, abrasion resistance and colour fastness to washing of dyed silk (94).

Epoxides react with amines, alcohols, phenols, carboxylic acids and thiols. Silk fibroin contains amino acid residues that include these functional groups within their side chains. The silk-epoxide reaction occurs predominately with the phenolic hydroxyl groups of the tyrosine residues. Epoxides also react with the basic amino acids, lysine, arginine, and histidine, and form ester links with the acidic amino acids of aspartic and glutamic acid. Bifunctional epoxides possess the ability to form cross-links between the fibroin side chains (95, 96). The incorporation of cross-links may in turn lead to an improvement in crease recovery properties.

The addition reaction of epoxides with silk fibroin is influenced by the nature of the salt catalyst and solvent used as well as the epoxide substituent. Thiocyanate, cyanide or chloride ions catalyse the reaction and tetrachloroethylene, toluene and ethanol are among the suitable solvents (80).

Epoxide treatment is conventionally carried out in two stages. The silk fabric is padded

to approximately 100% wet pick up with the catalyst, e.g. a salt solution, usually 1N NaSCN. This is followed by treatment with the epoxide in a solvent, e.g. tetrachloroethylene at 60 - 80°C for different times depending on the total weight gain required (94). Weight gains varying from 15-28% have been obtained with various epoxides (80). The disadvantages of this method include the environmental pollution caused by the solvent and the risk of damage to the silk fibre due to prolonged treatment times (2 - 3h) at relatively high temperatures (60 - 80°C).

Tsukada et al. have studied the structural changes induced by the reaction of silk with bifunctional epoxides. X-ray diffraction curves were used to show that the crystalline regions remained unchanged. Thermoanalysis revealed the epoxide-treated silk to be more thermally stable and mechanical analysis showed an improvement in both tensile strength and elongation at break. They attributed the changes in physical structure and thermal behaviour to the formation of cross-links between the hydroxyl groups of epoxide molecules and the functional groups in silk fibroin (97). The treated fabric also showed improved stability to photoyellowing in sunlight, good crease recovery in both wet and dry states, lower solubility in both acid and alkaline media and better colour fastness to washing for dyed samples. The dyeing behaviour of epoxide-treated silk was equivalent to that of the untreated fabric.

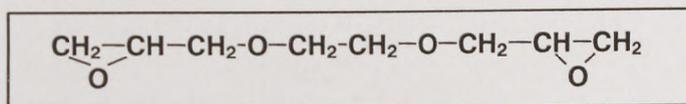


Figure 1. 21 Chemical formula of EDGE.

Silk treated with EDGE shows an increase in fibre regain at more than 4% weight gain, a significant increase in wet crease recovery values, a decrease in photoyellowing, and a slight increase in strength retention (94). An increase in DCRA from 117° to 140° (warp only), and a corresponding increase in WCRA from 115° to 158° have been reported (80). The glass transition temperature decreased significantly which led Tsukada et al. to suggest that the molecules not only react in the amorphous regions of the fibre but also in the laterally ordered regions even at low weight gains (96, 98). The bending rigidity and bending hysteresis of silk increased, and this was higher in the weft than in the warp direction. This was attributed to an increase in contact pressure and surface friction between the warp and weft yarns resulting in a tightening of the fabric texture after treatment with epoxides (95).

Sano et al. (98) proposed a method for applying epoxides by a pad-dry (2min at 100°C), -cure (20 min at 102°C), and wash off process. The finishing process was most effective when using EDGE with sodium chloride as a catalyst.

1.2.2.4 Grafting.

Among the chemical modification techniques, graft-copolymerisation of vinyl monomers on to silk fibres has been suggested as a potentially effective means to improve the crease recovery, easy-care, and photo-degradation behaviour of silk fabrics. A variety of vinyl monomers, with different functional groups at the side chains, have been applied to silk with varying degrees of success. Styrene (St), methyl methacrylate (MMA), ethoxyethylmethacrylate (ETMA), methacrylamide (MAA), 2-hydroxy-ethyl methacrylate (HEMA), and methacrylonitrile (MAN) have been used as grafting agents for silk (99).

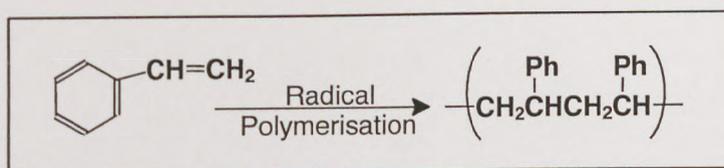


Figure 1.22 Radical polymerisation of styrene.

The grafting of vinyl monomers on to silk fibroin can be activated by a variety of methods commonly used to initiate chain-growth polymerisation reactions (see Figure 1.22). Generally, grafting of silk fibres occurs in an aqueous medium, with an initiator such as potassium or ammonium persulphate at temperatures above 75°C for several hours. The difficulty in achieving high add-on values and the damage to the silk fibres due to the severe conditions means that milder grafting techniques are now preferred (100).

The reaction involves the formation of free radicals on the silk fibroin backbone at the side groups of acidic, basic and hydroxyl amino acid residues. These radical sites on the fibroin backbone initiate polymerisation of the vinyl monomer that then polymerises within the amorphous regions of the fibre. X-ray diffraction curves indicate that the crystalline regions of the fibre remain unchanged even at high weight gains, suggesting that the graft-copolymerisation reaction does not occur here. Studies have shown that at high weight gains grafting occurs in the laterally ordered regions located at the end of each crystalline segment as well as in the amorphous regions of the fibre.

Thermoanalytical studies show that the decomposition temperature of silk fibroin shifts slightly upwards. An additional thermal transition can be detected whose intensity is roughly proportional to the graft yield attributed to the vinyl polymer within the silk fibroin. Infra-red spectra of silk fibres containing vinyl polymers show absorption bands characteristic of silk fibroin with a β -conformation and of the vinyl polymer. These results suggest that the polymerisation or copolymerisation of the vinyl monomer occurred within the fibre matrix. Further studies are needed to elucidate whether the vinyl monomers are chemically grafted or just trapped within the amorphous regions of the fibre.

The physico-chemical properties of the grafted silk fibres are determined by the extent of grafting and/or weight gain, and by the characteristics of the functional group within the monomer that has become an integral part of the silk fibre. Table 1.9 summarises the properties of silk fabrics grafted with different vinyl monomers.

Vinyl Monomer	Hand	Crease Recovery	Hydrophilicity	Affinity for Acid Dyes	Disperse Dyeable	Transfer Printable	Photo-yellowing
Styrene	Full, Bulky, Stiff, Hard	Increased	Large decrease	Decreased	Yes	Yes	-
MMA	Above 30% wt. gain stiff hand	Increased wt. gain 30-60%	Decreased	Decreased	Yes	Yes	-
ETMA	-	-	-	Increased	-	Yes	-
MAA	-	No improvement	Increased	Decreased	-	-	-
HEMA	Low bulkiness	No improvement	Increased	-	-	-	-
MAN	Soft, smooth	-	Slight decrease	-	-	-	-
BMA	Minimal change	-	Increased	-	-	-	Decreased

Table 1.9 Summary of properties of silk fabrics after grafting with various vinyl monomers (99-104).

Styrene was the first vinyl monomer to be used to modify silk fibres by graft-copolymerisation. Styrene-grafted silk fabrics showed an increase in bulkiness and in fabric crease recovery. Due to the strong hydrophobic properties of the polystyrene chains, styrene-grafted fibres show an increased hydrophobicity and consequently an

affinity for disperse dyes. There are several drawbacks of styrene-grafted silk fibres, at high graft yields they have a stiff, harsh handle, they are highly flammable, have strong hydrophobic properties and cause smells and air pollution problems during industrial application (99, 101). As a result new vinyl monomers were studied.

The crease-recovery of MMA-grafted silk fibres increased when the weight gain was in the range of 30-60%, without significantly affecting the tensile properties (100, 102, 103, 104). There is a decrease in fibre moisture content due to the hydrophobic nature of the poly-MMA chains, and consequently an affinity for disperse dyes and an increase in the resistance to water staining. Above 30% weight gain there is an increase in fabric stiffness and a harsher handle. SEM studies show the presence of polymer granules adhering to the surface of the silk fibre when the weight gain exceeds 85%.

MAA and HEMA improve the hydrophilicity of silk fibres. Both polymers, particularly MAA, are used as synthetic weighting agents in Japan. Treated fibres show an increase in moisture content without affecting the handle and lustre, and this plays an important role in improving the comfort of silk fabrics. There is no significant increase in crease-recovery values and the fabric drape can be maintained if the add-on does not exceed 30%. The disadvantage of MAA-grafted fibres is that silk dyed with acid and reactive dyes has a slight colour variation. Grafting of silk fibres using HEMA with high weight gains causes stiffness and a hard handle (105, 101).

Grafting with vinyl monomers can be used to manufacture different products with specific end properties. A soft finish can be achieved by altering the mechanical properties of MAN-grafted fibres (99), whereas silk fibres with an increased affinity for acid dyes and good transfer printability can be obtained by treatment with ETMA. Tsukada et al. (106) showed that the rate of photoyellowing of silk fabrics could be decreased when grafted with poly(N(n-butoxymethyl) methacrylamide) BMA, (see Figure 1. 23).



Figure 1. 23 N(n-butoxymethyl) methacrylamide (BMA)

1.2.2.5 Chemical Modification of silk with acid anhydrides.

Tsukada et al (1992-4) have studied the modifications of silk fibres treated with

aliphatic and aromatic dibasic acid anhydrides (107, 108, 109, 110). The aim was to improve both the crease resistance, mechanical and anti-photoyellowing properties of silk by reacting the anhydrides with the phenolic hydroxyl groups in tyrosine side chains (108). They demonstrated that modification of silk with acid anhydrides occurred under milder conditions than grafting silk with vinyl monomers (107).

The process involves treating the silk fibres with the acid anhydride in dimethylformamide under reflux for varying periods of time. The excess anhydride is removed with acetone at 55°C for 1 hour and finally washed off with water. Acylation of silk with acid anhydrides occurs within the amorphous regions of the fibre, mainly at the side chains of the basic amino acid residues lysine, histidine and arginine and the hydroxyl groups of tyrosine, serine and threonine.

Dibasic Acid Anhydride	Crease Resistance	Moisture Regain	Affinity for Acid Dyes	Affinity for Basic Dyes	Thermal Properties	Photo-yellowing
Glutaric Acid	Increased	Increased	Decreased	Slight increase	Endothermic reaction 210°C	Decreased
Succinic Acid	No change	Increased	Large decrease	Slight increase	No change	-
Itaconic Acid	No change	No change	-	-	Increased decomposition temperature	-
Phthalic Acid	Increased	Small decrease	Decreased	Slight increase	Endothermic reaction 210°C	-
o-sulfo-benzoic Acid	Slight increase	Increased	Very little	Large increase	No change	-

Table 1. 10 Summary of properties of silk fabrics after acylation with various acid anhydrides (107-110, 111).

The properties of silk fibroin after acylation with acid anhydrides vary depending on the anhydride used, the treatment can alter the moisture regain, crease recovery and dyeability of silk fabrics, see Table 1. 10.

Tsukada et al studied the effect of acylation by the above anhydrides and concluded that the structure of silk fibroin was not significantly altered (107). X-ray diffraction curves were used to demonstrate that treatment with acid anhydrides did not change the crystalline structure of silk fibroin. The thermal stability and tensile properties were

also largely unaltered.

Acylation with acid anhydrides can be used to alter the dyeability of silk fibroin. Following acylation the absorption for cationic dyes was significantly enhanced for all samples, the maximum dye uptake being achieved by *o*-sulfo-benzoic-treated silk fabrics, whereas their affinity for acid dyes was reduced. The presence of a high number the electronegative sulfonic groups in *o*-sulfo-benzoic anhydride-treated silk increases the number of available acidic groups in silk fibroin for reaction with cationic dyes.

Acylation with aliphatic anhydrides, glutaric anhydride appears to be the most promising. Glutarylation has been found to protect silk fibres against photoyellowing and improves the crease resistance of silk. Tsukada et al. proposed that succinylation of silk only forms single-ended attachment leaving free carboxyl groups present in the fibre after acylation (see Figure 1. 24). In contrast, ester cross-links are more easily formed by reaction with the larger glutaric anhydride (108). Itaconic anhydride showed a 10°C temperature increase in thermal decomposition suggesting a higher thermal stability induced by this chemical modification.

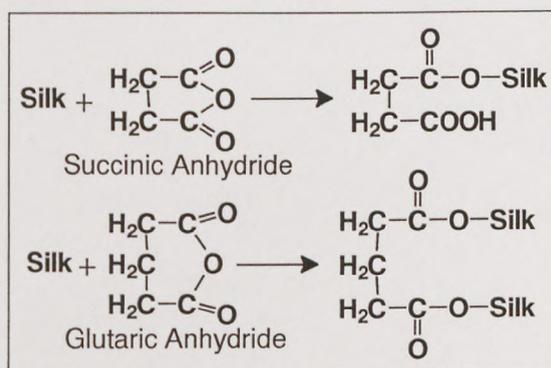


Figure 1. 24 Proposed mechanism by Tsukada et al. for the reaction of succinic and glutaric anhydrides with silk (108)

Of the aromatic anhydrides studied, *o*-sulfo-benzoic anhydride was more reactive towards silk fibroin than phthalic anhydride. This was attributed to the presence of the electronegative sulfonic group. *o*-sulfo-benzoic anhydride-treated fibres showed only a slight increase in fabric crease-recovery whereas silk treated with phthalic anhydride had increased crease recovery properties. The number of both the acidic and the basic amino acid residues in silk fibroin had decreased after modification with aromatic acid anhydrides (110).

Modification of silk fabrics with acid anhydrides could prove promising in the future for changing dyeing properties, or improving crease recovery and resistance to photoyellowing of silk fabrics. One disadvantage of this technique is that it is a solvent finishing process.

1.2.2.6 Polycarboxylic Acids.

A non-formaldehyde crease-resistant finish using polycarboxylic acids, (PCAs), as inter-fibre cross-linking agents have been studied by Yang and Li, 1993 (112). The addition of chemical cross-links to polymers restricts the relative movement of the chain monomers in water and increases the wet resiliency. Treatment of silk with 1,2,3,4-butane tetracarboxylic acid (BTCA) or citric acid (CA) was studied in the presence of sodium hypophosphite (SHP) as a catalyst, and 8% w/w formic acid (FA) as a swelling agent and a 1% w/w non-ionic aqueous polyethylene emulsion softener.

Yang and Li found that the treated silk fibres showed improved dry and wet crease recovery angles which were relatively stable to 50 wash cycles. The finished silk retained 80% of its original breaking strength and showed an increase of more than 100% in tear strength. There was a decrease in fabric whiteness and an increase in fabric stiffness. Yang and Li compared the finish to that of trimethylolmelamine; one of the most successful formaldehyde-containing easy-care finishes for silk, see Table 1. 11.

Reactant	DCRA (degrees)	WCRA (degrees)	% Retention Tensile Strength		Stiffness mg.cm	Whiteness Index CIE
			Warp	Weft		
Control	265	217	100	100	67.7	75.7
BTCA/SHP cure 180°C/1.5min	311	263	92	81.8	83.3	56.6
BTCA/FA/SHP cure 180°C/1.5min	309	253	96.9	89.1	81.7	59.4
CA/FA/SHP/TEA cure 180°C/1.5min	286	294	97.8	83.8	88	48.8
TMM/FA/Catalyst cure 135°C/3min	293	256	96.9	82.1	148.8	71.5

Table 1. 11 Summary of properties comparing TMM and PCA finishing of silk fibroin (112, 113).

FA has been used to notably improve the finishing effectiveness of TMM-treated fabrics (82), by aiding full swelling of silk to assist penetration of the finishing agent. PCAs are organic acids and as such can swell silk; therefore the addition of FA may not be

needed.

Triethanolamine (TEA) was added to the pad bath containing 7% w/w CA and 6% w/w SHP to act as a synergist for the cross-linking agent; FA and a non-ionic aqueous emulsion of polyethylene as a softener were also present. At a concentration above 7% w/w citric acid the finish formed a thick layer on the surface of the fabric decreasing the resiliency and the whiteness of the fabric. They found that conditions that favoured good DCRA were unfavourable to WCRA and vice versa. An increase in concentration of TEA in the pad bath aids WCRA but not DCRA. An increase in curing temperature from 150°C to 190°C improves DCRA but decreases the WCRA and increases fabric yellowing. However, at temperatures above 180°C decomposition of citric acid decreases the effectiveness of the finish.

Yang and Li (114) looked at the dyeability of PCA-finished silk fabrics using acid, basic and direct dyes. They found that if the fabric was dyed prior to finishing there was a decrease in colour strength of the silk fabric but an increase in colourfastness to laundering. If pre-finished the dyeability for anionic dyes e.g., acid and direct dyes, decreased, but the dyeability of cationic dyes increased. Generally silk fabrics finished with PCAs had good dyeability.

This initial study of PCA-finishing of silk fibroin indicates that it could provide good easy-care characteristics. PCAs are non-odorous, non-toxic, and have low oral and dermal toxicity, making them safe finishing agents.

1.2.2.7 Polyurethane Coatings.

More recently Tsang and Dhingra (1996) have studied the use of polyurethane coatings to enhance the performance of silk textiles. These have been used in conjunction with a sandwash finish, (see section 2.7.3.3), to help reduce the problem of garment care, creating silk products which are water-resistant, shrinkage-resistant, and crease-resistant (115, 116).

Polyurethane polymers contain urethane linkages and can be prepared by the polymeric addition reaction of diols and diisocyanates (see Figure 1. 25). A number of different kinds of polyurethanes can be produced depending on the nature of the monomers used

and the degree of cross-linking, and the resultant polymers can range from soft elastomeric to hard glassy materials. They have various end uses, as foams, elastomers, coatings, adhesives, sealants, films, and plastics (115).

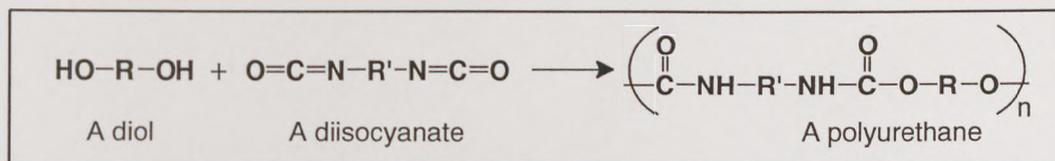


Figure 1.25 Nucleophilic addition of a diol to a diisocyanate to give a polyurethane (20).

Polyurethane elastomers can be 'tailor-made' according to the specific needs of the coating. Mechanical properties such as elasticity, tensile strength, tear resistance and hardness of the polymer depend on the degree of cross-linking of the chain structures and the relative amounts of soft, flexible and hard, rigid chain segments. The coating needs to be soft, transparent, and elastic, have good adhesion to the substrate and be resistant to degradation by light and polar solvents.

The polyurethane coating is applied to the back of the silk fabric by a direct or a transfer coating process. These coatings are generally classified as reactive coatings as they cross-link with the silk fibroin. The mechanical properties of polyurethane-coated silk fabrics are slightly altered compared with untreated samples. Tsanga and Dhingra (116) showed that generally there was an increase in the resistance to shear and bending but a decrease in the resistance to tearing. The coated side of the silk fabric is essentially a composite structure hence the relative movement of the threads within the structure is reduced, but the fibre-to-fibre adhesion is improved resulting in increased tensile strength retention.

1.3 OVERVIEW OF RESEARCH IN THIS THESIS.

The necessity of garment easy-care characteristics is becoming more and more important due to the change in modern living styles. If silk is to maintain its market share the inferior fabric properties of silk such as, poor wet resiliency, low resistance to abrasion and photoyellowing in sunlight, need to be improved during silk fabric processing. In silk finishing there is a gap in the market for a product that can impart true easy-care characteristics and thus further investigations were deemed desirable.

1.3.1 Literature Review.

Previously in this chapter (section 1.1) a review of the structure and properties of silk fabrics was undertaken as it was thought important to update any previous literature reviews and to look at the structure of silk fibroin with a chemical bias. A literature review of previous easy-care finishing treatments for silk fabrics was also undertaken, see section 1.2. Of the techniques previously studied to improve the easy-care characteristics of silk fabrics polycarboxylic acid (PCA) finishing was seen to be the most promising. It is a non-toxic, non-odorous, aqueous finishing system that has been used to cross-link cotton cellulose with some success. Treatment of silk fabrics with epoxides, grafting agents or acylating agents all take place in organic solvents. These increase the cost of the finishing system and are not as environmentally friendly as an aqueous system.

There is very little work reported in the literature on the chemical modification of silk fabrics with PCAs. The author drew upon the literature associated with PCA easy-care finishing of cotton cellulose (section 3.1) as it was expected that the hydroxyl-containing amino acids of serine, threonine and tyrosine in silk fibroin would react similarly to the hydroxyl groups of cotton. It is the hydroxyl groups in cotton cellulose that are believed to react with the PCAs during high temperature curing to form stable di-ester bonds (117).

1.3.2 Experimental Work

The practical work associated with this thesis is the first work to undertake a comprehensive study of the finishing of silk fibres using a PCA cross-linking system. This was split into the following three chapters.

1.3.2.1 Chapter Three.

Initial experiments verified the possibility of using PCAs as zero-formaldehyde chemical modification agents to improve the easy-care characteristics of silk fabrics. A comparison was made with that of the more traditional methylol melamine-finishing agent. Investigations were carried out into optimising the effectiveness of the process by maximising the quantity of chemical add-on achieved during the finishing process.

1.3.2.2 Chapter four.

An in-depth analysis of PCA/catalyst systems was undertaken using thermoanalytical and Fourier-transform infra-red spectroscopic techniques in which the conditions encountered by the polycarboxylic acids during curing were mimicked. It was hoped that an alternative method would be found for determining the effectiveness of a PCA/catalyst system as an easy-care finish. Selected systems were investigated by the more traditional methods of padding and testing and their suitability as chemical modification agents for silk fibroin reported.

1.3.2.3 Chapter five

Finally in chapter five research was undertaken into the effect of pad bath additives in the form of softening and stiffening agents either on their own or in combination with PCA cross-linking systems, to provide a multi-functional easy-care finish. The properties of the fabrics treated with these finishes were assessed.

2. EXPERIMENTAL AND FABRIC TEST METHODS.

2.1 EXPERIMENTAL PROCEDURE.

The experimental procedure involved preparing the samples, padding them in an aqueous pad bath, followed by drying and high temperature curing. The fabric samples were processed at open width to prevent the development of latent creases.

2.1.1 Sample Preparation.

The fabric, Habutai Silk, obtained from Whaleys of Bradford Ltd. There were five different rolls of fabric used in the practical work associated with this thesis; the fabric specifications for these fabrics are outlined in Table 2. 1.

Roll Number	Fabric Type	Ends/cm	Picks/cm	Fabric Weight g/m ²
1	Silk Noil	23.2	18.7	163.91
2	Habutai Silk (Medium)	51.2	46.5	35.95
3	Habutai Silk (Medium)	51.1	47.7	36.21
4	Habutai Silk (Heavy)	60.2	40.2	44.06
5	Habutai Silk (Heavy)	60.7	39.8	43.39

Table 2. 1 Fabric specifications of silk fabrics used in this thesis.

The silk fabric was cut into samples 250mm by 400mm. The silk samples were pre-shrunk by immersing them in cold water for 20 minutes, line dried and conditioned for 48h at $21 \pm 1^\circ\text{C}$ and $65 \pm 2\%$ relative humidity. The moisture content of the fabric sample must be uniform and constant in order to achieve an even pick-up.

2.1.2 Padding.

The chemical reagents used in the experimental work associated with this thesis are listed in Table 2. 2.

Chemical Reagent	Supplier
Permafresh Mel 68% solution (MF)	Warwick International Specialists Ltd.
Magnesium chloride hexahydrate (MgCl ₂)	BDH, Merck Ltd.
1,2,3,4-Butane tetracarboxylic acid (BTCA)	Lancaster Synthesis
Citric acid (CA)	Aldrich Chemical Company
Maleic acid (MA)	Lancaster Synthesis
DL-Malic acid (MLA)	BDH, Merck Ltd.
Itaconic acid (IA)	Aldrich Chemical Company
Pyromellitic acid (PMA)	Aldrich Chemical Company
Succinic acid (SA)	Aldrich Chemical Company
Glutaric acid (GA)	Aldrich Chemical Company
Phthalic acid (PA)	Aldrich Chemical Company
Terephthalic acid (TPA)	Aldrich Chemical Company
Sodium hypophosphite hydrate(SHP)	Aldrich Chemical Company
Monosodium citrate (MSC)	Aldrich Chemical Company
Disodium citrate (DSC)	Aldrich Chemical Company
Trisodium citrate (TSC)	Aldrich Chemical Company
Monosodium maleate (MSM)	Sigma Chemicals
Disodium maleate dihydrate(DSM)	Lancaster Synthesis
Monosodium tartrate (MST)	Lancaster Synthesis
Disodium tartrate (DST)	BDH, Merck Ltd.
Cyanamide (CY)	Aldrich Chemical Company
Ceranine L (CL)	Clariant
Polyethylene glycol 200 (PEG 200)	BDH, Merck Ltd.
Polyethylene glycol 400 (PEG 400)	BDH, Merck Ltd.
Polyethylene glycol 600 (PEG 600)	BDH, Merck Ltd.
Polyethylene glycol 1000 (PEG 1000)	BDH, Merck Ltd.
Ultratex SW (SW)	Ciba Dyes and Chemicals
Ultratex FEW (FEW)	Ciba Dyes and Chemicals
Acrylic acid (AA)	Aldrich Chemical Company
Polyacrylic acid (AA)	BDH, Merck Ltd.
Formic acid (FA)	Lancaster Synthesis
Sodium iodide (NaI)	Aldrich Chemical Company
Zinc chloride (ZnCl ₂)	Aldrich Chemical Company
Lithium chloride (LiCl)	BDH, Merck Ltd.

Table 2.2 Chemical reagents used in the experimental work associated with this thesis

The fabric samples were dipped in the pad liquor for a few seconds to allow the sample to wet out before being squeezed in-between the rubber bowls of the Ernst Benz Laboratory Padding Mangle under 4.5 kg/mm pressure. The process was repeated, giving a two dip, two nip padding process; this aids the uniform impregnation of the finishing agent. The speed of rotation of the rubber squeeze rollers and the pressure on the rolls were adjusted to achieve the desired fabric wet pick-up. The percentage wet pick-up was set between 90-95% and calculated as follows:

$$\text{Wet pick-up (\%)} = \frac{(\text{Weight of fabric after padding} - \text{Conditioned Weight})}{\text{Conditioned Weight}} \times 100$$

2.1.3 Batching.

After padding, the samples that underwent a batching process were individually placed and sealed inside plastic bags to avoid the pad liquor of one sample contaminating another and placed on a slow rotating batching roller for five hours. Fabric is rotated to ensure that the aqueous liquor remains evenly distributed throughout the batching process.

Batching allows additional time for both fibre swelling and diffusion of the padded chemicals inside the fibre to take place. In a swollen fibre there is an increase in the accessible area within the fibre for the padded chemicals to migrate to, and it is anticipated that both the evenness and the efficiency of the process would be improved.

2.1.4 Drying.

Traditional padding or batching processes involve impregnating the fabric with an aqueous solution and then removing the water to leave the finish trapped inside the fibre. In the drying process the fabric was mounted on the pin-frame of the Ernst Benz drying oven and passed through the oven at 80°C for two minutes. The samples were dried at a controlled temperature using hot air currents that were kept constant by the electrical heating system and a circulating fan (118). It is important during drying that the distribution of the reagents within the fibre is not disturbed. The water must evaporate off the surface of the fabric quicker than it diffuses out from the interior. This prevents the water-soluble matter concentrating on the surface. The oven must be kept at a constant temperature in order to prevent the migration of the reagents towards hotter parts of the fabric (81).

2.1.5 Curing.

The high temperature curing process provides the necessary energy for a reaction to take place, either a self-reaction with the finish or a reaction between the finish and the fabric, thus fixing the finish inside the fabric. It is important that the fabric finish once applied will remain operational for the useful life of the textile.

The dried fabric was mounted on a pin frame and cured for a pre-scheduled time period at a controlled temperature using the Werner Mathis AG curing oven. The hot air currents were maintained at a constant temperature by a heating device and a fan. Again it is important to keep the oven at a constant temperature as an uneven distribution of heat gives rise to uneven results. The fabric can be heated either by dry heat or by steam. Dry heat is the more common curing state.

Dry curing of fabrics is carried out at temperatures in excess of the boiling point of water. As the fibre dehydrates, the fibre swelling is reduced and the molecular entanglements within the amorphous regions are brought closer together to form a three-dimensional lattice with an improved response to deformation in the dry state. The absorption of moisture from the atmosphere and also fibre swelling are restricted due to the cross-links inserted during dry curing. As the fibre tries to swell the cross-links become taut and it is these forces that lead to improved fabric dry crease recovery (45).

It has been shown (119) that by steam curing it is possible to produce cotton goods with improved resistance to abrasion. This is due to the fabric being cured in the swollen state. The presence of moisture prevents the formation of hydrogen bonds between the molecular chains in the amorphous regions of the fibre. This gives rise to fabrics that are more relaxed with an improved recovery to wet creasing but no improvement in the dry state (81).

2.1.6 Washing.

All cured samples were after-washed at open width in a liquor containing 2g/l Sandozin NI (Clariant) for about 10 minutes at 50°C, followed by a thorough rinsing in cold tap water to ensure the removal of any uncombined reagents. The washed samples were dried on the Ernst Benz drying oven for two minutes at 80°C.

2.1.7 Conditioning.

In any given atmosphere textile fibres take up or lose water at a gradually decreasing rate until an equilibrium is reached (120). A dynamic equilibrium is reached where the number of water molecules evaporating from the specimen in a given time is equal to the number condensing and being absorbed at any one time. The properties of fibres and fabrics are altered by the quantity of moisture they have absorbed. The absorption of moisture causes fibres to swell and alters the dimensions of yarns and fabrics. Thus changes can occur in the size, shape, stiffness, and permeability of yarns and fabrics. The mechanical and frictional properties of yarns and fabrics vary with moisture content and consequently the behaviour of yarns and fabrics in processing and use also varies.

In order to be able to compare the results of one test with another all finished fabrics were conditioned in the standard atmosphere of $21\pm 1^{\circ}\text{C}$ and $65\pm 2\%$ relative humidity for at least 48 hours prior to testing.

2.2 CHEMICAL TEST METHODS.

The finished samples were tested for percent chemical add-on, moisture regain and the chemical reaction of the finish with the fabric was evaluated using Fourier transform infra-red spectroscopic analysis. In addition a few samples were tested for solubility in 97% formic acid solution.

2.2.1 Moisture Regain (121).

Silk, like most natural fibres, is hygroscopic; it absorbs water vapour from a moist atmosphere and loses water in a dry atmosphere. Many of the physical properties of silk are affected by the quantity of water it has absorbed e.g. crease recovery angle, tensile strength, elastic recovery, bending rigidity, etc. Therefore before testing these physical properties the moisture regain under standard conditions was calculated. The insertion of additional cross-links during fabric finishing may restrict fabric swelling and decrease the amount of water that the fabric is able to absorb (45).

“Regain is defined as the weight of water in a material expressed as a percentage of the oven dry weight (45)”.

$$\text{Regain} = ((\text{Conditioned Weight} - \text{Bone Dry Weight}) / \text{Bone Dry Weight}) \times 100\%$$

The regain of a sample is dependent on time, temperature and the previous history of the specimen. Sufficient time is needed for the sample to reach equilibrium before testing can commence. There is a hysteresis in the relation between the regain of a sample and the atmosphere with which it is in equilibrium. A sample that has been taken from a wetter atmosphere has a higher regain than a sample taken from a dryer atmosphere prior to conditioning. As can be seen from Table 2.3, a plot of the desorption isotherm for a specimen initially wet at successively lower humidities, does not follow the same route as the adsorption isotherm, a plot of equilibrium regains at successively higher humidities.

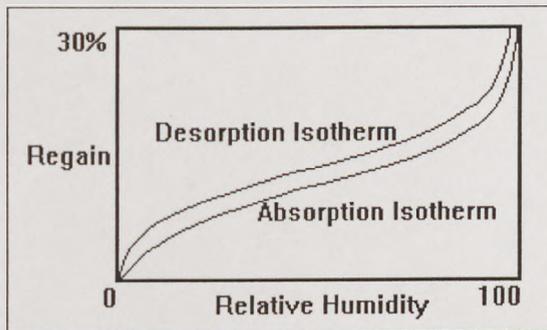


Table 2.3 Typical hysteresis of silk fabric with respect to fabric regain (45).

The conditioned samples (250mm²) were placed in numbered, pre-weighed weighing bottles, weighed and their conditioned weight calculated. The bottles were then placed in a ventilated drying oven for 2 hours at 110°C, placed immediately inside a vacuum desiccator over silica gel and allowed to cool for 30 minutes. The desiccator was opened, the weighing bottles were quickly sealed and weighed using an electronic balance. This process was repeated until a constant weight was achieved. Fabric regains were calculated using the above equation for all finishing methods after padding.

2.2.2 Chemical Add-On.

The bone-dry weights calculated as for moisture regain in section 3.2.1. were used to determine the percent chemical add-on for each finished sample.

$$\text{Chemical Add-on (\%)} = [((W_a - W_b) / W_b) \times 100\%] + \text{correction factor \%}$$

Where W_a = Bone dry weight of finished sample, W_b = bone dry weight of the sample prior to finishing, and the correction factor is the chemical add-on for a control sample that is padded with deionized water. A correction factor takes into consideration the small loss of fibre that occurs during the finishing process and any slight alteration in

conditions of the weighing process.

2.2.3 Infra-Red Analysis.

The infra-red region of the electromagnetic spectrum, ranges from 7.8×10^{-5} cm, which is just above visible to 10^2 cm. Only the middle portion from 2.5×10^{-3} cm to 2.5×10^4 cm is used in chemical analysis of organic compounds. Wavelengths within the spectrum are usually given in micrometers, $1\mu\text{m} = 10^{-4}$ cm, and frequencies are expressed in wave numbers, which are the reciprocal of the wavelengths in cm, expressed in cm^{-1} .

Infra-red spectroscopy involves the irradiation of organic compounds with infra-red light, whereby certain frequencies are absorbed, but others are not. The absorbed frequencies correspond to the amounts of energy distributed throughout the structure of the compound. These relate to specific molecular vibrations such as bending and stretching. A molecule can stretch, bend or vibrate only at those frequencies that correspond to specific energy levels. Every functional group has a characteristic set of infra-red absorptions, because each light frequency absorbed by the molecule corresponds to a particular type of molecular motion.

It is possible to use infra-red analysis to analyse the functional groups in a molecule by observing which frequencies of infra-red radiation are absorbed and which are not. A complete interpretation of an infra-red spectrum of large organic molecules is difficult because there are so many different bond stretching and bending vibrations. However, valuable structural information can be obtained from the infra-red spectrum by observing characteristic absorptions of functional groups (20).

2.2.3.1 Fourier transform infra-red (FTIR) spectroscopy.

A Fourier transform infra-red spectrophotometer was used to analyse the chemical finishing agents and finished silk fabrics used in this thesis. It combines infra-red spectroscopy with on-line data analysis and computing facilities. This allows for direct analysis of spectra either on their own or in combination. Two different methods of infra-red spectroscopy were used: attenuated total internal reflectance (ATR) spectroscopy was used to analyse the finished silk fabrics; and transmission spectroscopy was used to analyse the finishing agents themselves.

2.2.3.1.1 ATR spectroscopy.

This technique was used for analysing silk fabric samples. The spectrophotometer was set up with a gain of 8, resolution of 4cm^{-1} and programmed to run 64 scans per sample. Between each sample a background scan of the ATR unit was run; this is automatically subtracted from the sample spectra. Two pieces of silk were cut out and placed one either side of the ATR crystal (KRS-5 thallium bromide, thallium chloride crystal). The ATR unit was done up very tight; the closer the contact between the ATR crystal and the silk the better the spectra obtained.

The ATR crystal is made of a high refractive index infra-red transmitting material and thus the infra-red radiation entering the crystal is totally internally reflected, see Figure 2. 1. This internal reflectance extends beyond the surface of the crystal creating a small evanescent wave that extends to the sample held in close contact with the crystal. This wave fades very quickly with distance and it is therefore important for the sample to be in very close contact with the crystal in order to analyse the absorption spectra of the sample.

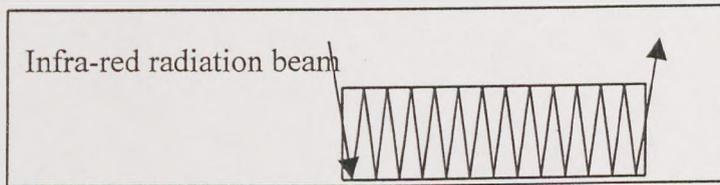


Figure 2. 1 ATR crystal with 25 points of reflection.

The absorption spectra were analysed using the data analysis package and semi-quantitative results were obtained by comparing one sample with another.

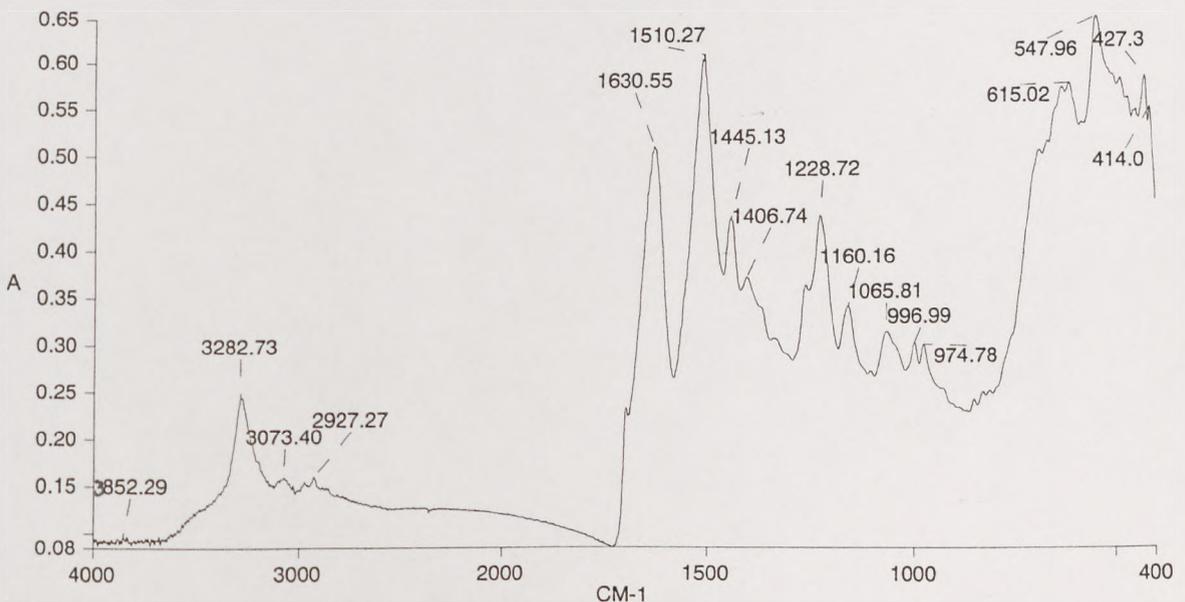


Figure 2. 2 ATR absorption spectra of silk fibroin.

Band Name	Wave number cm ⁻¹	Description of Band	Description of Molecular Vibration
Amide A	3280	N-H Sensitive to changes in degree of crystallinity and isotope exchange	N-H
Amide B	3080	N-H Stretching	N-H Stretching
Amide I	1660	α -(random coil conformation) form	C=O Stretching (principal) N-H deformation
	1630	β -(pleated sheet conformation) form	C-N Stretching
Amide II	1540	α -form	C-N Stretching
	1530	β -form	N-H deformation (principal)
Amide III	1234	α -form	C-N Stretching (principal)
	1265	β -form	N-H deformation
Amide V	650	α -form	N-H deformation
	700	β -form	
	975	Ala-Gly	
	998	Gly-Ala	

Table 2.4 Frequency and assignment of infra-red bands for silk fibroin (13).

Figure 2.2 shows an ATR absorption spectra for untreated silk fibroin. The absorption bands are described in Table 2.4. This untreated ATR silk fabric spectra was used as a control; this was subtracted from the ATR spectra of the treated samples. The difference between the two ATR spectra was used as a semi-quantitative analysis tool. ATR spectra of the same scale were printed out and the relevant peak heights were measured in mm using a ruler.

2.2.3.1.2 Transmission spectroscopy.

This technique was used for analysing the chemical reagents used in this thesis. 1mg of the chemical to be studied was ground into a fine powder with 150mg of potassium bromide (KBr) and a disc made by placing the sample mixture in a die and subjecting it to high pressure. KBr is used as a carrier for the sample. The KBr in the disc does not absorb infra-red radiation within the frequencies normally employed in infra-red analysis. The spectrophotometer was set up with a gain of 1, resolution of 4cm⁻¹ and programmed to run 16 scans per sample. Prior to scanning the KBr disc a background scan with nothing in the beam was taken; this was automatically subtracted from the sample spectra. The transmission spectra were analysed using the data analysis package on the computer.

2.2.4 Solubility In Formic Acid Solution.

It is known that a concentrated solution of organic acids such as formic acid can

dissolve silk (82), and in the past it has been used as a method for indicating the presence of cross-links in silk fabrics treated with methylol compounds. The solubility of selected samples in 97% formic acid solution was observed. 0.5g of silk was cut up into very small pieces, placed in a test tube in a fume cupboard and 5cm³ of formic acid (97%) was added at room temperature. The samples were left for three days at room temperature and visual comparisons with a control sample (untreated silk) were made.

2.3 PHYSICAL TEST METHODS.

The physical properties of a material depend on the nature and stereochemistry of the molecules from which it is composed. These vary within a fabric, from one fibre to another and from one condition of the material to another. The condition of a specific material depends on its processing history, including mechanical treatment, on its moisture content and temperature. All testing was carried out in the standard atmosphere of $21\pm 1^\circ\text{C}$ and $65\pm 2\%$ relative humidity, thus minimising the variation in moisture content and temperature of the tested samples. Conditioned samples are referred to as 'dry' samples in this experimental work. Wet samples refer to conditioned samples that have been immersed in deionised water and placed between two pieces of blotting paper to remove any excess water before the sample was tested.

The physical changes in fabric properties of the treated samples have been evaluated with respect to their crease recovery angle, tensile strength, elongation at break, fabric abrasion, and bending length. The samples for testing were cut out from the centre of the specimen leaving a 50mm perimeter.

2.3.1 Tensile Properties Of Fabrics.

If a small force is applied to a silk fabric extension occurs due to a slight stretching of the fibroin chain molecules and a straightening of chain molecules in the non-crystalline regions of the fibre, with a resultant straining of the ionic bonds (hydrogen bonds and salt links) between chains. The total extension will be proportional to the applied force. On removal of the force the molecules and cross-links in silk fibroin will normally spring back to their initial positions (45).

If the force applied is increased some of the more highly strained cross-links in the amorphous regions of the fibre will break. Under conditions of increased stress the

most strained cross-links become less stable and are easily broken by thermal vibrations within the fibre (48). This results in an increased straightening of the fibre and transfers the increased force to other cross-links. When the force is removed recovery is incomplete because some of the original cross-links are now broken and hence they cannot spring back to their initial positions, while new hydrogen bonds that were formed in the extended state tend to stabilise a new deformed state.

Under conditions of further stress a point is reached where further extension and straightening of the fibre molecules becomes difficult as an increasing strain is put on the cross-links and molecules, and finally breakage occurs.

Easy-care finishing of cotton cellulose has an adverse effect on the tensile properties of fabrics (81). A number of factors could contribute to this effect including, high curing temperatures, increased fibre cross-linking making the fibre brittle, the use of a softener decreasing inter-fibre friction, or acid or alkaline reagents in the pad bath causing hydrolysis of the cellulose chains, etc (81). The tensile properties of silk fabrics treated with various finishing agents were studied using an Instron tensile testing machine.

2.3.1.1 Instron Tensile Testing Machine (122).

The Instron 1026 tensile testing machine is a versatile instrument that is attached to a computer and can be programmed to operate a large variety of tensile tests. The machine was programmed to test for

- **Breaking Load:** The load at which the fabric specimen breaks. This is a measure of the steady force necessary to break the fabric specimen and was given experimentally by the maximum load developed in a tensile test.
- **Breaking Extension:** The elongation necessary to break the fabric sample. This is a measure of the resistance of a material to elongation and was expressed as the actual increase in length of the specimen.

Samples for testing were cut out, 120mm by 10mm, and the yarns were teased out to incorporate exactly 20 threads. The samples were mounted vertically between the upper moveable jaws of the Instron. A small weight was attached to the bottom of the sample to ensure that when the fabric sample was clamped between the lower fixed jaws the

same amount of tension was applied to each sample. The upper and lower fixed jaws were set at a distance of 75mm apart. The jaw clamps were opened and closed using high air pressure that was controlled by the operator's foot. The dimensions of the specimens have a direct effect on the results of the test; breaking load increases with an increase in volume of the specimen and elongation is proportional to the length of the sample. All samples tested consisted of 20 warp threads and the length tested was kept constant at 75mm.

A 5kg load cell was inserted above the upper jaws and the machine was programmed to begin the required tests. The upper jaws moved upwards during the test extending the sample until finally the sample broke. In order to standardise the conditions of the test, all tests used a 5kg load cell and the samples were extended at a constant rate of extension (50mm/min) throughout the test. The tensile strength and elongation at break were displayed directly on the computer screen. Ten samples per specimen were tested, five dry and five wet and the mean values and standard deviations were calculated by the computer.

2.3.1.1.1 Variation in tensile strength tests.

There was variation in the tensile strength tests, both breaking strength and elongation at break, between the five samples tested, in the dry state and in the wet state. Silk fabrics exhibit some variation in properties; there is some variation between filaments spun by different silkworms as well as variation along the length of the filament. There may also be some variation in yarn construction and in fabric weaving. To minimise this variation the tested fabric contained exactly 20 warp threads and a fixed length of 75mm was tested each time.

It can be assumed that the tensile strength test from one fabric sample has a fixed probability distribution that satisfies standard normal distribution, (also known as Gaussian distribution) (123). This has the probability density function,

$$P(x) = \frac{1}{(2\pi\sigma^2)^{1/2}} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right) \text{ for } -\infty < x < \infty$$

where μ is the true mean and σ^2 is the variance of the true mean.

To ascertain the statistical properties within a set of tensile strength test results the sample mean, $\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i$ and the sample variance, $s^2 = \frac{1}{n-1} \left[\sum_{i=1}^n x_i^2 - n\bar{x}^2 \right]$ were calculated by the computer. As n approaches ∞ , the sample mean and sample variance tend towards the true mean and variance of the sample.

For a random variable x_k the probability that it lies within the interval $a \leq x_k \leq b$ is,

$P(a \leq x_k \leq b) = \int_a^b P(x) dx$. There is a probability of approximately 0.95 that a random

variable x_k will be contained in the interval $\mu - 2\sigma \leq x_k \leq \mu + 2\sigma$. This rule cannot be applied directly to the tensile strength test results in this thesis, because the sample size taken was too small to calculate the true mean and standard deviation. However, a standard probability correction table, called the t-distribution table, accounts for uncertainty of this type.

Given a sample of n observations, the confidence level required for the data (i.e. 95%) is selected. The probability correction value α_r is found for the appropriate number of degrees of freedom ($\nu = n - 1$) for the sample.

	α_{10}	α_5	α_1		α_{10}	α_5	α_1
V	90%	95%	99%	ν	90%	95%	99%
2	2.920	4.303	9.925	18	1.736	2.101	2.880
4	2.132	2.776	4.604	20	1.725	2.086	2.845
5	2.017	2.572	4.034	30	1.697	2.042	2.750
6	1.943	2.447	3.707	40	1.684	2.021	2.704
8	1.860	2.306	3.355	50	1.678	2.011	2.682
10	1.812	2.228	3.169	∞	1.645	1.960	2.576

Figure 2.3 t-distribution table (123)

Using the calculated sample mean \bar{x} and variance s_x^2 , the standard error $s_{\bar{x}} = \frac{s_x}{n}$ and the confidence level for the population mean $\bar{x} - \alpha_r s_{\bar{x}} \leq \mu \leq \bar{x} + \alpha_r s_{\bar{x}}$ for the sample can be calculated. The true mean has a set probability of being within this range of values.

The mean values for the dry and wet tensile strength test results were calculated as a percent retention of the untreated sample. It was assumed that each test specimen within a sample was independent. Taking n tests for each (in this thesis $n = 5$), the test

results can be written,

Untreated control x_1, x_2, \dots, x_n ; mean = \bar{x} ; standard deviation = s_x

Treated sample y_1, y_2, \dots, y_n ; mean = \bar{y} ; standard deviation = s_y

The means \bar{x} and \bar{y} and the standard deviations s_x and s_y were calculated and from

these the mean percent retention of the treated fabric sample $\bar{T} \% = \left(\frac{\bar{x} - \bar{y}}{\bar{x}} \right) \times 100\%$ and

its standard error $s_{\bar{T}} \% = \left(\frac{s_x^2 - s_y^2}{s_x^2} \right) \times 100\%$ can also be calculated.

These were used to calculate the fabric tensile properties confidence limits $\bar{T} \pm \alpha_r s_{\bar{T}}$,

where α_r is taken from the t-distribution table above and has $\nu = (n-1)$ degrees of freedom. For each experiment a 95% confidence level was calculated

$\bar{T} - \alpha_r s_{\bar{T}} < \mu < \bar{T} + \alpha_r s_{\bar{T}}$ to show that there is a 95% certainty that the true mean lies within this range. The 95% confidence limits for fabric tensile strength tests are given in Table 2. 5; these are reported as maximum percent mean variation for each type of test at 95% confidence levels.

Fabric Tensile Strength tests	95% Confidence Levels
Dry Fabric Percent Retention Maximum Load at Break	< \pm 8.7%
Wet Fabric Percent Retention Maximum Load at Break	< \pm 9.1%
Dry Fabric Percent Retention Elongation at Break	< \pm 7.3%
Wet Fabric Percent Retention Elongation at Break	< \pm 5.5%

Table 2. 5 The maximum variation in fabric tensile strength tests expressed as 95% confidence levels.

2.3.1.2 Martindale Abrasion Tester (124).

Abrasion is the rubbing away of component fibres and yarns on the surface of the fabric. This test was undertaken to analyse any changes on this aspect of fabric wear caused by the applied finishes. Fabric wear refers to a combination of external forces that decrease the serviceability of a fabric; forces such as bending, stretching, tearing, abrading and laundering are important factors determining fabric wear (125).

The instrument chosen for the test was the Martindale Abrasion Tester. This operates by using a flat, multi-directional rubbing motion to abrade the sample. A standard cotton fabric (plain woven, scoured and bleached cotton fabric, 23 ends and picks per

cm) was used as the abradant; every sample was abraded against a fresh abradant. Circles of cotton fabric 155mm in diameter were cut out and mounted on to the machine using a flat weight to minimise variations in tension of the abradants. Four circles, 35mm in diameter, were cut out from each specimen, placed over a piece of foam of the same size and screwed into the sample holder using the mounting area provided on the machine. By minimising the variation in the technique used to mount the sample, the variations in tension of the samples were minimised. Care was taken to prevent either the samples or the abradant from becoming soiled prior to testing. The number of cycles necessary to abrade the samples were noted and an average from the four samples per specimen was calculated.

2.3.1.3 Fast-2: Bending Length.

The bending properties of fabrics are important when concerned with the aesthetic characteristics of fabrics such as handle and drape. Fabric bending length is a measure of fabric stiffness (120). This is the length of fabric that will bend to a specific angle under its own weight. The Fast-2 bending meter provides a direct measure of fabric bending length (mm).

The Fast-2 bending meter is designed to measure the bending length in mm of a 50mm wide strip of fabric to an angle of 41.5° from the horizontal. It is a fixed angle flexometer, and the fabric bends under its own weight until its leading edge cuts a beam of light inclined at 41.5° to the horizontal.

The specimen is cut to size with the aid of a template, and transferred to the platform, a metal slider is placed over the sample leaving at least 10mm of the leading fabric edge free. The fabric is moved slowly forward with the metal slider towards and over the edge of the cavity, where it is allowed to drape. The Fast-2 bending meter measures the bending length of the fabric at 41.5° and displays the result digitally. The samples were measured four times by turning the sample over and measuring both ends, face and back and the mean value calculated. Samples were cut in both warp and weft directions.

2.3.2 Creasing Behaviour Of Fibres.

When a fabric is creased, the fibres bend placing them in a position of strain additional

to that imposed from spinning or weaving (81). The fibres on the outer edge of the crease are held under tension, while the inner fibres are compressed. Elod, Holz and Graeser (126) showed that the recovery from creasing of a fibre is largely dependent on the elastic recovery from extension. Although some extension of the fibre must take place when a fabric is bent in a position of strain, this cannot be greater than the elastic recovery of the fibre at that given extension if creasing is to be avoided.

Elasticity is defined as 'the property of a body by virtue of which it tends to recover its original size and shape after deformation,' and is opposite to plasticity (45).

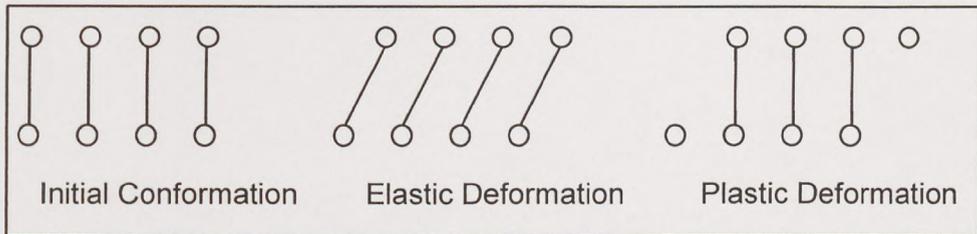


Figure 2. 4 Schematic illustration of elastic and plastic deformations (45).

At the molecular level, elastic deformation involves the stretching of inter-atomic and inter-molecular bonds, whereas plastic deformation involves the breaking of bonds and the formation of new bonds in new positions thus stabilising a new chain conformation. It follows that a deformation may be divided into elastic and plastic parts, that which is recoverable and that which is not. Elastic recovery can be quantitatively defined using the following equation:

$$\text{Elastic Recovery (\%)} = \frac{\text{Elastic Extension}}{\text{Total Extension}} \times 100\%$$

The elastic recovery from extension of silk fibres is 92% at 2% extension and 70% at 5% extension (44).

The creasing properties of a fabric are influenced by the force applied to the fabric. The permanence of a crease depends upon the mass of the load and the length of time for which it is applied. When the force applied is large enough to exceed the initial elastic limit of the fibre (that is the linear portion of the stress/strain curve) primary creep occurs. New forces of attraction form in the direction of the stress while the old forces tend to relax, producing strain in the fibre. This primary creep is reversible with time under the same conditions of temperature and humidity. Secondary creep occurs when the immediate elastic limit of the fibre is exceeded; it is not reversible. The chain

molecules are able to slip apart from one another and take up new preferred positions (45). The total extension of a fibre can be thus divided into three parts: the immediate elastic deformation, which is instantly recoverable; primary creep which is recoverable with time; and secondary creep which is not recoverable.

The polypeptide chains in silk fibroin are pleated and it is the stretching and contracting of these folded chains that allows for the good extensibility and recovery properties of the fibre. In the amorphous regions the large numbers of bulky side-groups give rise to a more open-packed structure leading to greater movement and flexibility within the fibre (44). Part of the flexibility and elasticity of a fibre at low extensions is due to the straightening of molecules within the amorphous regions. A limited amount of extension and compression can occur in these regions where the hydrogen bonds are few in number and widely distributed.

The moisture absorbed by the fibre from the atmosphere acts as an internal fibre lubricant breaking some of the hydrogen bonds and allowing the molecular chains to slide over one another in the outer curve of the creased fabric. When the molecular chains move so far that some of the hydrogen bonds within the amorphous regions reform in new positions, a crease is formed (45).

The amount of moisture absorbed by a fibre greatly influences its elastic properties. Water acts both as a lubricant and a plasticiser; when silk fibroin absorbs water and swells the ionic linkages are broken leaving the chain molecules to slip easily and be deformed by any sufficient creasing force. Upon drying or with a decrease in fibre moisture absorption, hydrogen bonding begins to reform in new positions, thus the original structure of the fibre is not retained, and fabric creases can be seen.

2.3.2.1 A Review of Crease Recovery Test Methods.

There are two main methods of measuring the creasing behaviour of fabrics. The first is based on the recovery angle method and the other is based on visual analysis.

2.3.2.1.1 The recovery angle method.

The recovery angle method involves the test specimens (40mm x 15mm) being folded in two, half creased face-to-face and half creased back-to-back in both warp and weft

directions under controlled conditions of temperature, $21\pm 1^\circ\text{C}$, pressure, $65\pm 2\%$ RH, time, $5\text{min}\pm 5\text{s}$, and under a force of 10N. After being creased for 5min the specimens are transferred to the wrinkle recovery tester. The free edge of the specimen is lined up with the vertical guide; in order to eliminate any gravitational effects the test instrument is rotated so as the free edge of the specimen is always in alignment with the vertical guide. The recovery angle of the crease when suspended in the test instrument for a controlled period of time, $5\text{min}\pm 5\text{s}$, is measured and recorded. The average recovery in degrees for each group of three specimens is calculated. If the difference in the face-to-face and back-to-back values for both warp and weft is less than 15 degrees then an average figure is stated for both warp and weft.

2.3.2.1.2 The visual analysis method.

The visual analysis method uses three pre-conditioned test specimens (150 mm weft x 280 mm warp) that have been wrinkled using an AATCC wrinkle tester under a load of 3500g for 20 minutes. The test specimens are then hung vertically from the shorter edge in a conditioned atmosphere for 24h before being mounted on a viewing board between the two nearest three-dimensional plastic replicas for comparison. There are five plastic replicas WR-5 - WR-1, to choose from; WR-5 represents the smoothest appearance and best retention of original appearance. Three trained observers stand directly in front of the specimen, 4 feet away from the board and the only light source should be that of the overhead fluorescent light. The nine observations, three for each specimen are averaged for the final result.

2.3.2.1.3 Alternative methods for assessing fabric creasing.

Assessment of wrinkling by both the recovery angle method and the visual analysis of trained observers are subjective methods of rating fabrics and are often sensitive to biases in perception. The advantages they possess is that they are cheap and simple to conduct. There is a need for a more objective method of testing and over the last few years, several alternatives have been suggested.

“Can wrinkle-prone fabrics be identified?”, a paper by A.E. Johnson, 1969 (127), describes an unusual wrinkle recovery test, “The CSI Wrinkle Rating System”, used mostly by Celanese fibre company laboratories. The test involves pre-wrinkling the fabric samples at various specified humidity levels in a glass cylinder with a collapsible

liner. A plunger arm repeatedly collapses and releases the liner inducing a state of random wrinkling. These fabrics are then spread out on a flat surface, and readings based on a subjective rating system according to shadings produced with an oblique source of light are taken after 1h and 24h.

The wrinkle patterns within the tested samples were rated according to five basic components. Each component was given a weighting factor (WF) as all are not considered to be of equal importance:

- **Profile (WF 5).** Wrinkle height or the degree to which the fabric surface is distorted from a plane.
- **Sharpness of creasing (WF 4).** The sharpness or roundness of the creases.
- **Musiness (WF 3).** The proportion of fabric with minute creases which give the fabric a crumpled appearance.
- **Wrinkle density (WF 2).** The number of wrinkles per unit area, assuming the wrinkle pattern is random.
- **Randomness (WF 1).** The extent to which a wrinkle pattern is repeated within the sample.

A rating of 0-4 was assigned to each component, 0, being low and 4 high. The assigned score was multiplied by its weighting factor and all scores were added together to produce a total. A satisfactory total weighted score depends on the end use of the test specimen. The Celanese use a sliding scale that takes into consideration fabric weight as well as end use when ranking samples for industry.

Another approach uses a Leica-Cambridge Quantimet 570 image analyser together with a video camera to record the image so that wrinkled fabrics can be quantified according to variations in intensities of light (128). Perfectly flat fabric under a given source of illumination appears as a uniform area of light intensity whereas a wrinkled fabric gives rise to an irregular distribution of differential intensities. If the illumination conditions are kept constant then changes in intensity across different samples can be quantified and compared.

The Quantimet stores the image and digitises the pixel intensities on a scale ranging

form 0, black, to 255, white. On a grid 50 x 50 pixels square a geometric representation of the fabric surface can be constructed to appear on the screen. For calculation purposes each grid contains 49 x 49 unit cells. In a perfectly flat fabric the grey levels of pixel-intensities will be identical, but in wrinkled fabrics the grey levels at the corners of individual unit cells will differ, producing curved or inclined "surface planes". Summation of these surface planes gives rise to a total surface area for the wrinkled fabric.

The 'surface plane' for a flat fabric will be level and thus fill the whole of the pixel square, allowing calculation of the total 'surface plane' area to be 100%.

$$\frac{\text{Total surface area of test fabric}}{\text{Total surface area of flat fabric}} \times 100 = \% \text{ Degree of Wrinkling}$$

Clearly the higher the value, the higher the degree of wrinkling.

A histogram of count against steepness can be plotted to quantify the number of cells having a specific steepness factor, and this is used to indicate the different degrees of creasing throughout the fabric. The steepness factor is a variable value and depends on the conditions of illumination.

With the rapid development and decreasing cost in computer technology the use of computer image analysis systems has become a viable tool for objective measurement of fabric appearance characteristics. Once the computer software is written, one person should be able to operate the system with little training. The VSI Video Shrinkage Inspector by Sick (129), (130), already monitors fabric shrinkage without touching the fabric, and it produces an immediate reading and print-out of relevant values.

Research projects have been set up in the USA to characterise and quantify the appearance properties of fabrics, such as wrinkling, staining, pilling, and colour, using image analysis algorithms and mathematical models with the goal of creating a comprehensive system for the evaluation of fabric appearance (131).

The evaluation of fabric appearance characteristics by computer image analysis systems can be thought of as a problem in pattern recognition. The first step involves capturing an image of the object, pre-processing any measurement errors, and then selecting the

desired characteristics for analysis.

2.3.2.2 Crease recovery tests used in this thesis.

2.3.2.2.1 The Shirley Crease Recovery Test (132).

This is a recovery angle method and was undertaken according with the European Standard CEN22313 (133). Fabrics that have good recovery from creasing during wear possess a high degree of recovery in both the wet and dry states. Samples that have a high degree of wet recovery and a moderate degree of dry recovery will exhibit good 'drip-dry' qualities but will be useless if tumble-dried (135). It was thus felt important to test the samples in both the dry and wet states.

Samples (40mm x 15mm) were cut out, 20 in the warp direction and 20 in the weft direction. Ten of these were used to measure the dry crease recovery angle (DCRA) and the other ten were used to measure the wet crease recovery angle (WCRA). The samples were creased for $5\text{min}\pm 5\text{s}$ under a force of 10N before being transferred to the Shirley Crease Test Machine and allowed to recover from creasing for $5\text{min}\pm 5\text{s}$. The Shirley crease test instrument consists of a circular-rotating dial mounted on a box-shaped platform. The bottom half of the dial is calibrated in degrees from 0-180°. At the centre of the dial there is a clamp for gripping the specimen during the test. Directly under the centre of the dial there is a marker for measuring the recovery angle, which is measured to the nearest degree. A recovery angle of zero indicates no recovery from creasing and an angle of 180° would indicate complete recovery.

The recovery angle was recorded for each sample and a mean value for both warp and weft directions calculated. The difference in CRA for both the warp and weft was less than 15° and thus the fabric mean crease recovery angle was calculated by adding the sums of the means of the warp and weft values. The results are given in the text in graphical form; a plot for both the instantaneous elastic recovery from creasing and a plot for the recovery from creasing after $5\text{min}\pm 5\text{s}$ are displayed. It was assumed that calculating both the initial elastic recovery and the creep after 5min was more informative than the more traditional method of only calculating the recovery from creasing after 5min. The results can be found in tabulated form in the Appendices at the back of this thesis.

2.3.2.2.1.1 Variation in Shirley crease recovery tests.

There was variation in the warp and weft DCRA and WCRA for the ten samples tested, five face-face and five back-back. Silk fabrics, because of the variation of the nature of the natural filaments, exhibit some variation in properties. Silk is a natural fibre and thus there is some variation between filaments spun by different silkworms as well as variation along the length of the filament. There may also be some variation in yarn construction and in fabric weaving.

It can be assumed that the result from a crease recovery test for one fabric sample has a fixed probability distribution. It can also be assumed that the distribution of the crease recovery test results satisfy standard normal distribution, (also known as Gaussian distribution) (123), see section 2.3.1.1.1.

To calculate the fabric crease recovery angle the sample mean value of the warp experiments was added to the sample mean value of the weft experiments. It was assumed that each piece of material is independent. That is $2n$ specimens of fabric were cut for the tests and half of them were used to test for warp recovery angle, and the other half for weft recovery angle. Taking n tests of each (in this thesis $n = 10$), the test results can be written,

Warp x_1, x_2, \dots, x_n ; mean = \bar{x} ; standard deviation = s_x

Weft y_1, y_2, \dots, y_n ; mean = \bar{y} ; standard deviation = s_y

The means \bar{x} and \bar{y} and the standard deviations s_x and s_y were calculated and from these the fabric mean total $\bar{T} = \bar{x} + \bar{y}$ and its standard error $s_T^2 = s_x^2 + s_y^2$ can also be calculated.

These were used to calculate the fabric crease recovery test confidence limits $\bar{T} \pm \alpha_r s_T$, where α_r is taken from the t-distribution table, see section 2.3.1.1.1, and has $\nu = 2(n-1)$ degrees of freedom. For each experiment a 95% confidence level was calculated $\bar{T} - \alpha_r s_T < \mu < \bar{T} + \alpha_r s_T$ and displayed graphically to show that there is a 95% certainty that the true mean lies within this range.

2.3.2.2.2 Visual analysis.

Selected samples were washed at 40°C in an automatic washing machine (Hotpoint,

electronic 1000 – De Luxe 9536), using a standard detergent (Persil non-biological), line dried and analysed visually. The washing machine was made up to a full 5kg load using towels and run on a delicate wash cycle (acrylic and wool cycle). The samples were washed and line dried and laid on a computer scanner and scanned into a computer for visual analysis. The computer software used was Deskscan and it was set up to scan the images with 300dpi as a black and white photograph. The brightness was set to 90, the contrast to 190 and the image was scaled to 70% of its original size. By keeping the scanning process constant throughout, it was possible to visually compare one image with another. The samples were then ironed quickly on a low heat and rescanned and visual comparisons were made.

2.3.3 ASTM Yellowness Index.

The yellowness of samples after finishing was measured using the ASTM yellowness index (YI) (134). Yellowness may be defined as a deviation in chroma from a white standard (white ceramic tile). A Colourgen DC M1100 Integrating Sphere machine with specular included was used to measure fabric yellowness. The measurement parameters used were 10° observer, CIE illuminant D65, and 8° illumination diffuse collection.

The fabric samples were measured with a thickness of four layers to obtain satisfactory opacity; four measurements were taken per sample, and two readings were recorded per measurement. The YI was measured according to ASTM American yellowness scale for near white opaque materials and the results were calculated by the on-line computer according to the following equation (134)

$$YI = [100/G(G - B)]$$

Where $G = (Y/Y_0) \times 100$, $B = (Z/Z_0) \times 100$, Y and Z are two of the three CIE tristimulus values that refer to the treated samples and Y_0 and Z_0 are two of the three CIE tristimulus values that refer to the white reference tile.

2.3.4 Thermoanalytical Analysis.

Two thermoanalytical techniques were used in this thesis, namely thermogravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC). These were undertaken on a DuPont 951 thermogravimetric analyser and a DuPont 910 differential

scanning calorimeter, respectively. The tests were controlled by an on-line computer and the results were automatically analysed using a DuPont data analysis package.

TGA involves the analysis of a sample weight as a function of temperature. The sample can be heated, cooled, or isothermed (kept at a constant temp). In the practical work associated with this thesis both the chemical reagents and the finished silk samples were analysed using the TGA. The heating rate and temperature range used varied with the experiment, but were kept constant within a set of results. The weight of the samples tested was approximately 5mg for the chemical reagents and 3mg for the finished silk samples.

The DSC instrument used was of the heat-flux type. The DSC cell uses a Constantan disk to transfer heat to the sample pan and a reference pan that sits on raised platforms on the Constantan disk (135). Heat is transferred via the disk up into the sample and reference via the sample pans. The differential heat flow to the sample and reference is monitored and the enthalpy values are calculated using the DSC data analysis software. The cell constant was calibrated using Indium metal. Because the heat of fusion of Indium metal (28.4J/g) is known the computer can calculate the cell constant. As before the heating rate and temperature range used varied according to the experiment, but were kept constant within a specific set of results. The weight of the chemical reagents tested was approximately 3mg.

3. CHEMICAL MODIFICATION OF SILK FABRIC WITH POLYCARBOXYLIC ACIDS. AN INITIAL STUDY.

3.1 INTRODUCTION.

Polycarboxylic acids (PCAs) have been investigated as an alternative to the conventional formaldehyde-based fibre cross-linking agents. It has been found that some of these compounds give good results when reacted with the hydroxyl groups in cotton cellulose, see section 3.1.2. The hydroxyl-containing side chains in silk fibroin could be capable of forming fibre inter-chain ester cross-links with the polycarboxylic acids that may lead to an improvement in the easy-care properties of silk fabrics.

This chapter summarises the structure and properties of carboxylic acids, reviews the literature on the cross-linking of cotton cellulose with polycarboxylic acids and investigates experimentally the possibility of using polycarboxylic acids as chemical modifying agents for silk fabric.

3.1.1 Summary Of The Structure And Properties Of Carboxylic Acids And Their Derivatives.

3.1.1.1 Carboxylic acids.

Carboxylic acids contain the group, $-\text{COOH}$, and are one member of the class of acyl derivatives, RCOY , where the acyl group is bonded to an electronegative substituent $-\text{Y}$. This electronegative substituent can act as a leaving group in nucleophilic acyl substitution reactions. Carboxylic-functional groups are structurally related to both ketones and alcohols. Like ketones the carbonyl carbon atom is sp^2 hybridised and has C-C-O and O-C-O bond angles of approximately 120° , whereas like alcohols carboxylic acids are associated via hydrogen bonding.

Carboxylic acids are acidic; they are weaker acids than mineral acids, such as HCl, but stronger acids than alcohols. Carboxylic acids dissociate more readily than alcohols because in the carboxylate ion of carboxylic acids the negative charge is delocalised over both oxygen atoms. This results in a stabilised resonance hybrid of two equivalent Kekulé structures, see Figure 3. 1.

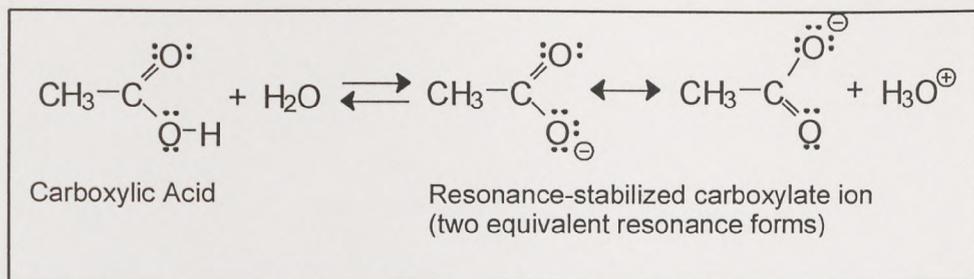


Figure 3. 1 Resonance-stabilised carboxylate ion in aqueous solution (20).

The acidity constant for most carboxylic acids is constant around $K_a = 10^{-5}$, where

$$K_a = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]} \quad \text{and} \quad \text{p}K_a = -\log K_a$$

The actual K_a value depends on the structure of the acid; carboxylic acids with electron-withdrawing substituents are more acidic because their carboxylate ions are stabilised, whereas carboxylic acids with electron-donating substituents are less acidic because their carboxylate ions are less stable. Like other Brønsted-Lowry acids they react with bases to give carboxylate salts, and they dissociate in aqueous solution to give H_3O^+ and carboxylate anion RCOO^- , see Figure 3. 1.

The general reactions of carboxylic acids are summarised in Figure 3. 2.

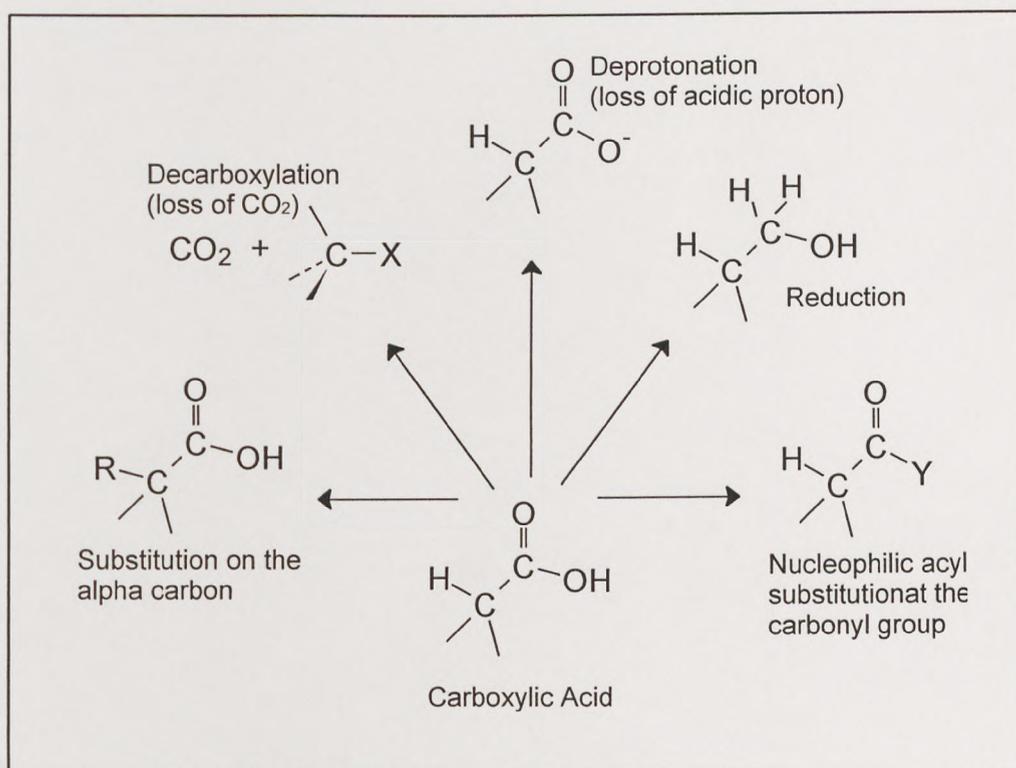


Figure 3. 2 Some general reactions of carboxylic acids (20).

Methods of synthesis of carboxylic acids include (20):

- Oxidation of alkylbenzenes with sodium dichromate or potassium permanganate.
- Oxidative cleavage of alkenes.
- Oxidation of primary alcohols or aldehydes with Jones' reagent.
- Hydrolysis of nitriles.
- Reaction of Grignard reagents with CO_2 (carboxylation).

Carboxylic acids have characteristic infra-red absorption spectra; the O-H bond gives rise to a broad absorption over the range $2500\text{-}3300\text{cm}^{-1}$, and the C=O bond absorbs between $1710\text{-}1760\text{cm}^{-1}$.

3.1.1.2 Carboxylic acid derivatives.

Carboxylic acids can be transformed into a variety of acid derivatives where the $-\text{OH}$ group has been replaced by other substituents; acid anhydrides, amides and esters are three of them. The chemistry of acid derivatives is dominated by one type of reaction, the nucleophilic acyl substitution reaction (20), see Figure 3.3.

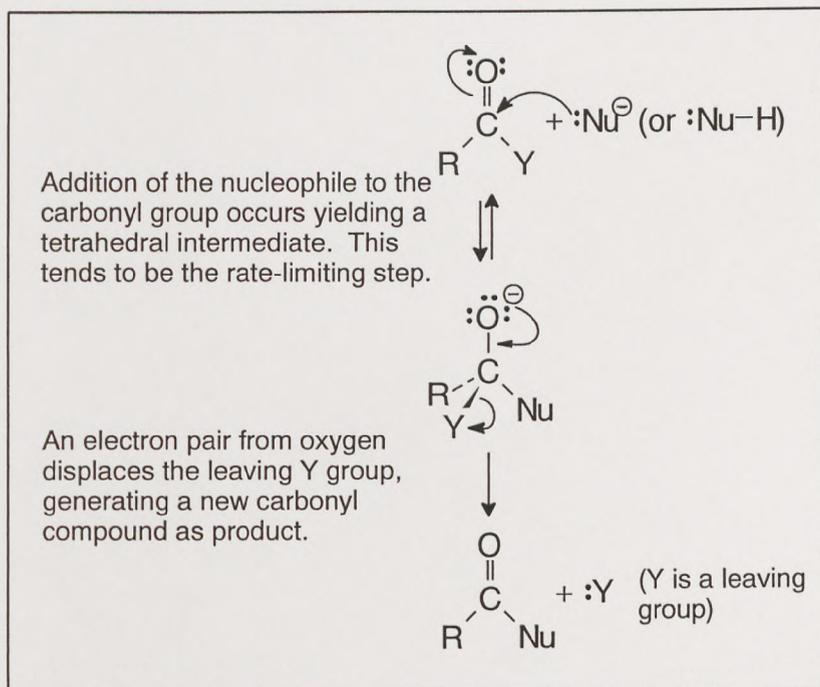


Figure 3.3 General mechanism of nucleophilic acyl substitution (20).

When nucleophiles add to carboxylic acid derivatives they initially form a tetrahedral intermediate that expels one of the two substituents originally bonded to the carbonyl carbon. As soon as the tetrahedral intermediate is formed the negative charge on the oxygen expels the leaving group, Y, which generates a new carbonyl compound. The reaction is favoured by any factor that allows the carbonyl group to be more easily

attacked; i.e. strongly polarised acyl derivatives are more readily attacked than less polarised acyl derivatives (20). An acid anhydride is more reactive than an ester derivative and it is therefore possible to transform an acid anhydride into its corresponding ester (20). Similarly an amide is less reactive than an ester derivative and thus the conditions required for amide hydrolysis are more severe than those required for ester hydrolysis. Some general reactions of carboxylic acid derivatives are shown in Figure 3. 4.

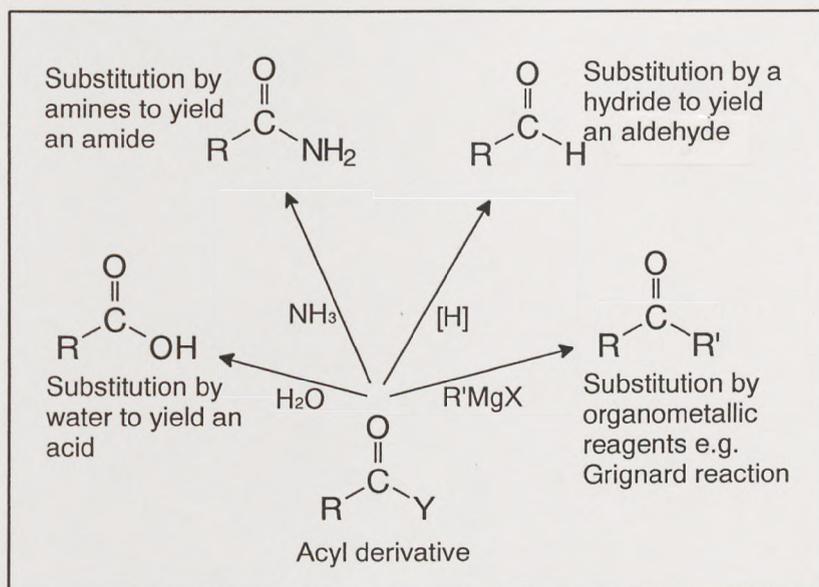


Figure 3. 4 Some general reactions of carboxylic acid derivatives (20).

3.1.1.2.1 Acid Anhydrides.

Acid anhydrides are formed by the elimination of water from two carboxylic acids, e.g. acetic anhydride is derived from two molecules of acetic acid, see Figure 3. 5.

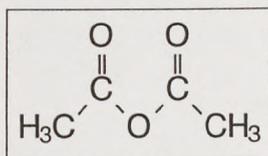


Figure 3. 5 Acetic anhydride.

Acid anhydrides react with water to form acids, with alcohols to form esters, with amines to form amides and with LiAlH_4 to form primary alcohols.

Acid anhydrides have characteristic infra-red absorption spectra; generally they show two carbonyl absorption bands, separated by approximately 60cm^{-1} in the region of $1740\text{-}1830\text{cm}^{-1}$.

3.1.1.2.2 Esters.

Esters have the general formula RCOOR' . The transformation of an acid to an ester can be achieved by several methods. Fischer and Speier discovered in 1895 that they could form esters by heating a carboxylic acid in methanol or ethanol in the presence of a small amount of mineral acid catalyst (20). Isotopic-labelling experiments have been used to support the mechanism, see Figure 3. 6.

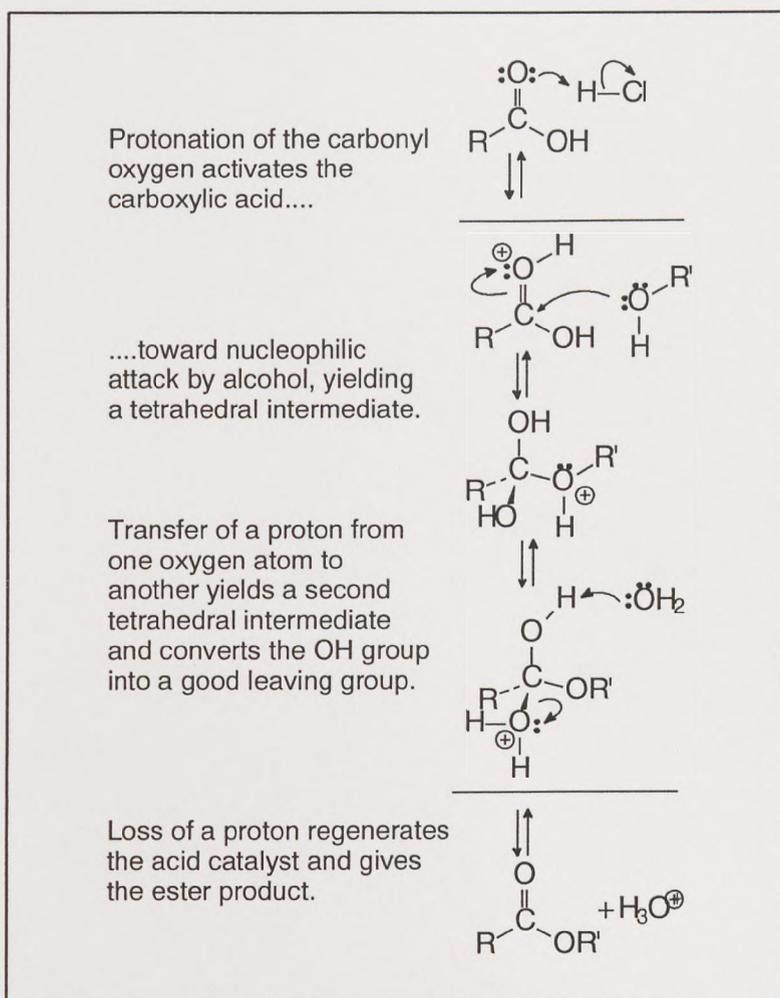


Figure 3. 6 Mechanism of Fischer esterification (20).

When ^{18}O -labeled methanol reacts with benzoic acid in accordance with the Fischer esterification reaction, the methyl benzoate formed is ^{18}O labelled and the water unlabelled. Thus, it can be concluded that the $\text{CO}-\text{OH}$ bond of the carboxylic acid is cleaved and not the $\text{COO}-\text{H}$ bond, and that it is the $\text{RO}-\text{H}$ bond of the alcohol that is cleaved, rather than the $\text{R}-\text{OH}$ bond.

Esters undergo the normal reactions for acid derivatives, see Figure 3. 4, but they are less reactive towards nucleophiles than acid anhydrides. Esters can be hydrolysed by either acid or base solution to yield the carboxylic acid and alcohol. The normal

pathway for acid hydrolysis is the reverse of the Fischer esterification reaction, see Figure 3.6. Ester hydrolysis in base solution is called saponification, and it usually occurs through a nucleophilic acyl substitution pathway, see Figure 3.3.

Esters have characteristic infra-red absorption spectra; they absorb around 1735cm^{-1} for saturated esters and 1715cm^{-1} for esters with either an aromatic ring or double bond in their structure.

3.1.1.2.3 Amides.

Carboxylic acids can be converted into amides by replacing the acid hydroxyl group with a nitrogen substituent. Amides are difficult to prepare by the direct reaction of a carboxylic acid with an amine (20); this is because amines convert the carboxyl group into their carboxylate anions, see Figure 3.7. The carboxylic anion has a negative charge and is therefore unable to be attacked by nucleophiles.

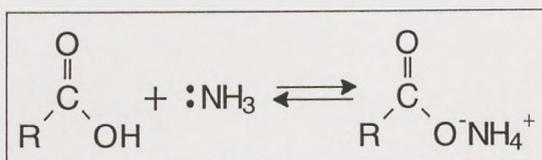


Figure 3.7 Reaction of a carboxylic acid with an amine (20).

Amides are much less reactive than either acid anhydrides or esters. They are hydrolysed on heating in aqueous acid or base yielding a carboxylic acid and an amine (20). Base hydrolysis occurs through nucleophilic addition of a hydroxide ion to the amide carbonyl group and subsequent loss of the amide ion, whereas acid hydrolysis occurs through the nucleophilic addition of water to the protonated amide followed by loss of ammonia. Amides also undergo reduction by LiAlH_4 .

Amides have characteristic infra-red absorption spectra; they absorb at the lower end of the carbonyl region, around $1650\text{-}1700\text{cm}^{-1}$. The exact position of the infra-red band is dependent on the degree of substitution on the nitrogen atom.

3.1.1.3 Di- and Polycarboxylic acids.

Di- and polycarboxylic acids, as their name suggests, contain more than one carboxylic acid group per molecule. These acids undergo the normal reactions of carboxylic acids as seen in Figure 3.2. In addition, some di- and polycarboxylic acids where the

carboxylic acid groups are on adjacent carbon atoms, can dehydrate at high temperatures to form stable five- or six-membered cyclic anhydrides, e.g. succinic anhydride, see Figure 3.8.

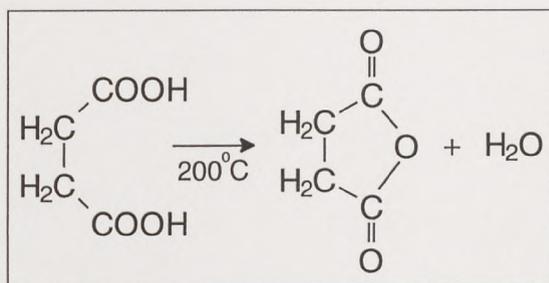
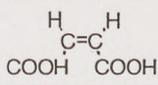
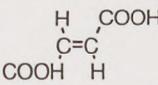
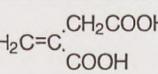
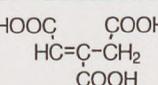
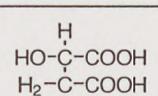
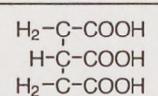
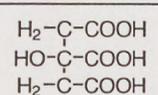
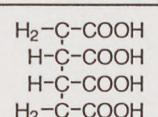
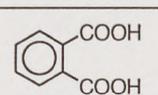
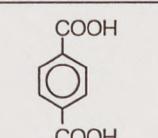
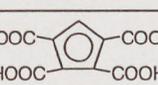
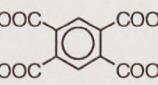


Figure 3.8 Succinic anhydride (20).

Table 3.1 displays some of the properties of di- and polycarboxylic acids used in this thesis. The properties of these acids are important for selecting an acid for a given purpose.

These di- and polycarboxylic acids are crystalline solids at room temperature. Their melting point and solubility in aqueous medium generally decrease as the number of carbon atoms per molecule increases (136). The unsubstituted aliphatic dicarboxylic acids exhibit an alternating effect; diacids with an odd number of carbon atoms have lower melting points and higher solubilities than their even counterparts. This is because odd numbered diacids cannot assume an in-plane orientation of both carbonyl groups with respect to the hydrocarbon chain (136). Di- and polycarboxylic acids are ionised in aqueous medium; the degree of ionisation depends on the proximity of the carbonyl groups within the individual structures. The carbonyl group is electron-withdrawing and causes the neighbouring carbonyl hydrogen to be more readily dissociated.

The unsaturated carboxylic acids are able to undergo typical reactions relating to the double bond in conjunction with the normal reactions for carboxylic acids (138). Similarly hydroxy- and aromatic carboxylic acids are capable of undergoing reactions characteristic of alcohols and the benzene nucleus respectively (137).

Common Name	Structure	Melting Point (°C)	Boiling Point (°C)	Dissociation Constants in aqueous solution (25°C)				Solubility g/100g (25°C)
				pK _{a1}	pK _{a2}	pK _{a3}	pK _{a4}	
Oxalic	HOOC-COOH	187	Decompose	1.27	4.27	-	-	9.5
Malonic	HOOC-CH ₂ -COOH	134-136	Decompose	2.85	5.70	-	-	152
Succinic	HOOC-(CH ₂) ₂ -COOH	187.6-187.9	Decompose	4.21	5.64	-	-	8.35
Glutaric	HOOC-(CH ₂) ₃ -COOH	98-99	200	4.34	5.54	-	-	130
Adipic	HOOC-(CH ₂) ₄ -COOH	153	265	4.41	5.41	-	-	3.08 at 34.1°C
Maleic		138-139	Decompose	1.94	6.23	-	-	44.1
Fumaric		287	290	3.02	4.38	-	-	0.70
Itaconic		-	-	3.85	5.45	-	-	9.5
Aconitic		190	-	-	-	-	-	Soluble
DL-Malic		131-133	-	3.40	5.11	-	-	-
TCA		159.62	-	-	-	-	-	Soluble
Citric		154.4	-	3.13	4.76	6.40	-	Soluble
BTCA		196	-	3.43	4.58	5.85	7.16	-
Phthalic		211	Decompose	2.95	5.41	-	-	0.7
Tere-phthalic		402	Sublimes	3.54	4.46	-	-	0.0017
CPTA		192.5	-	-	-	-	-	Soluble
Pyro-mellitic		282	-	1.92	2.87	4.49	5.63	Soluble

Where TCA = Tricarballic Acid, BTCA = 1,2,3,4-Butanetetracarboxylic Acid, and CPTA = 1,2,3,4-Cyclopentanetetracarboxylic Acid

Table 3. 1 Some properties of di- and polycarboxylic acids (136, 137, 138).

Di- and polycarboxylic acids form component parts of a large number of materials including polymers i.e., polyesters and polyamides, plasticising agents, lubricants, heat transfer fluids, surface inks and coatings, resins and surfactants. In general these acids are recognised to be ocular and dermal irritants and inhalation of the dust of these acids is irritating to the mucous membrane and respiratory system (136-138). The dust from some of these acids is combustible on exposure to heat or flames (136-138). The level of toxicity varies; citric acid is considered non-toxic whereas glutaric acid is a known kidney toxin (136).

3.2 CHEMICAL MODIFICATION OF COTTON CELLULOSE WITH POLYCARBOXYLIC ACIDS.

3.2.1 Initial Studies.

In 1963 Gagliardi and Shippee reported on a potentially new method for producing dimensionally stable and crease resistant cotton, linen and viscose fabrics (139). They examined the reaction of various polyfunctional carboxylic acids with the hydroxyl groups of cotton cellulose in the absence of an esterification catalyst at elevated temperatures. The reaction between polycarboxylic acids and cellulose was known, McIntyre, (1948), reported on the ion-exchange properties of succinic acid half esters of cotton (140).

In the absence of a catalyst, the pad, dry, cure treatment of cotton with polycarboxylic acids (PCA) imparted moderate crease resistance to cotton (141). Citric acid (CA) gave the best DCRA results (250-270°), but caused fabric yellowing under the severe conditions of high acidity and high temperature (143° -163°C for 15-60 min). The cross-links were formed in cellulose by acid-catalysed esterification between accessible hydroxyl groups in cotton cellulose, with the CA, itself furnishing the protons needed for autocatalysis (139), see Figure 3. 6. Permanent acid-catalysed cellulose chain cleavage occurred that resulted in a loss of tensile strength. The incorporation of unesterified carboxyl groups in the CA-modified cellulose resulted in an increased affinity for basic dyes.

The first evidence that PCAs could impart crease-resistance to cotton together with higher than normal strength retention compared to amino-formaldehyde reagents, was

obtained by Rowland et al. in 1964 (142). They impregnated cotton cellulose with di- and polycarboxylic acids that had been either partially or wholly converted to the mono-sodium or mono-triethylammonium salt, followed by drying and curing. The mono-sodium or mono-amine salts of polycarboxylic acids appeared to be autocatalytic for the cellulose esterification reaction. These salts also acted as buffers and greatly decrease the acid-damage to cotton cellulose during high temperature curing.

The ester cross-links inserted by the polycarboxylic acid finishing process were found to be recurable (143). At high temperatures the transesterification of ester cross-links on neighbouring cellulose hydroxyl groups causes the cross-links to be mobile, even in the absence of a catalyst. It was postulated that the ester cross-links dissociate at high temperatures to form cyclic anhydrides of the polycarboxylic acid followed by re-formation of the ester cross-link (143).

In another paper (1967) Rowland et al. (144) reported that cellulose impregnated with an aqueous solution of a polycarboxylic acid containing three or four carboxyl groups and a partial sodium or amine salt of the acid was insoluble in 0.5M cupriethylenediamine hydroxide. The insolubility of the treated cotton cellulose in this solvent was used as an indication for the existence of ester cross-links. These acids all have carbonyl groups attached to adjacent carbon atoms and are therefore capable of forming cyclic anhydride rings. These anhydrides may form an intermediate step in the esterification reaction. Cotton cellulose treated with the dicarboxylic acid, maleic acid and a partial sodium or amine salt of the acid, was also found to be insoluble in 0.5M cupriethylenediamine hydroxide. It would therefore appear that this acid is capable of forming ester cross-links in cotton cellulose. If maleic acid can form ester cross-links with cotton cellulose, it would seem to suggest that it is not essential for the acid to be able to form a cyclic anhydride intermediate in order for a reaction to occur with cotton. This was also insinuated in the slight reaction of terephthalic acid and its partial sodium or amine salt with cotton cellulose.

The quantities of free and total carboxyl groups in the cotton cellulose treated with cyclopentanetetracarboxylic acid (CPTA) were estimated by direct titration and saponification, respectively (144). The results suggested that approximately half of the carbonyl groups of CPTA had formed ester cross-links with cotton cellulose. It was

believed previously that ester linkages were not hydrolytically stable (see section 3.1.1.2.2) and therefore would not be able to survive a large number of home launderings. But Rowland et al. (144) demonstrated that these ester cross-links were found to be largely stable to hydrolysis during laundering. With cyclopentanetetracarboxylic acid there was only a small decrease in DCRA after five laundry cycles (144).

3.2.2 Polycarboxylic Acids As Fibre Cross-Linking Agents For Cotton Cellulose.

Since the late 1980's, Welch et al. at the Southern Regional Research Centre in New Orleans, Louisiana have continued research into the esterification of cotton cellulose with polycarboxylic acids as non-formaldehyde easy-care finishing agents. Polycarboxylic acids (PCAs), especially 1,2,3,4 butanetetracarboxylic acid (BTCA), have proved to be good fibre cross-linking agents, with excellent durability to laundering and good fabric strength retention. The polycarboxylic acids react with the hydroxyl groups in cotton cellulose to form ester cross-links that connect adjacent cellulose chain molecules in a three-dimensional network inside the fibre (145). The presence of ester links has been proven through infra-red spectral analysis (146). The cross-linking reaction is catalysed by weak bases and takes place at 160-215°C (145).

3.2.2.1 Tetracarboxylic acids.

1,2,3,4-butanetetracarboxylic acid (BTCA) and 1,2,3,4-cyclopentanetetra-carboxylic acid (CPTA) have been studied as easy-care finishing agents for cotton cellulose. Both these acids form ester cross-links with cotton cellulose when applied in the presence of an esterification catalyst (141). The physical properties of the treated fabrics, fabric crease recovery angles, fabric strength retention and fabric bending movements were comparable with cotton cellulose treated with DMDHEU (1,3-dimethylol-4,5-dihydroxyethylene urea). Fabric treated with BTCA is more durable to laundering than fabric treated with CPTA (141). The difference in laundering durability of the treated fabrics may be due to the difference in molecular structure of the tetracarboxylic acids, see Table 3.1. CPTA has a more rigid molecular structure than BTCA. The BTCA molecule has a highly flexible chain; the carbon atoms bearing the carbonyl groups are free to rotate, to allow maximum distance between the carbonyl groups. It is therefore

possible for the BTCA molecule to form more flexible ester cross-links in cotton cellulose.

The carbonyl groups in both BTCA and CPTA are on adjacent carbon atoms; this permits the formation of cyclic anhydrides at high temperatures. Because there are four carbonyl groups per acid, each molecule is capable of forming a dianhydride, see Figure 3.9.

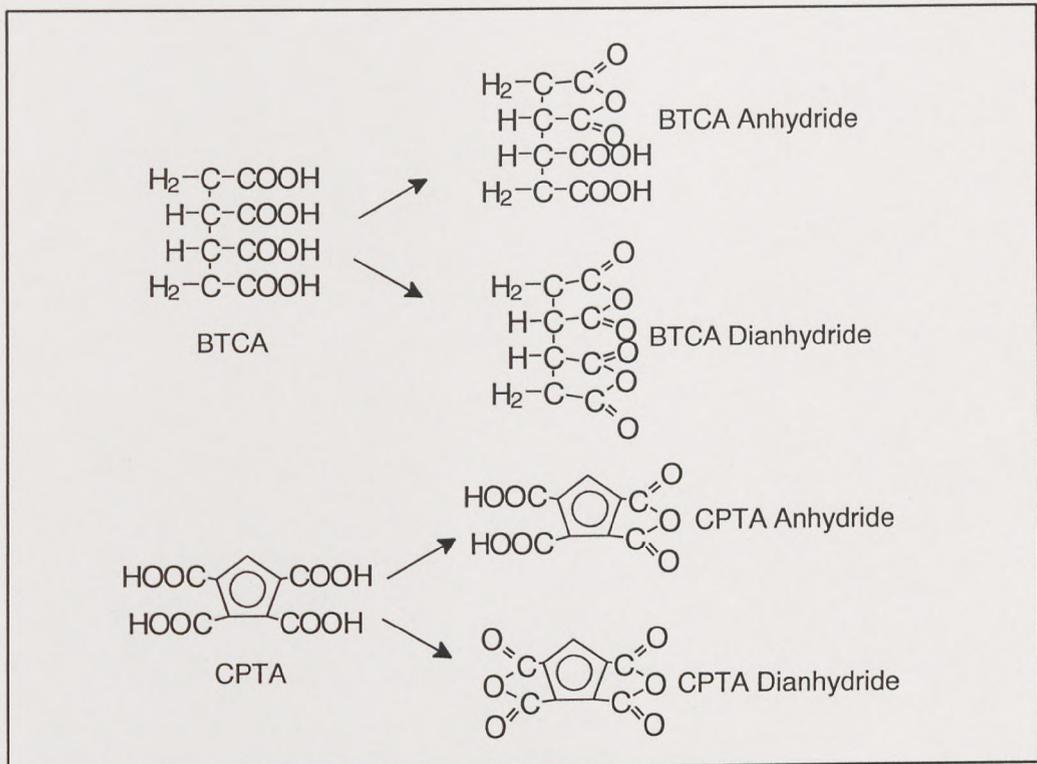


Figure 3.9 Tetracarboxylic acid anhydrides.

BTCA and CPTA have been found to be the most efficient polycarboxylic acids for cross-linking cotton cellulose tested to date (145). It was found that weak bases accelerated the esterification reaction of these acids at high temperatures. Strong acids are generally required to catalyse the esterification reaction of a monocarboxylic acid and an alcohol, see section 3.1.1.2.2, whereas weak bases are known to catalyse the esterification reaction of an acid anhydride and an alcohol (147).

It has been proposed that the base-catalysed esterification reaction of these acids with cotton cellulose occurs through the formation of an anhydride intermediate, see Figure 3.10 (145). In agreement with this hypothesis it follows that only acids that can form an anhydride intermediate will be effective esterification reagents for cotton cellulose under these conditions. In order for a diester cross-link to be formed in cotton cellulose

each acid molecule needs to be able to form two anhydride intermediates. If an acid is to be capable of forming either a five- or a six-membered anhydride intermediate the carbonyl groups should be on adjacent, or next but one, carbon atoms and a minimum of three carboxyl groups per molecule is needed to form a diester cross-link.

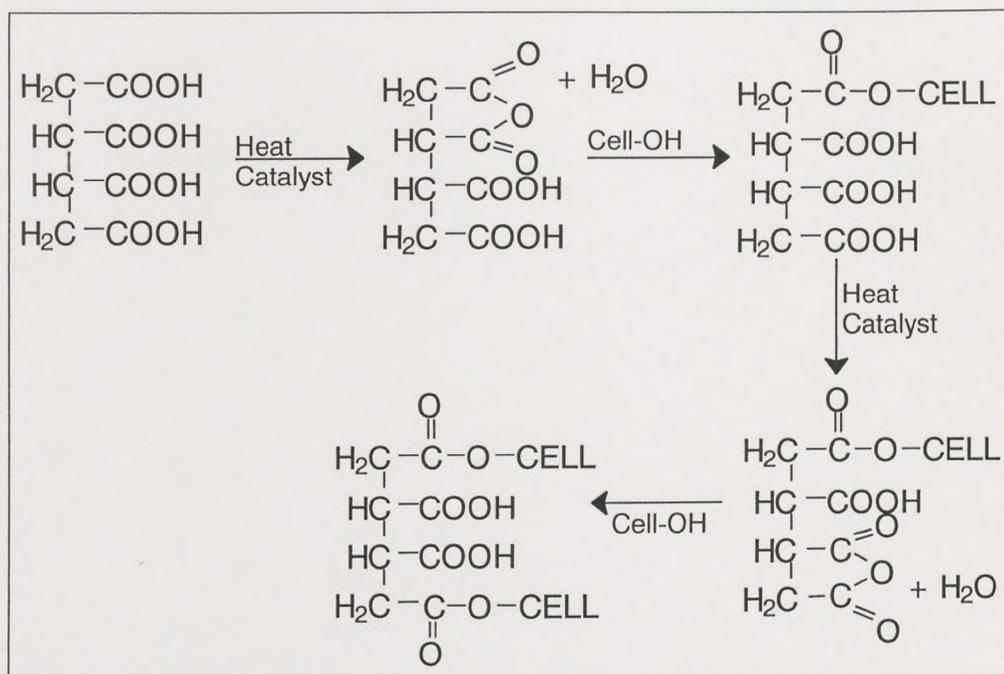


Figure 3.10 Proposed mechanism by Welch for the esterification reaction of cotton cellulose with BTCA (145).

While BTCA appears to be a suitable alternative to conventional DMDHEU reactants the market for BTCA is uncertain due to its projected high production cost. It is expected to be at least three times more expensive than conventional DMDHEU reactants and it is uncertain as to whether consumers will be willing to pay the increased cost (148). A secondary problem is the catalyst, the best catalyst to date for BTCA finishing is sodium hypophosphite monohydrate (SHP), but this catalyst is expensive and causes shade changes on sulphur dyeings and some reactive dyeings. Further research is therefore necessary to find a cheaper solution.

3.2.2.2 Tricarboxylic acids.

Suitable tricarboxylic acids, such as citric acid (CA), tricarballic acid (TCA), and aconitic acid (AA) (see Table 3.1) can impart moderate to good easy-care properties to cotton cellulose (149). The order of effectiveness of the acids is TCA, AA, and then CA. TCA is very expensive, approximately five times as expensive as BTCA and aconitic acid produces severe fabric discolouration; this precludes these acids as useful textile

finishing agents. The degradation of the vinyl group in aconitic acid is thought to be responsible for the colour change (150). Citric acid is cheap and non-toxic (151) and is therefore a suitable alternative for BTCA. However, fabric whiteness of citric acid-finished fabrics is low and does not compare with fabrics treated with BTCA or conventional N-methylol agents. The fabric yellowing may be due to dehydration of some of the CA molecules to form AA. A spot test with KMnO_4 on the cured fabric treated with citric acid indicated the presence of double bonds (152). The fabric whiteness can be improved by laundering (151), but this adds cost to an already costly finishing system.

SHP has been found to be the best catalyst for cross-linking cotton cellulose with tricarboxylic acids (149). If the concentration of SHP is increased, when used with CA, the fabric yellowing caused by the finish can be decreased (151). The addition of boric acid to the finish formulation in very small quantities can improve the fabric whiteness of samples treated with CA. This is possibly due to the boric acid reacting with the alpha hydroxy and carbonyl groups in the citric acid and preventing dehydration to the unsaturated acid (150). Unfortunately the inclusion of boric acid in the pad bath decreases the rate of esterification of the citric anhydride with cellulose (150). The inclusion of polyethylene glycol 400 or triethanolamine hydrochloride to the finish formulation also improved the fabric whiteness of the samples treated with CA (152).

Tricarboxylic acids suitable as easy-care finishing agents contain three carboxyl groups on adjacent or next but one carbon atoms. These acids are capable of forming five- or six-membered cyclic anhydrides. On forming an ester linkage one carboxyl group is recovered and thus the acid is capable of forming a second cyclic anhydride and consequently a diester linkage, according to the mechanism proposed by Welch (141) shown in Figure 3. 10.

CA can be used in conjunction with BTCA, to decrease the cost of the more effective but more expensive BTCA. The easy-care properties of cotton fabrics treated with a finish formulation of three parts CA and one part BTCA with SHP catalyst were intermediate to the properties of either agent used alone. Welch et al. proposed a possible intermediate for the reaction of BTCA with the α -hydroxyl groups of several CA molecules, see Figure 3. 11.

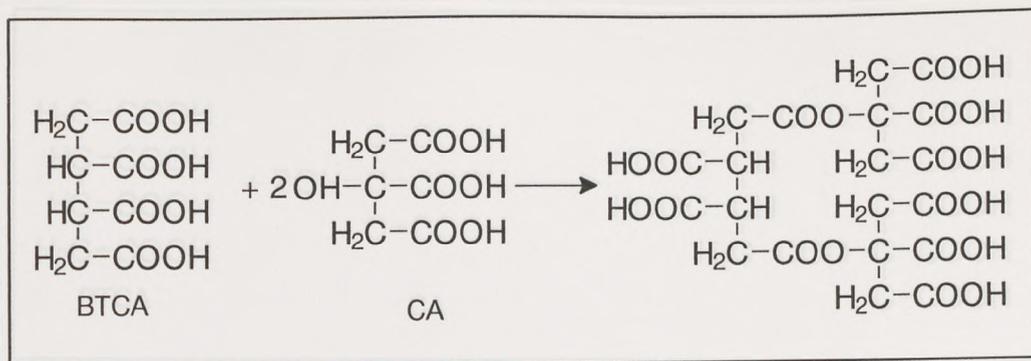


Figure 3. 11 Possible intermediate of the reaction of BTCA with several CA molecules.

It is hypothesised (153) that the BTCA forms an ester bond with the hydroxyl group in CA molecules during the first stage of the heat curing process to give higher molecular weight polycarboxylic acids. These higher molecular weight polycarboxylic acids can in turn form ester links with the cotton cellulose. A marked degree of yellowing was still evident in fabrics treated with this finishing process (153).

3.2.2.3 Dicarboxylic acids.

According to the proposed esterification mechanism by Welch (141) carboxylic acids require three carboxylic acid groups per molecule in order to form a diester link with cotton cellulose. However, unsaturated dicarboxylic acids, such as maleic acid (MA) in the presence of a free-radical initiator, e.g. potassium peroxydisulphate, can polymerise or copolymerise with another monomer to yield polycarboxylic acids with multiple carbonyl groups. If the carbonyl groups are on adjacent or next but one carbon atoms these polymers, in the presence of an esterification catalyst, can cross-link cotton cellulose.

Hydroxy acids such as DL-malic acid (MLA) could react with unsubstituted aliphatic di- and polycarboxylic acids according to the mechanism proposed by Welch et al. (shown in Figure 3.12) to yield higher molecular weight polycarboxylic acids. These in turn would be capable of forming di- or multi-ester linkages with cotton cellulose. MLA was found to impart easy-care characteristics to cotton cellulose when applied with BTCA and the catalyst SHP. These finished fabrics retained a high level of whiteness. Thermal dehydration of MLA would yield maleic acid (MA), which itself produces very little yellowing under the normal conditions used for the esterification of cotton cellulose (153).

3.2.2.4 Comparison of di- and polycarboxylic acids as easy-care finishing agents for cotton cellulose.

Acid	Catalyst	% Weight Gain	DP Rating	Fabric DCRA (degrees)	% Tear Strength Retained	% Breaking Strength Retained	No of Laundering cycles (DP > 3.5)	CIE Whiteness Index
6.3% BTCA	6.5% SHP	-	4.5	300	60	54	120	65
6.4% TCA	4.8% SHP	7.4	4.6	285	60	63	74	53
7% CA	4.8% SHP	8.0	4.2	278	56	58	22	41
7% CA, 1.7% BTCA	4.7% SHP	9.6	4.6	281	53	55	103	59
5.4% MLA 3% BTCA	3.2% SHP	8.9	4.4	273	52	64	126	65
6% MA, 1.5% BTCA	4.8% SHP	10.3	4.0	267	61	67	79	60
12% MA	1.5% KPS, 6% SHP	9.1	3.5	219	70	56	-	-
12% PCA MA:IA 1:1	1.5% KPS, 6.4% SHP	11.6	4.4	268	83	49	-	68.7
6% DMDHEU	1.5% MgCl ₂	-	4.7	303	68.1	43.7	>100	67

Where KPS = potassium persulphate, MgCl₂ = magnesium chloride

Table 3. 2 Summary of the results of the different di-and polycarboxylic acids researched as easy-care finishing agents for cotton cellulose, discussed in section 3.2.2.

Table 3. 2 summarises the results of the different di- and polycarboxylic acids researched as easy-care finishing agents for cotton cellulose, and discussed in section 3.2.2. The highest durable press ratings are achieved with BTCA, this acid is also more stable to laundering than the other PCAs tested.

3.2.3 Esterification Catalysts Used In The Fibre Cross-Linking Of Polycarboxylic Acids To Cotton Cellulose.

Initial research into the easy-care finishing of cotton cellulose with polycarboxylic acids found that the curing temperature and time could be greatly reduced by the addition of weak bases to the finish formulation (142). Welch et al. found that a number of alkali metal salts of phosphorus-containing mineral acids, of which sodium hypophosphite (SHP) was the most efficient, to be more effective catalysts than weak bases such as sodium carbonate. SHP is the most effective catalyst found to date, however it is expensive and it produces shade changes on sulphur dyeings and some reactive dyeings. Thus, alternative catalysts have been sought.

An effective catalyst accelerates the rate of the cellulose cross-linking reaction, lowers the curing temperature, minimises the strength loss of cotton cellulose and minimises any fabric yellowing (148).

3.2.3.1 Alkali metal salts of phosphorus-containing mineral acids.

In the absence of a catalyst BTCA can form ester linkages with cotton cellulose. High curing temperatures are required to force the reaction to completion. The high curing temperatures cause high fabric strength loss and severe fabric yellowing.

Alkali metal salts of phosphorus-containing mineral acids significantly lower the curing temperature required for the esterification of cotton cellulose with polycarboxylic acids. These salts also act as buffers and lower the acid degradation of cotton cellulose (148). In order to aid the formation of a cyclic anhydride by the acid the catalyst may function by some other mechanism besides converting the polycarboxylic acid to a basic salt.

Welch has proposed that the acid anhydride esterification of an alcohol can be catalysed by a weak base, see Figure 3. 10. This reaction also occurs with heat alone, or can be catalysed by acids. The esterification reaction between carboxylic acids and alcohols is known to be catalysed by strong acids, see section 3.1.1.2.2. It is possible that these catalysts exert both acid and base catalysis simultaneously; this dual catalysis has been reported before for the mutarotation of saccharides and enolisation of ketones (141). Brown suggested an alternative mechanism with the formation of a mixed anhydride intermediate between the carboxylic acid and the phosphoric acid, in which the mixed anhydride intermediate would be more reactive than the carboxylic acid itself (148).

Brown compared the catalytic action of mono- (MSP), di- (DSP), trisodium phosphate (TSP) and SHP on the esterification of cotton cellulose with BTCA (148). MSP, DSP, and TSP are all salts of phosphoric acid, whereas SHP is a salt of hypophosphorous acid. The pKa values for these acids are compared with BTCA in Table 3. 3.

Acid	Structure	pK _{a1}	pK _{a2}	pK _{a3}	pK _{a4}
Phosphoric acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{OH}-\text{P}-\text{OH} \\ \\ \text{OH} \end{array}$	2.12	7.21	12.67	-
Hypophosphorous acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{P}-\text{OH} \\ \\ \text{H} \end{array}$	2.00	-	-	-
BTCA	$\begin{array}{c} \text{H}_2\text{C}-\text{COOH} \\ \\ \text{HC}-\text{COOH} \\ \\ \text{HC}-\text{COOH} \\ \\ \text{H}_2\text{C}-\text{COOH} \end{array}$	3.43	4.58	5.85	7.16

Table 3. 3 pK_a values of phosphoric, hypophosphorous, and 1,2,3,4-butanetetracarboxylic acids (148).

MSP was found to be an efficient catalyst for the esterification of cotton cellulose (148). MSP (pK_{a1} 2.12) is a salt of a stronger acid than BTCA (pK_{a1} 3.43) and thus the Na⁺ ions are more strongly associated with the phosphoric acid and will not hinder the reaction with cotton cellulose by neutralising the carboxyl groups in BTCA. Brown proposed that the MSP acted as a buffer controlling the pH during the drying and curing stages and thus minimising acid degradation of the cotton cellulose. He proposed that the esterification reaction was catalysed by two protons provided by the unneutralised POH groups in the phosphoric acid.

DSP was found to be a less effective catalyst than MSP (148). pK_{a2} = 7.21 for phosphoric acid and thus DSP is a stronger base than MSP. Some neutralisation of the carboxylic acid groups in BTCA may occur hindering the esterification reaction. There was still a proton on the unneutralised POH group to catalyse the esterification reaction, but higher temperatures were required to activate the system (148).

Brown found that TSP-catalysed esterification of cotton cellulose produced fabrics with high levels of strength retention, but the high temperatures required to activate the system caused severe fabric yellowing. This catalyst is a stronger base than DSP, (pK_{a3} = 12.67) and it is thought to completely neutralise the carboxyl groups in BTCA. High levels of fabric strength retention were attributed to the buffering action of the stronger base. No additional protons were available for esterification catalysis.

SHP was found to be the most efficient of the catalysts tested by Brown. SHP is a salt of a stronger acid than BTCA, and thus neutralisation of the carboxyl groups in BTCA is unlikely to occur. The sodium salt of hypophosphorous acid does not have any

available protons to assist in the esterification catalysis. However, hypophosphorous acid and its salts are strong reducing agents. The $\text{PO}_2^{-(p+3)}$ anion can be oxidised to the phosphate anion $\text{PO}_4^{-(p+5)}$ with the release of two hydrogen ions. Brown proposed that SHP catalyses BTCA by forming a mixed anhydride intermediate with the carboxyl group of BTCA which either promotes the formation of the cyclic anhydride of BTCA or directly esterifies the cotton cellulose, see Figure 3. 12. The SHP is converted to MSP in the process which Brown suggests acts as a proton donor and buffer. Andrews et al. (154) reported that the $\text{PO}_2^{-(p+3)}$ anion remained unchanged after curing; however, this does not follow because catalysis with SHP is known to cause shade changes on sulphur dyeings due to its reductive nature.

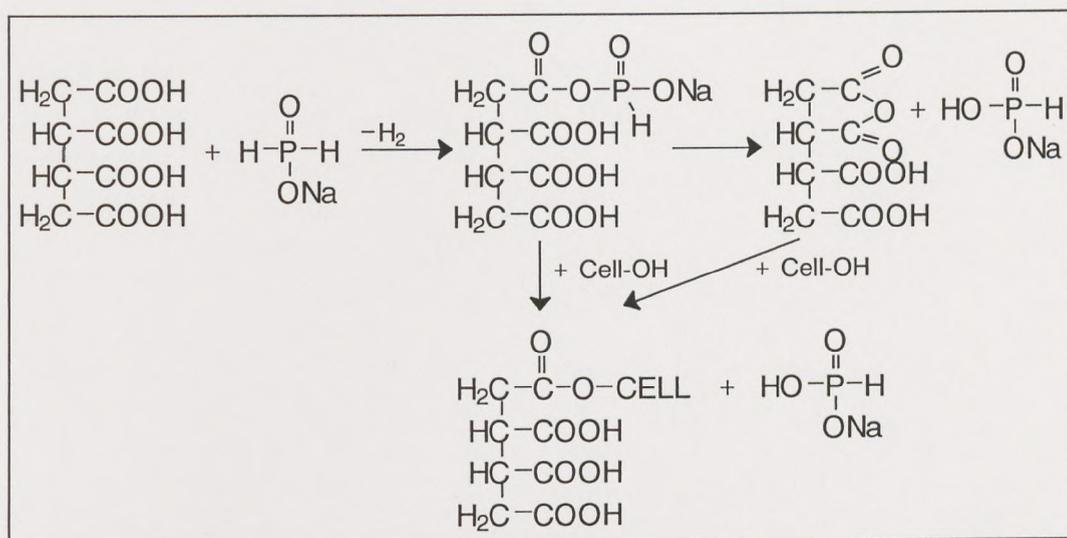
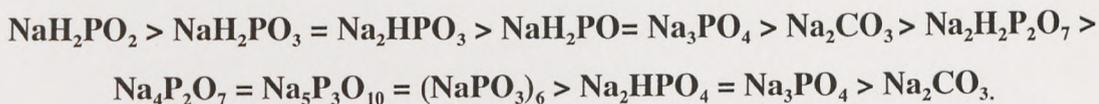


Figure 3. 12 Proposed mechanism by Brown for the sodium hypophosphite catalysed esterification reaction of cotton cellulose with BTCA (148)

Several alkali metal salts of phosphorus-containing acids have been investigated as catalysts for the esterification of cotton cellulose with polycarboxylic acids. They include salts of phosphoric, phosphorus, hypophosphorous, and polyphosphoric acids and the order of decreasing effectiveness as esterification catalysts is as follows (165):



The alkali metal salts of phosphorus-containing mineral acids are an environmental hazard; the combined phosphorus may serve as a nutrient for algae. This dissolves the oxygen needed by the fish and lowers the quality of the water for drinking (145). Alternative catalysts have therefore been investigated.

3.2.3.2 Non-phosphorus catalysts.

Various sodium salts of di- and tricarboxylic acids have been reported as alternative non-phosphorus catalysts of the cross-linking of cotton cellulose with polycarboxylic acids. These include the sodium salts of the saturated carboxylic acids, oxalic, malonic, succinic, glutaric and adipic acids, the unsaturated carboxylic acids, maleic, fumaric and itaconic acids, and the α -hydroxy acids such as citric, malic, and tartaric acids. These acids have been found to be more effective esterification catalysts than sodium carbonate but not as effective as SHP (155). However, strength retention of the treated cotton cellulose is better for fabrics catalysed by the sodium salts of di- and tricarboxylic acids (156).

The α -hydroxy acids appear to be the most promising replacement for SHP; the sodium citrates produced fabric with the best easy-care properties (157). Andrews and Morris suggested that the sodium citrates not only catalyse the esterification reaction but that the citric acid is available for cellulose cross-linking. The efficiency of the sodium citrates as catalysts was found to improve with an increase in the number of Na^+ ions attached to the citric acid (157). Improved strength retention was achieved with these systems in comparison with using SHP as the catalyst. This could be attributed to the higher pH value of the pad bath. Trisodium citrate gave the best retention of whiteness (145). Additives such as boric acid were generally needed to maintain the whiteness of these fabrics (145).

Aromatic N-heterocyclic compounds (imidazole and its derivatives) were found to be effective catalysts, giving similar DP ratings for fabrics catalysed with SHP (158). Cotton cellulose catalysed with imidazole derivatives had improved mechanical properties; these were attributed in part to the disruption of hydrogen bonds in cotton cellulose by these polar catalysts (158). If this is true, the polycarboxylic acids would be able to penetrate more readily throughout the cellulose molecules. The higher pH of the finish bath may also prevent acid degradation of cotton cellulose. This system caused slight fabric yellowing (158).

Esterification of cotton cellulose catalysed by imidazole imparted the highest fabric durable press rating in comparison to other aromatic N-heterocyclic compounds tested (158). Choi et al. proposed that an acylimidazolium salt was formed as a reaction

intermediate, in addition to general base catalysis, see Figure 3. 13. The pyridine nitrogen in imidazole derivatives could form an acylimidazolium salt with the polycarboxylic acid as a reaction intermediate through nucleophilic attack on the carbonyl carbon. This reaction would be pushed to the right by the reaction of the liberated imidazole with more polycarboxylic acid anhydride (158).

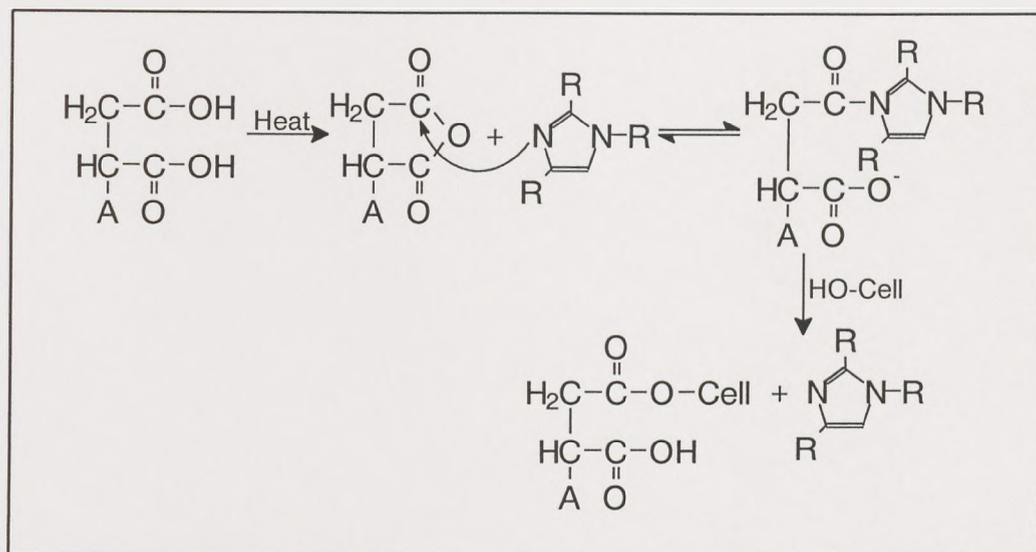


Figure 3. 13 Proposed mechanism by Choi et al. for the imidazole derivative catalysed esterification reaction of cotton cellulose with PCA (158)

Infra-red spectrophotometric analyses of cotton cellulose treated with BTCA using SHP and imidazole derivative catalysts were compared. These suggested that SHP was a more effective catalyst (158).

3.2.3.3 Comparison of the different catalytic systems employed for polycarboxylic acid easy-care finishing of cotton cellulose.

Table 3. 4 is a summary of the results of the different catalytic systems employed for the PCA easy-care finishing of cotton cellulose, and discussed in section 3.2.3. The highest durable press ratings are achieved with SHP as catalyst; however this catalyst acts as a reducing agent and therefore produces finished fabrics with minimum discoloration.

Acid	Catalyst	% Weight Gain	DP Rating	Fabric CRA (degrees)		% Tear Strength Retained	% Breaking Strength Retained	No of Laundry cycles (DP>3.5)	CIE Whiteness Index
				Dry	Wet				
6.3% BTCA	3.27% NaH ₂ PO ₂	5.41	4.4	255	250	57	44	120	65
6.3% BTCA	4.57% NaH ₂ PO ₃	6.35	3.9	268	240	53	41	-	-
6.3% BTCA	6.63% Na ₂ HPO ₃	6.14	3.8	250	197	62	47	90	-
6.3% BTCA	4.23% NaH ₂ PO ₄	5.26	4.0	262	233	47	40	-	-
6.3% BTCA	4.37% Na ₂ HPO ₄	5.93	3.8	241	197	52	43	70	-
6.3% BTCA	4.07% Na ₄ P ₂ O ₇	6.17	3.8	266	220	61	42	80	-
6.3% BTCA	1.63% Na ₂ CO ₃	4.23	3.6	245	208	56	50	-	-
6.5% BTCA	NaHFA 1:1 mole ratio	5.0	3.8	281	-	115.4	72.9	-	79.0
6.5% BTCA	Na ₂ FA 1:1 mole ratio	4.9	4.0	257	-	101.7	75.6	-	80.6
6.5% BTCA	NaHMA 1:1 mole ratio	6.3	3.3	266	-	108.2	64.9	-	76.7
6.5% BTCA	Na ₂ MA 1:1 mole ratio	5.8	3.8	250	-	75.0	73.8	-	78.1
6.5% BTCA	Na ₂ IA 1:1 mole ratio	5.6	3.5	265	-	112.5	78.8	-	73.8
6.0% BTCA	Na ₂ MLA 0.5:1 mole ratio	6.6	4.4	272	-	62	65	114	-
6.0% BTCA	Na ₂ TA 0.5:1 mole ratio	7.5	4.2	266	-	59	61	89	-
6.0% BTCA	Na ₂ HCA 0.5:1 mole ratio	7.3	4.3	276	-	58	60	107	-
6.5% BTCA	Imidazole 1:1 mole ratio	4.6	3.8	275	261	116.1	71.3	-	56.8

Where NaHFA = sodium hydrogen formate, Na₂FA = disodium formate, Na₂I = disodium itaconate, Na₂MLA = disodium malate, Na₂TA = disodium tartrate, Na₂HCA = disodium citrate.

Table 3.4 Summary of the results of the different catalytic systems employed for the PCA easy-care finishing of cotton cellulose, discussed in section 3.2.3.

3.2.4 Proposed Mechanisms Of The Fibre Cross-Linking Of Cotton Cellulose With Polycarboxylic Acids.

Yang (159, 160) has researched the mechanism of cotton cellulose cross-linking with polycarboxylic acids. He proposed that the esterification of cotton cellulose proceeded by two steps. The formation of a five-membered cyclic anhydride intermediate by the dehydration of two adjacent carbonyl groups on the polycarboxylic acid and followed by the reaction of the anhydride intermediate with the hydroxyl groups in cotton cellulose to form an ester link (160).

Yang studied the two isomers of butanedicarboxylic acid, i.e. the cis-isomer maleic acid and the trans-isomer fumaric acid. Infra-red spectral data indicated that only the maleic acid was able to form ester links with cotton cellulose. Infra-red spectroscopy was also used to reveal the anhydride intermediate during the curing of cotton cellulose (160). Yang compared the reaction of polyacrylic acid and polymaleic acid with cotton cellulose and concluded that polycarboxylic acids which could form five-membered cyclic anhydrides were capable of cross-linking cotton cellulose more effectively than polycarboxylic acids that formed six-membered cyclic anhydrides (161).

Using an infra-red spectroscopic study Yang was able to study the effect of pad bath pH on both the formation of the anhydride intermediate and on the formation of the ester links (159, 160). He reported that the formation of an anhydride intermediate was accelerated by an increase in proton concentration of the pad bath whereas the formation of an ester reached an optimum at around pH 3. Ester formation was not increased by a further increase in proton concentration.

The pH of the finish bath is influenced by the polycarboxylic acid and the catalyst in the finish formulation. Two ionisation equilibria co-exist, one for the polycarboxylic acid and the other for the catalyst. These ionisation equilibria interact with one another and thus the pH of the finish bath is determined by the concentration of the relevant acid and catalyst species in the aqueous solution.

There are five different species in the ionisation equilibrium for BTCA: H_4B , H_3B^- , H_2B^{2-} , HB^{3-} , B^{4-} , where the B^{4-} represents the butanetetracarboxylate anion. Table 3.5 shows the relative concentrations (α) of the five different ionisation species of BTCA at different pH values. Yang et al. (162) calculated these based on the ionisation equilibria for BTCA, see Figure 3.14. At any given temperature the pKa values remain constant and therefore proton concentration is the only variable in the ionisation equilibria for BTCA. Thus the relative concentration of the polycarboxylic acid species in the finish bath are determined by the proton concentration of the solution at any given temperature.

$$\alpha_{H_4B} = \frac{[H_4B]}{\{[H_4B] + [H_3B^-] + [H_2B^{2-}] + [HB^{3-}] + [B^{4-}]\}}$$

$$= \frac{\{[H^+]^4\}}{\{[H^+]^4 + K_{a1}[H^+]^3 + K_{a1}K_{a2}[H^+]^2 + K_{a1}K_{a2}K_{a3}[H^+] + K_{a1}K_{a2}K_{a3}K_{a4}\}}$$

$$\alpha_{H_3B^-} = \frac{[H_3B^-]}{\{[H_4B] + [H_3B^-] + [H_2B^{2-}] + [HB^{3-}] + [B^{4-}]\}}$$

$$= \frac{\{[H^+]^3 K_{a1}\}}{\{[H^+]^4 + K_{a1}[H^+]^3 + K_{a1}K_{a2}[H^+]^2 + K_{a1}K_{a2}K_{a3}[H^+] + K_{a1}K_{a2}K_{a3}K_{a4}\}}$$

$$\alpha_{H_2B^{2-}} = \frac{[H_2B^{2-}]}{\{[H_4B] + [H_3B^-] + [H_2B^{2-}] + [HB^{3-}] + [B^{4-}]\}}$$

$$= \frac{\{[H^+]^2 K_{a1}K_{a2}\}}{\{[H^+]^4 + K_{a1}[H^+]^3 + K_{a1}K_{a2}[H^+]^2 + K_{a1}K_{a2}K_{a3}[H^+] + K_{a1}K_{a2}K_{a3}K_{a4}\}}$$

$$\alpha_{HB^{3-}} = \frac{[HB^{3-}]}{\{[H_4B] + [H_3B^-] + [H_2B^{2-}] + [HB^{3-}] + [B^{4-}]\}}$$

$$= \frac{\{[H^+] K_{a1}K_{a2}K_{a3}\}}{\{[H^+]^4 + K_{a1}[H^+]^3 + K_{a1}K_{a2}[H^+]^2 + K_{a1}K_{a2}K_{a3}[H^+] + K_{a1}K_{a2}K_{a3}K_{a4}\}}$$

$$\alpha_{B^{4-}} = \frac{[B^{4-}]}{\{[H_4B] + [H_3B^-] + [H_2B^{2-}] + [HB^{3-}] + [B^{4-}]\}}$$

$$= \frac{\{K_{a1}K_{a2}K_{a3}K_{a4}\}}{\{[H^+]^4 + K_{a1}[H^+]^3 + K_{a1}K_{a2}[H^+]^2 + K_{a1}K_{a2}K_{a3}[H^+] + K_{a1}K_{a2}K_{a3}K_{a4}\}}$$

$$\alpha_{H_4B} + \alpha_{H_3B^-} + \alpha_{H_2B^{2-}} + \alpha_{HB^{3-}} + \alpha_{B^{4-}} = 1$$

Figure 3. 14 Ionization equilibria for BTCA (162).

pH	α_{H_4B}	$\alpha_{H_3B^-}$	$\alpha_{H_2B^{2-}}$	$\alpha_{HB^{3-}}$	$\alpha_{B^{4-}}$	% conversion carboxyl \Rightarrow carboxylate
1.0	0.996	0.004	0.000	0.000	0.000	0.0
2.0	0.964	0.036	0.000	0.000	0.000	0.9
3.0	0.724	0.269	0.007	0.000	0.000	7.1
4.0	0.175	0.651	0.171	0.002	0.000	25.0
5.0	0.007	0.248	0.625	0.092	0.001	43.5
6.0	0.000	0.015	0.392	0.554	0.038	65.0
7.0	0.000	0.000	0.040	0.567	0.392	83.7
8.0	0.000	0.000	0.001	0.126	0.873	96.8
9.0	0.000	0.000	0.000	0.014	0.986	99.9
10.0	0.000	0.000	0.000	0.001	0.999	100.0
11.0	0.000	0.000	0.000	0.000	1.000	100.0

Table 3. 5 The relative concentrations (α) of the five different ionization species of BTCA at different pH values (162).

From Table 3. 5 it can be seen that the carbonyl group is the predominant species in the BTCA solution in the pH range 1-3. Yang confirmed this using infra-red analysis (159). As the pH is increased, the carbonyl species is converted to carboxylate.

Yang (159) compared the catalysis of the different sodium salts of phosphoric acid and found their catalytic effectiveness to be pH-dependent. The relative concentrations of the different species of both acid and catalyst were dependent on the pH of the padding solution. Yang proposed that the main catalyst species in the pad bath was $H_2PO_4^-$ regardless of whether the initial catalyst was the mono-, di-, or trisodium salt. He indicated that the difference in catalytic effectiveness was due to the different pH values of the finish bath rather than to the different chemical form of the catalyst as suggested

by Brown (148).

After cotton cellulose has been finished with a polycarboxylic acid easy-care finishing agent, such as BTCA, the newly inserted carbonyl groups in the fabric exist in three forms. Intermolecular ester links, uncombined carbonyl end groups (the acid form of the free carbonyl) and uncombined carboxylate ions (the basic form of the free carbonyl). FT-IR spectroscopy has been used to measure the quantity of ester links in cotton cellulose. This is achieved by measuring the ester carbonyl band in the infra-red spectrum at around 1735cm^{-1} . The ester band and the acid carbonyl band overlap in the infra-red spectrum of the cured cotton cellulose, however treatment with a dilute solution of NaOH separates the bands by converting the acid carbonyl into a carboxylate ion. Yang (162) suggested that because the carbonyl to carboxylate conversion reaches 100% above pH 9 (see Table 3.5) treatment of the finished cotton cellulose with a 0.1M solution of NaOH at room temperature for two minutes converted the acid carbonyl in the cotton cellulose to carboxylate ions. Care must be taken not to hydrolyse the ester links during the NaOH treatment.

The intensity of the ester carbonyl band has been used as a basis for semi-quantitative analysis in relation to the total number of ester links in the fabric (163). Acid-base titration was used to quantitatively determine the concentration of the polycarboxylic acid and its ester cross-links in the treated cotton fabrics. A linear relation was found between the intensity of the ester carbonyl band absorbance from the infra-red spectrum and the ester concentration in the fabric calculated by acid-base titration (164). BTCA was found to be the most effective polycarboxylic acid for cotton cellulose cross-linking.

3.3 AN INITIAL STUDY INTO THE CHEMICAL MODIFICATION OF SILK FABRIC WITH POLYCARBOXYLIC ACIDS.

As discussed in the previous section, polycarboxylic acids have been investigated as alternative fibre cross-linking agents to formaldehyde-based chemicals for improving the easy-care characteristics of cotton cellulose fabrics. Reagents, such as BTCA, have been found to give equivalent durable press values to DMDHEU, the most popular formaldehyde reagent, when used in conjunction with SHP as a catalyst.

3.3.1 Treatment Of Silk Fabric With BTCA And CA With SHP As Catalyst.

In this initial study silk fabric was treated with two different polycarboxylic acids as chemical modification agents in the presence of a catalyst. The polycarboxylic acids selected for this initial study were BTCA and CA. BTCA was chosen as it has been reported in the literature to be the most effective polycarboxylic acid for improving the easy-care characteristics of cotton cellulose (164). Whereas CA was selected because of its proven non-toxic nature and its ability to impart moderate easy-care characteristics to cotton cellulose (136, 149). These polycarboxylic acids were applied to silk fabric samples in the presence of SHP as a catalyst; this catalyst has been reported to allow the lowest cure temperature and to inhibit fabric yellowing in the reaction of polycarboxylic acids with cotton cellulose (145).

3.3.1.1 Experimental procedure.

Plain-woven, silk noil fabric, see section 2.1, was treated with 5% w/w BTCA or 7% w/w CA and different molar ratios of SHP catalyst, see Table 3. 6. A two dip, two nip padding process was used and the samples were dried at 80°C for 2min followed by curing at 165°C for 1.5min, as described in section 2.1. The treated samples were conditioned for 48h and tested with respect to percent chemical add-on, crease recovery angle, and degree of sample yellowing. Sample testing was carried out according to the test methods described in section 2.2 and comparisons of the results were made with an untreated silk fabric control.

Sample Number	% w/w PCA	PCA:SHP Molar Ratio	Pad Bath pH
1	5% w/w BTCA	1:0.5	2.27
2	5% w/w BTCA	1:0.75	2.36
3	5% w/w BTCA	1:1	2.41
4	5% w/w BTCA	1:1.25	2.46
5	5% w/w BTCA	1:1.5	2.50
6	7% w/w CA	1:0.5	2.11
7	7% w/w CA	1:0.75	2.17
8	7% w/w CA	1:1	2.23
9	7% w/w CA	1:1.25	2.28
10	7% w/w CA	1:1.5	2.33

Table 3. 6 Summary of padding conditions of silk fabric treated with 5% w/w BTCA or 7% w/w CA and SHP catalyst.

The BTCA pad baths were clear yellow/green liquids, whereas the CA pad baths were clear to slightly cloudy liquids. SHP dissolves in aqueous solution to form a clear solution. CA dissolves at room temperature in aqueous solution whereas BTCA requires heating to dissolve it in aqueous solution, but once dissolved, it remains dissolved for several hours.

Table 3. 6 is a summary of the padding conditions used to treat silk fabrics with BTCA or CA and SHP catalyst. As the quantity of SHP was increased in the pad bath, the pad bath pH value increased. The pH of 5% w/w BTCA in solution was 2, whereas the pH of 7% w/w CA in solution was 1.78. With the addition of SHP the pH value increased for both pad baths because the pH of an equivalent molar ratio of SHP in solution is higher, approximately pH 6. The CA finishing baths had pH values slightly lower than the equivalent BTCA finishing baths. This is due in part to the higher concentration of CA in the finishing baths and to the fact that CA is slightly more acidic than BTCA, pK_{a1} 3.13 versus 3.43 respectively, see Table 3. 1.

3.3.1.2 Results and discussion.

The test results are tabulated in Appendix 1, Table A1.1 and plotted in the text in Figure 3. 15 to Figure 3. 18.

The treated samples were allowed to condition for 48h before being measured for shrinkage. No shrinkage occurred in the weft direction and less than 0.5% shrinkage occurred in the warp direction. Treatment of silk fabrics with either BTCA or CA according to the above method does not cause the fabric to shrink. By pre-shrinking the fabric prior to application of the finish any tensions put in the fabric during its previous processing history, e.g. weaving, were relaxed.

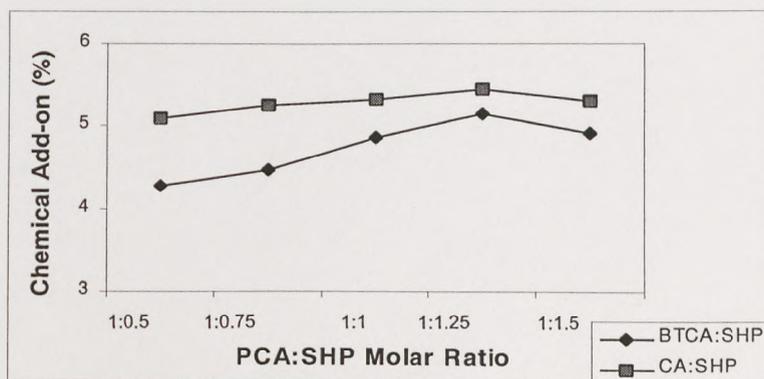


Figure 3. 15 Percentage chemical add-on of silk fabric treated with 5% w/w BTCA or 7% w/w CA and different molar ratios of catalyst SHP.

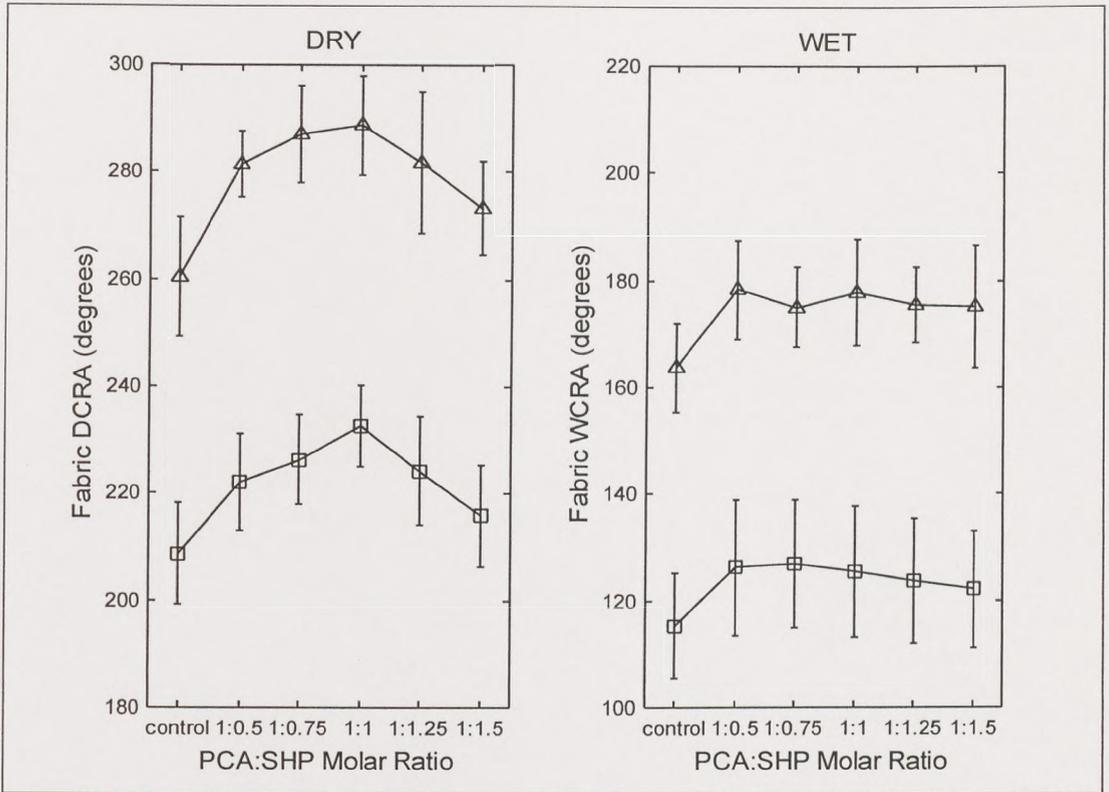


Figure 3.16 CRA of silk fabric treated with 5% w/w BTCA and different molar ratios of catalyst SHP.

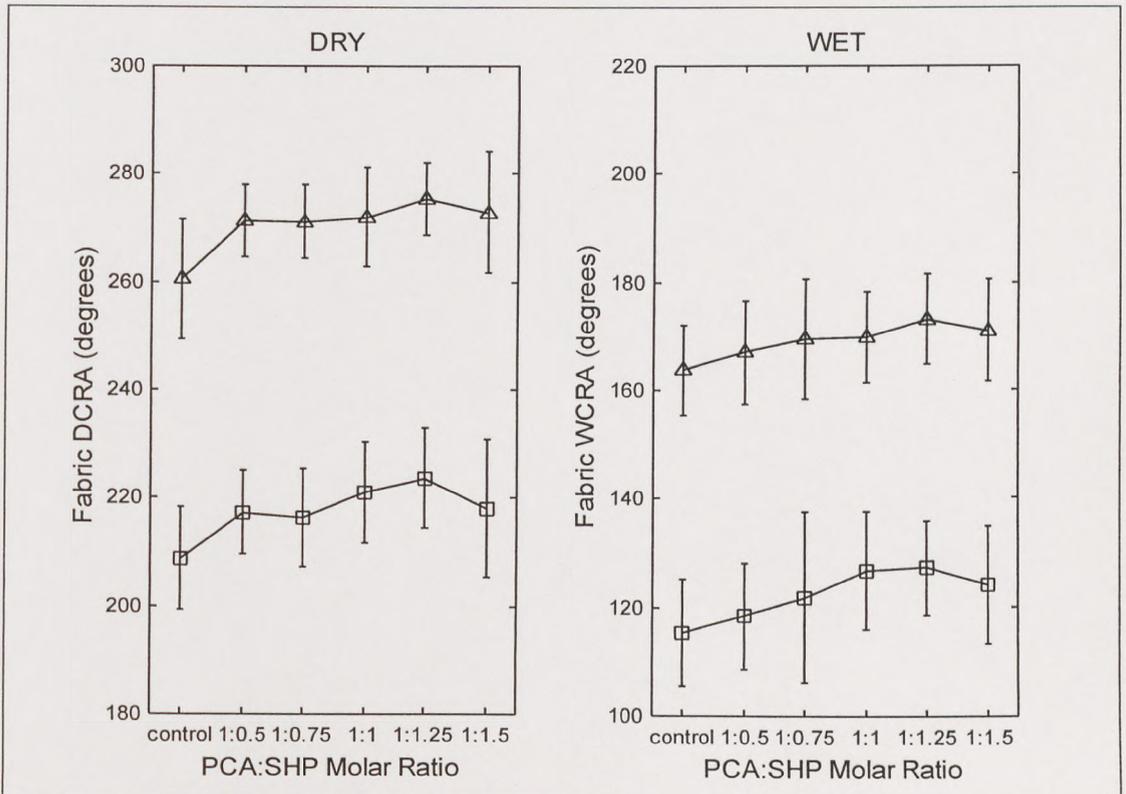


Figure 3.17 CRA of silk fabric treated with 7% w/w CA and different molar ratios of catalyst SHP.

Figure 3. 15 compares the chemical add-on of BTCA/SHP treated samples with samples treated with CA/SHP. The graph indicates that the chemical add-on on the fabric increases as the molar ratio of polycarboxylic acid:catalyst SHP (PCA:SHP) increases in the pad baths. Fabrics treated with CA show a higher percent chemical add-on than those treated with BTCA due to the higher concentration of CA in the CA pad baths compared with the BTCA pad baths, 7%w/w compared with 5%w/w respectively. For fabrics treated with either BTCA or CA the highest percent chemical add-ons were achieved with a 1:1.25 molar ratio of PCA:SHP. It appears from Figure 3. 15 that the addition of more catalyst above this acid:catalyst molar ratio causes a decrease in chemical add-on, hindering the reaction of the silk fibroin with the PCA. This may be due to a decrease in the reaction at the higher pH value or saturation of the available reaction sites within the accessible regions of the silk fibres.

The fabric crease recovery angles, dry crease recovery angle (DCRA) and wet crease recovery angle (WCRA), for silk fabric treated with BTCA or CA and different molar ratios of SHP catalyst are plotted in Figure 3.16 and Figure 3.17, respectively. The dry and wet crease recovery angles of the treated fabrics are compared with a control sample the dry and wet crease recovery angles of the untreated fabric. Figure 3.16 shows that the fabric DCRA increases, both the plot of the initial elastic recovery and the plot of the recovery from creasing after five minutes, increase as the concentration of SHP increases in the pad bath and reaches a maximum at a molar ratio of BTCA:SHP of 1:1. An increase in the molar ratio of BTCA: SHP above 1:1 does not improve the fabric DCRA further. The fabric WCRA for silk fabric treated with BTCA and varying ratios of SHP catalyst shows a slight increase in comparison to the untreated control. Figure 3.16 indicates that the fabric WCRA, both the plot of the initial elastic recovery and the plot for recovery from creasing after five minutes, are unaffected by the quantity of SHP in the pad bath. The wet and dry crease recovery angle graphs suggest that a molar ratio of BTCA:SHP of 1:1 leads to optimum crease recovery performance.

In contrast Figure 3.17 displays the results of the recovery from creasing of silk fabric treated with CA and varying molar ratios of SHP catalyst. These graphs show a slight increase in crease recovery angles for both the DCRA and WCRA in comparison with the untreated control. An increase in SHP in the pad bath gives rise to a very slight improvement in crease recovery angles. According to Figure 3.17 a molar ratio of

CA:SHP of 1:1.25 gives optimum crease recovery performance. A comparison of the crease recovery graphs for silk fabric treated with BTCA and CA indicates that samples treated with BTCA lead to higher recovery angles despite the lower molecular quantity of polycarboxylic acid in the BTCA pad bath. 5% w/w BTCA is equivalent to 0.214mol/l BTCA in the BTCA/SHP pad bath, whereas 7% w/w CA is equivalent to 0.364mol/l CA in the CA/SHP pad baths. This would suggest that BTCA is a more effective polycarboxylic acid in comparison with CA for improving the crease recovery properties of silk fabrics.

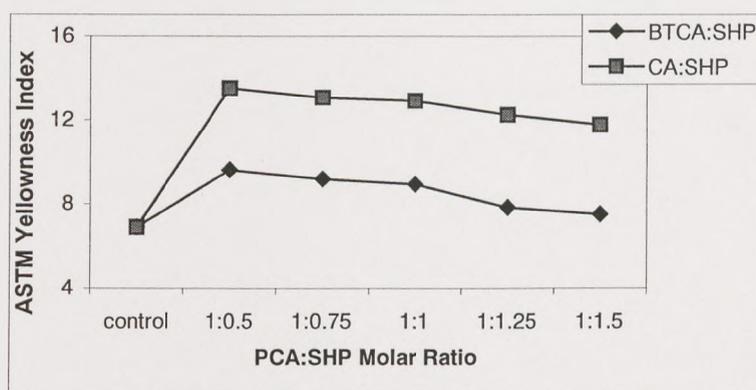


Figure 3. 18 Degree of yellowing of silk fabric treated with 5% w/w BTCA or 7% w/w CA and different molar ratios of catalyst SHP.

The degree of fabric yellowing of the treated samples was measured according to the ASTM yellowness index. Figure 3. 18 displays the results in graphical format. The yellowness of all the treated samples was greater than the control and in all cases the yellowness decreased with an increase of SHP in the pad bath. With high molar ratios of BTCA:SHP in the pad bath, greater than 1:1, very little fabric yellowing was observed. Treatment with CA caused the fabric to yellow more than samples treated with BTCA.

It has been reported in the literature that treatment with CA causes visible fabric yellowing (151). This is thought to be due to dehydration of some CA molecules to form aconitic acid (AA) at high curing temperatures (149). AA is an unsaturated acid and the large discoloration observed with fabrics treated with this acid at high temperatures could be due to the degradation of the double bond, see section 3.2.2.2. A variety of methods for suppressing this fabric discoloration are also reported in section 3.2.2.2.

The fabric yellowing of the treated samples decreased for samples treated with higher quantities of SHP in the pad baths. This has been reported to be due to the reducing properties of SHP (145). This is advantageous where fabric whiteness is concerned but fabrics treated with SHP as catalyst are known to cause shade changes on some sulphur and reactive dyeings (145).

3.3.1.3 Conclusions.

The results from this experiment on the chemical modification of silk fabric with polycarboxylic acids, follow the general trends expected when compared with polycarboxylic acid finishing of cotton cellulose reported in section 3.2. BTCA would appear to be a more efficient polycarboxylic acid than CA as an easy-care finishing agent. BTCA-treated fabrics had higher crease recovery values in both the dry and wet state, and the fabric showed considerably less yellowing than CA treated samples, despite lower number of molecules of BTCA in the BTCA pad bath compared to the CA pad bath. As the molar ratios of PCA:SHP were increased fabric yellowing was decreased and both the dry and wet crease recovery angles were increased. Above a molar ratio of PCA:SHP of 1:1.25, the chemical add-on decreased and a corresponding decrease in crease recovery angles was observed. This would seem to suggest that the optimum molar ratio of PCA:SHP is 1:1.25 for BTCA and CA.

3.3.2 Comparison Of Silk Fabrics Finished With BTCA And A Methylol Melamine Reagent.

In order to gauge the effectiveness of BTCA as an easy-care finishing agent for silk fabric a comparison with a traditional methylol melamine reagent was undertaken. It has been reported in the literature that methylol melamine is one of the most efficient formaldehyde-based easy-care finishing agents for silk (82). The methylol melamine reagent used in this experiment was Permafresh Mel (Warwick). This was used in conjunction with magnesium chloride as catalyst.

3.3.2.1 Experimental procedure.

Plain woven silk habutai heavy, roll 4, see section 2.1.1, was treated with varying quantities of BTCA and a 1:1 molar ratio of SHP catalyst or Permafresh Mel (MEL) and magnesium chloride catalyst, see Table 3. 7. The silk fabric samples were padded by a

two dip, two nip process, dried at 80°C for 2min and cured at 165°C for 1.5min according to the method described in section 2.1. The treated samples were conditioned for 48h and tested with respect to percent chemical add-on, dry and wet crease recovery angles, fabric warp and weft bending length, fabric tensile strength and fabric elongation at break.

Sample Number	% w/w Finish	Catalyst	Pad Bath pH
1	2% w/w BTCA	1:1 BTCA:SHP Molar Ratio	2.34
2	4% w/w BTCA	1:1 BTCA:SHP Molar Ratio	2.19
3	6% w/w BTCA	1:1 BTCA:SHP Molar Ratio	2.10
4	8% w/w BTCA	1:1 BTCA:SHP Molar Ratio	1.98
5	5% w/w MEL	1% w/w Magnesium Chloride	7.36
6	7.5% w/w MEL	1.5% w/w Magnesium Chloride	7.56
7	10% w/w MEL	2% w/w Magnesium Chloride	7.77
8	12.5% w/w MEL	2.5% w/w Magnesium Chloride	7.93
9	15% w/w MEL	3% w/w Magnesium Chloride	8.07

Table 3. 7 Summary of the pad bath conditions for silk fabric treated with varying quantities of BTCA or MEL.

BTCA is an off-white fine powder that dissolves in water on heating to produce a pale yellow/green liquid that remains dissolved for several hours whereas MEL is a clear viscous solution that turned cloudy on dilution with water. Both SHP and magnesium chloride dissolve in water to form clear solutions.

Table 3. 7 is a summary of the padding conditions used to treat silk fabric with BTCA or MEL. The pad baths containing BTCA are acidic in comparison to the MEL pad baths which are weakly alkaline. BTCA is an acidic finishing reagent, whereas MEL is an alkaline finishing reagent. As the quantity of BTCA increases in the pad bath the pH decreases and becomes more acidic, whereas as the quantity of MEL increases in the pad bath the pH increases and becomes more alkaline.

3.3.2.2 Results and discussion.

The test results are tabulated in Appendix 1, Tables A1.2 and the results appear in graphical form in the text in Figure 3.19 to Figure 3.24. The percent chemical add-on increases with an increase in finishing reagent in the pad bath for silk fabric treated with both BTCA and MEL. In order to compare samples treated with BTCA and MEL the fabric properties tested were analysed with respect to percent chemical add-on.

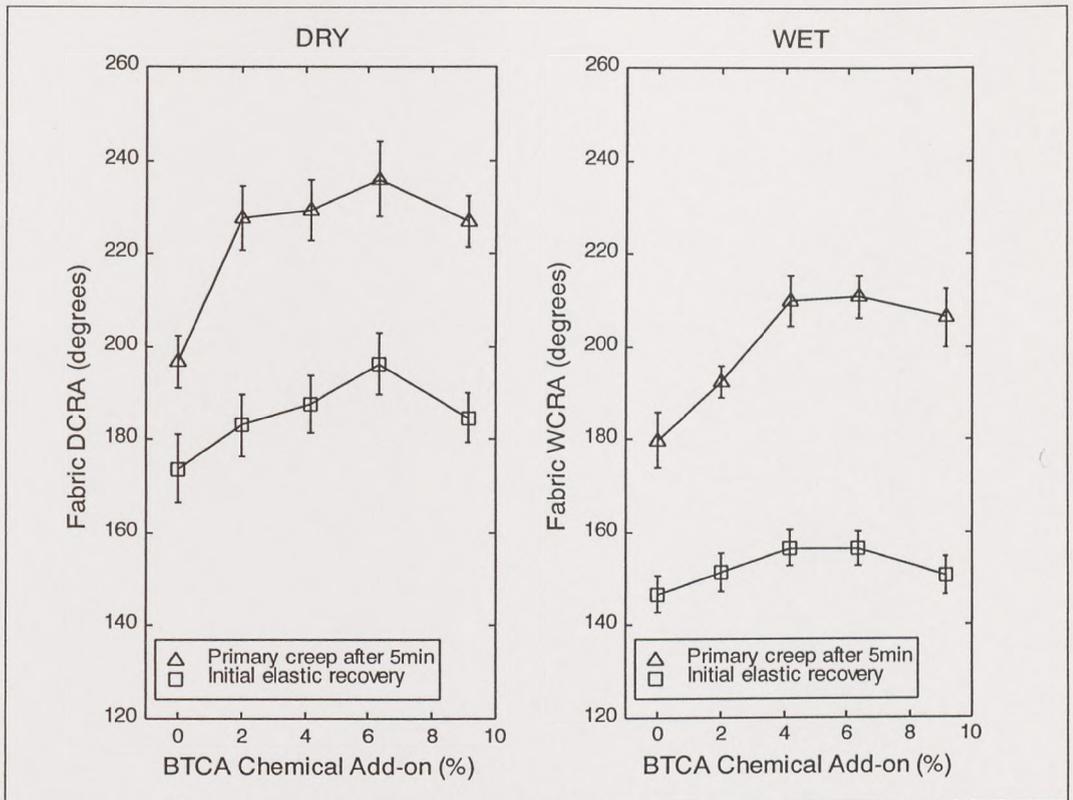


Figure 3. 19 Fabric CRA values of silk fabric treated with BTCA and a 1:1 molar ratio of SHP.

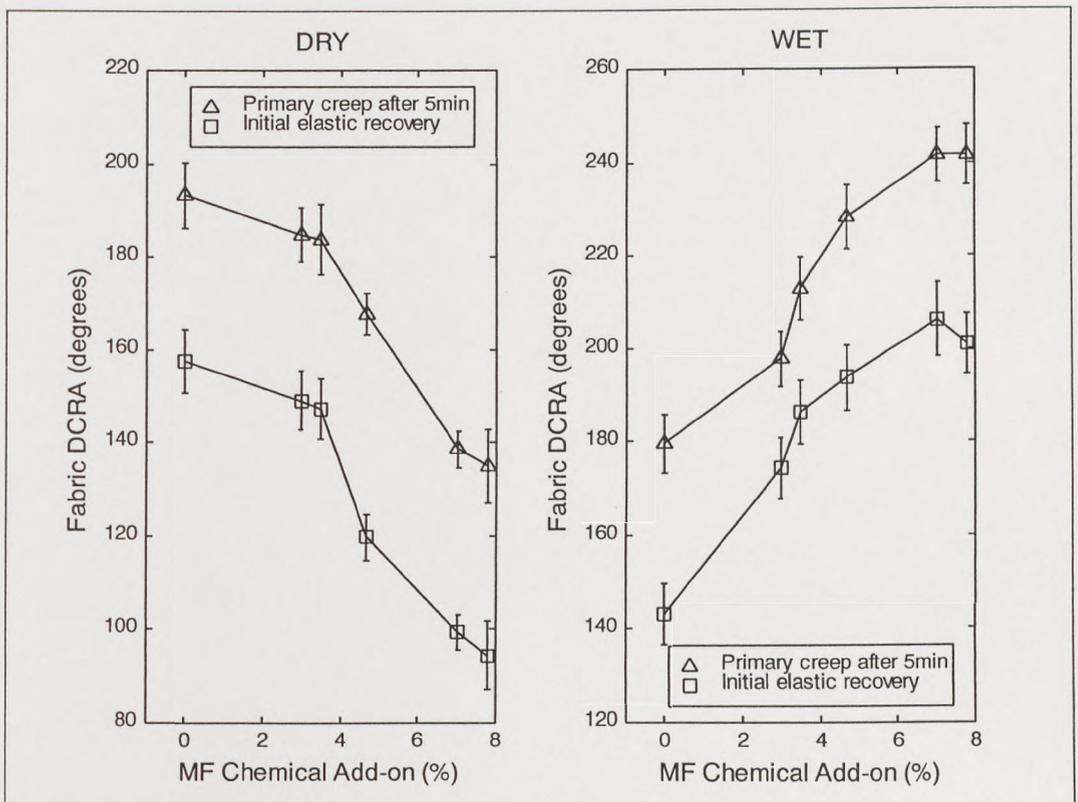


Figure 3. 20 Fabric CRA values of silk fabric treated with Permafresh Mel and magnesium chloride catalyst.

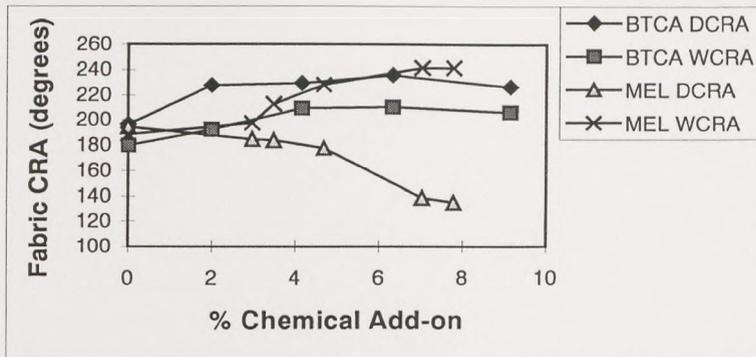


Figure 3. 21 Comparison of fabric dry and wet CRA values for silk fabric samples treated with BTCA or Permafresh Mel.

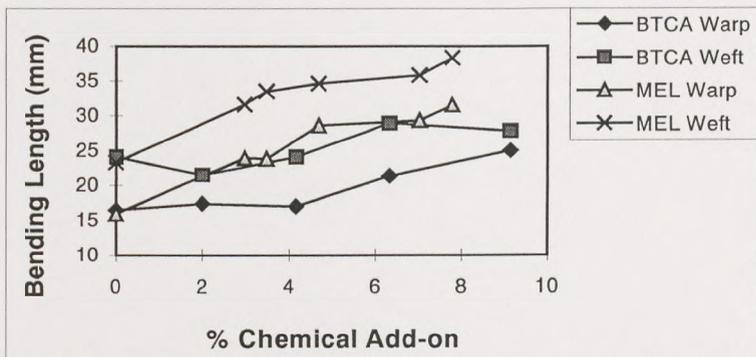


Figure 3. 22 Comparison of fabric warp and weft bending length for silk fabric samples treated with BTCA or Permafresh Mel.

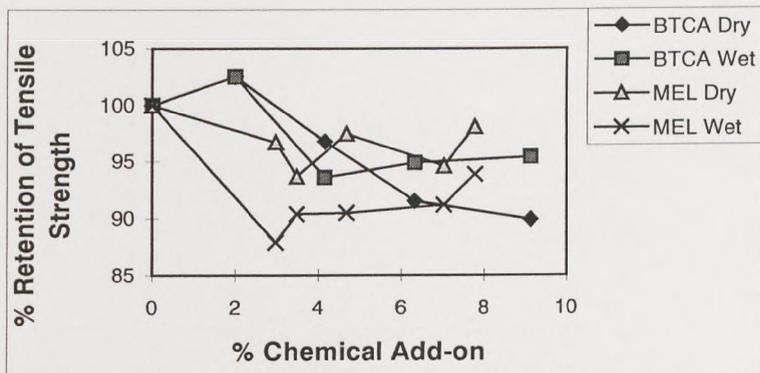


Figure 3. 23 Comparison of fabric dry and wet retention of fabric strength for silk fabric samples treated with BTCA or Permafresh Mel.

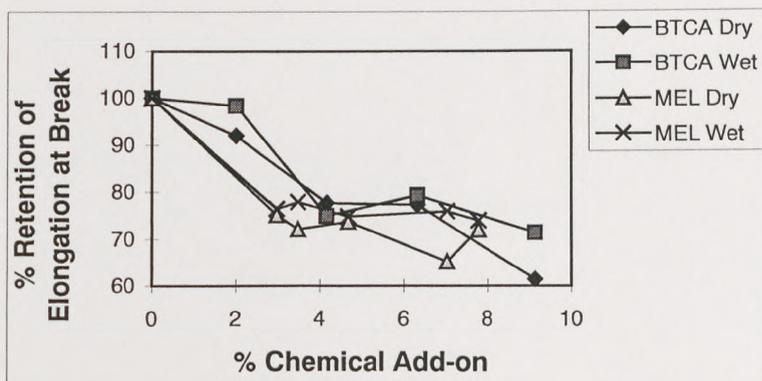


Figure 3. 24 Comparison of fabric dry and wet retention of elongation at break for silk fabric samples treated with BTCA or Permafresh Mel.

Fabric crease recovery angles were plotted against percent chemical add-on and are displayed in Figures 3.19 and 3.20. Silk fabric treated with BTCA and SHP catalyst has higher dry and wet crease recovery angle values. This improvement in crease recovery increases with percent chemical add-on to a maximum at approximately 6%. According to figure 3.19 high percent chemical add-on values have a detrimental affect on the fabric DCRA and do not further improve the fabric recovery from creasing in the wet state. In comparison silk fabric treated with Permafresh Mel (MEL) and magnesium chloride catalyst show opposite trends for dry and wet crease recovery angles. The fabric DCRA decreases significantly with an increase in percent chemical add-on whereas the fabric WCRA shows an increase with an increase in percent chemical add-on. A comparison of the dry and wet fabric crease recovery angles for silk fabric treated with BTCA or MEL are plotted in figure 3.21. Fabric treated with BTCA showed better recovery from creasing in the dry state but worse recovery from creasing in the wet state when compared with MEL at equivalent percent chemical add-on values.

Treatment of silk fabric with MEL made the fabric stiff; this is reflected in the high bending length results, see Table A1.2. Figure 3.22 compares the bending length results of silk fabric treated with BTCA or MEL. For both finishes the warp and weft bending lengths increase with an increase in percent chemical add-on. Fabric treated with MEL showed a much higher increase in bending length values for both warp and weft than silk fabric treated with BTCA. An increase in bending length is accompanied by an increase in fabric stiffness. From these results it can be inferred that silk fabric treated with MEL produces a fabric with a stiffer handle. This induced fabric stiffness precludes the use of the fabric for textile purposes particularly at high chemical add-on values.

The fabric stiffness of melamine formaldehyde finishes is discussed in section 1.2.2.2. It has been reported that melamine finishes produce hard resins (81). This may be due to the close lattice structure formed during the curing process or to the rigidity of the ring structure (81). It may be possible to control the fabric stiffness by the addition of suitable reagents into the pad bath such as fabric softeners.

The tensile properties of silk fabric treated with BTCA or MEL are compared in Figure 3.23 and Figure 3.24. There is a slight reduction in tensile strength of the treated silk

fabric samples for both finishes. Generally samples treated with BTCA showed less reduction in tensile strength than samples treated with MEL. The reduction in tensile strength for silk fabric treated with both BTCA or MEL showed improved retention of tensile strength in comparison to the results reported for easy-care finishing of cotton cellulose (81). The retention of elongation at break of silk fabric decreased with an increase in percent chemical add-on for both finishes. Again silk fabric treated with BTCA showed higher values of retention of tensile strength in comparison with samples treated with MEL at equivalent values of percent chemical add-on. The retention of fabric mechanical properties for silk fabric treated with BTCA are slightly higher than for samples treated with MEL. A similar trend has been reported when comparing the finishing of cotton cellulose with polycarboxylic acids such as BTCA and formaldehyde based reagents such as DMDHEU (165).

3.3.2.3 Conclusions.

As with experiment 3.3.1, the results reported here for the comparison of silk fabric finished with BTCA or MEL follow the expected trends when compared to the easy-care finishing of cotton cellulose reported in section 3.2. A comparison of the recovery from creasing of BTCA-finished silk fabric with MEL-finished silk fabrics leads to equivalent results. At 6.33% chemical add-on of BTCA compared with 4.68% chemical add-on MEL, the most suitable observed levels for each finish. The DCRA values were 235.9 for BTCA and 177.7 for MEL whereas the WCRA values were 210.7 for BTCA and 228.2 for MEL. BTCA-finished silk fabric showed better recovery from creasing in the dry state but showed lower values of recovery from creasing in the wet state. Additional BTCA in the pad bath above 6% w/w was not found to give any further increase in the fabric crease recovery angles. The optimum pad bath concentration of BTCA for finishing of cotton cellulose was also found to be approximately 6% w/w (154).

A comparison of the mechanical properties of silk fabric treated with BTCA or MEL showed that these decreased with an increase in percent chemical add-on. Samples treated with BTCA showed higher retention of both tensile strength and elongation at break when compared with samples treated with MEL. This trend has also been observed when comparing polycarboxylic acid finishing with the more traditional formaldehyde finishing for cotton cellulose (165). However, the percent reduction in

tensile strength was considerably less for the finishing of silk fabric compared with that of cotton cellulose.

Silk fabric treated with MEL particularly at high add-on values led to increased fabric stiffness. This has also been found to be true for cotton cellulose treated with melamine resins (81). However Yang and Li (85) stated that the stiffness of silk fabric treated with melamine resins could be overcome by suitable after-treatments.

3.3.3 Optimisation Of The Conditions For Curing Silk Fabrics Finished With BTCA.

Experiments 3.3.1 and 3.3.2 proved that it is possible to obtain an improvement in crease recovery properties for silk fabric treated with BTCA. Good fabric easy-care performance is obtained with fabrics that have high crease recovery properties in both the dry and wet states. In order to achieve maximum easy-care performance of silk fabrics treated with BTCA an investigation of the method of application of the fabric finish was undertaken in order to find the optimum conditions. This experiment researched different methods of curing the treated fabric samples (see section 2.1.5) and investigates the influence of curing on various fabric properties.

3.3.3.1 Experimental procedure.

Plain woven silk habutai medium, roll 2, see section 2.1.1, was treated with 6% w/w BTCA and a 1:1 molar ratio of SHP catalyst. The silk fabric samples were padded by a two dip, two nip process, dried at 80°C for 2min and cured under a variety of conditions according to the method described in section 2.1. The treated samples were conditioned for 48h and tested with respect to the carbonyl bond frequency peak height at 1735cm⁻¹ in FT-IR spectra of the treated silk fabric, fabric dry and wet crease recovery angles, fabric warp and weft bending length, fabric tensile strength and fabric elongation at break.

3.3.3.2 Results and discussions.

The test results are tabulated in Appendix 1, Tables A1.3a and A1.3b and the results appear in graphical form in the text in Figure 3.25 to Figure 3.29.

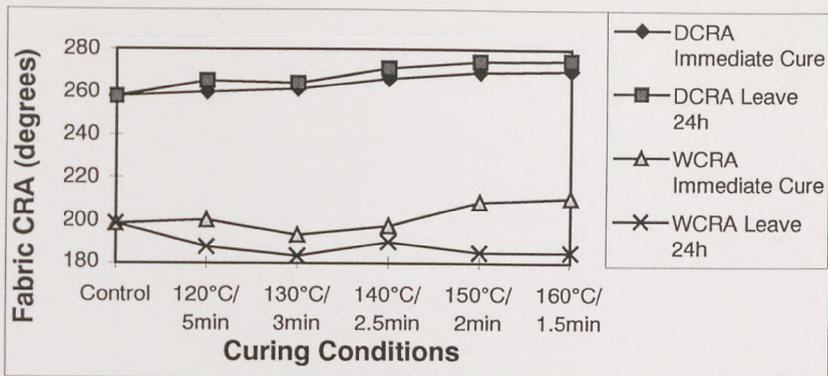


Figure 3.25 Fabric CRA values for silk fabric treated with 6% BTCA and 1:1 molar ratio of SHP cured under different conditions.

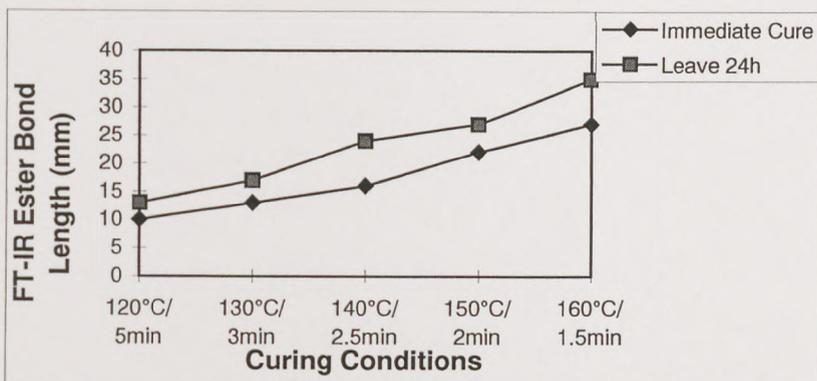


Figure 3.26 Peak height measured in mm for the carbonyl band frequency at 1735cm^{-1} from FT-IR spectra from silk fabric treated with 6% BTCA and 1:1 molar ratio of SHP cured under different conditions.

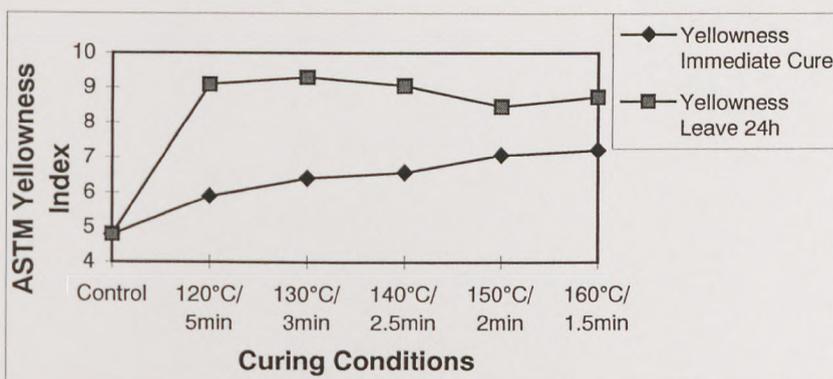


Figure 3.27 ASTM yellowness index for silk fabric treated with 6% BTCA and 1:1 molar ratio of SHP cured under different conditions.

Figure 3.25 shows a plot of the recovery from creasing after five minutes for silk fabric treated with 6% w/w BTCA and a 1:1 molar ratio of SHP under different curing conditions. As the temperature of the cure increases, there is a slight increase in the recovery from creasing for the treated silk fabrics in both the dry and wet state. The treated fabric samples that were left for 24h after drying and then cured showed higher DCRA values but lower WCRA values when compared with samples cured immediately after drying.

The high temperature curing process provides the necessary energy for a reaction to take place between the silk fabric and BTCA. The higher the temperature the greater the fabric recovery from creasing in both the wet and dry state. At a cure temperature above 170°C fabric yellowing was observed even for the untreated samples, and for this reason the highest curing temperature used in this experiment was 165°C.

It follows that the improved recovery from creasing may be as a result of an increase in chemical reaction with the fibre. Figure 3.26 plots the peak height measured in mm for the carbonyl band frequency from FT-IR spectra at 1735cm^{-1} for silk fabric treated with BTCA and SHP under different curing conditions, according to the method described in section 2.2.3.1.1. At a frequency of 1735cm^{-1} the carbonyl band of the carboxylic acid group overlaps with the carbonyl band of the ester link. The carbonyl frequency peak heights measured increased with an increase in curing temperature. This is indicative of an increase in carboxylic acid and ester bonds in the treated fabric samples as the curing temperature increased. Figure 3.26 also indicates that there is a greater increase in carboxylic acid and ester bonds in the delayed cured samples compared with samples cured immediately after drying.

The improvement in DCRA for the delayed cured samples may be attributed to the breaking of hydrogen bonds within the treated fabric after drying caused by the absorption of moisture from the atmosphere; this allows for a greater migration of the easy-care finish to new more effective positions. Subsequent curing fixes the resin within the silk fibroin. FT-IR spectra indicate that there is an increased quantity of ester links formed in the delayed cured samples compared to samples cured immediately after drying.

The decrease in WCRA of the delayed cured samples when compared to samples cured immediately after drying could be caused by the prolonged exposure of silk fabric to acid conditions. After drying the treated samples have a low pH value because of the low pH value of the reagent solution. Although it may be possible to achieve an increase in ester bond formation with samples subjected to the delayed cure process, any advantages this may offer over the immediate cure process appear to be offset by an increase in acid degradation of the treated samples.

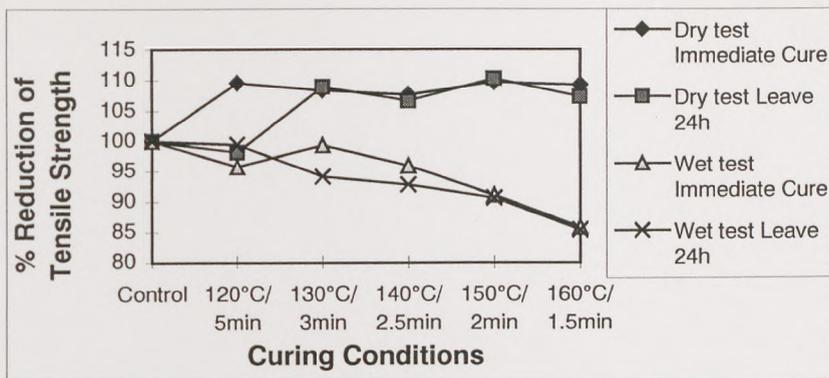


Figure 3.28 Fabric tensile strength for silk fabric treated with 6% BTCA and 1:1 molar ratio of SHP cured under different conditions.

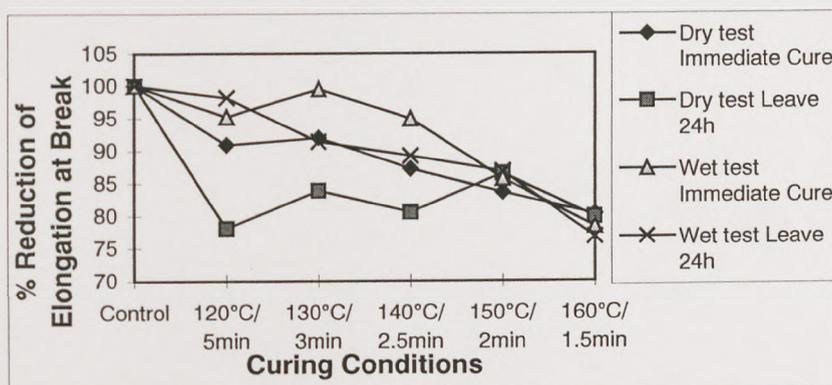


Figure 3.29 Fabric elongation at break for silk fabric treated with 6% BTCA and 1:1 molar ratio of SHP cured under different conditions.

This postulated theory of an increase in acid hydrolysis of the treated silk fabric samples subjected to the delayed cure process may also explain the lower percent retention of both tensile strength and elongation at break and the increase in fabric yellowing, see figures 3.27 to 3.29. Figure 3.27 is a plot of the ASTM yellowness index for samples treated under different curing conditions. As the curing temperature increases, there is an increase in fabric yellowing. Samples subjected to the delayed cure process show a marked increase in fabric yellowing. It has been reported that the yellowing of silk in the presence of ultra-violet light is primarily due to the degradation of the tyrosine residues (42), see section 1.1.4.10. It is possible therefore that the increased yellowing of the treated silk samples in the delayed cure process could be caused by a greater degradation of the tyrosine side chains due to prolonged exposure to acid conditions.

The increase in recovery from creasing in the dry state as the curing temperature is increased is accompanied by an increase in fabric strength, see figure 3.28. The increase in fabric strength suggests that at high cure temperatures more reaction has occurred; this is shown by an increase in FT-IR spectra carbonyl band frequency at 1735cm^{-1} . The fabric becomes more stable in the dry state. This would tend to suggest the

incorporation of new additional cross-links within silk fibroin caused by treatment with BTCA. However, there is a reduction in the dry retention of elongation at break as the cure temperature increases, so despite becoming stronger, the treated fabric samples become less extensible.

The increase in WCRA as the curing temperature increases is only very slight and is not accompanied by an increase in fabric strength. Figure 3.28 shows that as the curing temperature increases the retention of tensile strength decreases. This would tend to suggest that as the fabric becomes more stable in the dry state it becomes less stable in the wet state.

The results of treated fabric samples subjected to steam curing can be found in Appendix 1 table A1.4. These results show that steaming has a detrimental affect on both dry and wet crease recovery angles. The lower crease recovery angle values for steam-treated samples may be due to degradation of silk fibroin caused by the steaming process itself. The acid pH of the treated fabric samples in the presence of steam may cause hydrolysis of the peptide chains. This is reflected in the slightly lower percent retention of tensile strength and elongation at break for the steam-treated samples in comparison with samples cured without steam, see Appendix 1, Table A1.3a and A1.3b.

3.3.3.3 Conclusions.

It can be deduced from the results discussed in section 3.3.3.2 that as the curing temperature of the treated silk samples is increased the quantity of carbonyl groups within silk fibroin increases. This increase in carboxylic acid and ester groups is accompanied by an increase in dry fabric stability to both recovery from creasing and fabric strength. However a corresponding increase in wet resiliency is not observed; there is a slight increase in fabric WCRA as the curing temperature is increased but this is not accompanied by an increase in fabric strength. As the curing temperature and the quantity of carbonyl groups increases there is a corresponding decrease in both fabric yellowing and retention of elongation at break.

It could be possible that the improved dry stability of silk fabrics treated with BTCA and cured at high temperatures occurs as a result of a combination of increased hydrogen-bonding and ester bonds formed within silk fibroin. On wetting these

hydrogen bonds would be broken and thus a corresponding increase in wet resiliency would not be observed. The results show that as the curing temperature is increased there is an increase in the number of ester links formed within silk fibroin. These bonds are covalent in nature, and are therefore not broken when the samples are wetted. The slight increase in WCRA suggests that only a very few covalent cross-links are formed within the fibre. It could be possible that the BTCA molecules form single ended ester bond attachments with the hydroxyl bonds in silk fibroin and that the remaining three carboxylic acid groups are free to form hydrogen bonds either with themselves or with appropriate side chains in silk fibroin. This would explain the improved fabric DCRA and strength. The decreased elongation at break could be caused by a restriction in extensibility caused by the presence of the additional di-ester and ester/hydrogen bond cross-links in the PCA-treated fabrics.

Treated fabric samples that were left 24h prior to curing showed increased carbonyl bonds, carboxylic acid and ester bonds after fabric curing. This increase in reaction was not accompanied by an improvement in fabric properties. It is possible that the prolonged exposure to acid conditions of the delayed cure samples causes acid hydrolysis of silk fibroin. Therefore, any improvement in reaction efficiency is outweighed by acid degradation of the silk fibroin.

The results from experiment 3.3.3 show that steam curing is not an appropriate method for improving fabric properties as it leads to lower values of both dry and wet crease recovery angles as well as to decreased retention of fabric strength and elongation at break. This may be due to increased acid hydrolysis of the treated silk fabrics as a result of the combination of the steam and the low acid pH of the padded samples.

3.3.4 Optimisation Of The Process For Padding Silk Fabrics Finished With BTCA.

3.3.4.1 Introduction.

From experiment 3.3.3 it has been established that treatment of silk fabric with BTCA under pad, dry, cure conditions, at high temperatures of curing produces a fabric with improved κ^{dry} stability both to recovery from creasing and fabric strength. A corresponding improvement in WCRA and wet strength was not observed. Untreated silk has a high DCRA and good fabric dry stability but silk fabrics crease easily when wetted. In order

to improve the easy-care properties of silk fabrics their wet stability, with regard to both wet creasing and dimensional stability need to be improved.

3.3.4.1.1 Swelling of silk fabrics in water.

When fabrics absorb water they change dimensionally due to fibre swelling; and this can cause fabric shrinkage. In silk fabrics the regions accessible for moisture absorption are either the non-crystalline regions or the surfaces of the crystalline regions. When silk fabrics are wetted the first water molecules to be absorbed become directly hydrogen bonded to the free accessible hydrophilic side-groups in silk fibroin. These water molecules are held firmly in position within the fibre. On further absorption the water molecules may be attached either to other available hydrophilic side-groups or they may form multi-layers on top of the mono-layer of water molecules already absorbed, see Figure 3. 30 (45).

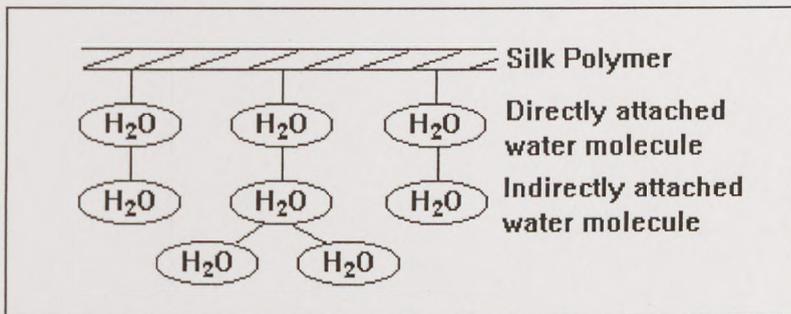


Figure 3. 30 Schematic diagram of the arrangement of water molecules in silk fibroin when wet.

The indirectly attached water molecules in the multi-layer are more loosely held in position than the directly attached water molecules in the mono-layer. As the absorption of water molecules increases the inter-fibre hydrogen bonds that give silk fibroin good dry stability break and are replaced by water molecules that become hydrogen bonded to the fibre, see Figure 3. 31.

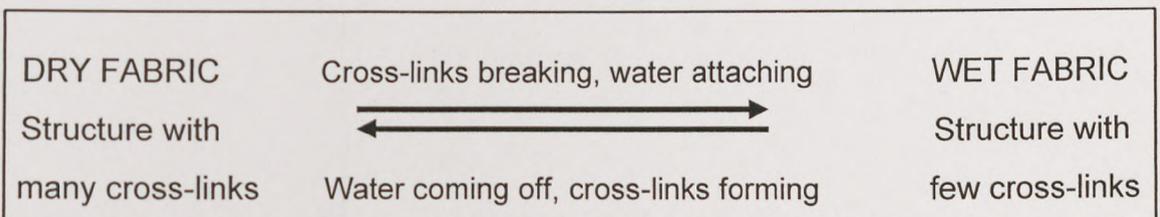


Figure 3. 31 Schematic diagram of the absorption and desorption of water from a fabric (45).

Fabric swelling is caused by the penetration of water molecules into the non-crystalline regions of the fibre and its failure to penetrate into the crystalline regions. Swelling

occurs because the fibre molecules are plasticised and move apart through molecular vibration and rotation. The fabric does not dissolve in water because the water molecules cannot penetrate the crystalline regions. In order to penetrate the crystalline regions it would be necessary for a large number of water molecules to simultaneously break a large number of inter-molecular hydrogen bonds. This is unlikely to occur as the reactions of each water molecule are independent.

3.3.4.1.2 A review of methods used to improve the wet stability of cotton cellulose.

Wet setting of fabrics is a two-stage process and takes place in the swollen state (86). Sufficient hydrogen bonds must first be broken for the structure to relax into a new stress-free state. This new structure is then stabilised by the formation of new bonds during de-swelling and drying.

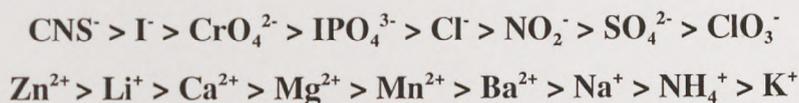
Several methods have been investigated for improving the WCRA of cotton cellulose. The general method is to stabilise the fabric in the swollen state. This is opposite to the dry cure process used in experiment 3.3.3. In the high temperature dry cure process fabric swelling is decreased because of the dehydration of the fibres and thus the molecular chains in the amorphous (or non-crystalline) regions are brought closer together. The fabric is stabilised by the formation of cross-links between the fibre chain molecules in this dehydrated/contracted state (81). The dry cured fabric has improved response to deformation in the dry state and lower fabric swelling and moisture regain values.

It has been reported that stabilisation of cotton cellulose in the swollen state yields cotton fabrics with a high degree of stability in the wet state but no improvement in stability in the dry state (81). In the swollen state the hydrogen bonds holding the molecular chains together are broken and the chain molecules can move further apart. The reaction occurs where the molecular chains are close enough to form cross-links, i.e., at the edge of the swollen amorphous sections. These cross-links hold the cotton cellulose in the swollen state and prevent the original hydrogen bonds from reforming. At Tootal Broadhurst Lee Co. Ltd. The use of pre-swelling treatments e.g. mercerisation was studied with the objective of making cotton fabrics more receptive to the action of an amino-formaldehyde resin finish (166, 167, 168). It was found that it was possible to

obtain a good combination of recovery from creasing and mechanical properties for cotton cellulose fabrics if the finishing treatment was carried out immediately after mercerisation when the fabric was still in the wet and swollen state (169). Mercerisation has also been studied in conjunction with BTCA as an easy-care finishing agent on cotton cellulose with improved performance characteristics (170).

Kärrholm and Åsnes (171) investigated the wet setting of cotton cellulose by swelling the fibre using alkali or salt solutions in order to minimise fabric shrinkage during re-wetting or laundering. They postulated that the increased wet stability was achieved by inserting hydrogen bonds into parts of the cotton cellulose when this was in a swollen, relaxed state but that after drying were no longer accessible to water. A high retention of wet stability was achieved by treating cotton cellulose in an almost saturated solution of KOH in either ethanol, 1-butanol or 1-octanol. The degree of fabric swelling was less in organic solvents compared with water, and thus improved wet stability of cotton cellulose was achieved with minimal fabric shrinkage.

Kärrholm and Åsnes (171) found that cotton cellulose swelled to a greater degree in strong salt solution compared with water. They found that one of the electrolyte ions, either the cation or the anion, was usually absorbed preferentially by the fibre. The ion is absorbed with its accompanying sphere of water molecules, providing that the ion binds more readily with water than with the fibre. The greater the absorption of the ions from the electrolyte solution the greater will be the degree of fibre swelling. The competition between the fibre and the solution for the ions means that the ions that bind with the smallest amount of water will be more readily absorbed by the cellulose chain molecules in the accessible regions of the fibre. The following lyotropic series is a list of ions in decreasing order of affinity for cotton cellulose:



Experiments showed that only ions at the beginning of the lyotropic series were effective cotton cellulose fabric swelling agents:



A high degree of dimensional stability to laundering was achieved by treating cotton cellulose with ZnCl_2 in water. An industrial experiment (171) which involved pre-setting cotton cellulose with a 63% ZnCl_2 solution prior to an amino-formaldehyde resin

finishing treatment produced fabrics with high WCRA, high retention of tensile strength and improved dimensional stability to washing. Smaller quantities of resin finish were required to obtain equivalent levels of easy-care performance when the pre-setting treatment was included.

Vapour phase cross-linking of cotton cellulose such as that used in the Marvelized 7 method (172) was found to be superior to conventional amino-formaldehyde resin finishing. It was found that the fabric moisture content at the time of cross-linking greatly influenced the resultant fabric properties. An increase in moisture content is accompanied by an increase in fabric swelling. Swindler et al. (173) found that improved easy-care characteristics were dependent on the simultaneous presence of moisture, resin and catalyst. If the initial moisture content on the fabric was too low or too high, too little or too much reaction took place respectively. With optimum treatment conditions good wet and dry crease recovery performance could be obtained with good laundering and abrasion durability.

Wet setting of cotton cellulose improves the fabric WCRA and the treated fabrics have a characteristic limp handle. This improved recovery from creasing in the wet state gives fabrics with good easy-care properties when line-dried. A high degree of stability in the dry state is also required if fabrics are to demonstrate good easy-care characteristics after being tumble-dried.

3.3.4.1.3 Methods for improving the wet stability of silk fabrics.

Lee and Sin (82) in their study of TMM finished silk, discussed in section 1.2.2.2, showed that the addition of formic acid (FA) into the finish bath aided the swelling of silk fibroin and assisted penetration of the finishing agent into the fabric, thereby improving the wet stability of silk. Yang and Li (174) investigated the finishing of silk fabric with BTCA, discussed in section 1.2.2.6, and found that the addition of FA into the pad bath did not improve the performance of the BTCA. This, they postulated, was because the BTCA is itself an organic acid and can therefore swell the silk fibre without the assistance of the formic acid.

In the following experiment, different padding conditions were investigated with the objective of establishing the most preferential conditions for maximum reagent reaction

to occur. Four different padding methods were used, pad-batch-wash-off (PBW), pad-batch-cure (PBC), pad-dry-cure (PDC), and pad-dry-(leave 24h)-cure (PDLC). The incorporation of selected fibre swelling/hydrogen bond breaking agents into the pad bath was also investigated; again to establish whether the incorporation of such additives could enhance the easy-care properties of the treated fabrics. The fibre swelling/hydrogen bond breaking agents used in this experiment were formic acid (FA), sodium iodide (NaI), zinc chloride ($ZnCl_2$), and lithium chloride (LiCl).

3.3.4.2 Experimental procedure.

Plain woven silk habutai medium, roll 3, see section 2.1.1, was treated with 6% w/w BTCA, a 1:1 molar ratio of SHP catalyst and a fibre swelling/hydrogen bond breaking agent, see Table 3. 8. Four different padding methods were used, pad-batch-wash-off (PBW), pad-batch-cure (PBC), pad-dry-cure (PDC), and pad-dry-(leave 24h)-cure (PDLC). The samples were treated according to the method described in section 2.1. A two dip, two nip padding process was used. Samples that required drying and/or curing were treated at 80°C for 2 min and 165°C for 1.5 min respectively. The treated samples were conditioned for 48h and tested with respect to percent chemical add-on, carbonyl bond frequency at $1735cm^{-1}$ in FT-IR spectra, dry and wet crease recovery angles, fabric tensile strength and fabric elongation at break.

Sample Number	% w/w BTCA	% w/w Pad Bath Additive	Padding Conditions	Pad Bath pH
1-4	6%	-	PBW, PBC, PDC, and PDLC	2.10
5-8	6%	8% w/w formic acid (FA)	PBW, PBC, PDC, and PDLC	1.50
9-12	6%	6% w/w sodium iodide (NaI)	PBW, PBC, PDC, and PDLC	1.87
13-16	6%	6% w/w zinc chloride ($ZnCl_2$)	PBW, PBC, PDC, and PDLC	1.52
17-20	6%	6% w/w lithium chloride (LiCl)	PBW, PBC, PDC, and PDLC	1.49

Where PBW = pad-batch-wash-off, PBC = pad-batch-cure, PDC = pad-dry-cure, and PDLC = pad-dry-leave-cure (PDLC)

Table 3. 8 Summary of the padding conditions for silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio BTCA:SHP and a fibre swelling/hydrogen bond breaking agent.

3.3.4.3 Results and discussion.

The test results are tabulated in Appendix 1, Tables A1.4a and A1.4b and the results appear in graphical form in the text Figure 3. 32 to Figure 3. 44.

Figure 3.32 is a plot of percent chemical add-on values for different padding conditions. Samples padded by the pad-batch-cure (PBC) method had the highest values of percent chemical add-on, followed by samples padded by the pad-dry-leave 24h-cure (PDLC) method, which were slightly higher than samples padded by the conventional dry curing process, pad-dry-cure (PDC). Samples padded by the pad-batch-wash-off method had the lowest percent chemical add-on values. This trend is reflected in Figure 3.36 a plot of the measure of the FT-IR carbonyl band at 1735cm^{-1} for the treated samples. The addition of fibre swelling/hydrogen bond breaking agents into the pad baths does not appear to aid the penetration of the reagent into the fabric. On the contrary samples treated with BTCA in the presence of one of these reagents all had lower percent chemical add-on and lower FT-IR carboxylic acid and ester bond frequency heights. This would suggest that the incorporation of hydrogen-bond breakers/swelling agents into the pad bath does not lead to an increase in reaction efficiency. The incorporation of these salts into the pad bath may cause a reaction to occur between either the salt and the BTCA or the salt and the SHP catalyst thus decreasing the quantity of BTCA or SHP available to take part in the cross-linking reaction with silk fibroin.

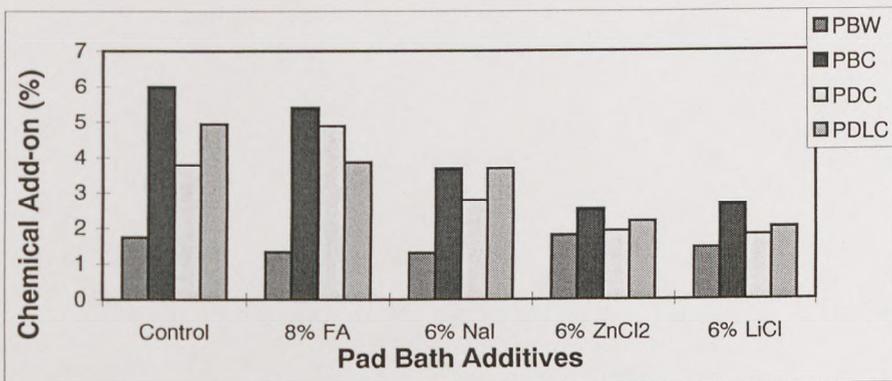


Figure 3.32 Percent chemical add-on of 6% w/w BTCA, a 1:1 molar ratio of SHP and different pad bath additives thought to act as hydrogen bond breakers.

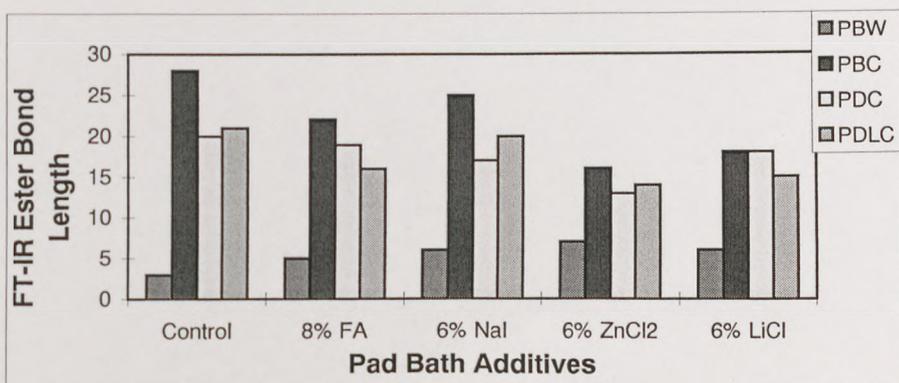


Figure 3.33 Measure of ester bond length in FT-IR spectra for silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and different pad bath additives thought to act as hydrogen bond breakers.

The dry and wet crease recovery angles are plotted in Figure 3.34 to Figure 3.38 and summarised in Figure 3.39 and Figure 3.40. From the graphs it can be seen that samples treated by the PBW method show little improvement in either dry or wet crease recovery angles. Samples treated by either of the other three methods, PBC, PDC, or PDLC, had similar dry and wet crease recovery angles. The trend seen in percent chemical add-on values in which PBC treated samples had the highest values is reflected in the creasing properties of the samples. In nearly all cases samples treated by the PBC method had very slightly higher dry and wet crease recovery angles.

Silk fabric samples treated with BTCA and the addition of FA in the pad bath showed improved WCRA values but lower fabric DCRA when compared with samples treated without the addition of FA in the pad bath. It may be possible that the addition of FA in the pad bath did improve the fabric swelling. This increased fabric swelling may allow for better penetration of the reagent inside the fabric. Percent chemical add-on values and FT-IR ester bond frequency lengths do not indicate a higher level of reaction with the fibre. However, if the reaction takes place in a more swollen state, the newly inserted cross-links could only be attached where the molecular chains are close enough for cross-linking to occur. These newly inserted cross-links would be able to stabilise the silk fibroin in this swollen state and prevent the original hydrogen bonds from reforming. The lower fabric DCRA compared with samples treated with BTCA without the addition of FA would therefore be as a result of fewer hydrogen bonds in the new stabilised swollen structure.

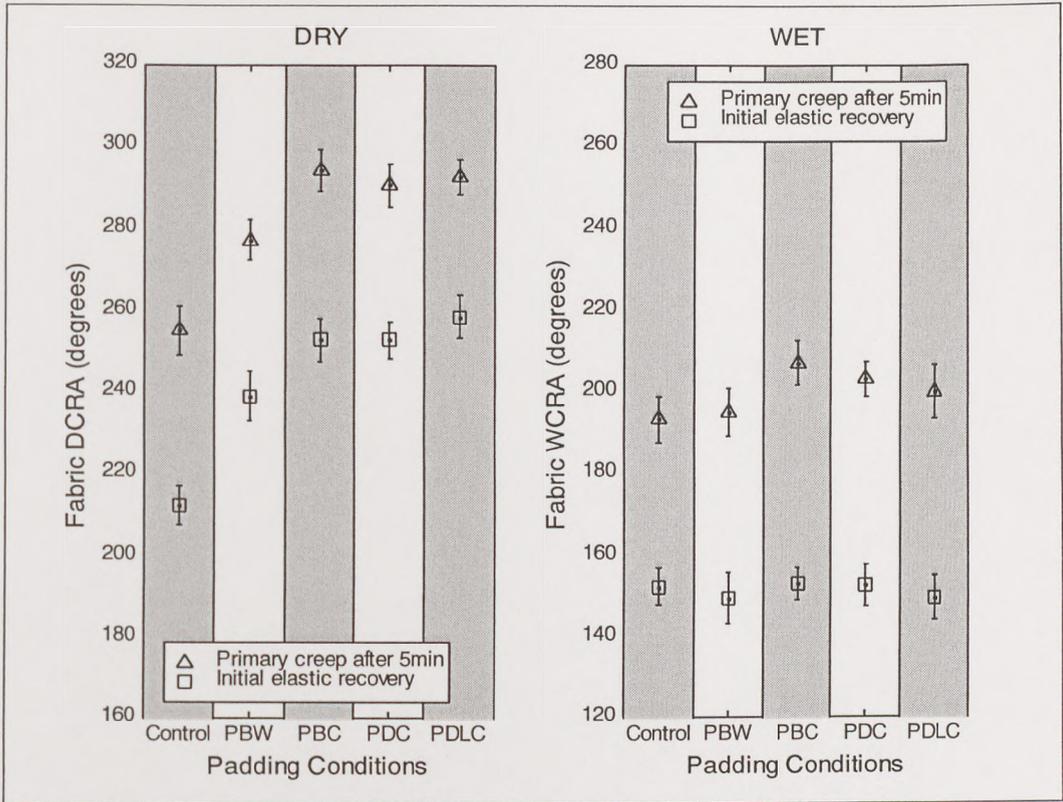


Figure 3.34 Fabric CRA values of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP catalyst.

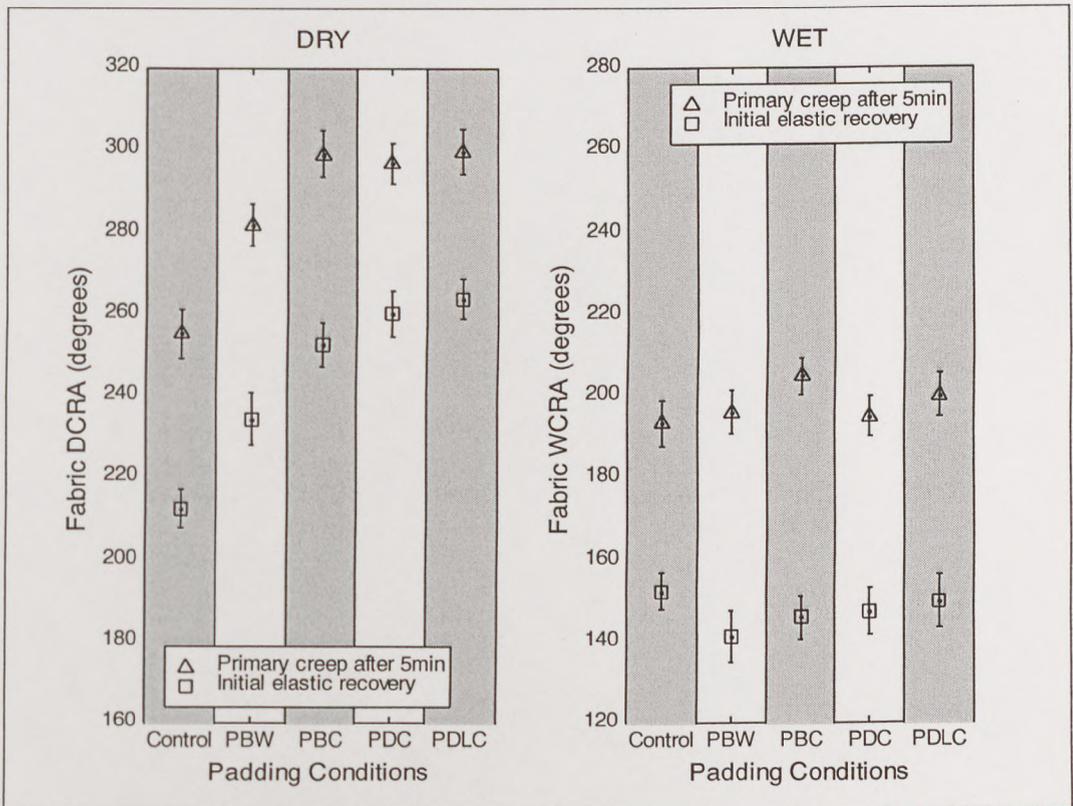


Figure 3.35 Fabric CRA values of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP catalyst, and 6% NaI.

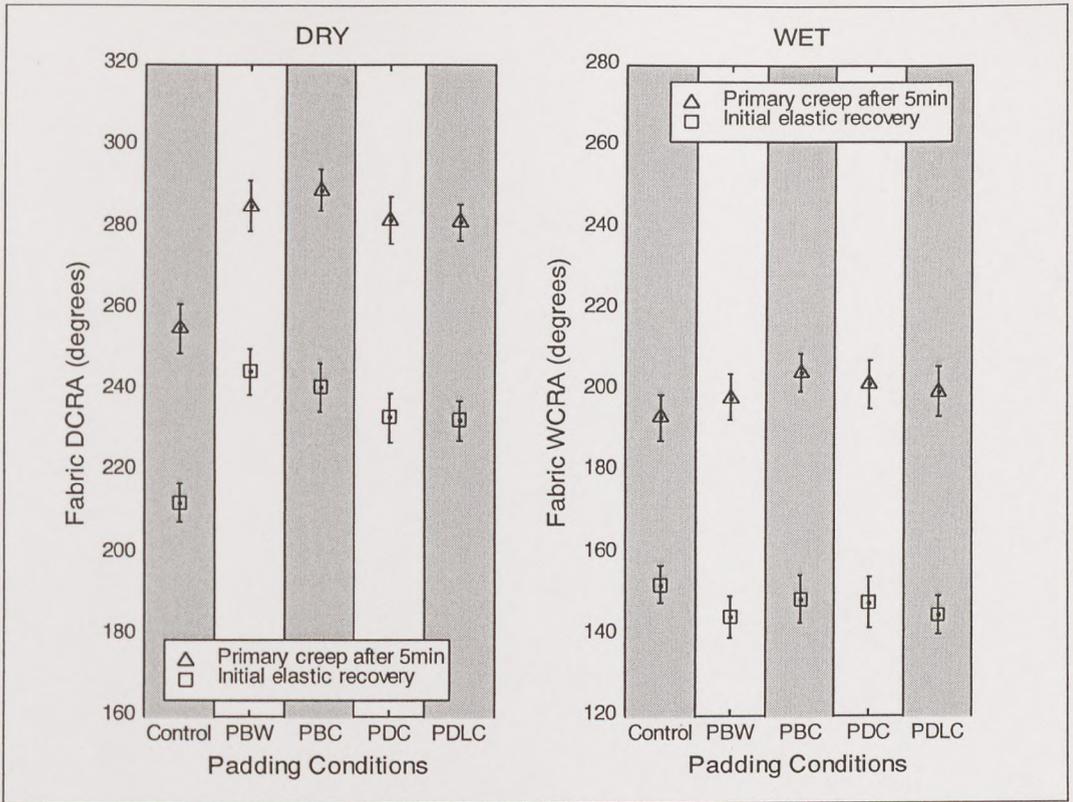


Figure 3.36 Fabric CRA values of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP catalyst, and 6% w/w $ZnCl_2$.

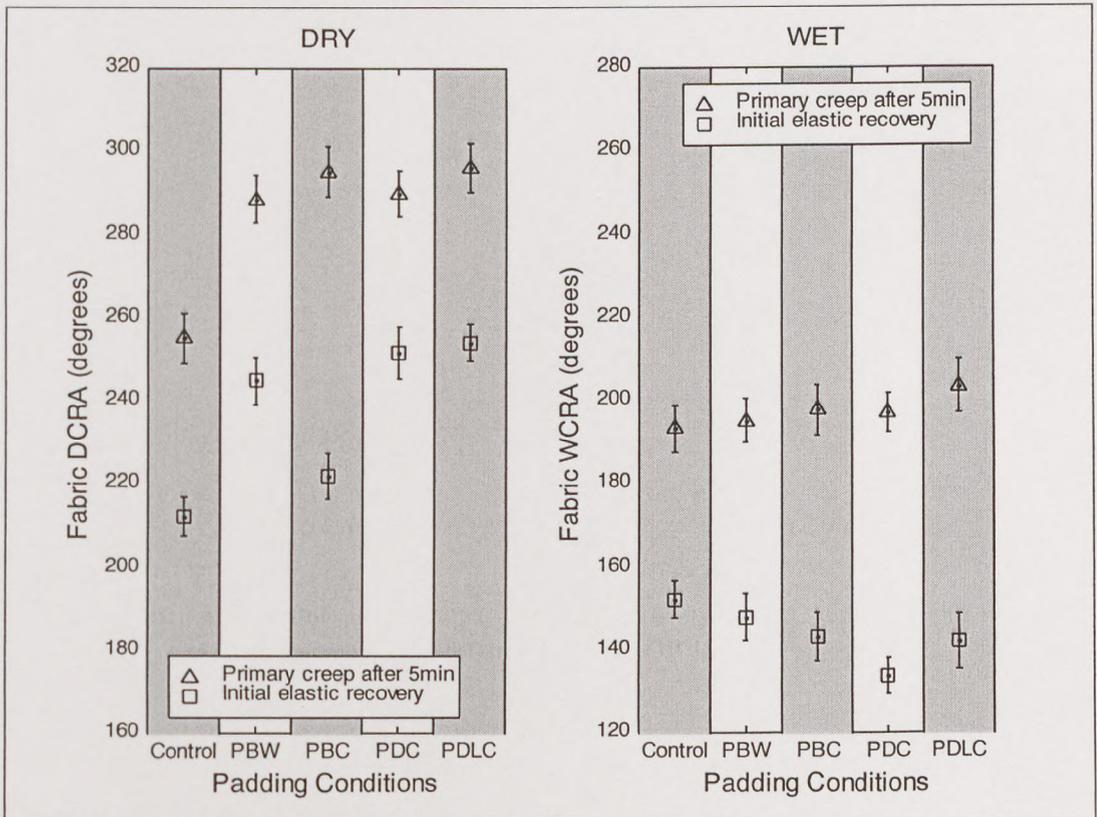


Figure 3.37 Fabric CRA values of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP catalyst, and 6% w/w $LiCl$.

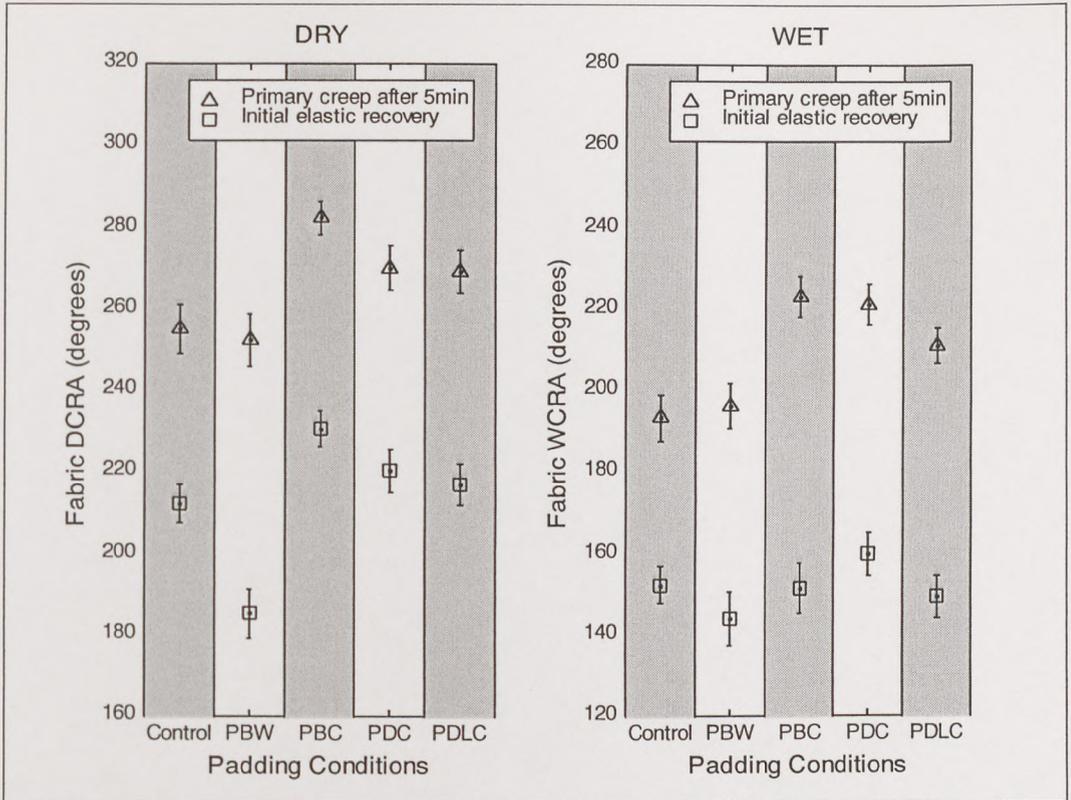


Figure 3.38 Fabric CRA values of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP catalyst, and 8% w/w FA.

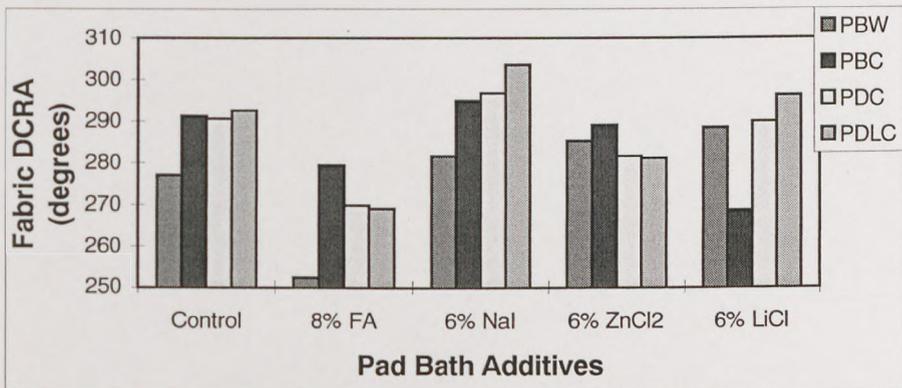


Figure 3.39 Fabric DCRA for silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and different pad bath additives thought to act as hydrogen bond breakers.

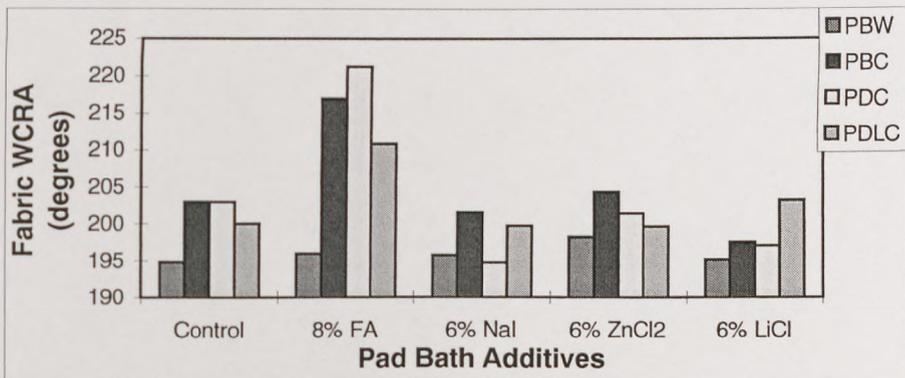


Figure 3.40 Fabric WCRA for silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and different pad bath additives thought to act as hydrogen bond breakers.

The tensile properties of the treated samples are plotted in Figure 3.41 to Figure 3.44. The retention of dry tensile strength is greater than 100% for all the treated samples and the retention of wet tensile strength is greater than 90%. Samples treated by the PBW method have the highest retention of tensile strength, and elongation at break, and in all cases this is greater than 100%. This improvement in tensile properties for the PBW samples seems to suggest that despite the absence of the high temperature curing process the silk fibroin has undergone a slight stabilisation in both the wet and dry states. The add-on values for the PBW process in all cases is between 1-2%. It is possible that a small amount of BTCA has formed hydrogen bond links with the silk fibroin in the swollen state that after drying were no longer accessible to water. This hypothesis is supported by the slight improvement in both dry and wet crease recovery angles of samples treated by the PBW method when compared with the untreated sample.

The tensile properties of the PBC process have slightly higher values when compared to either the PDC or PDLC processes. This could be as a consequence of increased fabric swelling and migration of the BTCA molecules during the batching process that leads to a greater efficiency of the cross-linking reaction. This method gives rise to improved dry and wet crease recovery properties and the higher values of percent chemical add-on and FT-IR ester bond frequency length.

The incorporation of metal salts into the pad bath as swelling agents does not improved the efficiency of the cross-linking reaction. Percent chemical add-on values and FT-IR ester bond frequency lengths are lower and there is no improvement in either dry or wet crease recovery angles when compared with samples treated with BTCA without the addition of a swelling agent. It is possible that the metal salts could have reacted with the BTCA to form carboxylic acid salts and neutralised the carboxylic acid side groups thus hindering the cross-linking reaction. The lower pH values of the pad baths containing the metal salts may slow down the rate of the chemical reaction between BTCA and silk fibroin.

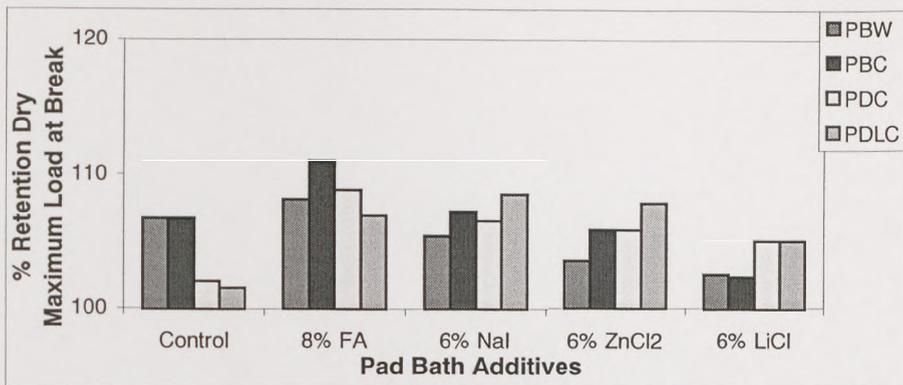


Figure 3. 41 Dry fabric percent retention maximum load at break for silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and different pad bath additives.

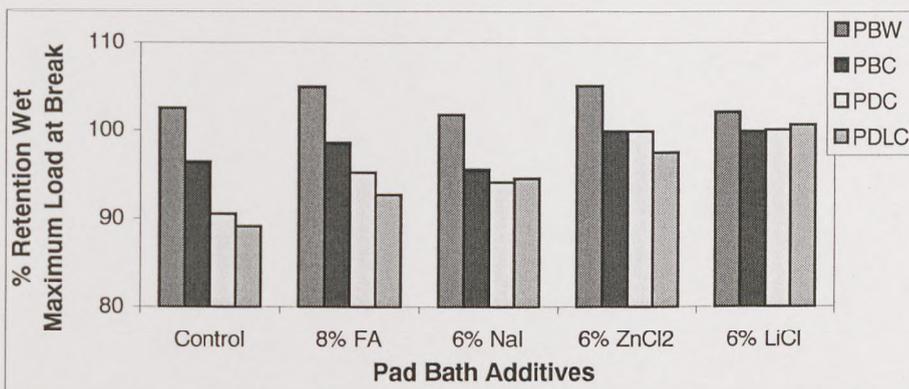


Figure 3. 42 Wet fabric percent retention maximum load at break for silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and different pad bath additives.

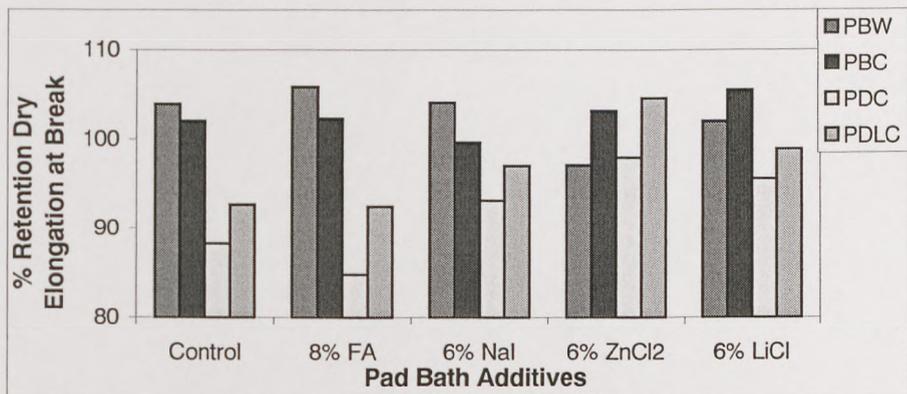


Figure 3. 43 Dry fabric percent retention elongation at break for silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and different pad bath additives.

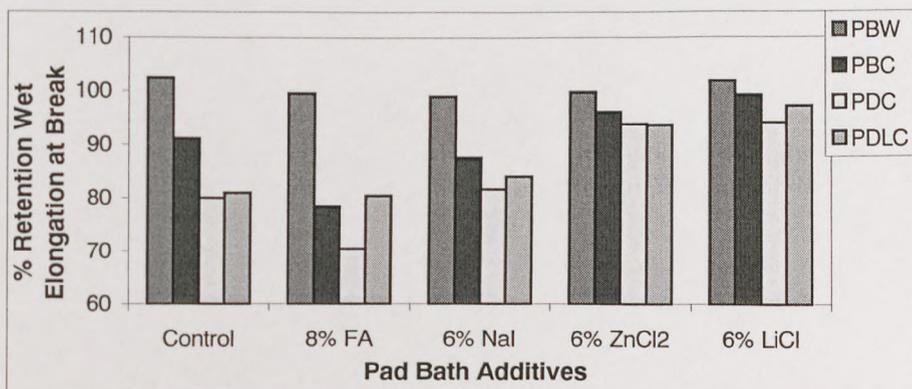


Figure 3. 44 Wet fabric percent retention elongation at break for silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and different pad bath additives.

3.3.4.4 Conclusions.

The results from experiment 3.3.4 discussed above suggest that silk fabrics padded by the pad-batch-cure method have superior properties. They exhibit the highest percent chemical add-on values and the greatest FT-IR ester bond frequency height values, and show the highest values of both dry and wet crease recovery angles. The batching process may allow sufficient time for the fabric to obtain maximum swelling and for greater penetration of the reagent inside the fibre. Fabric samples treated by the pad-batch-wash-off method showed improved stability to creasing and fabric strength in the dry state. It is postulated that this may be caused by the insertion of new hydrogen bond links between BTCA and silk fibroin chain molecules. The absence of the curing step prevents the formation of ester cross-links. However, fabric samples that underwent the pad-batch-cure method would have been capable of forming more stable ester cross-links in place of the hydrogen bonds formed in the pad-batch-wash-off samples. The superior fabric properties observed by samples treated by the pad-batch-cure method in comparison with fabric samples treated by the pad-dry-cure or pad-dry-leave-cure methods may be due to increased fibre swelling and better reagent penetration.

The incorporation of fibre swelling/hydrogen bond breaking agents into the pad bath did not improve the percent chemical add-on or FT-IR ester bond frequency length values. In fact the use of metal salts to swell the silk fibroin does not appear to have improved the fabric properties when compared with fabric samples treated without the inclusion of metal salts in the pad bath. It may be possible that the metal salts react with either the BTCA or the SHP in the pad bath decreasing the efficiency of the reaction. The inclusion of the metal salts in the pad baths lowers the pH value of the reagent solutions and this may slow down the rate of the reaction of the BTCA with silk fibroin.

However, the incorporation of formic acid in to the pad bath did improve the WCRA of the treated samples. This could have been as a result of improved fibre swelling and subsequent cross-linking in a more swollen condition. The lower DCRA of samples treated with BTCA and the inclusion of FA in the pad bath could be as a result of fewer hydrogen bonds in this new, more swollen structure.

3.3.5 Summary Of The Experimental Work In Chapter 3.

This initial study of the chemical modification of silk fabric with polycarboxylic acids has demonstrated that it is possible to improve the dry and wet crease recovery of silk fabrics by treating them with either BTCA or CA. The results reported in Chapter 3 reflect the general trends found in polycarboxylic acid finishing of cotton cellulose, reported in section 3.2. BTCA is a more effective acid than CA for improving the crease recovery properties of silk fabrics and causes considerably less fabric yellowing.

A comparison of treatment of silk fabric with BTCA or MEL led to equivalent results. BTCA-treated fabrics showed a greater improvement in DCRA values whereas MEL treated fabrics showed a greater improvement in WCRA values. BTCA treated silk fabrics had improved fabric strength retention and the treatment did not cause severe fabric stiffness, unlike samples treated with MEL. The percent retention of tensile strength of BTCA-treated silk samples was considerably more than that reported for the finishing of cotton cellulose with BTCA. The optimum percent BTCA was found to be 6% w/w and the optimum PCA:SHP molar ratio was found to be 1:1.25.

An investigation of the finishing method reported in sections 3.3.3 and 3.3.4 showed that as the curing temperature was increased up to 165°C for samples treated by the PDC method the quantity of ester bonds formed within the silk fabric increased. This increase in ester bond formation was accompanied by an increase in dry fabric stability, both recovery from creasing and fabric strength. However, a corresponding increase in wet stability was not observed. It was postulated that the BTCA may form a mixture of di-ester and ester/hydrogen bond cross-links within the silk fibre. These ester/hydrogen bond cross-links would be broken when the fabric was re-wetted and thus an increase in fabric wet stability would not be observed. The optimum curing condition found in this experiment was 165°C for 1.5min. A further increase in curing temperature caused severe fabric yellowing.

In order to improve the wet stability of silk fabrics, a variety of different padding methods were investigated. The use of a pad-batch-cure method produced fabrics with superior properties over the pad-dry-cure fabrics. It is postulated that this occurs as a consequence of increased fibre swelling and improved penetration of the reagent inside the fibre during the batching process. There was a slight increase in dry fabric stability

to creasing and fabric strength observed with silk samples treated by the pad-batch-wash-off method. It is postulated that this occurs as a result of the formation of new hydrogen bond links between the BTCA and the silk fibroin chain. In the fabric samples that were subsequently cured these hydrogen bonds would be converted to stable ester covalent bonds.

The incorporation of FA in the pad bath produced fabrics with improved wet recovery from creasing. FA is a known hydrogen bond breaker, but concentrated solutions can dissolve silk. The addition of 8% w/w FA into the pad bath could improve fibre swelling by acting as a hydrogen bond breaker, and thus improve the migration of the PCA within the silk fibre. It is postulated that the PCA forms hydrogen bonds links with the available sites in silk fibroin, i.e. at the edges of the swollen amorphous section, during the batching process that hold the silk fibroin in its new swollen state during the drying process. During fabric curing of the treated sample the hydrogen bonds are converted into new PCA ester cross-links that can stabilise the silk fibres in their new, more swollen condition.

The incorporation of FA in the pad bath does not improve the dry stability of fabrics. If, as postulated the silk fabrics have been wet set, there would be less hydrogen bonds in the new swollen structure when dry to hold the chain molecules in place when compared with the untreated control, and therefore the dry stability of the silk fabrics would not be improved. Because the dry stability of the untreated sample is already high, and it is the wet stability that needs improving in order to improve the easy-care characteristics of silk fabrics, it is concluded that the addition of FA in the pad bath could prove beneficial.

4. CHEMICAL MODIFICATION OF SILK FABRIC WITH POLYCARBOXYLIC ACIDS. AN IN-DEPTH STUDY.

Chapter three investigated the possibility of chemically modifying silk fabric with polycarboxylic acids. The reported results indicated that it was possible to improve the easy-care characteristics of silk fabrics by treating them with a polycarboxylic acid finishing system. The acid BTCA when used in conjunction with the catalyst SHP was found to give improved recovery from creasing in both the wet and dry state. This acid/catalyst system is reported to be the most efficient polycarboxylic acid finish for improving the easy-care properties of cotton cellulose, see section 3.2.

This BTCA/SHP polycarboxylic acid finishing system is expensive. As reported in section 3.2.2.1 the production cost for producing BTCA on an industrial scale is expected to be at least three times more expensive compared with the cost of producing the conventional finish DMDHEU. In addition, SHP is also expensive, it is an environmental hazard and has the drawback of producing shade changes on some reactive and sulphur dyeings. Alternative acid/catalyst systems are therefore desirable.

In this chapter the polycarboxylic acid finishing system is investigated. Rowland et al in 1967 (144) first reported that cellulose impregnated with an aqueous solution of a PCA containing three or four carboxyl group and a partial sodium or amine salt of the acid were insoluble in 0.5M cupriethylenediamine hydroxide. The insolubility of the cotton cellulose in this solvent was reported to be as a result of the existence of ester cross-links. It was suggested that these PCAs were capable of forming cyclic acid anhydrides and that these anhydrides may form an intermediate step in the esterification reaction. Welch et al (145) postulated that the cross-linking reaction between PCAs and the hydroxyl groups in cotton cellulose is catalysed by weak bases and takes place at 160-215°C. Only PCAs with three or more carboxylic acid groups on adjacent or next but one carbon atoms that can form cyclic anhydride intermediates were found to be effective at forming a diester cross-links according to the mechanism outlined by Welch, see Figure 3.10.

A number of polycarboxylic acids and a variety of catalysts were tested for their suitability as easy-care finishing agents. The suitability of an acid/catalyst system was

studied using thermoanalytical and Fourier Transform-Infra-red techniques. These techniques were used to study the behaviour of the PCA and the catalyst under conditions equivalent to those used in silk fabric curing. Dependent on the results of this experiment a number of different acid/catalyst systems were applied to silk fabric and the results compared for different acid/catalyst systems.

4.1 THERMOANALYTICAL AND FT-IR ANALYSIS OF POLY-CARBOXYLIC ACIDS EASY-CARE FINISHING SYSTEMS.

4.1.1 Introduction.

The aim of this experiment was to establish a method for pre-determining the effectiveness of an acid and catalyst system as an easy-care finish. Thermoanalytical techniques were used to heat the acid or acid and catalyst system at temperatures simulating conditions used in curing. The heated samples were then subjected to transmission FT-IR analysis and any chemical changes brought about by the simulated curing thermoanalysis were noted. The samples were also heated to high temperatures and their thermoanalytical behaviour was analysed using TGA and DSC techniques.

4.1.1.1 A review of previous research into thermoanalytical analysis of polycarboxylic acid finishing systems.

Trask-Morrell, Kottes Andrews, and Graves (175, 176, 177, 178) have investigated the thermal characteristics of a series of di-, tri-, and tetrafunctional PCAs with and without a catalyst using differential scanning calorimetric (DSC), thermogravimetric (TG), and differential thermogravimetric (DTG) techniques. Individual acids were tested pure and in combination with a catalyst. Pad solutions (1:1 molar ratio) were made up and oven dried to a constant weight in a vacuum oven at 60°C. All DSC sample weights were normalised to 5mg.

The acids were tested under nitrogen and heated under programmed conditions that varied according to the experiment. Three different heating conditions were used:

1. Simulated cure conditions: Samples were maintained isothermally at 60°C for 1 minute, heated at 25°C/minute to a maximum of either 160 or 180°C and held at the maximum temperature for a further 3 minutes. Percent residue of the sample was measured at these maximum temperatures. These conditions were studied to

approximate the cure conditions on fabrics in pad-dry-cure experiments, see Table 4.

1. A system that volatilises too early, decomposes completely or too rapidly will lead to poor results as it will not be available to react with the fabric.

Polycarboxylic Acid	Molecular Weight	Melting Point (°C)	Percent Residue (%) 160°C	Percent Residue (%) 180°C
Succinic Acid (SA)	118	287-289	97.5	92
Maleic Acid (MA)	115	134-136	5	5
DL-Malic Acid (MLA)	134	131-133	96	87
Tricarballic Acid (TCA)	176	159-162	97	91
Trans-Aconitic Acid	174	190 dec	93	54
Citric Acid (CA)	192	152-154	96	53
BTCA	234	196	100	99
All-cis-cyclopentanetetra-carboxylic Acid (CPTA)	246	192-195 dec	100	97

Table 4. 1 A comparison of the percent residue data from TGA for some polycarboxylic acids (175).

- High-temperature conditions: Samples were heated at 15°C/minute from 50°C to a maximum of 600°C. Percent residue of the sample was measured at 575°C. This high temperature study was used to completely evaluate the PCAs reaction to thermal stress.
- Intermediate heating conditions: Samples were maintained isothermally at 60°C for 3 minutes, heated at 15°C/minute to a maximum 300°C and held at this maximum temperature for a further 3 minutes. DSC thermograms were used to measure the total heat of reaction. The temperature range, from when the curve left the base line to where thermal activity ceased when the curve returned to the base line, was used to calculate the total heat of reaction in J/g. The sample must be heated to a sufficiently high temperature for the thermal activity to cease in order to calculate this quantity. TG data was used to record the percent residue on completion of the thermal analysis and the maximum rate of weight loss in percent weight/minute. When tested on fabrics, acid/catalyst systems with high percent residues, low rates of weight loss and high total heat values, improve the fabric durable press property (177).

Trask-Morrell and Kottes Andrews (177) suggested the use of a single prediction factor

based on data collected with samples treated to 300°C to calculate and rank acid/catalyst efficiency as easy-care finishing reagents.

$$\text{Prediction factor} = \frac{(\text{percent residue}) \times (\text{total heat, J/g})}{(\text{maximum rate of weight loss, \%/minute})}$$

A high value was indicative of an acid/catalyst system that should make a good easy-care finish.

Acid/Catalyst System	Percent Residue at 300°C (%)	Maximum Rate of Weight Loss (%/min)	Total Heat of Reaction (J/g)	Prediction Factor /1000
MA/SHP	59	8	1950	14.38
MA/MSP	32	23	2000	2.78
MA/DSP	56	16	2800	9.8
CA/SHP	52	32	1800	2.93
CA/MSP	37	31	1300	1.55
CA/DSP	41	22	1600	2.98
TCA/SHP	73	9	1900	15.41
TCA/MSP	43	15	1800	5.16
TCA/MSP	59	16	1550	5.72
BTCA/SHP	72	18	1900	7.60
BTCA/MSP	47	22	1800	3.85
BTCA/DSP	63	16	1300	5.12
CPTA/SHP	57	23	1650	4.09
CPTA/MSP	59	10	2100	12.39
CPTA/DSP	61	15	1700	6.91

Where SHP = Sodium hypophosphite, MSP = Monosodium phosphate, DSP = Disodium phosphate

Table 4.2 Thermoanalytical prediction factor calculated for five carboxylic acids (177).

The results from this prediction factor when compared to the experimental results for polycarboxylic acid finishing of cotton cellulose reported in section 3.2 do not appear to follow the same trends. It is possible that this variation in trends is caused by the different temperatures used; the prediction factor was calculated for samples heated to a temperature of 300°C, whereas the temperature used to cure the treated cotton cellulose fabrics is usually less than 200°C.

4.1.2 Experimental Procedure.

The acids and catalysts used in this experiment were all commercially available reagent grade chemicals, see Table 2.2. The acid catalyst mixtures were prepared by dissolving a 1:1 molar ratio of the acid and catalyst in water; heat was used to dissolve the reagents where necessary. These mixtures were dried in a vacuum oven at 60°C until equilibrium was reached, see Table 4.3. The pure acid and catalyst compounds were tested as solids, these were ground into a fine powder using a pestle and mortar prior to thermal analysis. The acid/catalyst mixtures that formed crystals or glassy solids were also ground into a fine powder prior to thermal analysis.

Polycarboxylic Acid	Catalyst	Solution	Oven Dried Sample
BTCA	SHP	Dissolved to form pale yellow/green liquid	Pale yellow/green crystalline solid
Citric Acid (CA)	SHP	Dissolved to form clear liquid	Amorphous resin (does not dry out completely)
DL-Malic Acid (MLA)	SHP	Dissolved to form clear liquid	Clear glassy resin
Succinic Acid (SA)	SHP	Dissolved to form clear liquid	White crystals
Itaconic Acid (IA)	SHP	Dissolved to form clear liquid	Crystalline white resin
Glutaric Acid (GA)	SHP	Dissolved to form pale brown liquid	Pale brown crystalline solid
Pyromellitic Acid (PMA)	SHP	Dissolved to form clear liquid	White crystals
Phthalic Acid (PA)	SHP	Dissolved to form clear liquid	White crystals
SA + CA	SHP	Dissolved to form clear liquid	Slightly tacky crystalline resin
SA + MLA	SHP	Dissolved to form clear liquid	Slightly tacky crystalline resin
BTCA	MSC	Dissolved to form clear liquid	Hard glassy resin
BTCA	DSC	Dissolved to form clear liquid	Hard glassy resin
BTCA	TSC	Dissolved to form clear liquid	Hard glassy resin
BTCA	MSM	Dissolved to form clear liquid	Hard glassy resin
BTCA	DSM	Dissolved to form clear liquid	Hard glassy resin
BTCA	MST	Dissolved to form clear liquid	Hard glassy resin
BTCA	DST	Dissolved to form clear liquid	Hard glassy resin

Table 4.3 Preparation of mixtures of polycarboxylic acids and catalysts for thermal analysis.

The acid/catalyst mixtures were heated on the TGA to simulate conditions encountered in fabric curing. The TGA was programmed to heat the sample at a rate of 10°C/min in

air to a maximum temperature, e.g. 180°C, and held at that temperature for a further 2min. The experiment was repeated for different maximum temperatures, varying between 130°C and 180°C. The heated samples were allowed to cool and then prepared for transmission FT-IR, as discussed in section 2.2.3.1.2. The infra-red spectra for different mixtures and different maximum temperatures were compared. Infra-red spectra were also prepared for the pure acid and catalyst reagents and for the unheated mixtures.

Thermoanalytical data were also acquired for acids, catalysts and their mixtures using thermogravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC) as discussed in section 2.3.5. The acid, catalysts and their mixtures were heated to a temperature of 350°C at a heating rate of 10°C/min under nitrogen (50ml/min) using both TGA and DSC techniques. The results were plotted on a single axis and compared for analysis. All thermal and infra-red data were repeated at least once in order to verify the reproducibility of the results.

4.1.3 Results And Discussion.

The results from experiment 4.1 are displayed in the text in Figure 4. 1 to Figure 4. 38 and in Table 4. 5 and Table 4. 6. Table 4. 4 shows some characteristic infra-red absorption peaks of some of the functional groups relevant to this research.

4.1.3.1 Tetrafunctional carboxylic acids and SHP.

4.1.3.1.1 1,2,3,4-Butanetetracarboxylic acid (BTCA).

Figure 4. 1 displays the FT-IR spectra for the unheated pure SHP catalyst, the unheated pure BTCA compound, the unheated mixture of BTCA and SHP and the heated mixture BTCA/SHP, heated by the TGA to 180°C and isothermed for 2min. The SHP spectra shows characteristic absorption peaks at 2353cm⁻¹ corresponding to P-H stretching vibrations, at 1231cm⁻¹ corresponding to vibrations of the P=O bond, and at 1057cm⁻¹ which may be associated with the ionic phosphite group.

Functional Group Class	Molecular Motions	Band Position (cm ⁻¹)	Intensity of Absorption
Carboxylic Acids	O-H stretching (free)	3560-3500	Medium
Carboxylic Acids	O-H stretching (bonded)	2700-2500	Weak
Carboxylic Acids (saturated)	C=O vibrations	1725-1700	Strong
Carboxylic Acids ($\alpha\beta$ -unsaturated)	C=O vibrations	1715-1690	Strong
Carboxylic Acids (hydrogen bonded)	C=O vibrations	1670-1650	Strong
Carboxylic Acids	C-O stretching, O-H deformation	1440-1395 1320-1211	Weak Strong
Carboxylic Acids	O-H deformation (out of plane)	950-900	Variable
Carboxylic Acids	-COO ⁻	1610-1550, 1420-1300	Strong Strong
Carboxylic Acid Anhydrides	C=O stretching	2 bands c.60cm ⁻¹ apart	Variable
Aliphatic Acid Anhydride	C=O stretching	1820, 1760	Variable
Typical Cyclic Anhydride	C=O stretching	1845, 1775	Variable
Open Chain Acid Anhydrides	C-O-C stretching	1175-1045	Strong
Cyclic Acid Anhydrides	C-O-C stretching	1310-1210 950-910	Strong
Esters (saturated)	C=O stretching	1735	Strong
Esters (with double bond or aromatic ring)	C=O stretching	1715	Strong
Alkanes, alkyl groups	C-H stretching	2850-2960	Medium
Alkenes	=C-H stretching	3020-3100	Medium
Alkenes	C=C stretching	1650-1670	Variable
Alcohols	O-H stretching	3400-3600	Strong
Primary Alcohols	O-H deformation, C-O stretching	1050, 1350-1260	Strong
Secondary Alcohols	O-H deformation, C-O stretching	1100, 1350-1260	Strong
Tertiary Alcohols	O-H deformation, C-O stretching	1150, 1410-1310	Strong
Organo-Phosphorus	P=O (free)	1350-1250	Strong
Organo-Phosphorus	P=O (bonded)	1250-1150	Strong
Organo-Phosphorus (aliphatic)	P-O-C	1050-990	Strong
Organo-Phosphorus	P-OH	2700-2560	Broad
Organo-Phosphorus	P-H	2440-2350	Medium
Ionic Phosphate Groups	Alkyl Substituents	1180-1150, 1080	Strong
Ionic Phosphate Groups	Aryl Substituents	1090-1040	

Table 4.4 Characteristic infra-red absorptions of some functional groups (179).

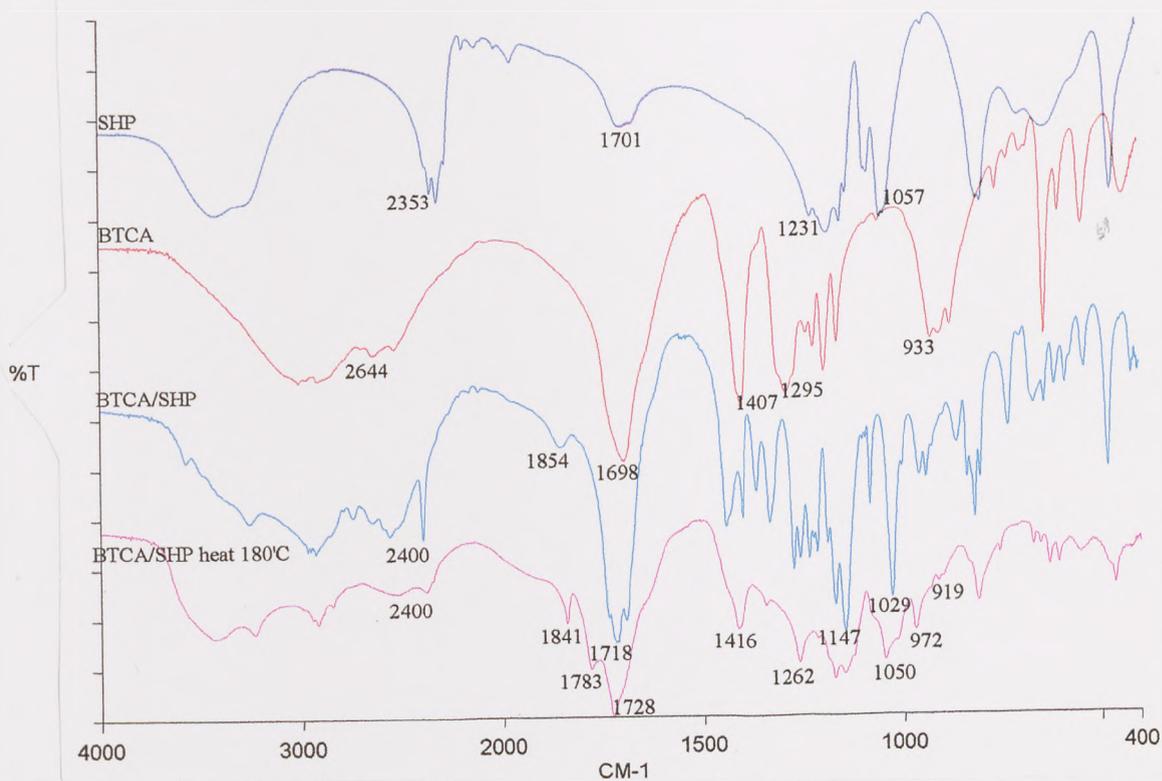


Figure 4.1 FT-IR spectra of BTCA, SHP and a 1:1 molar ratio mixture of BTCA and SHP.

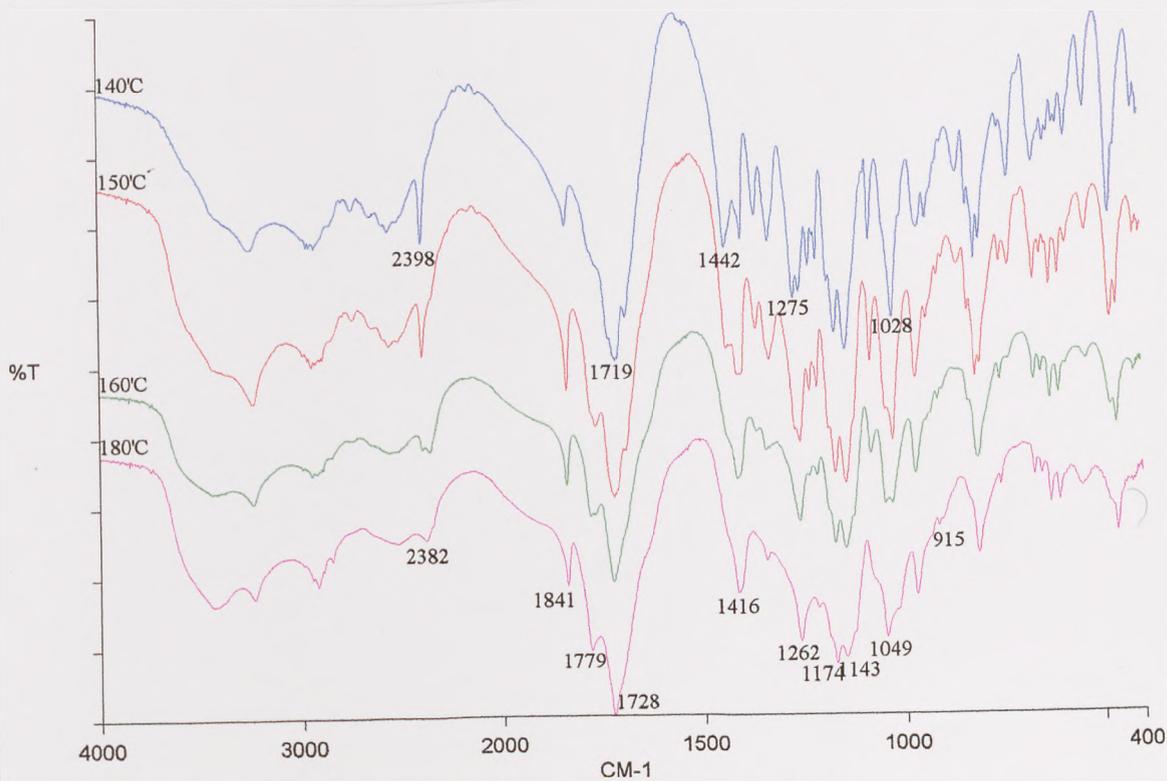


Figure 4.2 FT-IR spectra of a 1:1 molar ratio mixture of BTCA and SHP heated to different temperatures and isothermed for 2min.

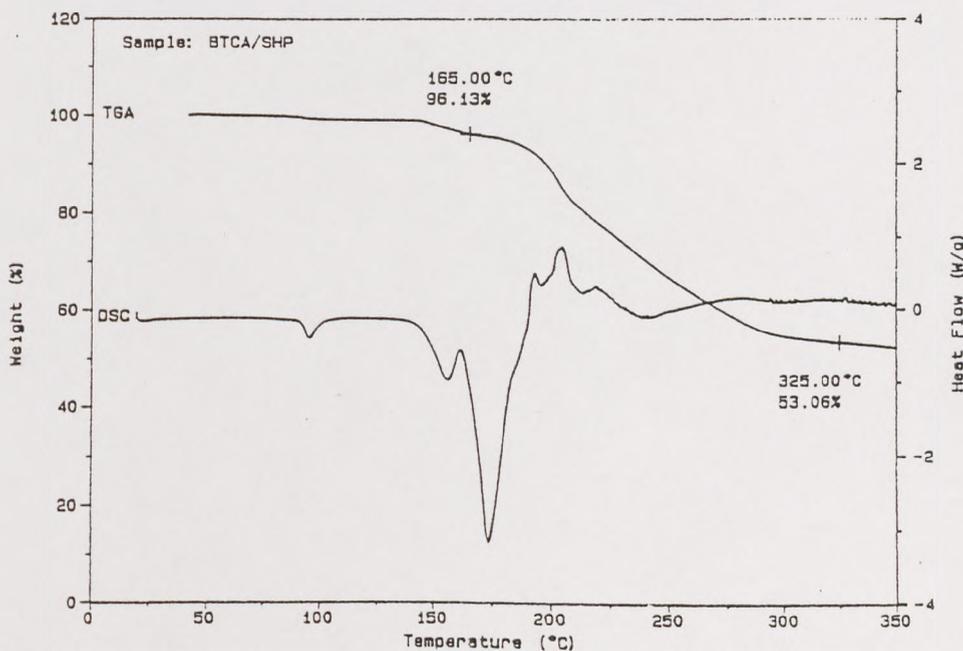
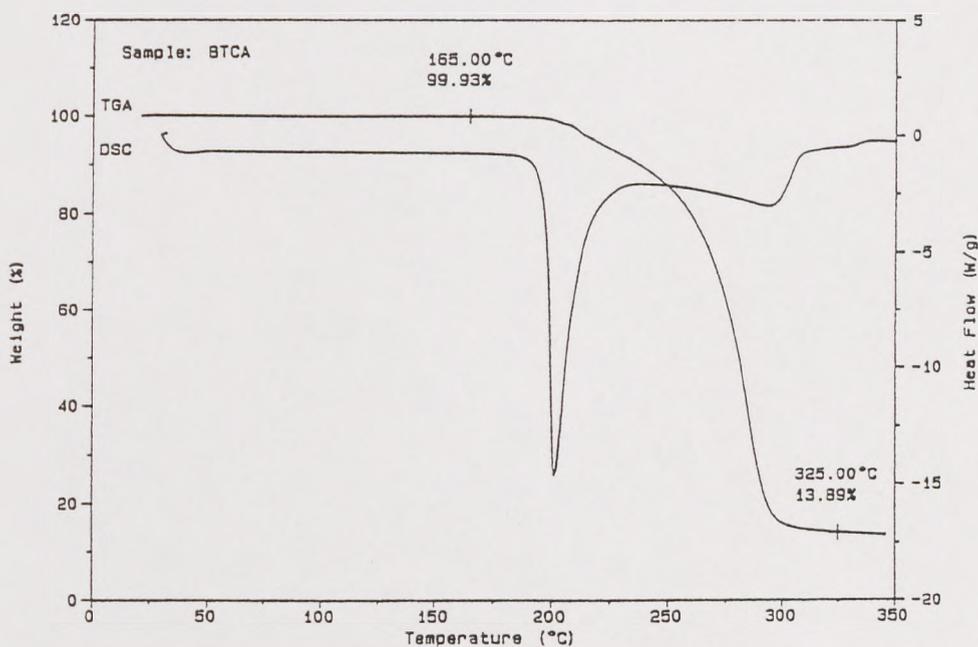
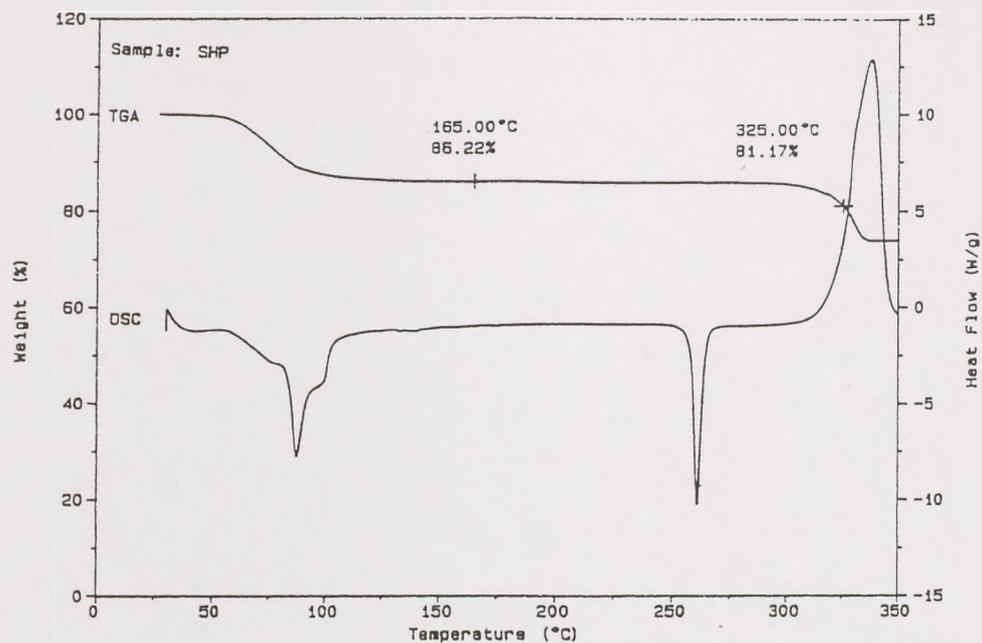


Figure 4.3 TGA and DSC analysis of SHP, BTCA, and a 1:1 molar mixture of BTCA and SHP.

The DSC and TGA thermograms for SHP are overlaid in Figure 4.3(b). The DSC curve contains both endothermic (downwards) peaks and exothermic (upwards) peaks. An endothermic reaction is one in which the sample absorbs heat as it is being heated, this includes water loss and melting peaks. An exothermic reaction is one in which the sample gives off heat as the sample is heated. The initial early endothermic peaks that also correspond to a reduction in mass of the SHP sample are probably due to the loss of water. Water of crystallisation generally has a sharp peak, whereas hydrogen-bonded water has a broader peak (179). SHP has one mole of water associated with it, the loss of which corresponds to 16.98% of the total weight of SHP monohydrate. The weight loss of the endotherm was 13.78%.

The TGA of SHP displayed in Figure 4.3 shows that at the temperature required to cure the PCA finish SHP does not produce any volatile components, such as phosphine that could be an environmental hazard. The results from this experiment suggest that SHP is safe to use as a catalyst for PCA finishing. Morris et al. (180) reported that the evolution of phosphine was not observed until temperatures in excess of 300°C. Thermal analysis of SHP depicted in Figure 4.3b shows SHP to be stable to temperatures above 300°C.

The FT-IR spectra for BTCA illustrated in Figure 4.1 show characteristic absorption peaks for a carboxylic acid. There is a broad band corresponding to O-H stretching between 2500-3500 cm^{-1} , a sharp peak at 1698 cm^{-1} corresponding to the carbonyl vibration, the two C-O stretching peaks can be seen at 1407 cm^{-1} and 1295 cm^{-1} , and there is a peak at 933 cm^{-1} that corresponds to O-H deformation. In the solid state carboxylic acids exist as dimers because of strong hydrogen bonding. The carbonyl band at 1698 cm^{-1} is shifted approximately 20 cm^{-1} when these dimers break down. This shift in the carbonyl stretching vibrations is visible in Figure 4.1. The FT-IR spectra of the mixtures of BTCA and SHP have carbonyl band absorptions at 1718 cm^{-1} which is again shifted slightly on heating to 180°C.

Figure 4.3 is a diagram of the TGA and DSC thermograms for BTCA. The TGA and DSC curves for the pure BTCA compound show a broad decomposition temperature range that begins just below 200°C with a melting peak and continues to approximately 300°C. This is in agreement with the melting point for BTCA at 196°C. There was a

small quantity of residue remaining after heating to 350°C. The TGA curve shows that BTCA is thermally stable at temperatures usually employed in silk fabric finishing; at 165°C there was 99.9% residue remaining.

The BTCA/SHP 1:1 molar ratio mixture was analysed prior to heating by FT-IR analysis. The mixture shows absorption bands with characteristics of both BTCA and SHP. The broad O-H stretching band of BTCA can be seen between 2500-3500cm⁻¹, and the carbonyl peak at 1718cm⁻¹ has been shifted because of a breakdown in hydrogen bonding of the BTCA. The P-H band for the SHP can be seen at 2400cm⁻¹. The spectrum becomes more complicated at the lower end of the scale. It would appear that the absorption peaks from the individual spectra have been shifted due to the presence of the other compound. The breakdown of the hydrogen bonding in the BTCA sample may also alter the position of the absorption bands.

The FT-IR spectra for the heated mixture of BTCA and SHP depicted in Figure 4. 2 clearly show two carbonyl peaks that are typical of a cyclic anhydride at 1779cm⁻¹ and 1841cm⁻¹. These bands begin to appear in the sample heated to 140°C for 2min. In the heated samples new bands are visible at 1262cm⁻¹ and 1049cm⁻¹ which may correspond to the C-O-C stretching typical of cyclic anhydrides and open chain anhydrides respectively. The band at 1049cm⁻¹ may also correspond to C-O-P vibrations. A small band at 915cm⁻¹ can be seen to be forming that may be associated with cyclic anhydride formation. The P-H band that appears in the unheated mixture at 2400cm⁻¹ slowly decreases as the samples are heated to a higher temperature. This may be indicative of the oxidation of the hypophosphite ion according to the reactions in Figure 4. 4.

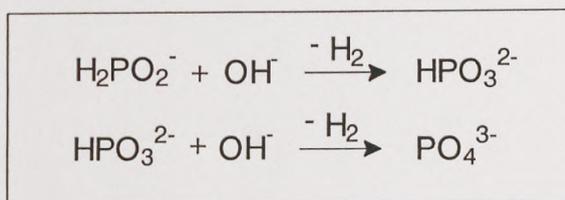


Figure 4. 4 Oxidation of the hypophosphite ion to the phosphate ion (181).

The PO₂⁻ anion is oxidised to PO₃²⁻ with the release of two hydrogens. Further oxidation of the PO₃²⁻ anion is also possible to PO₄³⁻ with the release of a further two hydrogen atoms. Both PO₂⁻ and PO₃²⁻ are known reducing agents (181). The reductive nature of SHP is evident during fabric finishing. Fabrics finished with PCA where SHP has been

used as the catalyst retain their whiteness properties better than fabrics finished with other catalysts and the finish can cause shade changes to some sulphur- and reactive-dyed goods (145).

The evidence from the infra-red analysis supports the mechanism proposed by Brown (148), see Figure 4. 5. This mechanism involves the formation of a mixed anhydride, a cyclic and a straight chain anhydride. There was possible evidence for both forms of anhydride in the FT-IR spectra of the heated BTCA/SHP mixture. The catalyst SHP is oxidised to sodium phosphite with the release of two hydrogen atoms. This reaction would cause a reduction in the P-H absorption band, which could be seen in infra-red analysis of the heated mixture. In the proposed mechanism Brown suggests that either the cyclic or the straight chain anhydride can form ester links with cotton cellulose. This has not been proven.

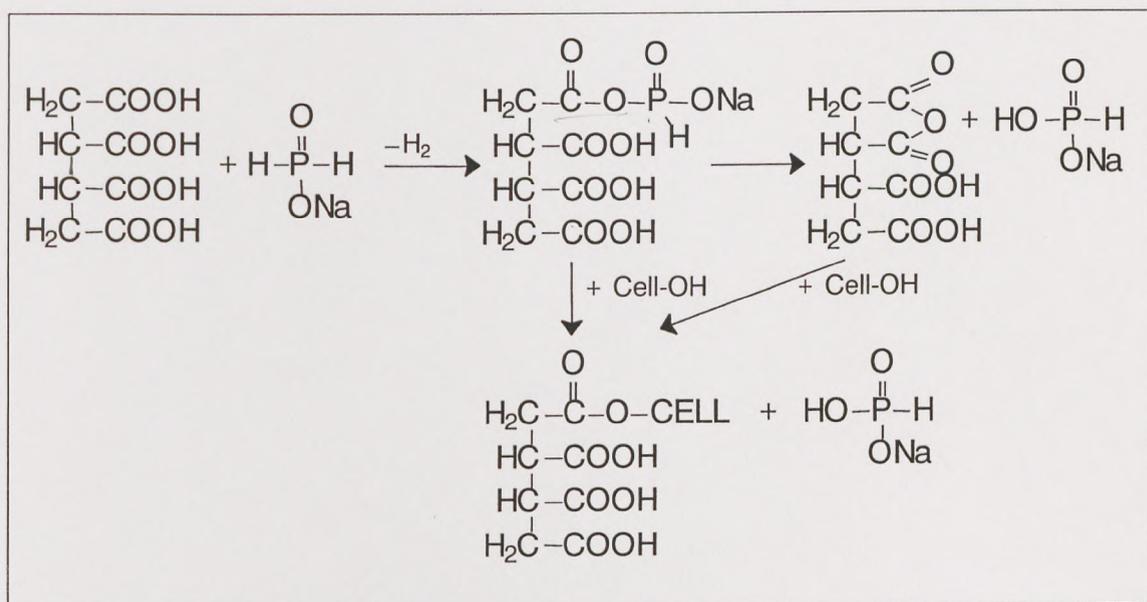


Figure 4. 5 Proposed mechanism by Brown for the SHP catalysed esterification reaction of cotton cellulose with BTCA (148).

The thermograms for the mixture of BTCA and SHP, see Figure 4. 3c, have different curves than either the BTCA or SHP pure compound thermograms. This is indicative of component interaction. There appears to be a loss of water that begins about 150°C to just below 200°C. The stepwise weight loss would suggest that after the initial loss of water there is some mixture stabilisation prior to decomposition that begins just above 200°C. The initial loss of water (approximately 4% of the total weight of the mixture) at 165°C may correspond to the loss of water by the formation of 1,2,3,4-

butanetetracarboxylic anhydride or the formation of a mixed anhydride with the SHP. The loss of one mole of water for a 1:1 molar ratio of the BTCA/SHP mixture corresponds to 5.29% of the total weight of the mixture. FT-IR spectra of the heated BTCA/SHP mixture showed evidence of anhydride formation beginning at 140°C. This is in agreement with the TGA and DSC thermograms. The small endothermic peak at just above 150°C may be as a result of anhydride formation. The endotherm at 175°C is probably as a result of melting.

4.1.3.1.2 Pyromellitic Acid (PMA).

Figure 4. 6 displays the FT-IR spectra for the unheated compound PMA, the unheated 1:1 molar ratio mixture of PMA and SHP and the heated mixture, heated to either 160°C or 180°C and isothermed for 2min. The spectrum for PMA shows bands typical of an aromatic carboxylic acid. The carbonyl stretching vibration can be seen at 1675cm⁻¹, this is overlapped with the band at 1712cm⁻¹ typically found in 1,2,4,5-substituted aromatic compounds. Another band at 817cm⁻¹ is also typical of 1,2,4,5- substituted aromatic structures. The C=C skeletal in-plane vibrations for aromatic compounds can be seen at 1607cm⁻¹ and 1510cm⁻¹. The frequencies corresponding to the carboxylic acid groups include a broad band corresponding to O-H stretching between 2500-3500cm⁻¹, two C-O stretching peaks that can be identified at 1413cm⁻¹ and 1282cm⁻¹, and a peak at 957cm⁻¹ that probably corresponds to O-H deformation.

Like BTCA, PMA exists as dimers in the solid state. The carbonyl band at 1675cm⁻¹ is shifted approximately 20cm⁻¹ when the hydrogen bonds in the PMA solid break down. In the PMA/SHP mixture the carbonyl band is shifted to 1693cm⁻¹ because of the decrease in hydrogen bonding in the mixture compared with the pure PMA compound. The spectrum for the unheated PMA/SHP mixture displays traits of both of the individual compound spectra. The shape of the FT-IR spectrum is similar to the spectrum for the unheated BTCA/SHP mixture. The peak at 2406cm⁻¹ corresponds to the P-H vibrations of the SHP, there is a broad band between 2500cm⁻¹ and 3500cm⁻¹ relating to the O-H vibration of the carboxylic acid group and the carbonyl band at 1693cm⁻¹ remains overlapping with the band typical of substituted aromatic compounds.

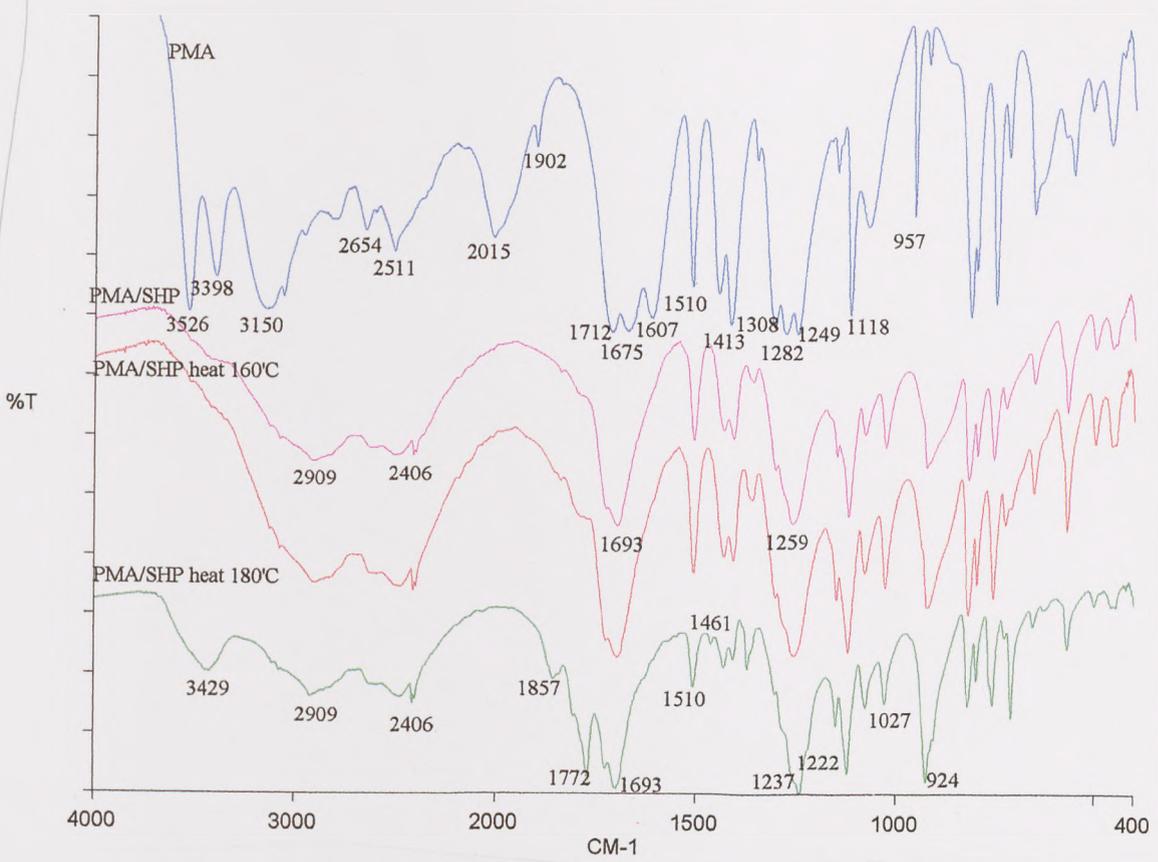


Figure 4. 6 FT-IR spectra for PMA and a 1:1 molar ratio of PMA and SHP.

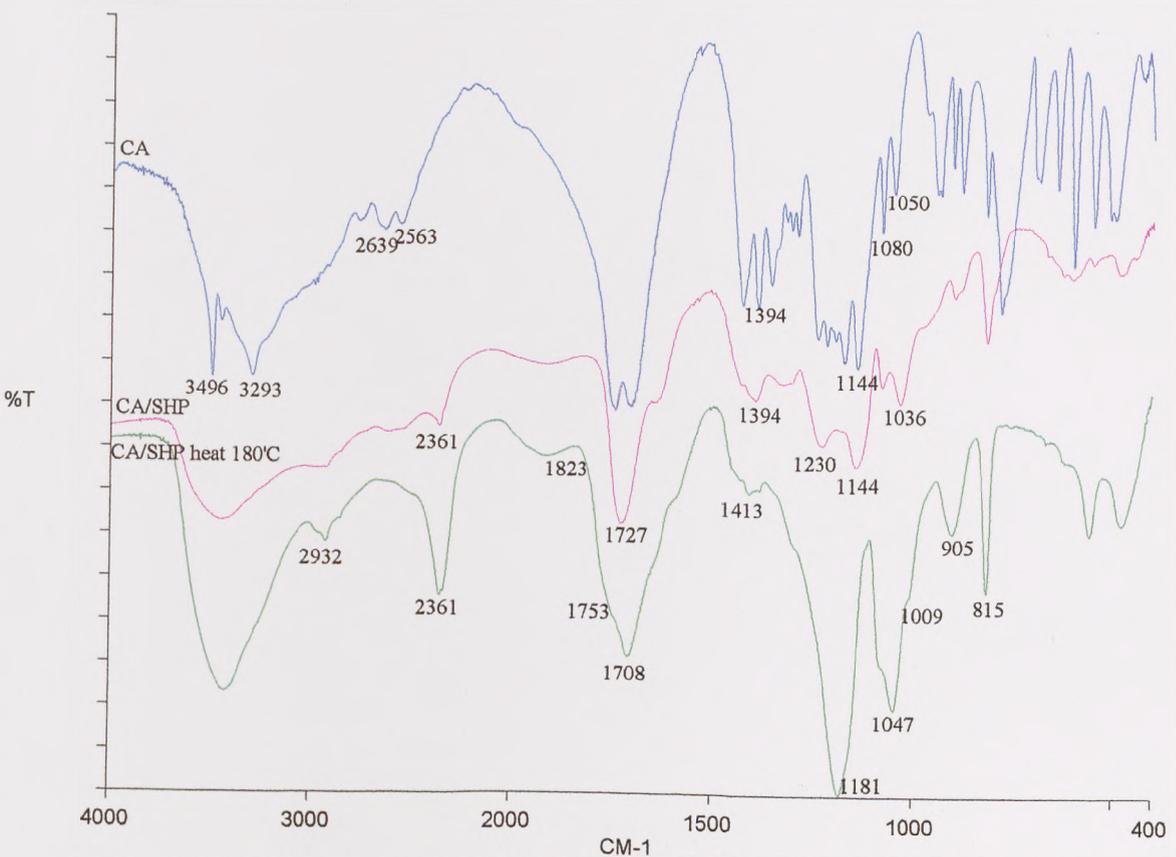


Figure 4. 7 FT-IR spectra for CA and a 1:1 molar ratio of CA and SHP.

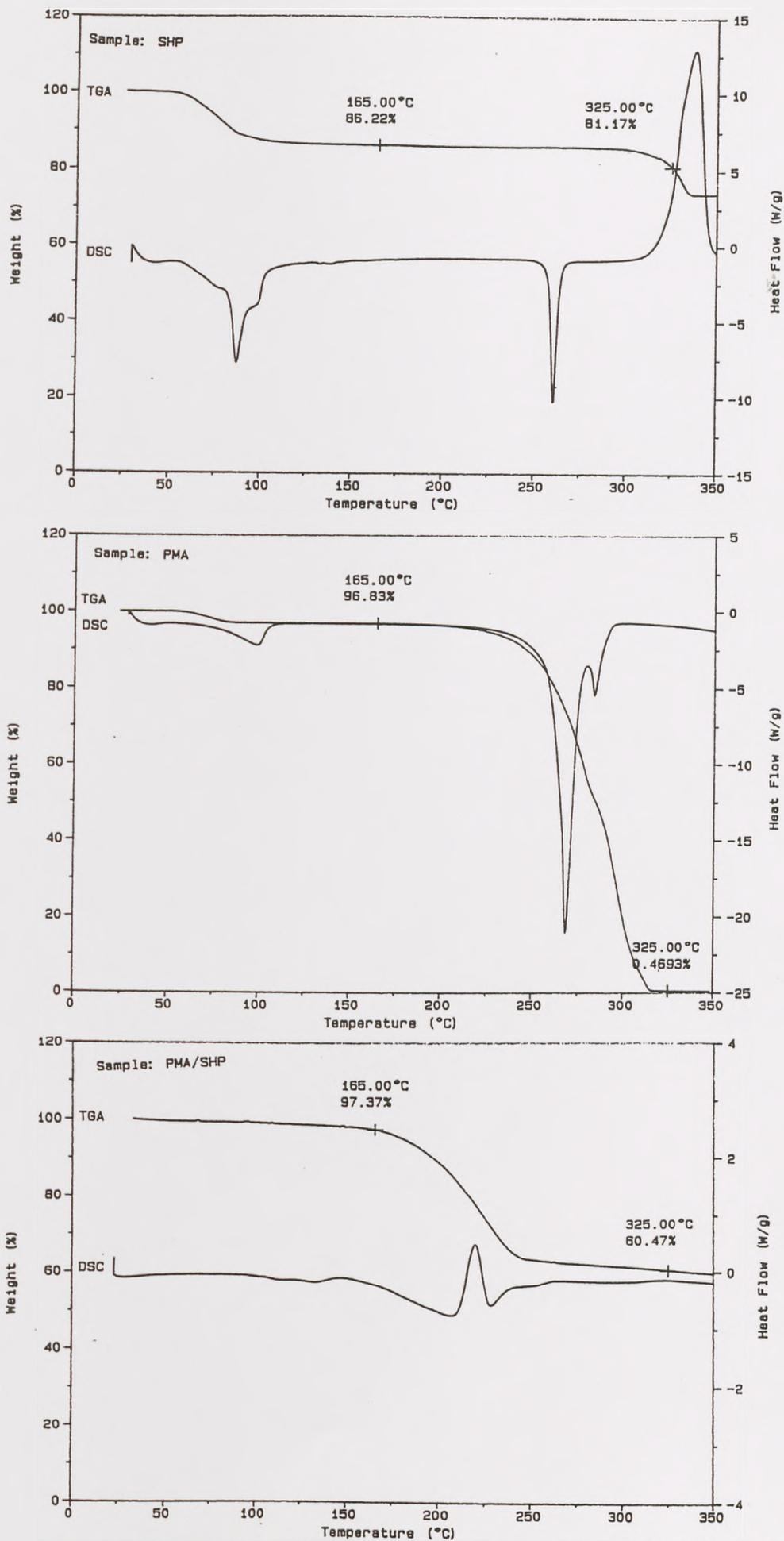


Figure 4. 8 TGA and DSC analysis of SHP, PMA, and a 1:1 molar mixture of PMA and SHP.

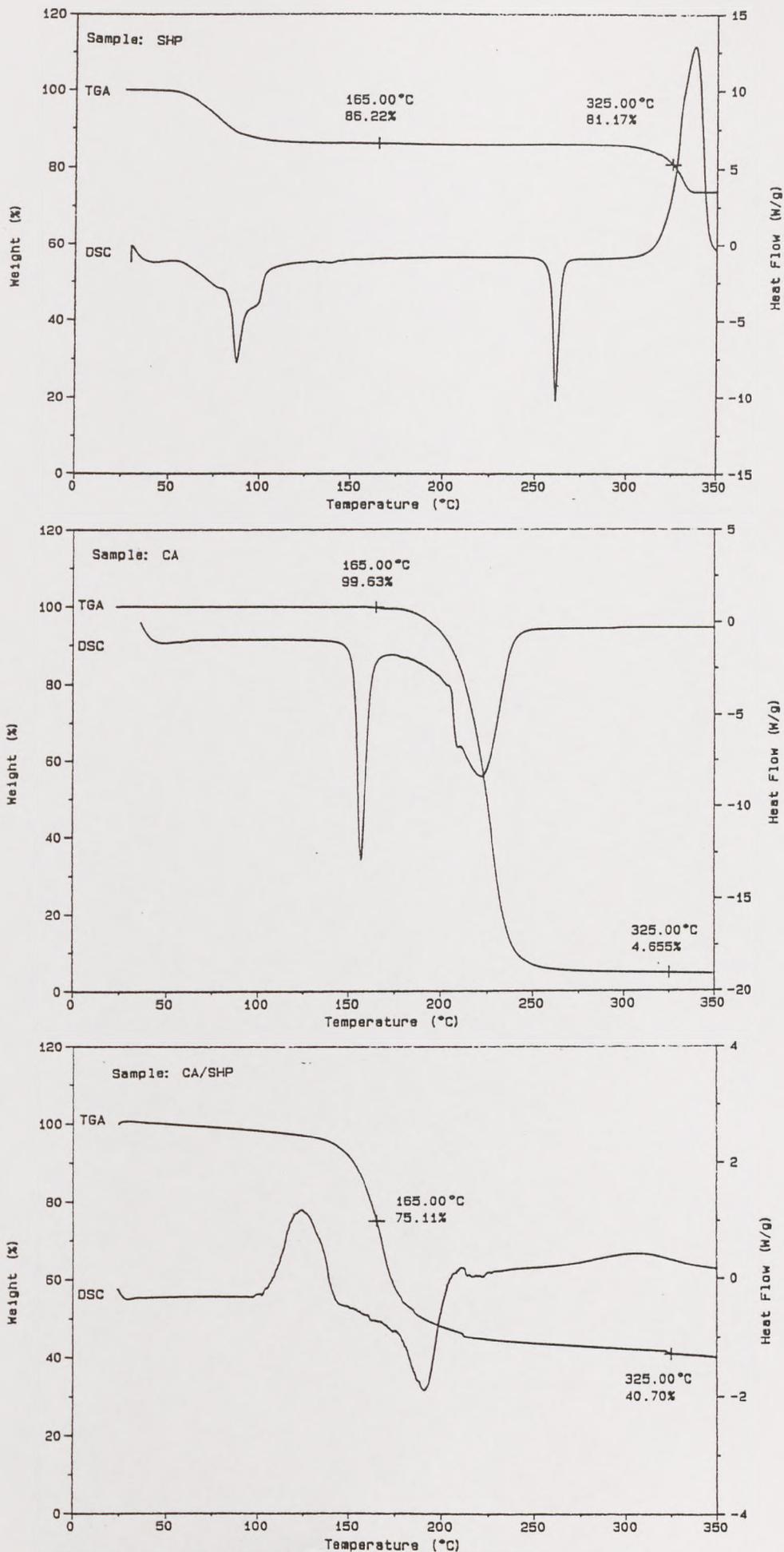


Figure 4.9 TGA and DSC analysis of SHP, CA, and a 1:1 molar mixture of CA and SHP.

The spectrum for the heated mixture clearly shows two new peaks corresponding to an anhydride at 1772cm^{-1} and 1857cm^{-1} . An additional new peak at 1237cm^{-1} probably corresponds to the C-O-C vibrations of a cyclic anhydride. There is no obvious new band that may correspond to the C-O-C vibrations of the straight chain anhydride or for the C-O-P vibration. The peak at 2405cm^{-1} typical of P-H vibrations in the SHP appears unchanged. In the spectrum for the heated BTCA/SHP mixture this peak showed a gradual decrease in height as the temperature of the heated mixture increased. The FT-IR spectral data for PMA and SHP tend to suggest that on heating to temperatures equivalent to those used in fabric curing this mixture forms a cyclic anhydride only, rather than a combination of both a cyclic- and an open chain- mixed anhydride.

Thermoanalysis depicted in Figure 4. 8 for PMA and a mixture of PMA and SHP shows both the single acid and the mixture to be stable to temperatures used in fabric curing. PMA melts and decomposes at around 270°C , in accordance with its melting point at 282°C . The PMA/SHP mixture begins to lose weight just above 175°C . This is accompanied by a slight endotherm on the DSC curve that may correspond to the formation of an anhydride visible on the FT-IR spectra in Figure 4.7 at 160°C . Above 200°C the PMA/SHP mixture begins to gradually decompose losing 40% of its initial weight by 250°C .

The FT-IR and thermal analysis of these tetracarboxylic acids in the presence of SHP as a catalyst indicate that these acids would be good fabric finishing agents. The acids and their mixtures are stable to temperatures in excess of those used in fabric finishing. From the FT-IR spectra it can be seen that the heated mixtures of these acids with SHP form anhydrides at temperatures used in fabric finishing. The formation of an anhydride is thought to be a necessary intermediate step in the formation of ester links between the PCA and silk fibroin.

4.1.3.2 Trifunctional carboxylic acids and SHP.

4.1.3.2.1 Citric Acid (CA).

The FT-IR spectra for the unheated pure CA compound, the unheated CA/SHP mixture and the CA/SHP mixture heated to 180°C and isothermed for 2min are shown in Figure 4. 7. The CA spectra is characteristic of a hydroxy carboxylic acid. There are peaks at 3496cm^{-1} and 3293cm^{-1} corresponding to the OH side groups, a broad band between

2500-3500 cm^{-1} corresponding to O-H stretching of the carboxylic acid and a double peaked carbonyl band between 1700 cm^{-1} and 1730 cm^{-1} .

Figure 4. 9 is a plot of the DSC and TGA thermograms from the tricarboxylic acid CA, the catalyst SHP and a 1:1 molar mixture of the pure compounds. The DSC and TGA thermograms of CA show a melting peak at just above 150°C followed by thermal decomposition of the compound that begins below 200°C. This corresponds with the melting point for CA of 154.4°C. The percent residue remaining above 300°C is low. TGA data suggests that CA is thermally stable at the temperature employed during curing.

The FT-IR spectrum for the unheated mixture, shown in Figure 4.8 is similar to the spectrum for the unheated BTCA/SHP mixture. There is a broad O-H stretching band for the CA between 2500-3500 cm^{-1} , a carbonyl peak at 1727 cm^{-1} and a band at 2361 cm^{-1} corresponding to the P-H vibration of the SHP. On heating the acid/catalyst mixture the carbonyl peak at 1727 cm^{-1} is shifted to 1708 cm^{-1} . This shift is in the opposite direction compared with the shift of the BTCA/SHP mixture shown in Figure 4. 1. It is possible that this shift is caused either by the formation of ester bonds between the CA anhydride molecules formed at the high temperature and the OH groups of adjacent CA molecules or by the dehydration of some CA molecules to form aconitic acid. Ester bonds characteristically absorb around 1735 cm^{-1} for aliphatic esters and around 1715 cm^{-1} for esters containing double bonds or ring structures. The C=C stretching vibration of a double bond absorbs between 1650 cm^{-1} and 1670 cm^{-1} . The anhydride bands at 1823 cm^{-1} and 1753 cm^{-1} are weak and this may be due to the anhydride forming ester bonds with adjacent OH groups. There is no band visible around 1260 cm^{-1} corresponding to C-O-C stretching vibrations of a cyclic anhydride. However, there is a sharp peak at 1047 cm^{-1} that may correspond to C-O-C stretching vibrations of open chain acid anhydrides or to C-O-P vibrations.

The thermograms in Figure 4. 9 for the CA/SHP mixture show a compound that appears less thermally stable than either of the two individual pure samples tested. Thermal decomposition begins below 150°C and the percent residue remaining at 165°C the optimum curing temperature for silk fabric is only 75.11%. The thermal data for this acid/catalyst mixture tend to suggest that decomposition occurs prior to the optimum

4.1.3.3 Difunctional carboxylic acids and SHP.

4.1.3.3.1 Maleic Acid (MA).

The FT-IR spectra for the pure unheated MA compound, the unheated MA/SHP mixture, and the heated MA/SHP mixture are shown in Figure 4. 11. MA is an unsaturated acid and peaks relating to its double bond can be identified at 3060cm^{-1} corresponding to =CH stretching and between 1650cm^{-1} and 1670cm^{-1} corresponding to C=C vibrations. The acid carbonyl peak can be seen at 1708cm^{-1} . This, like the BTCA acid carbonyl peak, shifts slightly due to a breakdown of hydrogen bonding in the acid when the acid and catalyst are mixed together.

The FT-IR spectrum of the heated MA/SHP mixture shows two peaks corresponding to the formation of an acid anhydride, at 1787cm^{-1} and 1846cm^{-1} . The higher peak is hard to identify as it overlaps within the shoulder of the next frequency. New bands appear in the spectrum of the heated samples at 1200cm^{-1} and 1050cm^{-1} that may correspond to the C-O-C stretching vibrations of the cyclic anhydride and the open chain anhydride, respectively. Alternatively the band at 1050cm^{-1} may relate to C-O-P vibrations, or the band could be a combination of the two frequencies. The FT-IR spectra show that MA is capable of forming an anhydride at temperatures equivalent to those used in fabric curing in the presence of SHP as a catalyst.

Figure 4. 13 displays the thermograms of the dicarboxylic acid MA, the catalyst SHP and a 1:1 molar mixture of MA and SHP. The MA thermograms show an initial melting peak that appears just before 150°C followed by immediate decomposition of the compound. The melting point for MA is $138\text{-}139^{\circ}\text{C}$. The percent residue remaining above 200°C is negligible. Evaporation or sublimation is probably responsible for the final weight of MA. The mixture of MA and SHP has a very different thermogram. This would be indicative of a reaction occurring between the MA and SHP that appears to make the mixture more thermally stable than the individual acid. At 165°C the percent residue remaining for the mixture is 85.27% almost twice that of the individual acid.



Figure 4.11 FT-IR spectra for MA, and a 1:1 molar ratio mixture of MA and SHP

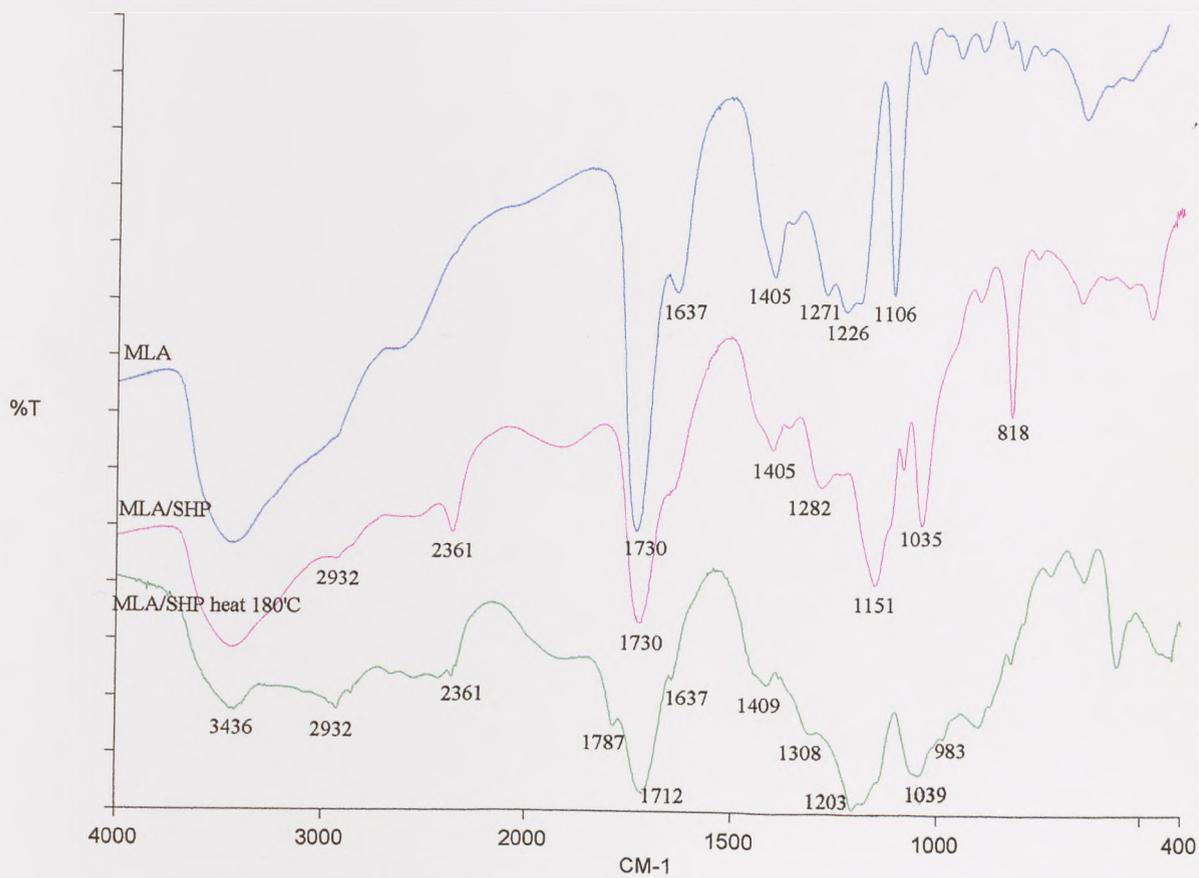


Figure 4.12 FT-IR spectra for MLA, and a 1:1 molar ratio mixture of MLA and SHP

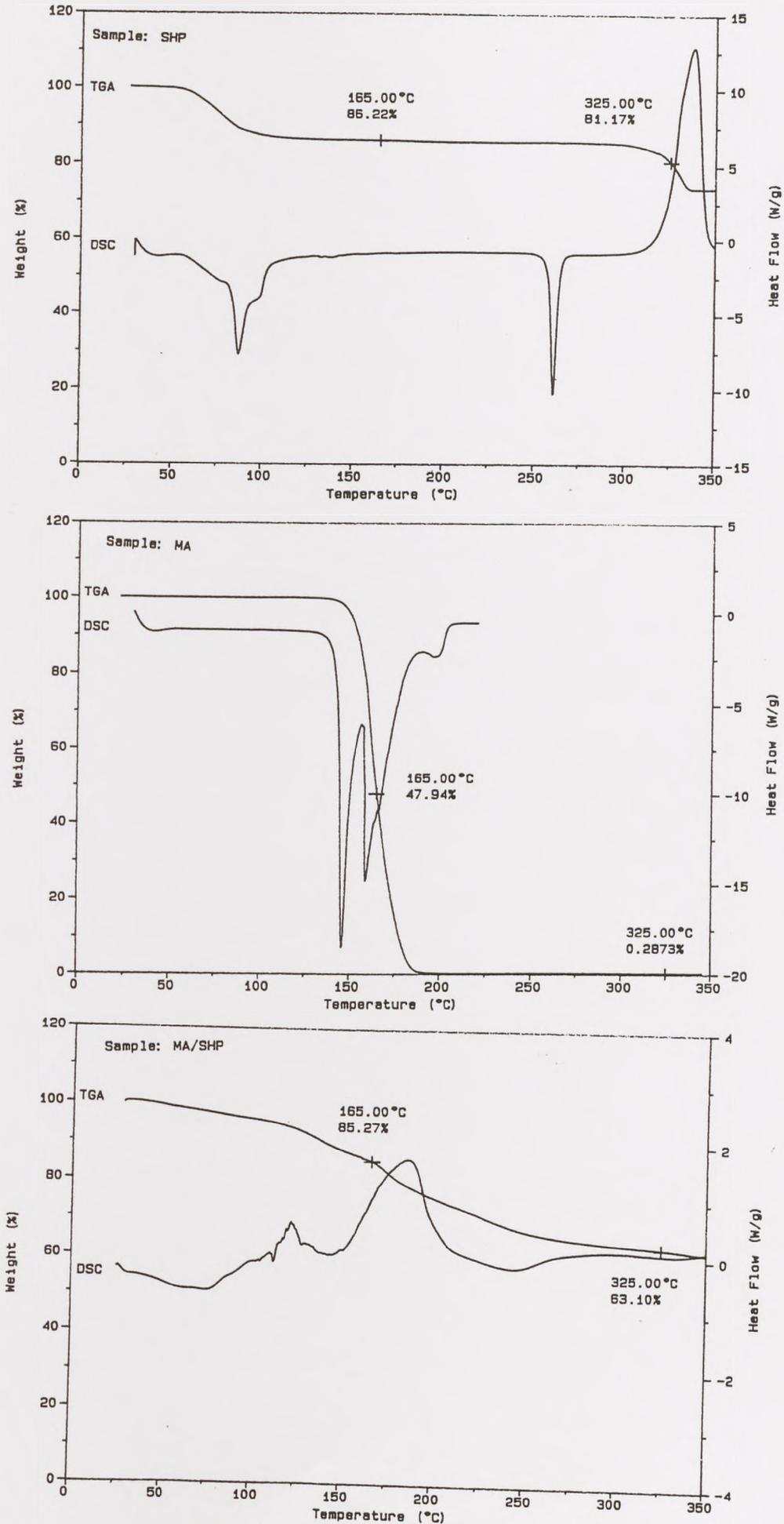


Figure 4. 13 TGA and DSC analysis of SHP, MA, and a 1:1 molar mixture of MA and SHP.

4.1.3.3.2 DL-Malic Acid (MLA).

The FT-IR spectra for the unheated pure MLA, the unheated MLA/SHP mixture and the heated MLA/SHP mixture are shown in Figure 4. 12. The shape of the three spectrum are similar to those shown for CA and CA/SHP mixture. MLA is a hydroxy dicarboxylic acid. There is a strong absorption around 3430cm^{-1} corresponding to the OH side groups, a broad band between $2500\text{-}3500\text{cm}^{-1}$ corresponding to O-H stretching of the carboxylic acid and the carbonyl band can be seen at 1730 cm^{-1} . The unheated MLA/SHP mixture shows the carbonyl band still at 1730cm^{-1} , the two C-O stretching peaks at 1405cm^{-1} and 1282cm^{-1} , and a peak at 2361cm^{-1} corresponding to the P-H bond of the SHP.

The FT-IR spectrum for the heated MLA/SHP mixture displays one new peak corresponding to the formation of an acid anhydride. A typical spectrum for an acid anhydride shows two peaks approximately 60cm^{-1} apart. The second anhydride band may be engulfed in the shoulder of the next peak. New peaks can also be seen at 1203cm^{-1} and 1039cm^{-1} that may represent C-O-C stretching vibrations of ring and open chain anhydrides, respectively. The acid carbonyl peak at 1712cm^{-1} has shifted approximately 20cm^{-1} lower than the value seen for the unheated MLA/SHP mixture. This shift in the carbonyl band was also observed in the spectra for the other hydroxy acid and SHP mixture, CA/SHP. It was hypothesised that this shift may be as a result of the formation of ester bonds between the OH side groups in CA and the acid anhydride formed or as a result of dehydration of the acid forming a double bond. Ester bonds characteristically absorb around 1735cm^{-1} for aliphatic esters and around 1715cm^{-1} for esters containing double bonds or ring structures. The C=C stretching vibration of a double bond absorbs between 1650cm^{-1} and 1670cm^{-1} .

Figure 4. 14 displays the MLA/SHP TGA and DSC curves. The DSC endotherm shows an initial exothermic peak just above 120°C , similar to that seen for the other hydroxy acid/catalyst mixture, CA/SHP. It was suggested that this exothermic peak in the CA/SHP could correspond to either dehydration of the hydroxy acid with the formation of a double bond or the formation of ester bonds. The MLA/SHP thermograms show the thermal degradation of the mixture begins above the temperature usually employed in curing silk fabrics.

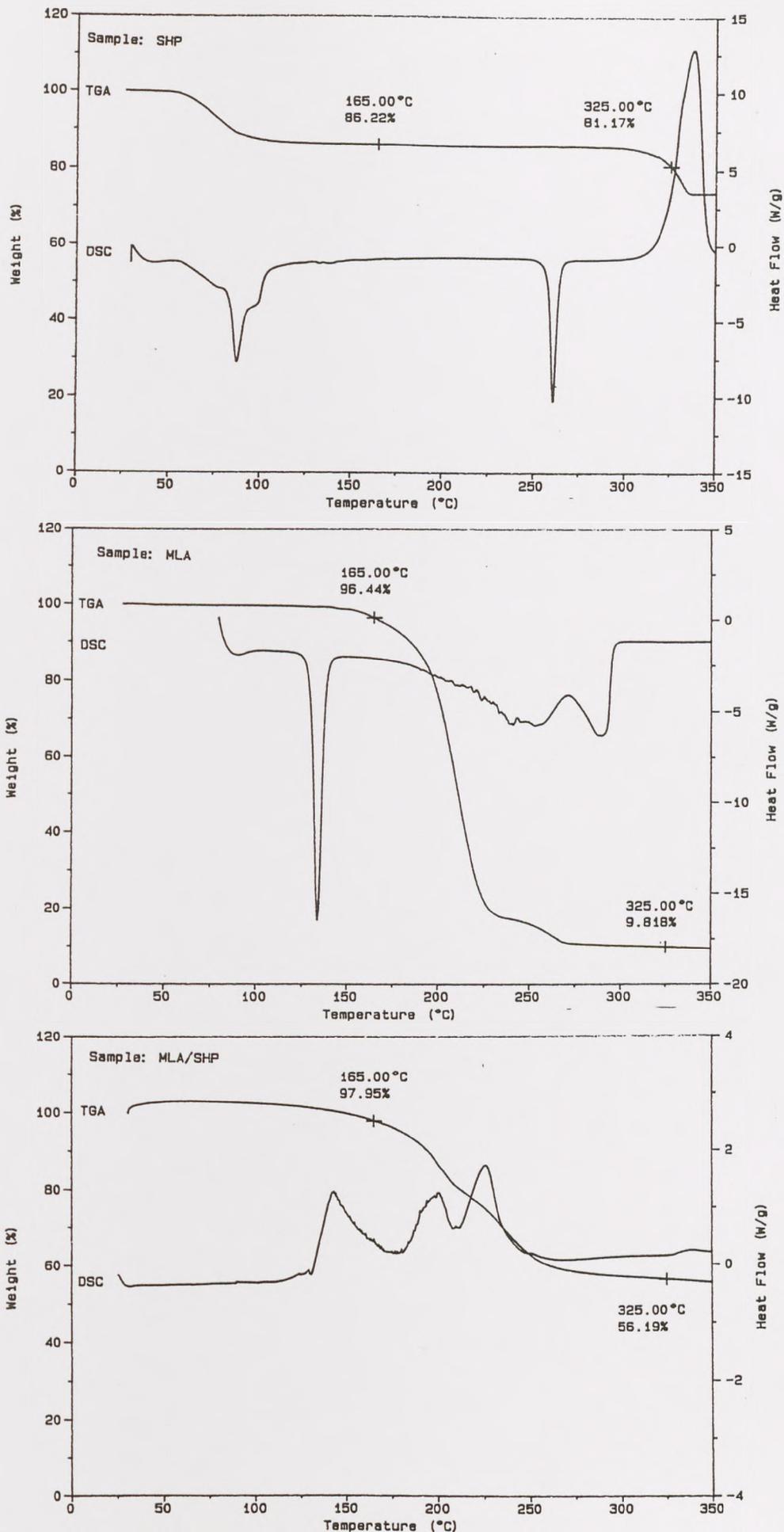


Figure 4. 14 TGA and DSC analysis of SHP, MLA, and a 1:1 molar mixture of MLA and SHP.

4.1.3.3.3 Aliphatic dicarboxylic acids.

The infra-red and thermal properties of succinic acid (SA), itaconic acid (IA), and glutaric acid (GA) were also studied. The DSC and TGA curves for the pure dicarboxylic acids all showed the same trends; an initial melt followed by decomposition of the dicarboxylic acid. They all have high percent residues remaining at 165°C and low percent residues remaining at 325°C. This is probably due to the acids thermally decomposing by evaporation or sublimation.

The FT-IR and thermal spectra for these acids and their mixtures with SHP are shown in Figure 4. 15 to Figure 4. 20. Figure 4. 15 is a diagram of the FT-IR spectra for SA and a 1:1 molar ratio mixture of SA and SHP. The spectrum of the heated mixture displays a slight inflection at 1771cm^{-1} and 1685cm^{-1} , the known absorption bands for succinic anhydride (180). The additional band for the heated mixture at 1046cm^{-1} is indicative of either open chain anhydride formation, or C-O-P vibrations. The alteration in the peak at 1170cm^{-1} may be as a result of some cyclic anhydride formation.

Additional indication of the formation of succinic anhydride is provided by thermal analysis of the SA/SHP mixture. The SA/SHP thermograms show curves indicating an initial weight loss corresponding to 8% of the weight of the initial mixture at 150°C followed by melting at around 175°C and immediate decomposition. The shape of the DSC and TGA curves are similar to those for BTCA/SHP mixture. The TGA curve shows two distinct weight loss regions, and seems to suggest some stabilisation after the initial loss of water at 150°C, this could be due to the formation of succinic anhydride as an intermediate step prior to decomposition. None of the other TGA curves for dicarboxylic acid and SHP mixtures showed the same stepwise degradation.

The thermograms of IA/SHP mixture show that degradation begins at around 125°C, and the percent residue remaining at 165°C, the ideal curing temperature for the chemical modification of silk fabric with polycarboxylic acids, is 73.60%. This reduced percent residue remaining at the curing temperature indicates that IA/SHP system would be unlikely to perform well as a silk fabric easy-care finish.

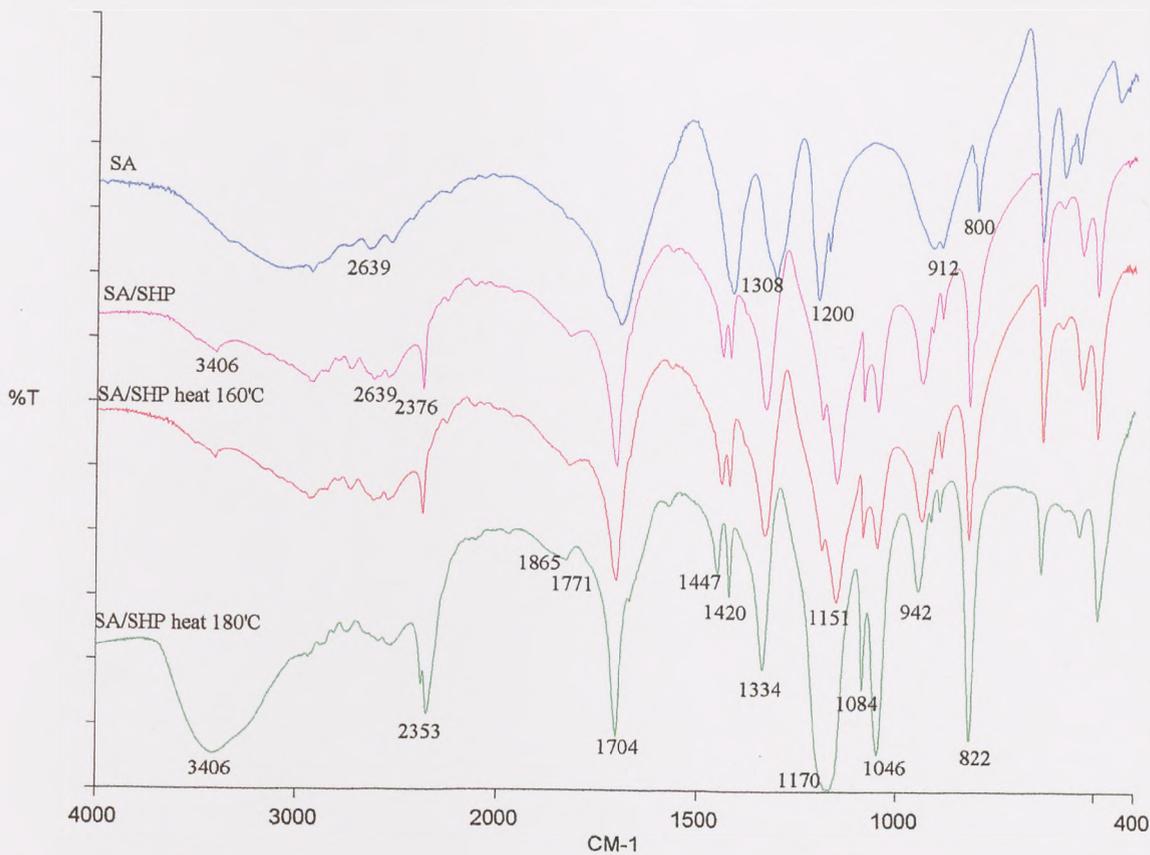


Figure 4.15 FT-IR spectra for SA and a 1:1 molar ratio of SA and SHP.

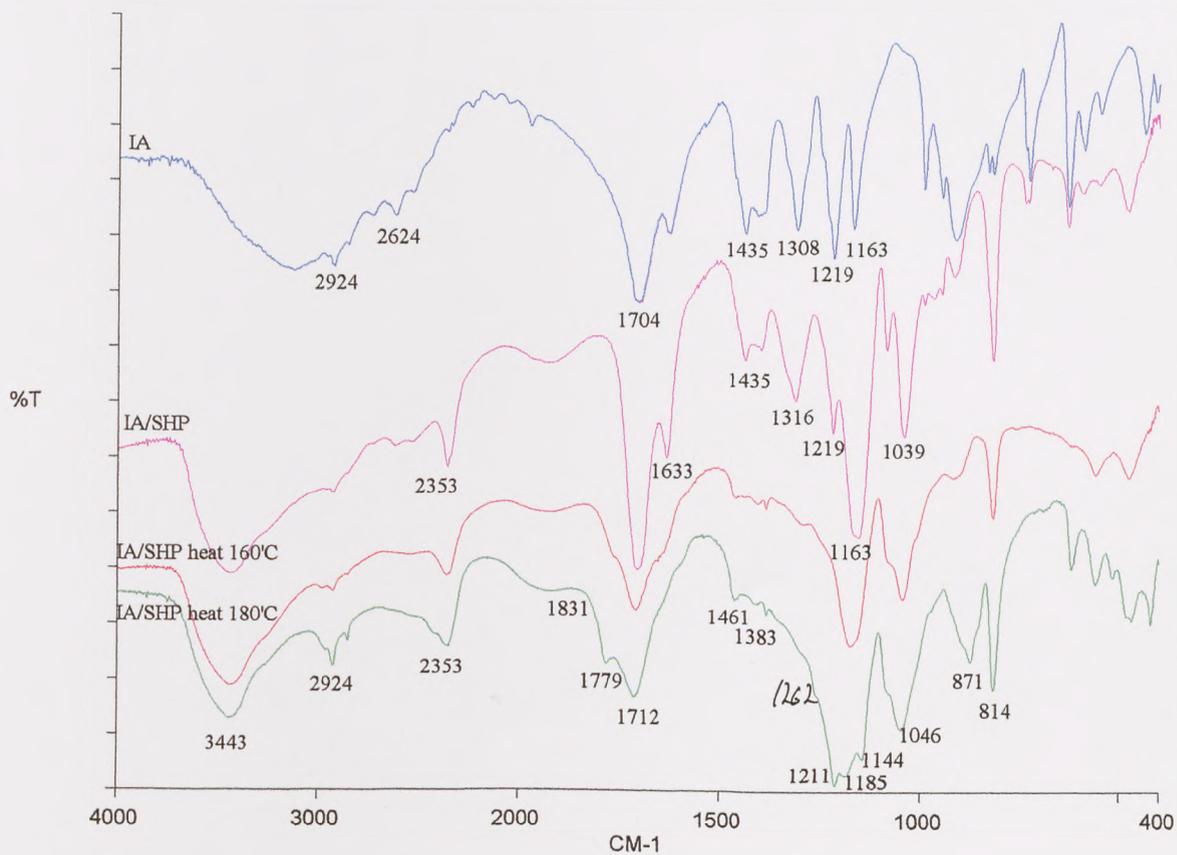


Figure 4.16 FT-IR spectra for IA and a 1:1 molar ratio of IA and SHP.

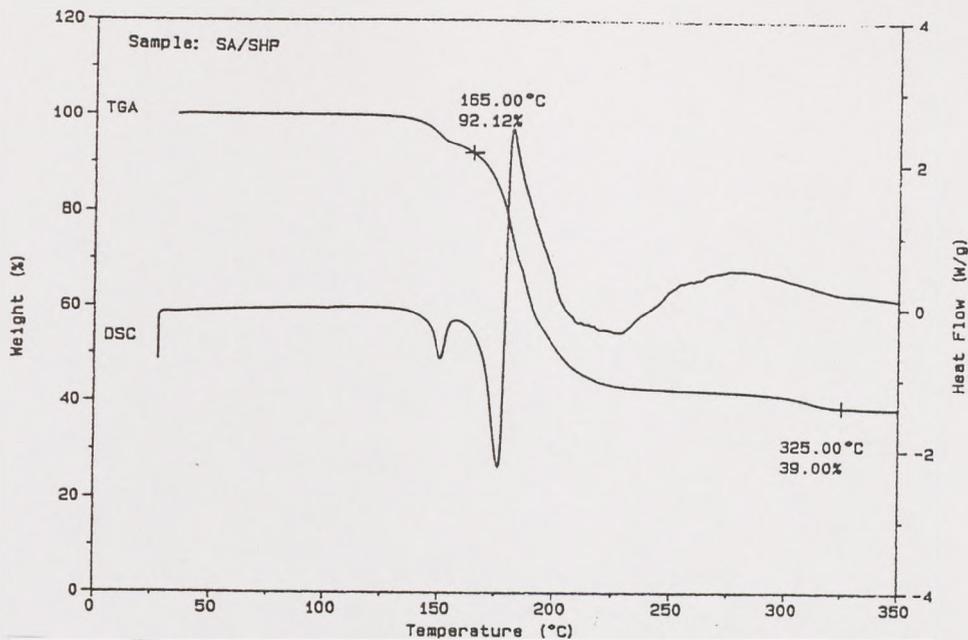


Figure 4. 17 TGA and DSC analysis of a 1:1 molar mixture of SA and SHP.

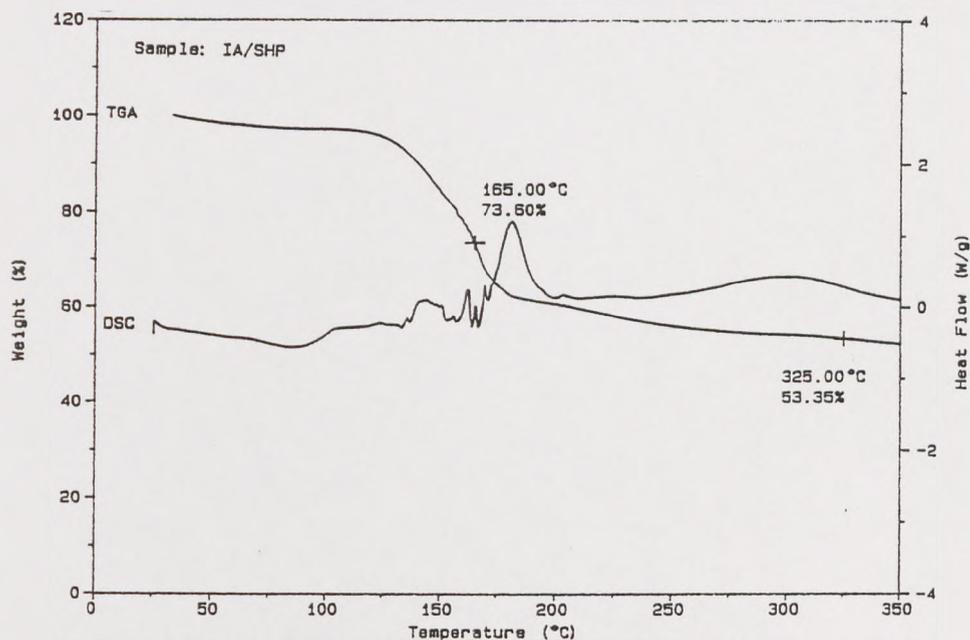


Figure 4. 18 TGA and DSC analysis of a 1:1 molar mixture of IA and SHP.

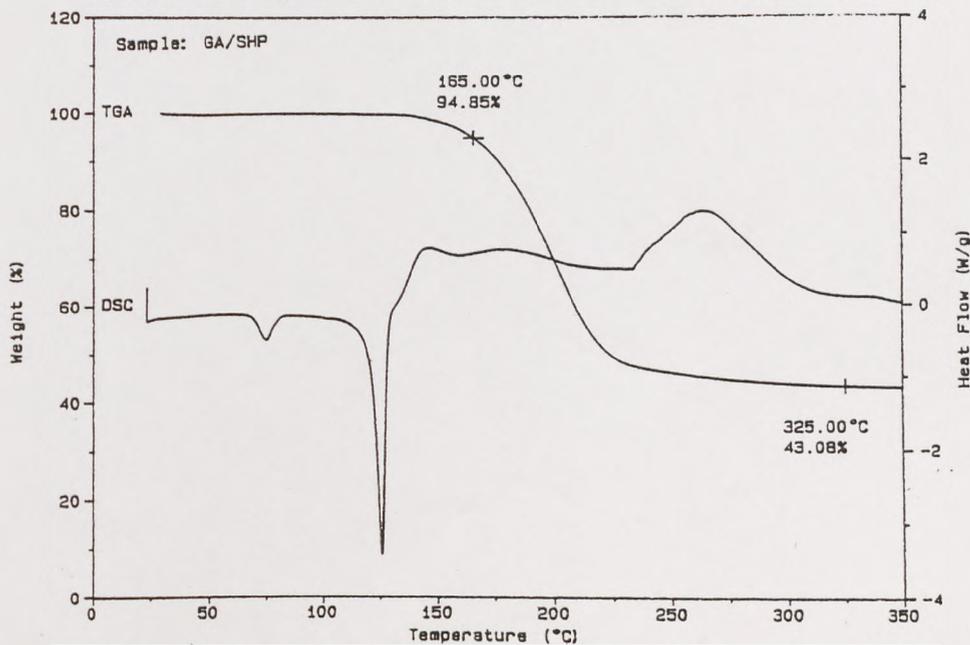


Figure 4. 19 TGA and DSC analysis of a 1:1 molar mixture of GA and SHP.

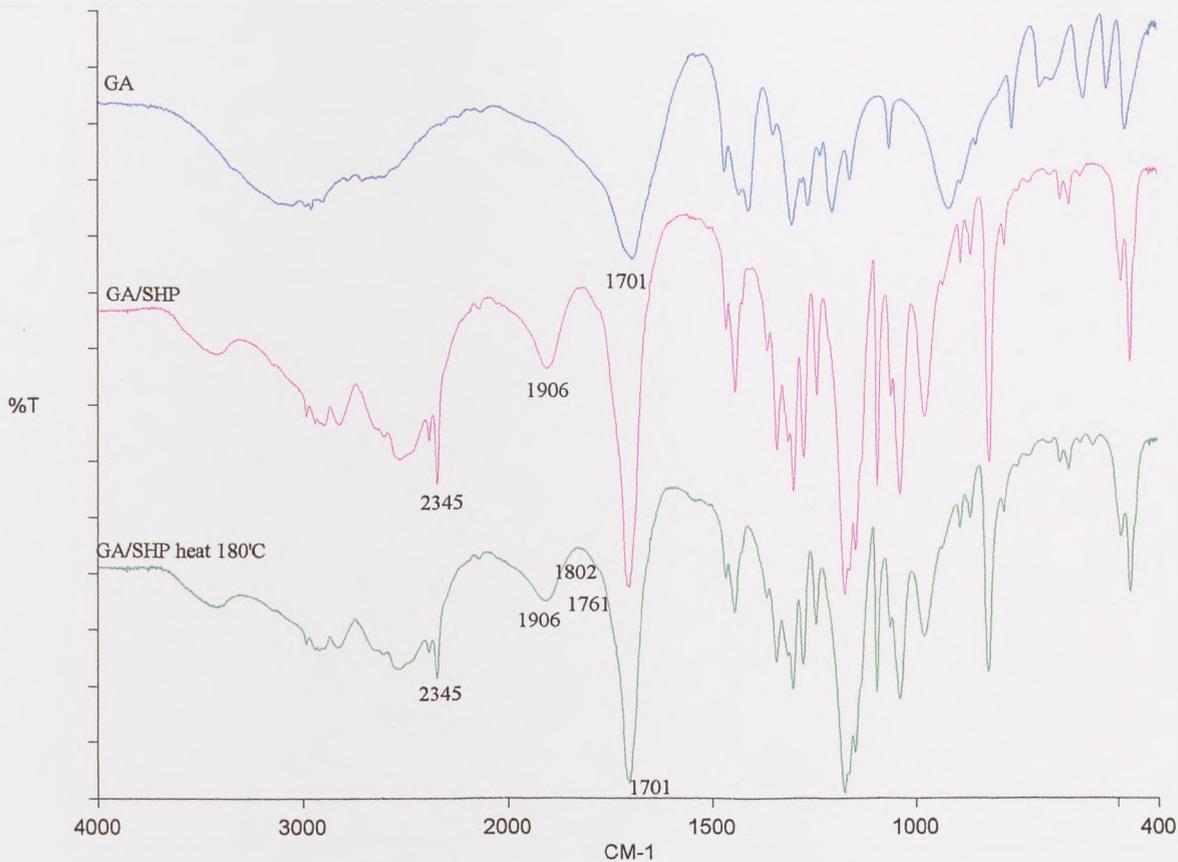


Figure 4. 20 FT-IR spectra for GA and a 1:1 molar ratio of GA and SHP.

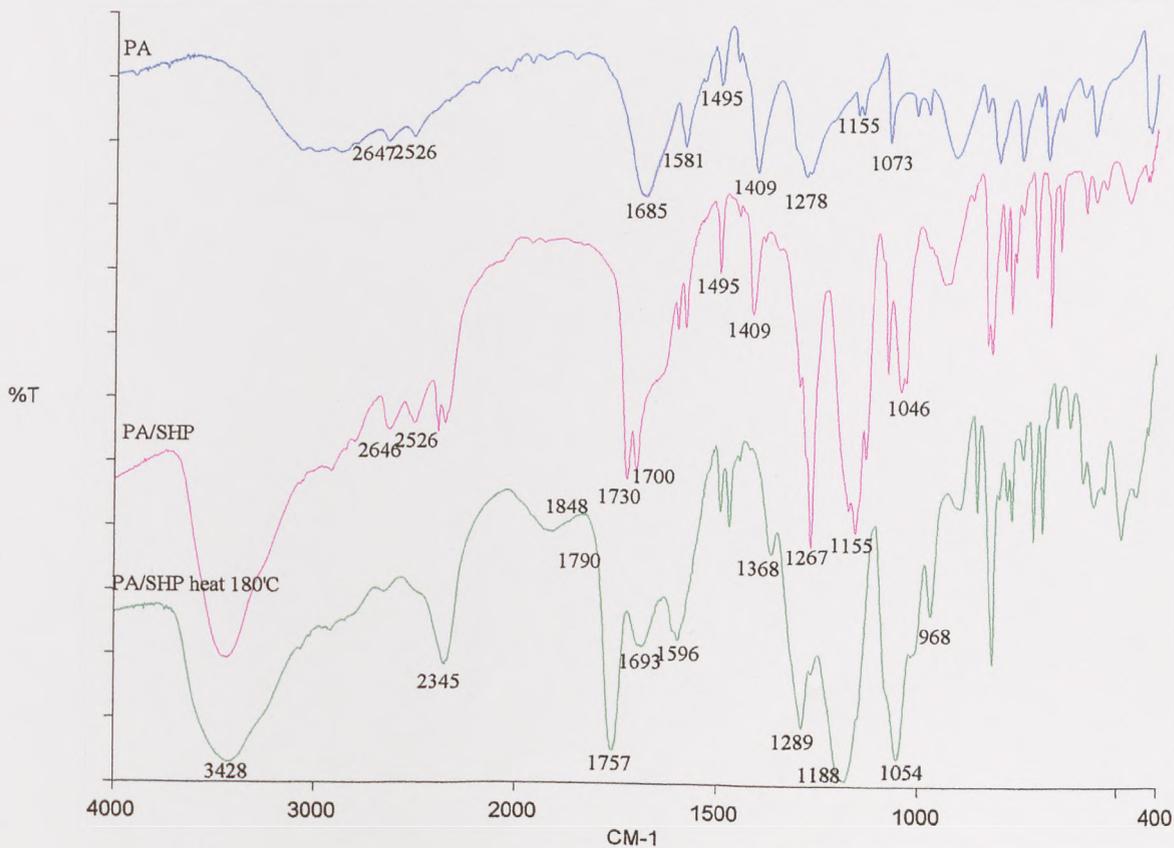


Figure 4. 21 FT-IR spectra for PA and a 1:1 molar ratio of PA and SHP.

The FT-IR spectrum for the heated GA/SHP mixture displayed in Figure 4. 20 shows no evidence of anhydride formation at the temperatures usually employed in silk fabric finishing and is therefore not thought suitable to be used as an easy-care finishing agent. GA/SHP thermograms, see Figure 4.19, show the mixture melting at 125°C and beginning to decompose above 150°C. This acid is a known kidney toxin and is therefore not suitable as an easy-care finish for silk fabric (136).

4.1.3.3.4 Phthalic Acid (PA).

The FT-IR spectrum for the heated PA/SHP mixture is pictured in Figure 4. 21 and shows no sign of anhydride formation at 180°C. This acid was therefore not thought appropriate as an easy-care finishing agent for finishing silk fabrics. The thermograms for PA/SHP were distorted, however decomposition of the mixture appeared to begin around 125°C.

4.1.3.4 A dicarboxylic acid, a hydroxy acid and SHP.

Succinic acid (SA) is a cheap, non-toxic dicarboxylic acid that is capable of forming a five-membered cyclic anhydride. If SA could react with the -OH group of a hydroxy acid such as citric acid (CA) or DL-malic acid (MLA) then a carboxylic acid with more than two carboxylic acid groups would be formed. This carboxylic acid may then be able to form an anhydride that would be capable of forming ester bonds with silk fibroin. In the proposed mechanism, by Welch (145), for the formation of ester cross-links by a PCA with cotton cellulose, the acid requires a minimum of three carboxylic acid groups. In Figure 4. 22 to Figure 4. 25 the FT-IR spectra and thermal graphs for mixtures of these acids with SHP are displayed.

Figure 4. 22 depicts the FT-IR spectrum for the heated SA/CA/SHP mixture. It shows the beginning of the formation of bands, at 1776cm^{-1} and 1830cm^{-1} , typical of anhydride formation at 160°C. New peaks at 1262cm^{-1} and 1045cm^{-1} are visible that may correspond to C-O-C stretching vibration of cyclic and open chain anhydrides respectively. As with the spectrum for the heated mixtures of a hydroxy acid and SHP the acid carbonyl peak has shifted on heating to a lower position by approximately 20cm^{-1} . It was hypothesised that this shift could be as a result of ester formation or as a result of dehydration of the acid to form an unsaturated compound, see Figure 4. 10.

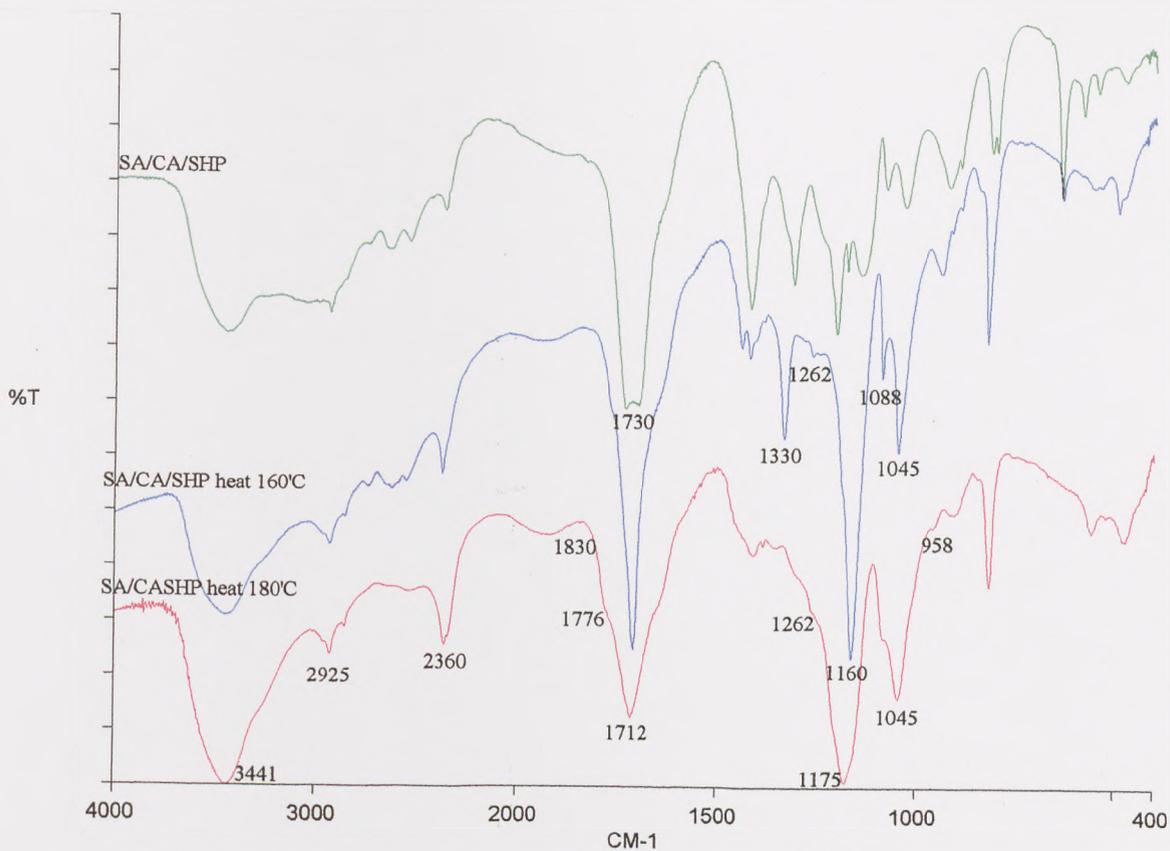


Figure 4.22 FT-IR spectra for a 1:1:0.5 molar ratio mixture of SA, CA and SHP.

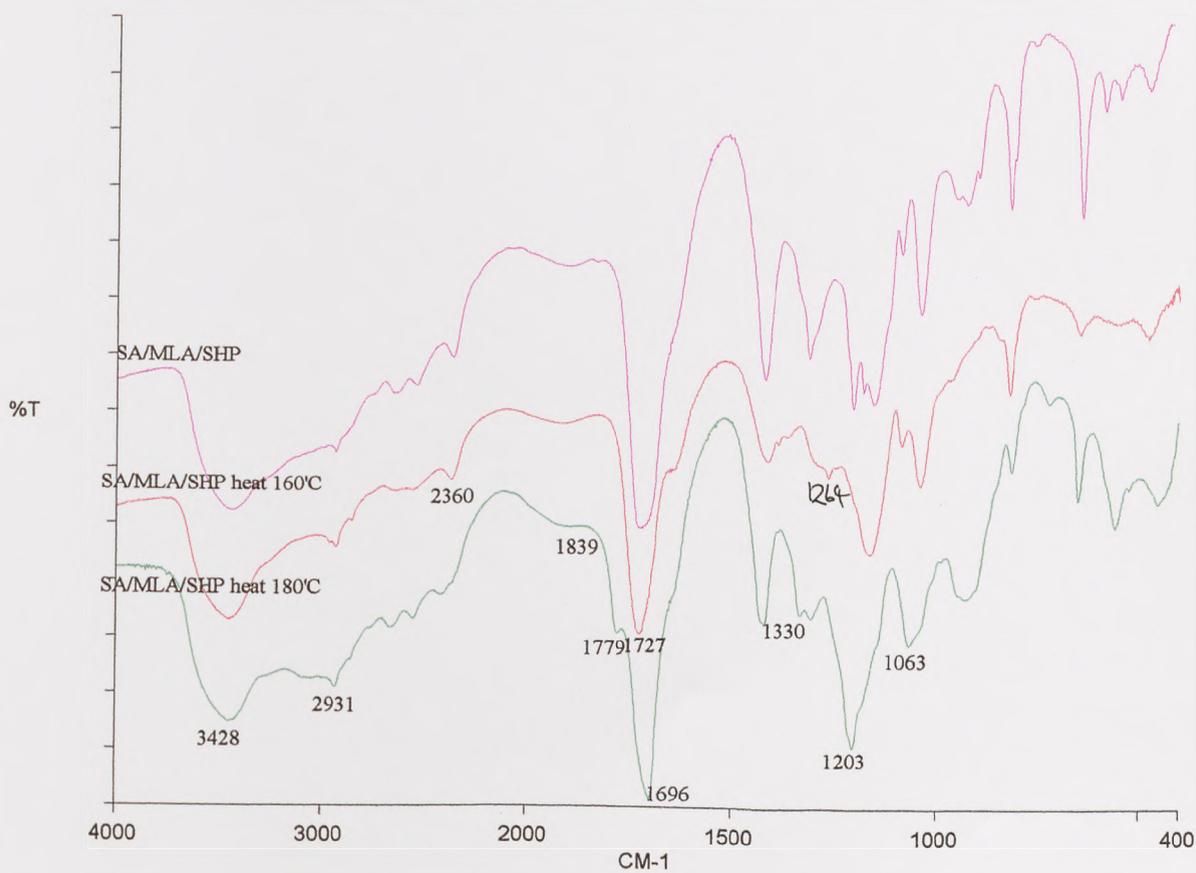


Figure 4.23 FT-IR spectra for a 1:1:0.5 molar ratio mixture of SA, MLA and SHP.

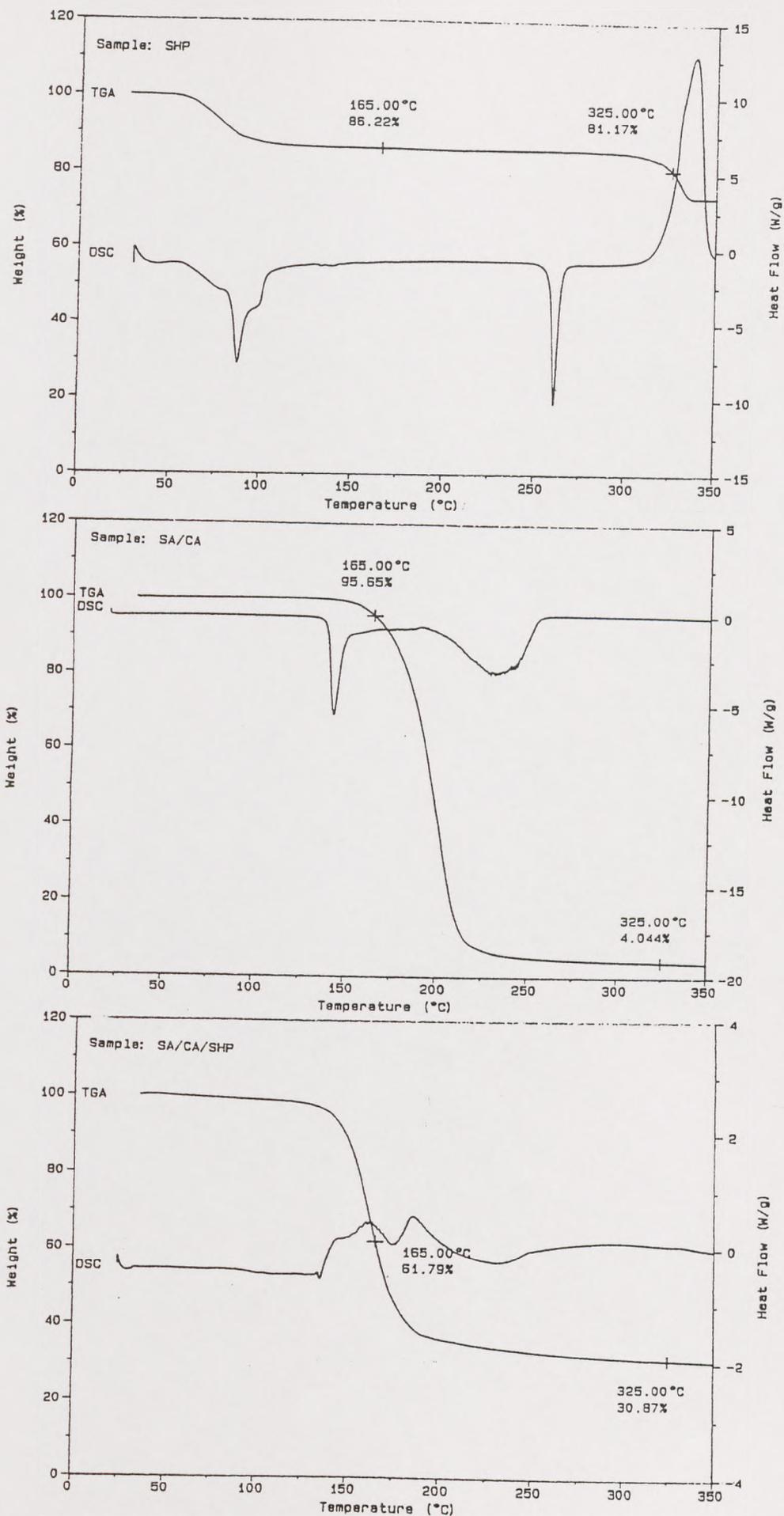


Figure 4. 24 TGA and DSC analysis of SHP, a 1:1 molar ratio mixture of SA and CA, and a 1:1:0.5 molar ratio of SA, CA and SHP.

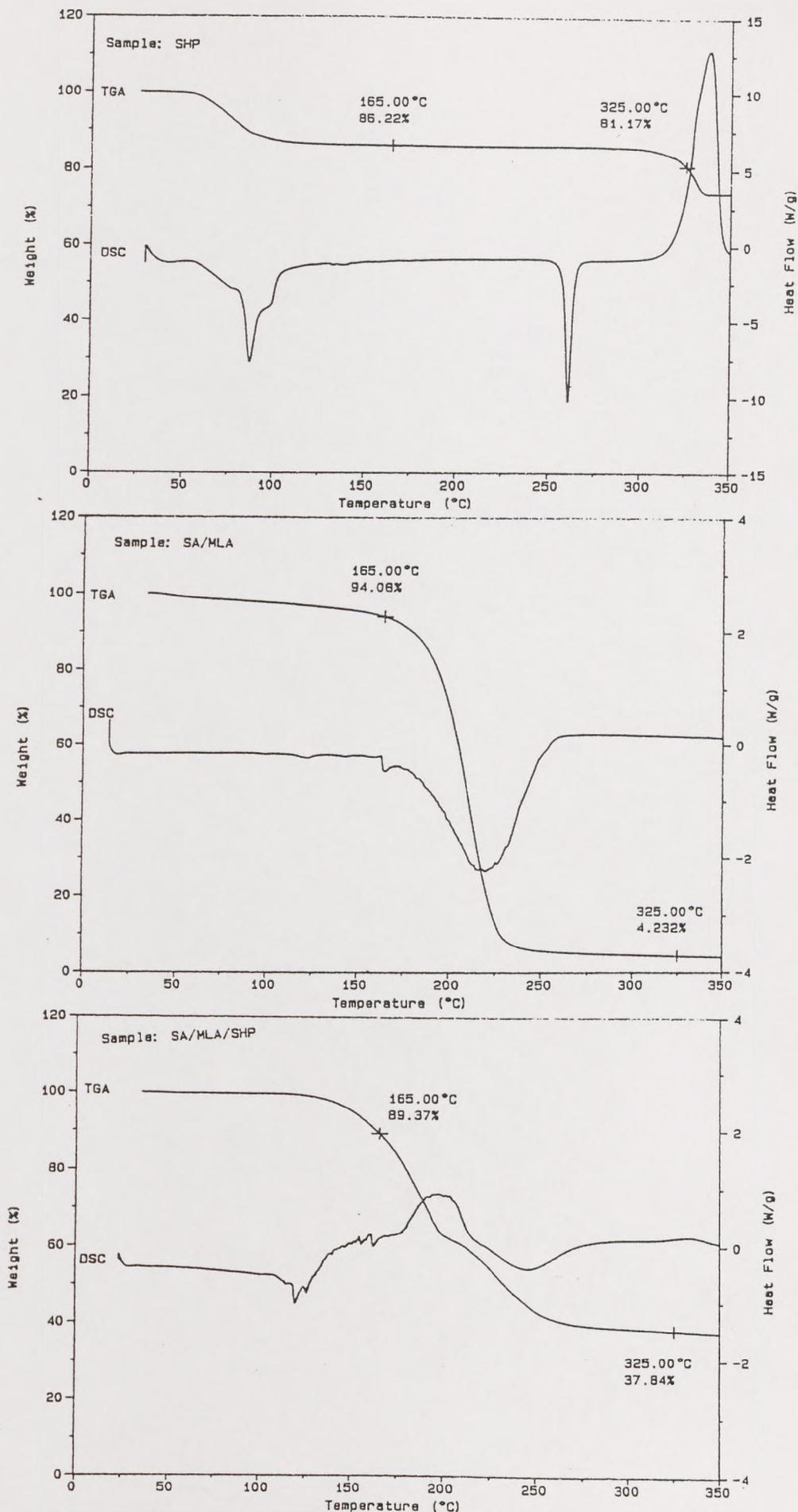


Figure 4. 25 TGA and DSC analysis of SHP, a 1:1 molar ratio mixture of SA and MLA, and a 1:1:0.5 molar ratio of SA, MLA and SHP.

The TGA and DSC thermograms for the SA/CA mixture and the SA/CA/SHP mixture are displayed in Figure 4. 24. The DSC thermogram for the acid mixture shows an endothermic peak that could correspond to the melting of the acid mixture followed by decomposition of the sample just above 150°C. The acid mixture and SHP also shows a decomposition beginning just above 150°C, but the melting endotherm is overlaid by an exothermic reaction. An exothermic peak was observed just below this temperature in the DSC thermogram for the CA/SHP mixture. It was postulated that this exothermic peak could correspond to either the formation of ester bonds or to the dehydration of the acid to form double bonds.

The infra-red spectra and thermoanalytical graphs for SA/MLA/SHP mixture show similar trends to those discussed for SA/CA/SHP mixture. Figure 4. 23 displays the FT-IR spectrum for the heated mixture and shows the formation of two anhydride C=O peaks for the mixture heated to 180°C. In the spectrum for the mixture heated to 160°C a new band at 1264cm⁻¹ is observed that may correspond to the C-O-C stretching vibrations of a cyclic anhydride. This band is not present in the mixture heated to 180°C, however, another band at 1063cm⁻¹ appears that may correspond to the C-O-C stretching vibrations of an open chain anhydride. Again there is a shift in the acid carbonyl peak from 1727cm⁻¹ to 1696cm⁻¹. The thermal data is displayed in Figure 4. 25 and is similar to that discussed for the SA/CA/SHP mixture.

The infra-red and thermoanalytical data for mixtures of succinic acid, a hydroxy acid and SHP indicate that these acid mixtures are capable of forming anhydrides at temperatures equivalent to those used in silk fabric curing. There is evidence, both from FT-IR analysis and the DSC thermograms, of a secondary reaction occurring simultaneously with the formation of the acid anhydride. What is unclear from these data however is the exact nature of the other reaction. Although, it is postulated that it may be either the dehydration of the acid forming double bonds, or the formation of ester bonds between the hydroxy acid and the acid anhydride formed during heating.

4.1.3.5 BTCA with alternative catalytic systems.

SHP is an expensive catalyst, it is an environmental hazard and has the drawback of producing shade changes on some reactive and sulphur dyeings. Alternative catalysts for cross-linking silk fibroin with PCAs are therefore desirable. Various sodium salts of

di- and tricarboxylic acids have been reported as alternative non-phosphorus catalysts for the cross-linking of cotton cellulose with polycarboxylic acids, see section 3.2.3.2. These acids have been found to be more effective esterification catalysts than sodium carbonate but not as effective as SHP (155). Of the di- and tricarboxylic acids tested as esterification catalysts, the sodium salts of α -hydroxy acids appear to be the most promising replacement for SHP (157). Andrews and Morris (157) found that the sodium citrates produced fabric with the best easy-care properties, and that the efficiency of the sodium citrates as catalysts improved with an increase in the number of Na^+ ions attached to the citric acid.

In this experiment the use of sodium salts of three carboxylic acids as catalysts are investigated by thermal and infra-red analysis; namely the sodium salts of the α -hydroxy acids citric and tartaric acids and the sodium salts of the unsaturated acid maleic acid. Figure 4. 26 to Figure 4. 38 display the thermal and infra-red graphs for these experiments.

Figure 4. 26 pictures the FT-IR spectra for the pure unheated monosodium citrate (MSC), the pure unheated BTCA compound, the unheated MSC/BTCA mixture and the mixture heated to 160°C and isothermed for 2min. The unheated pure MSC and the unheated pure BTCA compounds have similar infra-red spectra characteristic of a carboxylic acid. They both show a broad absorption band around $2500\text{-}3500\text{cm}^{-1}$ corresponding to the O-H stretching of the carboxylic acid group. A sharp carbonyl peak can be identified near 1700cm^{-1} ; the carbonyl peak for MSC appears at 1734cm^{-1} that is slightly higher than the carbonyl band for BTCA that can be seen at 1698cm^{-1} . This difference in position of the carbonyl band is caused by the BTCA molecules existing as hydrogen-bonded dimers and appears as a double peak absorption in the unheated BTCA/MSC mixture. Carbonyl absorptions for the two C-O stretching peaks can also be identified around 1400cm^{-1} and 1295cm^{-1} .

The spectrum for the unheated mixture shows the characteristics of both the individual compounds and has the expected absorption bands corresponding to a carboxylic acid. The spectrum for the heated mixture clearly displays the two C=O absorption peaks characteristic of an acid anhydride at 1768cm^{-1} and 1843cm^{-1} . Strong new bands have also appeared at 1262cm^{-1} and 1050cm^{-1} that may correspond to the C-O-C stretching

vibrations typical of a cyclic and open chain anhydride, respectively.

Figure 4. 26 is a plot of the FT-IR spectra for the heated BTCA/MSM mixture heated to different temperatures and isothermed at that temperature for 2min. From this figure it is clearly visible that the formation of an acid anhydride begins below 130°C. The two acid anhydride carbonyl peaks at 1768cm⁻¹ and 1843cm⁻¹ are evident at 130°C. The bands typical of an acid anhydride appear to shift when the BTCA/MSM mixture is heated to 180°C; this may be due to degradation of the mixture at this temperature.

Figure 4. 28 displays the thermograms for MSM, BTCA and a 1:1 molar ratio mixture of BTCA/MSM. The DSC thermogram for the BTCA/MSM mixture has an endothermic peak just above 100°C that is accompanied by a small loss in weight shown in the TGA curve. This could be attributed to the loss of water that may be associated with the formation of an acid anhydride. FT-IR analysis showed that acid anhydride formation began below 130°C. The DSC thermogram displays two more endothermic peaks, one that begins just below 150°C, and the other just below 175°C. This DSC curve is very similar to that seen for the BTCA/SHP mixture. In this thermogram it was hypothesised that the first of these endothermic peaks could be associated with anhydride formation and that the second could be attributed to the melting and decomposition of the mixture. The melting and decomposition of the BTCA/MSM mixture that begins around 175°C could explain the shift seen in the FT-IR spectrum for the mixture heated to 180°C.

Infra-red and thermal analysis of this BTCA/MSM mixture suggests that this acid/catalyst system would be a good easy-care finish. Acid anhydride formation, thought to be the rate-determining intermediate step in the esterification reaction for PCA and cotton cellulose, is clearly evident in the FT-IR spectrum of the heated mixture at temperatures as low as 130°C.

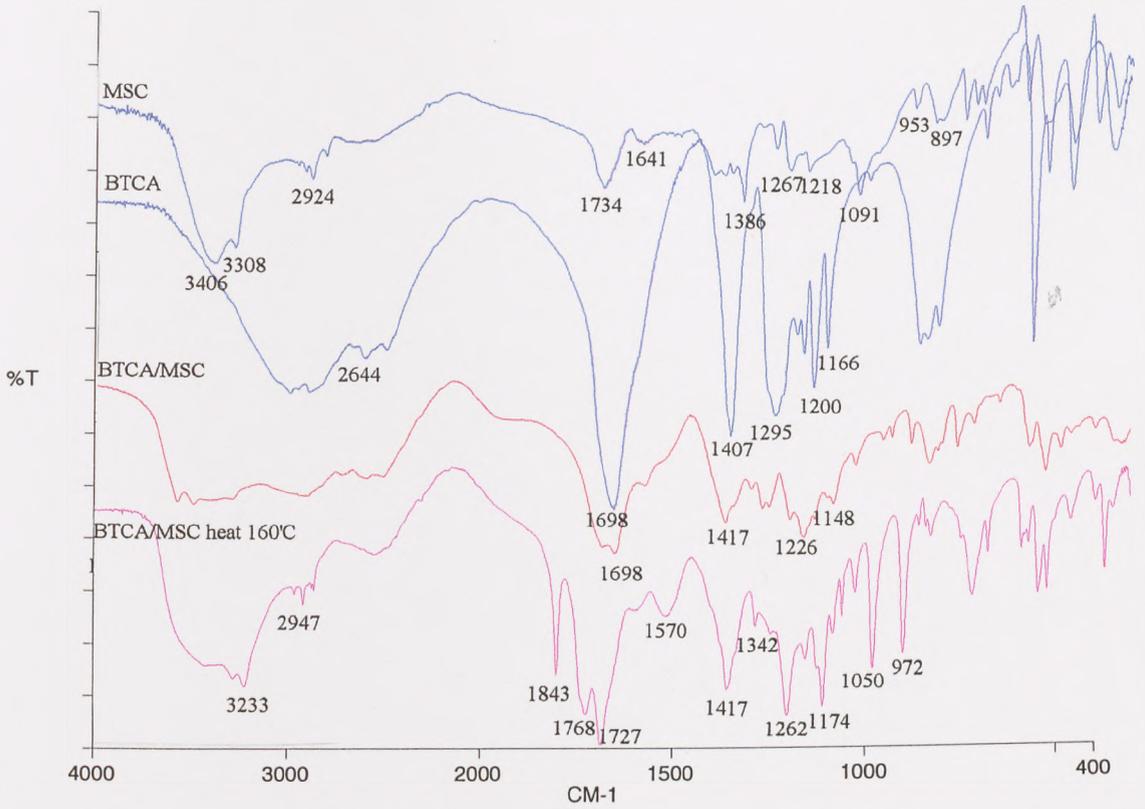


Figure 4.26 FT-IR spectra for MSC, BTCA, and a 1:1 molar ratio mixture of BTCA and MSC.

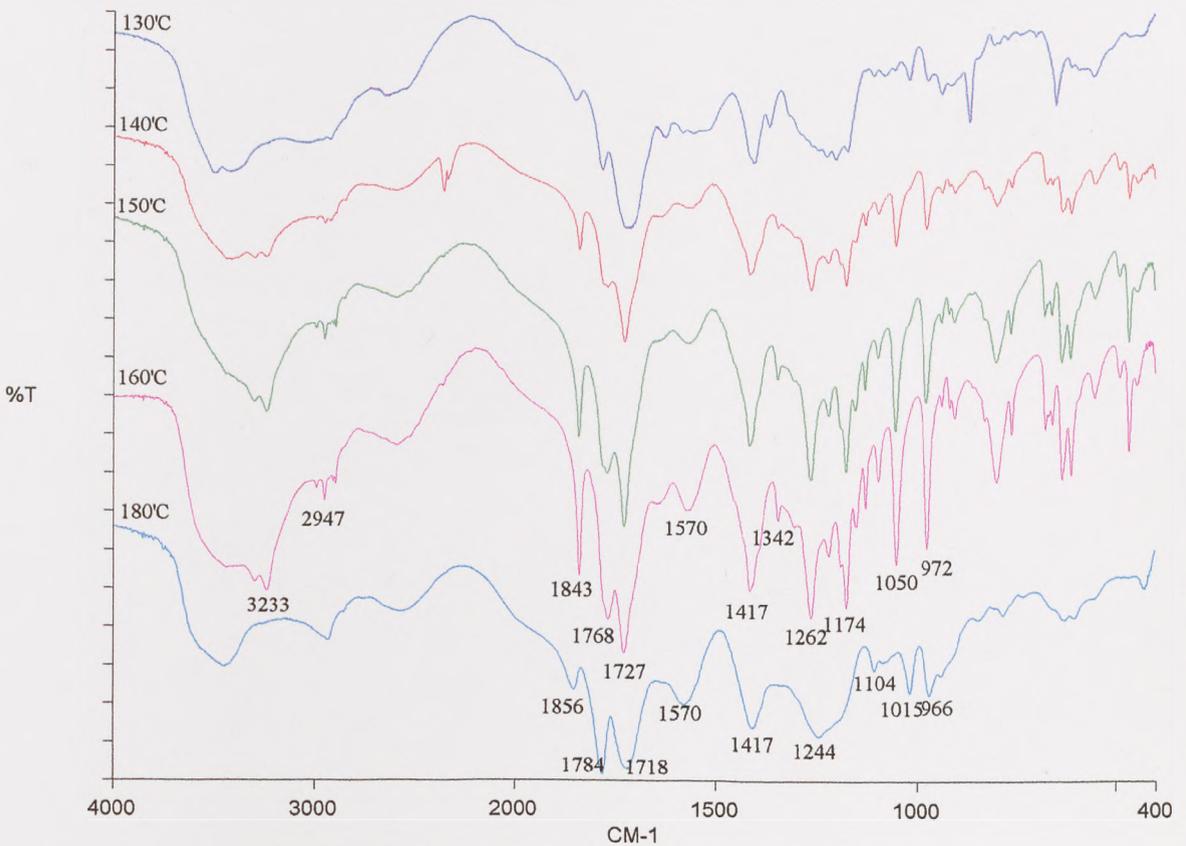


Figure 4.27 FT-IR spectra for a 1:1 molar ratio mixture of BTCA and MSC heated to different temperatures.

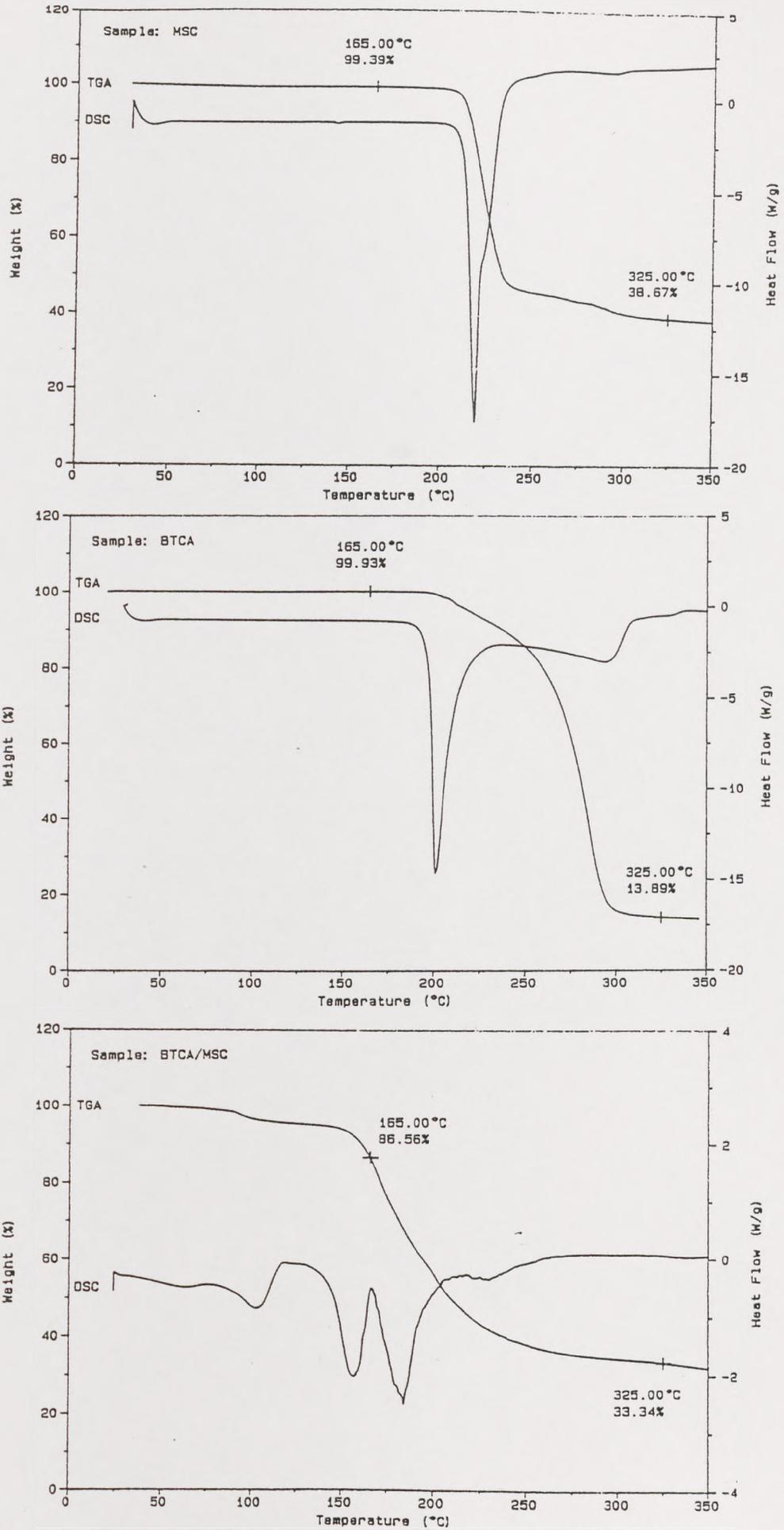


Figure 4. 28 TGA and DSC analysis of MSC, BTCA, and a 1:1 molar ratio mixture of BTCA and MSC.

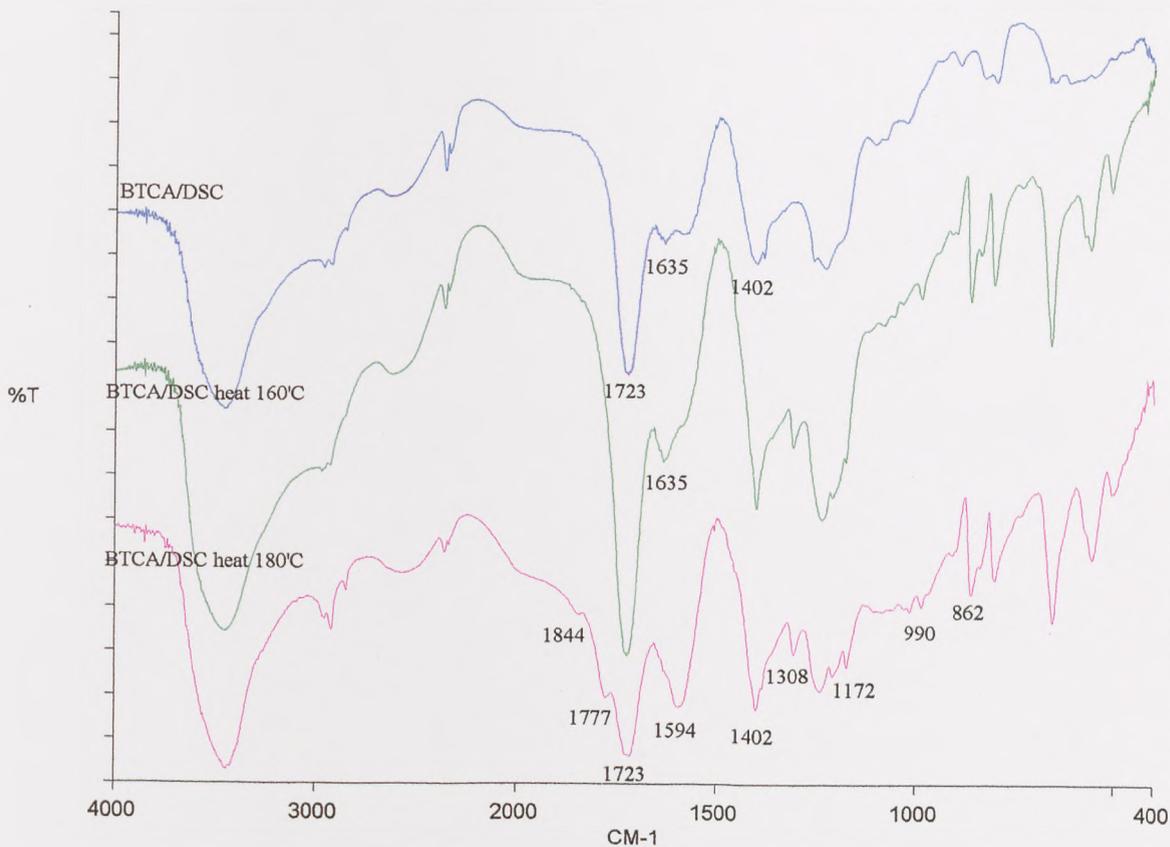


Figure 4.29 FT-IR spectra for and a 1:1 molar ratio mixture of BTCA and DSC.

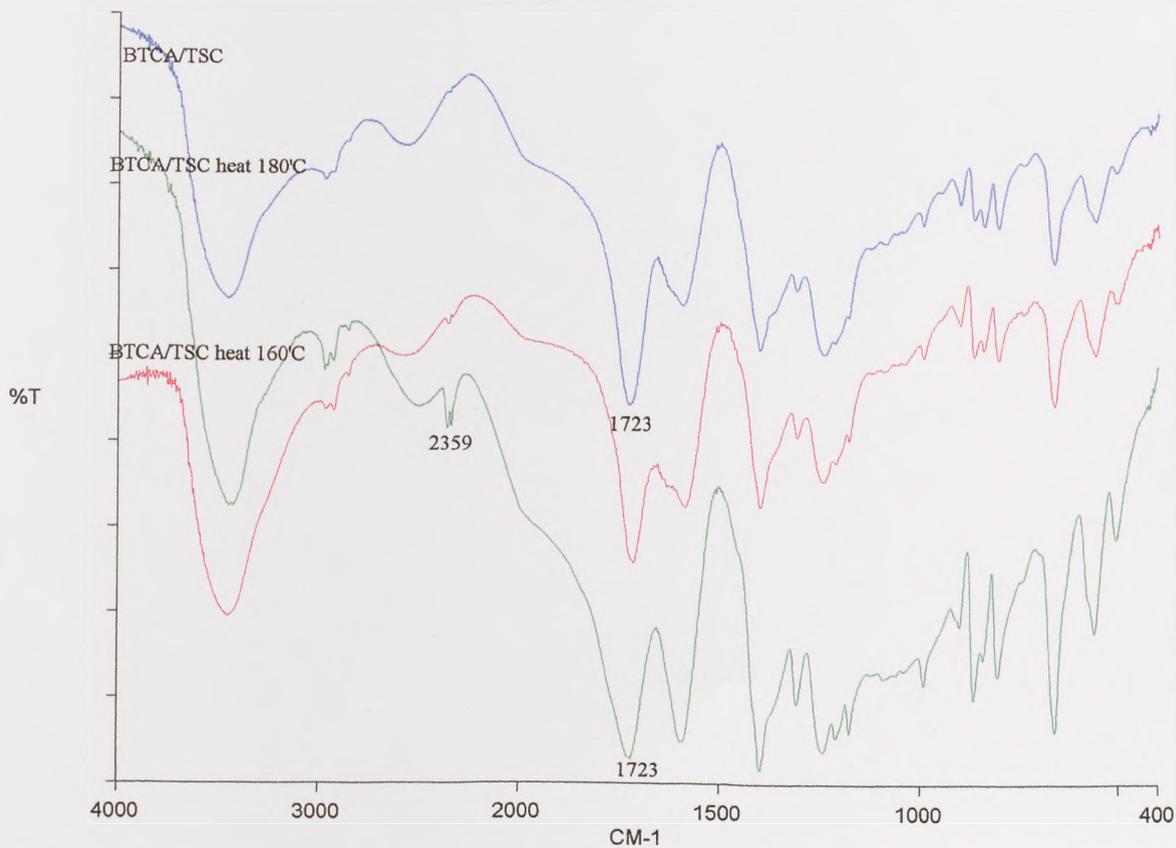


Figure 4.30 FT-IR spectra for and a 1:1 molar ratio mixture of BTCA and TSC.

Figure 4.29 and Figure 4.30 display the infra-red analysis data for mixtures of BTCA with disodium citrate (DSC) and trisodium citrate (TSC), respectively. From these spectra it can be seen that neither of these acids appear to catalyse the formation of the BTCA anhydride at as low a temperature as seen with MSC. The BTCA/DSC mixture depicted in Figure 4.29 shows no sign of anhydride formation at 160°C, however the two anhydride carbonyl bands are shown when the mixture is heated to 180°C. The spectrum for the BTCA/TSC mixture displayed in Figure 4.30 does not show any evidence of anhydride formation at temperatures usually employed in fabric finishing.

Figure 4.31 and Figure 4.32 display the infra-red spectrum for mixtures of BTCA with monosodium tartrate (MST) and disodium tartrate (DST). From these spectra it can be identified that both these catalysts are capable of reducing the temperature for anhydride formation of BTCA. Figure 4.31 shows the spectra for a 1:1 molar ratio mixture of BTCA and MST. These spectra are similar to those displayed in Figure 4.26 and Figure 4.27 for BTCA/MSM system. The spectra for the heated BTCA/MST mixture clearly show the two C=O absorption bands characteristic of an acid anhydride at 1777cm⁻¹ and 1845cm⁻¹ in the spectrum for the mixture heated to 150°C, and are just visible in the spectrum for the mixture heated to 140°C. New bands appear in the heated mixture at 1263cm⁻¹ and 1051cm⁻¹ that may correspond to the C-O-C stretching vibrations typical of a cyclic and open chain anhydride, respectively.

In the spectra displayed in Figure 4.32 new bands that are equivalent to those seen for BTCA/MST heated mixture can be identified for BTCA/DST mixture when heated to 160°C. Anhydride formation can be seen to be starting at 150°C. From these infra-red spectra it can be inferred that the catalyst MST is capable of lowering the temperature of BTCA anhydride formation to a lower temperature than the catalyst DST. The same trend was identified when using the sodium citrates as catalysts; the monosodium salt appeared to be a more effective catalyst than the disodium salt that in turn was a more effective catalyst than the trisodium salt.

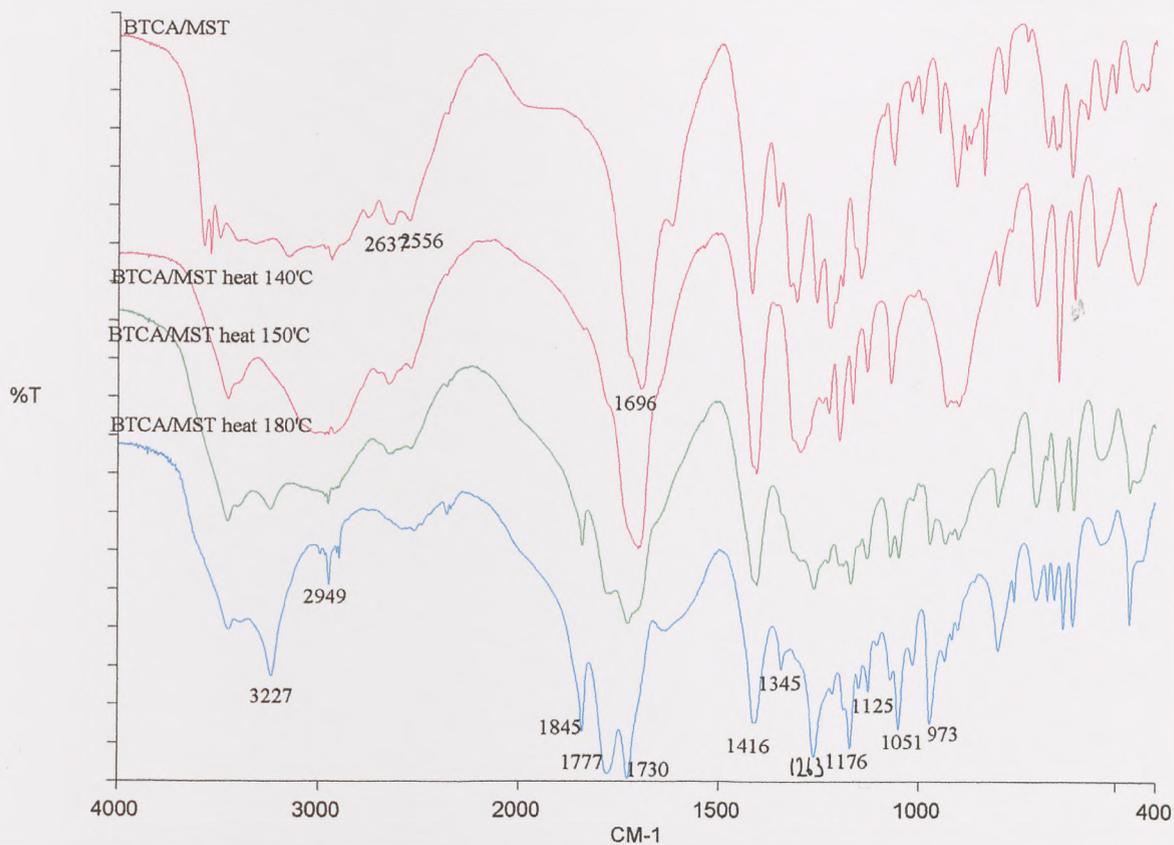


Figure 4.31 FT-IR spectra for and a 1:1 molar ratio mixture of BTCA and MST.

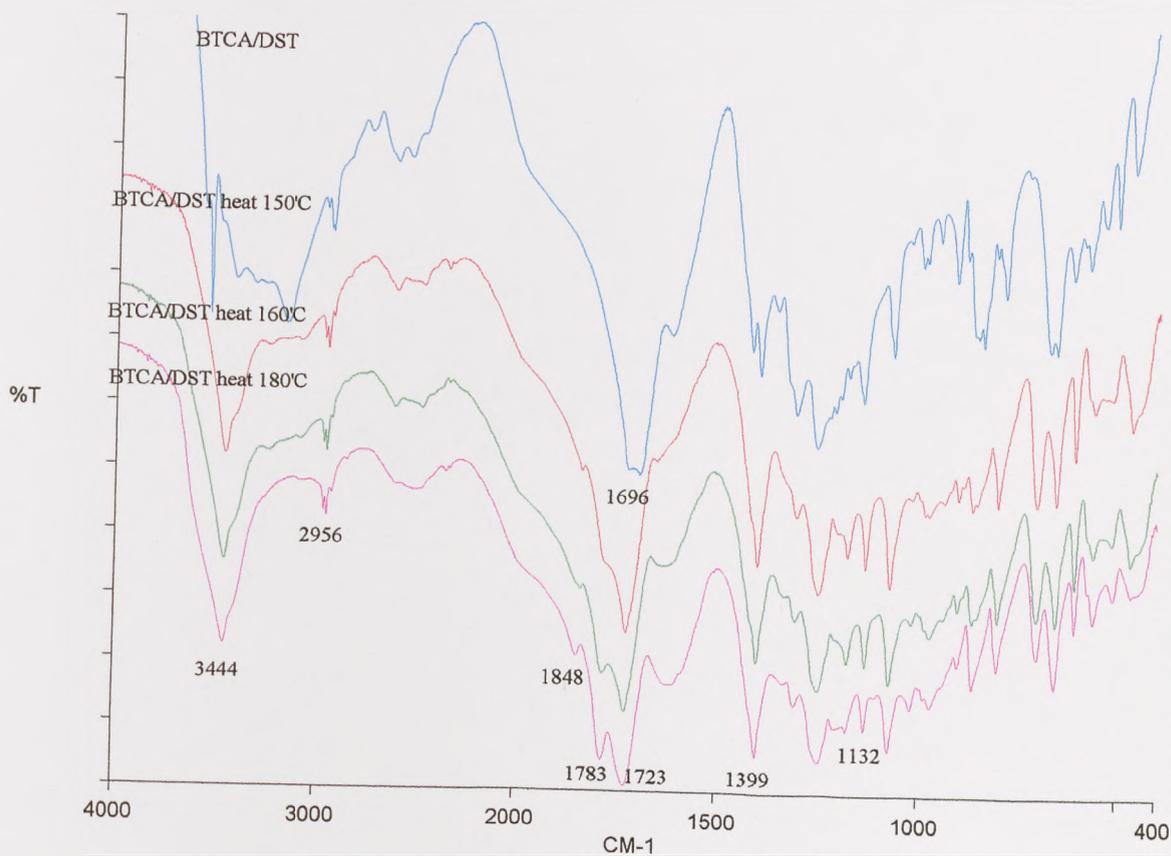


Figure 4.32 FT-IR spectra for and a 1:1 molar ratio mixture of BTCA and DST.

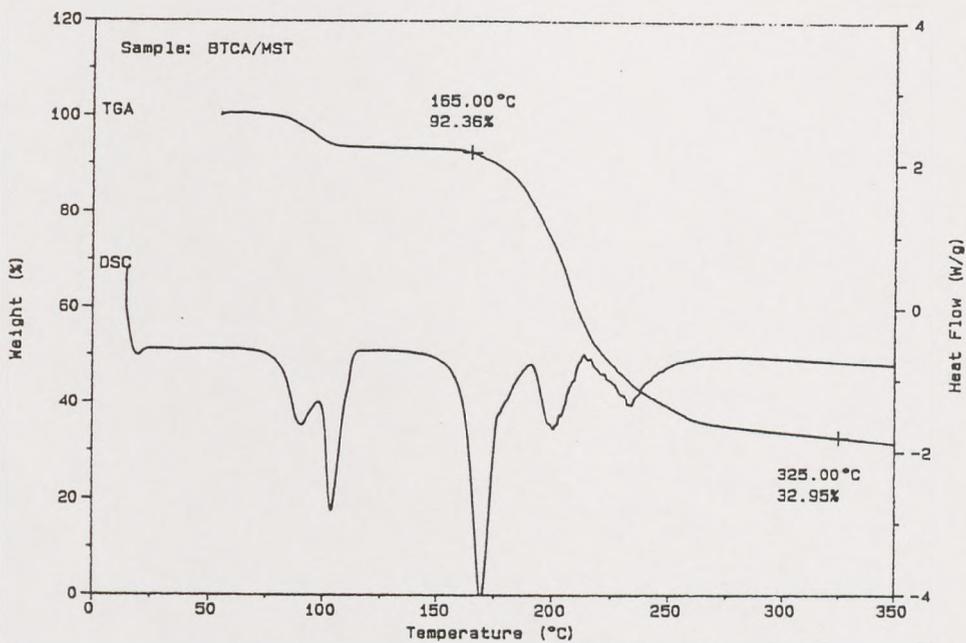


Figure 4.33 TGA and DSC analysis of a 1:1 molar ratio mixture of BTCA and MST.

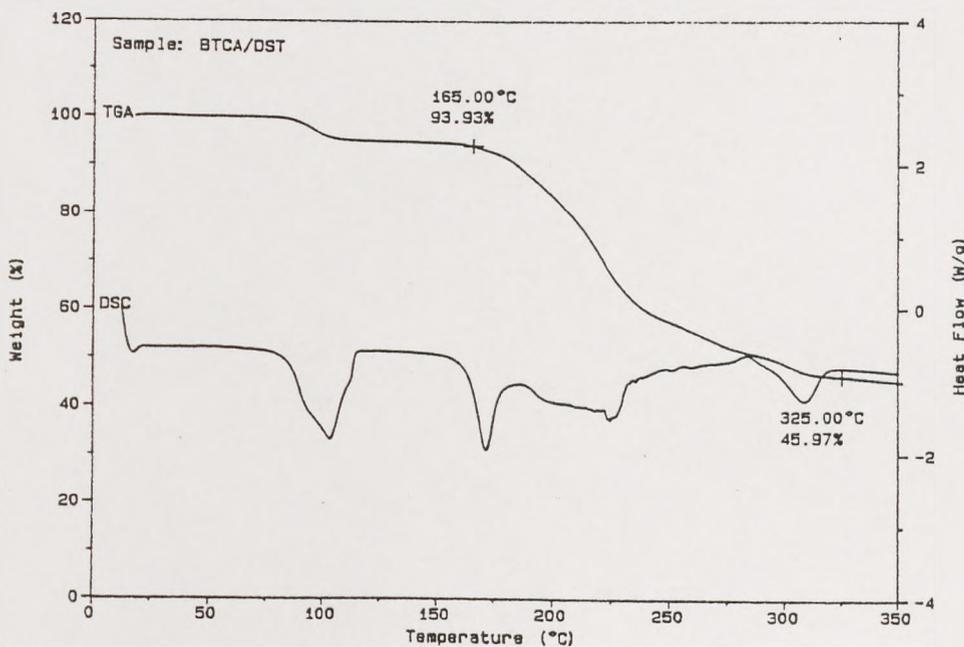


Figure 4.34 TGA and DSC analysis of a 1:1 molar ratio mixture of BTCA and DST.

Thermoanalytical data for BTCA/MST and BTCA/DST systems are pictured in Figure 4. 33 and Figure 4. 34. Both TGA thermograms show a stepwise degradation with a small initial weight loss occurring just above 100°C. The initial weight loss is accompanied by an endothermic peak shown in the DSC thermogram that could correspond with the loss of water and the formation of BTCA anhydride. Further degradation of the acid/catalyst systems occurs near 180°C. This stepwise degradation was also identified in the BTCA/SHP system.

Infra-red and thermoanalytical results suggest that either MST or DST would be good catalysts for reducing the temperature of acid anhydride formation in PCA easy-care finishing systems. FT-IR analysis indicated that anhydride formation begins at temperatures below 150°C for both BTCA/MST and BTCA/DST systems.

Figure 4. 35 and Figure 4. 36 display the infra-red spectra for 1:1 molar ratio mixtures of BTCA and monosodium maleate (MSM), and BTCA and disodium maleate (DSM), respectively. In the spectra pictured in Figure 4. 35 for BTCA/MSM system the formation of an acid anhydride can clearly be seen in the spectrum for the mixture heated to 130°C. The two acid anhydride carbonyl peaks are visible in the spectrum for the heated BTCA/MSM mixture at 1781cm⁻¹ and 1844cm⁻¹ and additional peaks at 1263cm⁻¹ and 1050cm⁻¹ that may correspond to C-O-C vibrations can also be seen. In Figure 4. 36 the spectrum for the BTCA/DSM system heated to 180°C shows slight carbonyl peaks at 1774cm⁻¹ and 1844cm⁻¹ corresponding to the formation of an acid anhydride. Again these spectra suggest that the monosodium salt of this dicarboxylic acid is a more efficient catalyst for PCA easy-care finishing systems than the corresponding disodium salt

Thermoanalytical analysis of BTCA/MSM and BTCA/DSM finishing systems depicted in Figure 4. 37 and Figure 4. 38, respectively indicate that the BTCA/MSM system would be unsuitable as an easy-care finishing system because the system begins to degrade at a very low temperature. At 165°C, the optimum temperature for silk fabric finishing, there is only 77% of the BTCA/MSM system available for reaction. In comparison the BTCA/DSM system is stable at temperatures usually employed in silk fabric finishing but this acid/catalyst system is unable to form an anhydride, thought to be a necessary intermediate step in PCA easy-care finishing, in this temperature range.

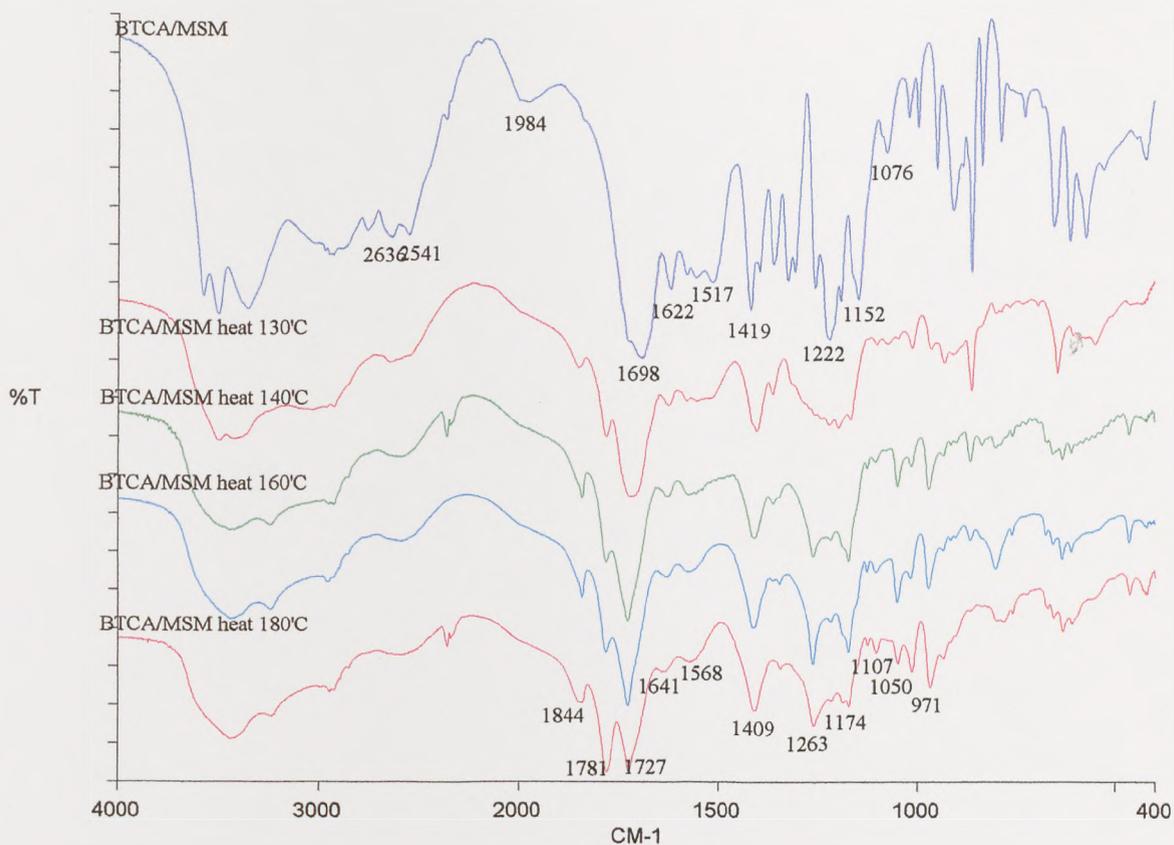


Figure 4.35 FT-IR spectra for and a 1:1 molar ratio mixture of BTCA and MSM.

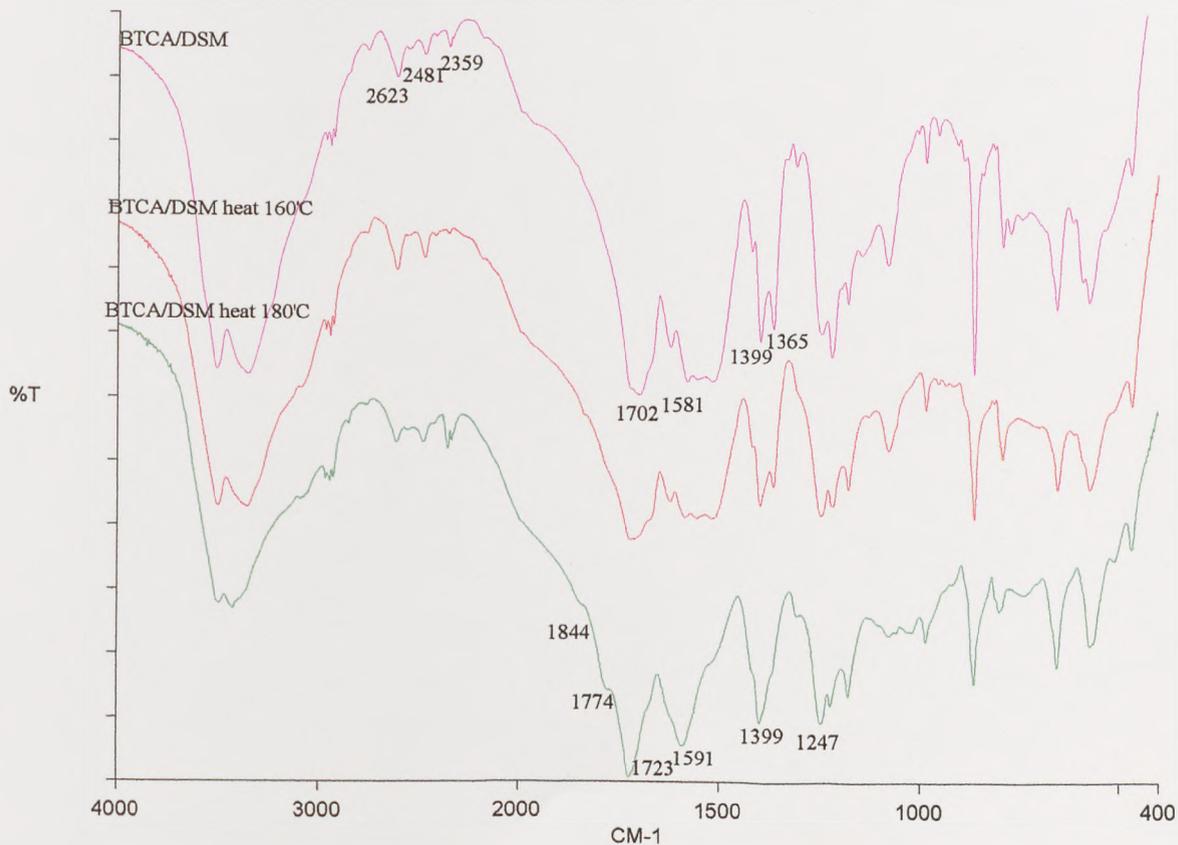


Figure 4.36 FT-IR spectra for and a 1:1 molar ratio mixture of BTCA and DSM.

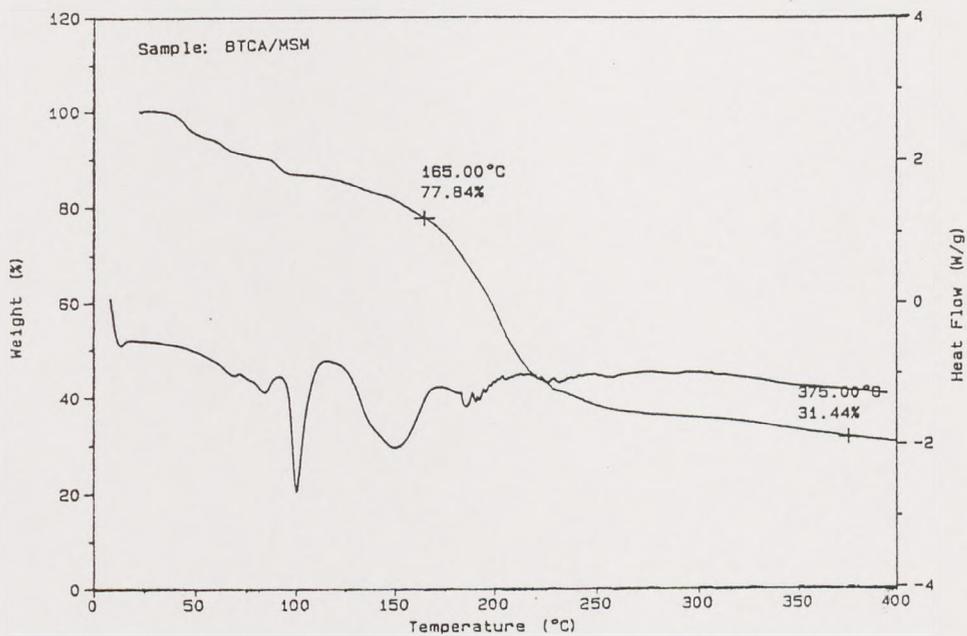


Figure 4.37 TGA and DSC analysis of a 1:1 molar ratio mixture of BTCA and MSM.

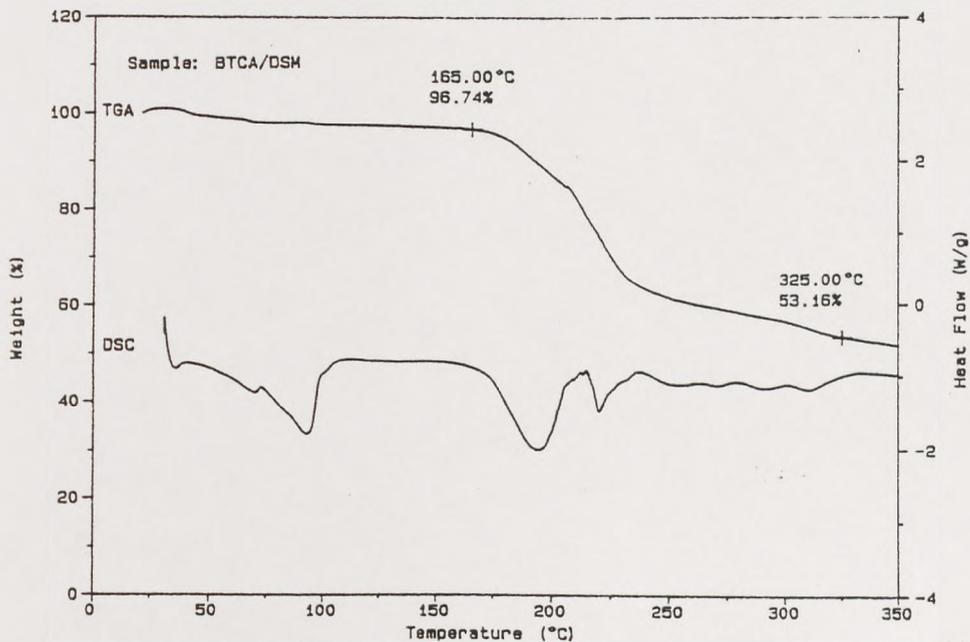


Figure 4.38 TGA and DSC analysis of a 1:1 molar ratio mixture of BTCA and DSM.

4.1.3.6 Comparison of Results.

PCA/ Catalyst	Colour of mixture heated to 180°C for 2min.	% Residue after heating the mixture to		Position of C=O peaks in FT-IR spectra of mixtures heated to 180°C/2min		Possible C-O-C peaks in FT-IR spectra of mixtures heated to 180°C/2min		Temperature at which C=O bands first appear in FT-IR spectra
		160°C/ 2min	180°C/ 2min					
BTCA/SHP	Cream char	94.88	94.49	1783	1841	1262	1050	140°C
PMA/SHP	Bright yellow char	98.48	92.93	1772	1857	1237	-	160°C
CA/SHP	Dark orange char	91.99	52.39	1753	1823	-	1047	180°C
MA/SHP	Yellow char	94.48	83.91	1787	1846	1211	1050	160°C
MLA/SHP	Cream sticky resin	95.75	87.72	1787	-	1203	1039	180°C
SA/SHP	White powder	92.91	66.21	1771	1865	-	1046	180°C
IA/SHP	Orange/brown resin	73.42	62.16	1779	1831	1211	1046	160°C
GA/SHP	Melted pale brown resin	98.02	89.41	-	-	-	-	-
PA/SHP	Pale green char	81.19	74.32	-	-	-	-	-
SA/CA/ SHP	Dark yellow sticky resin	65.61	40.61	1776	1830	1262	1045	160°C
SA/MLA/ SHP	Clear sticky resin	82.80	61.78	1779	1839	1264	1063	160°C

Table 4. 5 Summary of the infra-red and thermal analysis of a 1:1 molar ratio mixture of different PCAs with SHP.

PCA/ Catalyst	Colour of mixture heated to 180°C for 2min.	% Residue after heating the mixture to		Position of C=O peaks in FT-IR spectra of mixtures heated to 180°C/2min		Possible C-O-C peaks in FT-IR spectra of mixtures heated to 180°C/2min		Temperature at which C=O bands first appear in FT-IR spectra
		160°C/ 2min	180°C/ 2min					
BTCA/SHP	Cream	94.88	94.49	1783	1841	1262	1050	140°C
BTCA/MSD	Dark yellow	79.04	58.92	1768	1843	1262	1050	130°C
BTCA/DSC	Dark yellow	81.12	69.00	1777	1844	-	-	180°C
BTCA/TSC	Dark yellow	88.51	83.17	-	-	-	-	-
BTCA/MSM	Dark yellow	77.84	70.46	1781	1844	1263	1050	130°C
BTCA/DSM	Yellow	96.74	93.21	1774	1844	-	-	180°C
BTCA/MST	Pale yellow	92.36	87.39	1777	1845	1263	1051	140°C
BTCA/DST	Mustard	93.93	90.08	1783	1848	-	-	150°C

Table 4. 6 Summary of the infra-red and thermal analysis of a 1:1 molar ratio mixture of BTCA with different catalysts.

Table 4. 5 displays a summary of the infra-red and thermoanalytical results for different 1:1 molar ratio mixtures of a variety of PCA and SHP systems. The results include the colour of the mixture after being heated to 180°C and isothermed for 2min. The colour of the char is important; a dark coloured char has been observed in this work that is indicative of a finish that will discolour the fabric during the curing process. Several acid/catalyst systems are thought to be unsuitable as easy-care finishing agents after analysis of the char colour; these are CA/SHP, IA/SHP and GA/SHP. Acid/catalyst systems that produced yellow chars on heating, PMA/SHP, MA/SHP and SA/CA/SHP systems may also discolour the fabric during the curing process.

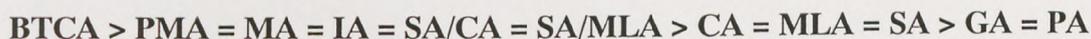
The percent residue after heating the mixtures to either 160°C or 180°C and isotherming for 2min were taken from TGA thermograms. At 160°C only the IA/SHP system had less than 80% of the initial weight of the mixture available to react. However at 180°C several of the acid/catalyst systems had started to degrade, e.g. CA/SHP, SA/SHP, PA/SHP, SA/CA/SHP, and SA/MLA/SHP. The degradation of the acid/catalyst system during heating is indicative of a system that will be less efficient as an easy-care finish because there is then less of the mixture available to react with the silk fibroin. At 165°C the optimum temperature for curing silk fabric finishes, it is proposed that only the IA/SHP system is unsuitable.

Table 4. 5 compares the position of the acid anhydride carbonyl peaks seen in the FT-IR spectra of the acid/catalyst mixtures heated to 180°C. The spectrum of the GA/SHP and the PA/SHP systems did not show any sign of these peaks and it is therefore concluded that these acid/catalyst systems are unable to form acid anhydrides at this temperature.

The position of new peaks in the infra-red spectra that might corresponding to C-O-C vibrations are listed in Table 4. 5. The BTCA/SHP system showed new additional peaks at 1262cm⁻¹ and 1050cm⁻¹ that may correspond to the C-O-C stretching of cyclic and straight chain anhydrides, respectively. The exact nature of these peaks is uncertain due to the large amount of infra-red absorptions at this end of the spectrum. Other acid/catalyst systems also display new bands in this region when heated to 180°C. The peak at 1262cm⁻¹ appears in the SA/hydroxy acid/SHP systems and a new peak is evident in the spectrum for PMA/SHP, MA/SHP, MLA/SHP, and IA/SHP at a lower frequency.

The band thought to correspond to the C-O-C stretching of a straight chain anhydride absorbs near 1050cm^{-1} . This peak was seen in all the mixtures that displayed acid anhydride carbonyl peaks with the exception of the PMA/SHP system. It would appear that in general acid/catalyst mixtures that are capable of forming acid anhydrides when heated to 180°C , assumed on the basis of the acid anhydride carbonyl peaks seen in the spectrum, form a mixed anhydride. Only the PMA/SHP system showed no sign of a new peak in the $1175\text{-}1045\text{cm}^{-1}$ range typical of open chain anhydride formation. This would suggest that this acid/catalyst system form only cyclic anhydrides when heated to 180°C . In the spectrum for the acid/catalyst mixtures that showed the first sign of acid anhydride carbonyl peaks at 180°C , there was little evidence of a peak corresponding to the C-O-C stretching typical of a cyclic anhydride. This may be because the open chain anhydride is an intermediate step in the formation of a cyclic anhydride, see the mechanism proposed by Brown, Figure 4.5.

From the summary of the different acid/catalyst systems displayed in Table 4.5 it can be concluded that when catalysed by SHP the order of ease with which a PCA is capable of forming an anhydride is as follows:



CA, IA, and GA form dark coloured chars on heating to 180°C and are therefore not suitable as easy-care finishing agents and IA was also found to degrade at too low a temperature to be available to act as an easy-care finishing agent.

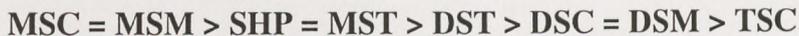
The acids that were thought to warrant further investigation as proposed easy-care finishing agents were BTCA, PMA, MA, SA/CA and SA/MLA. In section 4.2.1 these acids, in conjunction with SHP, were tested as easy-care finishes for silk fabrics.

Table 4.6 displays a summary of the infra-red and thermal analysis of 1:1 molar ratio mixtures of BTCA with a variety of different catalysts. A number of sodium salts of carboxylic acids were tested as alternative catalysts to SHP. All these catalysts when heated with BTCA to 180°C formed yellow chars; these may discolour the fabric during curing. The percent residues of the mixtures remaining after being heated to 160°C and isothermed for 2min are generally lower than that seen for SHP, but in all cases more

than 75% of the initial mixture remains.

Analysis of the infra-red data for BTCA/sodium salt of carboxylic acid systems show that the monosodium salt of the carboxylic acids tested are more efficient catalysts than either the di- or trisodium salts. BTCA anhydride forms more readily and at a lower temperature when the monosodium salt of the carboxylic acid is used as catalyst. Only in the spectra for BTCA/monosodium salt catalysts were infra-red absorbance peaks identified that may correspond to C-O-C stretching vibrations.

From the summary of the different acid/catalyst systems displayed in Table 4. 6 it can be concluded that the order of catalyst efficiency calculated by ease with which BTCA is capable of forming an anhydride, is as follows:



The monosodium salts were thought to warrant further investigation as an alternative catalyst to SHP for PCA easy-care finishing. In section 4.2.2 these catalysts, in conjunction with BTCA, were tested as easy-care finishes for silk fabrics.

4.2 TREATMENT OF SILK FABRIC WITH POLYCARBOXYLIC ACIDS.

The aim of this experiment was to investigate the suitability of a variety of different polycarboxylic acid/catalyst systems for improving the easy-care characteristics of silk fabric. In section 4.1 a new system was developed to study the suitability of a number of different acid/catalyst systems as easy-care finishing agents. The PCA/catalyst systems were analysed using thermoanalytical and infra-red techniques that mimicked the conditions used during fabric curing to analyse the chemical reaction occurring between the acid and catalyst. The acid/catalyst systems that were capable of forming an acid anhydride that did not degrade and did not form a dark coloured char at a temperature usually employed in the finishing of silk fabrics were thought to warrant further investigation.

4.2.1 Treatment Of Silk Fabric With PCAs And SHP Catalyst.

Infra-red and thermoanalytical analysis of a selection of PCAs with SHP catalyst are

summarised in Table 4. 5. From these results it was concluded that the ease with which a PCA is capable of forming an anhydride in the presence of SHP is as follows:



CA, IA, and GA were thought to be unsuitable as easy-care finishing agents because they formed dark coloured chars at temperatures usually employed in silk finishing and could therefore cause fabric discoloration on curing. IA was also thought to be unsuitable because it degraded at too low a temperature to be available to act as an easy-care finishing agent.

In this section BTCA, PMA, MA, SA/CA, and SA/MLA were tested as easy-care finishing agents in conjunction with SHP catalyst.

4.2.1.1 Experimental procedure.

Plain woven silk Habutai heavy, roll 4, see section 2.1.1, was treated with different quantities of PCA and SHP, see Table 4. 7. These acid/catalyst systems were applied to silk fabric via a pad-batch-cure method, as described in section 2.1. This technique was found to give superior results compared with other methods tested in section 3.3.4. Each acid/catalyst system was investigated with regard to different percent chemical add-ons, different acid:catalyst molar ratios, and a variety of pad bath pH values and curing conditions, see Table 4. 7.

The treated samples were conditioned for 48h and tested with respect to percent chemical add-on, regain, infra-red ester frequency peak height, fabric dry and wet crease recovery angles, fabric warp and weft bending length, fabric retention of tensile strength and fabric retention of elongation at break. Sample testing was carried out according to the test methods described in section 2.2 and comparisons of the results were made with an untreated control.

The BTCA pad baths required a small amount of heat to dissolve the BTCA. Once the BTCA had dissolved it remained in solution for several hours; only the 8%w/w BTCA pad bath had a tendency to recrystallise. This was also true for MA pad baths, these were clear in colour. PMA pad baths formed a dusky pink colour when dissolved; this

acid only dissolved in a warm aqueous solution and when this solution cools the PMA recrystallises. This caused problems during padding. Not only does the PMA need to be padded warm but on contact with the cold fabric it again falls out of solution and fine acid dust particles are produced in the air on drying and curing. For this reason this acid was felt to be a health risk and therefore not suitable as an easy-care finishing agent. SA and CA dissolve to produce clear solutions and MLA solutions were pale yellow.

4.2.1.2 Results and Discussion.

The test results are tabulated in Appendix 2, Table A2.1 to Table A2.4 and the results appear in graphical form in the text, Figure 4. 39 to Figure 4. 70.

4.2.1.2.1 BTCA/SHP finishing system.

Figure 4. 39 and Figure 4. 40 graphically display the results of silk fabric treated with different quantities of BTCA and a 1:1 molar ratio of SHP. As the quantity of BTCA in the pad bath is increased the percent BTCA chemical add-on increases and the quantity of ester bonds formed in the silk fabric during curing also increases.

The increase in ester bond formation is measured using FT-IR analysis. The ATR spectroscopic technique was used to analyse the treated silk fabrics, according to the method described in section 2.2.3.1.1. The silk fabrics were measured after rinsing in running water and conditioning and after treatment for 2min in 0.1M NaOH solution. The infra-red carbonyl absorption bands associated with esters and polycarboxylic acids overlap in the infra-red spectra. The silk fabrics were treated with a 0.1M sodium hydroxide solution to convert any unreacted carboxylic acid side groups to their sodium salt. Conversion of the unreacted carboxylic acid groups to their sodium salt shifts the carbonyl absorption band to a lower position and results in a decrease in the carbonyl absorption band, around 1735cm^{-1} , associated with carboxylic acids and esters when compared with the spectrum of the rinsed samples.

Care must be taken when treating the silk fabrics with sodium hydroxide solution not to degrade the silk fabrics or to break the ester bonds. Prolonged exposure of silk fabrics to 0.1M NaOH solution could result in degradation of the silk fibroin and cleavage of the ester links. The high pH value of the 0.1M NaOH solution means that some degradation may have occurred, however the treatment time and conditions were

carefully controlled to minimise any variation in results as a consequence of this degradation.

% w/w PCA	PCA:SHP Molar Ratio	Pad Bath pH	Curing Conditions
2%, 4%, 6%, and 8% w/w BTCA	1:1		165°C for 1.5min
6% w/w BTCA	1:0.5, 1:0.75, 1:1 and 1:1.25		165°C for 1.5min
6% w/w BTCA	1:1	pH1.5, pH2.1, pH3.5 and pH5	165°C for 1.5min
6% w/w BTCA	1:1		120°C for 5min, 150°C for 2min and 165°C for 1.5min
2%, 4%, 6%, and 8% w/w PMA	1:1		165°C for 1.5min
6% w/w PMA	1:0.5, 1:0.75, 1:1 and 1:1.25		165°C for 1.5min
6% w/w PMA	1:1	pH1.5, pH2.5, pH3.5 and pH5	165°C for 1.5min
6% w/w PMA	1:1		120°C for 5min, 150°C for 2min and 165°C for 1.5min
2%, 4%, 6%, and 8% w/w MA	1:1		165°C for 1.5min
6% w/w MA	1:0.5, 1:0.75, 1:1 and 1:1.25		165°C for 1.5min
6% w/w MA	1:1	pH1.5, pH2.5, pH3.5 and pH5	165°C for 1.5min
6% w/w MA	1:1		120°C for 5min, 150°C for 2min and 165°C for 1.5min
1%SA:1.6%CA, 2%SA:3.2%CA, 3%SA:4.8%CA and 4%SA:6.4%CA	1:1		165°C for 1.5min
3% w/w SA: 4.8% w/w CA	1:0.5, 1:0.75, 1:1 and 1:1.25		165°C for 1.5min
3% w/w SA: 4.8% w/w CA	1:1	pH1.5, pH1.9, pH3 and pH5	165°C for 1.5min
3% w/w SA: 4.8% w/w CA	1:1		120°C for 5min, 150°C for 2min and 165°C for 1.5min
2%SA:3%MLA, 3%SA:4.5%MLA, 4%SA:6%MLA and 5%SA:7.5%MLA	1:1		165°C for 1.5min
4% w/w SA: 6% w/w MLA	1:0.5, 1:0.75, 1:1 and 1:1.25		165°C for 1.5min
4% w/w SA: 6% w/w MLA	1:1	pH1.5, pH2.05, pH3 and pH5	165°C for 1.5min
4% w/w SA: 6% w/w MLA	1:1		120°C for 5min, 150°C for 2min and 165°C for 1.5min

Table 4.7 Summary of the conditions used for the treatment of silk fabric with PCA and SHP catalyst.

The infra-red spectra of the treated silk fabrics were normalised at 1228cm^{-1} and subtracted from a normalised, untreated control. The subtracted spectra were assumed to correspond to alterations in the silk fabrics as a consequence of the different finishing treatments. The peak height at around 1735cm^{-1} was measured for the subtracted spectrum from printouts of spectra of the same scale. The measurements of the ester peak heights for the spectra of silk fabrics treated under different finishing conditions were used as a semi-quantitative analysis tool for analysing the quantity of finish that had reacted with the silk fabric during curing.

In Figure 4. 40 the FT-IR ester peak height increases linearly with an increase in BTCA chemical add-on for the fabric rinsed after finishing and for the fabric treated with 0.1M NaOH. As the quantity of BTCA is increased in the pad bath, the greater the percent chemical add-on and the greater the height of the ester bond frequency band in the infra-red spectrum of the treated sample. It therefore follows that there was an increase in the quantity of ester linkages with the silk fibres with an increase in chemical add-on.

From Figure 4. 39 and Figure 4. 40 it can be seen that as the BTCA percent chemical add-on increases there is:

- An increase in chemical reaction, shown by an increase in FT-IR ester bond peak height.
- A slight increase in both fabric warp and weft bending length above 4% w/w BTCA chemical add-on. The increase in fabric bending length is indicative of an increase in fabric stiffness.
- A negligible change in fabric strength, shown by the percent retention maximum load at break that shows an initial slight increase followed by a slight decrease.
- A decrease in percent retention elongation at break.
- An increase in wet and dry crease recovery angle, both initial elastic recovery and recovery from creasing after five minutes. This increase in crease recovery angle appears to meet a maximum at around 7% w/w BTCA chemical add-on.

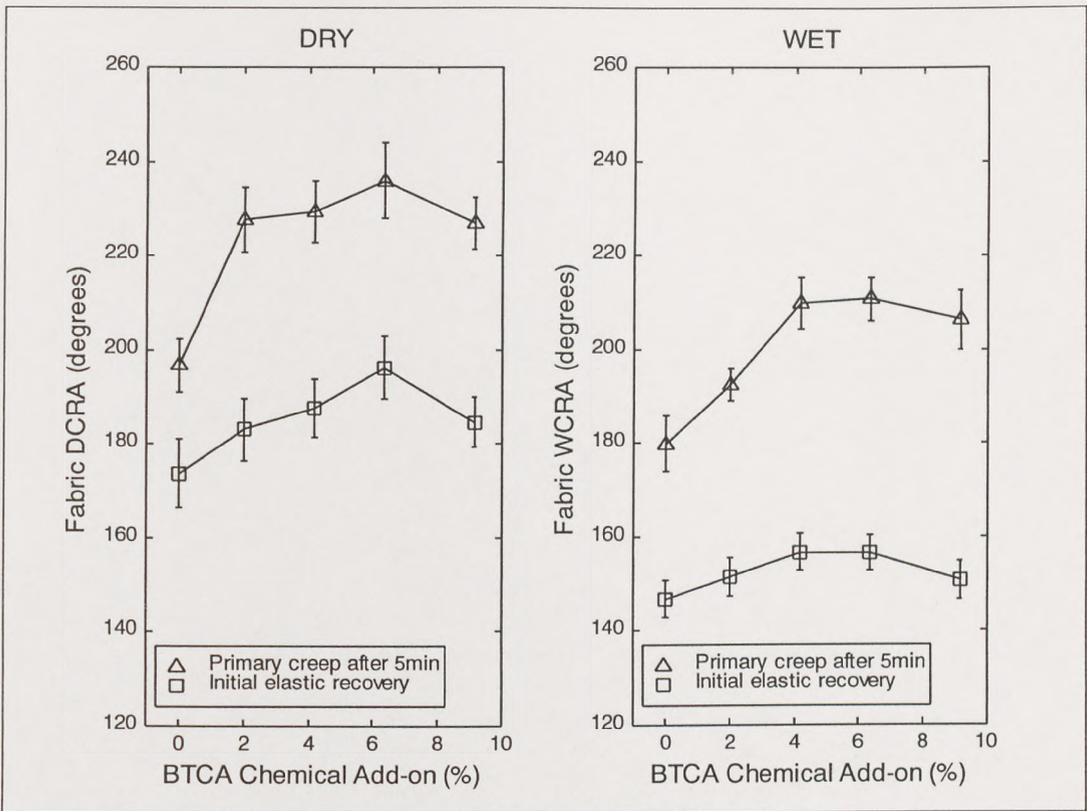


Figure 4.39 Fabric CRAs of silk fabric treated with different quantities of BTCA and a 1:1 molar ratio of SHP.

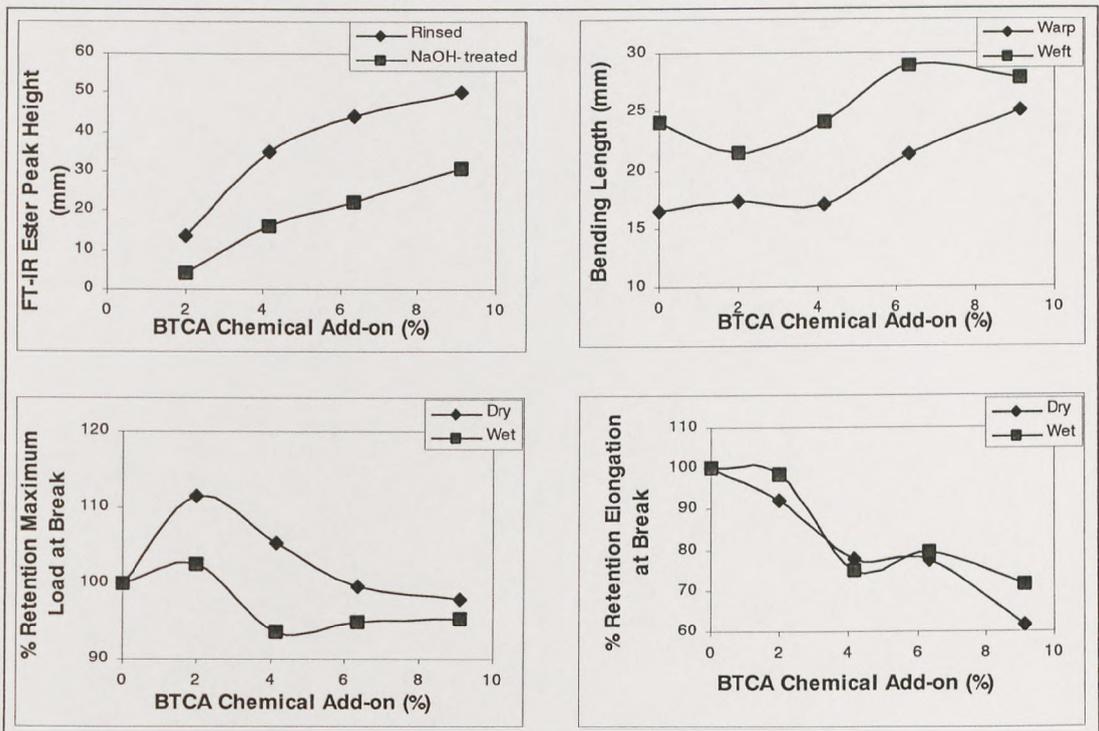


Figure 4.40 Graphical representation of the properties of silk fabric treated with different quantities of BTCA and a 1:1 molar ratio of SHP. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

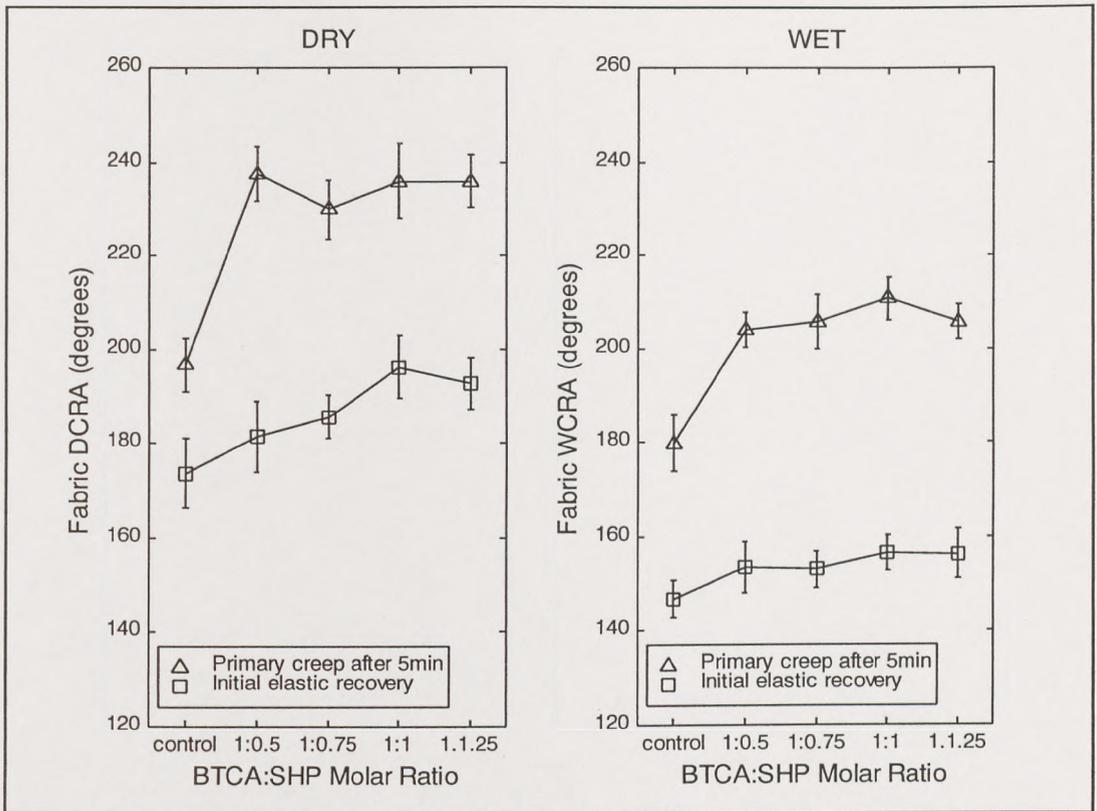


Figure 4.41 Fabric CRAs of silk fabric treated with 6% w/w BTCA and varying molar ratios of SHP.

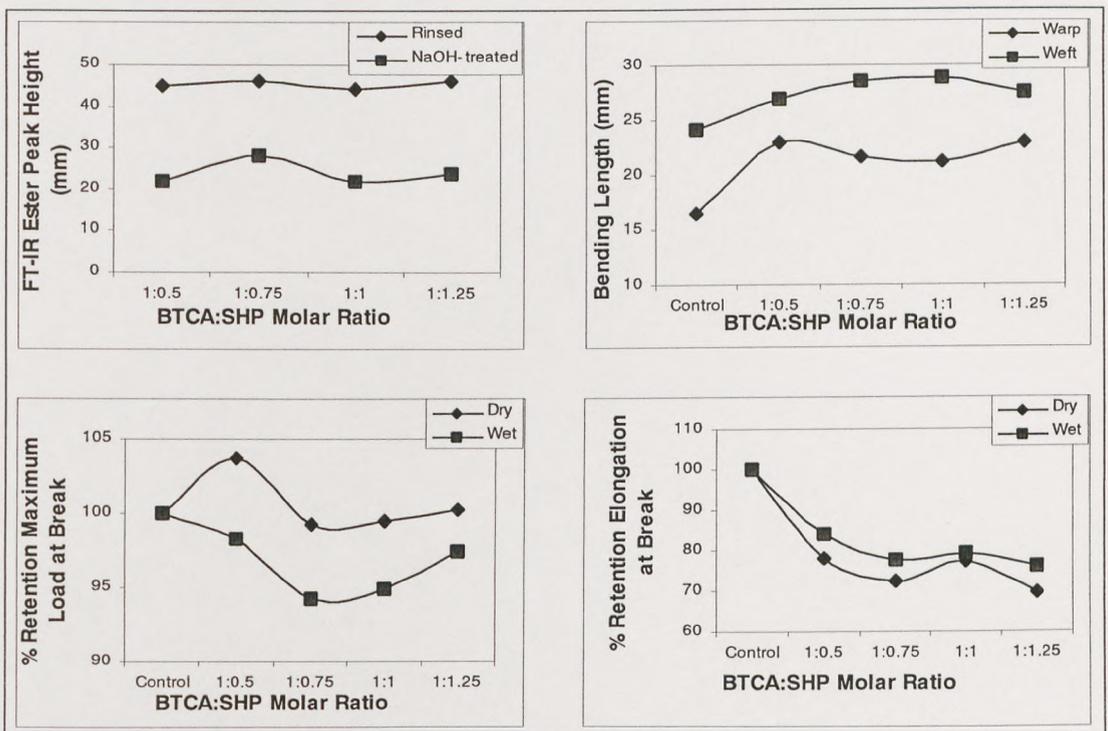


Figure 4.42 Graphical representation of the properties of silk fabric treated with 6% w/w BTCA and varying molar ratios of SHP. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

Analysis of these results suggest that the optimum percent chemical add-on of BTCA both in terms of an improvement in crease recovery angle and the other fabric properties tested is around 6-7% w/w BTCA chemical add-on.

The optimum treatment conditions for treating silk fabric with BTCA were further investigated with respect to BTCA:SHP molar ratio, pad bath pH and fabric curing conditions. Figure 4. 41 and Figure 4. 42 graphically display the results with regards to treating silk fabric with BTCA and different molar ratios of SHP as catalyst. These results are tabulated in Appendix 2, Table A2.1. From this table it can be seen that as the BTCA:SHP molar ratio increases the percent chemical add-on also increases. However, the FT-IR ester peak height does not increase with an increase in SHP in the pad bath, as shown in Figure 4. 42. It therefore follows that there is not an increase in ester links within the treated silk samples when the BTCA:SHP molar ratio is increased in the pad bath above 1:0.5. From Figure 4. 41 and Figure 4. 42 it can be seen that as the BTCA:SHP molar ratio increases there is:

- An increase in both dry and wet crease recovery angle both with regards to initial elastic recovery and recovery from creasing after five minutes up to a BTCA:SHP molar ratio of 1:1. The improved crease recovery properties of the treated fabrics suggest that as the BTCA:SHP molar ratio is increased, to an optimum ratio at 1:1, there is an increased fabric stability to creasing that suggests that there may be an increase in the number of di-ester cross-links produced within the fabric.
- A slight increase in fabric warp and weft bending length and a decrease in tensile properties. The increased fabric stiffness, signified by an increase in bending length, and a reduction in tensile properties are typical characteristics found in fabrics that have been treated with a cross-linking agent (81).

Treatment of silk fabric with 6% w/w BTCA and a 1:1 molar ratio of BTCA:SHP was investigated at different pad bath pH. The pH of the pad bath was 2.1; this was made more acidic with the addition of 1M HCl solution and more alkaline with the addition of 1M NaOH solution. Figure 4. 43 and Figure 4. 44 graphically illustrate the alteration in fabric properties brought about by the treatment of silk fabric with BTCA and SHP at different pad bath pH values. The results show that as the pH value increases from 1.5 to 5

- There is a decrease in FT-IR ester peak height above a pH value of 2.1. This

suggests that a more alkaline pad solution limits the quantity of ester links formed during fabric curing. A more acidic pad solution had little effect on FT-IR ester peak height.

- From Appendix 2, Table A2.1 it can be seen that the highest percent chemical add-on was achieved without altering the pad bath pH. A slight reduction in BTCA percent chemical add-on can be seen for samples treated in a more acidic pad bath and a large reduction in BTCA percent chemical add-on can be seen for samples treated in a more alkaline pad solution.
- The fabric bending length both in warp and weft are basically unaffected by the pH of the pad solution.
- The tensile properties of the fabric show a slight increase in retention of elongation at break as the pH value increases. This increase could be caused by the higher pH value of the pad solution resulting in less acid degradation of the silk fibroin and the reduced percent chemical add-on of BTCA. The retention of maximum load at break is mostly unaffected by the change in pH of the pad solution.
- Altering the pH of the pad solution does not improve the dry fabric crease recovery angle. The wet crease recovery angle is improved by increasing the acidity of the pad bath; this may be as a result of increased fibre swelling in the more acidic conditions.

The results show that altering the pH of the pad solution either to make it more acid or more alkaline did not improve the easy-care properties of the silk fabrics treated with the BTCA/SHP system. The addition of either HCl or NaOH into the pad bath decreases the total reaction; these additives could react with either the PCA or the catalyst forming salts thus lessening the quantity of these chemicals available to take part in the cross-linking reaction. The optimum pad bath pH was found to be around pH2.1.

The curing conditions of silk fabric treated with 6% w/w BTCA and a 1:1 BTCA:SHP molar ratio were investigated. The results are displayed in Figure 4.45 and Figure 4.46. It can be seen that as the curing temperature is increased from 120°C to 150°C there is:

- An increase in percent chemical add-on, shown in Appendix 2, table A2.1.
- An increase in FT-IR ester peak height. As the curing temperature was increased there was an increase in the quantity of ester links formed within the fabric.

- This increase in chemical reaction is accompanied by an increase in fabric stiffness shown by an increase in fabric warp and weft bending lengths.
- A reduction in fabric tensile properties. As the quantity of ester links formed within the fabric increases there is a corresponding decrease in the tensile properties of the fabric.
- There is an increase in both dry and wet crease recovery angles, both initial elastic recovery and recovery from creasing after 5min.

As the curing temperature is increased the quantity of chemical reaction occurring during the curing process also increases. The optimum curing conditions for the treatment of silk fabric with BTCA/SHP system is 165°C for 1.5min. If the temperature is increased above 165°C it was found that the silk fabric began to visibly yellow. The T_g for silk fibroin is known to be around 175°C (41), and the observed yellowing of silk fabrics cured above 165°C was thought to be due to thermal degradation of the silk fibroin.

In conclusion the optimum treatment conditions for treating silk fabric with BTCA/SHP system were achieved with a 6% w/w solution of BTCA, a 1:1 molar ratio of BTCA:SHP, a pad bath pH of 2.1 and a curing temperature of 165°C for 1.5min. These treatment conditions were found to give an increase in dry crease recovery angle from 196.7° to 235.9° and an increase in wet crease recovery angle from 179.9° to 210.7°. These results are indicative of a fabric that has been cross-linked with a fibre inter-chain cross-linking agent; this is discussed in more detail in section 4.2.1.4 on the possible mechanisms for improving the easy-care properties of silk fabrics. The properties of silk fabric treated with BTCA/SHP system under these conditions are compared with the other PCA/SHP systems tested in section 4.2.1.3.

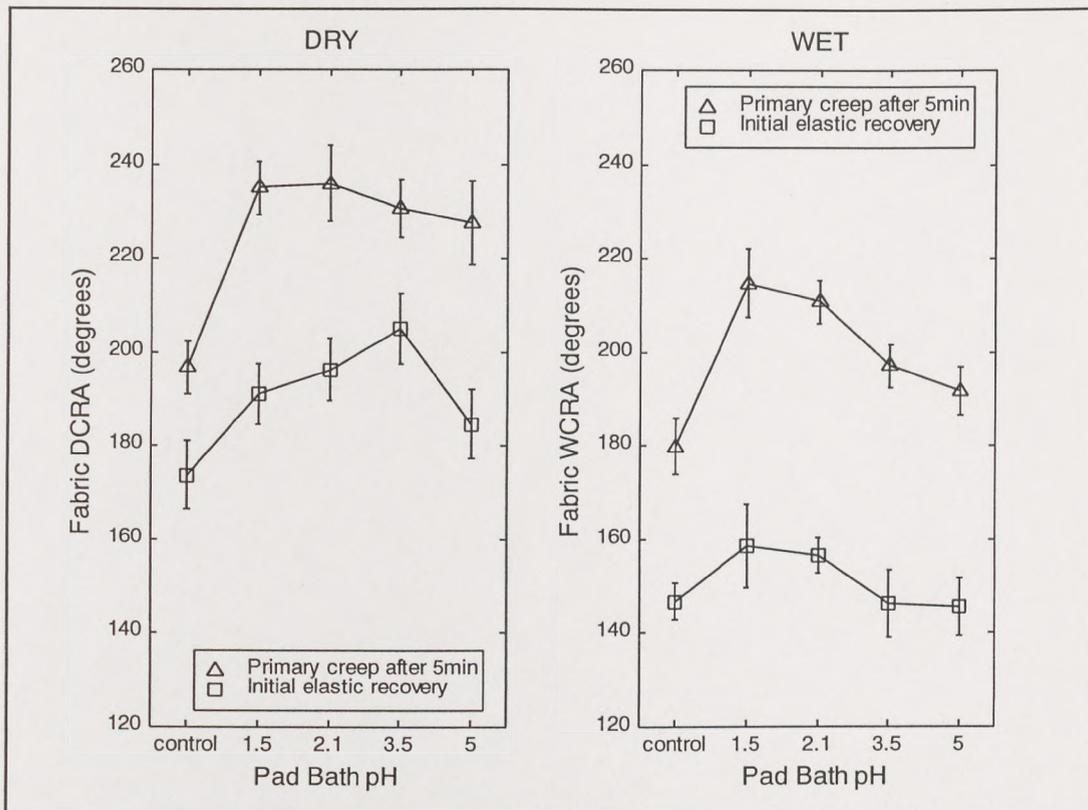


Figure 4.43 Fabric CRAs of silk fabric treated with 6% w/w BTCA and a 1:1 molar ratio of SHP at different pad bath pH.

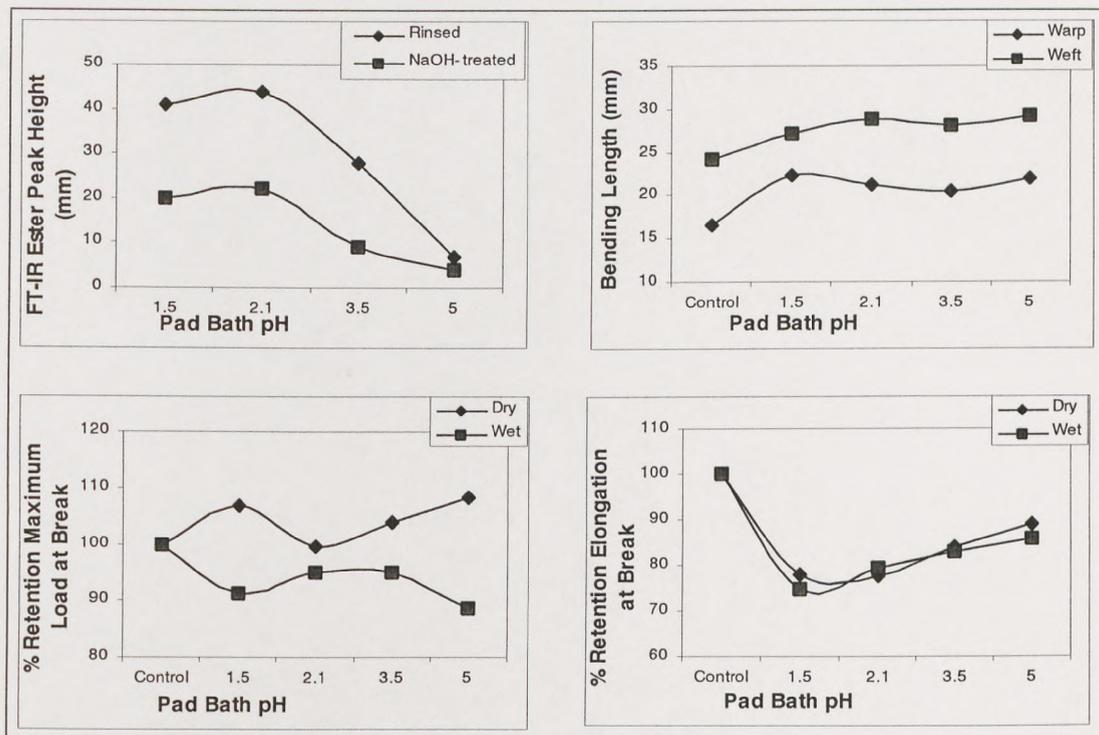


Figure 4.44 Graphical representation of the properties of silk fabric treated with 6% w/w BTCA and a 1:1 molar ratio of SHP at different pad bath pH. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

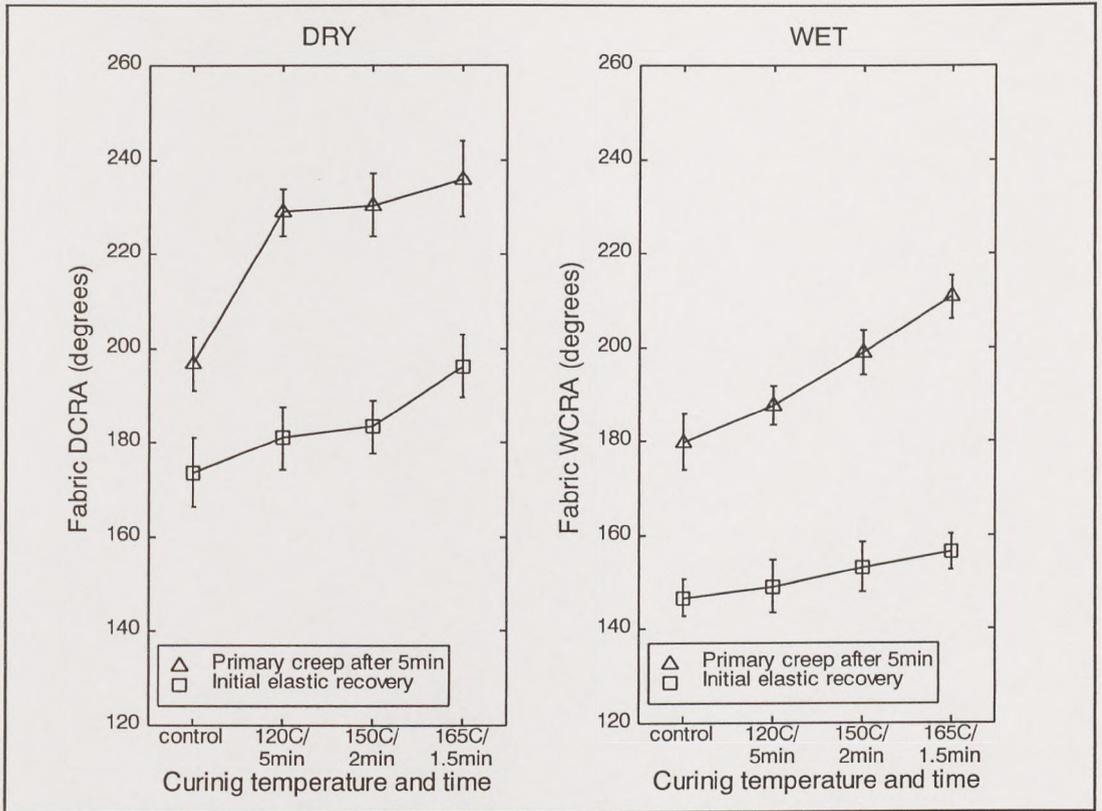


Figure 4.45 Fabric CRAs of silk fabric treated with 6% w/w BTCA and a 1:1 molar ratio of SHP and cured under different conditions.

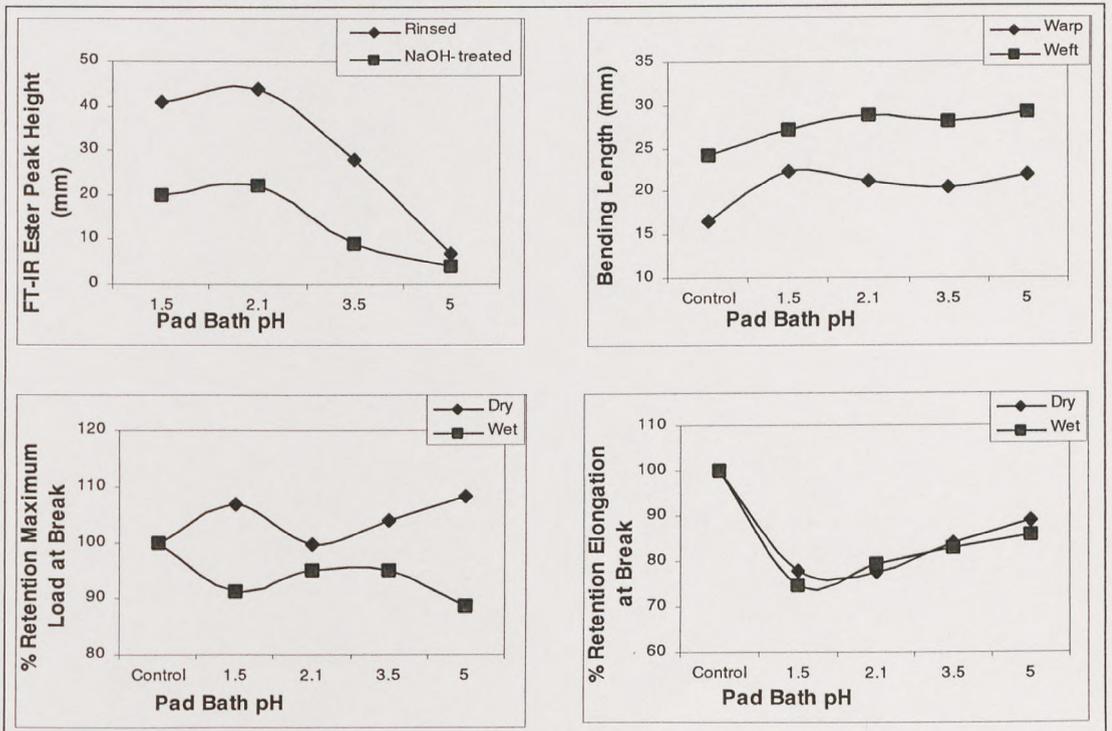


Figure 4.46 Graphical representation of the properties of silk fabric treated with 6% w/w BTCA and a 1:1 molar ratio of SHP and cured under different conditions.. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

4.2.1.2.2 MA/SHP finishing system.

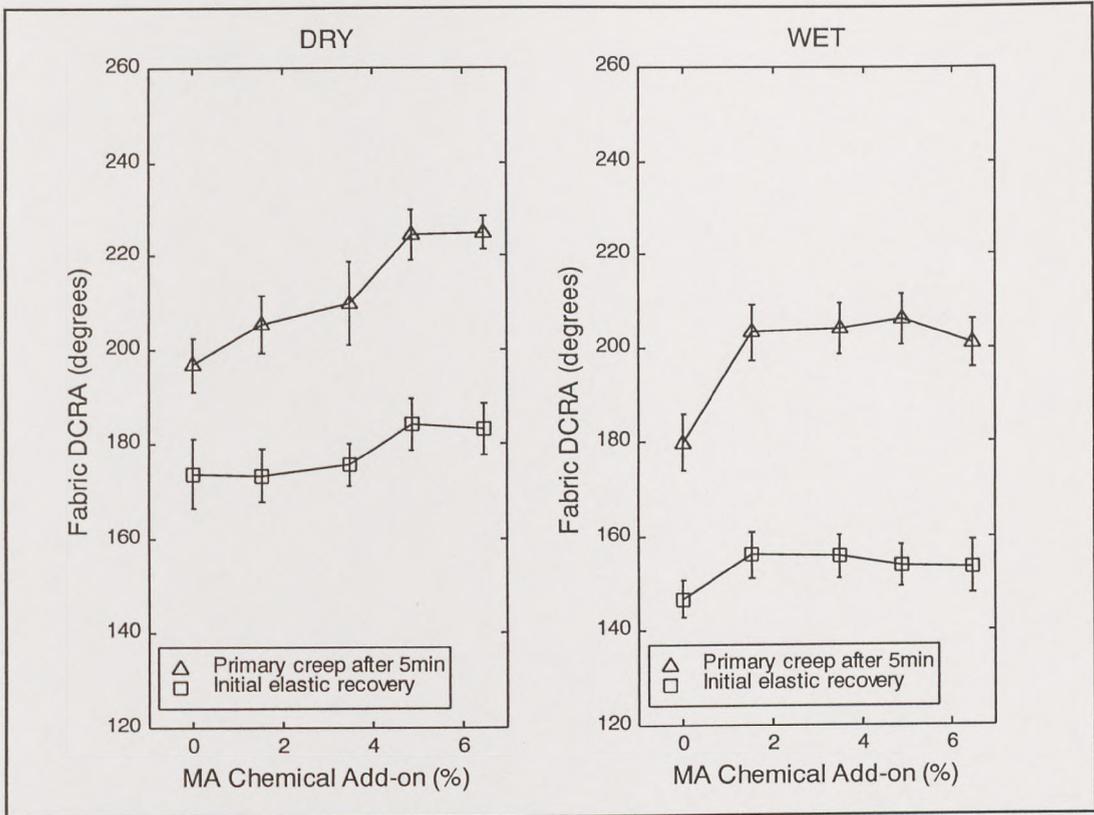


Figure 4.47 Fabric CRAs of silk fabric treated with different quantities of MA and a 1:1 molar ratio of SHP.

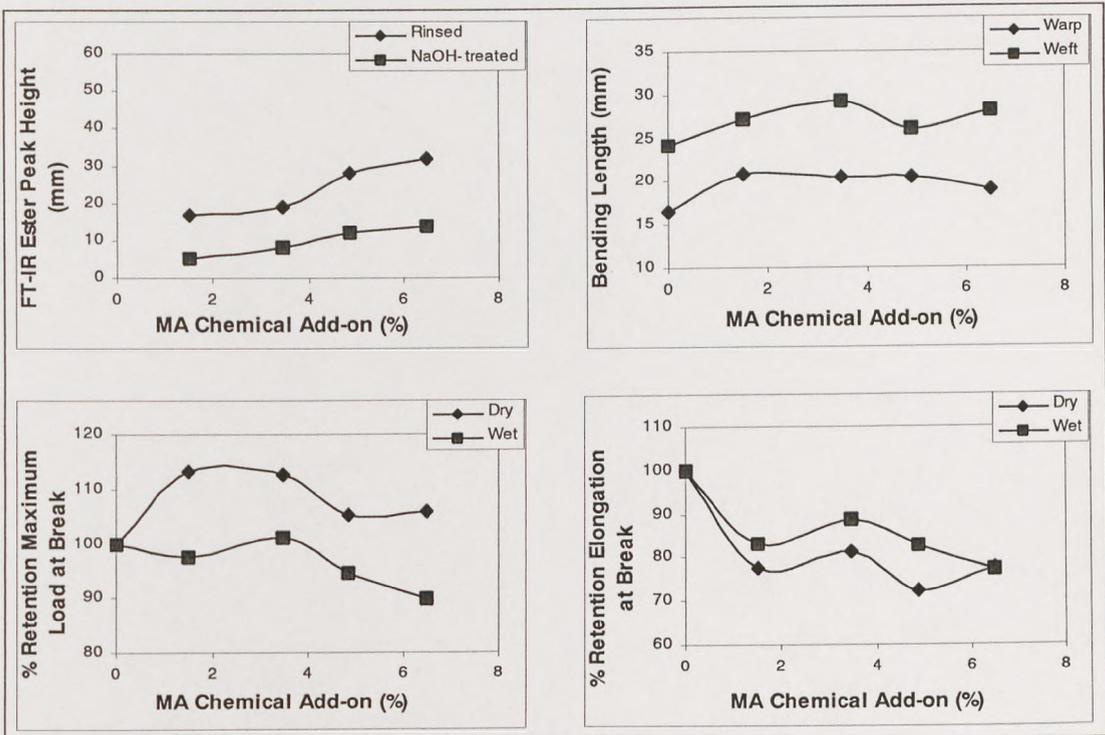


Figure 4.48 Graphical representation of the properties of silk fabric treated with different quantities of MA and a 1:1 molar ratio of SHP. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

The treatment of silk fabric with MA/SHP system was investigated as an alternative finishing system to BTCA/SHP. The optimum treatment conditions for treating silk fabric with MA/SHP were investigated with respect to percent MA chemical add-on, MA:SHP molar ratio, pad bath pH and curing conditions.

Figure 4. 47 and Figure 4. 48 graphically display the results of silk fabrics treated with different quantities of MA and a 1:1 molar ratio of SHP. As with the BTCA/SHP system, as the quantity of MA in the pad bath increased the percent MA chemical add-on increased, see Appendix 2, table A2.2, and the quantity of ester bonds in the treated fabric also increased, see Figure 4. 48. The greater the quantity of MA molecules in the pad bath the greater the chemical reaction with the fabric. From Figure 4. 47 and Figure 4. 48 it can be seen that as the percent MA chemical add-on increases there is:

- An increase in FT-IR ester peak height
- A slight increase in fabric stiffness demonstrated by the slight increase in fabric warp and weft bending length
- A slight increase in fabric dry retention maximum load at break, but a slight decrease in fabric wet retention maximum load at break
- A decrease in fabric dry and wet retention elongation at break
- An increase in fabric dry and wet crease recovery angle both initial elastic recovery and recovery from creasing after five minutes.

These results are typical of a fabric that has been treated with a fibre cross-linking agent. The greater the quantity of chemical add-on the greater the quantity of fibre inter-chain cross-links, shown by an increase in ester links within the fabric, an increase in crease recovery angle and an increase in dry retention of maximum load at break. A reduction in elongation at break and an increase in fabric stiffness are characteristic side-effects of the process. The increases in fabric warp and weft bending lengths are only slight and the reduction in fabric elongation at break is low when compared with the reduction in tensile properties of cotton fabrics treated with fibre cross-linking agents (81).

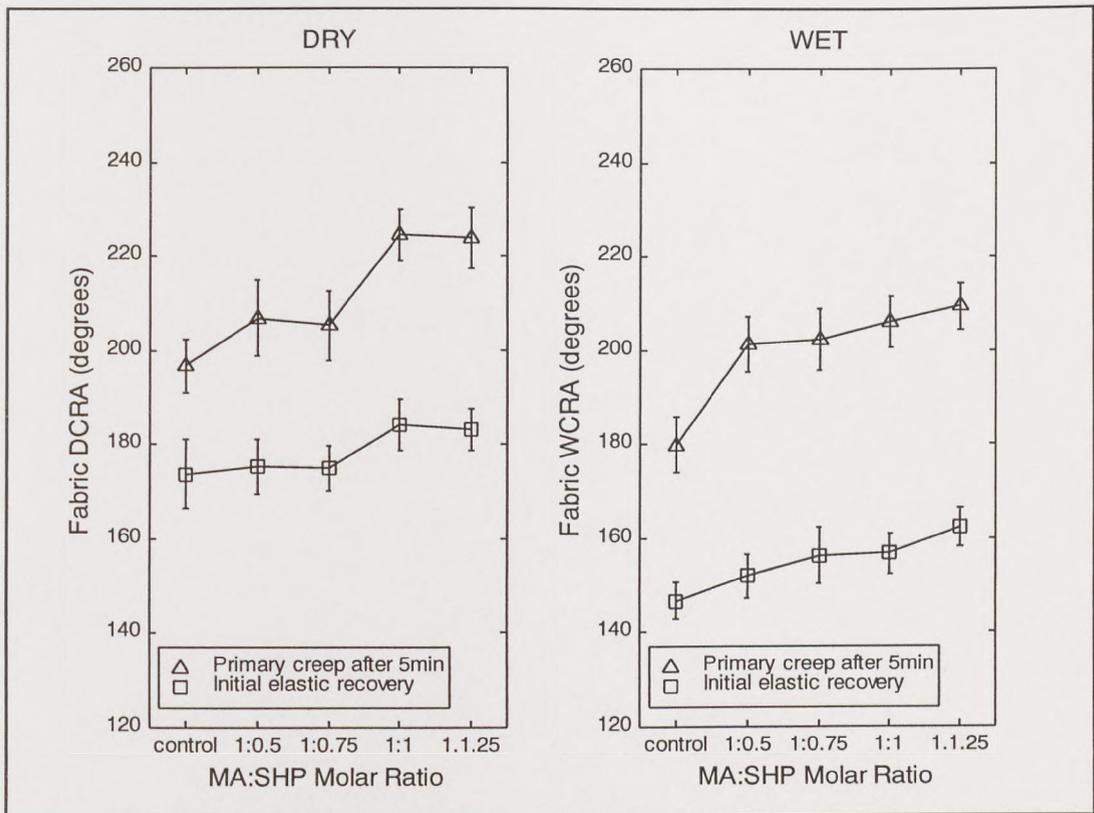


Figure 4.49 Fabric CRAs of silk fabric treated with 6% w/w MA and varying molar ratios of SHP.

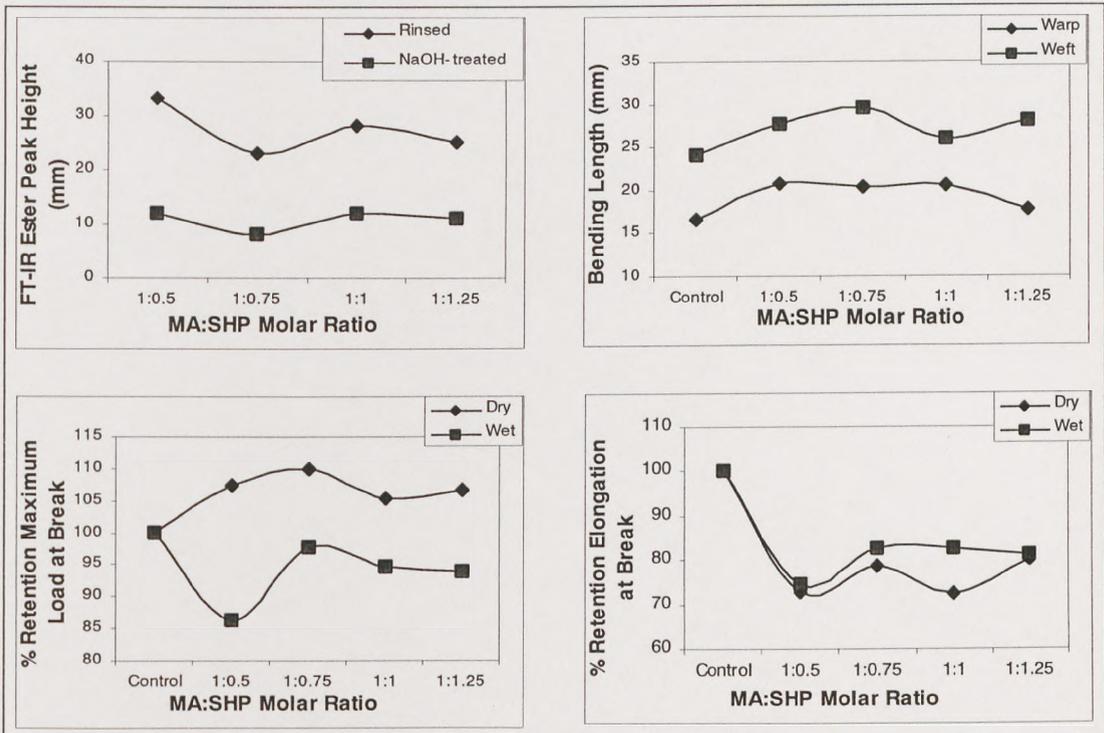


Figure 4.50 Graphical representation of the properties of silk fabric treated with 6% w/w MA and varying molar ratios of SHP. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

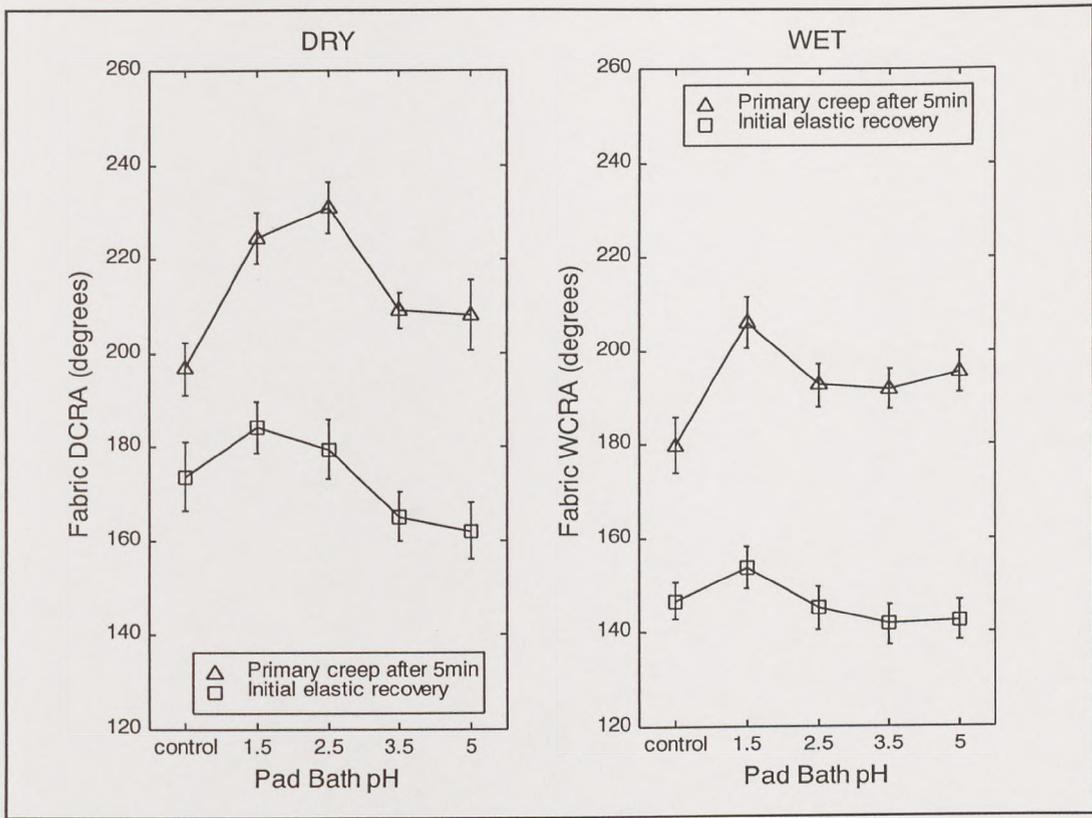


Figure 4.51 Fabric CRAs of silk fabric treated with 6% w/w MA and a 1:1 molar ratio of SHP at different pad bath pH.

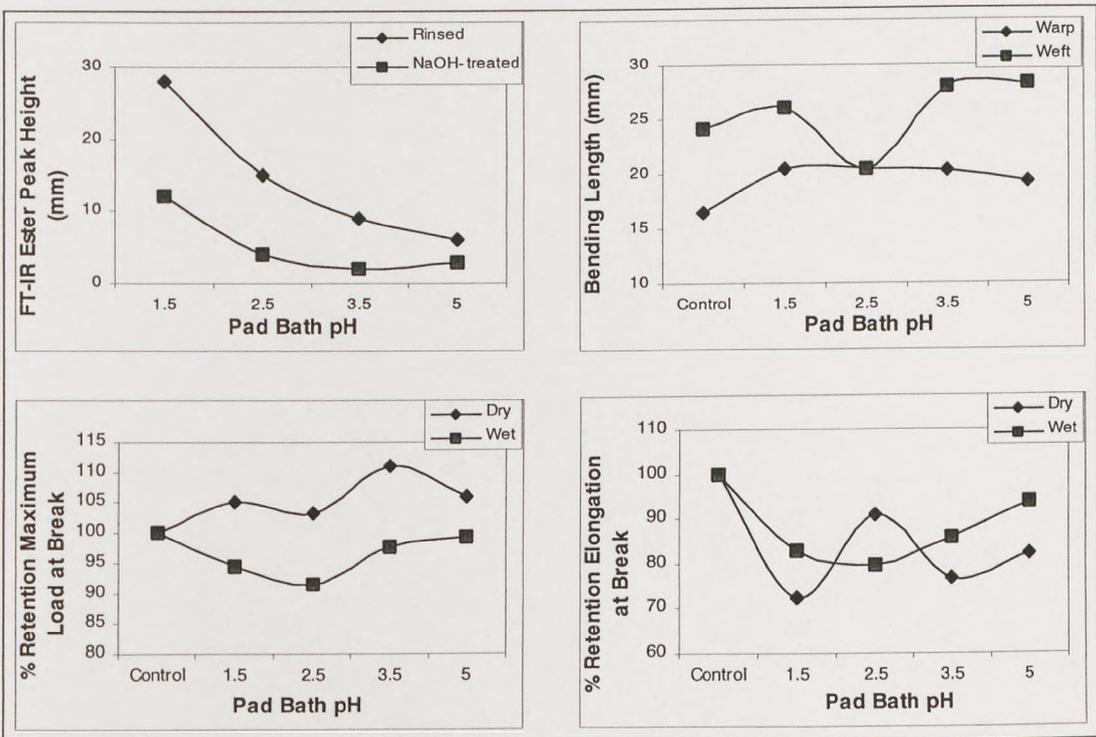


Figure 4.52 Graphical representation of the properties of silk fabric treated with 6% w/w MA and a 1:1 molar ratio of SHP at different pad bath pH. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

High concentrations of MA, above 6% w/w, only dissolve in warm aqueous solutions and have a tendency to fall out of the solution on cooling. This recrystallising of the MA at high concentrations causes problems during padding. Fine crystals get deposited on the surface of the silk fabric that can become airborne during subsequent drying and curing processes and could cause a health risk. The optimum concentration of MA that can safely be used as an easy-care finishing agent is 6%w/w.

The optimum concentration of SHP in the pad bath was also investigated. In Figure 4.49 and Figure 4.50 the properties of silk fabrics treated with different molar ratios of MA:SHP are displayed. As the concentration of SHP in the pad bath increases there is

- An increase in percent chemical add-on of MA, see Appendix 2, table A2.2. This increase in chemical add-on was not accompanied by an increase in the number of ester links in the treated fabrics, see Figure 4.50. Similar to the BTCA/SHP system there is not an increase in ester links with an increase in PCA:SHP molar ratio above 1:0.5.
- No change in the fabric warp and weft bending lengths, or tensile properties of the fabric
- An increase in the fabric dry and wet crease recovery angles, both initial elastic recovery and recovery from creasing after five minutes. This increase in crease recovery angle is not accompanied by an increase in the number of ester links formed within the fibre.

The pH of a 1:1 molar ratio MA:SHP pad bath was investigated. The pH of the pad solution was 1.5. A 1M NaOH solution was used to alter the pad bath pH to 2.5, 3.5 and 5. As can be seen from Figure 4.51 and Figure 4.52 by increasing the pad bath pH value from 1.5 to 5 there is:

- A decrease in fabric dry and wet crease recovery angles, both initial elastic recovery and recovery from creasing after five minutes.
- A decrease in the percent MA chemical add-on, see Appendix 2, table A2.2, and a corresponding decrease in the FT-IR ester bond frequency.
- Alteration of the pad bath pH has little effect on either the fabric warp and weft bending lengths or the fabric mechanical properties.

From these results it can be concluded that the optimum pad bath pH for the treatment

of silk fabric with MA/SHP system is pH 1.5. A more acidic pH could cause the silk fibroin to degrade.

The optimum curing conditions for treating silk fabric with the MA/SHP finishing system were investigated. It can be seen from Figure 4.53 and Figure 4.54 that as the curing temperature is increased there is a corresponding increase in the number of cross-links formed within the silk fibre. As the curing temperature is increased there is

- An increase in dry and wet crease recovery angle, both initial elastic recovery and recovery from creasing after 5 min.
- An increase in the percent MA chemical add-on, see Appendix 2, table A2.2, and a corresponding increase in FT-IR ester peak height.
- A slight increase in fabric warp and weft bending length, and therefore a slight increase in fabric stiffness.
- A decrease in fabric tensile properties, shown by a decrease in the fabric percent retention of maximum load at break and a decrease in the fabric percent retention elongation at break.

In a similar manner to the BTCA/SHP finishing system as the curing temperature is increased the quantity of chemical reaction occurring during the curing process also increases. The optimum curing conditions for the treatment of silk fabric with MA/SHP system are 165°C for 1.5min.

In conclusion the optimum treatment conditions for treating silk fabric with MA/SHP system were achieved with a 6% w/w solution of MA, a 1:1 molar ratio of MA:SHP, a pad bath pH of 1.5 and a curing temperature of 165°C for 1.5min. These treatment conditions were found to give an increase in the dry crease recovery angle from 196.7° to 224.4° and an increase in the wet crease recovery angle from 179.9° to 206.0°. Both the dry and wet crease recovery angle for silk fabric treated with MA/SHP finishing system are slightly lower when compared with silk fabric treated with BTCA/SHP finishing system. This increased fabric crease recovery stability of the treated samples may be caused by MA molecules forming diester and/or ester/hydrogen bond cross-links within the fabric. This is discussed further in section 4.2.1.4.

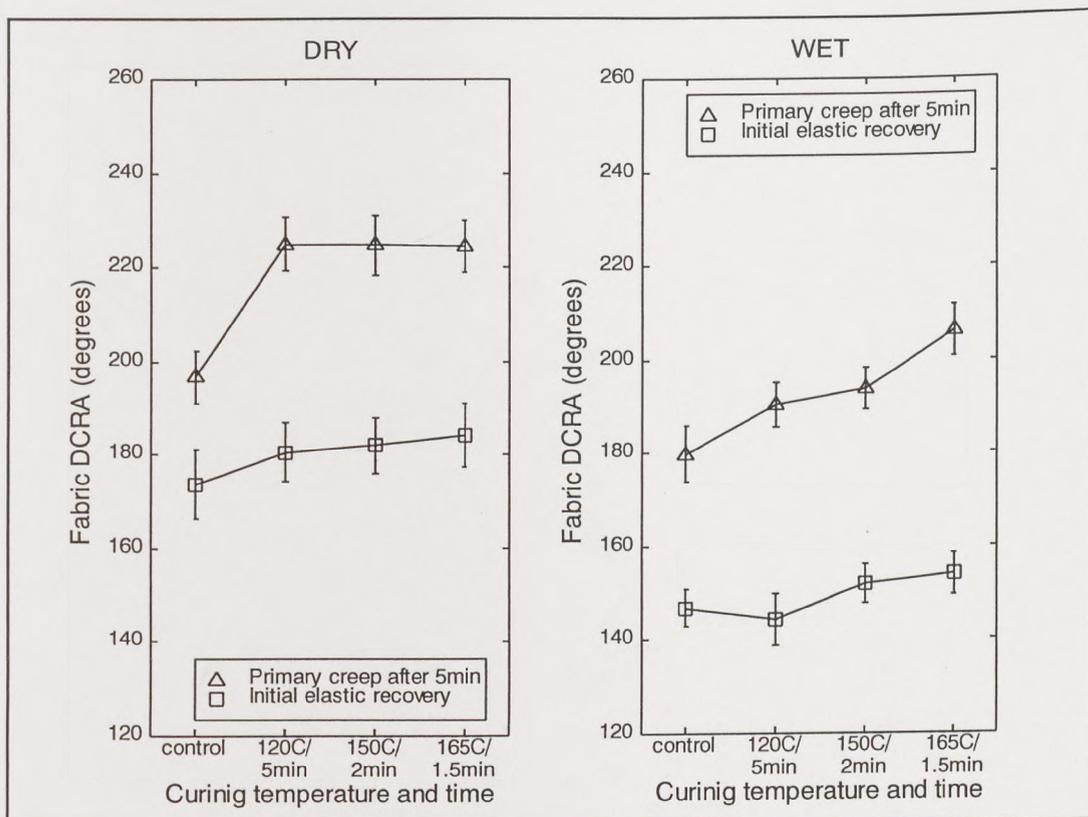


Figure 4.53 Fabric CRAs of silk fabric treated with 6% w/w MA and a 1:1 molar ratio of SHP and cured under different conditions.

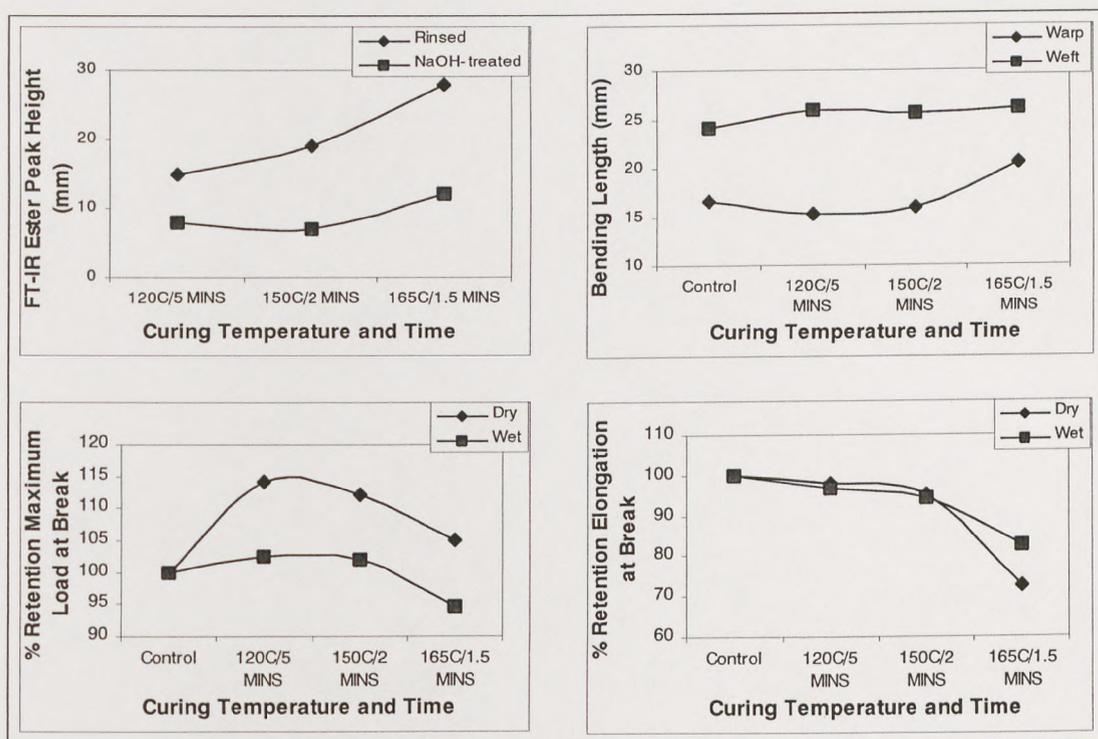


Figure 4.54 Graphical representation of the properties of silk fabric treated with 6% w/w MA and a 1:1 molar ratio of SHP and cured under different conditions. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

4.2.1.2.3 SA/CA/SHP finishing system.

Infra-red and thermoanalytical analysis of mixtures of succinic acid, a hydroxy acid, namely citric acid (CA) or DL-malic acid (MLA), and SHP indicate that these acid mixtures were capable of forming acid anhydrides at temperatures equivalent to those used in silk fabric finishing, see section 4.1.3.4. Evidence, at high temperatures, for a secondary reaction occurring simultaneously with the anhydride formation was observed, although the exact nature of this secondary reaction is uncertain. It was postulated that this secondary reaction could be either as a result of the hydroxy acid dehydrating to form an unsaturated acid or as a result of a reaction between the acid anhydride formed and the hydroxyl groups in the hydroxy acid, or a combination of these reactions. If the acid anhydride formed is capable of forming ester links with the hydroxyl groups in the hydroxy acid combination acids could be formed containing more carboxylic acid groups per molecule.

These combination acids containing a larger quantity of carboxylic acid groups per molecule could be capable of forming cross-links with silk fibroin. These di- and tri-carboxylic acids are cheap and non-toxic and are therefore suitable alternative easy-care finishing agents to BTCA. The treatment of silk fabric with SA/CA/SHP and SA/MLA/SHP finishing systems was investigated. The optimum treatment conditions for treating silk fabric with these acid systems were investigated with respect to PCA chemical add-on, PCA:SHP molar ratio, pad bath pH and fabric curing conditions.

Figure 4.55 and Figure 4.56 graphically display the results of silk fabrics treated with different quantities of a 1:1 molar ratio of SA:CA and a PCA:SHP molar ratio of 1:1. As the quantity of PCA in the pad bath increases there is a corresponding increase in the percent PCA chemical add-on, see Appendix 2, Table A2.3. High quantities of PCA in the pad bath do not improve the fabric percent PCA chemical add-on. It would appear that a saturation point is reached above a PCA chemical add-on of around 7%. This may be caused by a larger proportion of the PCA being deposited on the fabric surface with higher concentrations of PCA in the pad bath that prevent the diffusion of more PCA inside the fibre.

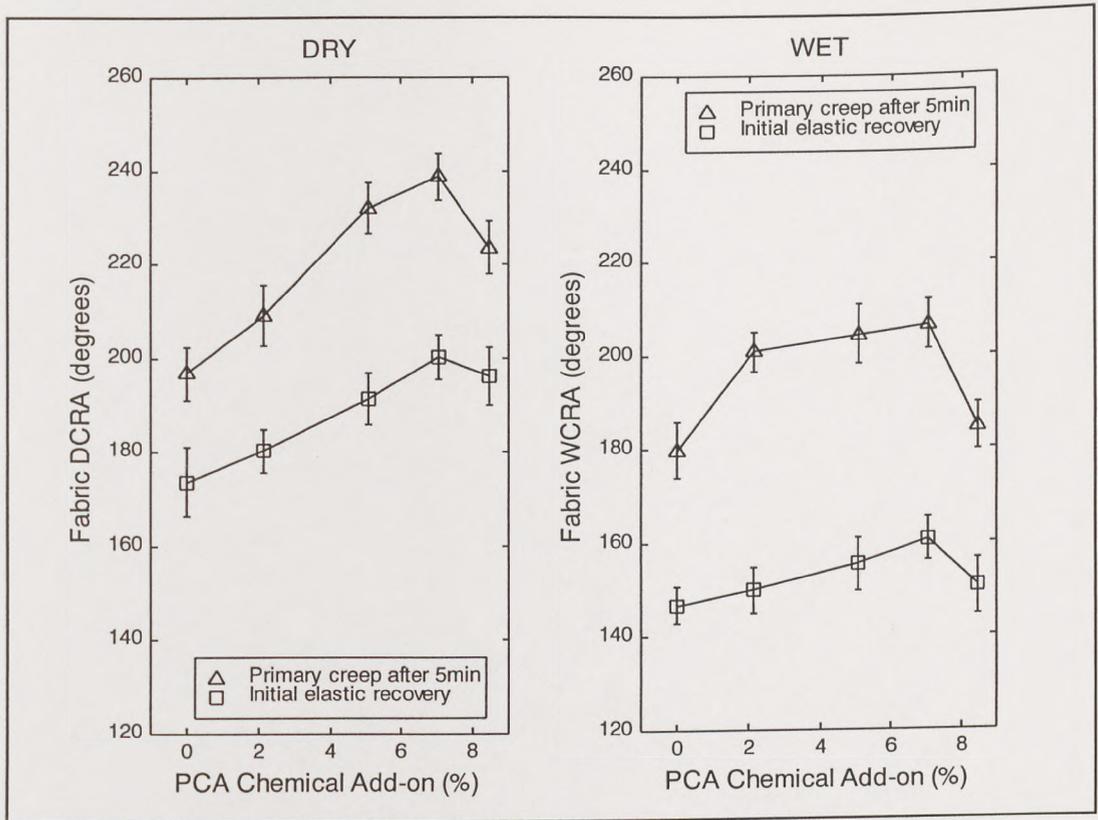


Figure 4.55 Fabric CRAs of silk fabric treated with different quantities of SA and CA and a 1:1 molar ratio of PCA:SHP.

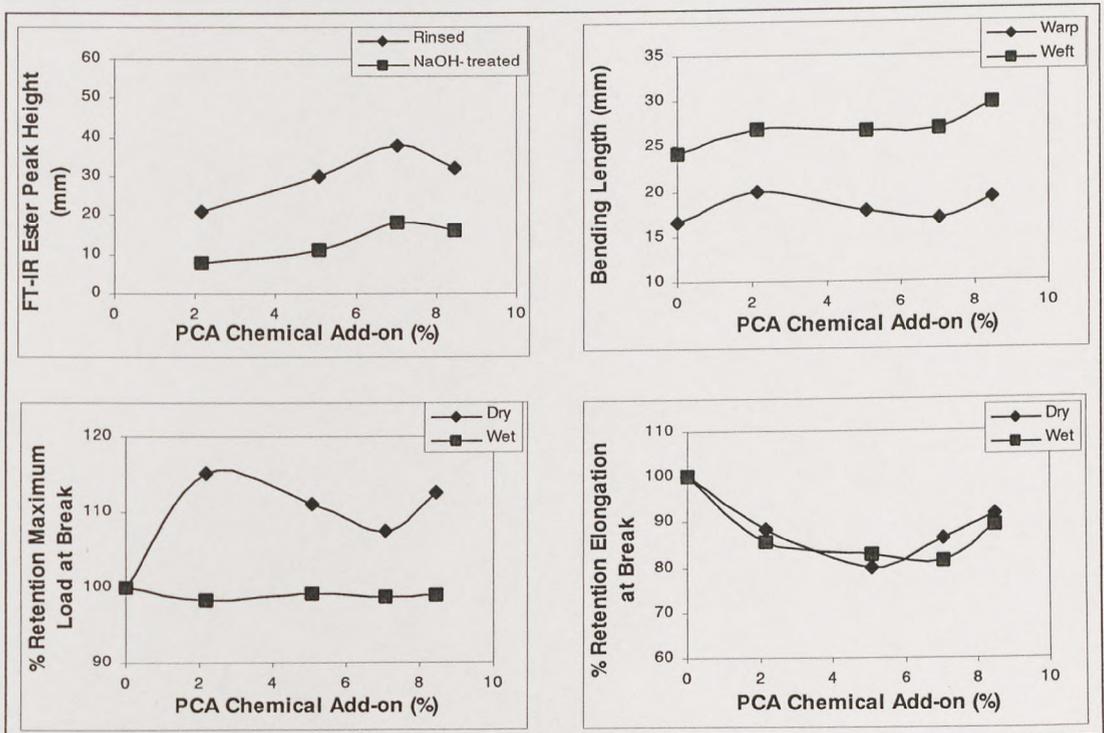


Figure 4.56 Graphical representation of the properties of silk fabric treated with different quantities of SA and CA and a 1:1 molar ratio of PCA:SHP. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

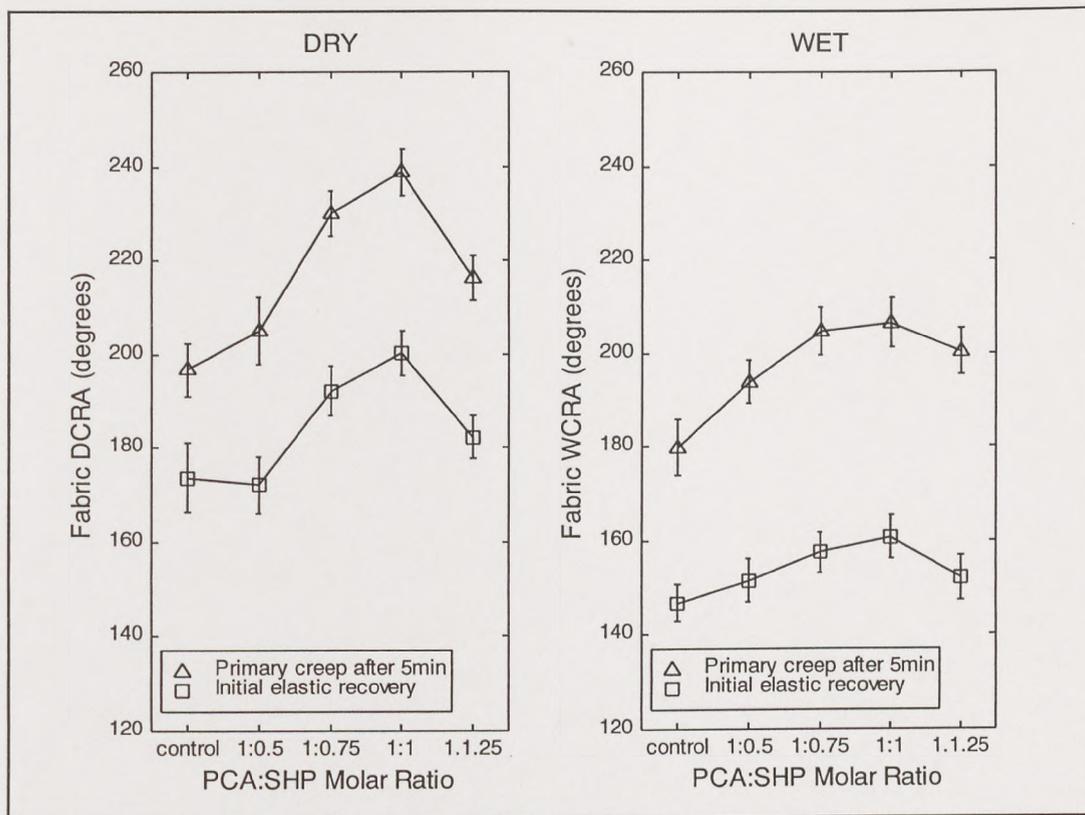


Figure 4.57 Fabric CRAs of silk fabric treated with 3% w/w SA, 4.8% w/w CA and varying molar ratios of SHP.

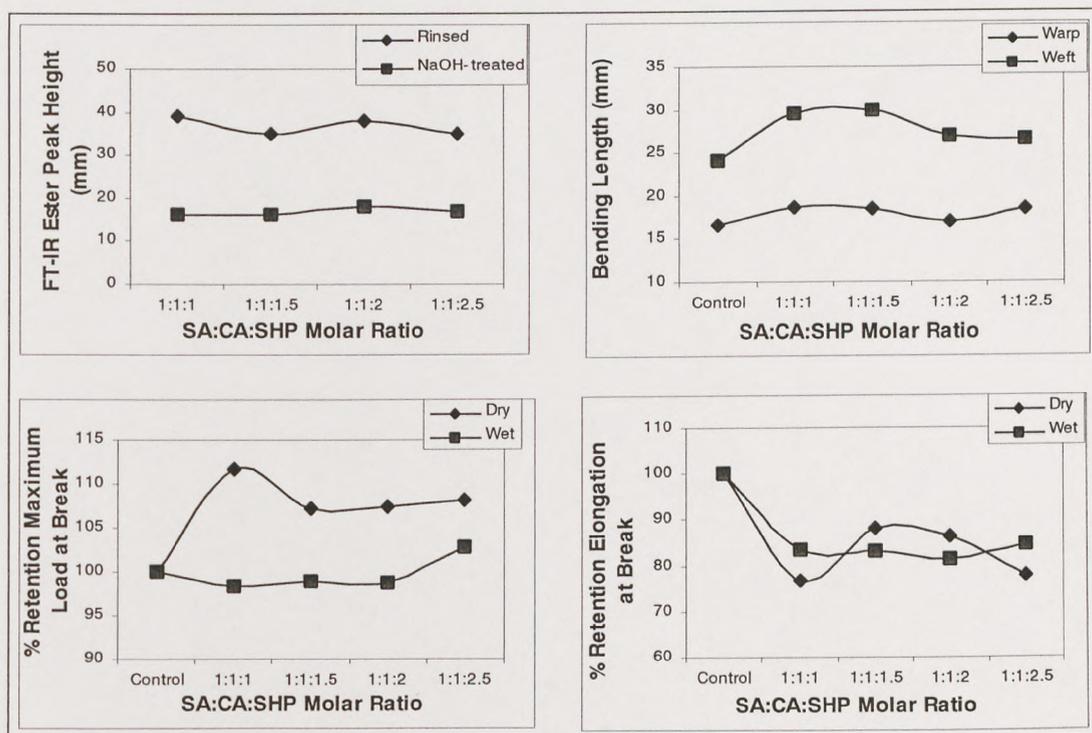


Figure 4.58 Graphical representation of the properties of silk fabric treated with 3% w/w SA, 4.8% w/w CA and varying molar ratios of SHP. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

From Figure 4.55 and Figure 4.56 it can be seen that as the percent PCA chemical add-on increases there is

- An increase in the quantity of ester links formed within the treated silk fabric shown by an increase in the FT-IR ester bond peak height.
- A small increase in fabric stiffness shown by a slight increase in the fabric warp and weft bending lengths.
- An increase in fabric dry percent retention maximum load at break compared with the untreated control and no change in the fabric wet percent retention maximum load at break.
- A decrease in the fabric percent retention elongation at break.
- An increase in fabric dry and wet crease recovery angles both in terms of initial elastic recovery and recovery from creasing after 5min.

These results are indicative of a fabric that has been cross-linked by a fibre inter-chain cross-linking agent. It can be concluded that treatment of silk fabric with SA/CA/SHP finishing system improves the fabric's recovery from creasing by inducing fabric stabilisation; this could be as a result of the incorporation of diester cross-links within the fibres.

The optimisation of this SA/CA/SHP finishing system was investigated. Figure 4.57 and Figure 4.58 display the results of silk fabric treated with 3%w/w SA, 4.8%w/w CA and varying PCA:SHP molar ratios. As the PCA:SHP molar ratio increases there is

- A slight increase in percent PCA chemical add-on up to PCA:SHP molar ratio of 1:1, see Appendix 2, table A2.3. This slight increase in PCA chemical add-on is not accompanied by an increase in ester links formed within the fibres.
- No change in the fabric warp and weft bending lengths, or tensile properties of the fabric.
- An increase in fabric dry and wet crease recovery angle, both initial elastic recovery and recovery from creasing after 5min up to a PCA:SHP molar ratio of 1:1.

These results show that as the PCA:SHP molar ratio is increased from 1:0.5 to 1:1 there is an increase in fabric crease recovery performance. However, this is not accompanied by an increase in the number of ester links formed within the fabric.

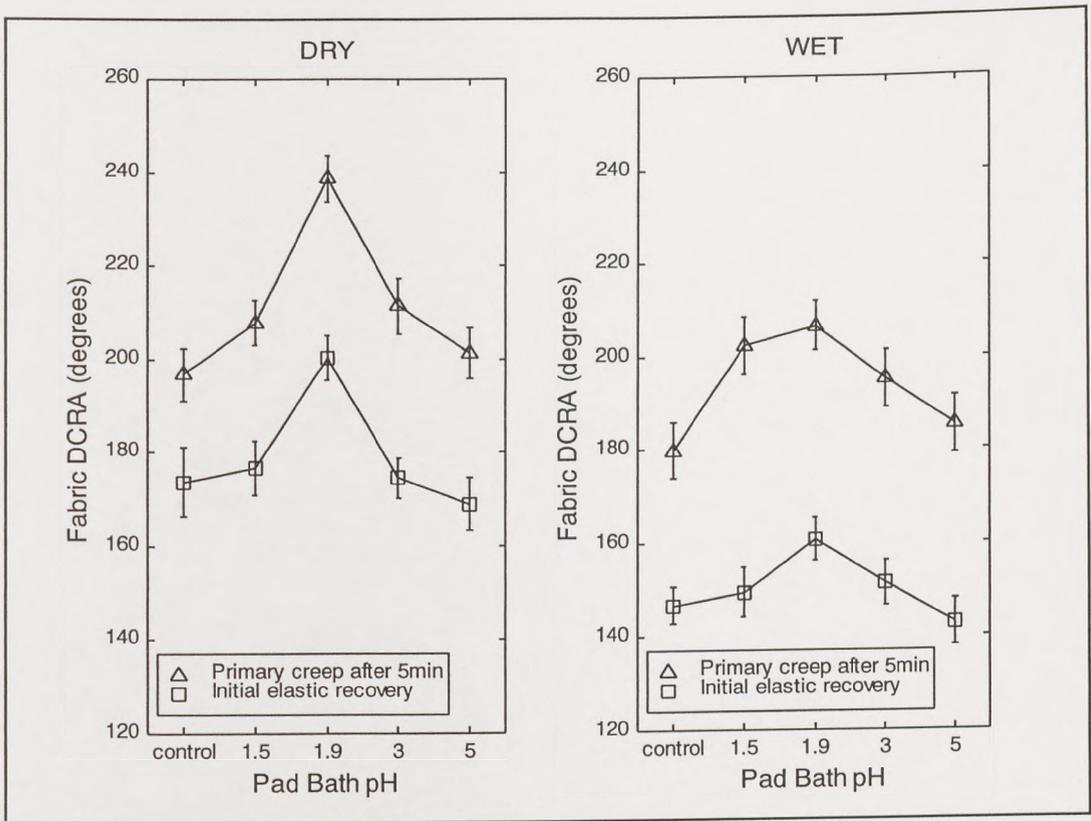


Figure 4.59 Fabric CRAs of silk fabric treated with 3% w/w SA, 4.8% w/w CA and a 1:1 molar ratio of PCA:SHP at different pad bath pH.

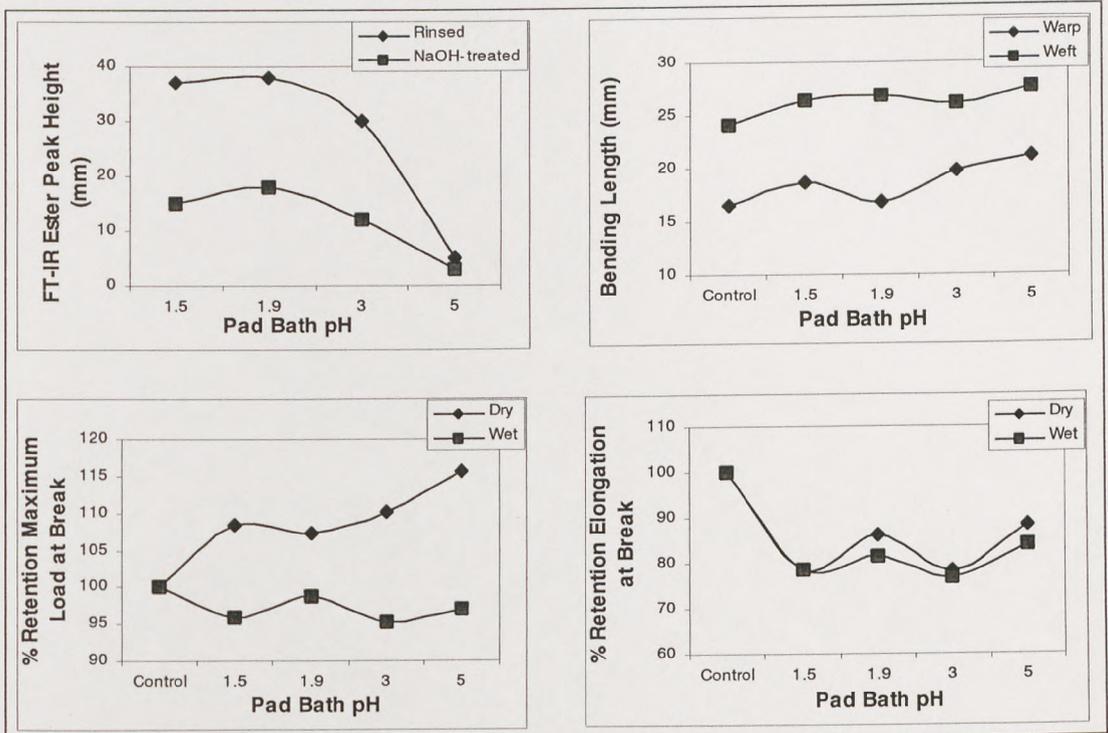


Figure 4.60 Graphical representation of the properties of silk fabric treated with 3% w/w SA, 4.8% w/w CA and a 1:1 molar ratio of PCA:SHP at different pad bath pH. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

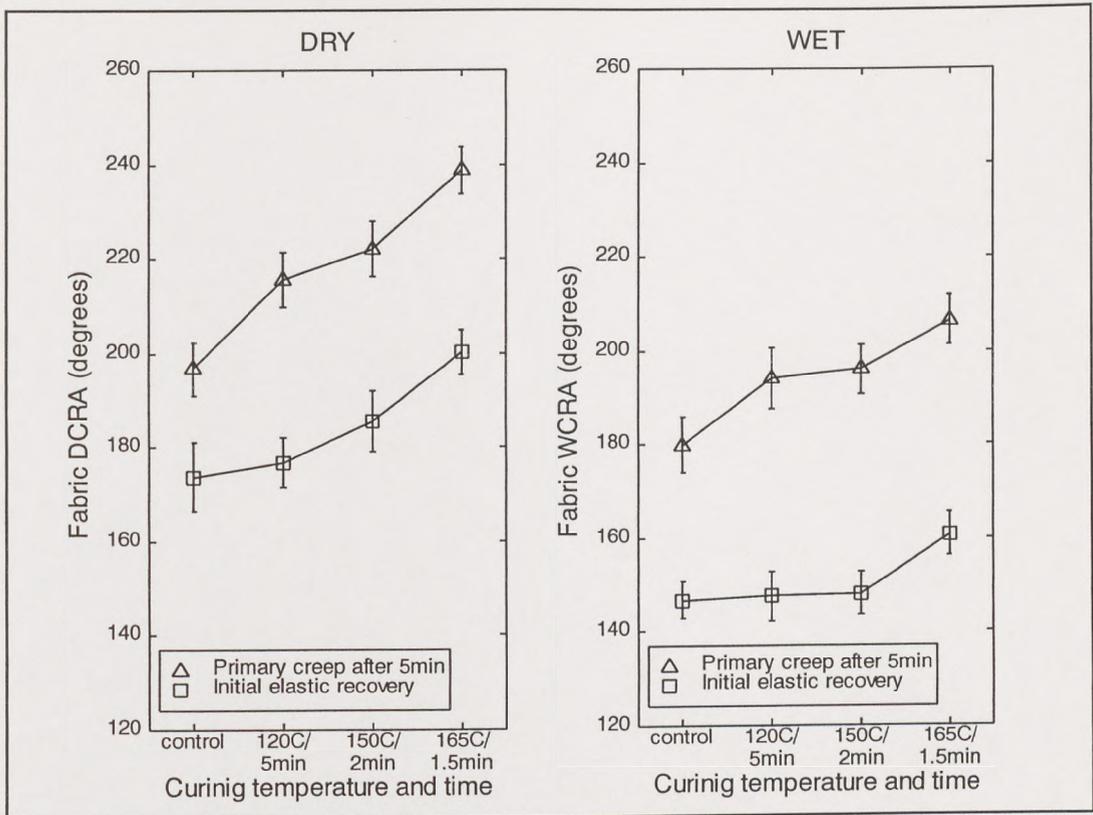


Figure 4.61 Fabric CRAs of silk fabric treated with 3% w/w SA, 4.8% w/w CA and a 1:1 molar ratio of PCA:SHP and cured under different conditions.

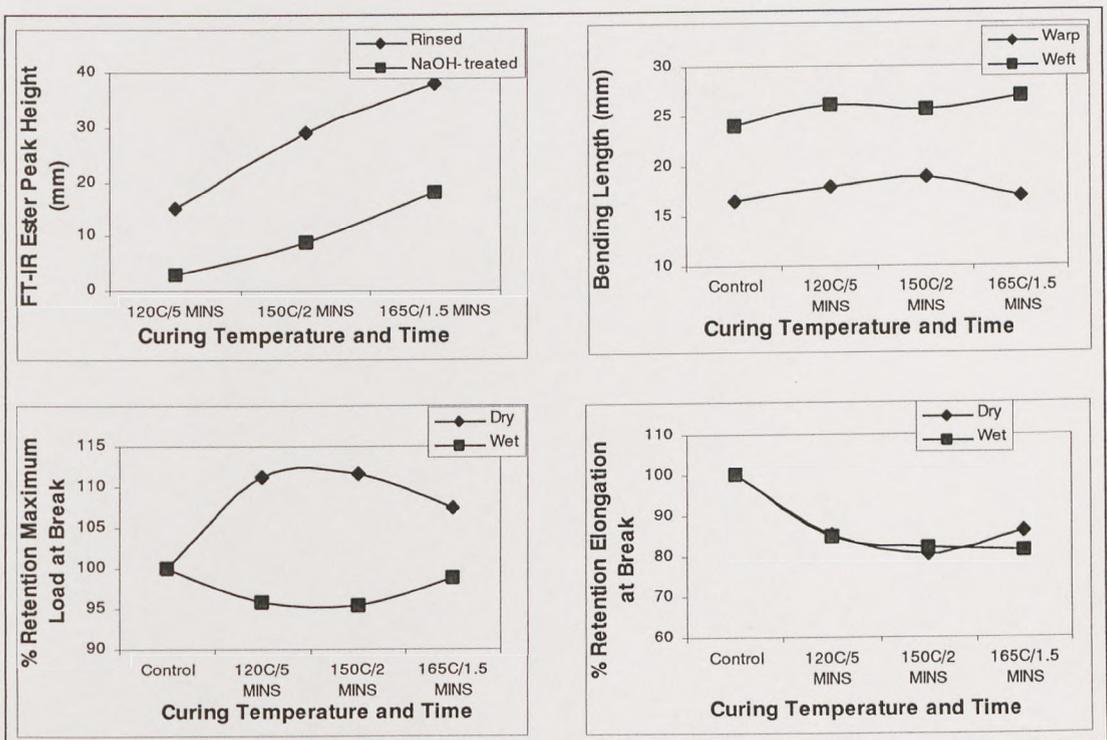


Figure 4.62 Graphical representation of the properties of silk fabric treated with 3% w/w SA, 4.8% w/w CA and a 1:1 molar ratio of PCA:SHP and cured under different conditions. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

In Figure 4. 59 and Figure 4. 60 the results of silk fabric treated with 3%w/w SA, 4.8%w/w CA, a PCA:SHP molar ratio of 1:1 at different pad bath pH values are displayed. The pH of the PCA:SHP 1:1 molar ratio solution was 1.9; this was made more acidic by the addition of 1M HCl to the pad bath and more alkaline with 1M NaOH. By altering the pH of the pad bath either to make the solution more acidic or more alkaline there is:

- A decrease in the percent PCA chemical add-on, see Appendix 2, table A2.3, and there is also a corresponding decrease in the quantity of ester links formed within the fibres. With the more alkaline pad solutions minimal reaction occurred.
- A slight decrease in fabric tensile properties. However the fabric percent retention of both maximum load at break and elongation at break show an increasing trend as the pad bath is made more alkaline.
- A decrease in fabric dry and wet crease recovery angles, both initial elastic recovery and recovery from creasing after 5min.

Increasing either the acidity or alkalinity of the pad bath has a detrimental effect on the cross-linking reaction. The optimum pH for treating silk fabric with SA/CA/SHP finishing solution is pH1.9.

The curing conditions of silk fabric treated with 3%w/w SA, 4.8%w/w CA and a PCA:SHP molar ratio of 1:1 were investigated. Figure 4. 61 and Figure 4. 62 graphically display the results from this experiment. As the curing temperature increases there is

- An increase in dry and wet crease recovery angle, both initial elastic recovery and recovery from creasing after 5 min.
- An increase in the percent PCA chemical add-on, see Appendix 2, table A2.3, and a corresponding increase in FT-IR ester peak height.
- Minimal variation in fabric warp and weft bending length and fabric tensile properties.

The optimum curing conditions for treating silk fabric with the SA/CA/SHP finishing system are 165°C for 1.5min. At a PCA chemical add-on of 7% the fabric DCRA was increased from 196.7° to 238.7° and the fabric WCRA was increased from 179.9° to 108.8°. The improvement in fabric recovery from creasing using a SA/CA/SHP finishing system is equivalent to that achieved with the BTCA/SHP finishing system.

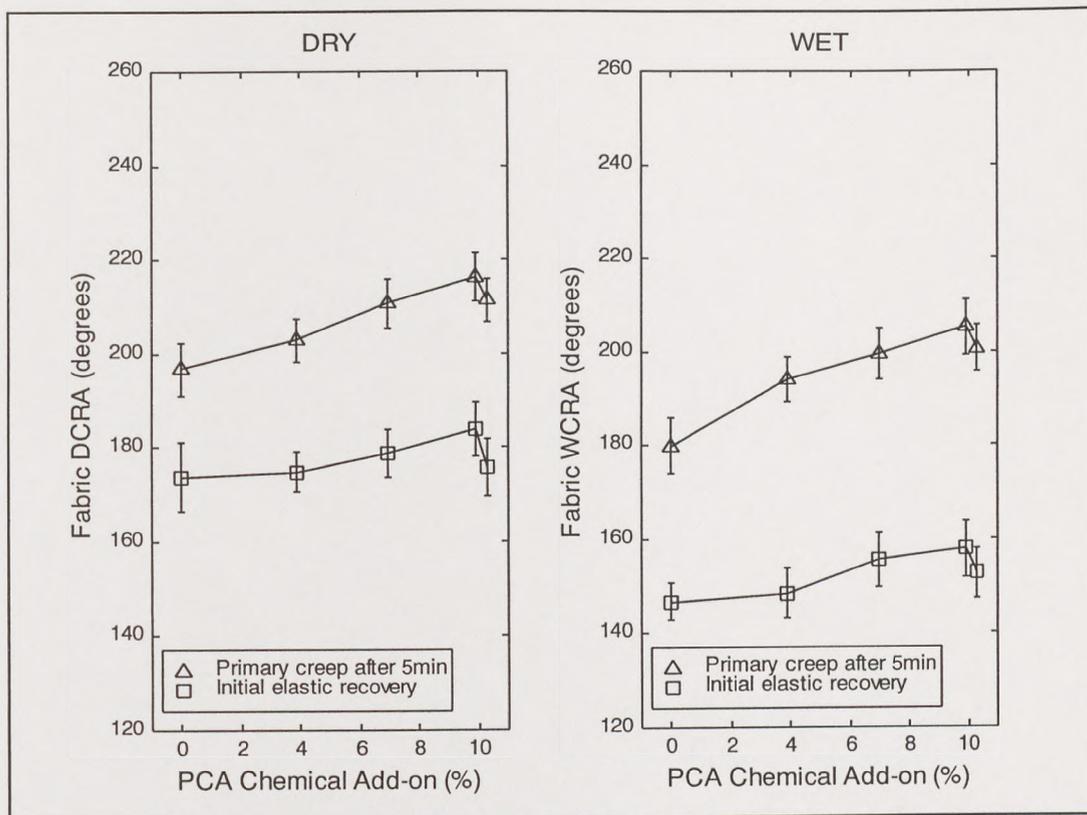


Figure 4.63 Fabric CRAs of silk fabric treated with different quantities of SA and MLA and a 1:1 molar ratio of PCA:SHP

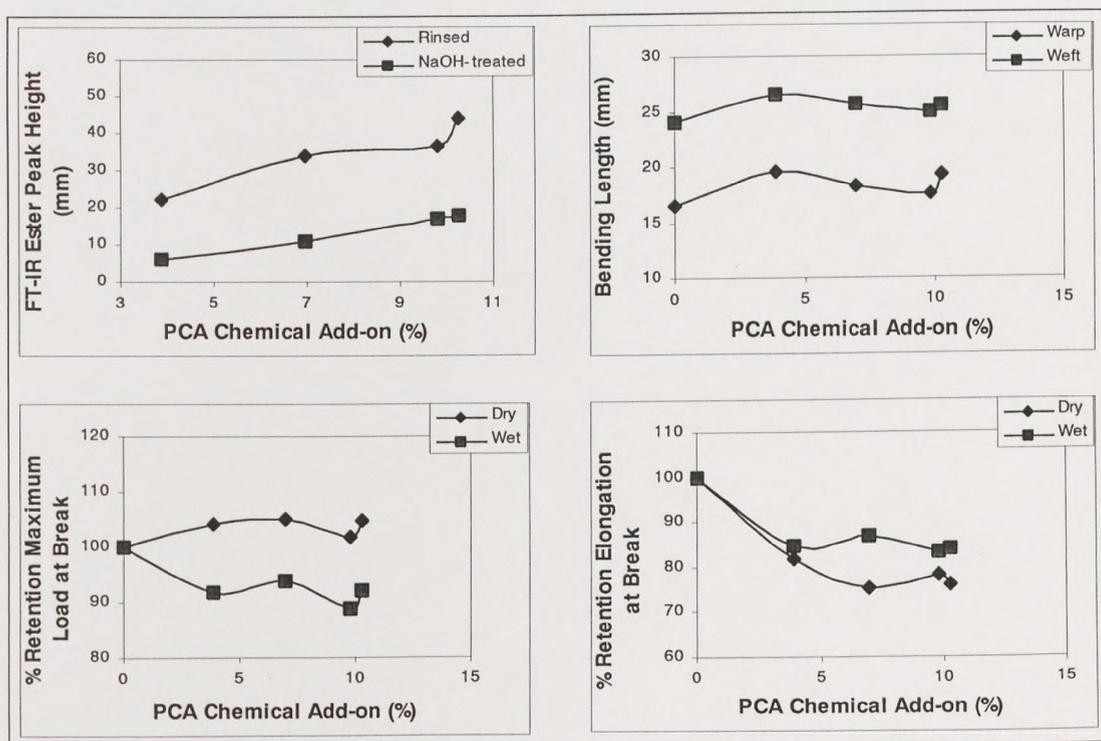


Figure 4.64 Graphical representation of the properties of silk fabric treated with different quantities of SA and MLA and a 1:1 molar ratio of PCA:SHP. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

In section 3.3.1 a comparison was made between treating silk with the BTCA/SHP finishing system and the CA/SHP finishing system. The CA/SHP finishing system was found to be inferior to the BTCA/SHP finishing system. In this experiment the addition of SA in the pad bath improved the efficiency of the finish so that it was comparable with the BTCA/SHP finish; this is discussed further in section 4.2.1.3. The proposed mechanisms for the reaction of various PCAs with silk fibroin are discussed in section 4.2.1.4.

4.2.1.2.4 SA/MLA/SHP finishing system.

Figure 4. 63 and Figure 4. 64 graphically illustrate the results of silk fabric samples treated with different quantities of a 1:1 molar ratio mixture of SA and MLA and a 1:1 molar ratio of PCA:SHP. As the quantity of PCA in the pad bath increases there is a corresponding increase in the percent PCA chemical add-on, see Appendix 2, table A2.4. From Figure 4. 63 and Figure 4. 64 it can be deduced that as the percent chemical add-on increases there is:

- An increase in fabric dry and wet crease recovery angles, both initial elastic recovery and recovery from creasing after 5min, up to a PCA add-on of approximately 9%.
- An increase in the FT-IR ester bond peak height that is representative of an increase in the quantity of ester links formed within the treated silk fabric.
- A slight increase in the fabric warp and weft bending lengths that is indicative of a slight increase in fabric stiffness
- A slight decrease in fabric tensile properties

The fabric properties induced by treatment of silk fabric with the SA/MLA/SHP finishing system are characteristic of fabric that has been treated with an easy-care finishing agent. Treatment of silk fabric with a SA/MLA/SHP finishing system improves the fabric crease recovery properties of the treated samples either by the incorporation of diester and/or ester/hydrogen bond cross-links within the fibre or by the formation of a PCA polymer network within the silk fibroin. It is possible that polycarboxylic acids with three or more carboxylic acid groups per molecule are formed by the reaction of the hydroxyl side groups of MLA with acid anhydrides formed during the high temperature curing process. This is discussed further in section 4.2.1.4.

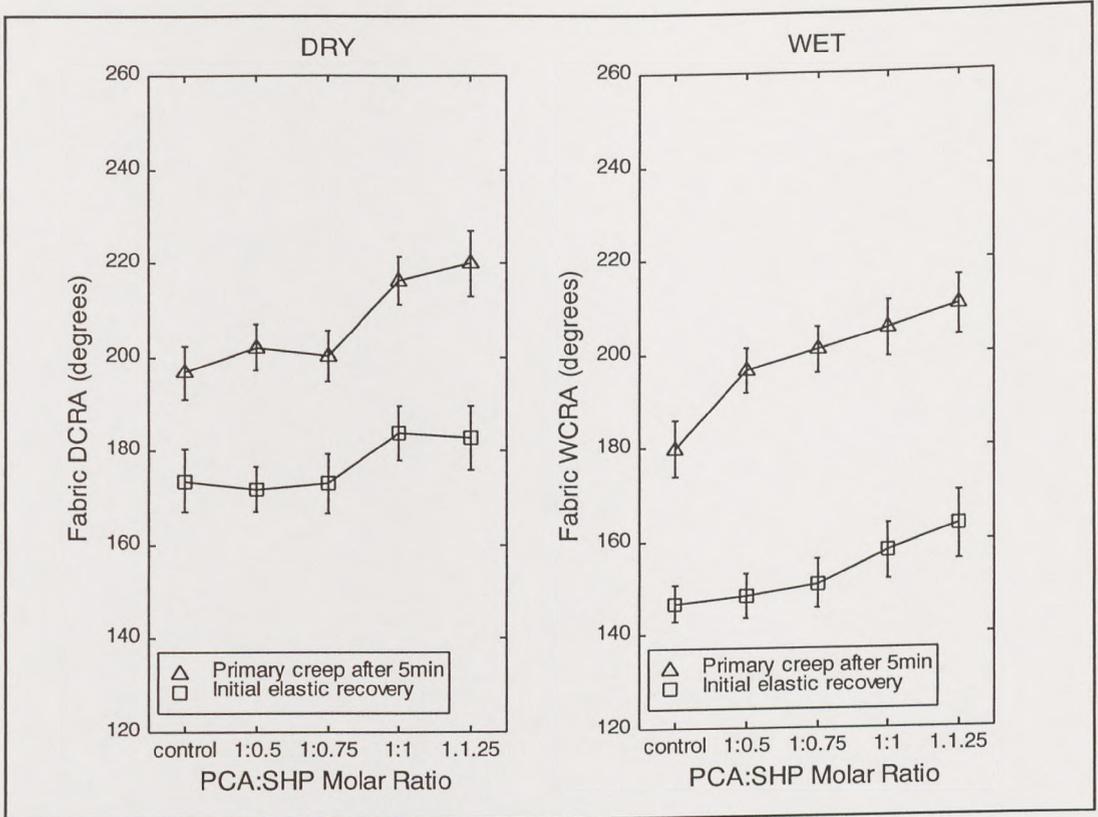


Figure 4.65 Fabric CRAs of silk fabric treated with 4% w/w SA, 6% w/w MLA and varying molar ratios of SHP.

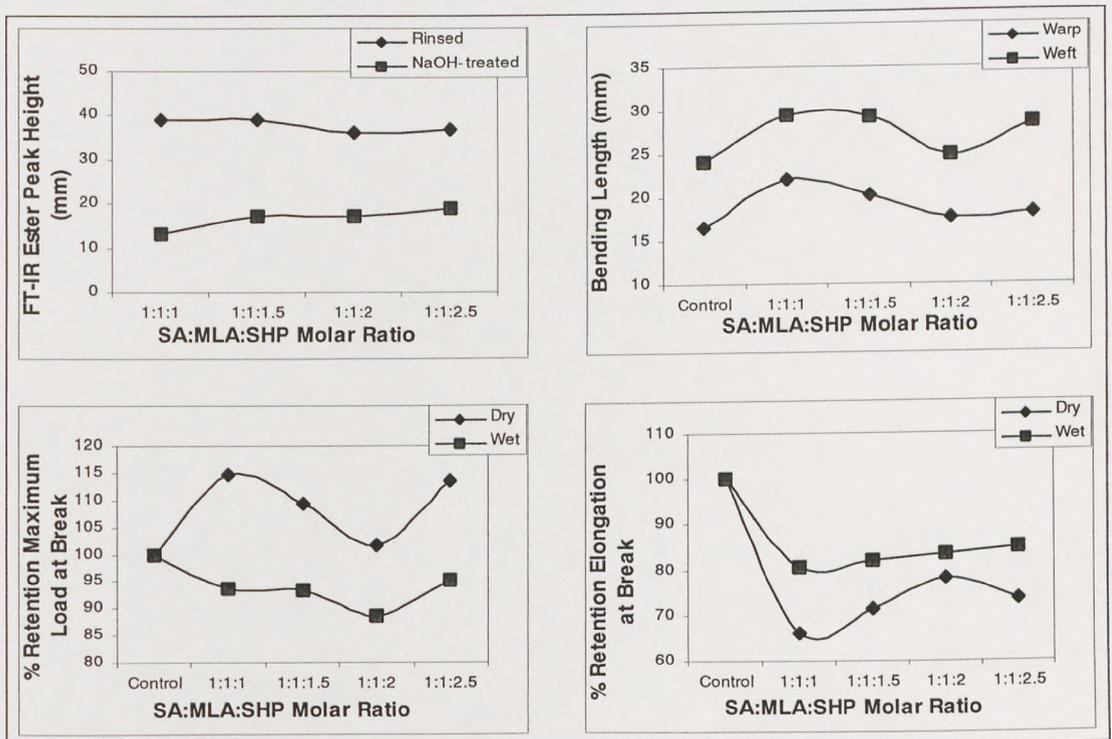


Figure 4.66 Graphical representation of the properties of silk fabric treated with 4% w/w SA, 6% w/w MLA and varying molar ratios of SHP. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

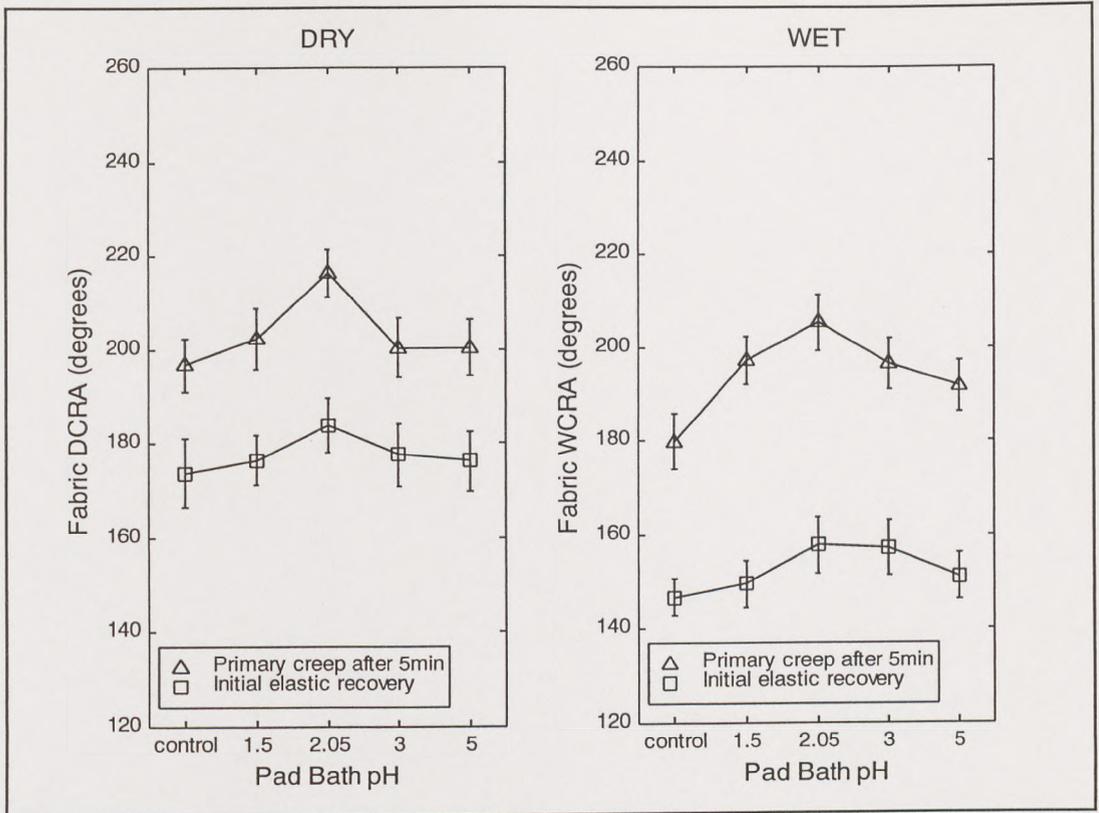


Figure 4.67 Fabric CRAs of silk fabric treated with 4% w/w SA, 6% w/w MLA and a 1:1 molar ratio of PCA:SHP at different pad bath pH.

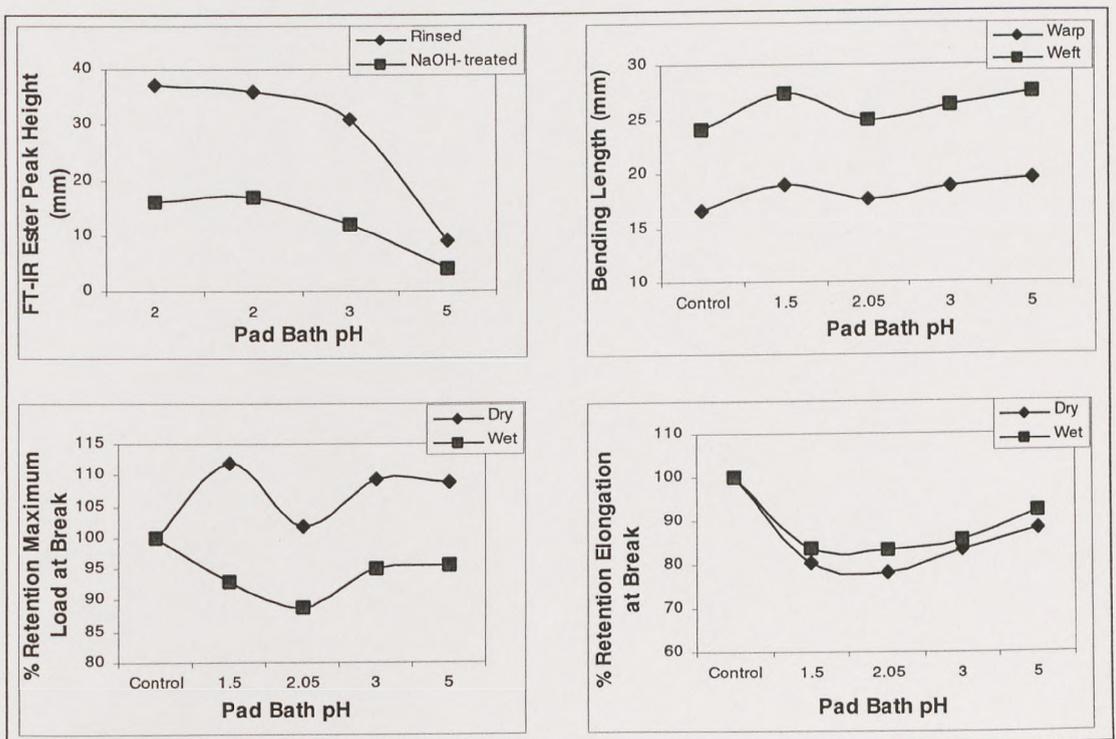


Figure 4.68 Graphical representation of the properties of silk fabric treated with 4% w/w SA, 6% w/w MLA and a 1:1 molar ratio of PCA:SHP at different pad bath pH. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

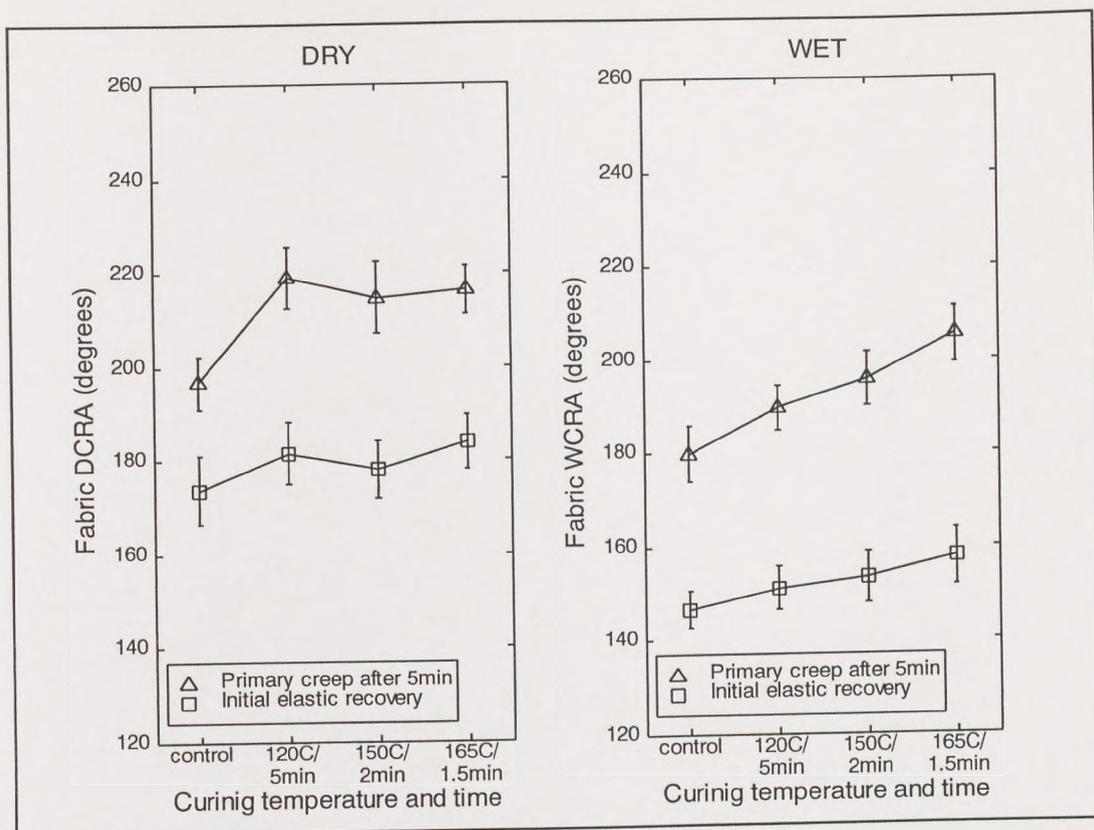


Figure 4.69 Fabric CRAs of silk fabric treated with 4% w/w SA, 6% w/w MLA and a 1:1 molar ratio of PCA:SHP and cured under different conditions.

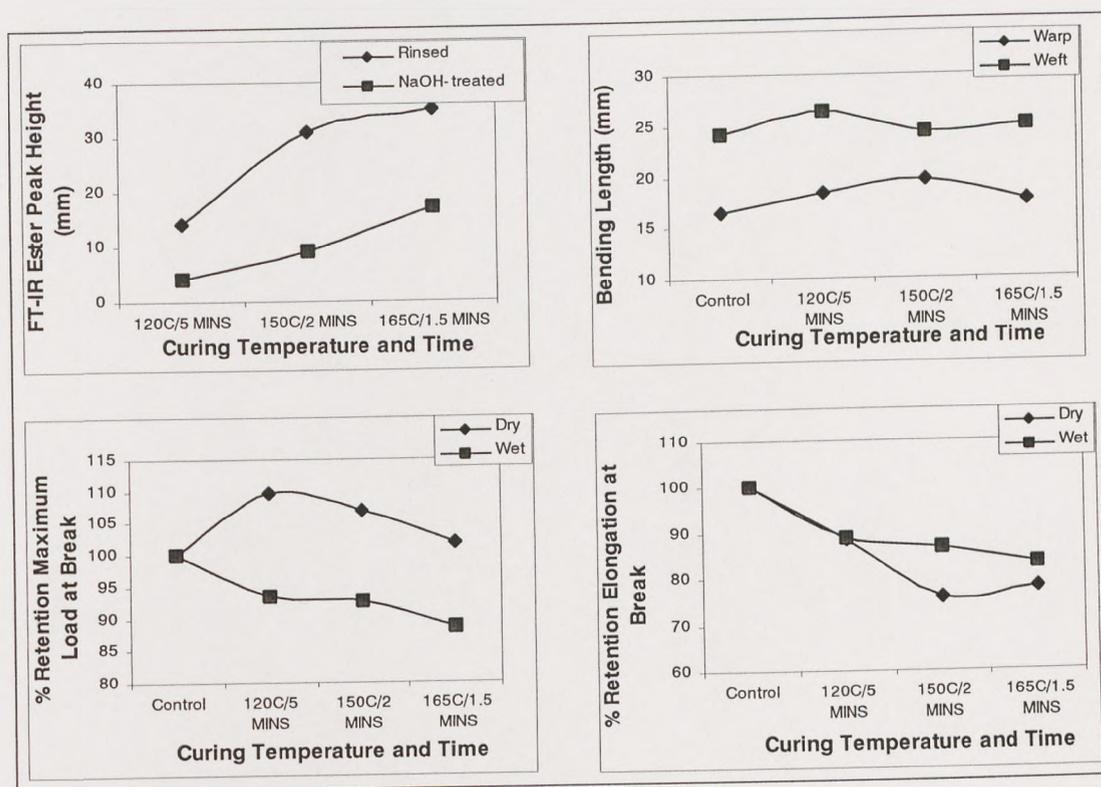


Figure 4.70 Graphical representation of the properties of silk fabric treated with 4% w/w SA, 6% w/w MLA and a 1:1 molar ratio of PCA:SHP and cured under different conditions. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

This SA/MLA/SHP finishing system was investigated with respect to optimising the PCA:SHP molar ratio, pad bath pH and curing conditions. Figure 4.65 and Figure 4.66 display the results of silk fabrics treated with 4g/l SA, 6g/l MLA and varying PCA:SHP molar ratios. As the PCA:SHP molar ratio increases there is

- A slight increase in percent PCA chemical add-on up to a PCA:SHP molar ratio of 1:1, see Appendix 2, table A2.3. This slight increase in PCA chemical add-on is accompanied by a slight increase in the number of ester links formed within the silk fabric.
- Minimal change in fabric warp and weft bending length and fabric tensile properties.
- An increase in fabric dry and wet crease recovery angle, both initial elastic recovery and recovery from creasing after 5min.

The optimum PCA:SHP molar ratio is 1:1.

Figure 4.67 and Figure 4.68 display the results of silk fabrics treated with 4%w/w SA, 6%w/w MLA, a PCA:SHP molar ratio of 1:1, and different pad bath pH values. The pH of the PCA:SHP finishing system was 2.05; this was made more acidic by the addition of 1M HCl and more alkaline by the addition of 1M NaOH. By altering the pH of the pad solution, either by decreasing or increasing the pad bath pH there is:

- A decrease in the percent PCA chemical add-on, see Appendix 2, table A2.4, and there is also a decrease in ester links formed within the silk fabric.
- Less reduction in fabric tensile properties and minimal change in fabric warp and weft bending length.
- A decrease in fabric dry and wet crease recovery angles, both initial elastic recovery and recovery from creasing after 5min.

Altering the pH of the pad bath has a detrimental effect on the reaction of the SA/MLA/SHP finishing system with silk fabric. The optimum pH for this finishing system is pH 2.05.

The curing conditions of silk fabric treated with 4%w/w SA, 6%w/w MLA and a PCA:SHP molar ratio of 1:1 were investigated and the results are displayed in Figure 4.69 and Figure 4.70. As the curing temperature is increased there is:

- An increase in dry and wet crease recovery angle, both initial elastic recovery and

recovery from creasing after 5min.

- An increase in percent PCA chemical add-on, see Appendix 2, table A2.4, and a corresponding increase in ester links formed within the treated fabric shown by an increase in FT-IR ester peak height.
- Minimal change in fabric warp and weft bending length and a decrease in fabric tensile properties.

The optimum curing conditions for treating silk fabric with SA/MLA/SHP finishing system is 165°C for 1.5min. At a PCA chemical add-on of 9.9% the average fabric DCRA was increased from 196.7° to 216.3° and the average fabric WCRA was increased from 179.9° to 205.2°. This improvement in fabric recovery from creasing in comparison with the untreated control for the SA/MLA/SHP finishing system was slightly less than the improvement in crease recovery angle seen with the BTCA/SHP finishing system, see section 4.2.1.3.

4.2.1.3 Comparison of results.

A number of trends can be identified in the treatment of silk fabrics with PCA/SHP finishing systems.

- As the PCA percent chemical add-on increased there was a corresponding increase in FT-IR ester frequency peak height within a PCA/SHP finishing system. This would suggest that as the quantity of chemical added to the fabric increases there is an increase in the number of ester links formed between the PCA and silk fibroin molecular chains.
- This increase in PCA percent chemical add-on eventually reaches a maximum above which no improvement in chemical reaction is achieved. There are only a limited number of available reactive side groups within silk fibroin. It has been reported that 50% of the serine and threonine and 100% of the tyrosine residues exist in the accessible regions of the fibre (34). Increasing the PCA:SHP molar ratio above 1:1 does not improve the PCA percent chemical add-on.
- Alteration of the pad bath pH either to a more acidic or to a more alkaline solution has detrimental effects on the reaction rate. The NaOH or HCl used to alter the pad bath pH, either to a higher pH value or a lower pH value, may have reacted with either the PCA or the catalyst decreasing the quantity of the acid or catalyst available to react with silk fibroin.

- The optimum pH for the reaction was between pH 1.5-2.1 dependent on the PCA/SHP finishing system. At pH 1.5-2.1 the conversion of PCA carbonyl groups to carboxylate ions would be very small. Silk has relatively high stability to acids, with the least degradation occurring between pH 4-8. Acid degradation leads to hydrolysis of the peptide links and subsequent loss in tensile strength and elasticity.
- Decreasing the curing temperature below 165°C decreases the reaction rate. At temperatures above 165°C fabric yellowing occurs due to degradation of the silk fibroin. The temperature at which silk fabric yellows is time-dependent. Fabric yellowing is expected if the time at 165°C is extended longer than 1.5min.
- As the quantity of ester links within the silk fibre increases there is an increase in fabric dry and wet crease recovery angles, both initial recovery from creasing and recovery from creasing after 5min. An improvement in the fabric stability to creasing is likely to be as a result of new fibre inter-chain cross-links being formed during the high temperature curing process or to an intra-molecular PCA polymer network being formed within the silk fibroin, see section 4.2.1.4.
- The increase in fabric recovery from creasing is accompanied by a slight increase in fabric stiffness. This could be as a result of an increase in fibre inter-chain cross-links or a three-dimensional PCA polymer network inside the silk fibroin that decreases the movement of the fibre chain molecules slightly restricting the bending properties of the silk fabrics.
- The improvement in fabric recovery from creasing is accompanied by a slight increase in dry fabric strength. The improvement in dry fabric strength could be as a result of additional cross-links being formed within the fibres. A greater force would be required to break the additional cross-links.
- This improvement in dry fabric strength is not mirrored by an improvement in wet fabric strength. If the PCA forms diester cross-links within the silk fibres then these cross-links should be stable to hydrolysis in water and there would be observed an increase in wet strength. The decrease in wet fabric strength could be caused by an increase in accessibility of the hydrogen bonds that hold the silk fibroin chains together by the water molecules caused by the fibre being cross-linked in a swollen state. The molecular chains within untreated silk fibroin are closely packed together to ensure maximum hydrogen bonding; if the fibre is cross-linked in a swollen state when some of these hydrogen bonds are broken, the structure may be more accessible to attack by water molecules on re-wetting. Alternatively, if the cross-

links consist of mono-ester/ hydrogen bonds, the hydrogen bonds would brake on re-wetting and thus would not contribute to an increase in wet stability.

- There is a decrease in fabric dry and wet elongation at break with an increase in ester links formed within the fibre. This is characteristic of fabrics that have been treated with an easy-care finishing agent. The increased stability of the silk fibroin chain molecules prevents the molecular chains slipping over one another as easily thus limiting the extension at break.

A comparison of the results for the optimum treatment conditions for each of the PCA/SHP finishing systems tested is shown in Table 4. 8. All four PCA/SHP finishing systems improve the crease recovery properties of silk fabric; the BTCA/SHP and the SA/CA/SHP finishing systems were found to give superior results compared with the MA/SHP and the SA/MLA/SHP finishing systems.

Fabric Properties	Control	BTCA/SHP	MA/SHP	SA/CA/SHP	SA/MLA/SHP
Percent Chemical Add-on (%)	0	6.33	4.87	7.05	9.92
FT-IR Ester Frequency Peak Height (mm) NaOH treated fabric	0	22	12	18	17
FT-IR Ester Frequency Peak Height (mm) after 1 wash	0	16	10	16	13
FT-IR Ester Frequency Peak Height (mm) after 10 washes	0	14	10	17	14
FT-IR Ester Frequency Peak Height (mm) after 25 washes	0	14	10	16	12
Fabric Moisture Regain (%)	8.62	7.65	7.39	6.98	6.66
Fabric DCRA (degrees)	196.7	235.9	224.4	238.7	216.3
Fabric WCRA (degrees)	179.9	210.7	206.0	206.5	205.2
Fabric Warp Bending Length (mm)	16.5	21.3	20.5	16.9	17.6
Fabric Weft Bending Length (mm)	24.1	28.9	26.0	26.9	24.9
% Retention Dry Fabric Maximum Load at Break	100	109.1	115.2	117.8	111.5
% Retention Wet Fabric Maximum Load at Break	100	94.9	94.5	98.7	88.7
% Retention Dry Fabric Elongation at Break	100	64.0	60.0	71.3	64.7
% Retention Wet Fabric Elongation at Break	100	79.3	82.7	81.3	83.3
ASTM Yellowness Index	5.11	7.28	7.59	8.04	5.57

Table 4. 8 Comparison of the properties of silk fabrics treated with different PCA/SHP finishing systems.

These results suggest that all four PCA/SHP finishing systems investigated are capable of improving the crease recovery properties of silk fabrics. Measurement of the ester peak height after 1, 10 and 25 washes demonstrate that the ester links are stable to hydrolysis during washing tested up to 25 washes. The fabric properties induced by treatment of silk fabric with a PCA/SHP system are characteristic of a fabric that has been either cross-linked with a fibre inter-chain cross-linking agent and/or treated with a self-cross linking resin.

The hydroxyl-containing amino acids in silk fibroin are capable of forming covalent ester links. Fibre inter-chain cross-links provide anchoring points for the molecular chains and limit excessive movement maintaining the positions of the molecular chains within the fibre. The insertion of strong covalent chemical bonds formed between the molecular chains by a cross-linking agent tend to improve the dimensional stability, improve the stability to heat, increase the strength and elastic recovery of the polymer and decrease fibre swelling in contact with solvents (67).

The results displayed in Table 4. 8 show that there is an increase in the number of ester bonds within the treated fabrics. It can be concluded that the PCAs are reacting with the hydroxyl-containing side groups in silk fibroin forming ester links. These ester links could be single ended, mono-ester, attachments or diester cross-links. Fibre inter-chain cross-links improve the stability of fibres by restricting the movement of the molecular chains. An improvement in the easy-care properties is attributed to an improvement in elastic properties of the fibre; this increased elasticity brings about a return to the original shape of the fabric. There are a number of ways in which the elastic properties of a fibre can be improved including the insertion of fibre inter-chain covalent cross-links between the molecular chains and by the insertion of an interlocking polymer network within the fibre (45). The results from the fabrics treated with PCA/SHP finishing systems displayed in Table 4. 8 suggest that the elastic properties of the fibres have been improved. A high degree of stabilisation within the fabric is necessary so that the relative positions of the fibres and yarns remain unchanged, and the original configuration of the fabric is restored. In order to verify the improved stability of the silk fabrics their behaviour to heat and in concentrated formic acid was investigated.

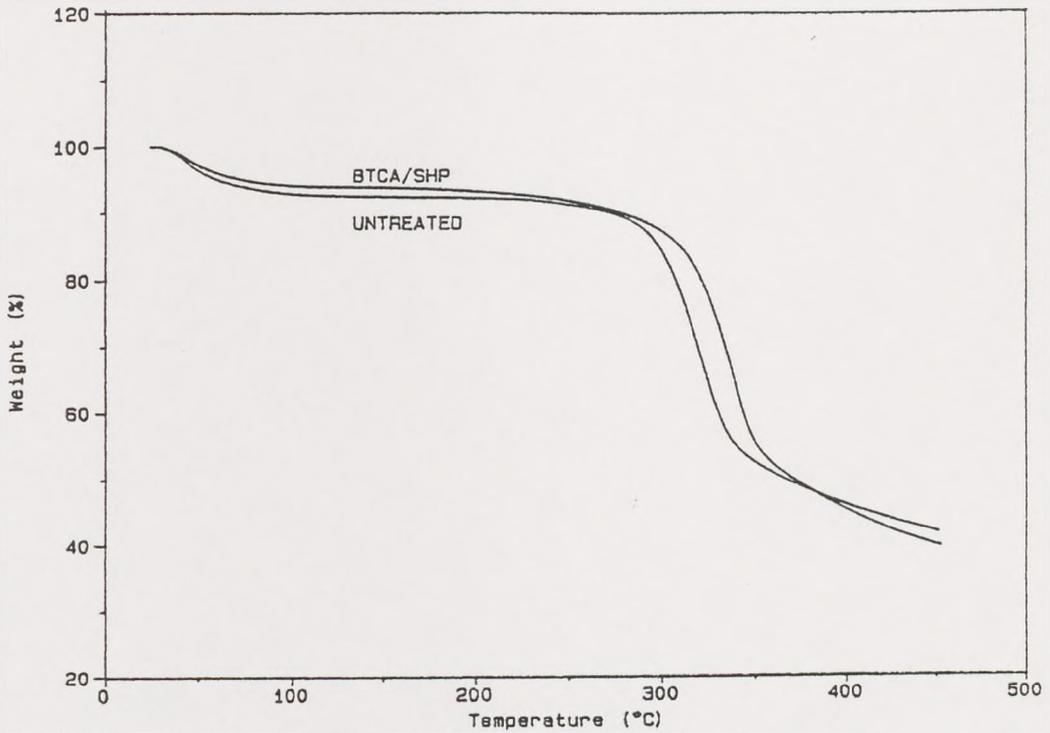


Figure 4. 71 TGA thermogram of silk fabric treated with 6% w/w BTCA and a 1:1 molar ratio mixture of BTCA:SHP compared with a TGA thermogram for the untreated control.

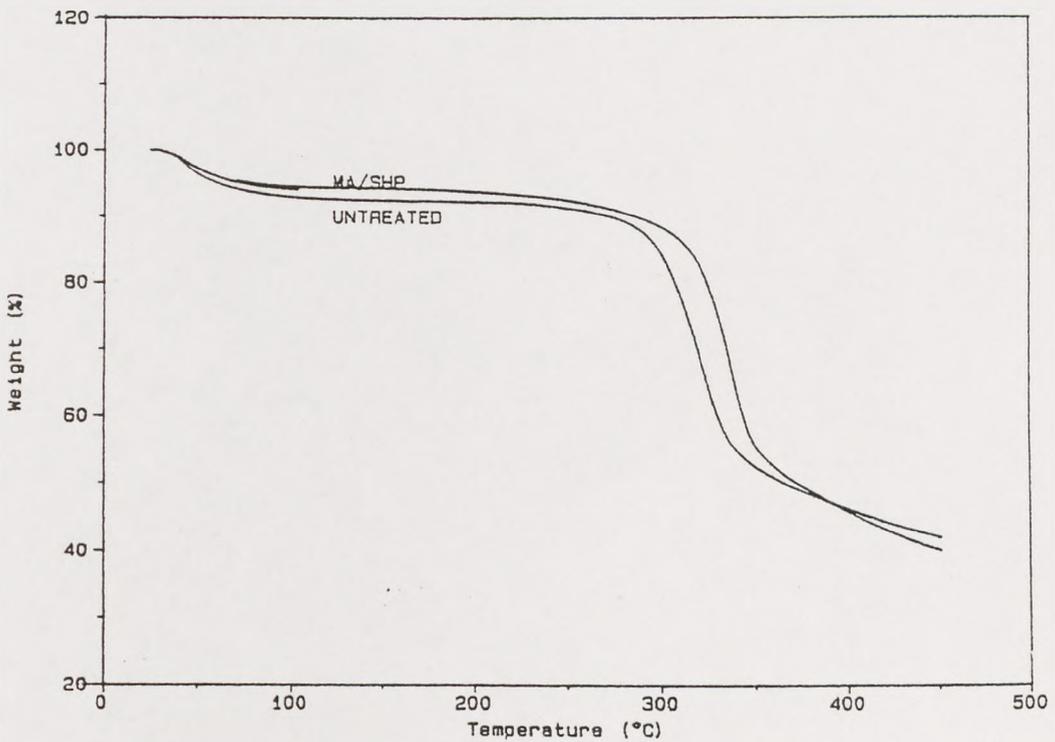


Figure 4. 72 TGA thermogram of silk fabric treated with 6% w/w MA and a 1:1 molar ratio mixture of MA:SHP compared with a TGA thermogram for the untreated control.

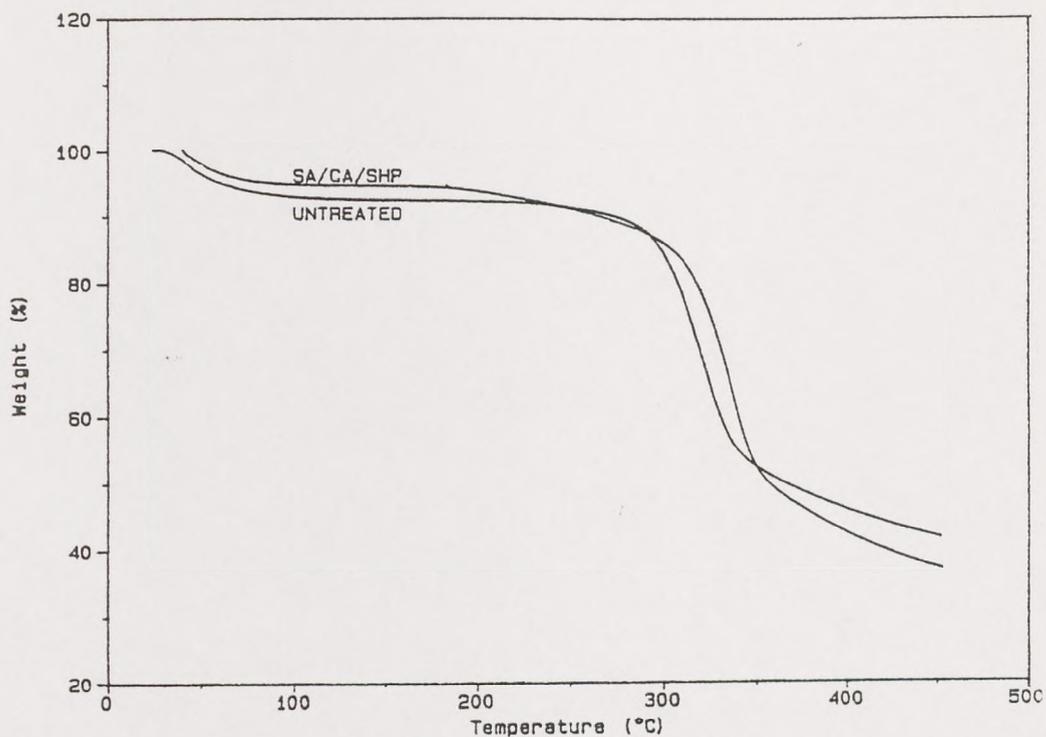


Figure 4. 73 TGA thermogram of silk fabric treated with 3% w/w SA, 4.8% w/w CA and a 1:1 molar ratio mixture of PCA:SHP compared with a TGA thermogram for the untreated control.

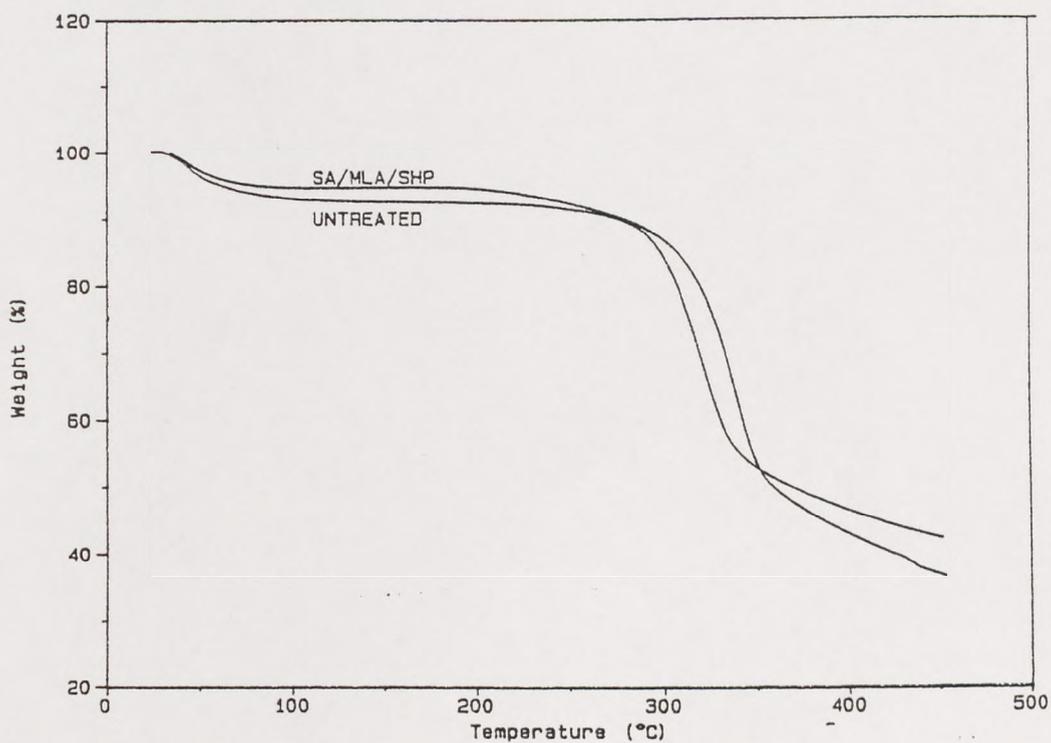


Figure 4. 74 TGA thermogram of silk fabric treated with 4% w/w SA, 6% w/w MLA and a 1:1 molar ratio mixture of PCA:SHP compared with a TGA thermogram for the untreated control.

The TGA thermograms for the PCA/SHP treated fabrics heated to 450°C are displayed in Figure 4. 71 to Figure 4. 72. For all four fabrics treated with the PCA/SHP finishing agent the initial weight loss is less for the treated fabrics compared with the untreated control. This is because the treated fabrics have lower moisture regain values and therefore there are fewer water molecules lost at the beginning of the heating process. It can be clearly seen that all four treated fabrics are stable to higher temperatures than the untreated control. The decomposition temperatures for the treated fabrics are approximately 20°C higher than for the untreated control. Treatment of silk fabrics with a PCA/SHP finishing system thus improves the stability of silk fabric to heat.

It is known that concentrated solutions of organic acids such as formic acid can dissolve silk (82) and in the past this has been used as a method for determining the presence of cross-links in silk fabrics treated with N-methylol compounds. The solubility in 97% formic acid solution was observed for the four treated silk fabrics and an untreated control. The untreated silk control fabric dissolved immediately whereas the silk fabrics treated with the PCA/SHP finishing systems did not completely dissolve even after three days. The treated fabrics do not swell as much in a concentrated solution of formic acid compared with the untreated control. Treatment of silk fabrics with a PCA/SHP finishing system improves the stability of silk fabric to concentrated formic acid solution.

There is strong evidence to support the improved stabilisation of silk fabrics treated with a PCA/SHP finishing system. This fabric stabilisation may be as a result of fibre inter-chain cross-links being inserted into silk fibres or as a result of a three-dimensional PCA polymer network being introduced through treatment with PCA/SHP finishing systems. The treated fabrics have improved stability to heat, reduced swelling in solvents, and improved elastic recovery giving rise to fabrics with improved easy-care properties.

4.2.1.4 Proposed mechanism for the treatment of silk fabric with PCA finishing system.

FT-IR spectra for the treated fabrics exhibit a new band at around 1735cm⁻¹ in common with carbonyl stretching of the ester bond overlapping with carbonyl stretching of the carboxylic acid bond. Treatment of the treated fabrics with a 1M NaOH solution separates the carbonyl band of the ester bond and the carboxylic acid bond by shifting

the carbonyl band of the carboxylic acid group as a result of it reacting with the NaOH forming the sodium salt of the carboxylic acid. It can be assumed that this new band at 1735cm^{-1} is associated with the new ester links formed within the treated fabrics during the high temperature curing process. Measurement of the ester bond peak height was undertaken as a semi-quantitative method of establishing the quantity of ester bonds formed within the treated samples. From Table 4. 8 it can be seen the highest quantity of ester links are formed with samples treated with the BTCA/SHP system, followed by the SA/CA/SHP system, the SA/MLA/SHP system and the lowest quantity with the MA/SHP system.

The quantity of ester links formed within the treated samples is a measure of the esterification reaction. The efficiency of the reaction at improving the easy-care properties of silk fabrics is dependent on the PCA improving the elastic properties and stability of the silk fabrics. Silk fabric treated with all four PCA/SHP finishing systems showed an improvement in initial elastic recovery from creasing in both the dry and wet states. This improvement in elastic properties of the treated silk fabrics could be as a consequence of new fibre inter-chain ester cross-links or a new intra-fibre PCA polymer network being formed within the silk fibres.

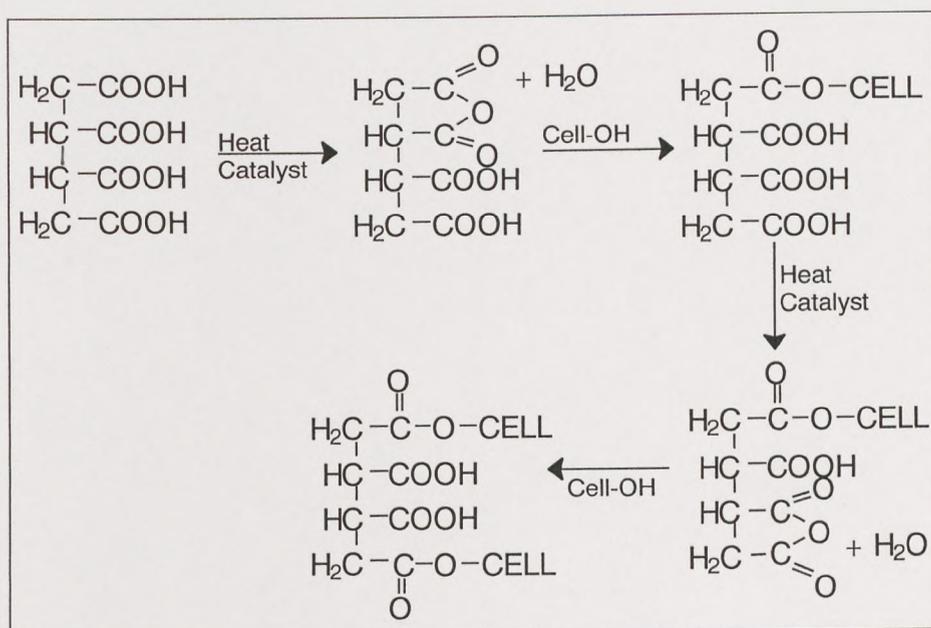


Figure 4. 75 Proposed mechanism by Welch for the esterification reaction of cotton cellulose with BTCA (145).

In the mechanism proposed by Welch (145) for the cross-linking of cotton cellulose by a PCA finishing system, it was considered that for a PCA to be capable of cross-linking

with cotton cellulose a minimum of three carboxylic acid groups per molecule was required, see Figure 4. 75. Welch proposed that the base-catalysed esterification reaction of PCAs with cotton cellulose occurred through the formation of an anhydride intermediate (145). In order that a PCA can form an anhydride intermediate the carboxylic acid side groups need to be on adjacent or next but one carbon atoms. For a di-ester cross-link to be formed within the fibre each acid molecule needs to be capable of forming two anhydride intermediates.

Thermoanalytical and infra-red analysis of the PCA/SHP finishing systems undertaken in section 4.1 concluded that all of the PCA/SHP finishing systems studied in this section were capable of forming an acid anhydride below 160°C, see Table 4.4. This mechanism proposed by Welch could explain the reaction mechanism for the BTCA/SHP system. According to the mechanism proposed by Welch dicarboxylic acids would not be capable of forming diester cross-links with silk fibroin. The results of the MA/SHP and the SA/MLA/SHP finishing systems suggest that silk fabrics treated with these dicarboxylic acid finishes have improved elastic and stability properties. However, these PCA/SHP finishing systems, according to the mechanism proposed by Welch, cannot form fibre inter-chain diester cross-links and the improvement in silk fabric properties must therefore be attributed either to a different mechanism or to a different reaction.

It is known (147) that strong acids are generally required to catalyse the esterification of a monocarboxylic acid and an alcohol, whereas weak bases are known to catalyse the esterification reaction between an acid anhydride and an alcohol. Maleic acid is a stronger acid than BTCA; $pK_{a1} = 1.94$ for maleic acid compared with $pK_{a1} = 3.43$ for BTCA. It is possible that there could be two different esterification reactions occurring between maleic acid and silk fibroin. Base-catalysed esterification of the maleic anhydride and silk fibroin according to the mechanism proposed by Welch (145) and acid-catalysed esterification of maleic acid and silk fibroin, see Figure 4. 76, according to the Fischer esterification mechanism (20), in which the maleic acid itself catalyses the reaction.

Silk fibroin treated with MA/SHP showed increased stability to heat and to dissolution in concentrated formic acid solution. This would suggest that new bonds have been

formed that are more stable. Single ended ester links could be formed within silk fibroin via base-catalysed esterification of maleic anhydride. When the maleic acid anhydride has formed an ester bond, one of the carboxylic acid groups is regenerated. This regenerated carboxylic acid group is unable to form a second anhydride, via the same mechanism, and therefore unable to form a diester cross-link. However, this second carboxylic acid group may be able to form a diester cross-link in silk fibroin via acid-catalysed esterification of maleic acid, according to the mechanism described in Figure 4. 76.

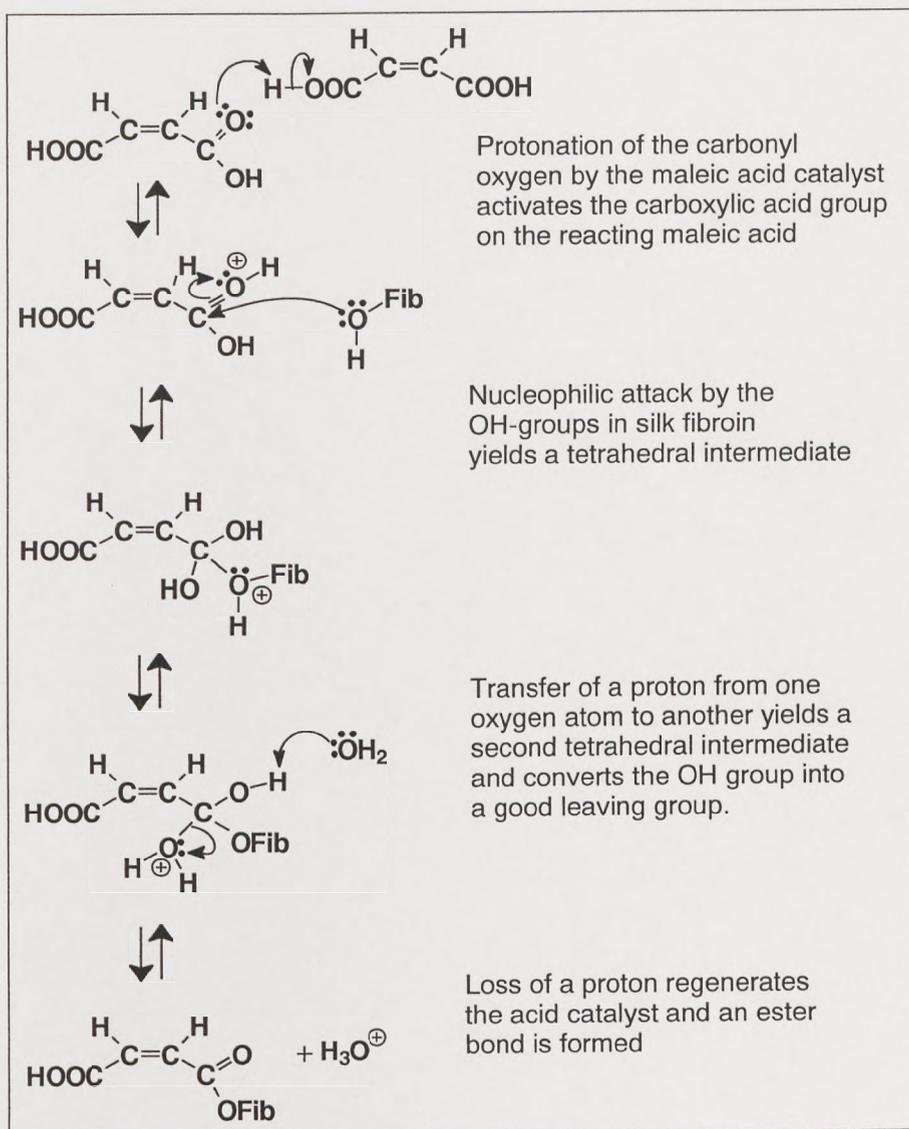


Figure 4. 76 Acid-catalysed esterification of maleic acid and silk fibroin according to the Fischer Esterification Mechanism.

Here the maleic acid itself acts as a catalyst by protonating the carbonyl oxygen of the carboxylic acid group in the reacting maleic acid molecule; this allows for nucleophilic attack by the OH-groups in silk fibroin and formation of a tetrahedral intermediate. The

transfer of a proton from one oxygen atom to another yields a second tetrahedral intermediate that expels this proton with the OH-group originally bonded to the carbonyl carbon. Loss of a proton regenerates the maleic acid catalyst and the ester link between maleic acid and silk fibroin is complete. If the other carboxylic acid group in the maleic acid molecule has already formed an ester link with silk fibroin then an inter-chain diester cross-link may be formed.

This acid-catalysed esterification mechanism for the cross-linking of silk fibroin with maleic acid could explain the large decrease in ester links formed within silk fibroin when the pH value was increased. An increase in the pH value from pH1.5 to pH2.5 saw a decrease in ester peak height measured from 12mm to 4mm. As the pad bath becomes less acidic it would be more difficult for the maleic acid to protonate the carbonyl oxygen in the carboxylic acid group of the maleic acid molecule participating in the reaction. This would also explain the decrease in ester links formed in fabric samples treated with a MA/SHP finishing system with an increase in SHP in the pad bath. An increase in SHP in the pad bath increases the pad bath pH value and decreases the esterification reaction. The incorporation of SHP in the pad bath may act as a buffer and help to prevent acid degradation of silk fibroin.

Alternatively, the unreacted carboxylic acid side groups could form hydrogen bonds with available side groups in silk fibroin. Single ended ester links could form a hydrogen bonded cross-link with the available carboxylic acid side group in maleic acid. These hydrogen bonds would be broken when the silk fabric was immersed in water and therefore would not improve the wet recovery from creasing of the silk fabrics. Silk fabric treated with the MA/SHP finishing system showed some improvement to recovery from creasing in the wet state, both initial elastic recovery and recovery from creasing after five minutes. This improvement in elastic recovery in the wet state could be as a result of di-ester cross-links being formed within the silk fibroin chain molecules. However, some of the maleic acid molecules may only form single ended ester links and therefore the unreacted carboxylic side group would be available to hydrogen bond with silk fibroin. These half-ester, half-hydrogen bonded cross-links would be capable of improving the dry elastic recovery and stability of silk fabrics, but under wet conditions it is presumed that hydrogen bonds would be broken, and the improvements would be lost.

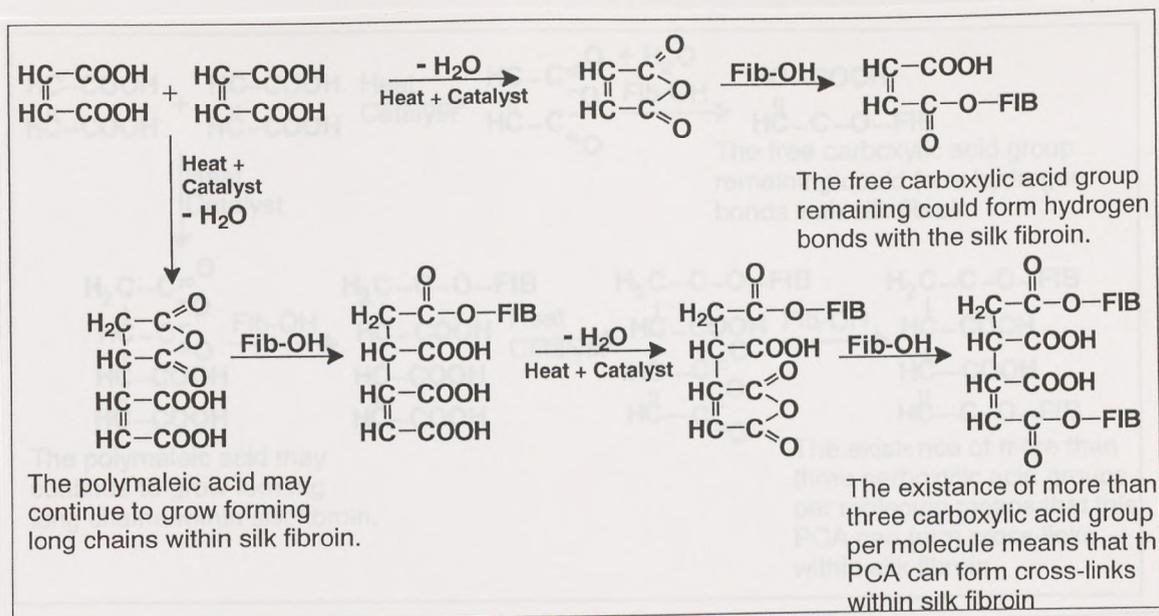


Figure 4. 77 Possible mechanism for the existence of cross-links in silk fabrics treated with Maleic acid.

Another possible mechanism for the existence of di-ester cross-links in silk fabric treated with a MA/SHP finishing system is shown in Figure 4. 77. This mechanism involves the breaking of the unsaturated double bond in the maleic acid molecule and the formation of polymaleic acid molecules. Under the temperature and catalysis conditions used to treat silk fabrics in this thesis this mechanism is unlikely to occur. The incorporation of a free-radical initiating catalyst in the pad bath would initiate the polymerisation reaction. However, when these catalysts were added to the pad bath they caused severe silk fabric discoloration during the curing process, and were therefore considered unsuitable for improving the easy-care properties of silk. This method has been used with some success for improving the easy-care characteristics of cotton fabrics (182)

Silk fabrics treated with the SA/CA/SHP finishing system had crease recovery properties equivalent to silk fabrics treated with BTCA/SHP finish. However, when CA was applied to silk without SA this treated fabric sample had inferior crease recovery properties to BTCA/SHP finished fabrics. This would suggest that the SA plays a key role in the reaction mechanism. As with the MA it is possible that the dicarboxylic acid SA could undergo acid-catalysed esterification of silk fibroin. The citric acid may act as the acid catalyst being more acidic than succinic acid; $pK_{a1} = 4.21$ for succinic acid and $pK_{a1} = 3.13$ for citric acid. Succinic acid is capable of forming a six-membered acid anhydride intermediate that would be capable of forming single ended ester links with

silk fibroin via the base-catalysed esterification mechanism. The unreacted carboxylic acid group may be capable of forming a di-ester link via acid-catalysed esterification of silk fibroin.

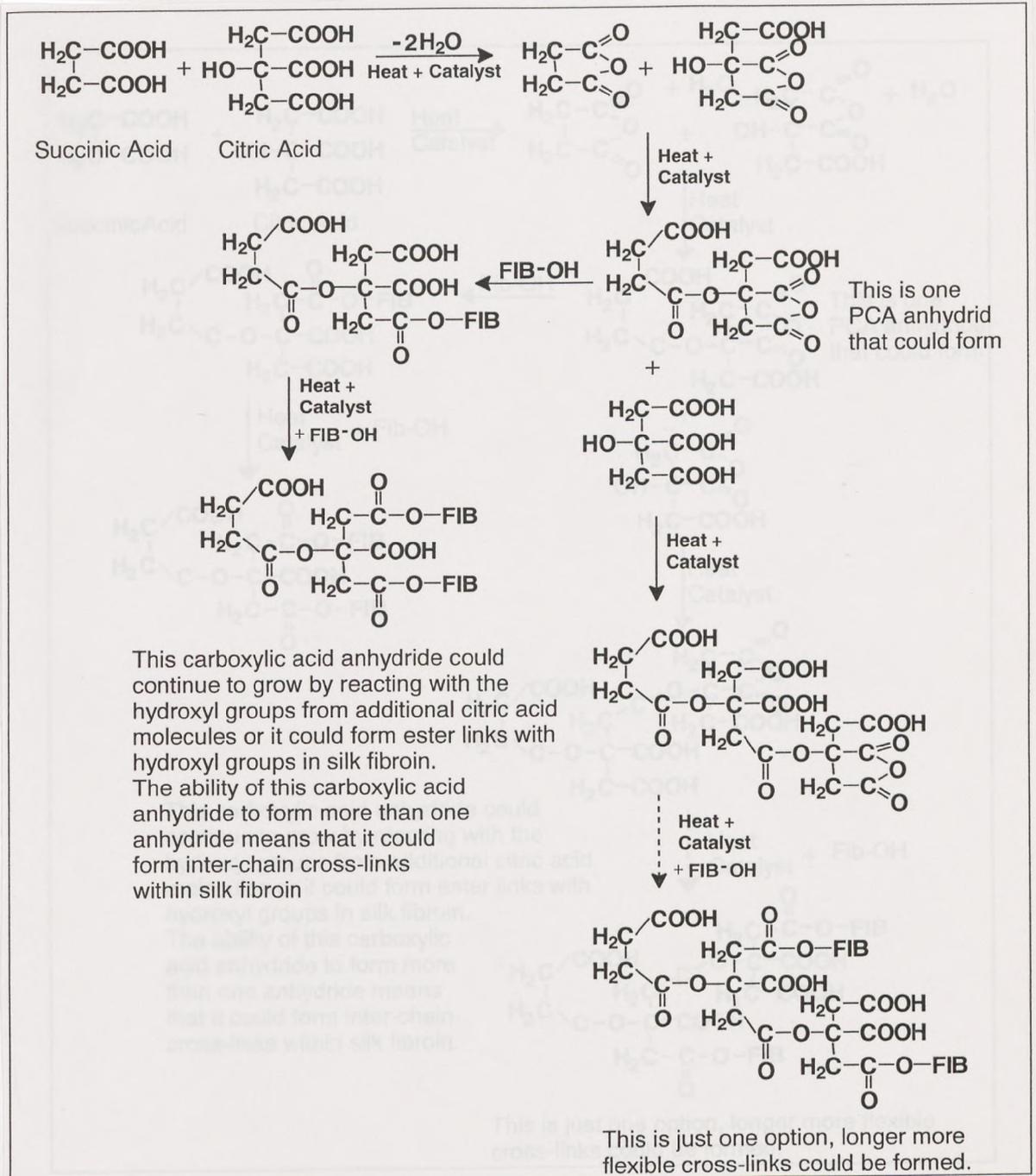


Figure 4.78 Proposed mechanism for one type of cross-link formed when silk fabrics are treated with SA/CA/SHP finishing system.

Alternatively, the succinic acid anhydride may react with the hydroxyl groups in the citric acid molecule, according to the proposed mechanism shown in Figure 4.78. Both citric acid anhydrides and succinic acid anhydrides formed during the high temperature

curing process would be available to react either with the reactive side groups in silk fibroin or with the OH-groups on adjacent citric acid molecules to form ester links.

This mechanism allows for both diester cross-links to be formed and a three-dimensional PCA lattice to form within silk fibroin. The citric acid molecules are capable of forming diester cross-links with silk fibroin and forming ester links with adjacent citric acid anhydrides or succinic acid anhydrides through their hydroxyl side groups. The improved elastic recovery properties and stability of silk fabrics treated with the SA/CA/SHP finishing system may thus be as a result either of diester cross-links being formed within silk fibroin and/or as a result of an interlocking intra-fibre PCA polymer network formed within silk fibroin.

The reduction in mechanical properties of silk fabrics treated with SA/CA/SHP system is less when compared with fabrics treated with either BTCA/SHP or MA/SHP finishes. This improved retention of fabric mechanical properties may be as a consequence of longer more flexible cross-links being formed within silk fibroin; short cross-links can make the fabric brittle. There is a larger reduction in fabric moisture regain with fabric samples treated with the SA/CA/SHP finishing system in comparison with BTCA/SHP or MA/SHP finishing systems. This could be due to large PCA polymers being formed within silk fibroin making the water sites less accessible, or to the amino acids reacting with the PCAs and therefore not being available to react with the water molecules.

Hydrogen bonding of the free carboxylic acid side groups in the PCA molecules would help to improve the dry stability of the treated silk fabric and reduce the available side groups to hydrogen bond with water, thus decreasing the fabric moisture regain. Improving the properties of silk fabric with SA/CA/SHP finish may occur via one of the above mechanisms or may be as a result of a combination of all of the different mechanisms.

The SA/MLA/SHP finishing system may operate according to similar mechanisms described above for the SA/CA/SHP finish. The improved elastic recovery of silk fabric samples treated with SA/MLA/SHP finishing system were not as high as those observed for the BTCA/SHP and the SA/CA/SHP treated samples. However, the improved crease recovery properties and stability to heat and concentrated formic acid solution of

the treated samples is indicative of improved elastic properties and fabric stability. This may arise as a consequence of either diester cross-links being inserted during the high temperature curing process or due to a three-dimensional PCA polymer network being inserted into the silk fibroin.

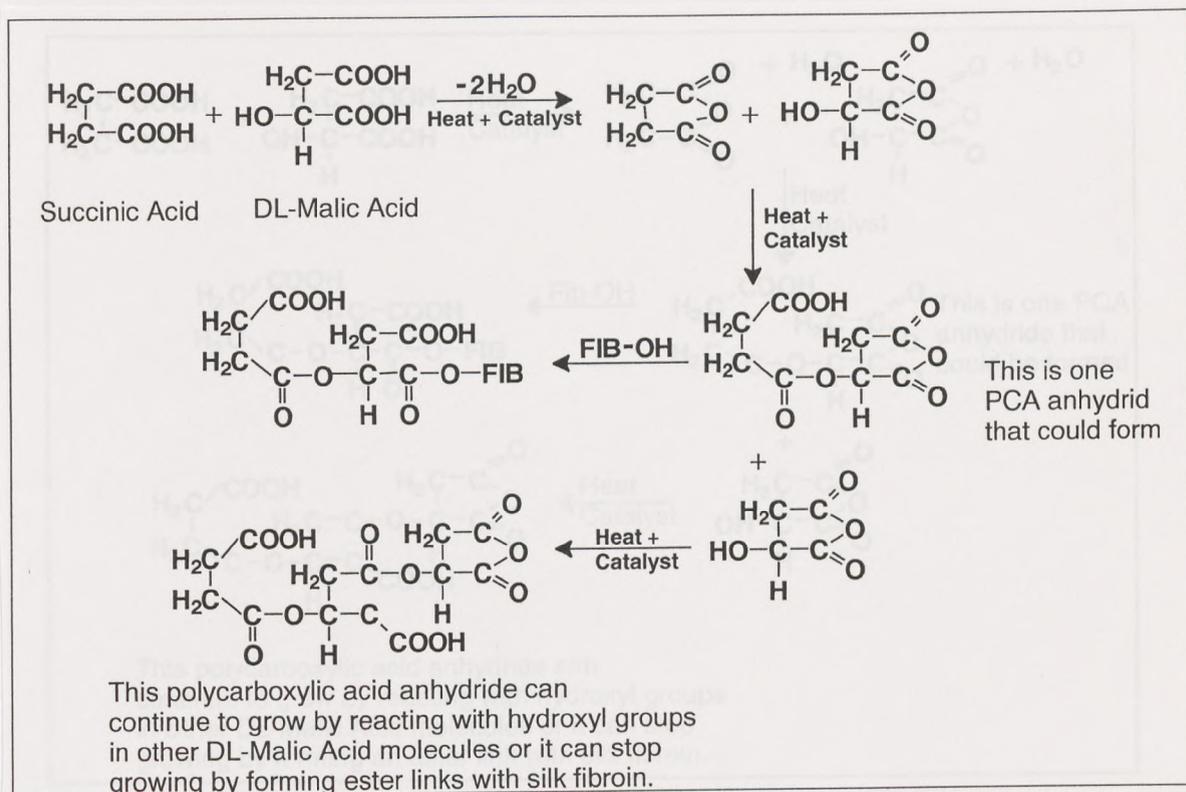


Figure 4. 79 Proposed mechanism for one type of cross-link formed when silk fabrics are treated with SA/MLA/SHP finishing system.

Succinic acid and DL-malic acid are both dicarboxylic acids and are therefore not capable of forming di-ester cross-links via base-catalysed esterification of their anhydrides. This method of esterification of silk fibroin only leads to single ended attachment of the dicarboxylic acid. The carboxylic acid group that is regenerated on formation of an ester cannot form a second anhydride and therefore cannot react with silk fibroin via base-catalysed esterification mechanism. Ester cross-links may be formed via acid-catalysed esterification, according to the mechanism described for maleic acid and depicted in Figure 4. 76, with the dicarboxylic acids themselves catalysing the reaction.

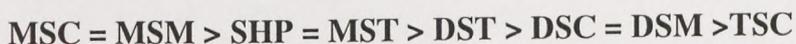
As with the SA/CA/SHP mechanism described the hydroxyl groups in the MLA molecules are capable of forming ester links with the dicarboxylic acid anhydrides formed during the high temperature curing process, see Figure 4. 79. The hydroxyl

groups could react either with another MLA molecule or a SA molecule to form combination acids capable of forming a three-dimensional PCA polymer network within silk fibroin. Unlike the SA/CA polymer network the SA/MLA polymer network is not capable of forming ester cross-links with silk fibroin. The polymer network continues to grow until the anhydride forms an ester link with silk fibroin rather than with a MLA hydroxyl group. The regenerated carboxylic acid groups from ester formation are available to form hydrogen bond links with available side groups in silk fibroin. The lower dry elastic recovery of this system may be as a result of fewer diester cross-links formed within the PCA polymer network.

A series of alternative carboxylic acid mixtures were tested with SHP catalyst, the results of which are displayed in Appendix 2, Table A2.5. None of these systems were as effective silk fabric easy-care finishing agents as BTCA/SHP, MA/SHP, SA/CA/SHP, or SA/MLA/SHP.

4.2.2 Treatment Of Silk Fabric With BTCA And Different Catalysts.

The suitability of using alternative catalysts to SHP was investigated using infra-red and thermoanalytical analysis, the results of which are summarised in Table 4. 6. From these results it was concluded that the order of catalyst suitability calculated by the ease with which BTCA is capable of forming an anhydride is as follows:



These catalysts are examined as alternatives to SHP and the results analysed for their suitability as PCA esterification catalysts.

Cyanamide was also studied as an alternative catalyst to SHP. Thermoanalytical and infra-red analysis of the BTCA/CY acid/catalyst system was not undertaken as CY was identified as a possible explosive and it was therefore thought unsafe to heat this chemical reagent in powder form to high temperatures (183). This catalyst has been used with some success in the dyeing of cotton fabric with reactive dyes containing phosphorus acid or carboxylic acid groups (184, 185). It is proposed that the cyanamide functions as a dehydrating agent (185), see Figure 4. 80. Cyanamide has been tested as a catalyst for the reaction of BTCA with cotton cellulose (186). FT-IR analysis of the

treated cotton fabric was found to form ester links when cured at 150°C.

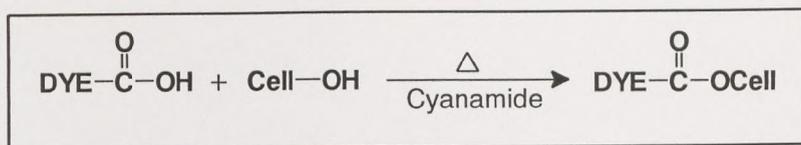


Figure 4. 80 Proposed reaction of a carboxylic acid reactive dye with cotton cellulose in the presence of heat and cyanamide catalyst.

4.2.2.1 Experimental procedure.

Plain woven silk Habutai heavy, roll 4, see section 2.1.1, was treated with 6%w/w BTCA and a variety of different catalysts, see Table 4. 9. These BTCA/catalyst systems were applied to silk fabric via a pad-batch-cure method, as described in section 2.1. Each BTCA/catalyst system was investigated with regard to different BTCA:catalyst molar ratios, and a variety of pad bath pH values and curing conditions, see Table 4. 9.

BTCA:Catalyst Molar Ratio	Pad Bath pH	Curing Conditions
BTCA:MSC 1:0.5, 1:1, 1:1.5 and 1:2	-	165°C for 1.5min
BTCA:MSC 1:1	pH1.5, pH2.5 and pH3.2	165°C for 1.5min
BTCA:MSC 1:1	-	120°C for 5min, 150°C for 2min and 165°C for 1.5min
BTCA:DSC 1:1	-	120°C for 5min, 150°C for 2min and 165°C for 1.5min
BTCA:TSC 1:1	-	120°C for 5min, 150°C for 2min and 165°C for 1.5min
BTCA:MST 1:0.5, 1:1, 1:1.5 and 1:2	-	165°C for 1.5min
BTCA:MST 1:1	pH1.5, pH2.9 and pH3.5	165°C for 1.5min
BTCA:MST 1:1	-	120°C for 5min, 150°C for 2min and 165°C for 1.5min
BTCA:DST 1:1	-	120°C for 5min, 150°C for 2min and 165°C for 1.5min
BTCA:MSM 1:0.5, 1:1, 1:1.5 and 1:2	-	165°C for 1.5min
BTCA:MSM 1:1	PH1.5, pH2.48 and pH3.5	165°C for 1.5min
BTCA:MSM 1:1	-	120°C for 5min, 150°C for 2min and 165°C for 1.5min
BTCA:DSM 1:1	-	120°C for 5min, 150°C for 2min and 165°C for 1.5min
BTCA:CY 1:0.5, 1:1, 1:2 and 1:3	-	165°C for 1.5min
BTCA:CY 1:1	pH1, pH1.8 and pH3	165°C for 1.5min
BTCA:CY 1:1	-	120°C for 5min, 150°C for 2min and 165°C for 1.5min

Table 4. 9 Summary of the conditions used for the treatment of silk fabric with BTCA and a variety of different catalysts.

The treated samples were conditioned for 48h and tested with respect to percent chemical add-on, regain, infra-red ester frequency peak height, fabric dry and wet crease recovery angles, fabric warp and weft bending length, fabric retention of tensile strength and fabric retention of elongation at break. Sample testing was carried out according to the test methods described in section 2.2 and comparisons of the results were made with an untreated control.

4.2.2.2 Results and discussion.

The test results are tabulated in Appendix 2, Table A2.6 to Table A2.9 and the results appear in graphical form in the text, Figure 4. 81 to Figure 4. 88.

4.2.2.2.1 BCTA/mono-, di- or trisodium citrate.

Figure 4. 81 and Figure 4. 82 graphically illustrate the results of silk fabric treated with 6%w/w BTCA and varying molar ratios of BTCA:MSC. As the molar ratio increases above a molar ratio of 1:1 there is very little increase in percent chemical add-on or FT-IR ester frequency peak height, see Appendix 2, table A2.6. The following observations were made.

- As the molar ratio increases there is a slight increase in dry crease recovery angle, both the initial elastic recovery and the recovery from creasing after 5min begin to level off after a molar ratio of 1:1. The wet fabric crease recovery angle peaks at a molar ratio of 1:1. When testing using the Shirley Crease Recovery Test the fabrics treated with BTCA/MSC finish sprung back after having been creased much more readily than fabrics treated with alternative PCA finishing systems.
- An increase in MSC in the pad path has minimal effect on fabric stiffness and slightly decreases the fabric tensile properties.
- Altering the pad bath pH or decreasing the curing temperature below 165°C decreases the rate of the reaction.
- Replacing MSC with either DSC or TSC does not improve the effectiveness of the PCA finishing agent.

The optimum BTCA:MSC molar ratio is 1:1 and MSC is a more efficient catalyst than either DSC or TSC. Thermoanalytical and infra-red analysis of these acid/catalyst systems showed that when using MSC as catalyst the BTCA formed an anhydride at a lower temperature than with either DSC or TSC. The results indicate that the acid anhydride formation is the rate-determining step in the reaction of a PCA with silk.

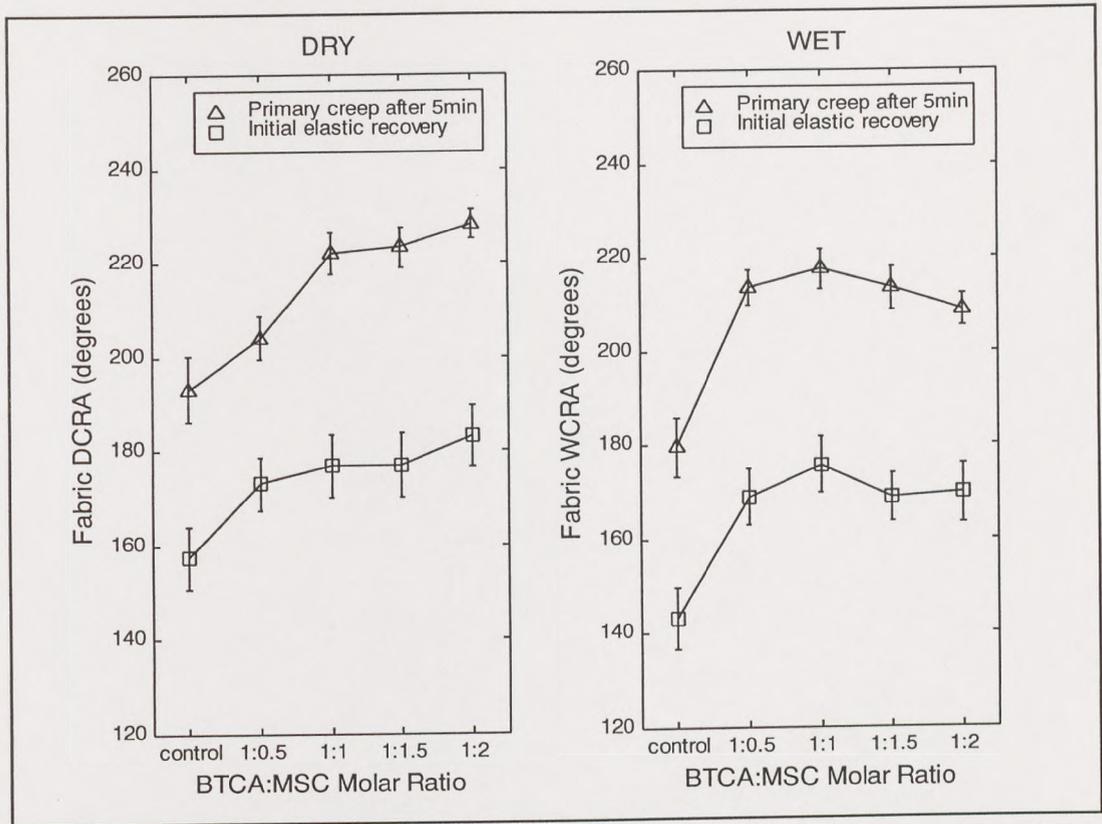


Figure 4.81 Fabric CRAs of silk fabric treated with 6% w/w BTCA and varying molar ratios of MSC.

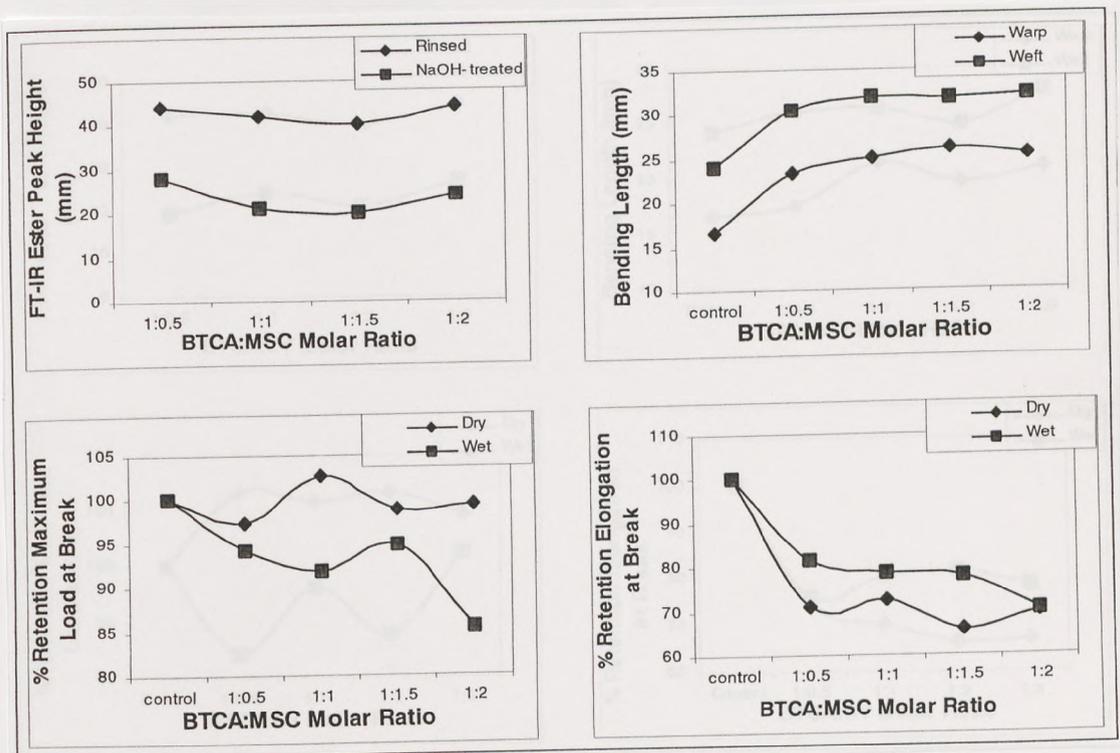


Figure 4.82 Graphical representation of the properties of silk fabric treated with 6% w/w BTCA and varying molar ratios of MSC. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

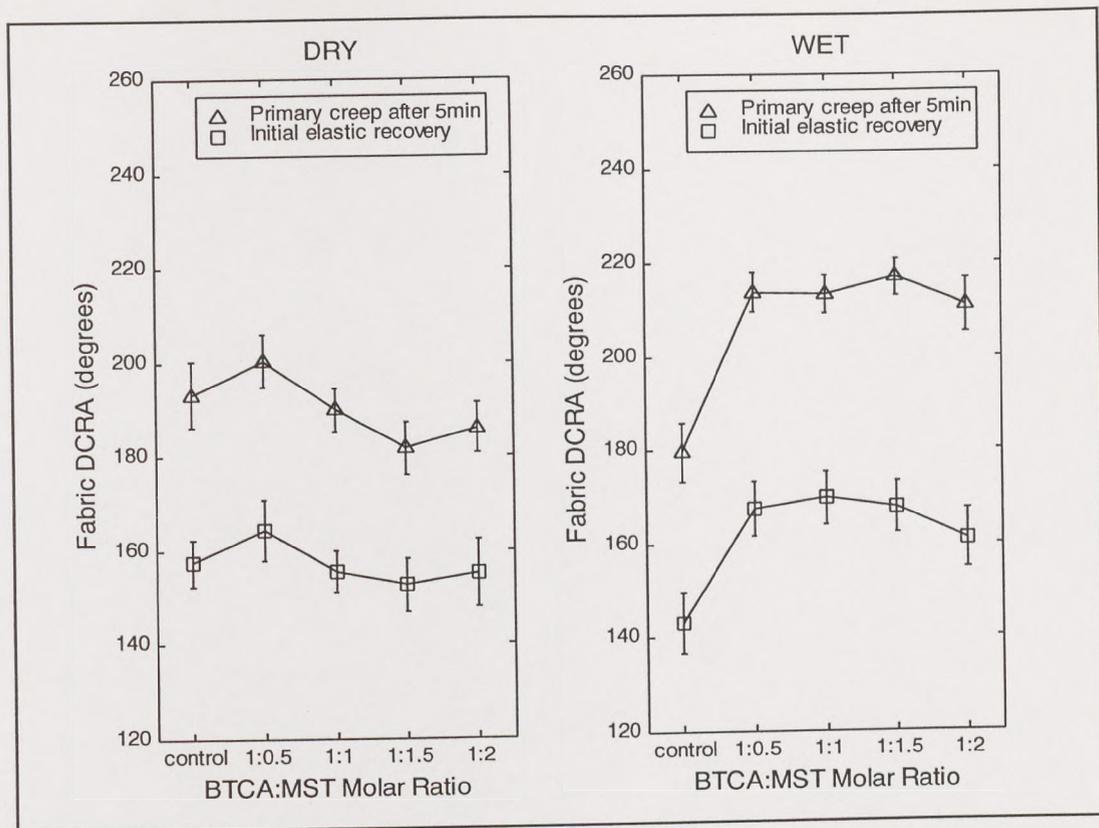


Figure 4.83 Fabric CRAs of silk fabric treated with 6% w/w BTCA and varying molar ratios of MST.

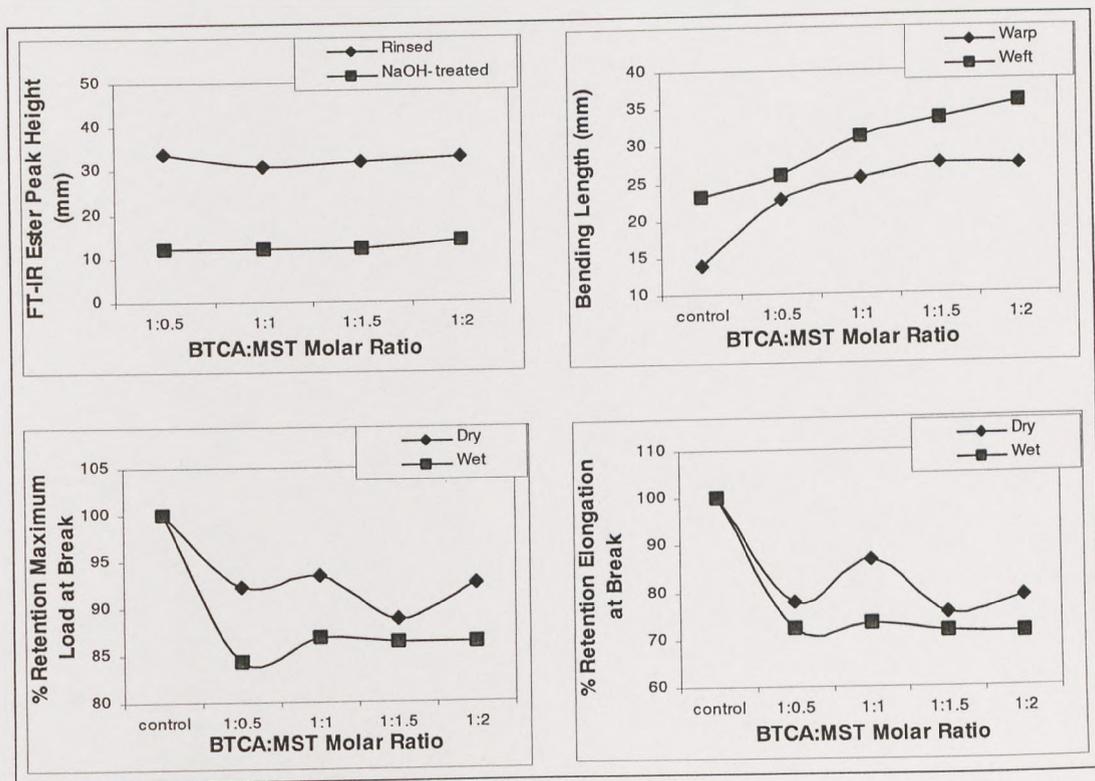


Figure 4.84 Graphical representation of the properties of silk fabric treated with 6% w/w BTCA and varying molar ratios of MST. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

4.2.2.2.2 BTCA/mono-, or disodium tartrate.

Figure 4. 83 and Figure 4. 84 display the results of silk fabric treated with 6%w/w BTCA and varying molar ratios of BTCA:MST. As the molar ratio increases above a molar ratio of 1:0.5 there is very little increase in percent chemical add-on or FT-IR ester frequency peak height, see Appendix 2, table A2.7. The following observations were made.

- An increase in BTCA:MST molar ratio decreases the dry crease recovery angle, both the initial elastic recovery and the recovery from creasing after 5min. This is accompanied by an increase in fabric stiffness shown by an increase in fabric warp and weft bending lengths. Increasing the BTCA:MST molar ratio above 1:0.5 does not improve the fabric wet crease recovery angle.
- An increase in MST in the pad path has minimal effect on fabric tensile properties.
- A more acid pH leads to an increase in percent chemical add-on and an increase in ester frequency peak height. However, this is not accompanied by an increase in wet crease recovery angle. A more alkaline pad bath pH or a cure temperature below 165°C decreases the rate of the reaction.
- Replacing MST with DST does not improve the effectiveness of the fabric finish.

The optimum BTCA:MST molar ratio is 1:0.5 and MST is a more efficient catalyst than DST. MST is not as efficient a catalyst as MSC. Thermoanalytical and infra-red analysis of these acid/catalyst systems showed that when using MSC as catalyst the BTCA formed an anhydride at a lower temperature than with either the MST or DST. The results support the theory that the acid anhydride formation is the rate-determining step in the reaction of a PCA with silk fibroin.

4.2.2.2.3 BTCA/mono-, disodium maleate.

Figure 4. 85 and Figure 4. 86 graphically show the results of silk fabric treated with 6%w/w BTCA and varying molar ratios of BTCA:MSM. As the molar ratio increases to a molar ratio of 1:1.5 there is a slight increase in percent chemical add-on and FT-IR ester frequency peak height, see Appendix 2, table A2.8. The following observations were made.

- An increase in BTCA:MSM molar ratio increases the dry and wet crease recovery angles, both the initial elastic recovery and the recovery from creasing after 5min
- An increase in MSM in the pad path has minimal effect on fabric bending or fabric

tensile properties.

- Altering the pad bath pH or decreasing the cure temperature below 165°C decreases the rate of the reaction.
- Replacing MSM with DSM does not improve the fabric properties.

The optimum BTCA:MSM molar ratio is 1:1.5 and MSM is a more efficient catalyst than DSM. MSM is not as an efficient catalyst as MSC, but is a more efficient catalyst than MST.

4.2.2.2.4 BTCA/Cyanamide.

Figure 4. 87 and Figure 4. 88 display the results of silk fabric treated with 6%w/w BTCA and varying molar ratios of BTCA:CY. As the molar ratio increases to a molar ratio of 1:3 there is a slight increase in percent chemical add-on and FT-IR ester frequency peak height, see Appendix 2, table A2.9. The following observations were made.

- An increase in BTCA:CY molar ratio to a molar ratio of 1:2 increases the dry and wet crease recovery angles, both the initial elastic recovery and the recovery from creasing after 5min. A BTCA:CY molar ratio above 1:2 leads to a decrease in both dry and wet crease recovery angles.
- An increase in CY in the pad path has minimal effect on fabric bending or fabric tensile properties.
- Altering the pad bath pH or decreasing the cure temperature below 165°C decreases the rate of the reaction.

The optimum BTCA:CY molar ratio is 1:2. CY is an effective esterification catalyst and is of equivalent efficiency to both SHP and MSC. Thermoanalytical and infra-red analysis of the BTCA/CY acid/catalyst system was not undertaken as CY was identified as a possible explosive and it was therefore thought unsafe to heat this chemical reagent in powder form to high temperatures (183). CY is a successful catalyst for the esterification of reactive dyes onto cotton cellulose (185). It has been used at temperatures in excess of those used to cure silk fabrics and is therefore not thought to be a safety risk. However, CY is not as effective an alternative to SHP as MSC because CY causes a higher degree of fabric yellowing, it is less environmentally friendly, its use involves careful handling and there is a small risk of explosion.

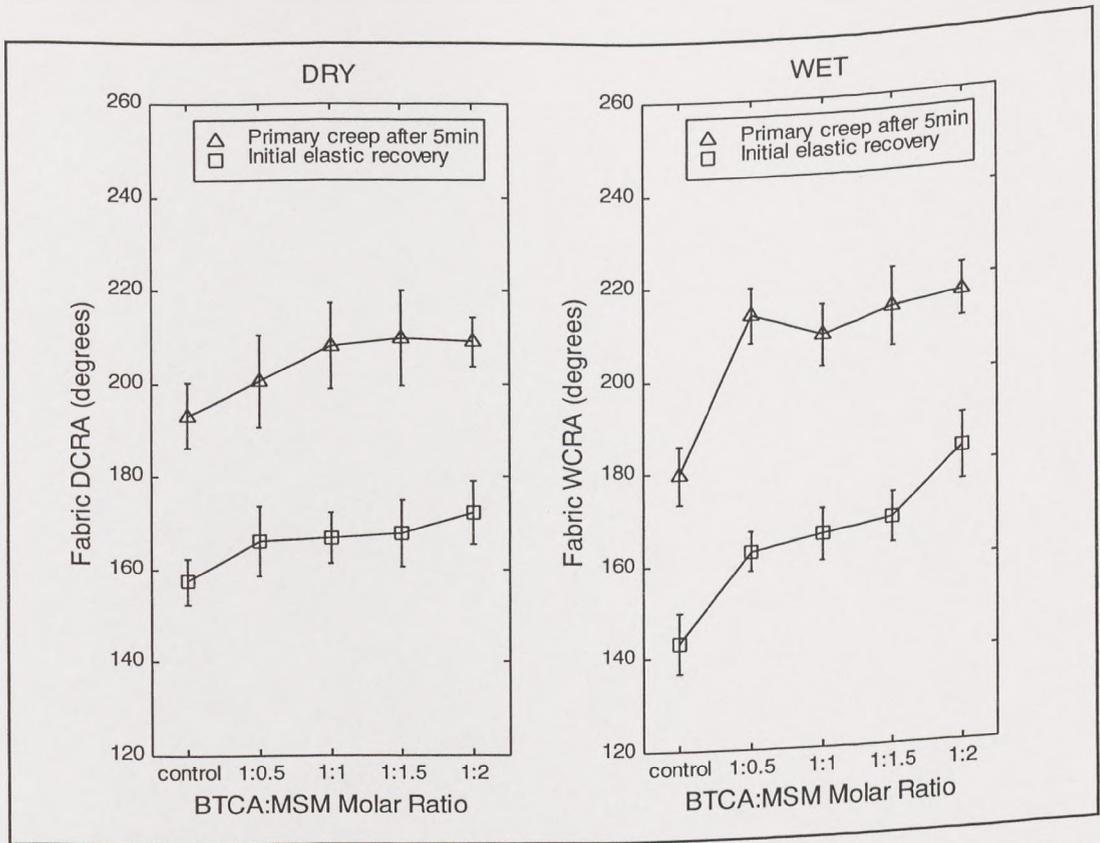


Figure 4.85 Fabric CRAs of silk fabric treated with 6% w/w BTCA and varying molar ratios of MSM.

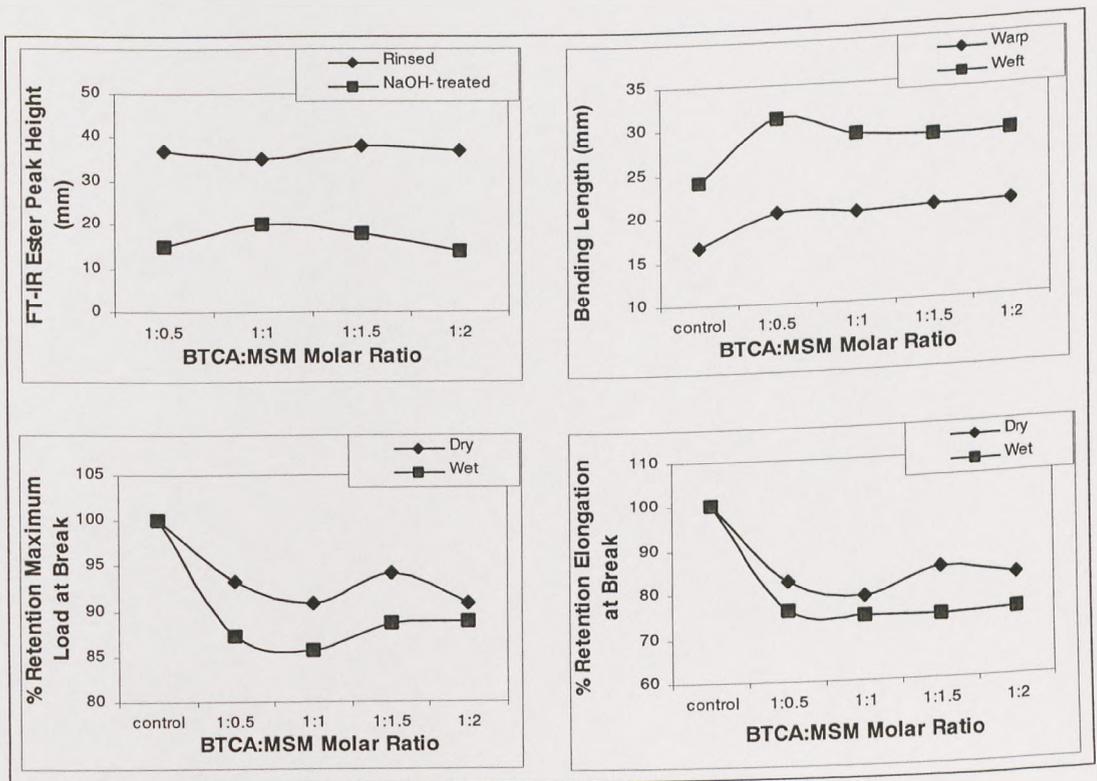


Figure 4.86 Graphical representation of the properties of silk fabric treated with 6% w/w BTCA and varying molar ratios of MSM. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

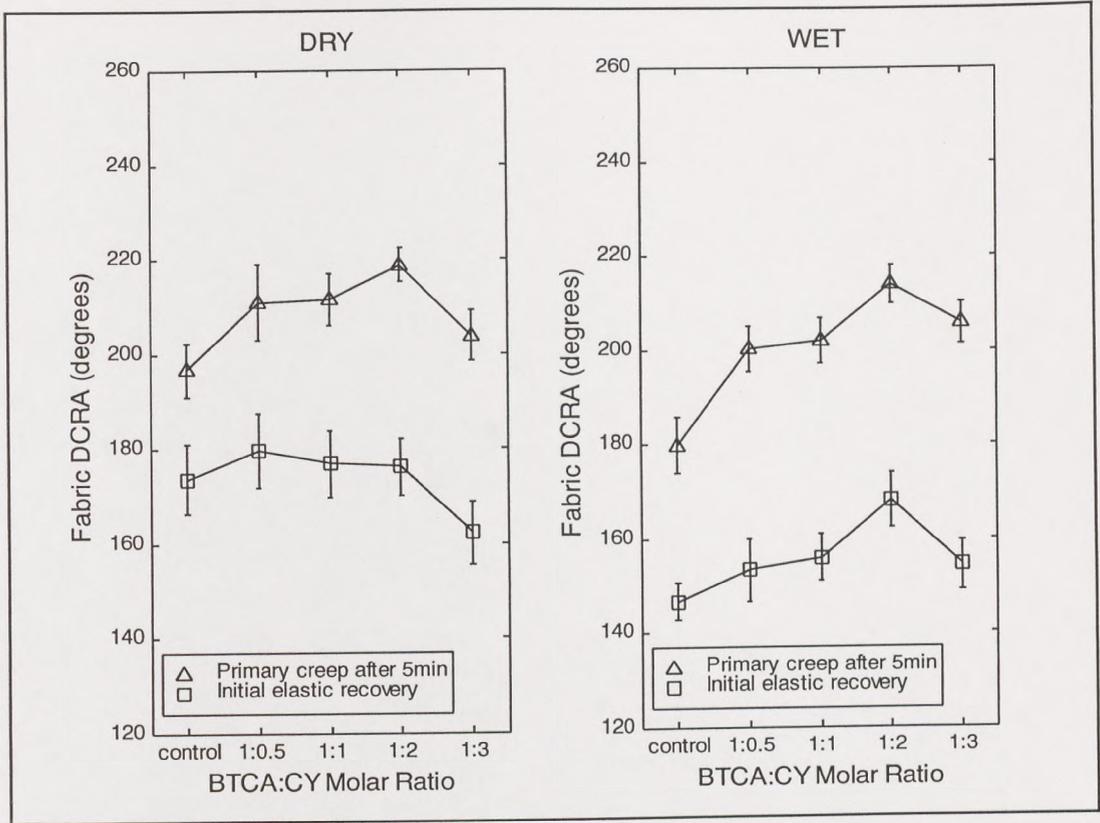


Figure 4.87 Fabric CRAs of silk fabric treated with 6% w/w BTCA and varying molar ratios of CY.

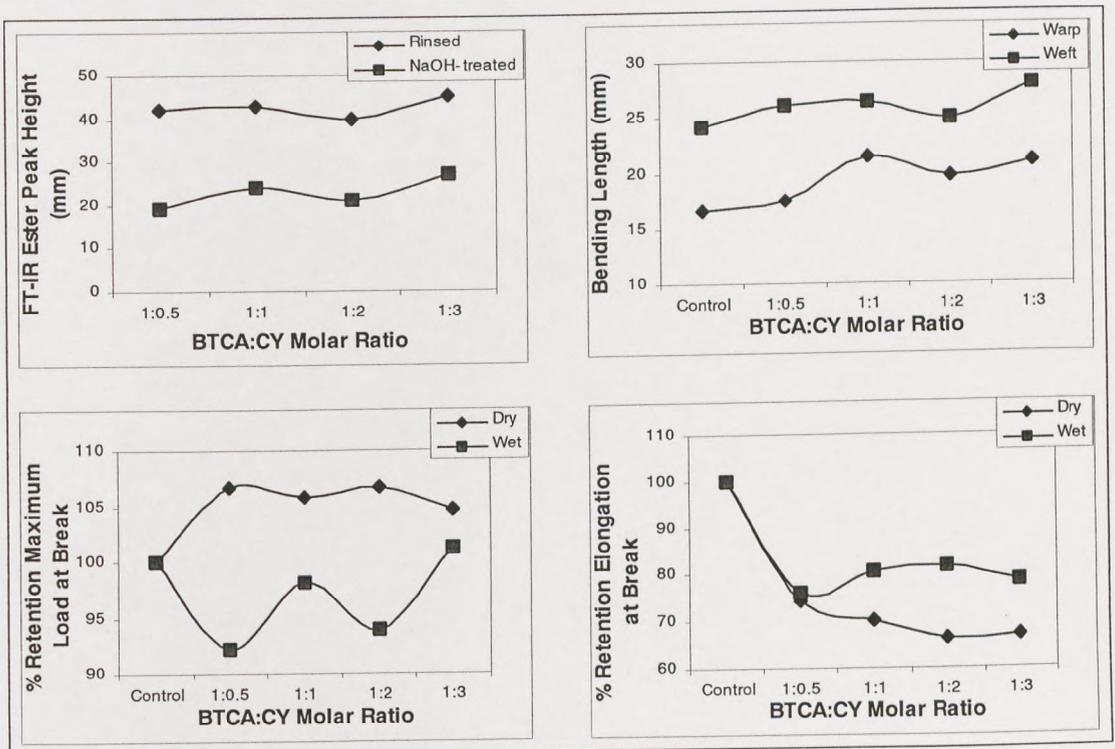


Figure 4.88 Graphical representation of the properties of silk fabric treated with 6% w/w BTCA and varying molar ratios of CY. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

4.2.2.3 Comparison of Results.

A number of trends can be identified in the treatment of silk fabrics with BTCA and sodium salts of di- and tricarboxylic acids as catalysts.

- The monosodium salts were more efficient catalysts than either the di- or tri- sodium salts. Thermoanalytical and infra-red analysis of these acid/catalyst systems showed that the monosodium salts lowered the temperature at which BTCA formed an anhydride more than the di- and trisodium salts. The results support the theory that the acid anhydride formation is the rate-determining step in the reaction of a PCA with silk fibroin.
- The more substituted is a carboxylic acid, i.e. the greater the number of sodium ions per carboxylic acid molecule, the less effective its catalytic action. Andrews and Morris (157) reported that the efficiency of the sodium citrates as catalysts for PCA finishing of cotton cellulose was found to improve with an increase in the number of Na⁺ ions attached to the citric acid. The reason for this opposing view may be due to the curing temperature used to cure the cotton fabrics. If a high temperature, ie above 200°C, was used to cure the cotton fabrics the monosodium citrate may have decomposed and therefore not been available to catalyse the reaction.
- BTCA percent chemical add-on eventually reaches a maximum above which no improvement in chemical reaction is achieved. Increasing the quantity of catalyst in the pad bath does not further improve the BTCA percent chemical add-on.
- Alteration of the pad bath pH either to a more acidic or to a more alkaline solution decreases the extent of the reaction. The addition of the pad bath additive used to alter the pad bath pH may have reacted with either the acid or catalyst in the pad bath; this would decrease the quantity of either the acid or catalyst available to take part in the esterification reaction.
- Decreasing the cure temperature below 165°C decreases the rate of the reaction.
- As the quantity of ester links within the silk fibre increases there is an increase in fabric dry and wet crease recovery angles, both initial recovery from creasing and recovery from creasing after 5min. An improvement in the elastic recovery from creasing could be as a result of new fibre inter-chain cross-links or an intra-fiber polymer network being formed during the high temperature curing process.
- Silk fabrics treated with BTCA are slightly stiffer and are have lower values of dry and wet elongation at break. This is characteristic of fabrics that have been treated

with either a fibre or a self cross-linking agent. The strong covalent cross-links hold the chain molecules in place more securely limiting the bending and extension properties of the fabric.

A comparison of the results for the optimum treatment conditions for each of the BTCA/Catalyst finishing systems tested is shown in Table 4. 10. All five BTCA/Catalyst finishing systems improved the crease recovery properties of silk fabrics compared with the untreated control and the ester links were found to be stable to washing tested up to 25 washes. The order of effectiveness of the catalysts is as follows:

$$\text{MSC} = \text{SHP} > \text{CY} > \text{MSM} > \text{MST}$$

MSC is a viable alternative to SHP as a catalyst for the PCA finishing of silk fabric. MSC is cheaper and more environmentally friendly than SHP.

Fabric Properties	Control	BTCA/ SHP	BTCA/ MSC	BTCA/ MST	BTCA/ MSM	BTCA/ CY
Percent Chemical Add-on (%)	0	6.33	9.12	8.82	9.18	8.12
FT-IR Ester Frequency Peak Height (mm) NaOH treated fabric	0	22	21	12	18	21
FT-IR Ester Frequency Peak Height (mm) after 1 wash	0	16	15	8	10	14
FT-IR Ester Frequency Peak Height (mm) after 10 washes	0	14	14	8	9	13
FT-IR Ester Frequency Peak Height (mm) after 25 washes	0	14	15	6	9	12
Fabric Moisture Regain (%)	8.62	7.65	7.74	7.82	7.79	7.44
Fabric DCRA (degrees)	196.7	235.9	222.1	200.3	209.8	218.8
Fabric WCRA (degrees)	179.9	210.7	217.6	213.7	214.1	214.0
Fabric Warp Bending Length (mm)	16.5	21.3	24.9	22.7	20.6	19.6
Fabric Weft Bending Length (mm)	24.1	28.9	31.9	25.9	28.6	24.9
% Retention Dry Fabric Maximum Load at Break	100	109.1	102.7	92.2	94.2	106.6
% Retention Wet Fabric Maximum Load at Break	100	94.9	91.9	84.3	88.7	93.9
% Retention Dry Fabric Elongation at Break	100	64.0	72.5	77.9	84.8	66.4
% Retention Wet Fabric Elongation at Break	100	79.3	78.7	72.4	74.4	81.4
ASTM Yellowness Index	5.11	7.28	8.93	8.21	8.33	11.14

Table 4. 10 Comparison of the properties of silk fabrics treated with different BTCA/Catalyst finishing systems.

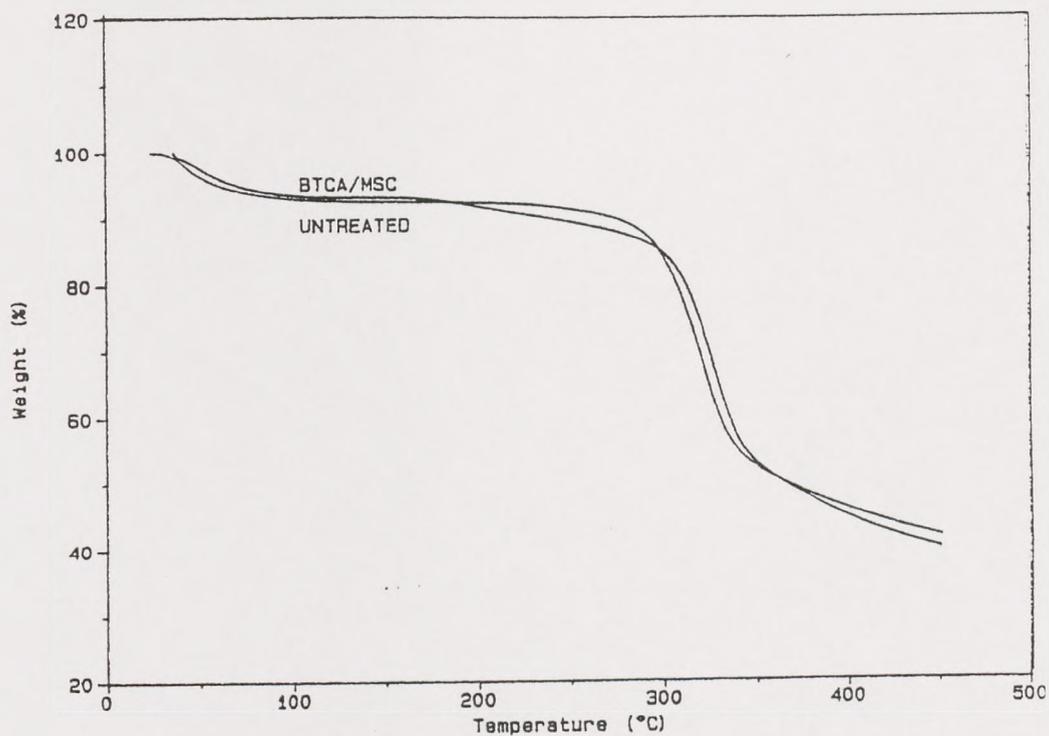


Figure 4.89 TGA thermogram of silk fabric treated with 6% w/w BTCA and a 1:1 molar ratio mixture of BTCA:MSC compared with a TGA thermogram for the untreated control.

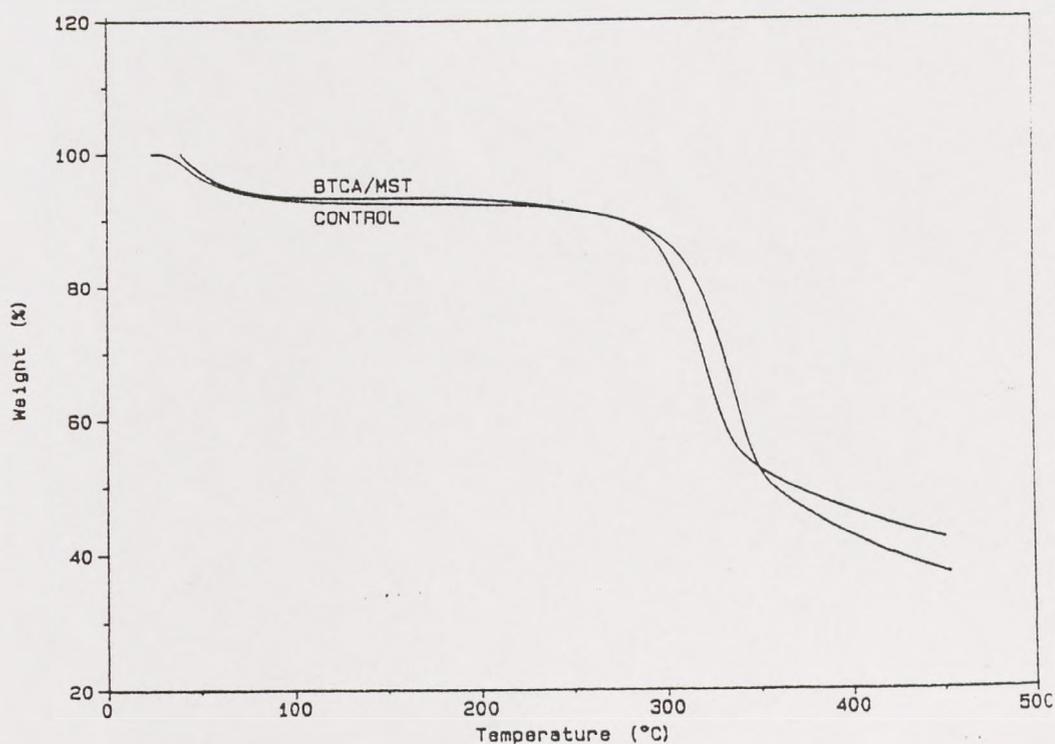


Figure 4.90 TGA thermogram of silk fabric treated with 6% w/w BTCA and a 1:1 molar ratio mixture of BTCA:MST compared with a TGA thermogram for the untreated control.

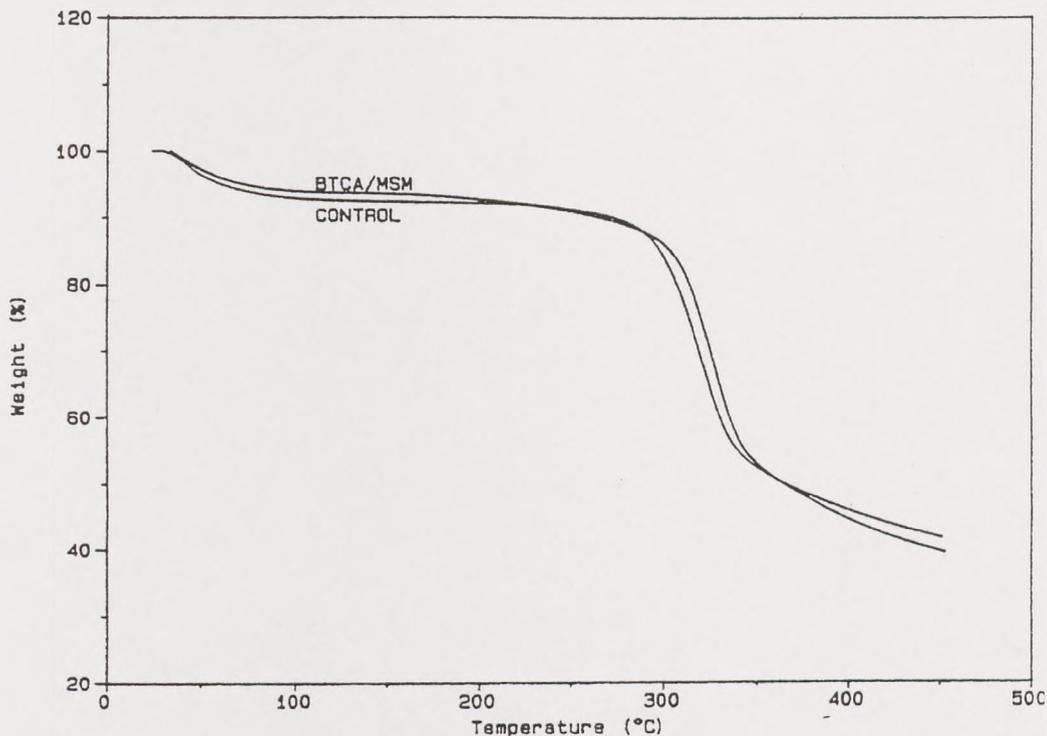


Figure 4.91 TGA thermogram of silk fabric treated with 6% w/w BTCA and a 1:1 molar ratio mixture of BTCA:MSM compared with a TGA thermogram for the untreated control.

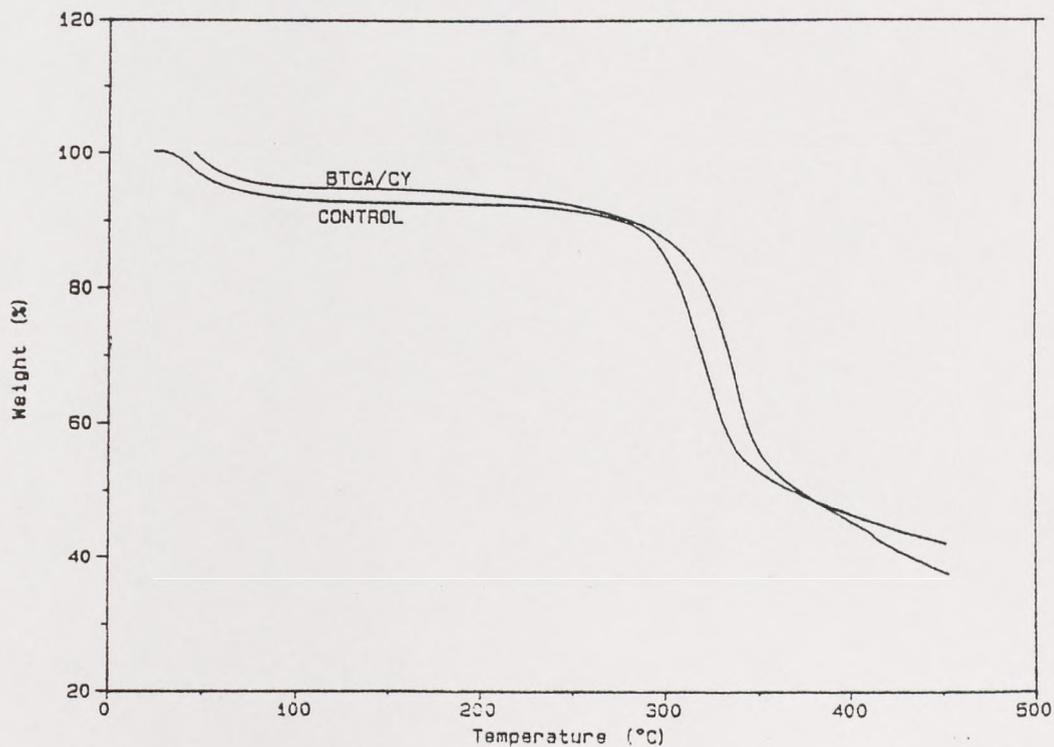


Figure 4.92 TGA thermogram of silk fabric treated with 6% w/w BTCA and a 1:1 molar ratio mixture of BTCA:CY compared with a TGA thermogram for the untreated control.

TGA thermograms for BTCA treated fabrics heated to 450°C are displayed in Figure 4. 89 to Figure 4. 92. When the reaction was catalysed by SHP, the monosodium salt of CA, TA and MA, or CY the treated fabrics were found to be stable to higher temperatures than the untreated control. The decomposition temperatures for the treated fabrics are approximately 20°C higher than for the untreated control. Treatment of silk fabrics with these finishing systems improves the stability of silk fabric to heat.

Treatment of silk fabrics with BTCA in the presence of SHP, the monosodium salt of CA, TA and MA, or CY improved the stability of the treated silk fabric to concentrated solutions of formic acid. The solubility in 97% formic acid solution was observed for the treated fabrics in comparison with an untreated control. The control silk dissolved immediately whereas the silk fabrics treated with the BTCA finishing systems did not completely dissolve even after three days. Treatment of silk fabrics with BTCA thus improves the stability of silk fabric to concentrated formic acid solution.

There is strong evidence to support the improved stabilisation of silk fabrics treated with a BTCA in the presence of SHP, the monosodium salt of CA, TA and MA, or CY. This fabric stabilisation may be as a result of fibre inter-chain diester cross-links being inserted into silk fabrics and/or as a result of a three-dimensional PCA polymer network being inserted. The treated fabrics have improved stability to heat, reduced swelling in solvents, and improved elastic recovery giving rise to fabrics with improved easy-care properties.

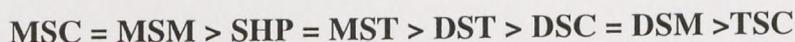
4.2.2.4 Proposed mechanism for the treatment of silk fabric with BTCA and different catalysts.

FT-IR spectra for the treated fabrics after treatment with a 1M NaOH solution have a new band at around 1735cm⁻¹ in common with carbonyl stretching of the ester bond. Measurement of the ester bond peak height was undertaken as a semi-quantitative method of establishing the quantity of ester bonds formed within the treated samples. From Table 4. 10 it can be seen the highest quantity of ester links were formed with samples treated with BTCA when SHP, MSC or CY were used as catalysts, followed by catalysis with MSM and the lowest quantity when MST was used as the catalyst.

The quantity of ester links formed within the treated samples is a measure of the

esterification reaction. The efficiency of the reaction at improving the easy-care properties of silk fabrics is dependent on the PCA improving the elastic properties and stability of the silk fabrics. Silk fabric treated with BTCA showed an improvement in initial elastic recovery from creasing in both the dry and wet states when SHP, CY or the monosodium salt of CA, TA, or MA were used. This improvement in elastic properties of the treated silk fabrics could be as a consequence of new fibre inter-chain diester cross-links being formed within the silk fibres.

Evidence from this study suggests that the temperature at which the BTCA forms an acid anhydride is directly proportional to the quantity of ester links formed within the treated silk fabric. It therefore follows that the efficiency of a catalyst is dependent on its ability to reduce the temperature at which BTCA forms an anhydride. Thermoanalytical and infra-red analysis of the BTCA/Catalyst finishing systems undertaken in section 4.1 concluded that all of the BTCA/Catalyst systems tested were capable of forming an acid anhydride below 160°C, see Table 4.6. The order of effectiveness of these catalysts at lowering the temperature at which BTCA formed an anhydride is:



This order is very similar to the order of effectiveness of BTCA when catalysed by the above catalysts at improving the elastic recovery properties of the treated fabrics.



It is known (147) that strong acids are generally required to catalyse the esterification of a monocarboxylic acid and an alcohol, whereas weak bases are known to catalyse the esterification reaction between an acid anhydride and an alcohol. As suggested in section 4.2.1.4 the mechanism proposed by Welch for the cross-linking of cotton cellulose by a PCA finishing system could explain the cross-linking mechanism for silk fabrics finished with BTCA/SHP, see Figure 4. 75. This mechanism may also be true for the BTCA/CY finish. Welch proposed that the base-catalysed esterification reaction of PCAs with cotton cellulose occurred through the formation of an anhydride intermediate (145). For a di-ester cross-link to be formed within cotton cellulose each acid molecule needs to be capable of forming two anhydride intermediates.

Catalysis of the BTCA finishing of silk fabric with sodium salts of di- and tricarboxylic

acids could occur through several different mechanisms. The different catalytic mechanisms may occur simultaneously or one of the mechanisms may predominate. The monosodium salts of the carboxylic acids may catalyse the esterification of BTCA with silk fibroin via base-catalysed esterification according to the mechanism proposed by Welch and/or acid-catalysed esterification mechanism, see Figure 4. 76. If the monosodium salt of the carboxylic acid was converted to its carboxylic acid in the pad bath, this carboxylic acid if it is more acidic than BTCA, as citric, tartaric and maleic acid all are, could catalyse the esterification via the acid route. Thus both acid and base catalysis may occur simultaneously.

Treatment of silk fibroin with BTCA using monosodium salts of carboxylic acids as catalysts could involve the esterification not only of BTCA within silk fibroin but the catalyst as well. These catalysts are also capable of forming ester bonds with silk fibroin and this could help improve the efficiency of the finish. Monosodium salts of hydroxy carboxylic acids could also become trapped inside the fibre by esterification of the hydroxy groups with anhydrides formed during the high temperature curing process and a three-dimensional PCA polymer lattice structure could be formed within silk fibroin, see Figure 4. 78.

4.2.3 Summary Of The Experimental Work In Chapter 4.

The aim of this study was to improve the properties of silk fabrics by chemically modifying silk fabric with a polycarboxylic acid finishing system. Chapter three concluded that it was possible to chemically modify silk fabric with the BTCA/SHP finishing system. Improved recovery to fabric creasing was reported. However, the BTCA/SHP finishing system is expensive and SHP is an environmental hazard and causes shade changes with some dyeing systems. This chapter investigated a number of alternative acids and catalysts as easy-care finishing agents.

TGA and infra-red analysis of a number of acid/catalyst systems, reported in section 4.1, investigated the suitability of an acid/catalyst system as an easy-care finishing agent. The PCA/catalyst systems were analysed using thermoanalytical and infra-red techniques that mimicked the conditions used during fabric curing to analyse the chemical reaction occurring between the acid and catalyst. The acid/catalyst systems that were capable of forming an acid anhydride, that did not degrade, and did not form a

dark coloured char at 165°C, the optimum temperature for curing silk fabrics were tested as easy-care finishes on silk fabrics.

This new method for testing the suitability of an acid/catalyst system as an easy-care finish was found to be very successful. The finishes that were capable of forming an acid anhydride, and that did not degrade significantly below 165°C when applied to silk fabric as an easy-care finish improved the elastic and stability properties of the treated fabrics. Notification of the char colour during TGA analysis proved important at identifying fabric finishes that would cause fabric discoloration during the high temperature curing process. Solubility of the finish in water was also important. Acids that fall out of solution during the padding operation can cause large amounts of fine acid dust particles to be emitted during the drying and curing operations that could cause a health risk.

FT-IR analysis of the treated silk fabrics was used to determine the quantity of ester links formed during the high temperature curing process. Measurement of the ester bond peak height was used as a semi-quantitative method to establish the quantity of ester bonds formed within the treated samples. The largest quantity of ester links were formed with samples treated with BTCA/SHP, BTCA/MSA, or BTCA/CY, followed by BTCA/MSM, SA/CA/SHP, and SA/MLA/SHP and the lowest quantity with the MA/SHP and BTCA/MST systems. These ester links were found to be stable to laundering, tested up to 25 washes.

The quantity of ester links formed within the treated samples is a measure of the esterification reaction. The efficiency of the reaction at improving the easy-care properties of silk fabrics is dependent on the PCA improving the elastic properties and stability of the silk fabrics. Silk fabric treated with selective PCA finishing systems showed an improvement in initial elastic recovery from creasing in both the dry and wet states, improved stability to heat and concentrated solution of formic acid solution. It is postulated that this improvement in elastic and stability properties of the treated silk fabrics could be as a consequence of new fibre inter-chain diester and or ester/hydrogen bond cross-links and/or a new intra-fibre PCA polymer network being formed within the silk fibres.

A number of proposed mechanisms were discussed for the treatment of silk fabric with a PCA easy-care finish. Esterification of silk fibroin may occur either through base-catalysed esterification of acid anhydrides or through acid-catalysed esterification of the PCA. These two esterification mechanisms may occur simultaneously or one mechanism may dominate. PCA that contain hydroxy side groups may form ester bonds with adjacent PCAs and a three-dimensional lattice structure may build up inside silk fibroin. This structure may be held in place by single ended ester attachment or through multiple ester links. Carboxylic acid groups that remain after the esterification reaction are available to hydrogen bond with silk fibroin. These hydrogen bonds would be broken in water and therefore not improve the wet stability of silk fabrics but could help increase the dry stability.

This work concludes that there is strong evidence to support the improved stabilisation of silk fabrics treated with selective PCA finishing systems. This fabric stabilisation may be as a result of fibre inter-chain diester and/or ester/hydrogen bond cross-links being inserted into silk fabrics and/or as a result of a three-dimensional PCA polymer network being formed within the silk fibroin. Amide links may also be formed between the basic amino acids, arginine, histidine and lysine in silk fibroin and acid anhydrides formed during the high temperature curing process. These bonds were not discussed due to the low occurrence of available basic side groups in silk fibroin. However a small number of amide links may contribute to an improvement in the easy-care performance of the treated silk fabrics. The treated fabrics have improved stability to heat, reduced swelling in solvents, and improved elastic recovery giving rise to fabrics with improved easy-care properties.

5. CHEMICAL MODIFICATION OF SILK FABRIC WITH POLYCARBOXYLIC ACIDS. PAD BATH ADDITIVES.

The aim of this thesis was to improve the easy-care properties of silk fabric. Commercially an easy-care fabric is one that does not crease readily while in use, can be washed and requires no or minimum ironing to restore the fabric to its original shape and appearance. Technically an easy-care finish enhances the fabric resistance to, and recovery from, creasing without any adverse affect on other intrinsic fabric properties. Silk fabric treated with selective PCA finishing systems, in chapter 4, showed improved stability to heat, reduced swelling in concentrated formic acid and improved elastic recovery from creasing. However, the treated fabrics were stiffer and less extensible when compared with the untreated control.

This chapter investigates the properties of silk fabric treated with various PCA finishes and the suitability of such finishes at improving the easy-care properties of silk fabric. The incorporation of additional chemicals into the pad bath was investigated to maximise the improvement in fabric properties brought about by the easy-care finish.

5.1 THE USE OF TEXTILE SOFTENING AGENTS TO OPTIMISE THE FINISHING OF SILK FABRIC WITH BTCA.

5.1.1 Introduction

Textile softeners can be added to the pad bath to help improve some of the side effects of resin finishing such as the stiffer handle, reduced fabric tensile strength, tear strength and abrasion resistance (81). Softeners also improve fabric handle, softness, and drape, decrease static and aid fabric cutting and sewability (187). Softeners fall into a number of basic types based on their polarity or ionic nature (194).

5.1.1.1 Nonionic Softeners.

Nonionic softeners have limited substantivity for the fibre (188). They include mono- and di-glycerides, glycol esters, stearamides, and some polyethylene and silicone emulsions (194). Most of these compounds are chemically stable and consequently do not discolour the fabric even when applied with other chemicals. Nonionic softeners are mainly used in combination with cationic softeners to act as lubricants, or due to their non-substantive nature as temporary softeners (188).

5.1.1.2 Cationic Softeners.

Cationic Softeners are the most extensively used class of softener. The compounds are positively charged structures derived from nitrogen-bearing moieties including fatty amidoamine acid salts, quaternary fatty amidoamides, quaternary tertiary amines, and quaternary imidazolines (194). Some cationic polyethylene emulsions and amino-functional silicones also come under this group. Cationic softeners are substantive to the fibres producing a finish that is more durable to washing than nonionic softeners (187). Cationic softeners are not compatible with anionic chemicals or detergents; a precipitate is formed that decreases the softening properties of the finish (187). The major advantages of cationic softeners are their efficiency at low add-on values, exhaustion from long liquors and moderate durability to washing (194).

5.1.1.3 Anionic Softeners.

These softeners have poor exhaustion, high cost, low fibre substantivity and poor wash fastness; thus they are only utilised in specific situations where nonionic and cationic softeners are incompatible (188). Anionic softeners include sulfated triglycerides, sulfated fatty alcohols, and anionically-emulsified glycerides (194).

5.1.1.4 Amphoteric Softeners.

These softeners possess both cationic and anionic charges and are thought to be universally compatible structures (194). They are more substantive than either nonionic or anionic softeners but not as durable as cationic softeners (188). They include imidazoline carboxylate salts, and imidazoline sulfonate salts. High cost has prevented amphoteric softeners from being commercially accepted within the textile industry (194).

5.1.1.5 Reactive Softeners.

These softeners react, under suitable conditions of catalysis, at elevated temperatures with the fibre to form a covalent bond between the softener and the substrate that yields a permanent softening effect that is fast to washing (187). Commercial reactive softeners consist of N-methylol stearamide, and octadecyl ethylene urea. Reactive softeners can be applied simultaneously with crease-resist finishes; they can impart a higher degree of crease-resistance, and/or reduce the loss in tensile strength, tear strength and/or abrasion resistance (187).

5.1.1.6 Polyethylene Emulsions.

Polyethylene emulsions can be applied with crease resistant finishes on cotton to act as a lubricating agent and hence decrease the inter-fibre friction. They improve the mechanical properties of the fibre and produce a soft, supple handle that is durable to laundering. The softener aids fabric sewability by allowing the needle a smooth passage through the fabric. Polyethylene emulsions consist of tiny particles of the insoluble polyethylene emulsified with a suitable emulsifying agent so as to give a fine dispersion in water. A nonionic emulsifying agent is usually chosen as it is compatible with the majority of the chemicals found in textile finishing.

5.1.1.7 Silicone Softeners.

The principal function of the fabric softener is that of surface lubrication by coating the substrate with a thin film or layer. Silicone softeners have been used by the textile industry since the 1940's primarily as softeners, lubricants, water-repellents and anti-foams (189). They impart what is commonly described as a super soft (i.e. luxurious) handle to the fabric.

Silicone softeners reduce the inter-yarn and inter-fibre friction and in so doing give rise to a number of improved fabric properties. A soft flexible handle is imparted to the fabric that has good resistance to washing; an improvement in abrasion resistance, tear strength and sewability, as well as a reduction in fabric creasing and shrinkage have been found on cotton fabrics (187). There is no significant reduction in moisture regain and any loss of fabric strength is slight (190).

Silicone softeners can be classified into three groups:

Non-reactive. These are based on polydimethylsiloxanes, see Figure 5. 1.

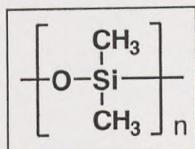


Figure 5. 1 A polydimethylsiloxane monomer.

Non-reactive silicones form a flexible film on the fibre surface that orientates itself so that the oxygen atoms are facing towards the fibre surface and the methyl groups away from it (187,189,190). This softener does not cross-link with the fibre and thus the film

is easily cracked during laundering when the fibre is more swollen (190).

2. **Conventional-reactive.** These are modified dimethylsiloxanes with silanol groups, see Figure 5. 2. Polymerisation of these modified dimethylsiloxanes takes place inside the fibre through condensation of the silanol groups (187,189, 191,190).

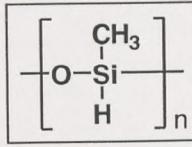


Figure 5. 2 A polymethyl hydrogen siloxane monomer.

This polymer network improves the durability of the softener. However, due to the difference in electronegativity of carbon in the fibre and silicon, stable chemical bonds between the softener and the fibre cannot be formed (190). Silane coupling agents have been used to try to improve this fixation (190). These facilitate cross-linking as well as condensation of the reactive softener with the fibre.

3. **Organo-functional.** These are manufactured from mixed polyorganosiloxanes, see Figure 5. 3 (187).

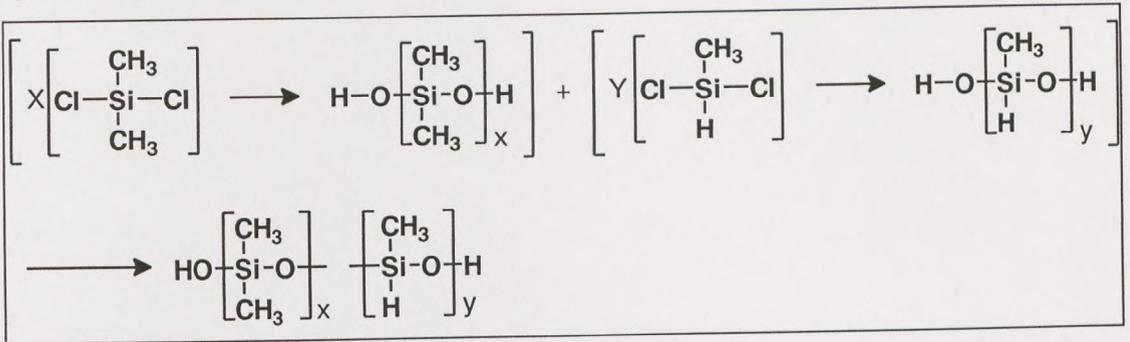


Figure 5. 3 A mixed polyorganosiloxane monomer.

These silicone finishes are modified with functional groups, see Figure 5. 4, that are able to react either with the fibre, a durable press resin, a latex system or with themselves (191).

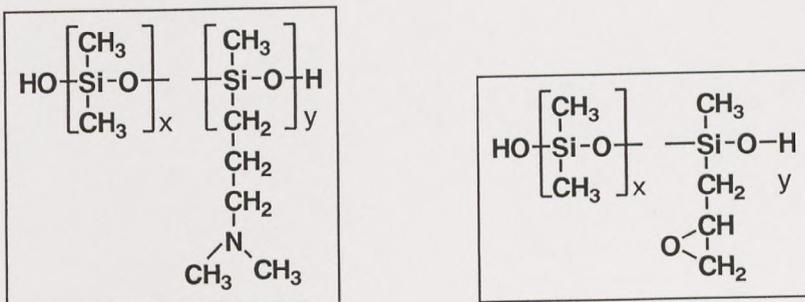


Figure 5. 4 An amino-functional polyorganosiloxane and an epoxy-modified polyorganosiloxane.

By varying the molecular weight of the polymer and the degree of modification of the

softener different finishes can be manufactured to produce optimum results and a variety of different fabric handles.

5.1.2 Experimental Procedure.

Plain woven silk Habutai medium, roll 3, see section 2.1.1, was treated with a variety of different softening agents, both with and without a PCA finish, see Table 5. 1. The PCA finish consisted of 6%w/w BTCA and a 1:1 molar ratio of SHP catalyst. These finishes were applied together to silk fabrics via a pad-dry-cure method, as described in section 2.1. The silk fabrics that were treated with the softening agent without the PCA were not cured; however the drying temperature was raised to 110°C for the samples treated with the silicone softeners. The treated samples were conditioned for 48h and the crease recovery properties of the treated fabrics were investigated according to the method described in section 2.3.2.2.1.

Softening Agent	Type of Softener	%w/w Softener	Applied with PCA finish
Ceranine L	Nonionic polyethylene dispersion	0.5%, 1%, 1.5%, and 2%	Yes
PEG 200	Poly(ethylene glycol) RMM 200	0.25%, 0.5%, 1%, 1.5%, and 2%	No & Yes
PEG 400	Poly(ethylene glycol) RMM 400	0.25%, 0.5%, 1%, 1.5%, and 2%	No & Yes
PEG 600	Poly(ethylene glycol) RMM 600	0.25%, 0.5%, 1%, 1.5%, and 2%	No & Yes
PEG 1000	Poly(ethylene glycol) RMM 1000	0.25%, 0.5%, 1%, 1.5%, and 2%	No & Yes
Ultratex SW	Reactive amine functional polysiloxane microemulsion	0.5%, 1%, 1.5%, 2% and 2.5%	No & Yes
Ultratex FEW	Reactive amine functional polydimethylsiloxane emulsion	0.5%, 1%, 2%, 3%, and 4%	No & Yes

Table 5.1 Summary of the different softening and PCA finishes used for the treatment of silk fabric.

5.1.3 Results And Discussion.

The aim of this experiment was to investigate the alteration in creasing properties of the treated silk fabrics brought about by the addition of different softeners into the pad bath. The crease recovery results are tabulated in Appendix 3, Table A3.1 and A3.2 and the results are displayed in graphical form in the text Figure 5. 5 to Figure 5. 17.

Figure 5. 5 displays the crease recovery results of silk fabric treated with 6%w/w BTCA, a 1:1 molar ratio of SHP and different quantities of Ceranine L (Clariant), a

nonionic polyethylene dispersion. Addition of the softener into the pad bath improves the dry crease recovery angles, both the initial elastic recovery and the recovery from creasing after five minutes. The wet crease recovery results remain almost unchanged by the addition of Ceranine L liquid into the pad bath.

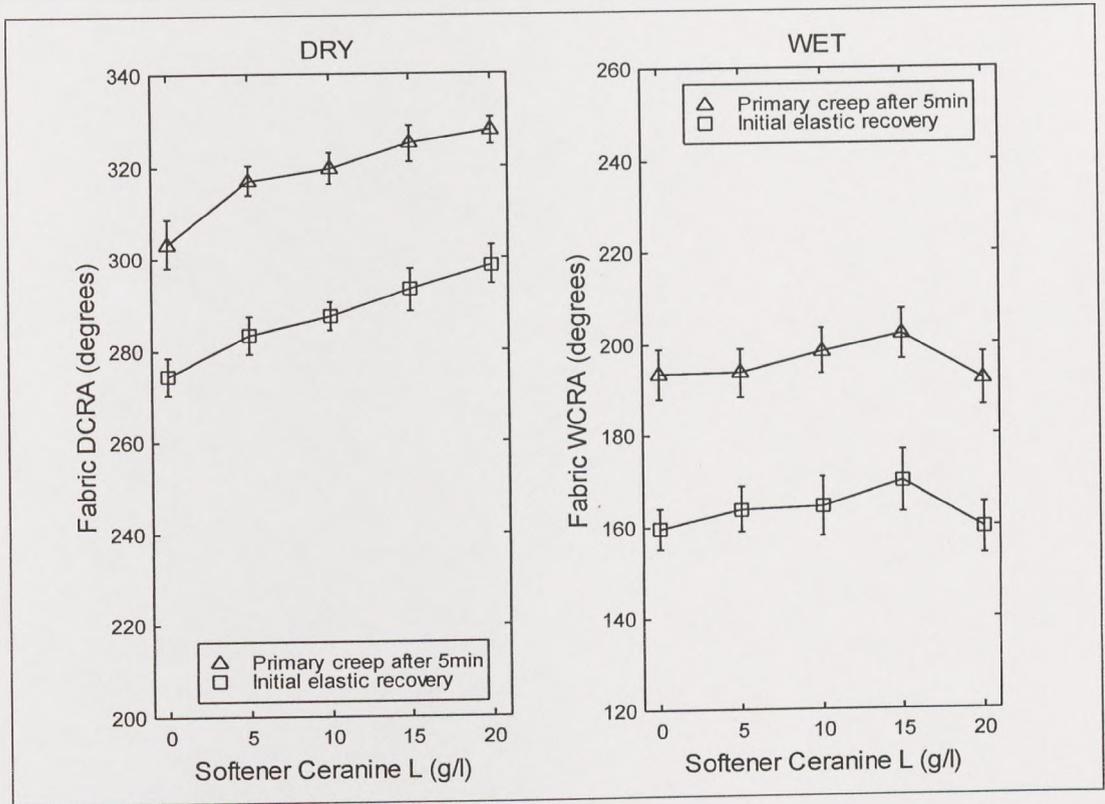


Figure 5.5 Fabric CRAs of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and varying amounts of softener Ceranine L (Clariant)

Figure 5.6 to Figure 5.13 display the results of silk fabrics treated with different quantities of polyethylene glycols (PEG) of various molecular weights with and without a PCA finish. The treatment of silk fabrics with different weight PEGs all had a similar effect on the creasing properties of the silk fabrics whether applied on their own or in conjunction with a PCA finish. Small quantities of PEG added to the pad bath improved the DCRA of the treated silk fabric; both the initial recovery from creasing and the recovery from creasing after 5min were improved. Above 0.5%w/w PEG in the pad bath there was no further improvement in DCRA. The WCRA showed, with small quantities of PEG in the pad bath, a sharp initial improvement; when more PEG was added to the pad bath this improvement in WCRA, both initial elastic recovery and recovery from creasing after 5min, was less sharp. Treatment of silk fabric with PEG softeners either on their own or in conjunction with a PCA finish improved the elastic properties of the treated silk fabric and this led to improved crease recovery properties.

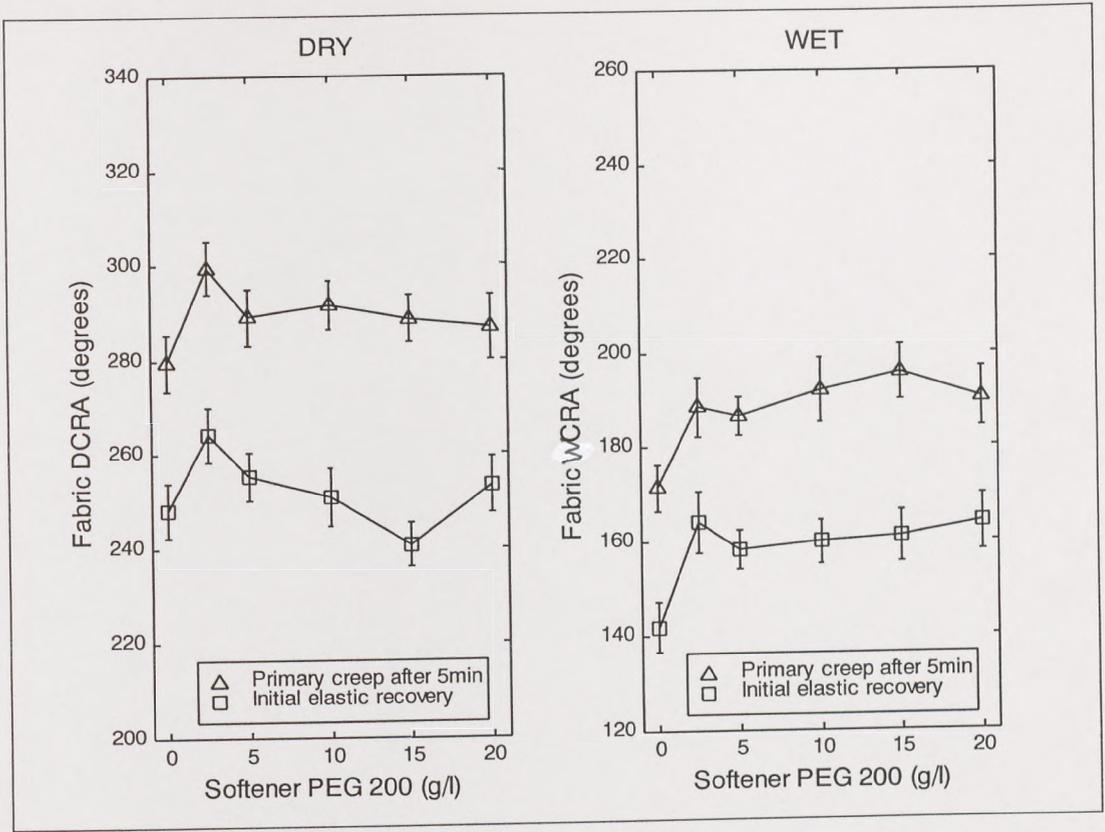


Figure 5. 6 Fabric CRAs of silk fabric treated with varying amounts of softener polyethylene glycol 200.

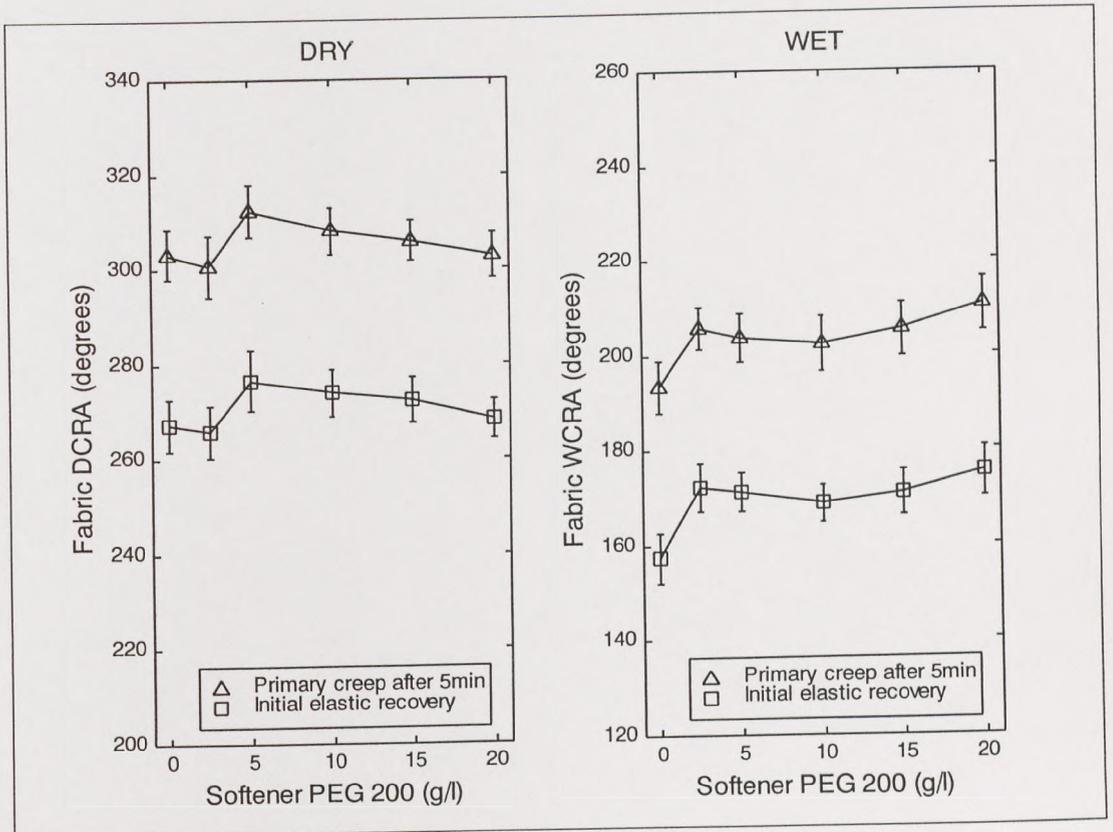


Figure 5. 7 Fabric CRAs of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and varying amounts of softener polyethylene glycol 200.

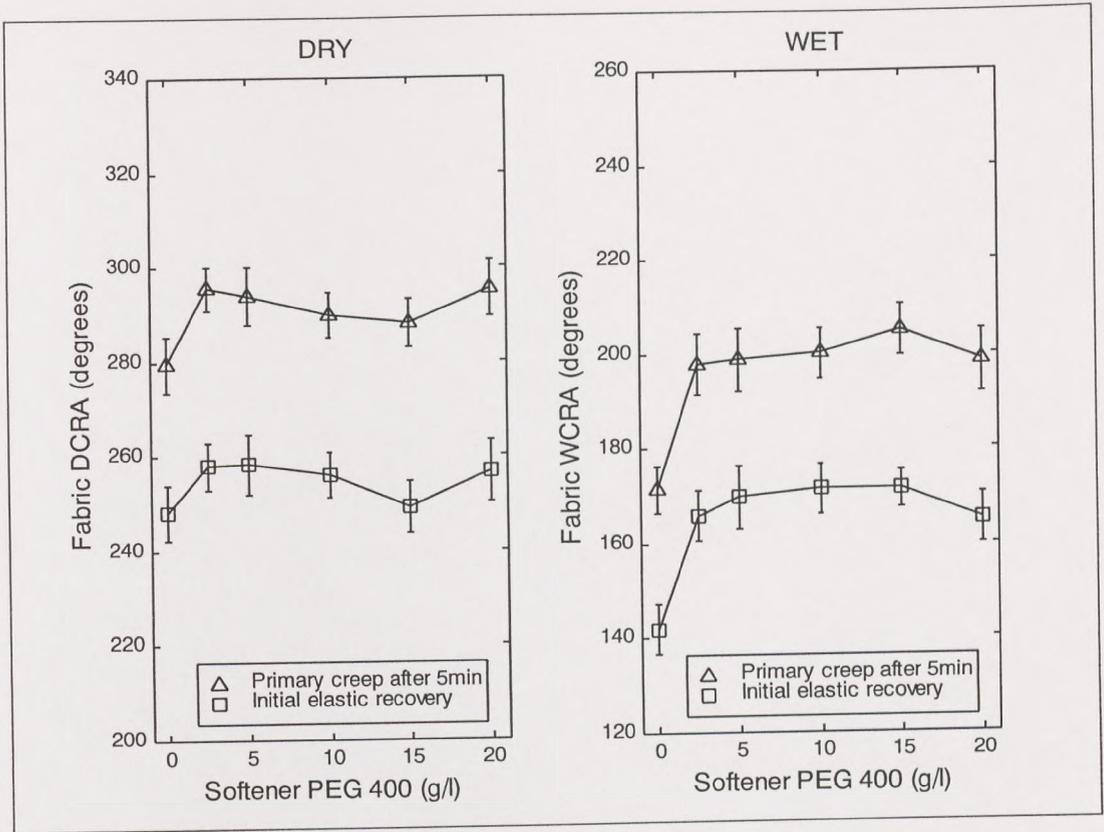


Figure 5.8 Fabric CRAs of silk fabric treated with varying amounts of softener polyethylene glycol 400.

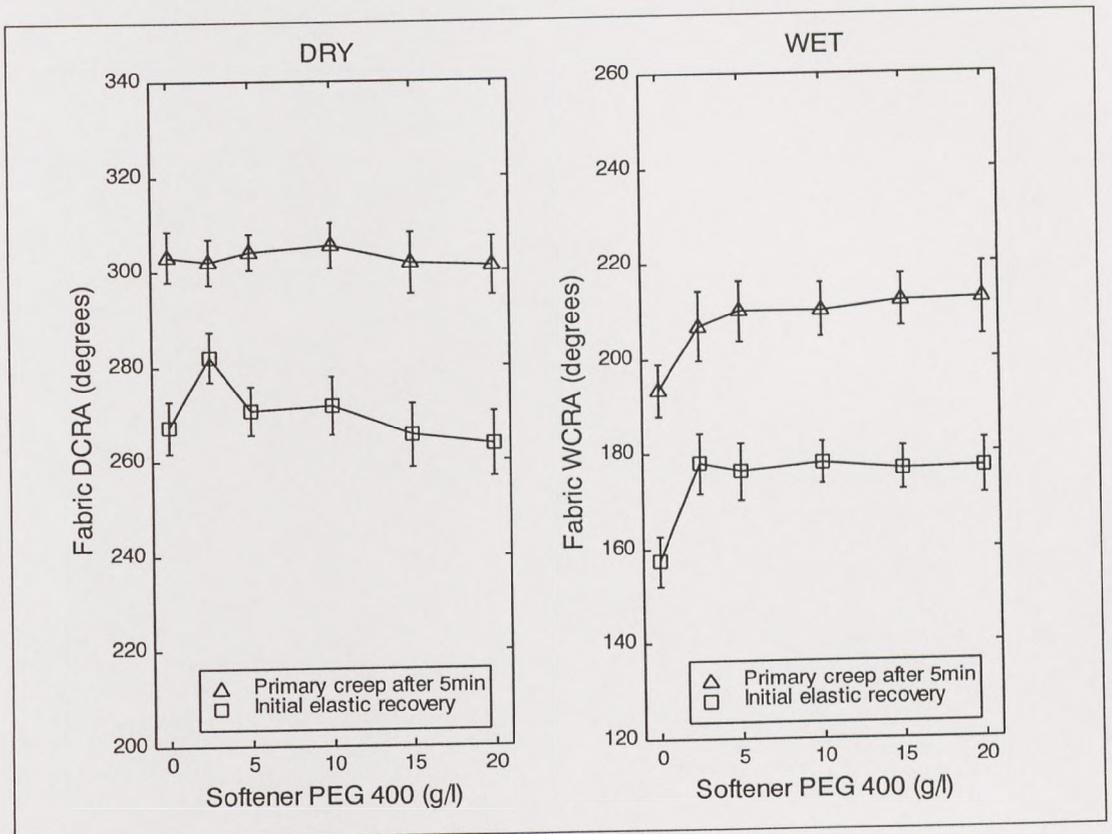


Figure 5.9 Fabric CRAs of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and varying amounts of softener polyethylene glycol 400.

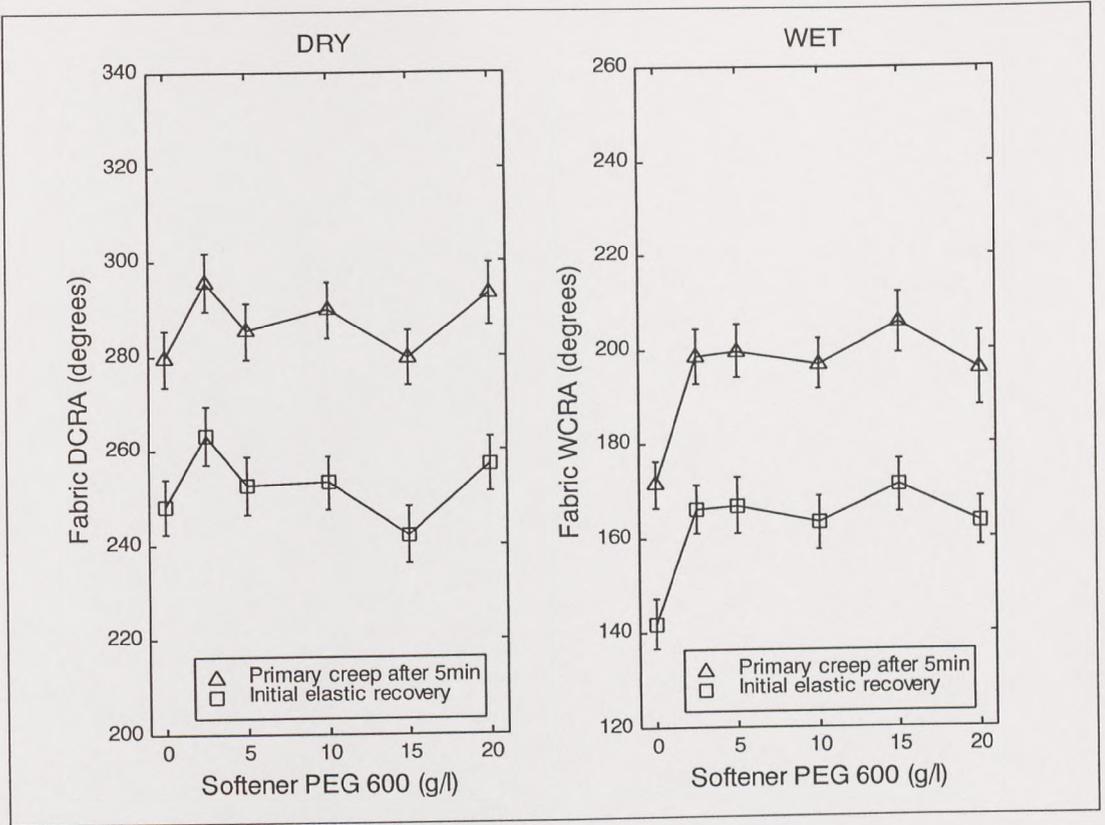


Figure 5.10 Fabric CRAs of silk fabric treated with varying amounts of softener polyethylene glycol 600.

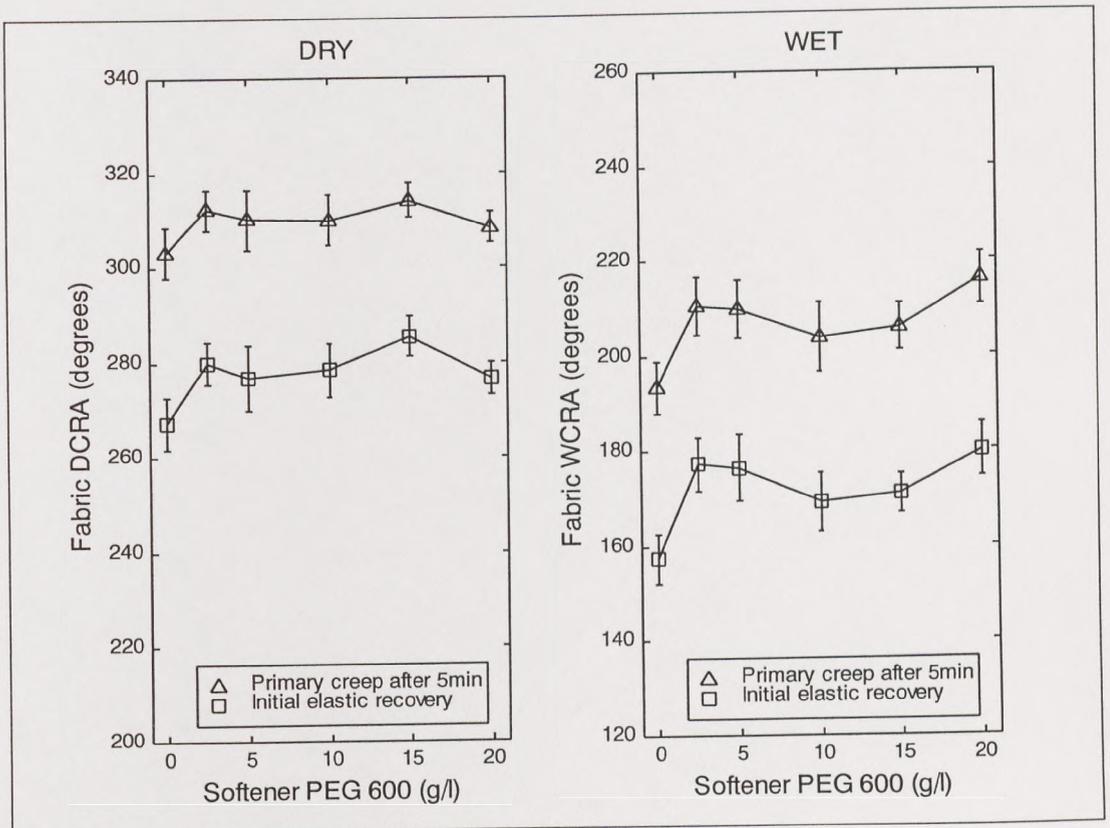


Figure 5.11 Fabric CRAs of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and varying amounts of softener polyethylene glycol 600.

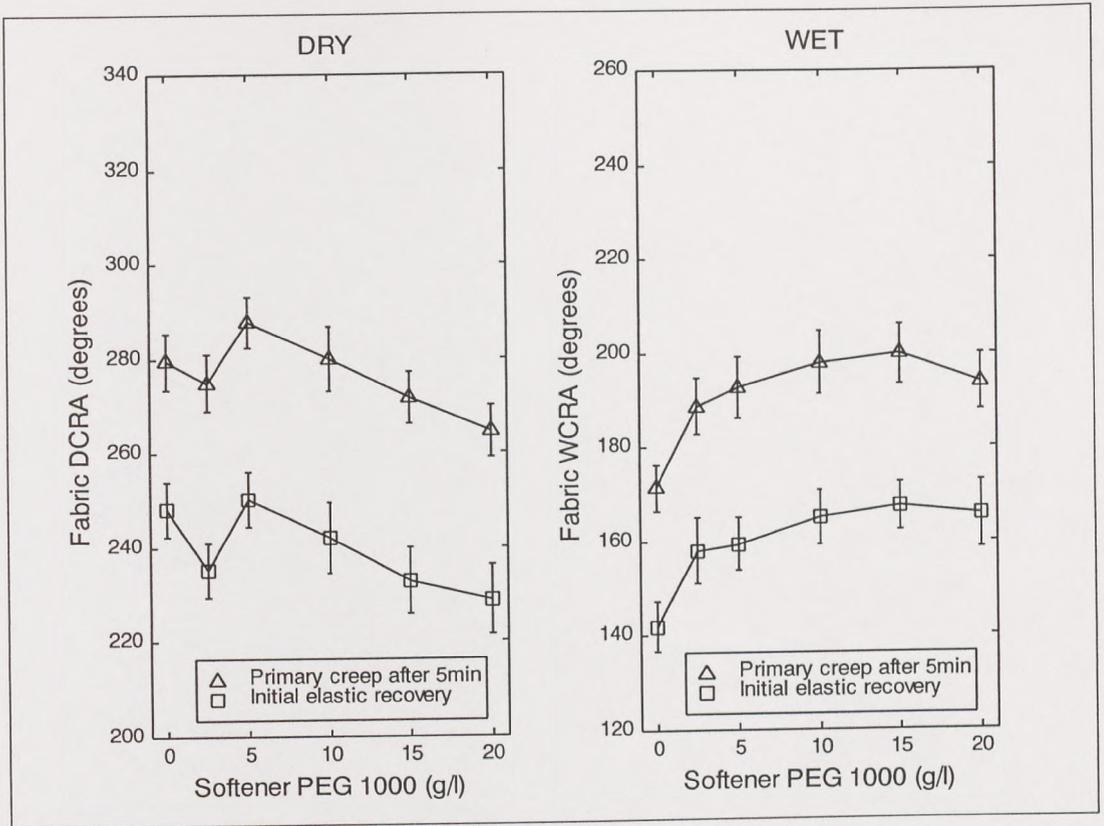


Figure 5.12 Fabric CRAs of silk fabric treated with varying amounts of softener polyethylene glycol 1000.

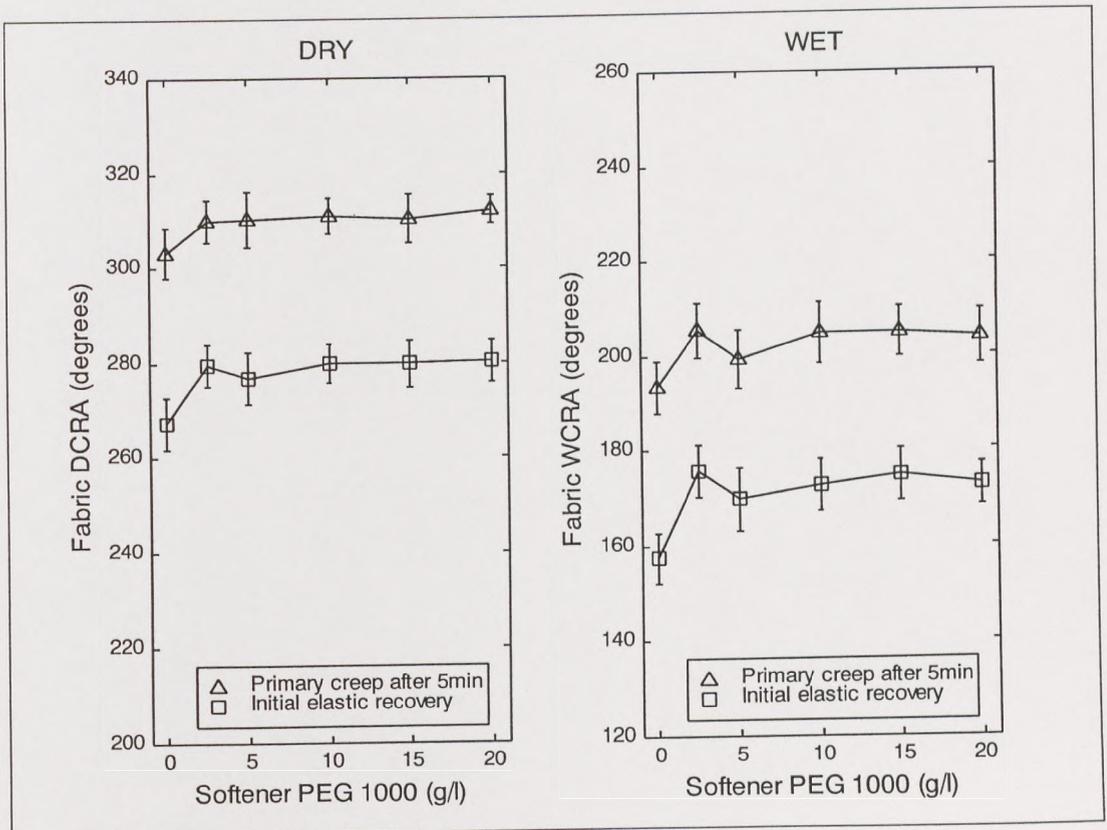


Figure 5.13 Fabric CRAs of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and varying amounts of softener polyethylene glycol 1000.

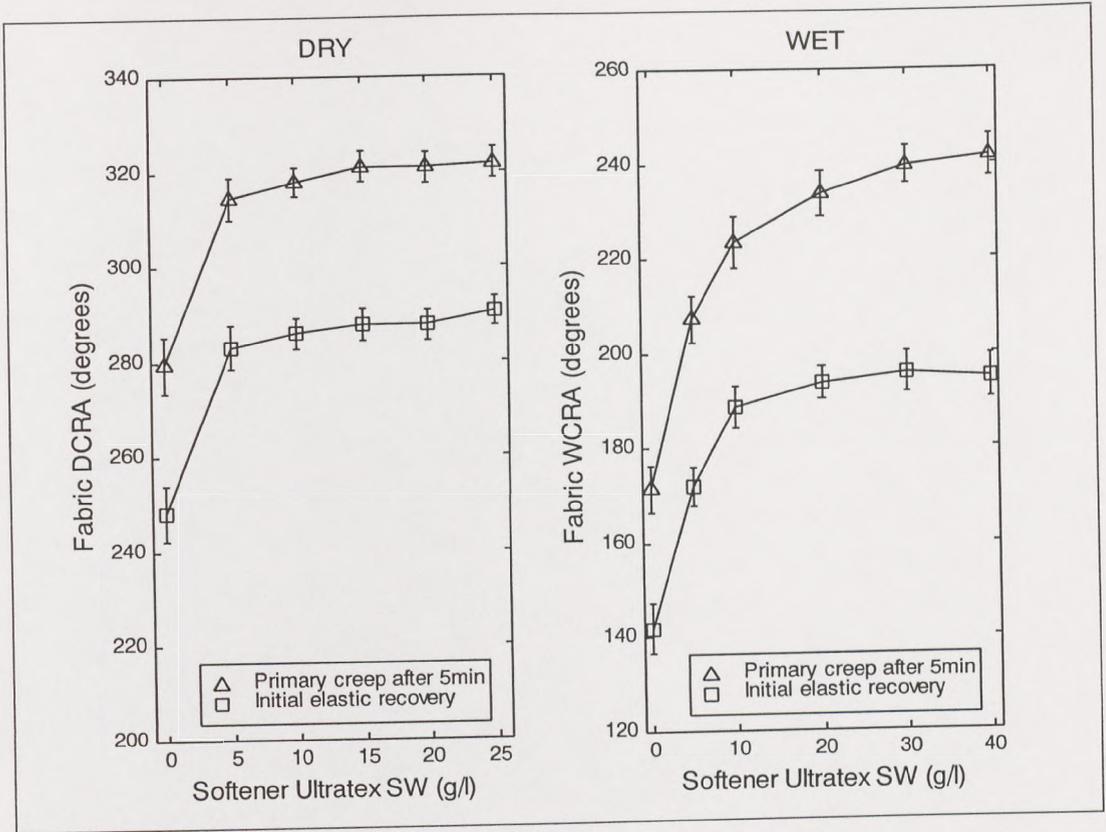


Figure 5.14 Fabric CRAs of silk fabric treated with varying amounts of silicone softener Ultratex SW (Ciba).

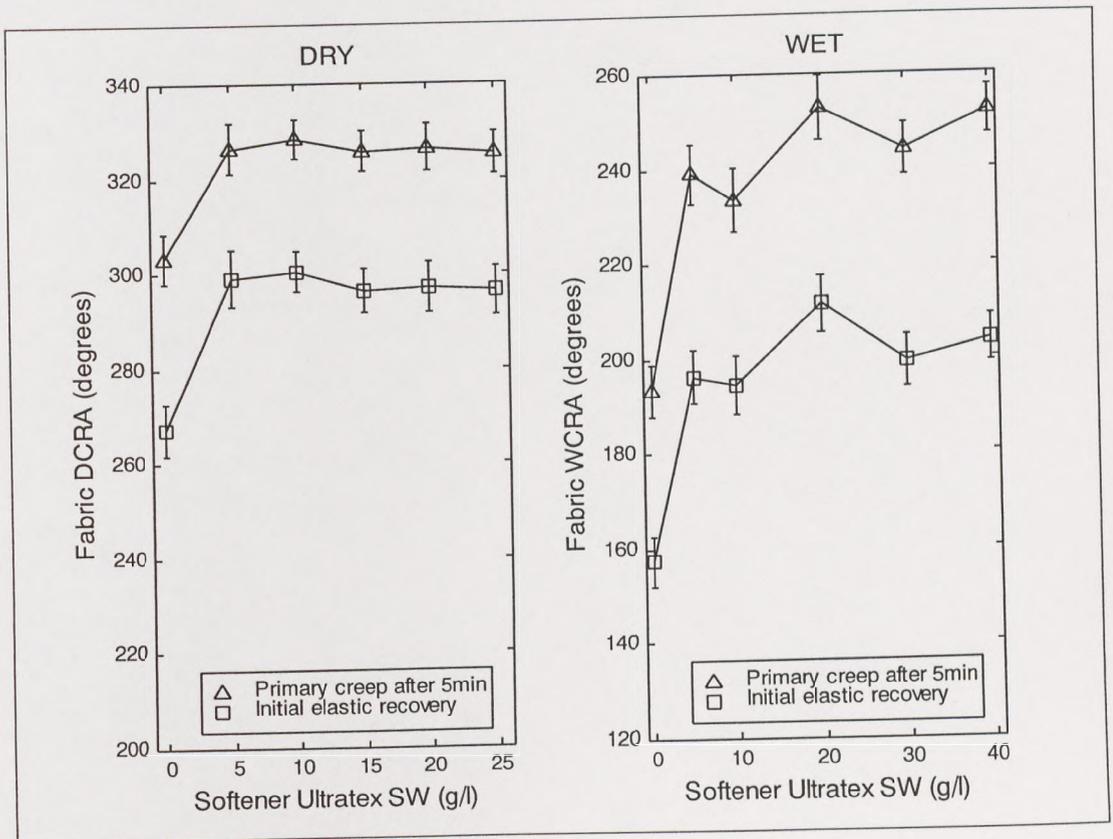


Figure 5.15 Fabric CRAs of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and varying amounts of silicone softener Ultratex SW (Ciba).

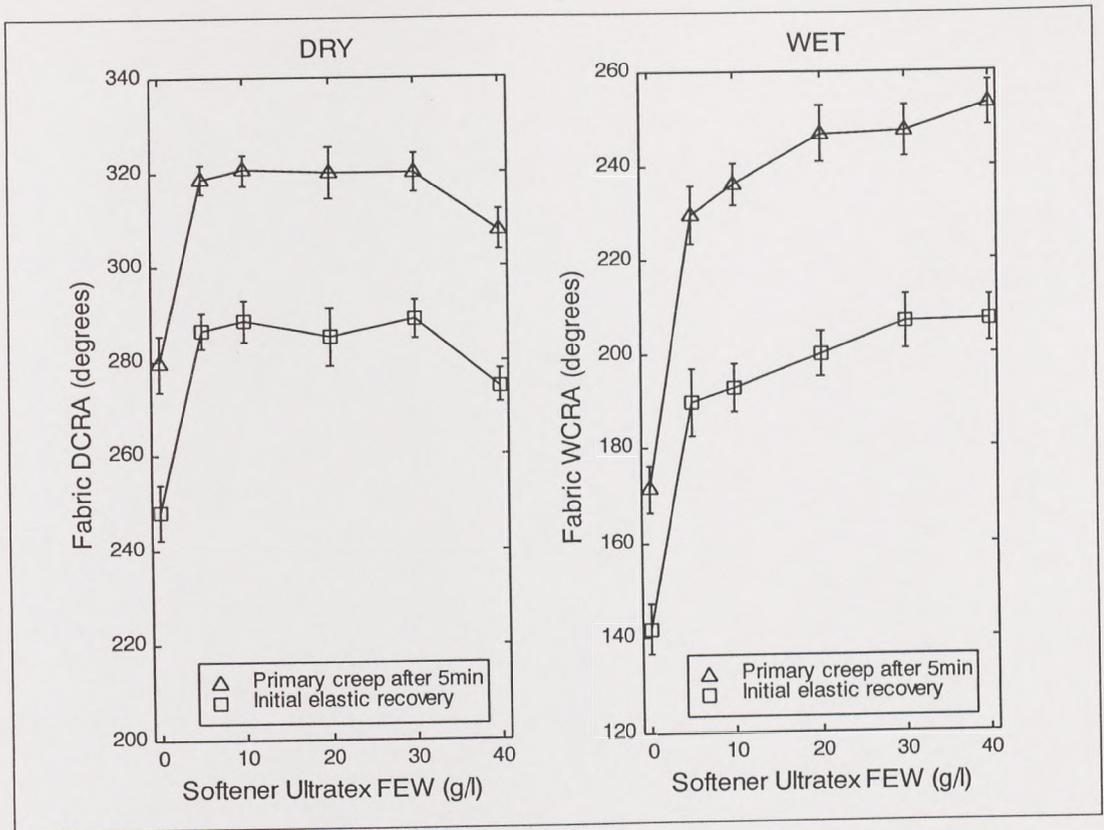


Figure 5.16 Fabric CRAs of silk fabric treated with varying amounts of silicone softener Ultratex FEW (Ciba).

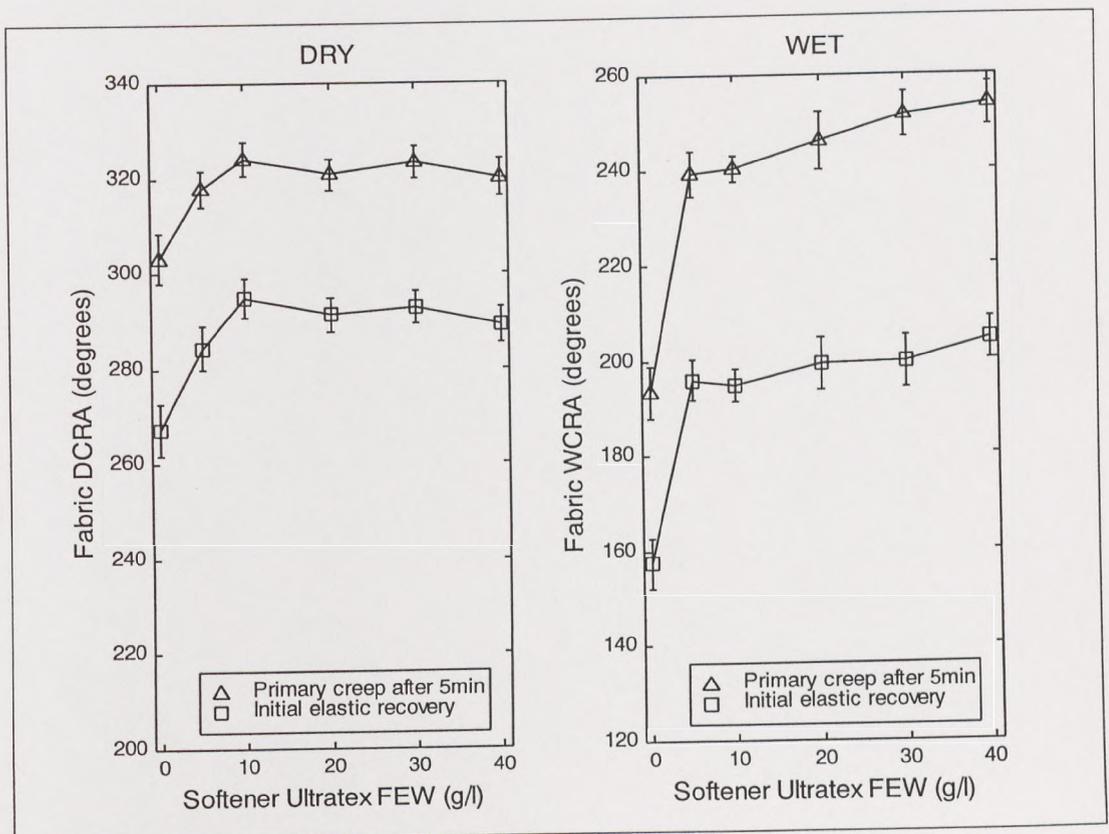


Figure 5.17 Fabric CRAs of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and varying amounts of silicone softener Ultratex FEW (Ciba).

Treatment of silk fabrics with silicone softeners Ultratex SW and Ultratex FEW (Ciba) with and without a PCA finish leads to large improvements in both DCRA and WCRA, see Figure 5. 14 to Figure 5. 17. The addition of even very small quantities of these silicone softening agents led to large improvements in crease recovery angles, both initial recovery from creasing and recovery from creasing after 5min. The improvement in both DCRA and WCRA is greater than 40°.

Silk fabrics treated with silicone softeners have a super-soft, luxurious handle. The silk fabrics become very limp when treated with the silicone softener without a PCA finish. The combined treatment of silk fabrics with a selective PCA finish and a silicone softener leads to a synergistic improvement in crease-recovery properties.

5.1.4 Conclusions.

Treatment of silk fabric with different softening treatments can improve the crease recovery properties of the fabric, see Table 5. 2. Silk fabric treated with PEGs, RMM 200, 400, 600, and 1000, have improved recovery from creasing in both the dry and wet states. Treatment of silk fabrics with silicone softeners, Ultratex SW and Ultratex FEW, markedly improves the recovery from creasing in both the dry and wet states. However, silk fabric treated with these silicone softeners has a very limp handle, due to a reduction in inter-fibre and inter-yarn friction.

Softener	Fabric DCRA (recovery after 5min)	Fabric WCRA (recovery after 5min)
Control	279.5 ± 5.9	171.5 ± 4.9
1%w/w PEG 200	291.4 ± 5.1	191.9 ± 6.8
1.5%w/w PEG 400	288.1 ± 5.0	205.0 ± 5.4
1.5%w/w PEG 600	289.5 ± 5.9	205.8 ± 6.6
1%w/w PEG 1000	279.9 ± 6.9	198.0 ± 6.5
2.5%w/w Ultratex SW	321.6 ± 3.2	241.5 ± 4.4
3%w/w Ultratex FEW	319.9 ± 4.2	247.4 ± 5.4

Table 5. 2 Comparison of the CRAs of silk fabrics treated with different softeners.

The addition of selected compatible softeners into the PCA finish pad bath and treatment of silk fabrics with the combined finish can lead to synergistic improvements in both DCRA and WCRA, see Table 5. 3. A slight improvement in recovery from

creasing was observed with silk fabric samples treated with Ceranine L and varying weight PEGs compared with samples treated with BTCA without the addition of a softener into the pad bath. A large improvement in crease recovery angles both dry and wet was observed when silicone softeners were added to the BTCA pad baths. These samples had a handle more characteristic of silk compared with the very limp handle of silk fabric treated with silicone softeners and no PCA finish.

PCA + Softener	Fabric DCRA (recovery after 5min)	Fabric WCRA (recovery after 5min)
6%w/w BTCA	303.2 ± 5.3	193.3 ± 5.5
6%w/w BTCA + 1.5%w/w Ceranine L	324.9 ± 4.0	201.9 ± 5.5
6%w/w BTCA + 1.5%w/w PEG 200	305.9 ± 4.2	205.2 ± 5.7
6%w/w BTCA + 1%w/w PEG 400	305.5 ± 4.9	210.2 ± 5.6
6%w/w BTCA + 1.5%w/w PEG 600	314.2 ± 3.5	205.8 ± 4.9
6%w/w BTCA + 1%w/w PEG 1000	311.0 ± 3.7	204.8 ± 6.5
6%w/w BTCA + 1.5%w/w Ultratex SW	325.8 ± 4.1	252.9 ± 6.8
6%w/w BTCA + 3%w/w Ultratex FEW	323.2 ± 3.4	251.4 ± 4.7

Table 5.3 Comparison of the CRAs of silk fabrics treated with 6% w/w BTCA, 1:1 molar ratio SHP and different softeners.

5.2 THE EFFECTIVENESS OF PCA EASY-CARE FINISHES FOR SILK FABRIC.

The aim of this experiment was to investigate the effectiveness of different PCA easy-care finishes for silk fabrics. Additional chemicals, such as fibre swelling agents, stiffening agents, and softening agents, were added to the pad bath and their effect on different fabric properties investigated. On cotton fabrics treated with DMDHEU the addition of polymeric additives, such as polyacrylates, polyurethanes, polyethers and polysilicones, to the pad bath can produce a fabric with a CRA in excess of 300° and improved resistance to fabric abrasion (192). The pad bath additives used in this experiment were the swelling agents formic acid and acrylic acid, the stiffening agent polyacrylic acid, and the softening agents, Ceranine L, PEG 1000, Ultratex SW and Ultratex FEW.

5.2.1 Experimental Procedure.

Plain woven silk Habutai heavy, roll 5, see section 2.1.1, was treated with a variety of different PCA finishes, with and without different pad bath additives, see Table 5. 4.

These finishes were applied to silk fabrics via a pad-batch-cure method, as described in section 2.1. The silk fabrics that were treated with a softening agent in addition to a PCA finish, the softening agent was applied as an after-treatment in the last wash bath prior to final drying. The whole process was pad-batch-dry-cure-wash-pad-dry. The final drying temperature was raised to 110°C for the samples treated with the silicone softeners.

The treated samples were conditioned for 48h and were tested with respect to percent chemical add-on, regain, infra-red ester frequency peak height, fabric dry and wet crease recovery angles, fabric warp and weft bending length, fabric retention of tensile strength and fabric retention of elongation at break. Selected fabrics were also tested with respect to fabric abrasion. Sample testing was carried out according to the test methods described in section 2.2 and comparisons of the results were made with an untreated control. The efficiency of the easy-care finishes were compared by washing the treated silk fabrics in a standard wash cycle with a full load, line drying and visually comparing the creasing both before and after ironing. The washed samples were scanned into a computer and the images printed out so a visual record could be made for this thesis.

PCA Finish	Pad Bath Additives	1% w/w Softener After-treatment
BTCA/SHP	-	Ceranine L, Ultratex FEW and SW
BTCA/SHP	1%w/w, 3%w/w, and 5%w/w FA	-
BTCA/SHP	5%w/w FA	Ceranine L, PEG 1000, Ultratex FEW and SW
BTCA/SHP	1%w/w, 3%w/w, and 5%w/w AA	-
BTCA/SHP	5%w/w AA	Ceranine L, PEG 1000, Ultratex FEW and SW
BTCA/SHP	1%w/w, 3%w/w, and 5%w/w PAA	-
BTCA/SHP	1%w/w PAA	Ceranine L, PEG 1000, Ultratex FEW and SW

Table 5.4 Summary of the different pad bath additives and softening treatments in addition to treatment of silk fabric with 6% w/w BTCA and a 1:1 molar ratio of SHP.

5.2.2 Results And Discussion.

The results are tabulated in Appendix 3, Table A3.3 and Table A3.4 and the results are displayed in graphical form in the text Figure 5. 18 to Figure 5. 55.

Figure 5. 18 and Figure 5. 19 graphically display the results of silk fabric treated with 6%w/w BTCA, a 1:1 molar ratio of SHP as catalyst. Some of these fabric samples were

given an additional finishing treatment in the final wash-off bath with 1%w/w of various softening agents.

- This additional softening finish has minimal effect on the fabric DCRA values but markedly improves the fabric WCRA, both initial elastic recovery and recovery from creasing after five minutes. Treatment with a silicone finish improves the recovery from creasing of the silk fabric more than that of the other softening treatments tested.
- The additional softening finish does not affect the reaction between BTCA and silk. FT-IR ester peak height was not affected by the additional softening finish. The softening treatment occurs after curing the resin finish and it therefore should not interfere with the reaction of the PCA with silk fibroin.
- The additional softening treatment improves the mechanical properties of the silk fabrics treated with BTCA. There was an observed decrease in bending length and thus a reduction in fabric stiffness imparted during the resin finishing process. There is an increase in the retention of breaking strength and elongation at break compared with samples that were only subjected to a resin finish.
- From Table 5.5 it can be seen that the additional softening treatment increases the fabric moisture regain by more than 1% and that the fabric resistance to abrasion is markedly improved.

PCA + Softener	Fabric Moisture Regain (%)	Abrasion Resistance (no. of rubs)	ASTM Yellowness Index
Untreated Control		775	
BTCA	7.65	725	7.28
BTCA + Ceranine L	9.06	2000	6.14
BTCA + PEG 1000	8.81	1300	5.58
BTCA + Ultratex FEW	8.78	2000	6.27
BTCA + Ultratex SW	8.76	1500	7.06

Table 5.5 Summary of additional fabric properties for silk fabrics treated with 6% w/w BTCA, a 1:1 molar ratio of SHP, and in the final wash 1% w/w softener.

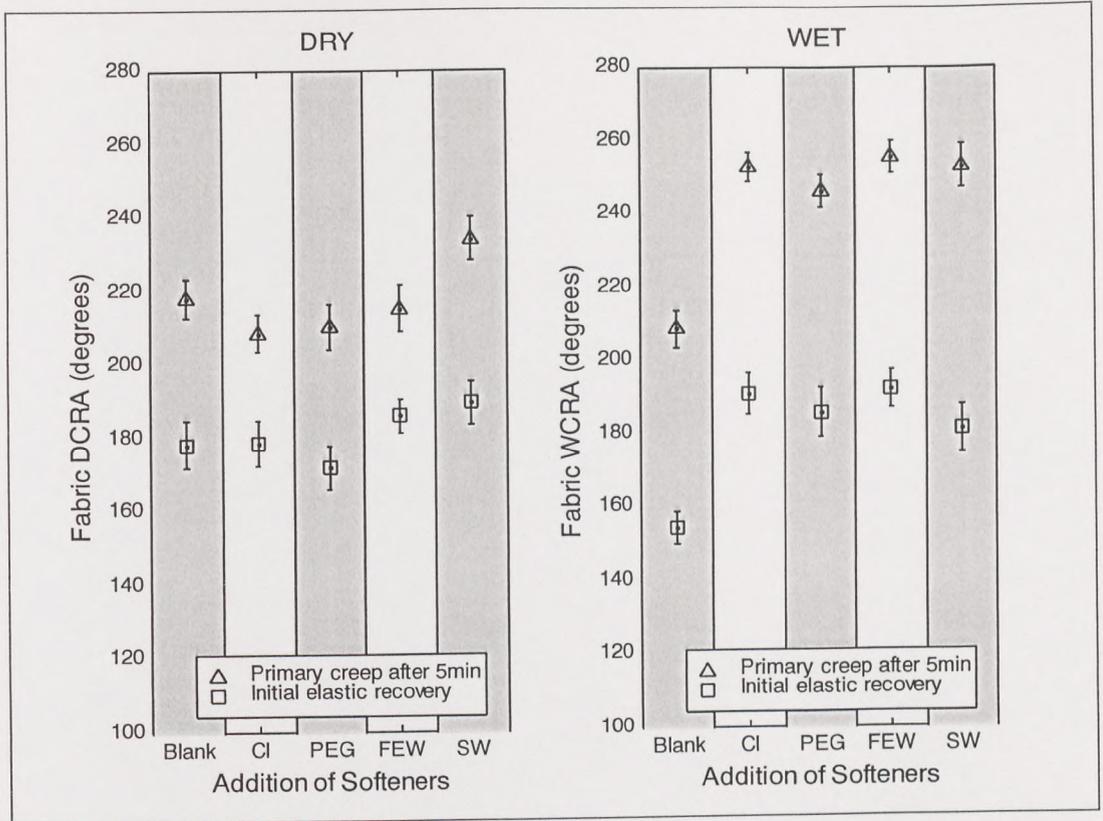


Figure 5.18 Fabric CRAs of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and 1% w/w of different softeners.

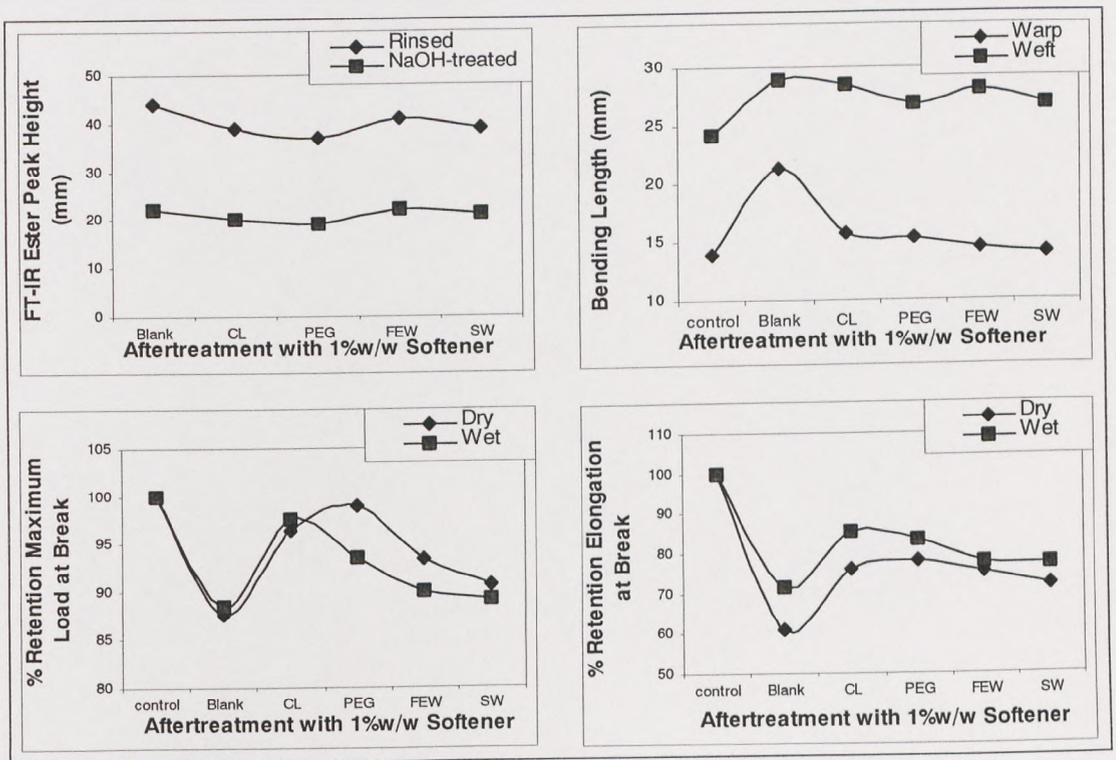


Figure 5.19 Graphical representation of the properties of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and 1% w/w of different softeners. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

In order to ascertain the effectiveness of the different finishes on silk fabrics at improving the easy-care properties the samples were washed and line dried and the extent of creasing after washing noted. These washed samples were lightly ironed and the visual appearance of the samples was again analysed. These washed and ironed samples were scanned into the computer and the scanned images printed out so that a permanent record could be kept of the fabric appearance, see Figure 5. 20 to Figure 5. 31. From these images a number of different types of creases can be identified: hard, sharp creases that are difficult to remove when ironed; moderate creases, which are less sharp and can be removed by ironing; mussiness or minute creases that give the fabric a crumpled appearance, these creases are easily removed by ironing.

PCA + Softener	Shrinkage after Washing (%)		Appearance after Washing	Fabric WCRA after 5min (degrees)
	Warp	Weft		
Untreated Control	4	0	Very creased. Hard creases and lots of mussiness. Mussiness removed when ironed.	179.6 ± 6.2
BTCA	2	0	Moderate creasing. Hard creases and some mussiness. Mussiness removed when ironed.	208.7 ± 5.0
BTCA + Ceranine L	0	0	Moderate creasing. Hard creases and minimal mussiness. Mussiness removed when ironed.	252.8 ± 4.0
BTCA + PEG 1000	2	0	Moderate creasing. Hard creases and minimal mussiness. Mussiness removed when ironed.	246.2 ± 4.5
BTCA + Ultratex FEW	1	0	Minimal creasing. Very hard creases only. These are difficult to remove during ironing.	255.5 ± 4.5
BTCA + Ultratex SW	2	0	Minimal creasing. Very hard creases only. These are difficult to remove during ironing.	252.9 ± 5.9

Table 5. 6 Summary of the appearance of treated silk fabric samples after washing and ironing.

Treatment of silk fabrics with BTCA and a 1:1 molar ratio of SHP improved the easy-care properties of silk fabric. It can be seen from Table 5. 6 that there is an improvement in WCRA after 5min, a decrease in warp shrinkage after washing and a decrease in the quantity of creases observed in the washed sample for the treated fabric compared with the untreated control. However, this improvement in easy-care performance is not sufficient to remove all the creases from the treated fabric after washing and ironing. The additional softening treatments further improve the easy-care characteristics of the treated fabric. There is a greater increase in fabric WCRA and a greater decrease in the quantity of creases observed after the treated fabric samples had been washed. The difference in the appearance of the samples treated with the additional softening treatments after washing was not mimicked by a difference in WCRA; it is therefore proposed that this measure is not sufficient on its own to identify the creasing performance of a fabric to washing.



Figure 5.20 Scanned image of untreated silk fabric that has been washed using a standard detergent on a delicate wash cycle and line dried.

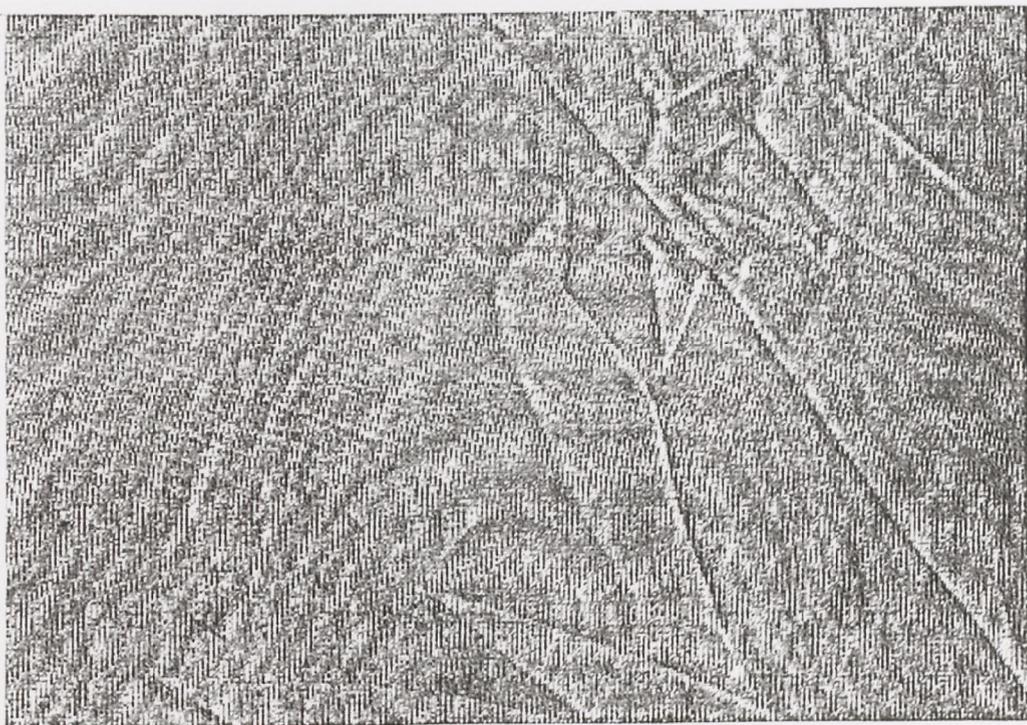


Figure 5.21 Scanned image of untreated silk fabric that has been washed using a standard detergent on a delicate wash cycle, line dried and ironed.



Figure 5. 22 Scanned image of silk fabric treated with 6% w/w BTCA, and a 1:1 molar ratio of SHP that has been washed using a standard detergent on a delicate wash cycle and line dried.

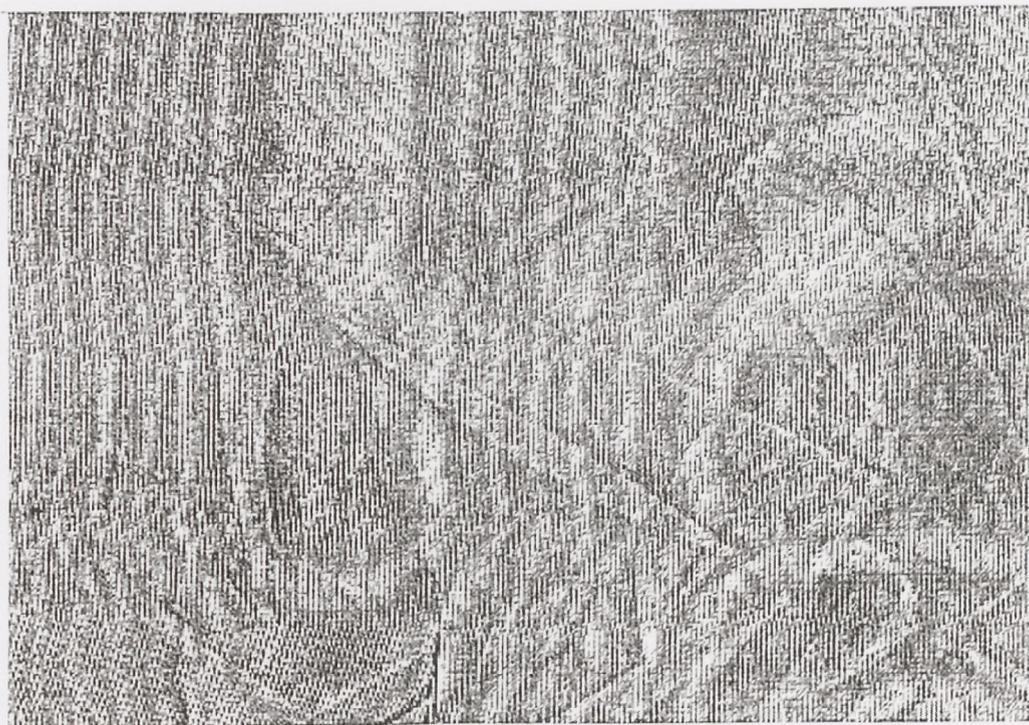


Figure 5. 23 Scanned image of silk fabric treated with 6% w/w BTCA, and a 1:1 molar ratio of SHP that has been washed using a standard detergent on a delicate wash cycle, line dried and ironed.



Figure 5. 24 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and 1% w/w Ceranine L (Clariant) that has been washed using a standard detergent on a delicate wash cycle and line dried.



Figure 5. 25 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and 1% w/w Ceranine L (Clariant) that has been washed using a standard detergent on a delicate wash cycle, line dried and ironed.

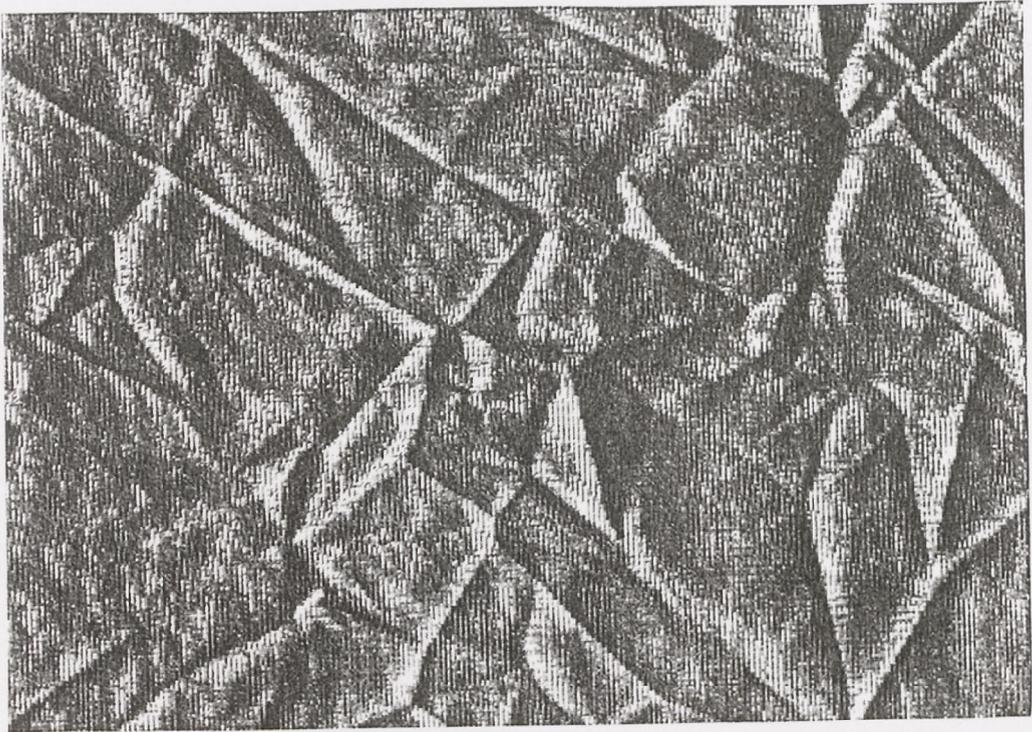


Figure 5. 26 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and 1% w/w polyethylene glycol 1000 that has been washed using a standard detergent on a delicate wash cycle and line dried.

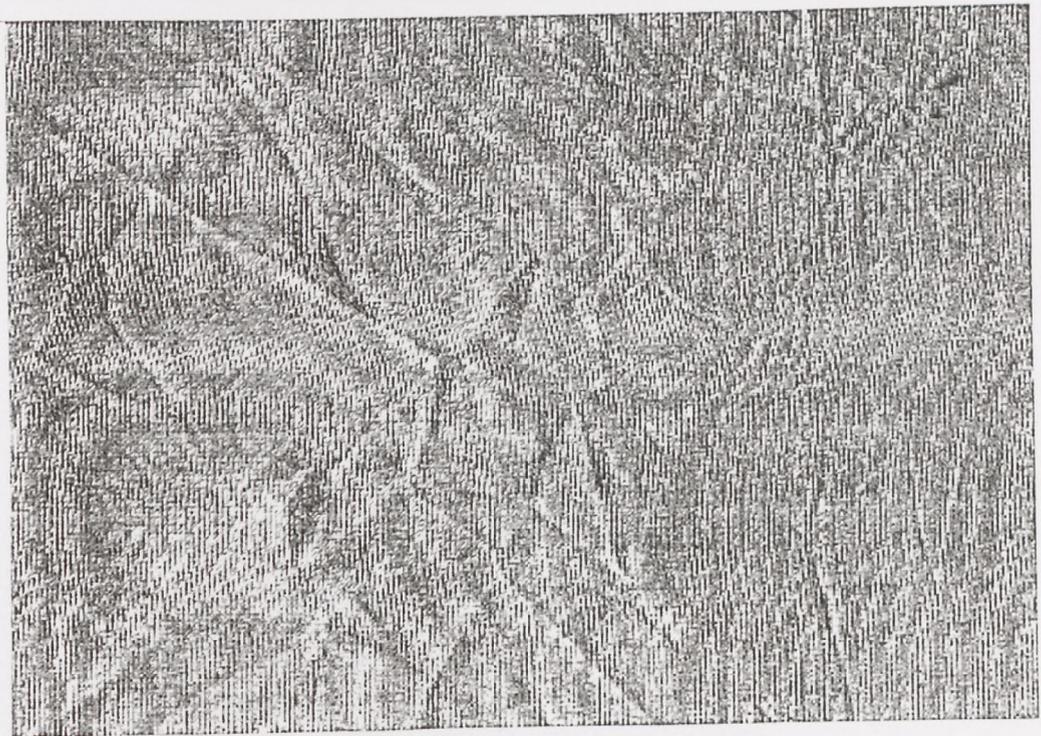


Figure 5. 27 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and 1% w/w polyethylene glycol 1000 that has been washed using a standard detergent on a delicate wash cycle, line dried and ironed.



Figure 5. 28 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and 1% w/w Ultratex SW (Ciba) that has been washed using a standard detergent on a delicate wash cycle and line dried.

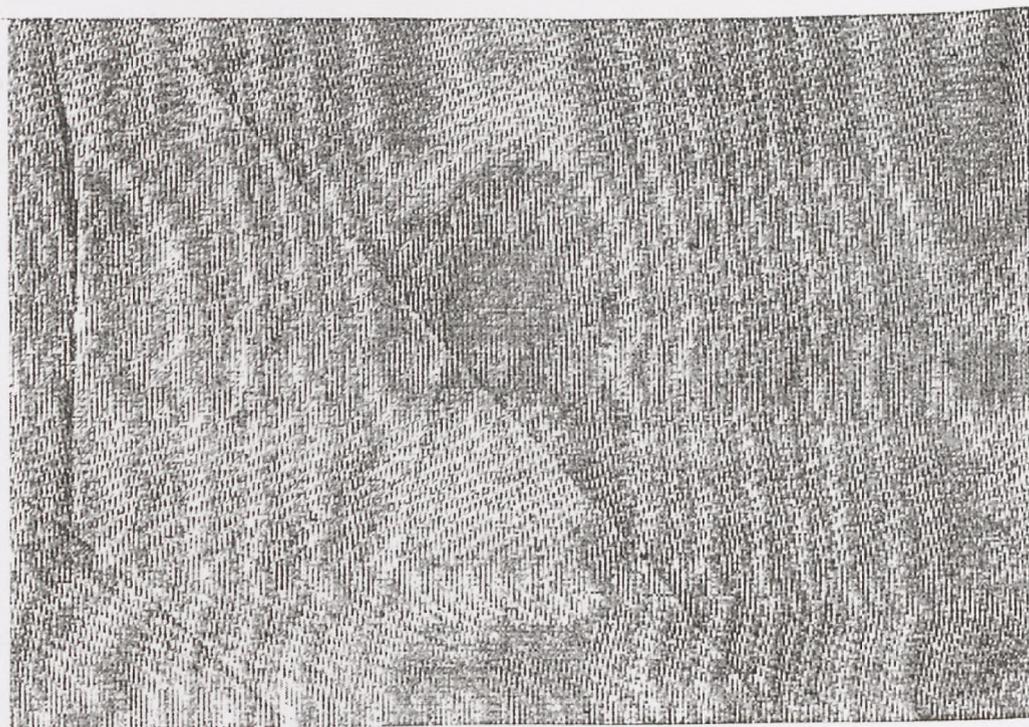


Figure 5. 29 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and 1% w/w Ultratex SW (Ciba) that has been washed using a standard detergent on a delicate wash cycle, line dried and ironed.

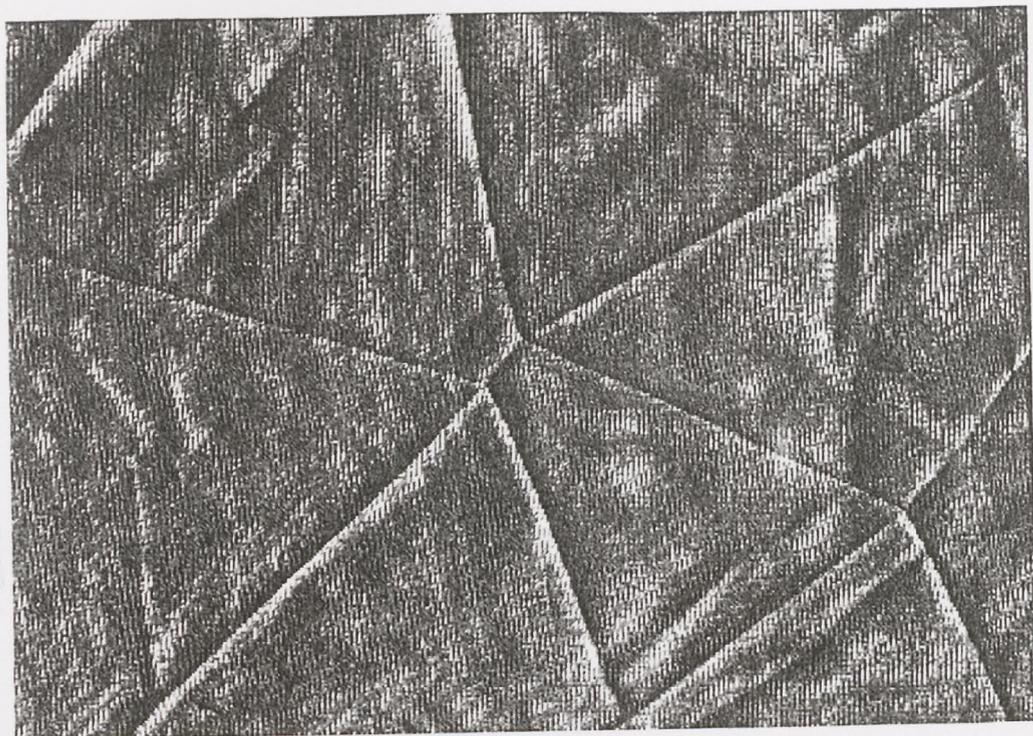


Figure 5.30 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and 1% w/w Ultratex FEW (Ciba) that has been washed using a standard detergent on a delicate wash cycle and line dried.

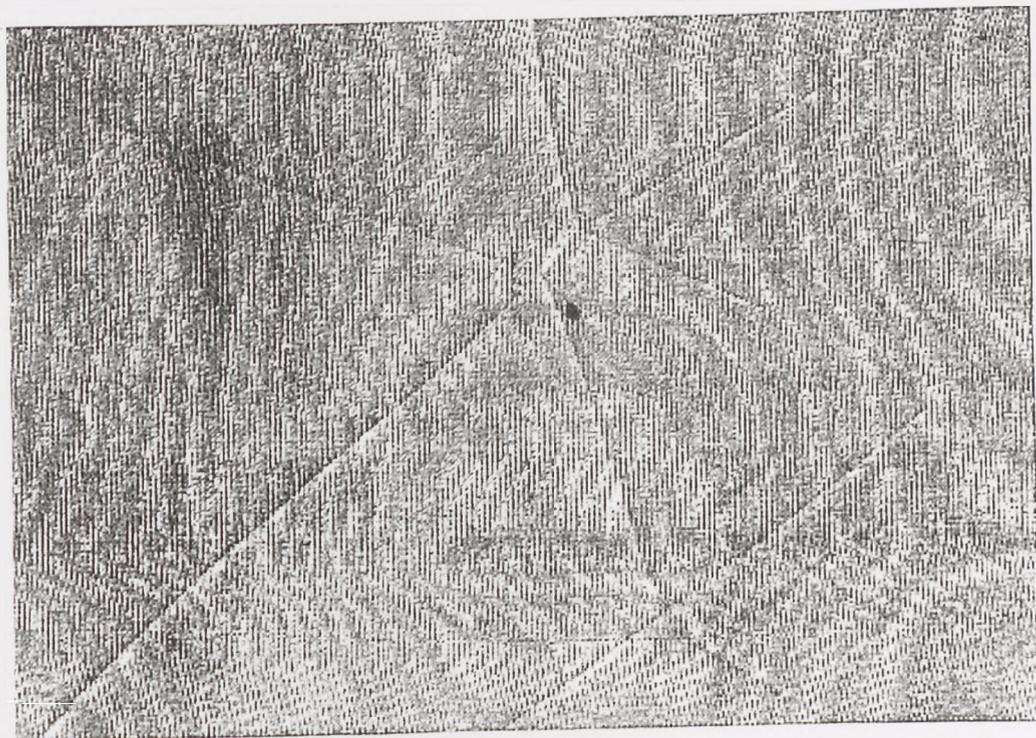


Figure 5.31 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and 1% w/w Ultratex FEW (Ciba) that has been washed using a standard detergent on a delicate wash cycle, line dried and ironed.

It can be seen from the scanned images of the silk fabrics treated with the BTCA/SHP finishing system with and without additional softening finish that there is a marked increase in easy-care properties of the silk fabric. The improvement in easy-care performance is at its greatest when a PCA finish is combined with a silicone finish. However, this finish does not lead to silk fabrics that when washed and ironed are completely free from creasing.

The improvement in easy-care properties is brought about by an improvement in the elastic properties of the fabric. Treatment with BTCA/SHP system improves the elastic properties of the fabric to an extent that a large majority of the minute creases that cause mussiness are removed, but the improvement in elastic properties is not sufficient to remove the hard, sharp creases or the moderate, less sharp creases. After-treatment with a silicone softener improves the elastic properties of the fabric further and the moderate, less sharp creases are removed. The improvement in elastic behaviour of the treated silk fabric is not sufficient to remove the hardest, sharpest creases. These creases are very difficult to remove by ironing. It is concluded that these finishes, despite their obvious improvement in easy-care properties of the treated silk fabrics, do not lead to sufficient improvement to be recommended as a new easy-care finish for silk fabrics.

The incorporation of additional pad bath additives was investigated as a means for improving the elastic properties of the treated silk fabrics to an extent that there would be no creases inserted into the silk fabrics during washing. The addition of formic acid and acrylic acid were investigated, as it has been reported that the addition of formic acid into the pad bath can improve silk fabric swelling and the easy-care performance of silk fabrics treated with TMM (82).

Figure 5. 32 and Figure 5. 33 graphically display the results of silk fabric treated with BTCA/SHP finishing system with different quantities of formic acid added to the pad bath. Figure 5. 34 and Figure 5. 35 show the results of silk fabric treated with BTCA/FA/SHP finishing system and an after-treatment with 1%w/w of different softeners.

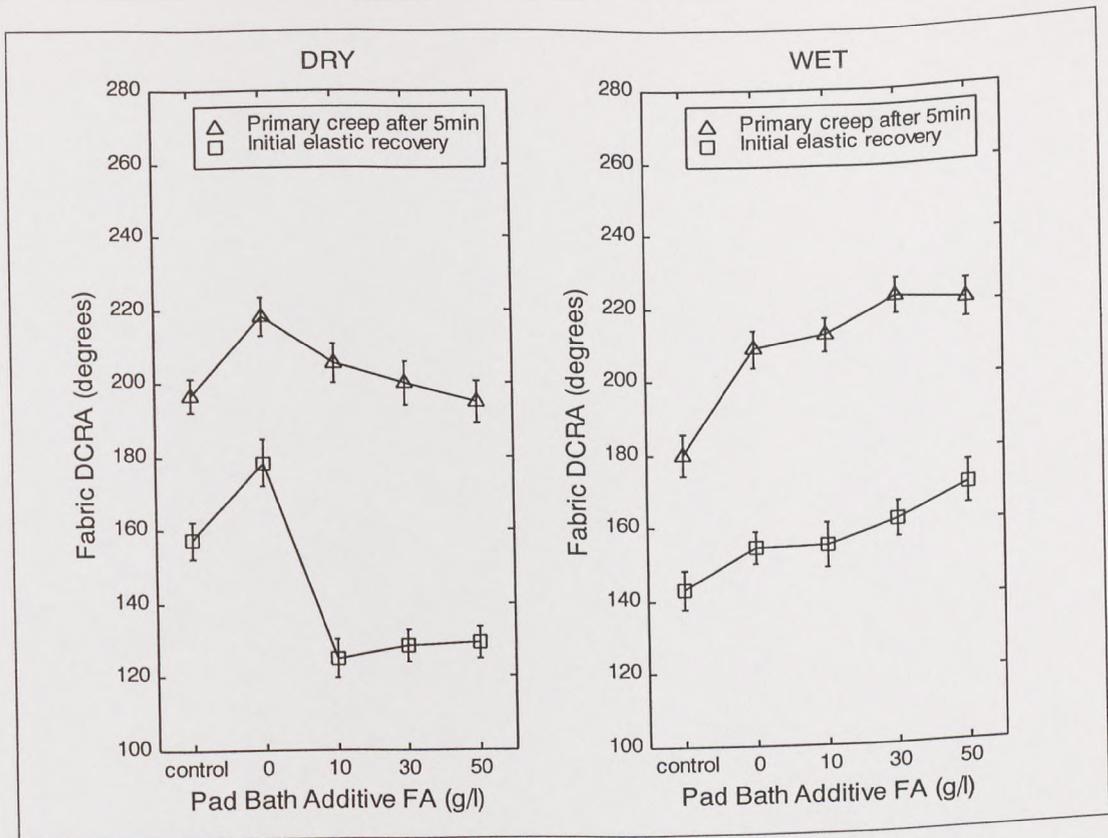


Figure 5.32 Fabric CRAs of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and varying amounts of formic acid (FA).

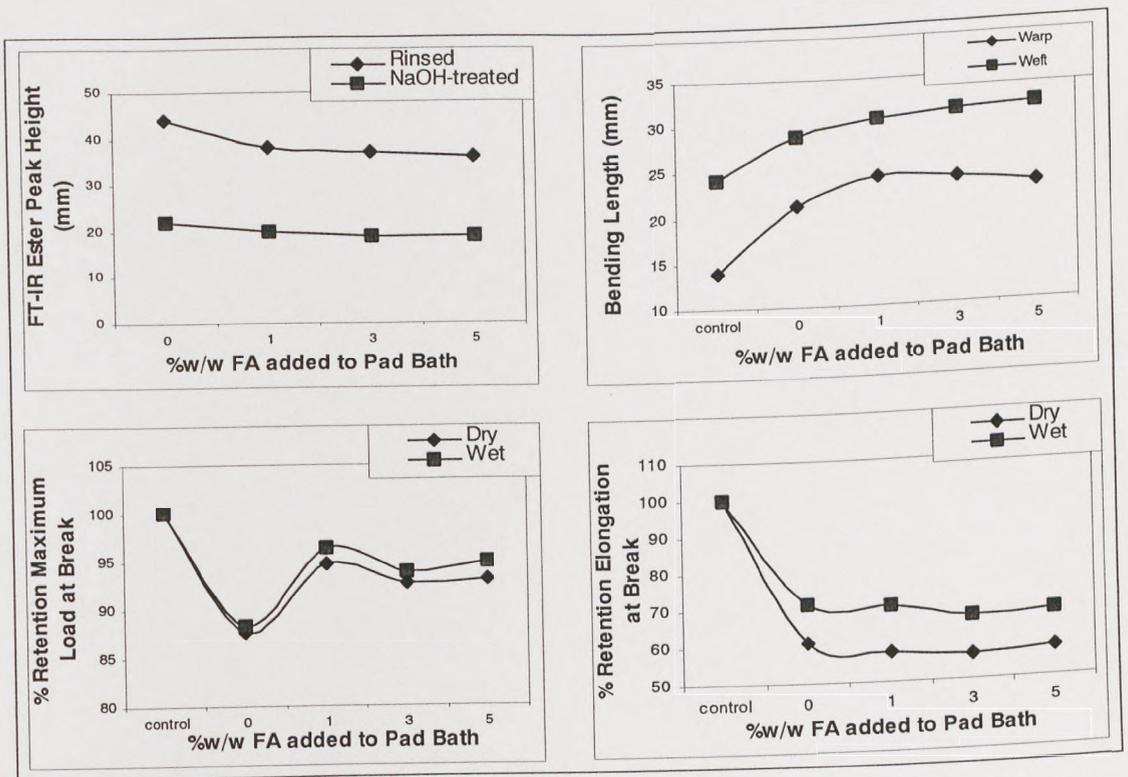


Figure 5.33 Graphical representation of the properties of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and varying amounts of formic acid. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

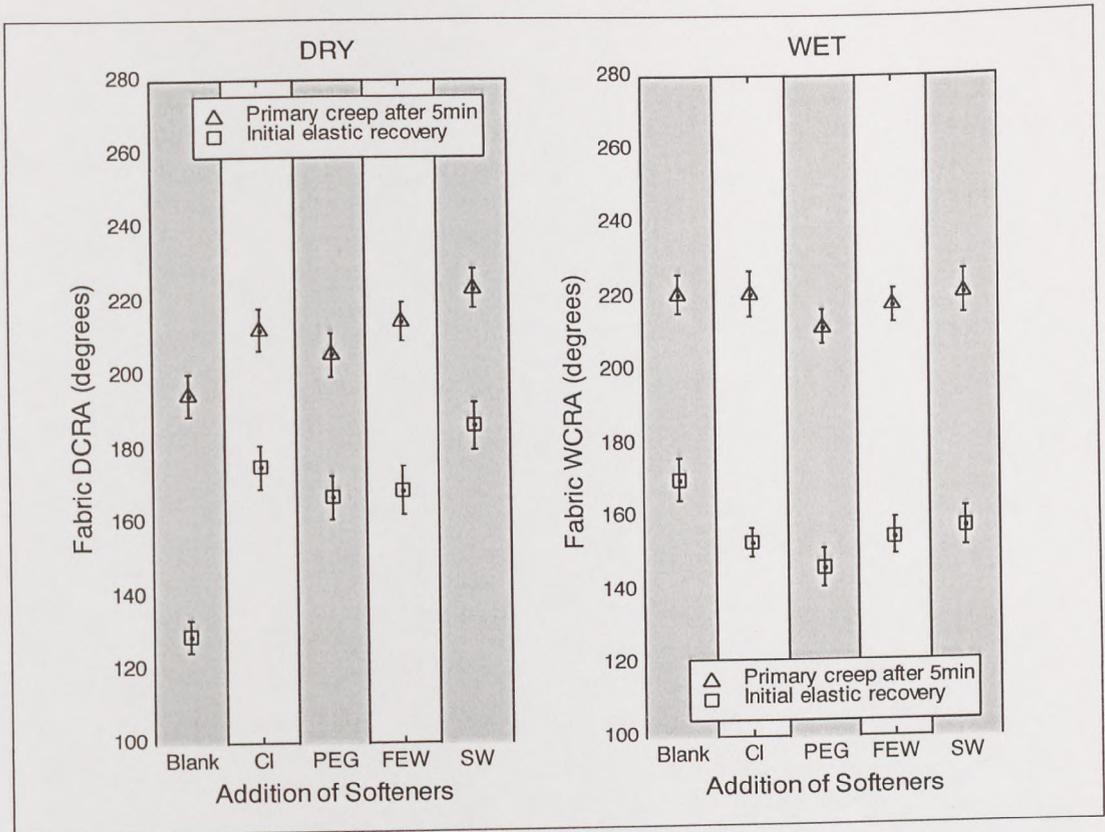


Figure 5.34 Fabric CRAs of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP, 5% w/w FA and 1% w/w of different softeners.

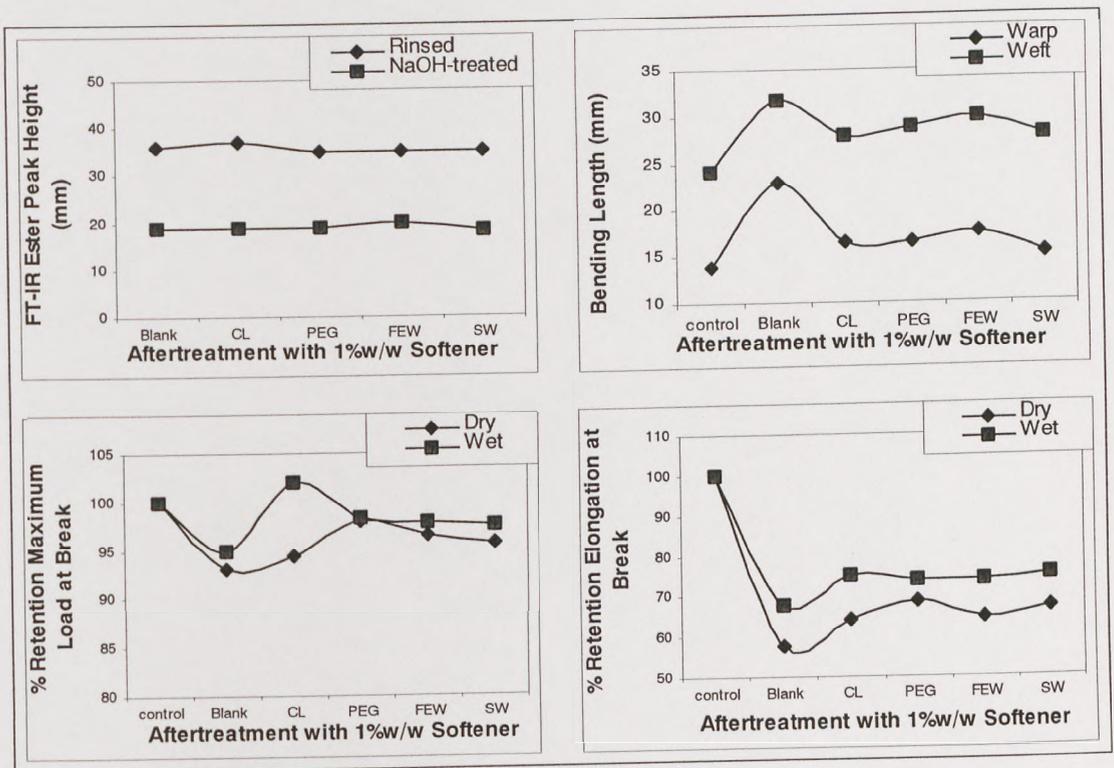


Figure 5.35 Graphical representation of the properties of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP, 5% w/w FA and 1% w/w of different softeners. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

In chapter three it was found that the addition of FA into the pad bath produced fabrics with improved wet recovery from creasing. However, the dry stability of the treated fabrics was not improved. The dry stability of the untreated sample is already high, and therefore it is the wet stability that needs to be improved to impart easy-care characteristics to silk fabrics. FA is a known hydrogen bond breaker and concentrated solutions can dissolve silk. It was proposed that the addition of FA into the pad bath could improve fibre swelling by acting as a hydrogen bond breaker, and thus improve the migration of the PCA within the silk fibre.

From Figure 5.32 and Figure 5.33 and from Appendix 3, Table A3.3 it can be seen that the addition of FA into the BTCA/SHP pad baths

- Improves the elastic recovery from creasing in the wet state but not in the dry state.
- Does not alter the quantity of ester links formed within the treated silk fabric.
- Increases the fabric stiffness slightly, shown by a slight increase in both warp and weft fabric bending length.
- Improves the fabric breaking strength, and has no effect on the fabric retention of elongation at break.
- Does not affect the fabric moisture regain or fabric yellowness.

From Figure 5.34 and Figure 5.35 and from Appendix 3, Table A3.3 it can be seen that after-treatment of silk fabrics treated with a BTCA/FA/SHP finish with various different softeners

- Improves the elastic recovery from creasing in the dry state but not in the wet state.
- Does not alter the quantity of ester links formed within the treated silk fabric.
- Decreases the fabric stiffness that was increased as a result of the PCA finish.
- Increases the fabric mechanical properties; fabric breaking strength and elongation at break.
- Slightly increases the fabric moisture regain and decreases the fabric yellowness.
- Imparts a large increase in fabric resistance to abrasion.
- Improves the fabric stability to washing and reduces the shrinkage in the warp direction.



Figure 5.36 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and 5% w/w formic acid that has been washed using a standard detergent on a delicate wash cycle and line dried.

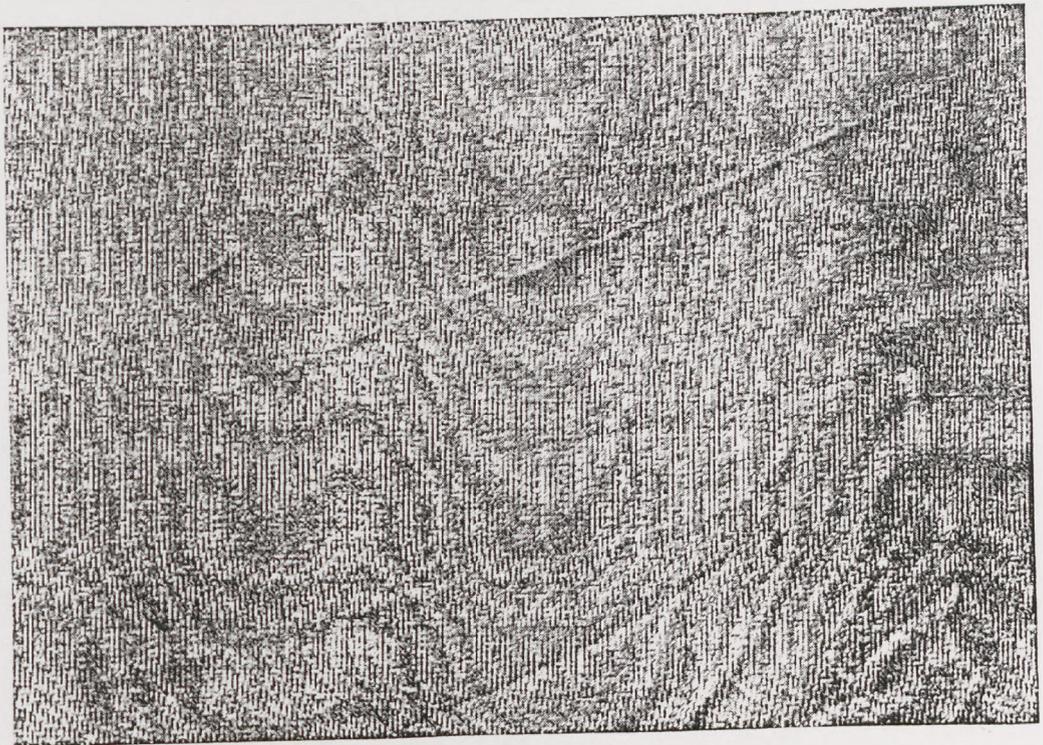


Figure 5.37 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and 5% w/w formic acid that has been washed using a standard detergent on a delicate wash cycle, line dried and ironed.



Figure 5. 38 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP, 5% w/w formic acid and 1% w/w Ultratex FEW (Ciba) that has been washed using a standard detergent on a delicate wash cycle and line dried.

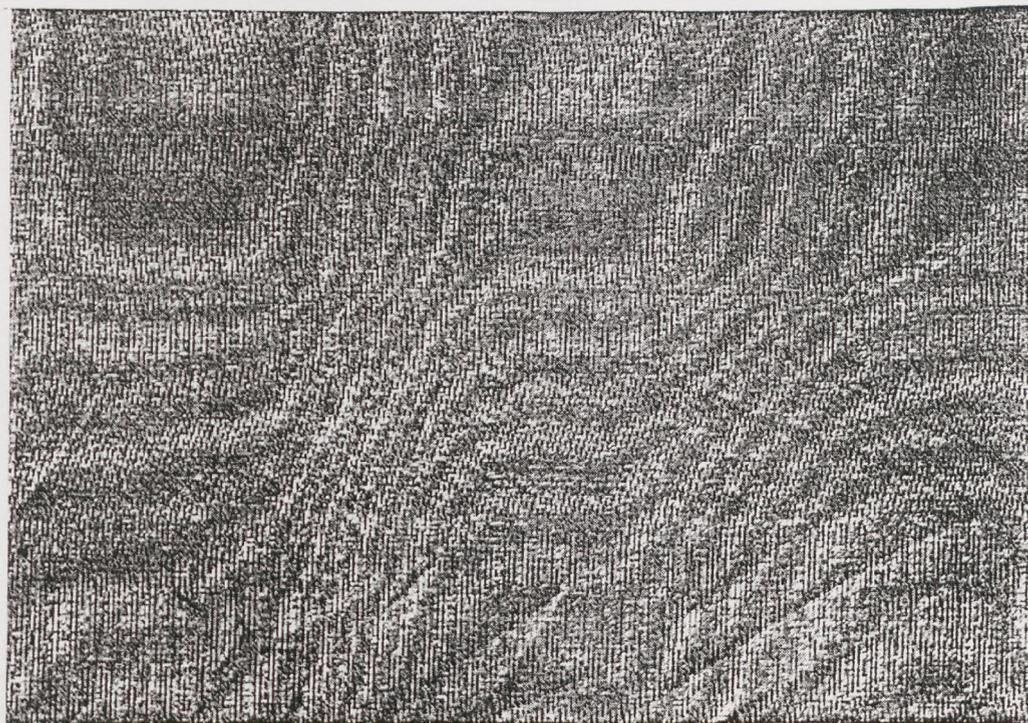


Figure 5. 39 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP, 5% w/w formic acid and 1% w/w Ultratex FEW (Ciba) that has been washed using a standard detergent on a delicate wash cycle, line dried and ironed.

In order to judge the effect of the incorporation of FA into the PCA pad bath with and without a softening after-treatment the treated samples were washed and line dried and the extent of creasing after washing analysed both before and after ironing, see Table 5.7 and Figure 5.36 to Figure 5.39.

PCA + FA + Softener	Shrinkage after Washing (%)		Appearance after Washing	Fabric WCRA after 5min (degrees)
	Warp	Weft		
Untreated Control	4	0	Very creased. Hard creases and lots of mussiness. Mussiness removed when ironed.	179.6 ± 6.2
BTCA + FA	1.5	0	Minimal creasing. Hard creases and some mussiness. Mussiness removed when ironed.	220.8 ± 5.4
BTCA + FA + Ceranine L	0	0	Minimal creasing. Hard creases and some mussiness. Mussiness removed when ironed.	220.7 ± 6.1
BTCA + FA + PEG 1000	0.5	0	Minimal creasing. Hard creases and some mussiness. Mussiness removed when ironed.	211.6 ± 4.6
BTCA + FA + Ultratex FEW	0	0	Very little creasing. A few sharp creases and some mussiness. Nearly all ironed out.	217.5 ± 4.6
BTCA + FA + Ultratex SW	1	0	Very little creasing. A few sharp creases and some mussiness. Nearly all ironed out.	220.9 ± 6.0

Table 5.7 Summary of the appearance of treated silk fabric samples after washing and ironing.

The incorporation of FA into the PCA pad bath markedly improves the easy-care properties of silk fabrics treated with BTCA. It is proposed that the FA improves the swelling of silk during the batching process. Some of the hydrogen bonds holding the chain molecules together in silk fibroin are broken and move apart and the silk fabric takes on a new, swollen relaxed state. The BTCA molecules migrate inside the fabric and during the curing process new cross-links are formed in the swollen silk fibroin where the molecular chains are close enough to form cross-links, i.e., at the edge of the swollen amorphous sections. These new cross-links hold the silk fibroin in the swollen state and prevent the original hydrogen bonds from reforming. The stabilised swollen silk fibre swells less when re-wetted and thus a reduction in fabric shrinkage was observed after washing.

FA may act as a catalyst for acid-catalysed cross-linking of BTCA with silk fibroin, according to the mechanism discussed in Section 4.2.1.4. The after-treatment with a silicone softener improved the dry elastic recovery and would help to prevent creases being formed in the dry state.

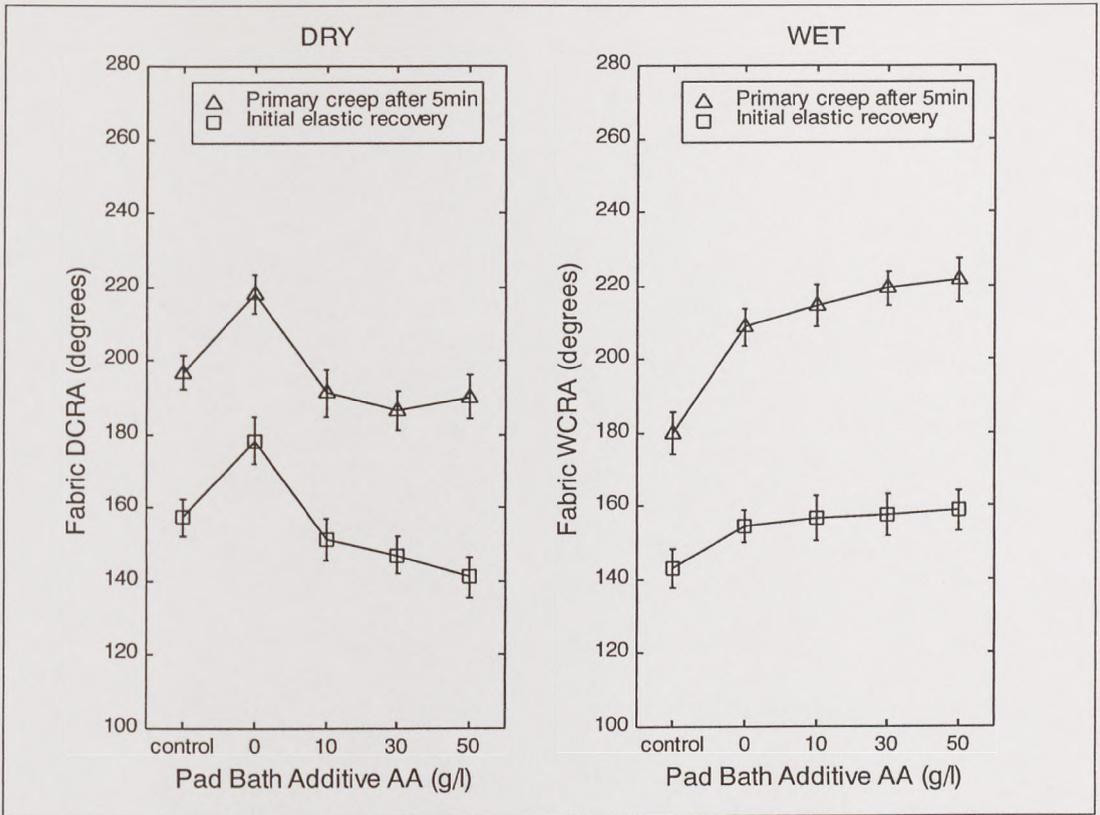


Figure 5.40 Fabric CRAs of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and varying amounts of acrylic acid (AA).

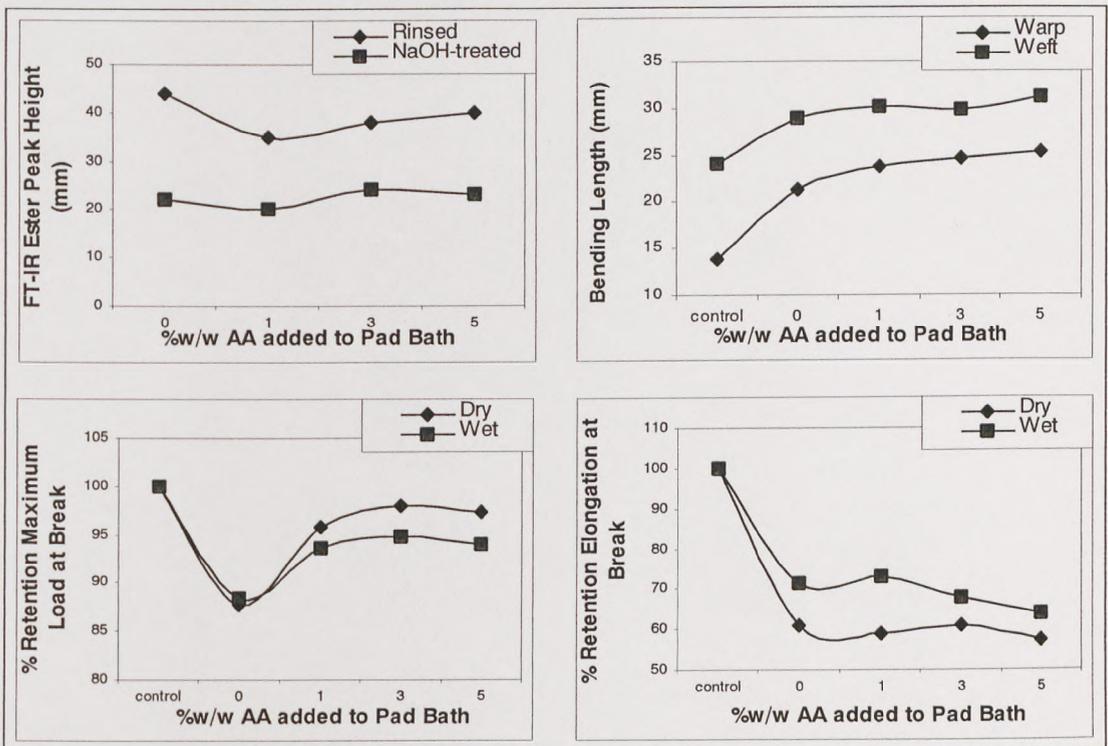


Figure 5.41 Graphical representation of the properties of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and varying amounts of acrylic acid. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

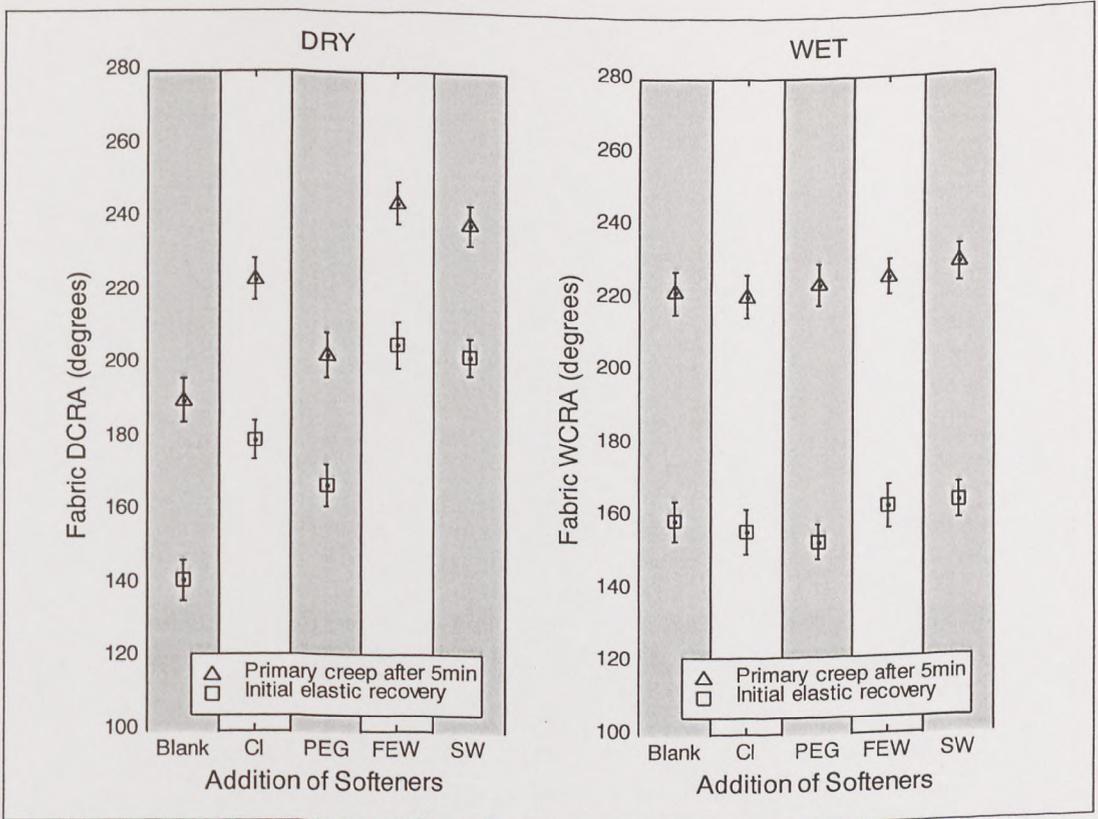


Figure 5.42 Fabric CRAs of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP, 5% w/w AA and 1% w/w of different softeners.

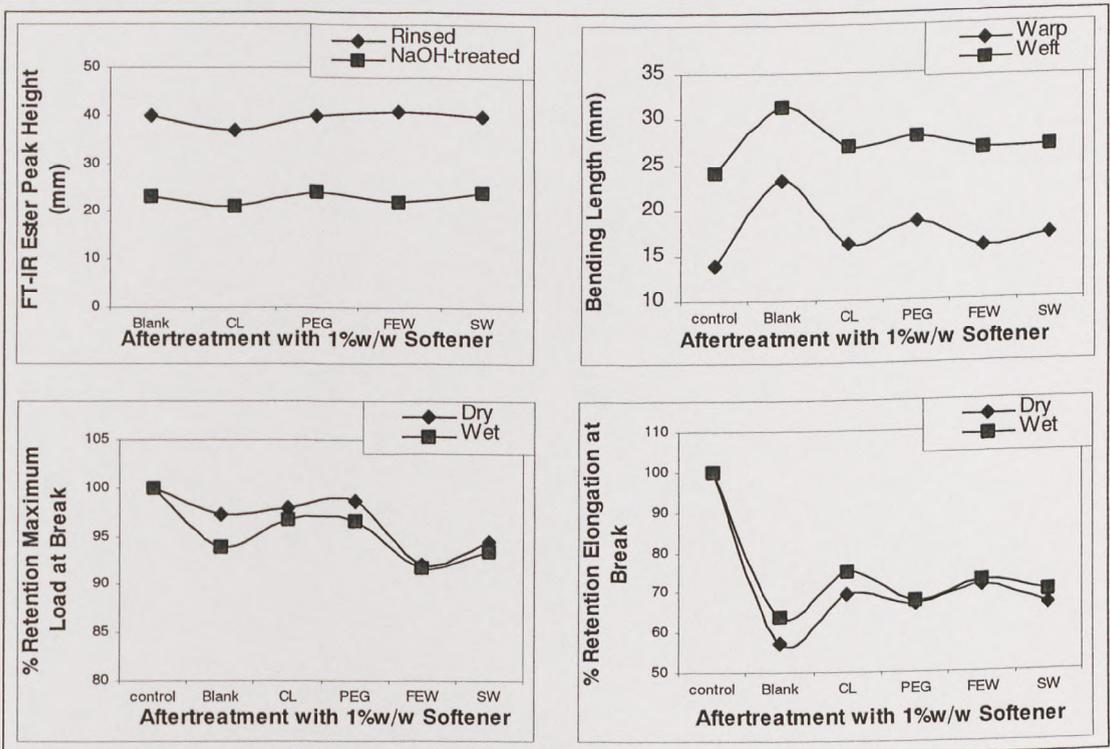


Figure 5.43 Graphical representation of the properties of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP, 5% w/w AA and 1% w/w of different softeners. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

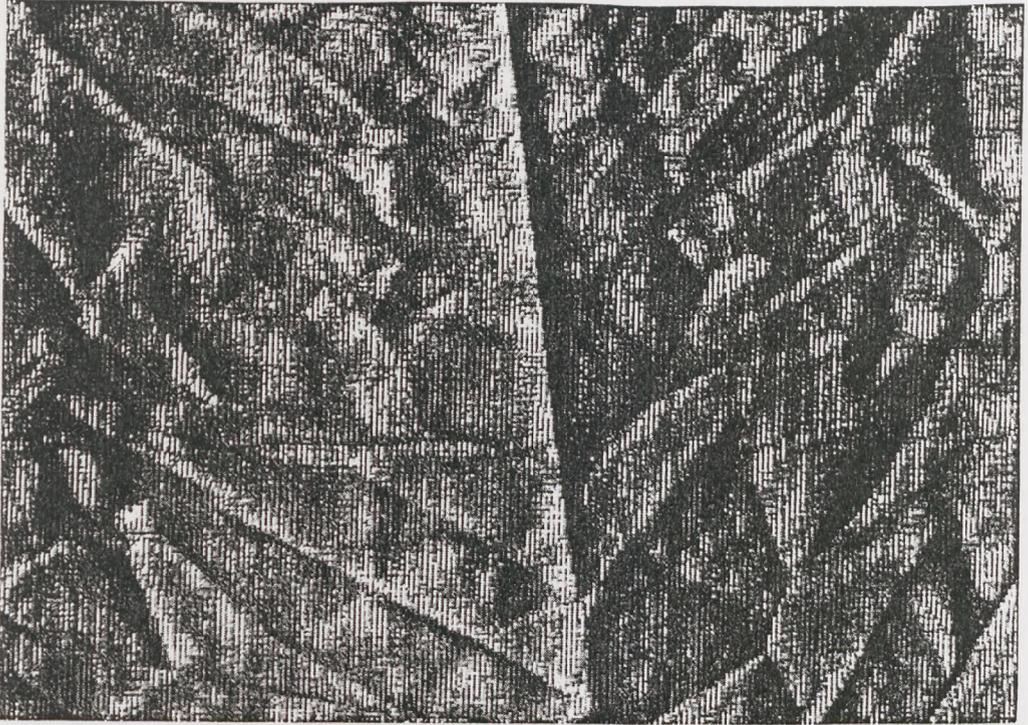


Figure 5. 44 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and 5% w/w acrylic acid that has been washed using a standard detergent on a delicate wash cycle and line dried.

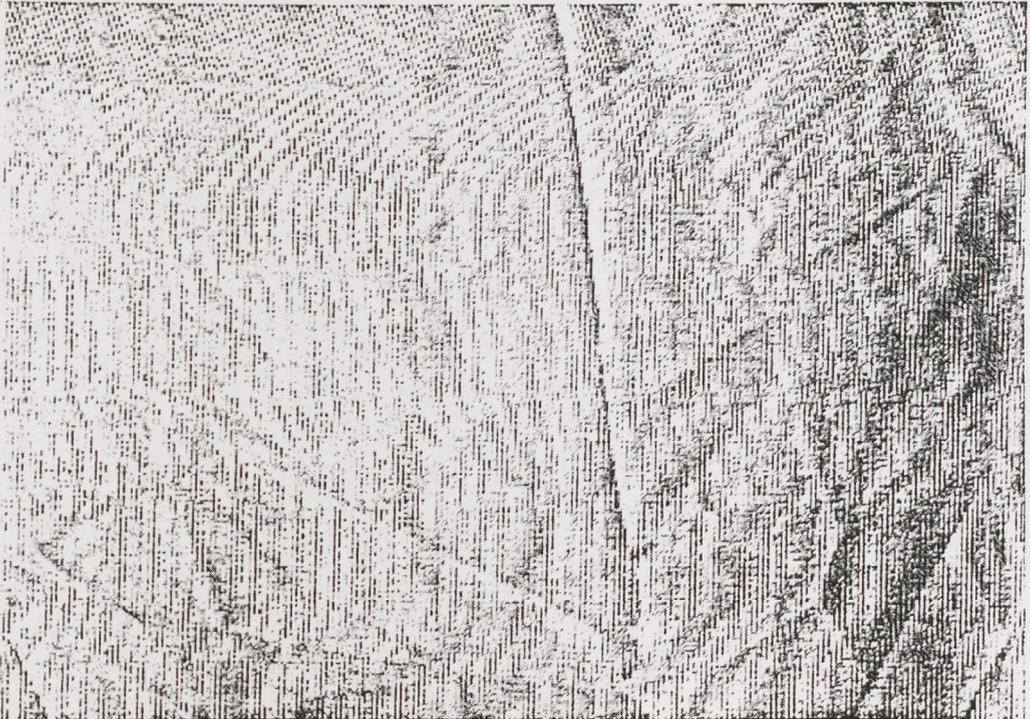


Figure 5. 45 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and 5% w/w acrylic acid that has been washed using a standard detergent on a delicate wash cycle, line dried and ironed.

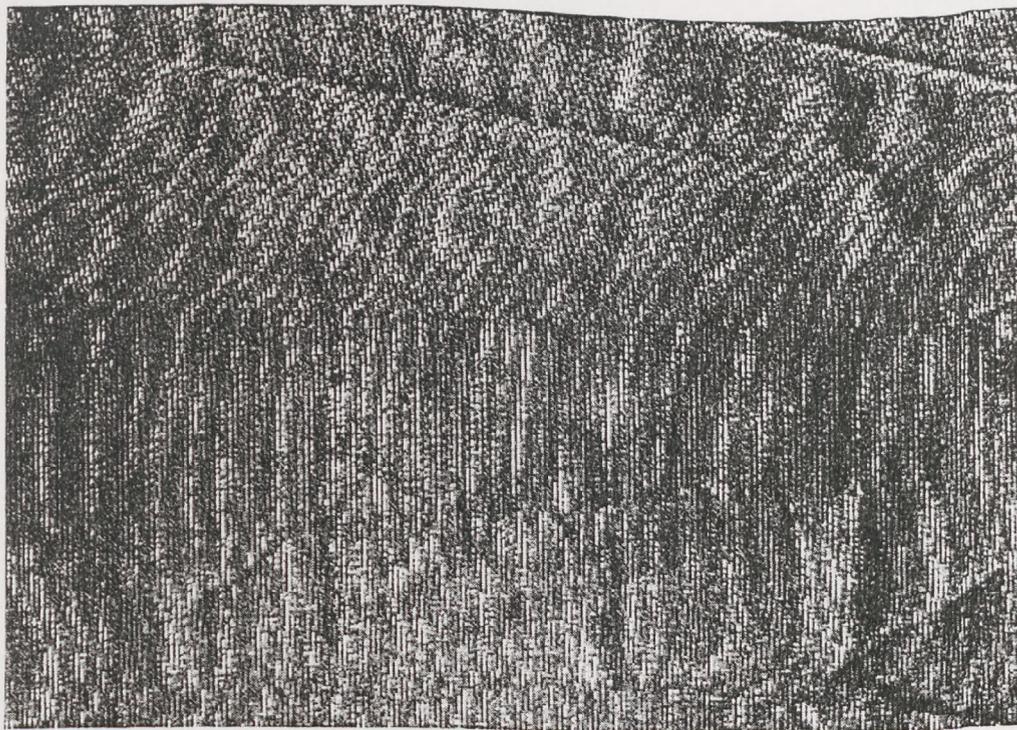


Figure 5. 46 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP, 5% w/w acrylic acid and 1% w/w Ultratex SW (Ciba) that has been washed using a standard detergent on a delicate wash cycle and line dried.

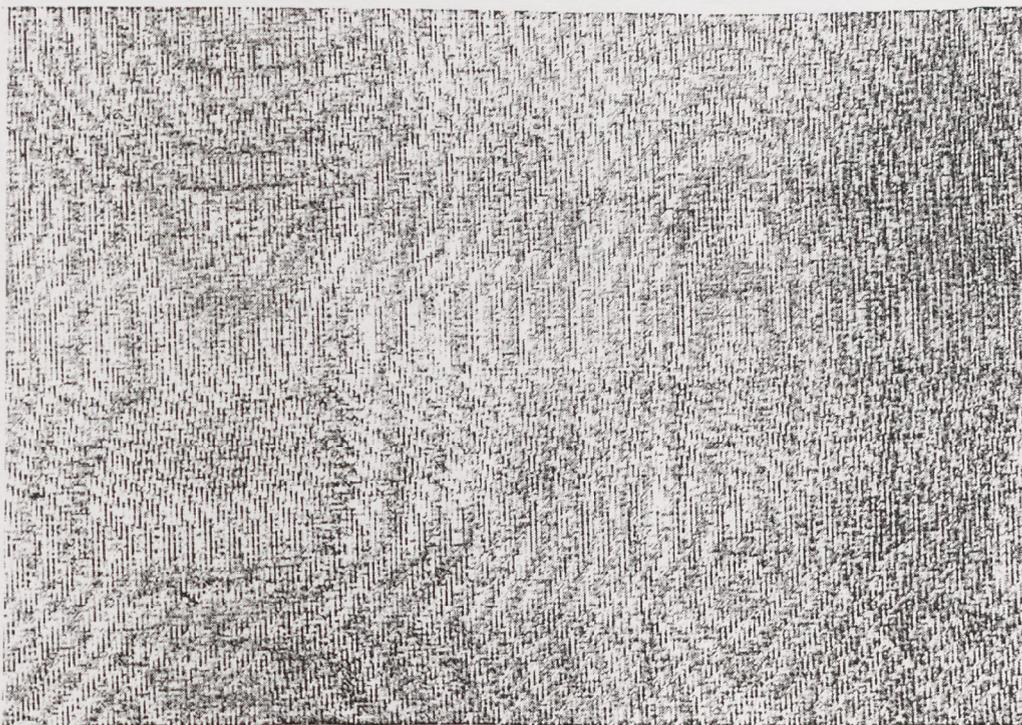


Figure 5. 47 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP, 5% w/w acrylic acid and 1% w/w Ultratex SW (Ciba) that has been washed using a standard detergent on a delicate wash cycle, line dried and ironed.

It is concluded that the incorporation of FA as a swelling agent and/or acid catalyst into the PCA pad bath improves the easy-care properties of the treated silk fabrics. As a consequence of the large improvement in elastic properties brought about by this finishing process the author recommends it for further study as a new easy-care finish for silk fabrics.

The use of acrylic acid (AA), $\text{H}_2\text{C}=\text{CHCOOH}$, was investigated as an alternative swelling agent/acid catalyst to FA. The results of which are displayed graphically both with and without a softening after-treatment in Figure 5. 40 to Figure 5. 43 and are tabulated in Appendix 3, Table A3.4. The results show that the incorporation of AA into the PCA pad bath has the same effect on fabric properties as did the addition of FA. AA treatment

- Improves the elastic recovery from creasing in the wet state but not in the dry state.
- Does not alter the quantity of ester links formed within the treated silk fabric.
- Increases the fabric stiffness slightly, shown by a slight increase in both warp and weft fabric bending length.
- Improves the fabric breaking strength, and has no effect on the fabric retention of elongation at break.
- It improves the fabric moisture regain and increases slightly the fabric yellowness.

It can be seen that after-treatment of silk fabrics treated with a BTCA/AA/SHP finish with various different softeners. Again there are close similarities with the BTCA/FA/SHP finish, e.g. the finish

- Improves the elastic recovery from creasing in the dry state but not in the wet state.
- Does not alter the quantity of ester links formed within the treated silk fabric.
- Decreases the fabric stiffness that was increased as a result of the PCA finish.
- Increases the fabric retention of elongation at break and has minimal effect on fabric breaking strength.
- Slightly increases the fabric moisture regain and decreases the fabric yellowness.
- Large increase in fabric resistance to abrasion.
- Improves the fabric stability to washing, reduces the shrinkage in the warp direction.

In order to judge the effect of the incorporation of AA into the PCA pad bath with and without a softening after-treatment the treated samples were washed and line dried and

the extent of creasing after washing analysed both before and after ironing, see Table 5.8, and Figure 5.44 to Figure 5.47.

The incorporation of AA into the PCA pad bath like FA markedly improves the easy-care properties of silk fabrics treated with BTCA. It is proposed that, like FA, AA improves the fibre swelling by acting as a hydrogen bond breaker and thus improves the migration of the PCA inside the fibre. New cross-links hold the silk fibroin in the swollen state and prevent the original hydrogen bonds from reforming. The stabilised swollen silk fibre swells less when re-wetted and again a reduction in fabric shrinkage was observed after washing for the treated samples. Again, it is proposed that AA may also act as a catalyst for the reaction of BTCA with silk fibroin, according to the mechanism described in section 2.4.1.4. The after-treatment with a silicone softener improved the dry elastic recovery and would help to prevent creases being formed in the dry state.

PCA + AA + Softener	Shrinkage after Washing (%)		Appearance after Washing	Fabric WCRA after 5min (degrees)
	Warp	Weft		
Untreated Control	4	0	Very creased. Hard creases and lots of mussiness. Mussiness removed when ironed.	179.6 ± 6.2
BTCA + AA	2	0	Minimal creasing. Hard creases and some mussiness. Mussiness removed when ironed.	221.4 ± 5.7
BTCA + AA + Ceranine L	0.5	0	Minimal creasing. Hard creases and some mussiness. Mussiness removed when ironed.	220.4 ± 5.9
BTCA + AA + PEG 1000	1.5	0	Minimal creasing. Hard creases and some mussiness. Mussiness removed when ironed.	223.4 ± 5.6
BTCA + AA + Ultratex FEW	2	0	Very little creasing. One or two moderately sharp creases that were removed on ironing.	225.2 ± 4.9
BTCA + AA + Ultratex SW	2	0	Very little creasing. One or two moderately sharp creases that were removed on ironing.	228.5 ± 4.9

Table 5.8 Summary of the appearance of treated silk fabric samples after washing and ironing.

It is concluded that the incorporation of AA, like FA, into the PCA pad bath improves the easy-care properties of the treated silk fabrics. The improvement in elastic properties brought about by this finishing process is sufficient for this finish to also be recommended by the author for further study as a new easy-care finish for silk fabrics.

Finally, the incorporation of polyacrylic acid, PAA, was investigated as a combination finish. PAA has been used in conjunction with N-methylol resins to improve the easy-

care properties of the finish (193). Figure 5. 48 and Figure 5. 48 display the results of silk fabrics treated with BTCA/SHP finishing system with different quantities of PAA added to the PCA pad bath. The incorporation of PAA into the pad bath

- Markedly improves the elastic recovery from creasing in the wet state but markedly decreases the elastic recovery from creasing in the dry state.
- Does not have any effect on the quantity of ester links formed within silk fibroin.
- Large increase in fabric stiffness as shown by the increase in both warp and weft fabric bending length.
- Has minimal effect on fabric tensile properties, either bending strength or retention of elongation at break.
- Increase in fabric moisture regain and no effect on fabric yellowness.

Due to the large increase in fabric stiffness and the large decrease in recovery from creasing in the dry state the addition of PAA to the pad bath was kept to a minimum, 1%w/w. The fabric properties of treated silk fabrics were observed following an after-treatment with 1%w/w of various softening agents. The results are displayed graphically in Figure 5. 50 and Figure 5. 51 and can be found in tabulated form in Appendix 3, Table A3.4.

The after-treatment with various softening agents

- Improves the elastic recovery from creasing in the dry state but has minimal effect in the wet state.
- Has no effect on the quantity of ester links formed within the treated silk fabrics.
- Slightly decreases the increase in fabric stiffness caused by the BTCA/PAA/SHP finish.
- Slightly improves the reduction in tensile properties caused by the BTCA/PAA/SHP finish.
- Small increase in fabric moisture regain and a slight decrease in fabric yellowness.
- A large increase in the resistance of the treated fabrics to abrasion.
- A decrease in the weft shrinkage during subsequent fabric washing.

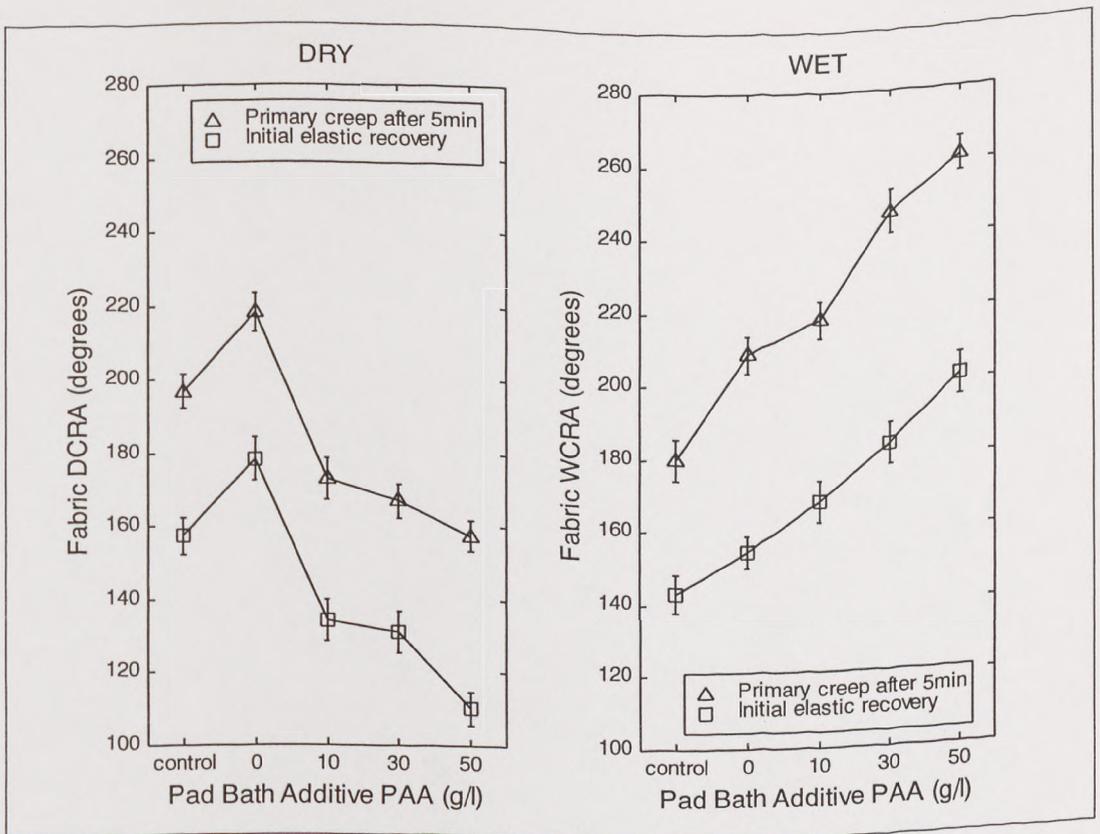


Figure 5.48 Fabric CRAs of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and varying amounts of polyacrylic acid (PAA).

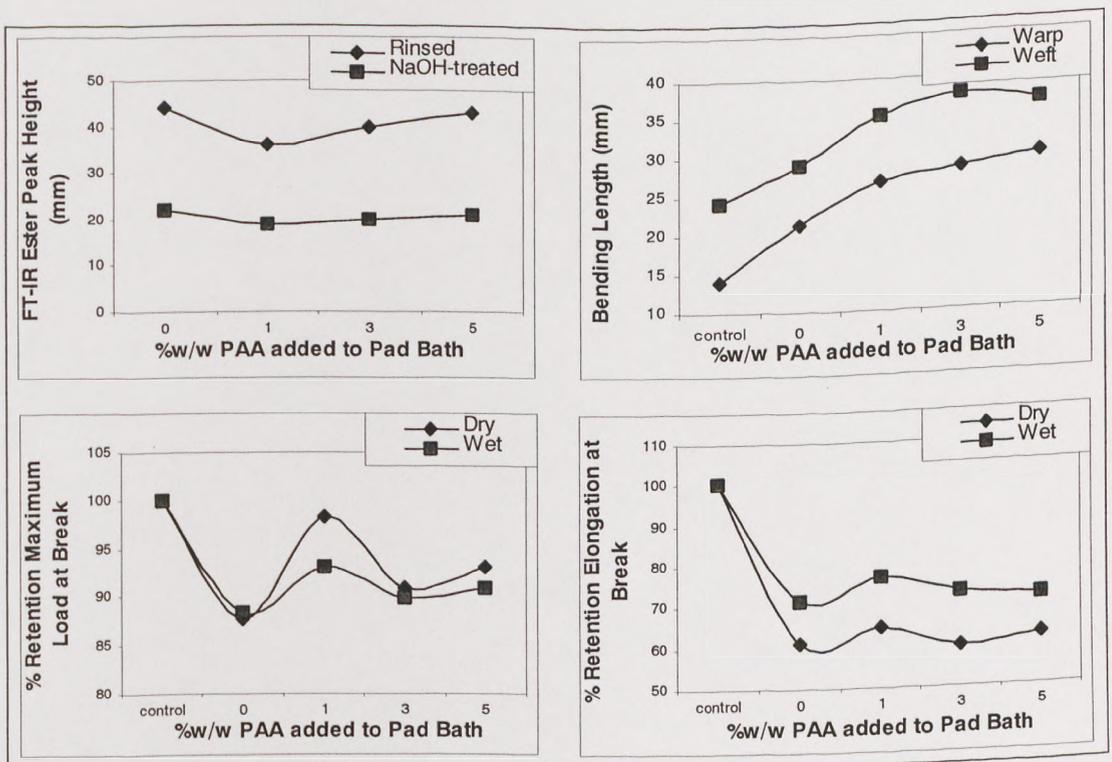


Figure 5.49 Graphical representation of the properties of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and varying amounts of polyacrylic acid. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.

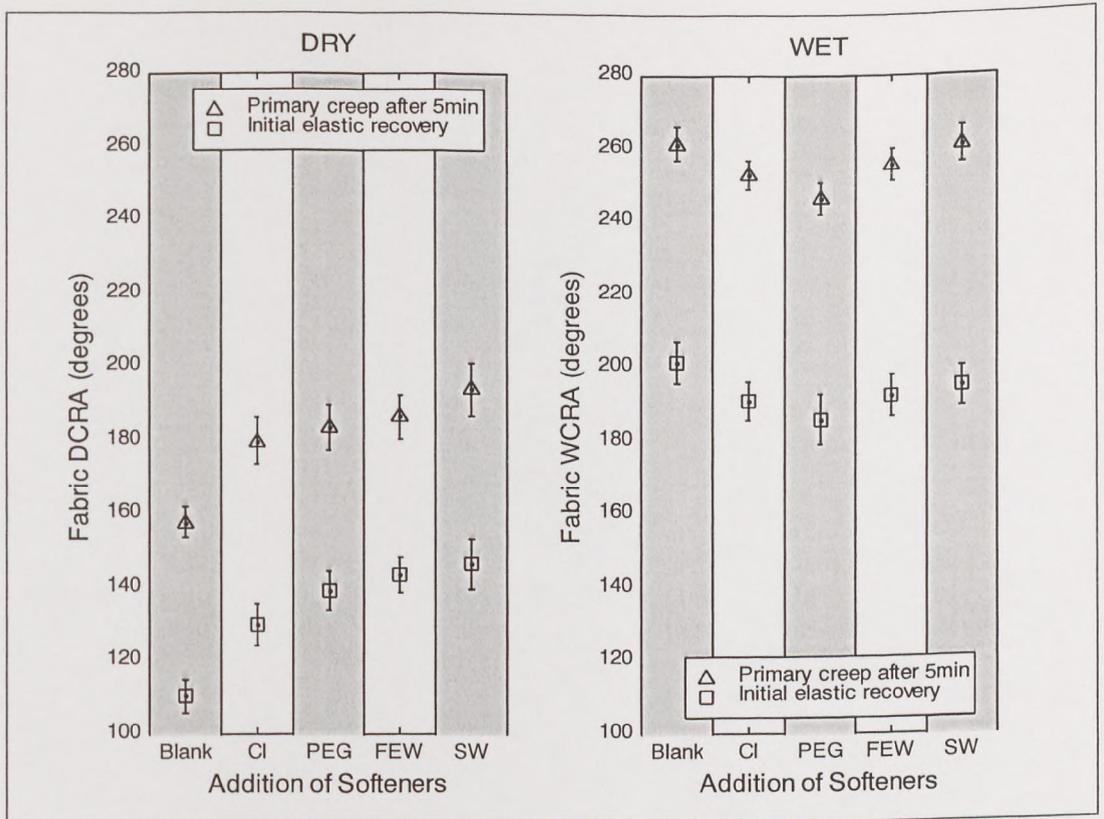


Figure 5.50 Fabric CRAs of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP, 5% w/w PAA and 1% w/w of different softeners.

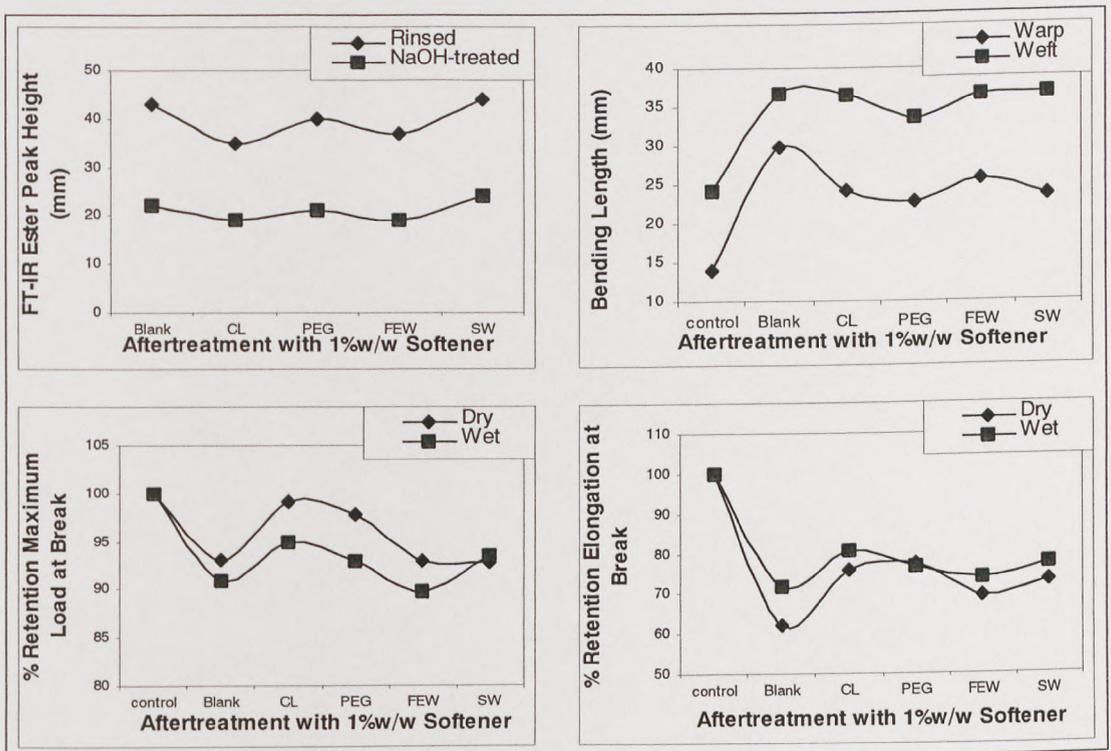


Figure 5.51 Graphical representation of the properties of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP, 5% w/w PAA and 1% w/w of different softeners. Top left, FT-IR ester peak height (mm); top right, fabric bending length, warp and weft; bottom left, percent fabric retention maximum load at break, dry and wet; and bottom right, percent fabric retention elongation at break, dry and wet.



Figure 5.52 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and 1% w/w polyacrylic acid that has been washed using a standard detergent on a delicate wash cycle and line dried.

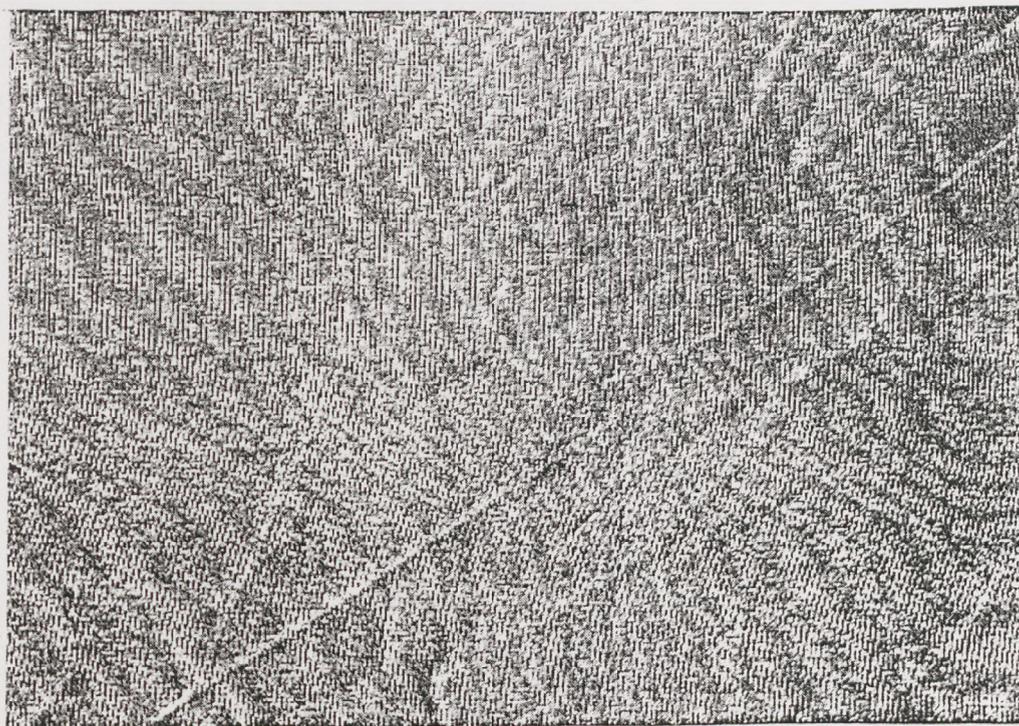


Figure 5.53 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP and 1% w/w polyacrylic acid that has been washed using a standard detergent on a delicate wash cycle, line dried and ironed.

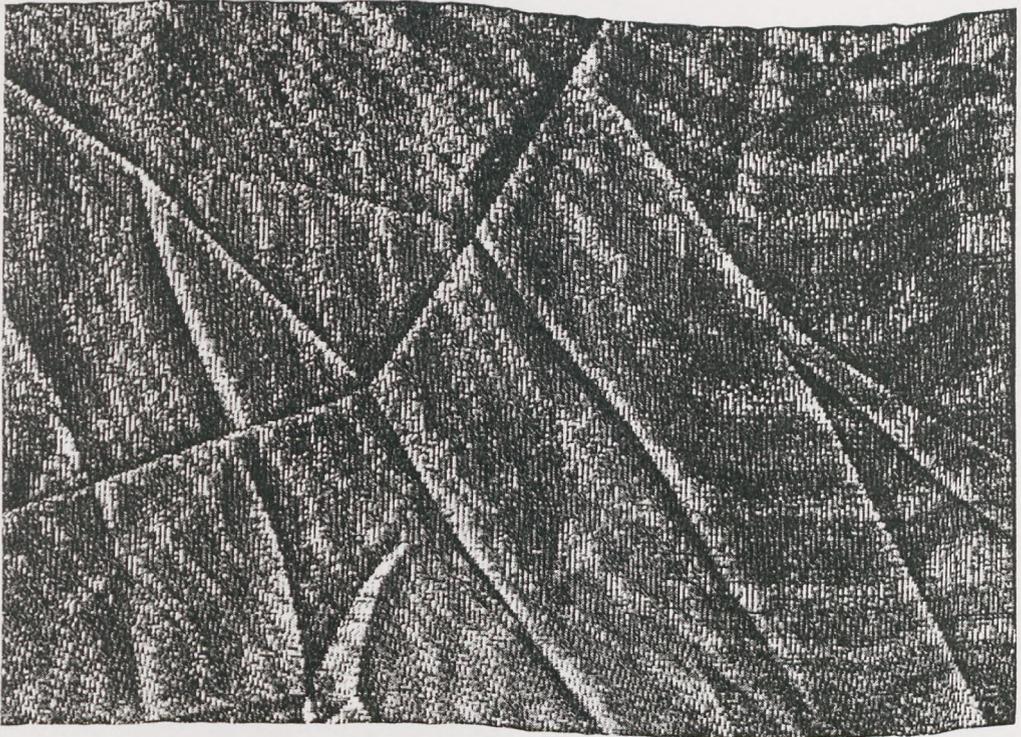


Figure 5.54 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP, 1% w/w polyacrylic acid and 1% w/w Ultratex SW (Ciba) that has been washed using a standard detergent on a delicate wash cycle and line dried.

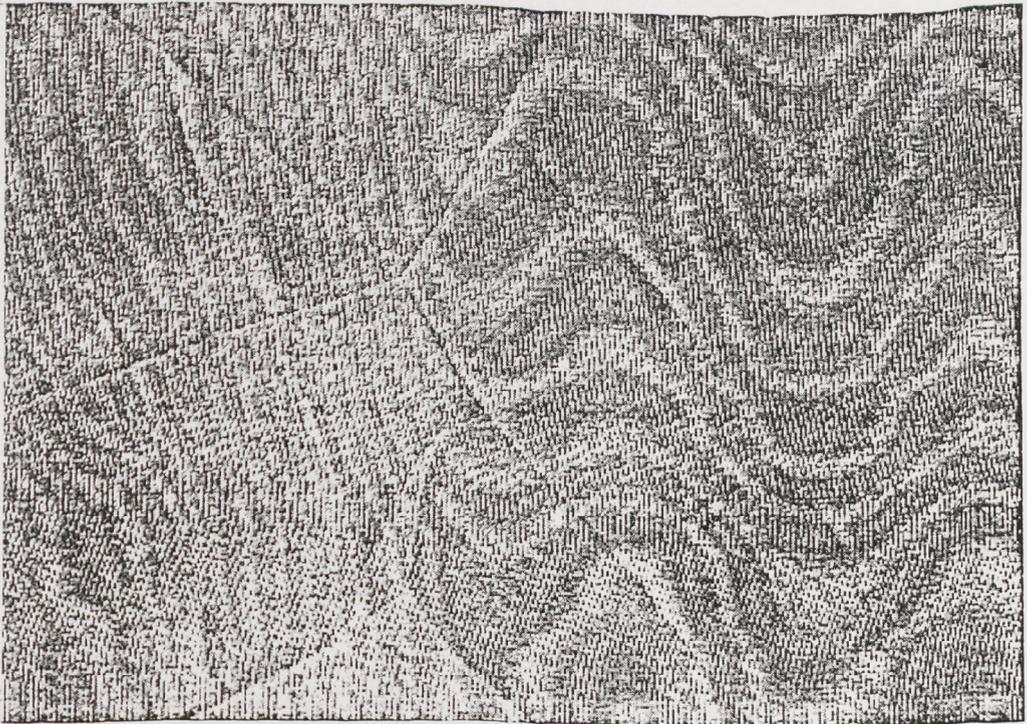


Figure 5.55 Scanned image of silk fabric treated with 6% w/w BTCA, a 1:1 molar ratio of SHP, 1% w/w polyacrylic acid and 1% w/w Ultratex SW (Ciba) that has been washed using a standard detergent on a delicate wash cycle, line dried and ironed.

PCA + PAA + Softener	Shrinkage after Washing (%)		Appearance after Washing	Fabric WCRA after 5min (degrees)
	Warp	Weft		
Untreated Control	4	0	Very creased. Hard creases and lots of mussiness. Mussiness removed when ironed.	179.6 ± 6.2
BTCA + PAA	2.5	0	Moderate creasing. Hard and moderate creases. Hard creases remain after ironing.	217.9 ± 4.9
BTCA + PAA + Ceranine L	2	0	Moderate creasing. Hard and moderate creases. Hard creases remain after ironing.	252.8 ± 4.0
BTCA + PAA + PEG 1000	1	0	Moderate creasing. Hard and moderate creases. Hard creases remain after ironing.	246.2 ± 4.5
BTCA + PAA + Ultratex FEW	1	0	Minimal creasing. Very hard creases only. These are difficult to remove during ironing.	255.5 ± 4.5
BTCA + PAA + Ultratex SW	2	0	Minimal creasing. Very hard creases only. These are difficult to remove during ironing.	260.9 ± 4.9

Table 5.9 Summary of the appearance of treated silk fabric samples after washing and ironing.

The performance of the treated fabrics as easy-care silk fabrics was observed after washing and line drying the treated fabrics both before and after drying, see Table 5.9, and Figure 5.52 to Figure 5.55. Despite the large increase in the elastic recovery from creasing measured in the wet state, there appeared to be little improvement in easy-care characteristics when compared with the silk fabrics treated with the BTCA/SHP finishing system without the addition of PAA in the pad bath. After-treatment with a silicone softener gave rise to a fabric that was super-soft and also had good draping properties. The inclusion of PAA in the pad bath increased the fabric stiffness and this improved the very limp handle characteristic of silk fabrics treated with silicone finishes. The inclusion of PAA in the pad bath does not improve the easy-care properties of the BTCA/SHP treated silk fabrics and therefore the author does not recommend the inclusion of PAA in such finishes except in circumstances where an increase in fabric stiffness is desirable.

5.2.3 Conclusions.

In this section the incorporation of additional chemicals into the pad bath was investigated and the suitability of the finish for improving the easy-care properties of silk fabrics was observed.

After-treatment of BTCA/SHP finished silk fabrics with a softening finish improved the easy-care characteristics of the treated fabrics. Of the softening agents used, the silicone

softeners, Ultratex FEW and SW, were more effective at improving the elastic recovery to creasing than Ceranine L, a nonionic polyethylene dispersion, and PEG 1000. Table 5. 10 displays a comparison of some of the results of silk fabrics treated with the BTCA/SHP finish, various pad bath additives and an after-treatment with Ultratex FEW.

Treatment	Warp Shrinkage after Washing (%)	Appearance after washing (rated 5-very creased to 0-no creases)	DCRA Recovery after 5min (degrees)	WCRA Recovery after 5min (degrees)	Abrasion Resistance (no. of rubs)	Fabric Moisture Regain (%)	ASTM Yellowness Index
Untreated control	4	5	193.2	179.6	775	8.62	5.1
BTCA	2	3	218.0	208.7	725	7.65	7.28
BTCA/FEW	1	2	235.2	255.5	2000	8.78	6.27
BTCA/FA/FEW	0	1	234.5	217.5	2300	8.60	5.27
BTCA/AA/FEW	2	1	244.6	225.2	2400	8.62	6.04
BTCA/PAA/FEW	1	2	186.3	255.5	2250	8.61	6.5

Table 5. 10 Comparison of results of silk fabrics treated with different easy-care finishes.

From Table 5. 10 it can be seen that the easy-care properties of silk fabrics are improved by treatment with BTCA; these properties are further improved if a silicone softening after-treatment is included, and improved further still if a swelling agent, such as FA or AA, is added to the PCA pad bath. Fabrics treated with a BTCA/FA/SHP or BTCA/AA/SHP finish a silicone softener after-treatment have good easy-care characteristics. The inclusion of the stiffening agent PAA in the pad bath does not improve the easy-care properties of the treated silk fabrics, however the induced fabric stiffness improves the limp handle characteristic of silk fabrics finished with a silicone softener to give a fabric with good draping characteristics.

5.2.4 Summary Of The Experimental Work In Chapter 5.

The aim of this study was to improve the easy-care properties of silk fabric. The low wet resiliency and severe laundry shrinkage of silk fabrics limit their commercial usage. In Chapters 3 and 4 it was established that it was possible to improve the elastic recovery from creasing in both the dry and wet state by treating silk fabrics with a PCA finishing system. In this chapter the properties of silk fabrics treated with a polycarboxylic acid (PCA) finish and the suitability of the finish at improving the easy-

care properties of silk fabric was investigated. The incorporation of additional chemicals into the pad bath was investigated to maximise the improvement in fabric properties brought about by the easy-care finish.

Untreated silk fabrics that were washed, line dried and analysed before and after ironing had very poor easy-care properties. The washed fabric was extremely crumpled and it was not possible to remove all the creases by ironing the fabric. The untreated control had low WCRA values both initial elastic recovery and recovery from creasing after 5min and there was a shrinkage in the warp direction of 4% after washing.

Treatment of silk fabric with a BTCA/SHP finishing system improved the easy-care properties of the silk fabric compared with the untreated control. After-treatment with various softening agents further improved the easy-care characteristics of the treated silk fabrics. An improvement in easy-care properties is brought about by an improvement in elastic recovery from creasing of the treated samples bringing about a return to the original shape of the fabric. A high degree of stabilisation within the fabric is necessary so that the relative positions of the fibres and yarns remain unchanged, and the original configuration of the fabric is restored. It was considered that by analogy with research work on cotton (145) that BTCA molecules are capable of forming di-ester cross-links that would provide anchoring points for the molecular chains that restrain excessive movement and maintain the position of the chain within silk fibroin.

Strong covalent chemical bonds formed between silk fibroin polymer chains by a cross-linking agent tend to improve the dimensional stability, improve the stability to heat, increase the strength and elastic recovery of the silk polymer and reduce its swelling in contact with solvents (48). In chapter 4 it was concluded that treatment of silk fibroin with a PCA finish improved the stability of silk fabrics to heat, improved the elastic recovery of the silk polymer to creasing both in the dry and wet states, and reduced the swelling of silk fabric in concentrated formic acid. In addition in this chapter it has been observed that treatment of silk fabric with a BTCA/SHP finish reduces the shrinkage after washing.

The synergistic improvement in easy-care characteristics brought about by the after-treatment of the BTCA/SHP finished silk fabrics with a softening finish could be

associated with the rubber-like properties of the surface elastomers and the coating may act as a rubbery cushion or mechanical buffer (81). Treatment with a reactive silicone softener increased the elastic recovery from creasing more in both the dry and wet states than treatment with either a non-ionic polyethylene dispersion or with a PEG. In addition treatment with a silicone softener gave rise to a fabric with a super-soft, luxurious, but floppy handle.

Treatment of silk fabrics with a BTCA/SHP finish even with a silicone softener after-treatment did not improve the elastic properties of the silk fibroin sufficiently for this finish to be recommended as a viable commercial easy-care finish for silk fabrics. However, the inclusion of a fibre swelling agent, FA or AA, into the PCA pad bath vastly improved the easy-care properties of the treated samples. It is proposed that the increased swelling brought about by the inclusion of a fibre swelling agent into the pad bath is as a result of new PCA ester cross-links being inserted into silk fibres that wet set the silk through stabilisation of its new swollen structure. After-treatment with a silicone softener improved the dry elastic recovery; this should help prevent creases being formed in the dry state.

Treatment of silk fabrics with a BTCA/FA/SHP, or BTCA/AA/SHP finish followed by an after-treatment with a silicone softener results in good easy-care performance. It is recommended that these systems should be considered as new easy-care finishes for silk fabrics. Not only do these finishes allow silk fabrics to be washed in a washing machine with minimal fabric creasing and minimal fabric shrinkage, but it should be possible to remove any creases inserted during washing by minimal ironing. This finish also markedly improves the fabric resistance to abrasion and thus would prolong the wear of garments made from the treated fabric.

The inclusion of PAA in the pad bath does not improve the easy-care properties of the BTCA/SHP treated silk samples and therefore it is not recommended except in circumstances where an increase in fabric stiffness is desirable.

6. CONCLUSIONS.

6.1 INTRODUCTION

Modern living styles necessitate garment easy-care characteristics. If silk is to compete with the technically advanced man-made fibre products in the future and maintain its market share the inferior fabric properties of silk such as, poor wet resiliency, low resistance to fabric abrasion and photoyellowing in sunlight, need to be improved during silk fabric processing.

This thesis extends the research into the chemical modification of silk fabric with a polycarboxylic acid (PCA) finishing system. This system was chosen because of its success as an easy-care finish for cotton fabric and because it is a non-toxic, non-odorous, aqueous finishing system. The author drew on the research reported for the PCA easy-care finishing of cotton cellulose, see section 3.1, as it was expected that the hydroxyl-containing amino acids in silk fibroin would react similarly to the hydroxyl groups in cotton cellulose.

6.2 EXPERIMENTAL WORK ASSOCIATED WITH THIS THESIS.

6.2.1 An Initial Study.

Initial experiments, reported in Chapter 3, confirmed that an improvement in elastic recovery from creasing in both the dry and wet states can be obtained by treating silk fabrics with selected PCAs, namely BTCA and CA. FT-IR analysis of the treated silk fabrics identified the existence of ester bonds. It is proposed that ester links are formed between the PCA and the hydroxyl-containing amino acids, serine, threonine, and tyrosine, in the accessible region of silk fibroin during fabric curing.

The basic amino acids arginine, histidine, and lysine may also react with the PCA forming amide links. The quantity of basic amino acids in silk fibroin is less than 3%, whereas the quantity of hydroxyl-containing amino acids is greater than 17%. Amides are difficult to prepare by direct action of a carboxylic acid and an amine (80); this is because amines convert the carboxyl group into their carboxylate anion. However, the basic side groups in silk fibroin may react with the acid anhydride formed during curing. In this thesis the reaction of PCA with the hydroxyl-containing amino acids only were

analysed; this is because they exist in a greater quantity in silk fibroin and because they have a characteristic infra-red absorption band around 1735cm^{-1} . However, amide links may also be formed between the PCA and accessible amine side groups in silk fibroin that may contribute to an improvement in easy-care performance.

A comparison with trimethylol melamine (TMM), one of the most effective formaldehyde-based easy-care finishing agents for silk (82), concluded that BTCA-treated silk fabric had better recovery from creasing in the dry state, but not in the wet state, had improved fabric strength retention and did not cause severe fabric stiffness. It was proposed that the improvement in DCRA may be as a result of a combination of diester and mono-ester/hydrogen bond cross-links being formed within the treated fabric. On re-wetting these hydrogen bonds would be broken; this would explain the lower improvement in WCRA compared with DCRA of the treated silk samples.

Investigations were carried out into optimising the process by maximising the quantity of ester links formed during the finishing process. The greatest quantity of ester bonds was formed in the samples treated by the pad-batch-cure process, cured at 165°C for 1.5min, see Table 6. 1. It is proposed that the batching process allows for increased fibre swelling and improved penetration of the reagent inside the fibre.

Padding Process	Chemical Add-on (%)	Fabric DCRA after 5min (degrees)	Fabric WCRA after 5min (degrees)
Untreated Control	0.00	255.1 ± 6.0	193.3 ± 5.6
BTCA/SHP (PBW)	1.75	277.2 ± 4.8	194.8 ± 5.9
BTCA/SHP (PDC)	3.79	290.6 ± 5.2	203.0 ± 4.3
BTCA/SHP (PBC)	6.00	294.2 ± 207.0	207.0 ± 5.4
BTCA/FA/SHP (PBC)	5.41	282.4 ± 4.2	222.9 ± 5.1

Where PBW = pad-batch-wash-off, PDC = pad-dry-cure and PBC = pad-batch-cure.

Table 6. 1 Comparison of the CRA values for silk fabric treated with 6% w/w BTCA, 1:1 molar ratio of SHP and/or 8% w/w FA, and cured at 165°C for 1.5min.

A slight increase in dry fabric stability to creasing and fabric strength was observed with silk samples treated by the pad-batch method that were not cured, see Table 6. 1. It is proposed that this may be caused by the insertion of new hydrogen bond links between BTCA and silk fibroin chain molecules during batching. In the fabric samples that were subsequently cured it is postulated that these hydrogen bonds would be converted into stable ester covalent bonds. These new ester cross-links improve the stability of silk fibroin in the dry and wet state.

The incorporation of formic acid (FA), as a swelling agent, into the pad bath further improved the wet stability of the treated sampled but not the dry stability. FA is a known hydrogen bond breaker (23) and has been used in TMM finishing of silk fabrics to improve the wet resiliency of silk (82). It is proposed that the addition of FA into the pad bath increased fibre swelling during the batching process. New hydrogen bond links between BTCA and silk fibroin would be inserted at the edges of the swollen amorphous sections during batching; these hold silk fibroin in its new swollen state during drying before being converted to stable ester covalent bonds during fabric curing. Fibre swelling on re-wetting is restricted; as the fibre tries to swell the cross-links become taut and it is these forces that lead to improvement in elastic recovery.

The dry stability of the untreated silk fabric is high, whereas the wet stability needs to be increased in order to improve the easy-care characteristics of silk fabrics.

6.2.2 Polycarboxylic Acid Finishing of Silk.

The BTCA/SHP polycarboxylic acid finishing system, reported to be the most successful PCA easy-care finish for cotton cellulose, is expensive (130). SHP is also an environmental hazard and has the drawback of producing shade changes on some reactive and sulphur dyeings (156). This thesis investigated alternative acid/catalyst systems.

A new analytical method was developed for pre-determining the suitability of an acid/catalyst system as an easy-care finishing agent. A number of PCA/catalyst systems were analysed using thermoanalytical and Fourier-transform infra-red spectroscopic techniques in which the conditions encountered by the finish during fabric curing were mimicked.

This new method for testing the suitability of an acid/catalyst system as an easy-care finish was found to be very successful. Acid/catalyst systems that formed an acid anhydride below 165°C, and that did not degrade significantly below this temperature when applied as a finish to silk fabrics were found to improve the elastic properties of the fibre. Formation of an acid anhydride is thought to be an intermediate step in the reaction of a PCA with cotton cellulose (117). Notification of the char colour during TGA analysis proved important at identifying fabric finishes that would cause fabric

discoloration during the high temperature curing process. Solubility of the finish in water was also important. Acids that fall out of solution during the padding operation can cause large amounts of fine acid dust particles to be emitted during the drying and curing operations that could cause a health risk.

A number of PCA/catalyst systems were identified as possible easy-care finishes for silk fibroin. These finishes were applied to silk fibroin by the pad-batch-method and their optimum treatment conditions investigated. A number of conclusions were drawn:

- The lower the temperature at which an acid/catalyst system formed an acid anhydride the greater the quantity of ester bonds formed within the treated fabric. It is therefore proposed that the formation of the anhydride is the rate-determining intermediate step.
- Optimum pad bath pH was 1.5-2.1. Altering the pH value with either NaOH or HCl decreased the quantity of ester bonds formed within the treated fabric. At pH 1.5-2.1 the conversion of carboxyl groups to carboxylate ions would be very small.
- Optimum curing temperature was 165°C for 1.5min. A cure temperature below 165°C decreased the quantity of ester bonds formed within the treated fabric. A cure temperature above 165°C caused fabric yellowing to occur.
- With an increase in ester bonds formed within the treated fabrics there was:
 - an increase in elastic recovery from creasing observed in the dry and wet states,
 - an increase in dry fabric strength,
 - a slight increase in fabric stiffness
 - a reduction in elongation at break
 - an increase in the stability to heat
 - an increase in the stability to formic acid
- These ester bonds were found to be stable to laundering tested up to 25 washes.

FT-IR analysis of the treated silk fabrics was used to determine the quantity of ester links formed during the high temperature curing process. The largest quantity of ester links were formed with samples treated with

$$\text{BTCA/SHP} = \text{BTCA/MSM} = \text{BTCA/CY} > \text{BTCA/MSM} = \text{SA/CA/SHP} = \\ \text{SA/MLA/SHP} > \text{MA/SHP} = \text{BTCA/MST}$$

As a result of the experimental work carried out in this thesis a number of interesting mechanistic possibilities have been proposed for improving the easy-care performance of silk fabrics with a PCA finishing system. It is postulated that the improvement in elastic and stability properties of the treated silk fabrics could be as a consequence of new fibre inter-chain diester and/or ester/hydrogen bond cross-links and/or a new intra-fibre PCA polymer network being formed within the silk fibres, see Figure 6. 1 and Figure 6. 2. Amide links may also be formed between the basic side chains in silk fibroin and acid anhydrides formed during curing.

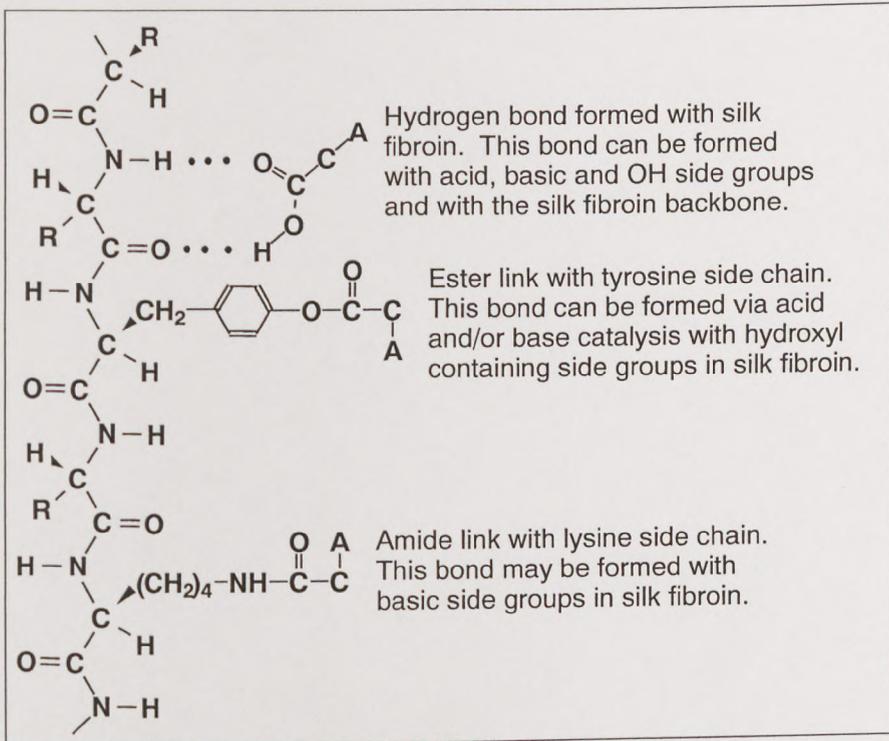


Figure 6. 1 Three different types of bonds formed between a carboxylic acid and silk fibroin.

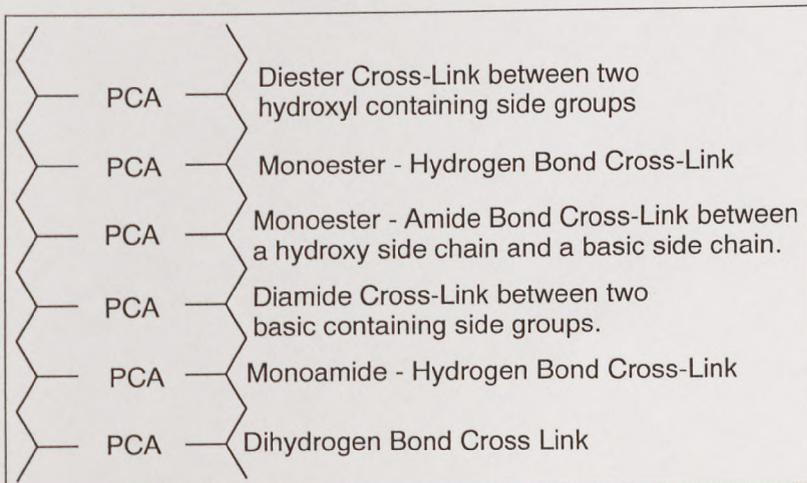


Figure 6. 2 A summary of the different cross-links that can occur between a PCA and silk fibroin.

Esterification of the hydroxyl side groups in silk fibroin may occur through base-catalysed esterification of acid anhydrides, as proposed by Welch (117), and/or through acid-catalysed esterification of the PCA. These two esterification mechanisms may occur simultaneously or one mechanism may dominate. PCA anhydrides may also form amide links with the basic side chains in silk fibroin. PCAs that contain hydroxy side groups may form ester bonds with adjacent PCAs and a three-dimensional lattice structure may build-up inside silk fibroin. This structure may be held in place by single ended ester attachment, multiple ester links, and/or amide links and/or hydrogen bonds. Carboxylic acid groups that do not form ester or amide links are free to hydrogen bond with silk fibroin. Hydrogen bonds are not stable to water and therefore do not contribute to an improvement in fabric wet stability, however they do contribute to an improvement in fabric dry stability.

This work concludes that treatment of silk fabric with selected PCA finishing systems improves the stability of silk fabric. The treated fabrics have improved stability to heat, reduced swelling in solvents, and improved elastic recovery in the dry and wet states giving rise to fabrics with improved easy-care properties.

This work proposes the use of BTCA, and SA/CA as successful PCAs for the easy-care finishing of silk. These acids were found to improve the elastic recovery from creasing more than MA and SA/MLA. However, these dicarboxylic acids warrant further investigation; SA/MLA finish produced the least fabric yellowing, if the reaction efficiency could be improved it is proposed that this finish could be a viable alternative to BTCA, and MA offers the possibility of polymerising within the fibre.

This research found an alternative catalyst to SHP, monosodium citrate (MSC). MSC is cheaper, more environmentally friendly than SHP and further decreases the temperature at which BTCA forms an anhydride. This catalyst may also react with silk fibroin and/or BTCA forming inter-chain cross-links and/or an intra-fibre polymer network. Silk fabric treated with BTCA/SHP or BTCA/MSC finishing systems led to equivalent improvements in easy-care characteristics.

6.2.3 Improving The Easy-Care Properties Of Silk.

Untreated silk fabrics have poor easy-care characteristics. They cannot be machine washed as it is impossible to remove all the creases inserted during washing by ironing, and they shrink. Treatment of silk fabric with a PCA finishing system improved the easy-care properties of the silk fabric compared with the untreated control. After-treatment with various softening agents further improved the easy-care characteristics of the treated silk fabrics. Treatment with a reactive silicone softener gave rise to a fabric with the greatest improvement in elastic properties and a super-soft, luxurious, but floppy handle.

Treatment of silk fabrics with a BTCA/SHP finish even with a silicone softener after-treatment did not improve the elastic properties of the silk fibroin sufficiently for this finish to be recommended as a viable commercial easy-care finish for silk fabrics. However, the inclusion of a fibre swelling agent, FA or AA, into the PCA pad bath vastly improved the easy-care properties of the treated samples. It is proposed that the increased swelling brought about by the inclusion of a fibre-swelling agent into the pad bath wet set the silk through stabilisation in its new swollen state. After-treatment with a silicone softener improved the dry elastic recovery; this should help prevent creases being formed in the dry state. The finish produced a super soft, minimum iron fabric with enhanced resistance to fabric abrasion. The treated fabric was machine-washable.

Treatment of silk fabrics with a BTCA/FA/SHP, or BTCA/AA/SHP finish followed by an after-treatment with a silicone softener results in good easy-care performance. This thesis recommends the use of selected PCAs, in the presence of either FA or AA with a suitable catalyst (MSC or SHP) followed by after-treatment with a silicone softener to be considered as a new easy-care finish for silk.

6.3 FUTURE WORK.

PCA finishes can be applied to many fibre types including silk, cotton, and wool. This thesis extends previous research with respect to PCA finishing; it proposes the use of a new analytical method to pre-determine the effectiveness of an acid/catalyst system as an easy-care finish, the use of new combination acids to compete with BTCA and an alternative catalyst to SHP, namely MSC. Previous research on cotton treated with a BTCA/MSC finish proved unsuccessful, it is proposed that this was due to too high a

curing temperature being used in which the MSC would have decomposed and therefore not been available to act as a catalyst. Future research with this catalyst for the PCA finishing of cotton cellulose is recommended using a curing temperature of 165°C.

The market place for easy-care cotton fabrics is much larger than that for silk fabrics and it is anticipated that research undertaken in this thesis could be a future starting point for further research into zero-formaldehyde PCA finishing of cotton cellulose. New acids and catalysts could be tested using the thermoanalytical and infra-red analysis technique proposed in section 4.1 and successful systems could then be tested as new easy-care finishes. Catalysts that are capable of lowering the temperature at which PCA anhydride formation occurs, decrease the temperature required for fabric curing and thus decrease the cost of the process.

Future work is recommended with regards to combination finishes that contain carboxylic acid reactive groups. Finishes that combine easy-care and flame retardancy with carboxylic acid reactive dyeing could be the future for cellulosic and protein fibres in the next millennium.

APPENDIX 1. RESULTS FROM SECTION 3.3.

A.1.1 Treatment of Silk Fibroin with BTCA and CA with SHP as catalyst.

% w/w PCA	PCA:SHP Molar Ratio	Chemical Add-on (%)	Fabric DCRA (degrees)		Fabric WCRA (degrees)		ASTM Yellowness Index
			Immediate Recovery	Recovery After 5min	Immediate Recovery	Recovery After 5min	
Untreated Control		0.00	208.8 +/- 5.7	260.6 +/- 7.5	115.3 +/- 7.8	163.7 +/- 6.6	6.88
5% w/w BTCA	1:0.5	4.27	222.2 +/- 6.6	281.6 +/- 4.0	126.2 +/- 7.2	178.4 +/- 6.9	9.61
5% w/w BTCA	1:0.75	4.47	226.3 +/- 7.2	287.1 +/- 6.7	126.9 +/- 10.7	175.0 +/- 6.2	9.18
5% w/w BTCA	1:1	4.87	232.7 +/- 6.3	288.8 +/- 4.3	125.4 +/- 4.3	177.8 +/- 6.4	8.93
5% w/w BTCA	1:1.25	5.14	224.3 +/- 6.3	281.9 +/- 8.7	123.7 +/- 9.0	175.5 +/- 4.9	7.83
5% w/w BTCA	1:1.5	4.92	215.9 +/- 5.2	273.4 +/- 5.4	122.1 +/- 8.2	175.2 +/- 9.5	7.51
7% w/w CA	1:0.5	5.09	217.2 +/- 4.9	271.4 +/- 5.3	118.3 +/- 7.3	166.9 +/- 7.4	13.52
7% w/w CA	1:0.75	5.25	216.2 +/- 5.6	271.1 +/- 4.7	121.8 +/- 9.6	169.4 +/- 6.3	13.07
7% w/w CA	1:1	5.32	221.1 +/- 9.2	272 +/- 7.9	126.7 +/- 7.7	167.7 +/- 5.3	12.91
7% w/w CA	1:1.25	5.45	223.7 +/- 7.2	275.4 +/- 4.6	127.1 +/- 4.0	173.0 +/- 6.2	12.25
7% w/w CA	1:1.5	5.31	218.1 +/- 8.9	272.8 +/- 8.0	124.0 +/- 8.2	170.9 +/- 8.9	11.76

Table A1. 1 Physical properties of silk fibroin treated with 5% w/w BTCA or 7% w/w CA and different molar ratios of SHP catalyst.

A.1.2 Comparison of polycarboxylic acid with methylol melamine easy-care finishing of silk fibroin.

% w/w PCA	Chemical Add-On (%)	Fabric Moisture Regain (%)	Fabric DCRA (degrees)			Fabric WCRA (degrees)		Bending Length (mm)		% Retention Tensile Strength		% Retention Elongation at Break	
			Immediate Recovery	Recovery After 5min	Recovery After 5min	Immediate Recovery	Recovery After 5min	Warp	Weft	Dry	Wet	Dry	Wet
Control Untreated	0.00	8.62	173.7 +/- 7.4	196.7 +/- 5.7	146.8 +/- 3.8	179.9 +/- 5.9	16.5	24.1	100.0	100.0	100.0	100.0	
2% w/w BTCA	2.00	7.88	183.1 +/- 6.7	227.6 +/- 6.8	151.4 +/- 4.2	192.5 +/- 3.4	17.4	21.5	102.5	102.5	92.0	98.4	
4% w/w BTCA	4.16	7.65	187.6 +/- 6.3	229.4 +/- 6.5	156.6 +/- 3.9	209.7 +/- 5.4	17.0	24.1	96.8	93.6	77.7	75.0	
6% w/w BTCA	6.33	7.65	196.3 +/- 6.6	235.9 +/- 8.0	156.5 +/- 3.7	210.7 +/- 4.6	21.3	28.9	91.5	94.9	77.3	79.3	
8% w/w BTCA	9.13	7.60	184.7 +/- 5.3	226.8 +/- 5.4	150.8 +/- 4.1	206.3 +/- 6.3	25.0	27.8	89.9	95.4	61.4	71.4	
5% w/w MEL	2.97	9.37	149.1 +/- 6.3	184.8 +/- 5.8	174.4 +/- 6.5	197.7 +/- 5.9	23.9	31.6	96.70	87.89	75.19	76.45	
7.5% w/w MEL	3.48	9.28	147.3 +/- 6.4	183.8 +/- 7.6	186.3 +/- 6.7	212.9 +/- 6.9	23.8	33.5	93.68	90.38	72.15	77.92	
10% w/w MEL	4.68	9.28	119.9 +/- 4.9	167.7 +/- 4.5	193.6 +/- 6.9	228.2 +/- 6.8	28.6	34.6	97.47	90.48	73.76	74.85	
12.5% w/w MEL	7.03	9.36	99.6 +/- 3.8	138.6 +/- 4.0	206.1 +/- 8.1	241.6 +/- 5.7	29.3	35.8	94.61	91.15	65.21	75.89	
15% w/w MEL	7.78	9.20	94.4 +/- 7.3	135.1 +/- 7.8	200.9 +/- 6.5	241.6 +/- 6.6	31.5	38.3	98.07	93.84	72.03	73.98	

Table A1. 2 Physical properties of silk fibroin treated with BTCA and SHP catalyst or Permafresh Mel 68 (MEL) and MgCl₂ catalyst.

A.1.3 Optimisation of the conditions for curing silk fabrics finished with BTCA.

Curing Conditions	FT-IR Ester Peak Height (mm)	Fabric DCRA (degrees)		Fabric WCRA (degrees)		% Retention Tensile Strength		% Retention Elongation at Break		ASTM Yellowness Index
		Immediate Recovery	Recovery After 5min	Immediate Recovery	Recovery After 5min	Dry	Wet	Dry	Wet	
Control Untreated		192.3 +/- 4.9	255.1 +/- 6.0	132.1 +/- 4.6	193.3 +/- 5.6	100.0	100.0	100.0	100.0	4.79
Leave 24hrs		196.3 +/- 6.6	255.0 +/- 6.8	144.1 +/- 4.3	202.1 +/- 5.3	110.2	98.4	93.1	97.0	9.6
Leave 48hrs		199.9 +/- 6.3	258.4 +/- 6.9	139.6 +/- 4.5	198.6 +/- 4.8	110.2	99.2	94.2	99.5	10.45
Cure 120°C/5min	10	195.7 +/- 7.3	259.9 +/- 5.1	136.7 +/- 5.7	200.3 +/- 4.9	109.5	95.7	90.9	95.2	5.9
Cure 130°C/3min	13	202.7 +/- 7.9	261.4 +/- 6.1	135.8 +/- 4.4	193.2 +/- 5.5	108.3	99.3	92.0	99.5	6.41
Cure 140°C/2.5min	16	207.8 +/- 5.6	266.3 +/- 5.8	135.7 +/- 4.8	197.5 +/- 6.1	107.6	95.9	87.2	94.9	6.57
Cure 150°C/2min	22	208.0 +/- 6.2	269.8 +/- 5.1	140.9 +/- 5.4	208.6 +/- 4.4	109.6	91.1	83.6	85.7	7.07
Cure 160°C/1.5min	27	202.0 +/- 7.3	260.1 +/- 5.8	143.5 +/- 5.0	210.5 +/- 5.3	109.2	85.8	80.3	78.4	7.21
Steam 5min	11	187.7 +/- 7.1	251.2 +/- 7.0	131.8 +/- 5.3	190.2 +/- 7.7	108.2	98.4	87.2	97.0	6.98
Steam 2min + Cure 150°C/2min	22	189.3 +/- 5.3	254.6 +/- 6.1	135.5 +/- 7.7	197.3 +/- 8.3	109.8	90.2	80.6	85.7	6.08
Steam 5min + Cure 150°C/2min	22	196.6 +/- 6.9	261.0 +/- 7.4	138.2 +/- 7.1	195.9 +/- 5.8	109.5	94.1	82.1	88.7	5.7
Cure 150°C/2min + Steam 2min	21	187.3 +/- 5.6	250.0 +/- 6.2	140.1 +/- 5.3	197.0 +/- 4.8	110.0	92.4	83.9	87.6	6.94
Cure 150°C/2min + Steam 5min	22	197.0 +/- 6.6	258.3 +/- 4.6	139.6 +/- 6.0	198.9 +/- 5.6	105.7	91.7	78.5	86.5	6.71

Table A1. 3a. Properties of silk fabrics treated with 6% w/w BTCA and a 1:1molar ratio of catalyst SHP under different curing conditions (continued overleaf).

Curing Conditions	FT-IR Ester Peak Height (mm)	Fabric DCRA (degrees)			Fabric WCRA (degrees)			% Retention Tensile Strength		% Retention Elongation at Break		ASTM Yellowness Index
		Immediate Recovery	Recovery After 5min	Recovery After 5min	Immediate Recovery	Recovery After 5min	Recovery After 5min	Dry	Wet	Dry	Wet	
Control Untreated	0	192.3 +/- 4.9	255.1 +/- 6.0	193.3 +/- 5.6	132.1 +/- 4.6	100.0	100.0	100.0	100.0	100.0	100.0	4.79
Leave 24hrs + Cure 120°C/5min	13	203.5 +/- 7.8	265.2 +/- 6.3	187.8 +/- 7.3	125.9 +/- 6.4	98.1	99.4	78.1	98.1	98.1	98.1	9.09
Leave 24hrs + Cure 130°C/3min	17	202.1 +/- 6.8	264.1 +/- 7.5	183.4 +/- 5.5	125.6 +/- 5.0	108.9	94.1	83.9	91.4	91.4	91.4	9.3
Leave 24hrs + Cure 140°C/2.5min	24	212.5 +/- 4.6	271.2 +/- 5.1	189.9 +/- 5.8	125.3 +/- 4.8	106.6	92.8	80.6	89.2	89.2	89.2	9.06
Leave 24hrs + Cure 150°C/2min	27	214.2 +/- 5.6	274.3 +/- 3.7	184.8 +/- 6.7	123.4 +/- 8.2	110.2	90.6	86.5	86.8	86.8	86.8	8.46
Leave 24hrs + Cure 160°C/1.5min	35	218.6 +/- 8.2	274.8 +/- 6.7	184.8 +/- 6.3	125.6 +/- 6.2	107.3	85.4	79.9	76.8	76.8	76.8	8.73
Leave 24hrs + Steam 5min	10	195.2 +/- 7.5	257.2 +/- 6.7	186.2 +/- 7.2	129.5 +/- 8.1	108.5	100.1	90.1	99.2	99.2	99.2	10.53
Leave 24hrs + Steam 2min + Cure 150°C/2min	25	214.2 +/- 7.3	275.7 +/- 9.3	191.6 +/- 7.3	128.6 +/- 6.6	99.2	89.5	78.8	86.8	86.8	86.8	8.21
Leave 24hrs + Steam 5min + Cure 150°C/2min	27	215.7 +/- 8.0	270.4 +/- 6.6	182.8 +/- 6.6	122.2 +/- 7.7	98.9	87.3	77.4	84.4	84.4	84.4	8.18
Leave 24hrs + Cure 150°C/2min + Steam 2min	30	211.3 +/- 6.0	267.8 +/- 6.7	190.5 +/- 8.2	128.2 +/- 6.0	98.9	88.1	71.9	79.8	79.8	79.8	8.44
Leave 24hrs + Cure 150°C/2min + Steam 5min	29	216.1 +/- 6.1	275.5 +/- 4.5	192.5 +/- 7.7	131.0 +/- 5.7	102.3	88.5	78.5	84.1	84.1	84.1	8.42

Table A1. 3b Properties of silk fabrics treated with 6% w/w BTCA and a 1:1molar ratio of catalyst SHP under different curing conditions (from previous page).

A.1.4 Optimisation of the process for padding silk fabrics finished with BTCA.

Padding Process + Pad Bath Additives	Chemical Add-On (%)	FT-IR Ester Peak Height (mm)	Fabric Moisture Regain (%)	Fabric DCRA (degrees)		Fabric WCRA (degrees)		% Retention Tensile Strength		% Retention Elongation at Break		ASTM Yellowness Index
				Immediate Recovery After 5min	Recovery After 5min	Immediate Recovery	Recovery After 5min	Dry	Wet	Dry	Wet	
Control Untreated	0.00	0	8.74	212.3 +/- 4.9	255.1 +/- 6.0	152.1 +/- 4.6	193.3 +/- 5.6	100.0	100.0	100.0	100.0	6.88
PBW	1.75	3	8.64	239.0 +/- 6.2	277.2 +/- 4.8	149.2 +/- 6.3	194.8 +/- 5.9	106.8	102.5	103.9	102.5	11.32
PBC	6.00	28	8.97	252.7 +/- 5.3	294.2 +/- 5.0	152.8 +/- 4.0	207.0 +/- 5.4	106.8	96.4	102.0	91.1	11.33
PDC	3.79	20	8.35	252.7 +/- 4.5	290.6 +/- 5.2	152.4 +/- 5.0	203.0 +/- 4.3	102.1	90.5	88.3	80.0	8.00
PDLC	4.93	21	9.07	258.5 +/- 5.4	292.7 +/- 4.2	149.4 +/- 5.5	200.0 +/- 6.5	101.6	89.1	92.6	81.0	7.54
PBW + 6% w/w NaI	1.31	6	8.56	234.3 +/- 6.4	281.8 +/- 5.1	141.1 +/- 6.2	195.8 +/- 5.3	105.5	101.8	104.1	99.0	6.95
PBC + 6% w/w NaI	3.69	25	8.88	252.5 +/- 5.3	299.0 +/- 5.7	145.7 +/- 5.3	204.6 +/- 4.5	107.3	95.5	99.6	87.6	7.27
PDC + 6% w/w NaI	2.80	17	8.42	260.2 +/- 5.7	296.8 +/- 4.9	147.0 +/- 5.7	194.7 +/- 4.8	106.6	94.1	93.1	81.6	7.31
PDLC + 6% w/w NaI	3.69	20	9.11	264.0 +/- 4.9	299.7 +/- 5.6	149.4 +/- 6.4	199.7 +/- 5.3	108.6	94.5	97.0	84.0	6.91
PBW + 6% w/w ZnCl ₂	1.80	7	8.51	244.5 +/- 5.6	285.3 +/- 6.3	144.2 +/- 5.0	198.2 +/- 5.6	103.6	105.0	97.1	99.8	7.34
PBC + 6% w/w ZnCl ₂	2.53	16	8.73	240.6 +/- 6.2	289.1 +/- 5.1	148.4 +/- 5.9	204.3 +/- 4.6	105.9	99.8	103.1	96.0	8.03
PDC + 6% w/w ZnCl ₂	1.92	13	8.45	233.3 +/- 6.0	281.7 +/- 5.8	147.7 +/- 6.4	201.4 +/- 6.0	105.9	99.8	97.9	93.8	8.10
PDLC + 6% w/w ZnCl ₂	2.19	14	9.17	232.4 +/- 4.9	281.2 +/- 4.3	144.6 +/- 4.6	199.6 +/- 6.2	107.9	97.5	104.6	93.6	7.79

Table A1. 4a. Physical properties of silk fabrics treated with 6% w/w BTCA and a 1:1 molar ratio of catalyst SHP under different padding conditions (continued overleaf).

Padding Process + Pad Bath Additives	Chemical Add-On (%)	FT-IR Ester Peak Height (mm)	Fabric Moisture Regain (%)	Fabric DCRA (degrees)		Fabric WCRA (degrees)		% Retention Tensile Strength		% Retention Elongation at Break		ASTM Yellowness Index
				Immediate Recovery After 5min	Recovery After 5min	Immediate Recovery After 5min	Recovery After 5min	Dry	Wet	Dry	Wet	
Control Untreated	0.00	0	8.74	212.3 +/- 4.9	255.1 +/- 6.0	152.1 +/- 4.6	193.3 +/- 5.6	100.0	100.0	100.0	100.0	6.88
PBW + 6% w/w LiCl	1.45	6	8.75	244.9 +/- 5.7	288.5 +/- 5.6	147.8 +/- 5.7	195.1 +/- 5.3	102.6	102.1	102.0	101.8	8.18
PBC + 6% w/w LiCl	2.65	18	9.04	221.9 +/- 5.5	295.1 +/- 6.1	143.0 +/- 5.8	197.5 +/- 6.0	102.4	99.8	105.5	99.2	8.41
PDC + 6% w/w LiCl	1.80	18	8.91	251.7 +/- 6.3	289.9 +/- 5.5	133.6 +/- 4.4	197.0 +/- 4.7	105.1	100.0	95.6	94.0	7.75
PDLC + 6% w/w LiCl	2.01	15	9.14	254.2 +/- 4.6	296.2 +/- 5.9	141.9 +/- 6.7	203.2 +/- 6.4	105.1	100.6	98.9	97.2	8.25
PBW + 8% w/w FA	1.33	5	8.63	185.2 +/- 6.1	252.4 +/- 6.5	143.8 +/- 6.8	196.0 +/- 5.5	108.2	104.9	105.8	99.6	7.27
PBC + 8% w/w FA	5.41	22	8.63	230.5 +/- 4.2	282.4 +/- 4.2	151.2 +/- 6.3	222.9 +/- 5.1	111.0	98.6	102.3	78.4	7.40
PDC + 8% w/w FA	4.89	19	9.27	220.3 +/- 5.3	269.9 +/- 5.4	159.7 +/- 5.3	221.2 +/- 5.1	108.9	95.2	84.8	70.5	6.28
PDLC + 8% w/w FA	3.88	16	8.91	217.1 +/- 5.1	269.1 +/- 5.3	149.1 +/- 5.4	210.8 +/- 4.3	107.0	92.7	92.4	80.4	7.49

Table AI. 4b. Physical properties of silk fabrics treated with 6% w/w BTCA and a 1:1 molar ratio of catalyst SHP under different padding conditions (from previous page)

APPENDIX 2. RESULTS FROM SECTION 4.2.

A.2.1 Treatment of Silk Fibroin with BTCA/SHP finishing system.

BTCA/SHP	Chemical Add-on (%)	FT-IR Ester Peak Height (mm)		Fabric Moisture Regain (%)	Fabric DCRA (degrees)		Fabric WCRA (degrees)		Fabric Bending Length (mm)		% Retention Tensile Strength		% Retention Elongation at Break		ASTM Yellowness Index
		Rinsed	NaOH-treated		Immediate Recovery	Recovery After 5min	Immediate Recovery	Recovery After 5min	Warp	Weft	Dry	Wet	Dry	Wet	
Untreated Control	0.01			8.62	173.7 ± 7.4	196.7 ± 5.7	146.8 ± 3.8	179.9 ± 5.9	16.5	24.1	100.0	100.0	100.0	100.0	5.1
20g/l BTCA	2.00	14	4	7.88	183.1 ± 6.7	227.6 ± 6.8	151.4 ± 4.2	192.5 ± 3.4	17.4	21.5	111.5	102.5	92.0	98.4	
40g/l BTCA	4.16	35	16	7.65	187.6 ± 6.3	229.4 ± 6.5	156.6 ± 3.9	209.7 ± 5.4	17.0	24.1	105.2	93.6	77.7	75.0	
60g/l BTCA	6.33	44	22	7.65	196.3 ± 6.6	235.9 ± 8.0	156.5 ± 3.7	210.7 ± 4.6	21.3	28.9	99.5	94.9	77.3	79.3	
80g/l BTCA	9.13	50	31	7.60	184.7 ± 5.3	226.8 ± 5.4	150.8 ± 4.1	206.3 ± 6.3	25.0	27.8	97.8	95.4	61.4	71.4	
BTCA:SHP 1:0.5	6.01	45	22	7.52	181.4 ± 7.4	237.4 ± 5.8	153.4 ± 5.5	204.0 ± 3.9	23.0	26.9	103.7	98.3	78.1	83.9	
BTCA:SHP 1:0.75	6.07	46	28	7.62	185.7 ± 4.6	229.8 ± 6.4	153.1 ± 3.9	205.8 ± 5.8	21.6	28.5	99.2	94.3	72.6	77.5	
BTCA:SHP 1:1	6.33	44	22	7.65	196.3 ± 6.6	235.9 ± 8.0	156.5 ± 3.7	210.7 ± 4.6	21.3	28.9	99.5	94.9	77.3	79.3	
BTCA:SHP 1:1.25	7.19	46	24	7.52	192.7 ± 5.4	235.9 ± 5.7	156.3 ± 5.4	205.7 ± 3.9	23.0	27.5	100.3	97.4	69.4	75.8	
Pad Bath pH 1.5	5.35	41	20	7.62	191.0 ± 6.6	235.0 ± 5.7	158.7 ± 8.9	214.7 ± 7.4	22.3	27.1	106.9	91.4	77.7	74.8	
Pad Bath pH 2.1	6.33	44	22	7.65	196.3 ± 6.6	235.9 ± 8.0	156.5 ± 3.7	210.7 ± 4.6	21.3	28.9	99.5	94.9	77.3	79.3	
Pad Bath pH 3.5	3.32	28	9	7.90	205.1 ± 7.4	230.6 ± 6.2	146.2 ± 7.1	197.1 ± 4.6	20.5	28.1	104.0	95.0	83.8	83.0	
Pad Bath pH 5	0.86	7	4	8.28	184.7 ± 7.5	227.7 ± 8.9	145.6 ± 6.3	191.8 ± 5.0	21.9	29.1	108.3	88.5	88.8	85.8	
Cure 120°C, 5min	1.83	23	6	7.74	181.0 ± 6.6	228.8 ± 5.1	149.1 ± 5.6	187.7 ± 4.0	18.1	24.9	109.0	94.2	90.6	89.9	7.81
Cure 150°C, 2min	4.97	37	9	7.66	183.5 ± 5.6	230.4 ± 6.7	153.2 ± 5.2	199.0 ± 4.8	18.3	26.5	102.7	91.0	79.1	79.5	8.08
Cure 165°C, 1.5min	6.33	44	22	7.65	196.3 ± 6.6	235.9 ± 8.0	156.5 ± 3.7	210.7 ± 4.6	21.3	28.9	99.5	94.9	77.3	79.3	7.28

Table A2.1 Properties of silk fibroin treated with a BTCA/SHP finishing system.

A.2.2 Treatment of Silk Fibroin with PCA/SHP finishing system.

PMA/SHP	Chemical Add-on (%)	FT-IR Ester Peak Height (mm)		Fabric Moisture Regain (%)	Fabric DCRA (degrees)		Fabric WCRA (degrees)		Fabric Bending Length (mm)		% Retention Tensile Strength		% Retention Elongation at Break		ASTM Yellowness Index
		Rinsed	NaOH-treated		Immediate Recovery	Recovery After 5min	Immediate Recovery	Recovery After 5min	Warp	Weft	Dry	Wet	Dry	Wet	
Untreated Control	0.01			8.62					16.5	24.1	108.8	100.0	100.0	100.0	
20g/l PCA	4.80	29		7.80	185.9 ± 5.7	225.5 ± 5.1	142.4 ± 5.3	185.2 ± 4.1	18.6	24.8	105.6	81.2	76.5	71.2	
40g/l PCA	3.35	27		7.91	184.5 ± 5.2	223.2 ± 5.1	139.8 ± 5.7	187.3 ± 4.8	19.0	24.1	108.6	93.9	79.7	80.3	
60g/l PCA	3.78	23		7.88	202.4 ± 6.6	236.5 ± 5.4	141.3 ± 5.3	189.3 ± 4.4	17.0	23.8	101.3	9.0	77.6	78.7	
80g/l PCA	2.99	23		8.13	178.5 ± 7.1	207.8 ± 6.7	146.5 ± 6.0	198.2 ± 4.5	18.6	24.8	107.4	89.1	75.0	71.9	
PCA:SHP 1:0.5	4.05	27		7.88	181.1 ± 5.7	211.6 ± 5.8	142.8 ± 5.2	189.9 ± 5.8	18.3	24.0	103.0	89.3	72.4	76.2	
PCA:SHP 1:0.75	3.88	29		7.93	185.0 ± 4.6	217.4 ± 6.8	144.4 ± 4.2	181.8 ± 6.3	18.5	25.4	102.4	86.0	76.2	71.7	
PCA:SHP 1:1	3.78	23		7.88	202.4 ± 5.1	236.5 ± 5.4	141.3 ± 5.3	189.3 ± 4.4	17.0	23.8	101.3	9.0	77.6	78.7	
PCA:SHP 1:1.25	3.98	26		7.89	211.6 ± 5.3	241.6 ± 4.9	142.5 ± 5.4	194.1 ± 4.5	17.6	26.3	105.1	92.7	85.7	79.8	
Cure 120°C, 5min	0.92	14		7.88	187.1 ± 6.8	224.0 ± 4.5	146.9 ± 5.2	187.7 ± 5.1	16.1	23.8	105.3	97.8	95.9	88.3	6.23
Cure 150°C, 2min	2.81	20		8.00	187.7 ± 5.7	220.7 ± 5.7	149.5 ± 6.4	188.2 ± 4.4	20.3	24.9	113.4	99.5	80.4	85.1	6.66
Cure 165°C, 1.5min	3.78	23		7.88	202.4 ± 5.1	236.5 ± 5.4	151.3 ± 4.3	189.3 ± 4.4	17.0	23.8	101.3	9.0	77.6	78.7	7.86

Table A2. 2 Properties of silk fibroin treated with a PCA/SHP finishing system.

A.2.3 Treatment of Silk Fibroin with MA/SHP finishing system

MA/SHP MA	Chemical Add-on (%)	FT-IR Ester Peak Height (mm)		Fabric Moisture Regain (%)	Fabric DCRA (degrees)		Fabric WCRA (degrees)		Fabric Bending Length (mm)		% Retention Tensile Strength		% Retention Elongation at Break		ASTM Yellowness Index
		Rinsed	NaOH-treated		Immediate Recovery	Recovery After 5min	Immediate Recovery	Recovery After 5min	Warp	Weft	Dry	Wet	Dry	Wet	
Untreated Control	0.01			8.09	173.7 ± 7.4	196.7 ± 5.7	146.8 ± 3.8	179.9 ± 5.9	16.5	24.1	108.8	100.0	100.0	100.0	
20g/l MA	1.52	17	5	7.37	173.4 ± 5.7	205.3 ± 6.2	156.1 ± 4.9	203.2 ± 6.0	20.9	27.3	113.3	97.5	77.5	83.1	
40g/l MA	3.48	19	8	7.48	175.8 ± 4.5	209.8 ± 8.9	155.7 ± 4.6	204.1 ± 5.5	20.5	29.3	112.6	101.0	81.3	88.8	
60g/l MA	4.87	28	12	7.39	184.2 ± 5.6	224.4 ± 5.4	153.8 ± 4.5	206.0 ± 5.3	20.5	26.0	105.1	94.5	72.4	82.7	
80g/l MA	6.49	32	14	7.32	183.2 ± 5.3	224.9 ± 3.6	153.6 ± 5.7	201.0 ± 5.1	18.9	28.1	105.8	89.8	77.6	77.3	
MA:SHP 1:0.5	4.67	33	12	6.97	175.3 ± 5.9	206.9 ± 8.0	152.0 ± 4.7	201.3 ± 5.9	20.8	27.6	107.1	86.2	72.9	74.5	
MA:SHP 1:0.75	4.73	23	8	7.10	175.0 ± 4.7	205.3 ± 7.3	156.3 ± 6.0	202.2 ± 6.4	20.4	29.5	109.7	97.5	78.7	82.5	
MA:SHP 1:1	4.87	28	12	7.39	184.2 ± 5.6	224.4 ± 5.4	156.8 ± 4.3	206.0 ± 5.3	20.5	26.0	105.1	94.5	72.4	82.7	
MA:SHP 1:1.25	6.01	25	11	7.24	183.2 ± 4.4	223.9 ± 6.5	162.4 ± 4.1	209.3 ± 5.0	17.8	28.1	106.5	93.8	80.2	81.1	
Pad Bath pH 1.5	4.87	28	12	7.39	184.2 ± 5.6	224.4 ± 5.4	153.8 ± 4.5	206.0 ± 5.3	20.5	26.0	105.1	94.5	72.4	82.7	
Pad Bath pH 2.5	1.42	15	4	7.35	179.5 ± 6.3	231.0 ± 5.4	145.1 ± 4.5	192.6 ± 4.7	20.4	20.5	103.2	91.6	90.7	79.4	
Pad Bath pH 3.5	1.06	9	2	7.63	165.2 ± 5.2	209.1 ± 3.9	141.7 ± 4.3	191.8 ± 4.3	20.3	28.0	110.9	97.5	76.5	85.7	
Pad Bath pH 5	0.47	6	3	7.85	162.1 ± 6.0	208.1 ± 7.4	142.7 ± 4.4	195.5 ± 4.4	19.3	28.3	106.0	99.3	82.0	93.8	
Cure 120°C, 5min	2.10	15	8	7.08	180.6 ± 6.2	225.0 ± 5.8	144.4 ± 5.5	190.3 ± 4.9	15.3	25.9	114.2	102.5	97.9	96.9	6.08
Cure 150°C, 2min	3.52	19	7	7.25	182.0 ± 5.8	224.7 ± 6.3	151.8 ± 4.1	193.7 ± 4.3	15.9	25.6	112.2	102.0	94.9	94.4	6.51
Cure 165°C, 1.5min	4.87	28	12	7.39	184.2 ± 6.7	224.4 ± 5.4	153.8 ± 4.5	206.0 ± 5.3	20.5	26.0	105.1	94.5	72.4	82.7	7.59

Table A2.3 Properties of silk fibroin treated with a MA/SHP finishing system.

A.2.4 Treatment of Silk Fibroin with SA/CA/SHP finishing system

SA/CA/SHP	Chemical Add-on (%)	FT-IR Ester Peak Height (mm)		Fabric Moisture Regain (%)	Fabric DCRA (degrees)		Fabric WCRA (degrees)		Fabric Bending Length (mm)		% Retention Tensile Strength		% Retention Elongation at Break		ASTM Yellowness Index
		Rinsed	NaOH-treated		Immediate Recovery	Recovery After 5min	Immediate Recovery	Recovery After 5min	Warp	Weft	Dry	Wet	Dry	Wet	
Untreated Control	0.01			8.09	173.7 ± 7.4	196.7 ± 5.7	146.8 ± 3.8	179.9 ± 5.9	16.5	24.1	108.8	100.0	100.0	100.0	
10g/l SA:16g/l CA	2.16	21	8	7.23	180.3 ± 4.7	209.2 ± 6.6	150.0 ± 5.0	200.8 ± 4.3	20.0	26.9	115.1	98.3	88.2	85.4	
20g/l SA:32g/l CA	5.07	30	11	7.23	191.5 ± 5.5	232.0 ± 5.4	155.4 ± 5.7	204.4 ± 6.4	17.8	26.6	111.1	99.1	79.9	82.7	
30g/l SA:48g/l CA	7.05	38	18	6.98	200.2 ± 4.7	238.7 ± 5.1	160.8 ± 4.7	206.5 ± 5.4	16.9	26.9	107.4	98.7	86.1	81.3	
40g/l SA:64g/l CA	3.46	15	8	7.75	196.1 ± 6.3	223.6 ± 5.7	150.6 ± 5.9	184.6 ± 5.0	19.3	29.6	112.5	99.0	91.4	89.0	
SA:CA:SHP 1:1:1	6.10	39	16	6.98	172.2 ± 6.0	205.1 ± 7.1	151.5 ± 4.5	193.9 ± 4.7	18.6	29.5	111.7	98.3	76.6	83.3	
SA:CA:SHP 1:1:1.5	6.56	35	16	6.77	192.2 ± 5.4	230.0 ± 4.8	157.5 ± 4.3	204.7 ± 5.0	18.5	29.9	107.2	98.9	88.0	83.2	
SA:CA:SHP 1:1:2	7.05	38	18	6.98	200.2 ± 4.7	238.7 ± 5.1	160.8 ± 4.7	206.5 ± 5.4	16.9	26.9	107.4	98.7	86.1	81.3	
SA:CA:SHP 1:1:2.5	6.38	35	17	7.05	182.3 ± 4.7	216.2 ± 4.7	152.1 ± 4.8	200.4 ± 4.8	18.5	26.6	108.2	102.8	77.9	84.4	
Pad Bath pH 1.5	6.08	37	15	7.26	176.8 ± 5.8	207.7 ± 4.8	149.5 ± 5.2	202.3 ± 6.1	18.6	26.4	108.3	96.0	78.5	78.4	
Pad Bath pH 1.9	7.05	38	18	6.98	200.2 ± 4.7	238.7 ± 5.1	160.8 ± 4.7	206.5 ± 5.4	16.9	26.9	107.4	98.7	86.1	81.3	
Pad Bath pH 3	4.22	30	12	7.40	174.5 ± 4.3	211.4 ± 6.0	151.3 ± 4.8	195.1 ± 6.1	19.6	26.0	110.1	95.3	78.2	76.9	
Pad Bath pH 5	0.45	5	3	7.99	169.0 ± 5.5	201.2 ± 5.5	143.0 ± 5.0	185.2 ± 6.0	21.0	27.6	115.6	96.9	88.2	83.8	
Cure 120C/5 MINS	1.55	15	3	7.69	176.8 ± 5.4	215.6 ± 5.7	147.6 ± 5.3	194.1 ± 6.4	17.9	26.1	111.2	95.7	85.3	84.7	5.31
Cure 150C/2 MINS	4.58	29	9	7.30	185.5 ± 6.5	222.0 ± 5.8	148.1 ± 4.6	196.0 ± 5.3	18.9	25.6	111.6	95.4	80.6	81.9	5.72
Cure 165C/1.5 MINS	7.05	38	18	6.98	200.2 ± 4.7	238.7 ± 5.1	160.8 ± 4.7	206.5 ± 5.4	16.9	26.9	107.4	98.7	86.1	81.3	8.04

Table A2. 4 Properties of silk fibroin treated with a SA/CA/SHP finishing system.

A.2.5 Treatment of Silk Fibroin with SA/MLA/SHP finishing system

SA/MLA/SHP	Chemical Add-on (%)	FT-IR Ester Peak Height (mm)		Fabric Moisture Regain (%)	Fabric DCRA (degrees)		Fabric WCRA (degrees)		Fabric Bending Length (mm)		% Retention Tensile Strength		% Retention Elongation at Brea		ASTM Yellowness Index
		Rinsed	NaOH-treated		Immediate Recovery	Recovery After 5min	Immediate Recovery	Recovery After 5min	Warp	Weft	Dry	Wet	Dry	Wet	
Untreated Control	0.01			7.94	173.7 ± 7.4	196.7 ± 5.7	146.8 ± 3.8	179.9 ± 5.9	16.5	24.1	108.8	100.0	100.0	100.0	
20g/ SA:30g/l MLA	3.89	22	6	6.92	174.7 ± 4.3	202.9 ± 4.7	148.5 ± 5.2	194.1 ± 4.7	19.5	26.5	104.2	91.7	81.7	84.6	
30g/ SA:45g/l MLA	6.95	34	11	6.57	178.6 ± 5.1	210.7 ± 5.3	155.6 ± 5.7	199.6 ± 5.4	18.3	25.6	105.1	93.8	75.2	86.8	
40g/l SA:60g/l MLA	9.92	35	17	6.66	183.9 ± 5.8	216.3 ± 5.2	157.8 ± 6.0	205.2 ± 6.1	17.6	24.9	101.7	88.7	78.1	83.3	
50g/l SA:75g/l MLA	10.27	44	18	6.46	175.6 ± 6.1	211.4 ± 4.7	152.7 ± 5.4	200.7 ± 4.9	20.1	25.5	118.4	96.0	75.8	83.9	
SA:MLA:SHP 1:1:0.5	9.19	39	13	6.49	171.8 ± 4.7	202.1 ± 5.0	148.4 ± 4.8	196.4 ± 4.8	22.0	29.5	114.7	93.5	66.1	80.4	
SA:MLA:SHP 1:1:0.75	9.39	39	17	6.65	173.1 ± 6.4	200.3 ± 5.5	150.9 ± 5.5	200.8 ± 5.0	20.1	29.3	109.2	93.2	71.4	82.1	
SA:MLA:SHP 1:1:1	9.92	36	17	6.66	183.9 ± 5.8	216.3 ± 5.2	157.8 ± 6.0	205.2 ± 6.1	17.6	24.9	101.7	88.7	78.1	83.3	
SA:MLA:SHP 1:1:1.25	9.44	37	19	6.51	182.7 ± 6.8	219.9 ± 7.1	163.3 ± 7.4	210.0 ± 6.3	18.1	28.6	113.6	95.2	73.3	84.7	
Pad bath pH 1.5	8.29	37	16	6.73	176.5 ± 5.2	202.3 ± 6.4	149.6 ± 4.9	197.2 ± 5.1	18.9	27.3	111.8	92.9	80.4	83.6	
Pad bath pH 2.05	9.92	36	17	6.66	183.9 ± 5.8	216.3 ± 5.2	157.8 ± 6.0	205.2 ± 6.1	17.6	24.9	101.7	88.7	78.1	83.3	
Pad bath pH 3	6.23	31	12	6.97	177.6 ± 6.6	200.3 ± 6.4	157.1 ± 5.8	196.6 ± 5.5	18.8	26.3	109.4	95.0	83.3	85.7	
Pad bath pH 5	1.24	9	4	7.59	176.2 ± 6.2	200.4 ± 6.1	151.2 ± 4.9	191.7 ± 5.5	19.5	27.5	108.8	95.6	88.2	92.3	
Cure 120C/5min	1.81	14	4	7.25	181.6 ± 6.8	219.0 ± 6.5	151.1 ± 4.6	189.6 ± 4.9	18.3	26.3	109.7	93.4	88.4	88.7	5.34
Cure 150C/2min	4.22	31	9	7.38	178.0 ± 6.1	214.7 ± 7.7	153.5 ± 5.6	195.7 ± 5.8	19.6	24.4	106.9	92.7	75.8	86.6	5.44
Cure 165C/1.5min	9.92	35	17	6.66	183.9 ± 5.8	216.3 ± 5.2	157.8 ± 6.0	205.2 ± 6.1	17.6	24.9	101.7	88.7	78.1	83.3	5.57

Table A2. 5 Properties of silk fibroin treated with a SA/MLA/SHP finishing system.

A.2.6 Treatment of Silk Fibroin with BTCA/mono-, di-, trisodium citrate finishing systems

BTCA/MSC	Chemical Add-on (%)	FT-IR Ester Peak Height (mm)		Fabric Moisture Regain (%)	Fabric DCRA (degrees)		Fabric WCRA (degrees)		Fabric Bending Length (mm)		% Retention Tensile Strength		% Retention Elongation at Break		ASTM Yellowness Index
		Rinsed	NaOH-treated		Immediate Recovery	Recovery After 5min	Immediate Recovery	Recovery After 5min	Warp	Weft	Dry	Wet	Dry	Wet	
Untreated Control					157.4 ± 6.8	193.2 ± 7.1	143.1 ± 6.5	179.6 ± 6.2							
BTCA:MSC 1:0.5	7.32	44	28	7.596	173.2 ± 5.7	204.1 ± 4.6	169.0 ± 6.0	213.5 ± 3.9	23.3	30.4	97.4	94.2	71.0	81.6	
BTCA:MSC 1:1	9.12	42	21	7.736	177.0 ± 6.6	222.1 ± 4.3	175.8 ± 6.0	217.6 ± 4.3	24.9	31.9	102.7	91.9	72.5	78.7	
BTCA:MSC 1:1.5	9.20	40	20	7.709	177.1 ± 6.9	223.4 ± 4.3	168.8 ± 5.1	213.5 ± 4.6	26.1	31.6	98.7	94.7	65.9	77.9	
BTCA:MSC 1:2	10.07	44	24	7.716	183.1 ± 6.5	228.2 ± 3.1	169.7 ± 6.2	208.9 ± 3.4	25.4	32.0	99.4	85.4	69.7	70.3	
Pad bath pH 1.5	9.77	31	15	7.714	173.6 ± 7.5	204.3 ± 7.1	162.5 ± 4.4	195.4 ± 5.9	27.1	34.0	98.0	90.9	85.8	80.8	
Pad bath pH 2.5	10.72	46	15	7.759	173.5 ± 4.2	211.4 ± 5.7	165.9 ± 4.9	208.7 ± 4.2	23.6	24.4	99.6	89.2	84.0	79.2	
Pad bath pH 3.2	9.12	42	21	7.736	177.0 ± 6.6	222.1 ± 4.8	175.8 ± 4.6	217.6 ± 4.3	24.9	31.9	105.7	91.9	81.1	78.7	
Cure 140C/3min	4.78	30	14	7.801	175.0 ± 5.7	213.3 ± 6.5	154.8 ± 4.2	206.1 ± 5.2	22.6	31.6	100.3	92.1	73.7	76.9	10.29
Cure 150C/2min	6.74	35	23	7.605	184.0 ± 5.5	227.2 ± 5.4	161.0 ± 6.2	204.4 ± 4.7	21.0	30.1	100.3	86.7	84.0	79.2	8.93
Cure 165C/1.5min	9.12	42	21	7.736	182.0 ± 5.8	222.1 ± 4.3	175.8 ± 6.0	217.6 ± 4.3	24.9	31.9	105.7	91.9	81.1	78.7	12.14
BTCA/DSC															
Cure 140C/3min	6.56	21	4	7.938	166.8 ± 5.8	207.1 ± 6.5	138.1 ± 5.7	182.9 ± 7.2	22.5	24.6	108.8	97.9	80.2	86.4	8.49
Cure 150C/2min	4.71	22	6	7.922	166.2 ± 6.5	209.3 ± 6.7	145.6 ± 5.6	193.6 ± 6.3	21.8	27.1	108.5	95.0	82.3	85.1	8.45
Cure 165C/1.5min	6.51	25	6	7.802	173.4 ± 6.7	210.1 ± 7.2	152.5 ± 4.9	185.7 ± 7.1	20.1	27.4	105.6	90.4	79.4	82.9	9.45
BTCA/TSC															
Cure 140C/3min	5.12	12	4	8.468	167.8 ± 6.1	211.4 ± 6.8	139.7 ± 6.5	189.6 ± 5.2	17.3	26.5	93.4	88.1	95.4	81.2	8.48
Cure 150C/2min	4.69	17	6	8.478	161.9 ± 9.1	205.1 ± 9.3	143.5 ± 5.6	190.2 ± 5.7	20.8	26.8	94.2	88.5	102.5	82.5	7.98
Cure 165C/1.5min	5.94	20	6	8.658	154.5 ± 6.1	199.8 ± 5.9	146.5 ± 8.5	195.6 ± 6.8	24.3	27.8	93.2	87.7	77.7	73.7	10.76

Table A2. 6 Properties of silk fibroin treated with a BTCA/MSC, BTCA/DSC, or BTCA/TSC finishing system.

A.2.7 Treatment of Silk Fibroin with BTCA/mono-, disodium tartrate finishing systems

BTCA/MST	Chemical Add-On (%)	FT-IR Ester Peak Height (mm)		Fabric Moisture Regain (%)	Fabric DCRA (degrees)		Fabric WCRA (degrees)		Fabric Bending Length (mm)		% Retention Tensile Strength		% Retention Elongation at Break		ASTM Yellowness Index
		Rinsed	NaOH-treated		Immediate Recovery	Recovery After 5min	Immediate Recovery	Recovery After 5min	Warp	Weft	Dry	Wet	Dry	Wet	
BTCA:MST 1:0.5	8.82	34	12	7.824	164.5 ± 6.5	200.3 ± 5.7	167.4 ± 5.8	213.7 ± 4.3	22.7	25.9	92.2	84.3	77.9	72.4	
BTCA:MST 1:1	8.33	31	12	7.825	155.6 ± 4.5	189.9 ± 4.7	169.7 ± 5.6	213.2 ± 4.2	25.5	31.3	93.5	86.9	86.7	73.2	
BTCA:MST 1:1.5	9.05	32	12	7.955	152.7 ± 5.6	181.7 ± 5.6	167.8 ± 5.5	216.9 ± 3.9	27.5	33.6	88.8	86.3	75.5	71.5	
BTCA:MST 1:2	9.00	33	14	7.875	155.2 ± 7.3	186.0 ± 5.4	161.1 ± 6.3	210.8 ± 5.8	27.3	35.6	92.6	86.3	78.7	71.3	
Pad bath pH 1.5	9.51	35	15	7.498	155.2 ± 6.0	192.0 ± 5.3	157.3 ± 5.0	206.4 ± 4.8	23.5	30.5	94.4	84.0	81.1	71.2	
Pad bath pH 2.9	8.33	31	12	7.825	155.6 ± 4.5	189.9 ± 4.7	168.7 ± 5.1	213.2 ± 4.2	25.5	31.3	93.5	86.9	86.7	73.2	
Pad bath pH 3.5	6.31	22	8	8.06	152.8 ± 5.5	191.4 ± 5.6	158.6 ± 6.9	202.2 ± 4.1	26.1	34.3	93.5	83.8	82.5	72.4	
Cure 140C/3min	7.30	20	3	7.71	164.5 ± 6.2	198.3 ± 6.5	147.0 ± 6.5	191.9 ± 4.0	17.3	28.5	95.1	85.9	85.4	75.7	8.77
Cure 150C/2min	7.31	31	7	7.741	157.3 ± 6.7	194.7 ± 4.6	155.7 ± 6.2	197.6 ± 5.0	22.3	29.3	89.6	81.1	84.8	72.3	9.37
Cure 165C/1.5min	8.33	31	12	7.825	155.6 ± 4.5	189.9 ± 4.7	168.7 ± 5.1	213.2 ± 4.2	25.5	31.3	93.5	86.9	86.7	73.2	8.21
BTCA/DST															
Cure 140C/3min	4.30	17	3	8.152	155.0 ± 5.4	192.8 ± 5.9	144.5 ± 6.1	185.4 ± 3.7	17.5	26.3	94.1	87.3	88.4	77.1	8.65
Cure 150C/2min	3.76	22	3	8.098	152.6 ± 5.5	194.0 ± 5.5	143.0 ± 5.5	189.6 ± 2.9	21.8	26.1	90.0	90.6	84.6	80.9	8.53
Cure 165C/1.5min	6.62	23	8	8.191	150.1 ± 6.1	183.8 ± 7.1	156.6 ± 5.6	208.0 ± 5.7	23.4	29.6	96.4	84.7	85.7	72.5	7.55

Table A2. 7 Properties of silk fibroin treated with a BTCA/MST or BTCA/DST finishing system.

A.2.8 Treatment of Silk Fibroin with BTCA/mono-, disodium maleate finishing systems

BTCA/MSM	Chemical Add-on (%)	FT-IR Ester Peak Height (mm)		Fabric Moisture Regain (%)	Fabric DCRA (degrees)			Fabric WCRA (degrees)			Fabric Bending Length (mm)		% Retention Tensile Strength		% Retention Elongation at Break		ASTM Yellowness Index
		Rinsed	NaOH-treated		Immediate Recovery	Recovery After 5min	Recovery After 5min	Immediate Recovery	Recovery After 5min	Warp	Weft	Dry	Wet	Dry	Wet		
BTCA:MSM 1:0.5	8.26	37	15	7.793	166.1 ± 7.6	200.5 ± 9.9	162.8 ± 4.2	213.8 ± 6.0	20.4	31.1	93.4	87.2	82.8	75.9			
BTCA:MSM 1:1	8.87	35	20	7.789	166.8 ± 5.4	208.0 ± 9.3	166.0 ± 5.7	209.0 ± 6.7	20.3	29.1	90.8	85.8	79.0	74.5			
BTCA:MSM 1:1.5	9.18	38	18	7.593	167.7 ± 7.1	209.8 ± 10.1	168.7 ± 5.5	214.1 ± 8.2	20.6	28.6	94.2	88.7	84.8	74.4			
BTCA:MSM 1:2	8.90	37	14	7.753	172.2 ± 6.9	209.0 ± 5.3	183.2 ± 7.3	216.7 ± 5.6	20.8	28.9	90.9	88.8	82.5	75.1			
Pad bath pH 1.5	9.77	40	15	7.467	160.2 ± 6.3	199.6 ± 4.9	155.9 ± 6.3	207.0 ± 5.5	21.1	27.9	91.7	85.6	81.7	75.6			
Pad bath pH 2.48	8.87	35	20	7.789	166.8 ± 5.4	208.0 ± 6.4	166.0 ± 5.7	209.0 ± 5.3	20.3	29.1	90.8	85.8	79.0	74.5			
Pad bath pH 3.5	6.83	23	10	8.241	167.8 ± 5.9	210.1 ± 5.3	165.7 ± 6.3	213.7 ± 3.8	21.8	31.4	92.4	85.8	91.0	72.9			
Cure 140C/3min	6.08	23	6	7.763	172.7 ± 6.1	217.9 ± 6.0	157.3 ± 5.7	201.5 ± 5.2	16.9	27.0	92.3	88.9	92.8	80.6	7.74		
Cure 150C/2min	7.18	33	17	7.743	174.6 ± 5.5	219.0 ± 5.0	161.8 ± 5.4	206.6 ± 4.7	19.3	29.6	93.0	87.9	93.6	80.0	8.16		
Cure 165C/1.5min	8.87	35	20	7.789	171.2 ± 4.6	208.0 ± 6.4	166.0 ± 5.7	209.0 ± 6.7	20.3	29.1	90.8	85.8	79.0	74.5	8.33		
BTCA/MSM																	
Cure 140C/3min	5.04	15	3	7.95	180.9 ± 6.7	208.3 ± 7.2	140.9 ± 5.1	184.7 ± 5.1	17.0	26.8	92.7	89.7	89.2	80.1	7.93		
Cure 150C/2min	4.66	19	5	7.929	158.3 ± 5.9	200.0 ± 4.6	152.3 ± 5.6	200.2 ± 4.9	18.1	26.4	93.7	90.4	89.5	82.1	8.36		
Cure 165C/1.5min	6.63	27	7	7.867	154.0 ± 4.9	193.7 ± 4.1	150.3 ± 5.0	202.0 ± 5.1	18.9	26.5	92.7	90.2	85.8	78.5	8.03		

Table A2. 8 Properties of silk fibroin treated with a BTCA/MSM or BTCA/DSM finishing system.

A.2.9 Treatment of Silk Fibroin with BTCA/cyanamide finishing systems

BTCA/CY	Chemical Add-On (%)	FT-IR Ester Peak Height (mm)		Fabric Moisture Regain (%)	Fabric DCRA (degrees)		Fabric WCRA (degrees)		Fabric Bending Length (mm)		% Retention Tensile Strength		% Retention Elongation at Break		ASTM Yellowness Index
		Rinsed	NaOH-treated		Immediate Recovery	Recovery After 5min	Immediate Recovery	Recovery After 5min	Warp	Weft	Dry	Wet	Dry	Wet	
Untreated Control					173.7 ± 7.4	196.7 ± 5.7	146.8 ± 3.8	179.9 ± 5.9							
20g/l BTCA	2.51	21	6	7.70	173.9 ± 6.5	212.5 ± 5.0	159.6 ± 4.8	203.7 ± 5.0	18.5	24.8	104.7	99.3	79.6	89.0	
40g/l BTCA	5.71	24	8	7.48	176.0 ± 6.1	217.6 ± 5.6	160.7 ± 5.6	204.5 ± 5.3	18.8	26.3	108.8	96.7	82.6	85.5	
60g/l BTCA	8.21	40	21	7.44	176.2 ± 6.0	218.8 ± 8.7	168.1 ± 5.7	214.0 ± 4.0	19.6	24.9	106.6	93.9	66.4	81.4	
80g/l BTCA	11.07	51	30	7.52	172.4 ± 5.8	217.3 ± 6.5	150.3 ± 6.3	202.9 ± 5.1	21.6	28.8	99.6	93.9	67.5	76.4	
BTCA:CY 1:0.5	7.47	42	19	7.43	179.7 ± 7.8	211.0 ± 7.9	153.3 ± 6.6	200.2 ± 4.8	17.5	26.0	106.7	92.2	74.4	76.1	
BTCA:CY 1:1	8.16	43	24	7.49	176.9 ± 6.9	211.4 ± 5.5	155.9 ± 4.9	201.9 ± 4.9	21.4	26.4	105.8	98.1	70.0	80.5	
BTCA:CY 1:2	8.21	40	21	7.44	176.2 ± 6.0	218.8 ± 3.6	168.1 ± 5.7	214.0 ± 4.0	19.6	24.9	106.6	93.9	66.4	81.4	
BTCA:CY 1:3	8.96	45	27	7.35	162.2 ± 6.6	203.8 ± 5.3	154.4 ± 5.2	205.7 ± 4.5	21.0	27.9	104.7	101.1	67.1	78.5	
Pad bath pH 1	8.75	39	17	7.52	170.1 ± 5.4	212.4 ± 4.3	158.1 ± 2.9	207.8 ± 4.6	18.9	24.8	109.3	99.8	78.4	81.6	
Pad bath pH 1.8	8.21	40	21	7.44	176.2 ± 6.0	218.8 ± 3.6	168.1 ± 5.7	214.0 ± 4.0	19.6	24.9	106.6	93.9	66.4	81.4	
Pad bath pH 3	7.76	35	19	7.55	159.8 ± 6.0	200.3 ± 3.5	161.8 ± 6.0	215.7 ± 5.0	23.6	28.5	110.8	100.9	74.7	84.5	
Pad bath pH 5	1.42	9	5	8.16	153.5 ± 6.1	193.8 ± 4.9	157.7 ± 4.2	201.1 ± 4.7	19.5	27.9	110.2	101.9	90.4	97.1	
Cure 140C/3min	3.96	23	7	7.57	172.2 ± 6.3	202.3 ± 7.3	155.2 ± 4.7	193.8 ± 6.0	20.1	24.9	112.5	100.1	85.9	92.8	9.81
Cure 150C/2min	7.77	41	19	7.76	177.0 ± 5.6	211.3 ± 5.6	159.9 ± 4.8	213.2 ± 6.4	19.5	23.5	110.2	98.4	81.7	88.4	11.21
Cure 165C/1.5min	8.21	40	21	7.44	178.2 ± 5.7	218.8 ± 3.6	168.1 ± 5.7	214.5 ± 4.2	19.6	24.9	106.6	93.9	66.4	81.4	11.14

Table A2.9 Properties of silk fibroin treated with a BTCA/CY finishing system.

A.2.10 Treatment of Silk Fibroin with BTCA/PCA/SHP and MA/PCA/SHP finishing systems

BTCA/MA, BTCA/CA, BTCA/SA	Chemical Add-on (%)	FT-IR Ester Peak Height (mm)		Fabric Moisture Regain (%)	Fabric DCRA (degrees)		Fabric WCRA (degrees)		Fabric Bending Length (mm)		% Retention Tensile Strength		% Retention Elongation at Break	
		Rinsed			Immediate Recovery	Recovery After 5min	Immediate Recovery	Recovery After 5min	Warp	Weft	Dry	Wet	Dry	Wet
Control					157.4 ± 6.8	193.2 ± 7.1	143.1 ± 6.5	179.6 ± 6.2						
60g/l MA	4.87	29		7.387	184.2 ± 5.6	224.4 ± 9.3	153.8 ± 4.5	206.0 ± 5.3	20.5	26.0	105.05	88.04	72.43	74.46
20g/l BTCA, 40g/l MA	5.63	33		7.69	157.0 ± 6.0	202.0 ± 6.1	158.5 ± 6.3	206.3 ± 4.0	20.8	26.0	95.76	91.60	69.81	74.46
30g/l BTCA, 30g/l MA	5.67	35		7.712	150.3 ± 4.8	196.5 ± 4.8	165.6 ± 7.5	211.9 ± 5.0	21.0	29.8	94.12	91.30	69.52	71.69
40g/l BTCA, 20g/l MA	5.79	37		7.852	148.4 ± 5.7	196.6 ± 6.2	154.7 ± 6.0	207.2 ± 5.4	23.3	28.6	96.64	92.01	68.26	71.13
60g/l BTCA	6.33	44		7.654	196.3 ± 6.6	235.9 ± 8.0	156.5 ± 3.7	210.7 ± 4.6	21.3	28.9	99.50	88.40	77.33	71.43
50g/l CA	4.13	28		8.258	148.4 ± 6.6	191.7 ± 6.3	151.6 ± 6.1	199.1 ± 4.6	21.5	28.0	96.48	85.90	71.01	69.23
20g/l BTCA, 33g/l CA	4.02	32		7.989	149.3 ± 6.5	192.9 ± 6.0	152.5 ± 8.0	209.4 ± 4.8	22.0	29.0	92.40	90.89	70.17	72.64
30g/l BTCA, 25g/l CA	4.00	34		8.051	149.3 ± 5.9	196.2 ± 7.2	158.0 ± 6.2	210.7 ± 4.7	24.1	29.1	93.48	89.31	62.58	68.28
40g/l BTCA, 16g/l CA	4.12	34		8.085	149.1 ± 4.4	197.3 ± 7.2	156.4 ± 6.6	215.6 ± 5.1	23.5	31.6	92.36	87.02	66.89	68.54
60g/l BTCA	6.33	44		7.654	196.3 ± 6.6	235.9 ± 8.0	156.5 ± 3.7	210.7 ± 4.6	21.3	28.9	99.50	88.40	77.33	71.43
30g/l SA	1.72	17		8.218	163.8 ± 10.3	208.3 ± 6.5	139.8 ± 5.0	184.9 ± 3.0	19.3	25.9	94.48	86.87	72.80	78.57
20g/l BTCA, 20g/l SA	2.24	27		8.477	157.4 ± 5.4	191.1 ± 5.2	151.8 ± 5.6	207.2 ± 5.1	18.1	27.1	89.00	88.19	69.52	70.35
30g/l BTCA, 15g/l SA	3.32	28		8.277	158.7 ± 5.5	197.2 ± 6.9	148.7 ± 3.5	207.8 ± 4.1	18.6	26.6	93.40	87.38	70.05	69.01
40g/l BTCA, 10g/l SA	3.62	32		8.28	155.6 ± 5.2	187.8 ± 6.5	153.0 ± 4.5	209.2 ± 5.4	21.0	27.5	94.68	90.59	66.65	69.62
60g/l BTCA	6.33	44		7.654	196.3 ± 6.6	235.9 ± 8.0	156.5 ± 3.7	210.7 ± 4.6	21.3	28.9	99.50	88.40	77.33	71.43

Table A2. 10a Properties of silk fibroin treated with a BTCA/PCA/SHP and MA/PCA/SHP finishing system (continued on next page).

BTCA/MLA, MA/CA, MA/MLA	Chemical Add-on (%)	FT-IR Ester Peak Height (mm)	Fabric Moisture Regain (%)	Fabric DCRA (degrees)		Fabric WCRA (degrees)		Fabric Bending Length (mm)		% Retention Tensile Strength		% Retention Elongation at Break	
				Immediate Recovery	Recovery After 5min	Immediate Recovery	Recovery After 5min	Warp	Weft	Dry	Wet	Dry	Wet
34g/l MLA	3.18	19	8.144	166.7 ± 6.9	199.1 ± 6.4	146.3 ± 5.9	189.2 ± 4.4	19.0	26.6	96.12	86.92	77.94	78.18
20g/l BTCA, 23g/l MLA	3.22	27	8.299	163.9 ± 6.8	194.2 ± 5.8	155.9 ± 7.0	212.2 ± 5.5	19.1	27.3	93.20	90.59	73.76	73.21
30g/l BTCA, 17g/l MLA	4.39	30	8.254	162.5 ± 6.3	193.1 ± 6.4	158.0 ± 5.8	204.9 ± 5.6	22.3	27.6	91.64	86.77	63.06	66.55
40g/l BTCA, 11g/l MLA	4.30	34	8.205	167.3 ± 6.6	199.0 ± 5.5	151.9 ± 5.8	206.6 ± 5.0	21.1	29.3	92.72	86.97	74.30	67.11
60g/l BTCA	6.33	44	7.654	196.3 ± 6.6	235.9 ± 8.0	156.5 ± 3.7	210.7 ± 4.6	21.3	28.9	99.50	88.40	77.33	71.43
50g/l CA	4.13	30	8.258	148.4 ± 6.6	191.7 ± 6.3	151.6 ± 6.1	199.1 ± 4.6	21.5	28.0	96.48	85.90	71.01	69.23
20g/l MA, 33g/l CA	4.36	28	8.261	147.2 ± 5.7	191.3 ± 5.5	152.8 ± 6.3	207.2 ± 5.4	20.3	26.9	92.16	90.99	71.91	75.06
30g/l MA, 25g/l CA	4.84	28	7.911	153.1 ± 6.9	200.2 ± 6.2	147.3 ± 5.3	196.8 ± 4.8	19.4	28.0	93.40	86.77	74.84	72.73
40g/l MA, 16g/l CA	5.08	27	8.034	149.6 ± 6.7	186.3 ± 5.4	151.8 ± 6.0	202.2 ± 3.8	20.3	28.3	94.04	87.38	70.59	73.42
60g/l MA	4.87	29	7.387	184.2 ± 5.6	224.4 ± 9.3	153.8 ± 4.5	206.0 ± 5.3	20.5	26.0	105.05	88.04	72.43	74.46
34g/l MLA	3.18	18	8.144	166.7 ± 6.9	199.1 ± 6.4	146.3 ± 5.9	189.2 ± 4.4	19.0	26.6	96.12	86.92	77.94	78.18
20g/l MA, 23g/l MLA	4.21	27	8.088	160.8 ± 6.1	183.9 ± 7.1	150.3 ± 6.7	196.8 ± 7.8	21.3	27.6	95.04	89.47	71.37	76.92
30g/l MA, 17g/l MLA	4.54	28	7.945	157.8 ± 5.6	186.1 ± 7.2	152.7 ± 7.4	196.1 ± 6.0	18.9	26.1	95.20	90.03	72.21	76.45
40g/l MA, 11g/l MLA	5.17	29	7.829	161.9 ± 5.8	188.0 ± 6.7	149.4 ± 5.8	196.8 ± 2.6	18.8	27.9	93.56	89.26	73.10	78.57
60g/l MA	4.87	28	7.387	184.2 ± 5.6	224.4 ± 9.3	153.8 ± 4.5	206.0 ± 5.3	20.5	26.0	105.05	88.04	72.43	74.46

Table A2. 10b Properties of silk fibroin treated with a BTCA/PCA/SHP and MA/PCA/SHP finishing system (continued from previous page).

APPENDIX 3. RESULTS FROM SECTION 5.**A.3.1 Treatment of silk fabric with different softening agents.**

Experiment E Untreated	Fabric DCRA (degrees)		Fabric WCRA (degrees)	
	Immediate Recovery	Recovery After 5min	Immediate Recovery	Recovery After 5min
Untreated Control	248.1 ± 5.7	279.5 ± 5.9	141.9 ± 5.3	171.5 ± 4.9
0.25% w/w PEG 200	264.2 ± 5.9	299.5 ± 5.6	163.9 ± 6.5	188.5 ± 6.2
0.5% w/w PEG 200	255.4 ± 5.2	289.1 ± 6.0	158.3 ± 4.0	186.6 ± 4.1
1% w/w PEG 200	250.9 ± 6.0	291.4 ± 5.1	159.9 ± 4.6	191.9 ± 6.8
1.5% w/w PEG 200	240.8 ± 4.8	288.6 ± 5.0	160.9 ± 5.5	195.7 ± 5.8
2% w/w PEG 200	253.4 ± 6.1	286.8 ± 6.8	163.9 ± 6.1	190.5 ± 6.3
0.25% w/w PEG 400	257.9 ± 5.0	295.5 ± 4.6	165.8 ± 5.3	197.7 ± 6.5
0.5% w/w PEG 400	258.3 ± 6.3	294.0 ± 6.1	169.8 ± 6.6	198.8 ± 6.7
1% w/w PEG 400	256.0 ± 4.8	289.9 ± 4.8	171.4 ± 5.2	200.1 ± 5.4
1.5% w/w PEG 400	249.2 ± 5.5	288.1 ± 5.0	171.4 ± 4.0	205.0 ± 5.4
2% w/w PEG 400	256.7 ± 6.5	295.4 ± 6.1	165.2 ± 5.4	198.4 ± 6.5
0.25% w/w PEG 600	263.2 ± 6.1	295.6 ± 6.0	166.1 ± 5.0	198.5 ± 5.9
0.5% w/w PEG 600	252.5 ± 6.1	285.3 ± 5.9	166.9 ± 5.9	199.7 ± 5.7
1% w/w PEG 600	253.1 ± 5.6	289.7 ± 6.0	163.2 ± 5.7	197.0 ± 5.3
1.5% w/w PEG 600	242.1 ± 5.9	189.5 ± 5.9	171.2 ± 5.6	205.8 ± 6.6
2% w/w PEG 600	256.9 ± 5.8	293.1 ± 6.7	163.3 ± 5.2	195.8 ± 7.8
0.25% w/w PEG 1000	235.2 ± 5.9	274.9 ± 5.9	158.0 ± 7.0	188.8 ± 6.1
0.5% w/w PEG 1000	250.2 ± 5.8	287.8 ± 5.6	159.4 ± 5.6	192.8 ± 6.6
1% w/w PEG 1000	242.0 ± 7.4	279.9 ± 6.9	165.1 ± 5.7	198.0 ± 6.5
1.5% w/w PEG 1000	232.9 ± 7.0	271.6 ± 5.4	167.4 ± 5.1	199.8 ± 6.3
2% w/w PEG 1000	228.8 ± 7.4	264.6 ± 5.4	165.8 ± 7.2	193.9 ± 5.9
0.5% w/w Ultratex SW	283.1 ± 4.6	314.4 ± 4.5	171.9 ± 4.2	207.3 ± 4.9
1% w/w Ultratex SW	285.9 ± 3.2	317.7 ± 3.1	188.5 ± 4.5	223.5 ± 5.3
1.5% w/w Ultratex SW	287.7 ± 3.5	321.0 ± 3.4	193.8 ± 3.5	233.8 ± 4.8
2% w/w Ultratex SW	287.6 ± 3.2	320.8 ± 3.3	195.9 ± 4.3	239.6 ± 3.9
2.5% w/w Ultratex SW	290.4 ± 3.1	321.6 ± 3.2	194.9 ± 4.5	241.5 ± 4.4
0.5% w/w Ultratex FEW	286.4 ± 3.7	318.5 ± 3.0	189.6 ± 7.2	229.7 ± 6.2
1% w/w Ultratex FEW	288.5 ± 4.5	320.4 ± 3.3	192.8 ± 5.0	236.1 ± 4.3
2% w/w Ultratex FEW	285.1 ± 6.2	319.9 ± 5.4	199.9 ± 4.7	246.8 ± 6.1
3% w/w Ultratex FEW	288.8 ± 4.2	319.9 ± 4.2	206.7 ± 5.7	247.4 ± 5.4
4% w/w Ultratex FEW	274.6 ± 3.5	307.7 ± 4.4	207.1 ± 5.0	253.3 ± 4.8

Table A3.1 Crease recovery angle results of silk fabric treated with different softening agents

A.3.2 Treatment of silk fabric with BTCA/SHP/Softener finish.

Experiment E Treated	Fabric DCRA (degrees)		Fabric WCRA (degrees)	
	Immediate Recovery	Recovery After 5min	Immediate Recovery	Recovery After 5min
6% w/w BTCA, SHP(1:1)	267.3 ± 5.5	303.2 ± 5.3	157.5 ± 5.2	193.3 ± 5.5
+ 0.5% w/w Ceranine L	283.3 ± 4.2	316.9 ± 3.2	163.8 ± 4.9	193.6 ± 5.4
+ 1% w/w Ceranine L	287.4 ± 3.1	319.6 ± 3.4	164.5 ± 6.5	198.3 ± 4.9
+ 1.5% w/w Ceranine L	293.1 ± 4.6	324.9 ± 4.0	170.0 ± 6.8	201.9 ± 5.5
+ 2% w/w Ceranine L	298.4 ± 4.2	327.6 ± 3.0	159.5 ± 5.7	192.1 ± 5.8
+ 0.25% w/w PEG 200	265.9 ± 5.4	300.8 ± 6.5	172.3 ± 5.2	205.8 ± 4.5
+ 0.5% w/w PEG 200	276.6 ± 6.3	312.4 ± 5.5	171.2 ± 4.1	203.7 ± 5.2
+ 1% w/w PEG 200	274.0 ± 5.0	308.1 ± 5.1	168.7 ± 4.0	202.2 ± 5.8
+ 1.5% w/w PEG 200	272.3 ± 4.8	305.9 ± 4.2	170.9 ± 4.8	205.2 ± 5.7
+ 2% w/w PEG 200	268.2 ± 4.1	302.9 ± 4.8	175.2 ± 5.2	210.4 ± 5.6
+ 0.25% w/w PEG 400	282.1 ± 5.3	302.1 ± 4.8	177.9 ± 6.4	206.9 ± 7.4
+ 0.5% w/w PEG 400	270.7 ± 5.2	304.2 ± 3.8	176.2 ± 6.1	210.0 ± 6.3
+ 1% w/w PEG 400	271.8 ± 6.2	305.5 ± 4.9	178.0 ± 4.5	210.2 ± 5.6
+ 1.5% w/w PEG 400	265.5 ± 6.7	301.8 ± 6.4	176.8 ± 4.7	212.2 ± 5.5
+ 2% w/w PEG 400	263.6 ± 6.8	301.1 ± 6.1	177.0 ± 5.8	212.5 ± 7.7
+ 0.25% w/w PEG 600	280.0 ± 4.4	312.2 ± 4.1	177.2 ± 5.7	210.4 ± 6.1
+ 0.5% w/w PEG 600	276.8 ± 6.7	310.2 ± 6.3	176.5 ± 6.9	209.8 ± 6.3
+ 1% w/w PEG 600	278.4 ± 5.6	310.0 ± 5.3	169.2 ± 6.1	203.8 ± 7.3
+ 1.5% w/w PEG 600	285.5 ± 4.3	314.2 ± 3.5	170.8 ± 4.2	205.8 ± 4.9
+ 2% w/w PEG 600	276.5 ± 3.5	308.3 ± 3.2	179.9 ± 5.6	216.0 ± 5.4
+ 0.25% w/w PEG 1000	279.6 ± 4.5	309.8 ± 4.4	175.7 ± 5.4	205.3 ± 5.9
+ 0.5% w/w PEG 1000	276.8 ± 5.5	310.2 ± 5.8	169.8 ± 6.7	199.3 ± 6.1
+ 1% w/w PEG 1000	280.0 ± 4.0	311.0 ± 3.7	172.5 ± 5.4	204.8 ± 6.5
+ 1.5% w/w PEG 1000	279.8 ± 5.0	310.4 ± 5.1	174.7 ± 5.4	204.8 ± 5.4
+ 2% w/w PEG 1000	280.3 ± 4.5	312.1 ± 2.8	172.6 ± 4.4	203.6 ± 5.9
+ 0.5% w/w Ultratex SW	299.1 ± 6.0	326.5 ± 5.3	196.3 ± 5.5	239.1 ± 6.3
+ 1% w/w Ultratex SW	300.5 ± 4.3	328.4 ± 4.2	194.4 ± 6.1	233.5 ± 6.6
+ 1.5% w/w Ultratex SW	296.4 ± 4.7	325.8 ± 4.1	211.4 ± 6.0	252.9 ± 6.8
+ 2% w/w Ultratex SW	297.1 ± 5.3	326.5 ± 5.0	199.2 ± 5.4	244.0 ± 5.5
+ 2.5% w/w Ultratex SW	296.2 ± 5.1	325.3 ± 4.3	203.7 ± 5.0	252.1 ± 5.2
+0.5% w/w Ultratex FEW	284.5 ± 4.7	317.8 ± 3.8	195.9 ± 4.2	239.2 ± 4.8
+ 1% w/w Ultratex FEW	295.0 ± 4.0	324.0 ± 3.6	194.8 ± 3.5	240.2 ± 2.8
+ 2% w/w Ultratex FEW	291.5 ± 3.6	320.8 ± 3.3	199.2 ± 5.6	246.0 ± 6.1
+ 3% w/w Ultratex FEW	292.8 ± 3.5	323.2 ± 3.4	199.5 ± 5.5	251.4 ± 4.7
+ 4% w/w Ultratex FEW	289.1 ± 3.8	320.0 ± 4.0	204.3 ± 4.4	253.7 ± 4.6

Table A3. 2 Crease recovery angle results of silk fabric treated with BTCA/SHP/Softener finish.

A.3.3 Treatment of silk fibroin with BTCA/SHP and various pad bath additives.

BTCA/SHP	Chemical Add-on (%)	FT-IR Ester Peak Height (mm)		Fabric Moisture Regain (%)	Fabric DCRA (degrees)		Fabric WCRA (degrees)		Fabric Bending Length (mm)		% Retention Tensile Strength		% Retention Elongation at Break		ASTM Yellowness Index
		Rinsed	NaOH-treated		Immediate Recovery	Recovery After 5min	Immediate Recovery	Recovery After 5min	Warp	Weft	Dry	Wet	Dry	Wet	
6%w/w BTCA	6.33	44	22	7.65	178.3 ± 6.5	218.0 ± 5.2	154.5 ± 4.3	208.7 ± 5.0	21.3	28.9	87.6	88.4	60.9	71.4	7.28
+ 1%w/w CL	4.64	39	20	9.06	178.5 ± 6.0	208.5 ± 5.1	190.9 ± 5.5	252.8 ± 4.0	15.8	28.5	96.4	97.6	76.1	85.4	6.14
+ 1%w/w PEG	4.23	37	19	8.81	171.8 ± 5.9	210.3 ± 6.1	185.8 ± 6.8	246.2 ± 4.5	15.3	26.9	98.9	93.6	77.9	83.1	5.58
+ 1%w/w FEW	5.60	41	22	8.78	185.9 ± 4.7	215.2 ± 6.3	192.2 ± 5.4	255.5 ± 4.5	14.5	28.0	93.4	90.0	75.1	77.7	6.27
+ 1%w/w SW	4.32	39	21	8.76	189.4 ± 5.9	234.1 ± 6.0	181.4 ± 6.6	252.9 ± 5.9	14.0	26.8	90.6	89.2	72.0	77.2	7.06
+ 1%w/w FA	5.61	38	20	8.39	125.0 ± 5.2	205.2 ± 5.3	155.0 ± 6.2	212.2 ± 4.7	24.3	30.5	94.7	96.3	57.9	70.4	7.49
+ 3%w/w FA	5.69	37	19	8.43	128.6 ± 4.5	199.9 ± 6.0	161.4 ± 4.9	222.5 ± 4.9	23.8	31.3	92.6	93.8	56.4	66.8	6.86
+ 5%w/w FA	6.43	36	19	8.34	129.4 ± 4.4	194.9 ± 5.7	170.4 ± 5.8	220.8 ± 5.4	22.9	31.6	93.0	94.9	57.8	67.6	6.3
+ 5%w/w FA, 1%w/w CL	5.01	37	19	8.78	175.3 ± 6.0	212.4 ± 5.6	153.0 ± 3.9	220.7 ± 6.1	16.5	27.9	94.4	102.0	64.1	75.2	6.14
+ 5%w/w FA, 1%w/w PEG	5.57	35	19	8.65	167.0 ± 5.8	205.7 ± 5.9	146.0 ± 5.4	211.6 ± 4.6	16.5	28.8	97.9	98.3	68.6	73.7	5.48
+ 5%w/w FA, 1%w/w FEW	5.42	35	20	8.60	168.9 ± 6.4	214.5 ± 5.2	154.5 ± 5.0	217.5 ± 4.6	17.5	29.8	96.4	97.7	64.3	73.7	5.27
+ 5%w/w FA, 1%w/w SW	5.11	35	18	8.65	186.3 ± 6.3	223.3 ± 5.2	157.1 ± 5.2	220.9 ± 6.0	15.3	27.9	95.6	97.5	67.1	74.9	4.65

Table A3.3 Properties of silk fabric treated with BTCA/SHP and/or the swelling agent formic acid (FA). Some fabrics were given an after-treatment with different softening agents.

BTCA/SHP	Chemical Add-On (%)	FT-IR Ester Peak Height (mm)		Fabric Moisture Regain (%)	Fabric DCRA (degrees)		Fabric WCRA (degrees)		Fabric Bending Length (mm)		% Retention Tensile Strength		% Retention Elongation at Break		ASTM Yellowness Index
		Rinsed	NaOH-treated		Immediate Recovery	Recovery After 5min	Immediate Recovery	Recovery After 5min	Warp	Weft	Dry	Wet	Dry	Wet	
6%w/w BTCA	6.33	44	22	7.65	178.3 ± 6.5	218.0 ± 5.2	154.5 ± 4.3	208.7 ± 5.0	21.3	28.9	87.6	88.4	60.9	71.4	7.28
+ 1%w/w AA	6.09	35	20	8.40	151.4 ± 5.7	191.2 ± 6.3	156.7 ± 6.1	214.6 ± 5.6	23.8	30.1	95.7	93.6	59.0	72.8	8.76
+ 3%w/w AA	6.79	38	24	8.28	147.0 ± 5.0	186.5 ± 5.3	157.5 ± 5.6	219.2 ± 4.5	24.5	29.9	97.9	94.7	60.8	67.6	8.61
+ 5% w/w AA	7.72	40	23	8.69	141.2 ± 5.5	190.1 ± 6.0	158.7 ± 5.4	221.4 ± 5.7	25.3	31.3	97.2	93.9	57.2	63.9	7.59
+ 5%w/w AA, 1%w/w CL	5.87	37	21	8.61	179.5 ± 5.1	223.2 ± 5.7	155.8 ± 6.1	220.4 ± 5.9	16.1	26.9	97.9	96.8	69.4	75.2	7.04
+ 5%w/w AA, 1%w/w PEG	6.45	40	24	8.89	167.0 ± 5.8	202.9 ± 6.1	152.7 ± 4.7	223.4 ± 5.6	18.6	28.0	98.6	96.5	67.0	67.6	8.61
+ 5%w/w AA, 1%w/w FEW	6.57	41	22	8.62	205.6 ± 6.4	244.6 ± 5.8	162.2 ± 5.8	225.2 ± 4.9	15.8	26.5	92.0	91.8	71.2	72.6	6.04
+ 5%w/w AA, 1%w/w SW	5.60	40	24	8.85	202.6 ± 5.0	238.6 ± 5.5	163.3 ± 4.9	228.5 ± 4.9	17.1	26.8	94.4	93.5	66.6	69.9	7.43
+ 1%w/w PAA	6.07	36	19	8.67	134.2 ± 5.8	172.8 ± 5.7	168.1 ± 5.8	217.9 ± 4.9	26.8	35.1	98.3	93.1	64.7	76.9	7.28
+ 3%w/w PAA	6.51	40	20	8.62	131.1 ± 5.8	167.0 ± 4.7	183.4 ± 5.5	246.8 ± 5.9	28.3	37.8	90.9	89.9	59.8	72.9	7.17
+ 5% w/w PAA	6.96	43	21	8.51	110.4 ± 4.5	157.7 ± 4.1	201.4 ± 5.7	261.2 ± 4.7	29.9	36.8	93.0	90.8	62.1	71.6	7.1
+ 1%w/w PAA, 1%w/w CL	4.75	35	19	9.12	129.8 ± 5.7	179.5 ± 6.3	190.9 ± 5.3	252.8 ± 4.0	24.1	36.4	99.2	94.9	76.0	80.7	6.55
+ 1%w/w PAA, 1%w/w PEG	5.56	40	21	8.71	139.2 ± 5.2	183.3 ± 6.1	185.8 ± 6.8	246.2 ± 4.5	22.8	33.6	97.9	92.9	77.4	76.5	6.67
+ 1%w/w PAA, 1%w/w FEW	6.73	37	19	8.61	143.4 ± 5.0	186.3 ± 5.8	192.2 ± 5.7	255.5 ± 4.5	25.6	36.4	93.0	89.7	69.4	73.9	6.5
+ 1%w/w PAA, 1%w/w SW	5.36	44	24	8.99	146.4 ± 6.7	193.8 ± 7.3	194.7 ± 5.6	260.9 ± 4.9	23.5	36.8	92.7	93.5	72.9	77.3	6.87

Table A3. 4 Properties of silk fabric treated with BTCA/SHP and/or the pad bath additives, acrylic acid (AA) or polyacrylic acid (PAA). Some fabrics were given an after-treatment with different softening agents.

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