WET AND DRY-JET WET-SPINNING OF ACRYLIC FIBRES

A thesis submitted for the degree of
Doctor of Philosophy

by

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An account of work carried out under
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To my Wife and my Children

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ABSTRACT

A comparison of the wet-spinning and dry-jet wet-spinning of acrylic fibres has been carried out using a commercial acrylic polymer (Courtelle) redissolved in dimethyl formamide. The higher speeds possible in dry-jet wet-spinning have been related to the higher free velocity and the higher draw ratios possible. It is believed that the presence of the air-gap in dry-jet wet-spinning allows the removal of the die-swell effects as well as other viscoelastic behaviour before coagulation and that this leads to fibres with superior mechanical properties, especially in improvements in extensibility. Conditions are described which allow the production of high tenacity acrylic fibres with tenacity up to 5.8 g/d tex.

In an attempt to produce fibres with better mechanical properties under hot-wet conditions, copolymers have been prepared using bicyclo [2,2,1] hepta-2,5-diene as a comonomer. Fibres from such copolymers have low extensibilities and satisfactory fibres could be made only by incorporating, in addition to the bicyclo [2,2,1] hepta-2, 5-diene monomer, itaconic acid and by dry-jet wet-spinning. In one such case a fibre was obtained with a slightly higher hot-wet modulus and a considerably reduced hot-wet extensibility when compared with Courtelle fibre.

CONTENTS

CHAPTER 1. INTRODUCTION

1.1 About a century ago the first successful man-made fibre created a sensation at the 1889 Paris Exposition[1]; this was Chardonnet's "artificial silk". During this past hundred years, scientists have developed a comprehensive, well ordered background of basic science, as a result of which, fibre production has improved enormously. In the man-made fibre industries the main process is the conversion of the raw material, which is polymer solid in the shape of chips, powder, etc., to the fibre form. This process involves changes of the physical state of the polymer, in that the solid polymer is converted to a liquid state, by means of heat or solvent (to give a polymer melt or polymer solution), and after shaping into filament form is converted back to the solid state (fibre). These processes have been done usually, either by the melt spinning method or by solution spinning methods. In the latter systems the fibre could be formed either by dry-spinning or by wet-spinning processes. Apart from these three spinning systems, which are fundamental procedures of fibre formation, there are less important methods, including spinning from emulsion and suspension[2,3], spinning with phase separation[4], and spinning with chemical reaction controlling the solidification of the spinning fluid.[5,6] There are also modifications of the fundamental spinning methods such as gel-spinning (semi-melt spinning[7]) and dry-jet wet-spinning[8].

1.2 Fibre production from polyacrylonitrile polymer and copolymers

1.2.1 Introduction

In 1948[9], the Du Pont company of the United States announced its intention to produce and market fibres prepared from polyacrylonitrile, and in 1950, acrylic fibre was produced commercially. Although acrylonitrile polymer and co-polymers had been known for many years, it was initially regarded as a useless raw material for fibre productions. In fact acrylonitrile was discovered in ~~1839~~ 1893[10], but the polymer and co-polymers of high acrylonitrile content could neither be melted, because of decomposition, nor could they be dissolved in all known solvents up to the 1930's. In 1938 Rein[11] discovered that polyacrylonitrile could be dissolved in certain aqueous solutions of some inorganic salts, such as zinc chloride or calcium thiocyanate. Also a wide range of organic solvents were found during the 1940s[12-22], which could dissolve the polymer and co-polymers. The concentrated solutions (dope), which were prepared from polyacrylonitrile in these organic and inorganic solvents are used for fibre production. Therefore, the usual processes for fibre production from acrylonitrile polymer and co-polymers are the solution spinning methods.

Since 1950, when the first commercial acrylic fibres were produced, production has increased very substantially. Although, in some years there was a decrease in production, related to a recession or a sudden increase in the price of raw material, the overall rate of growth of output has been rather rapid during the last 30 years. The production of these fibres in 1952 was only 6.37 x 10^3 tonnes[23], while the production of acrylic and modacrylic fibres for 1980 was 2083 x 10^3 tonnes[24], which means there has been an average annual rate of growth of 23% in the production of these fibres.

Table 1.1[24] and Fig. 1.1 show the annual production figures for acrylic fibre during the period 1974 to 1980 and the available capacity for 1981 and 1982 together with the annual production of the all non-cellulosic man-made fibres for the same years. Today there are about 60 plants in 29 countries, which are producing fibres from acrylonitrile polymer and co-polymers, (Table 1.2[24]).

This rapid growth has been attributed to some of the physical and chemical properties of acrylic fibre, namely those of lightweight, handle, warmth, good chemical and weathering resistance, and its resemblence to wool. Another factor for this growth is certainly related to the methods of synthesis of acrylonitrile monomer, especially those processes based on the use of propylene, such as the Sohio process, which was a considerable break from the traditional technology of acrylonitrile production. Owing to the availability of propylene at a low cost as the by-product of refining and cracking processes, the production cost of acrylonitrile using propylene therefore, could be as low as about one third of that using other methods.[25]

The success of these fibres has been almost entirely in staple form, while the production of filament form in

Table 1.1 World acrylic and total synthetic fibres production (in metric tonnes x 10^3)

Year	Acrylic and modacrylic fibre metric tonnes x 10^3	Total synthetic fibre metric tonnes x10^3	%
1973	1577	7674	20.64
1974	1449	7487	19.35
1975	1391	7353	18.90
1976	1742	8601	20.25
1977	1790	9149	19.56
1978	2021	10034	20.14
1979	2069	10608	19.50
1980	2083	10487	19.86
1981*	2602	13283	19.59
1982*	2681	13969	19.19

* producing capacity

Fig 1.1 World acrylic and modacrylic fibre production[24]

Table 1.2 World distribution of acrylic and modacrylic plants

Place	No. of countries	No. of plants
Western Europe	11	23
Eastern Europe	6	7
America	6	13
Asia, Oceania	6	17
Total	29	60

comparison with staple is very low (less than 0.3%)[24]. The main use of these fibres is in the knitwear trade, imitated fur, upholstery, blankets and carpets. The success of acrylic fibres in different applications is mainly due to their ease of processability on a variety of textile processing machinery, including woollen, and cotton spinning systems, (and to some extent on worsted spinning systems), and essentially all knitting, tufting and weaving machinery which are used for spun yarns.

1.2.2 Fibre spinning

The solution spinning for acrylonitrile polymer and co-polymers can be done either by the wet-spinning system, or through the dry-spinning method. Both methods are used industrially at present. Apart from solution spinning methods, the fibre can also be produced by some other methods, such as semi-melt spinning[26,27], which operates with the aid of a suitable plasticising substance, such as DMF, propylene carbonate, or ethylene carbonate, which is mixed with the polymer before spinning. However, due to the difficulty of obtaining a stable phase of the molten polymer, the melt-spinning of acrylic fibres has not been used commercially. Therefore, in order to produce acrylic fibres, it has been the common practice to prepare a spinning solution by dissolving an acrylonitrile polymer or co-polymers in a concentrated aqueous solution of an inorganic salt or in an organic solvent, and to form fibre therefrom by a wet-spinning or dry-spinning system. Table 1.3[28,30] shows the spinning systems used for most of the commercially produced acrylic fibres. As can be seen from Table 1.3, it is obvious that the majority of the commercial acrylic fibres are produced by the wet-spinning method. Also, there is a good deal of published work[29] dealing with this process of fibre formation reflecting the importance of this method of spinning for acrylonitrile polymer and co-polymers.

In the wet-spinning process, a polymer solution with very high viscosity is extruded through the small holes of a spinneret, which is immersed in a liquid bath (coagulation bath) at angles which may vary from +90° to -90° with respect to the liquid surface. As the gel-thread passes through the coagulation bath, it solidifies in a process which is called coagulation. During coagulation in the coagulation bath, there is a diffusional interchange between polymer solution and the coagulation bath. The spinning solution contains 10 - 30% of polymer and the spinnerets which are used in the wet spinning have a minimum of 1000 holes and a maximum of 120,000 holes[31,32]. of diameters from about 60 to 150 micron. Generally speaking, the speed of spinning is considerably lower in this process than in the dry-spinning process (5 to 20 m/min). This has the advantages of allowing the after treatment and the finishing processes be effected continuously.

Table 1.3 Spinning methods of some commercial acrylic fibres[28,30]

Trade name	Producer	Spinning procedure
Acribel	Fabelta	Wet
Acrilan	Monsanto	"
Beslon	Toho	"
Cashmilon	Asahi	"
Courtelle	Courtaulds	"
Creslan	Cyanamid	"
Crylor	C.T.A.	"
Dolan	Hoechst	Wet,dry
Dralon	Bayer	Dry
Euroacril	A.N.I.C.	Wet
Exlan	Exlan	"
Leacril	Chatillon	"
Nitron	U.S.S.R.	"
Nymacron	N.V.Nyma	"
Orlon	Du Pont	Dry
Pan	Cassella F.	"
Redon	Phrix G mbh	Wet
Sircril	S.I.R.	"
Tacryl	Stockholm S.	"
Toraylon	Toray	"
Velicren	Snia Viscosa	"
Vonnel	Mitsubishi	"
Wolpryla	Wolfen	"
Zefran	Dow-Badische	"

The dry-spinning process consists in extruding the polymer dope through a spinneret into a heated shaft (chamber), where the solvent evaporates gradually. The spinning system is generally carried out with DMF as solvent. The type of spinneret used has a varying number of holes usually from 200 to 600, and the polymer dope is fed at a temperature of 80-150°C, while the temperature of the air in the heated chamber is about 230-260°C. Since the boiling temperature of DMF is 153°C it evaporates, causing the filaments to solidify as solvent diffuses from the thread-line, so that a substantially dry fibre leaves the bottom of the shaft and is wound onto bobbins at a speed of 100-300 m/min . An additional washing of fibre is usually included because the last residues of solvent are very difficult to remove.[33]

Particular attention must be given to the possible formation of turbulence in the heated shaft which can disturb the regular formation of the yarns. Another factor that must be carefully checked is the hygrometric state as well as the oxygen content of the atmosphere used in the shaft to accelerate the removal of the solvent. This is to prevent discoloration and spoiling of the yarns.[34]

The major advantages of this method, if compared with wet-spinning, lies in the several times higher spinning velocity and in the 1.5-2 times higher concentration of spinning solution (and, thus, in a higher output of the equipment and a smaller amount of solvent to be recovered). The disadvantages of dry-spinning are the considerable losses of the solvent and the considerable height of the device, if a reasonable spinning velocity is to be achieved.

However, both, dry-spinning and wet-spinning have various drawbacks of a technological nature which considerably limit their application. Thus the dry-spinning method, permitting a much higher speed of take-up compared with that possible in the wet-spinning system, requires, in view of the low volatility of the solvents normally employed, the use of very high temperatures in order to be able to eliminate the solvent in acceptable quantity and in an acceptable period of time. The use of such high temperatures can sometimes lead to the phenomenon of degradation and to the production of discoloured yarns. On the other hand, in the wet-spinning process, the extruded polymer dope leaves the spinneret hole forming a jet streaming through a surrounding fluid medium; in this case, because of hydrodynamic resistance together with the viscoelastic behaviour of the polymer dope, the spinning speed is very low, especially in comparison with the dry-spinning speed. However, because of the compact nature of this method of fibre spinning it can achieve a high productivity.

In Table 1.4 some of the advantages and disadvantages of these two spinning systems for polyacrylonitrile are summarised.

Table 1.4 The main advantages and disadvantages of the wet-spinning and dry-spinning processes

Wet-spinning	Dry-spinning
ADVANTAGES	
1. Economic: (a) continuous system (b) elimination of heat (c) use of more holes per spinneret	1. Higher spinning speed
2. Use of any solvent (volatile or non-volatile)	2. Positive jet-stretch ratio for very fine fibres
3. Simple process: (a) a much wider choice of temperature, coagulation rate, and dope concentration (b) greater flexibility of equipment (c) relatively easier solvent recovery	3. Higher dope concentration
4. No danger of degradation	4. Fibre has better cover, lustrous, softer handle, and soil-hiding properties.
DISADVANTAGES	
1. Low spinning speed	1. Discoloration and degradation of the polymer due to heat
2. Maintaining of the uniformity of composition and temperature of the coagulation bath	2. Difficulty of solvent recovery
3. Use of finer spinnerets	3. Hazard and danger of the plant and solvent
4. Low jet stretch ratio	4. Use of very high temperatures in the dry spinning
	5. Health hazard
	6. Limited choice of solvent (volatile only)

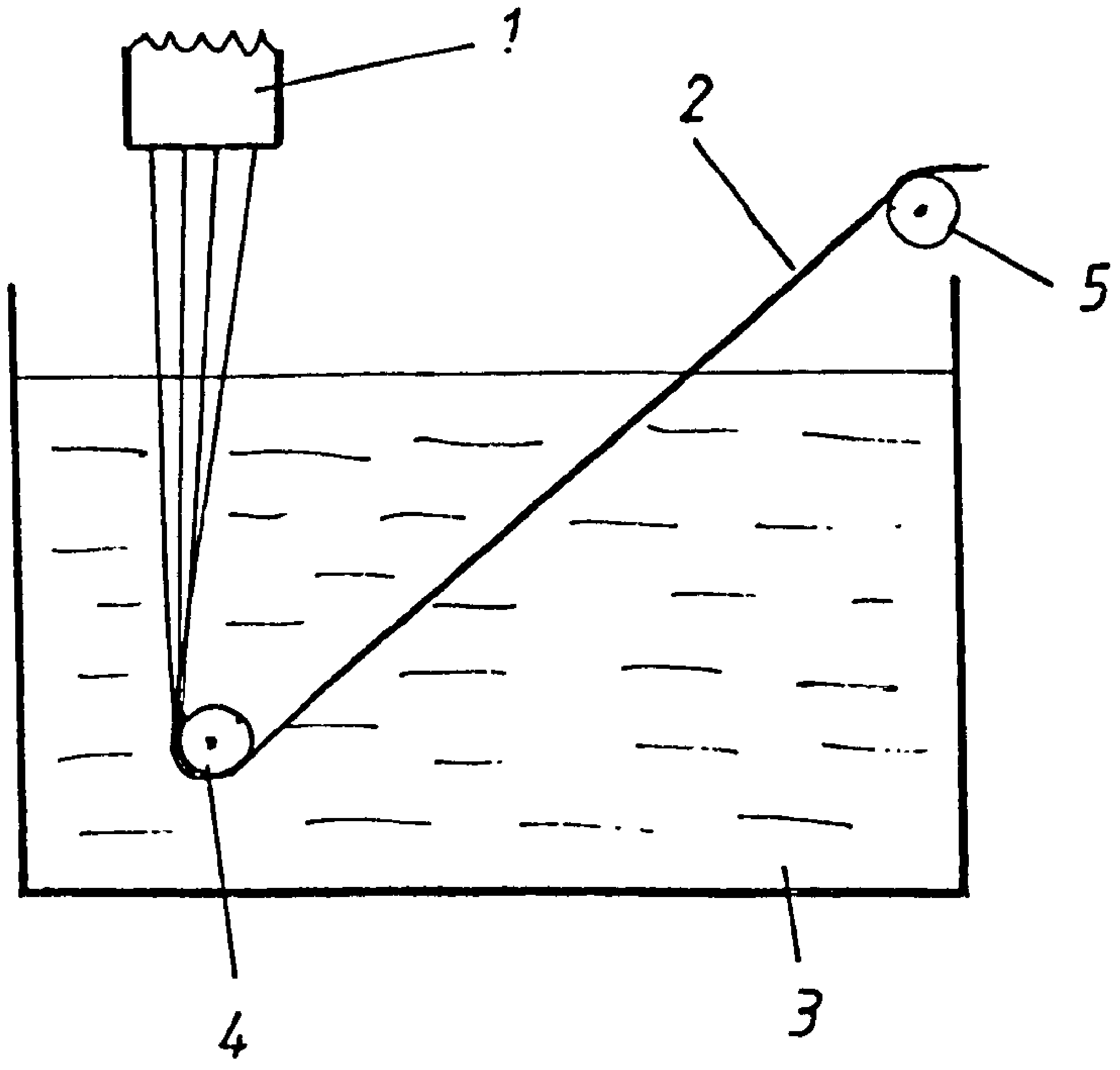
1.3 The dry-jet wet-spinning method

1.3.1 Introduction

The known spinning methods, which have been used commerically up to now, for the production of fibres from acrylonitrile polymer and co-polymers are the dry-spinning and the wet-spinning methods. However, such methods have various drawbacks of a technical nature, which limit considerably their application. To overcome the drawbacks, without sacrificing the advantages at the same time is an attractive goal and some research has been directed to this end. From the beginning of the 1960's, there have been some patents[8,33,35-60] and a few papers[61-64] describing methods in which, in contrast to the above mentioned methods, the solidification process takes place in two stages, namely, the non-liquid stage and the liquid stage. In this method the polymer solution is extruded through a spinneret, which is positioned vertically above a liquid surface, initially into the air or into a stream of an inert gas (non-liquid stage), the spinneret never entering the liquid. Then the fluid thread lines enter a coagulation bath (liquid stage) as shown in Fig.1.2.

The principle of both dry-spinning and wet-spinning methods are thus employed in this method. Hence, it is called the dry-jet wet-spinning method[8], though some other names, such as dry-jet spinning, wet-dry spinning[47], dry-wet spinning[64], and air-gap spinning[62] have been used. This method is a modified

Fig. 1.2 Dry-jet wet-spinning



1. Spinneret
2. Filaments
3. Coagulating bath
4. Guide roller
5. Take-up roller

system for wet-spinning, because all other procedures for fibre processing in this system are the same as in the wet-spinning method, and the only difference between these two methods of fibre production is the way in which the solidification of the polymer solution takes place.

The main object of this method is to increase the speed of the wet-spinning process though it also gives rise to an improvement in the physical and the mechanical properties of the fibres produced. So in all patents, which consider this method of fibre spinning, high speeds of spinning, up to 1500 m/min[52] have been claimed.

1.3.2 Spinning

The essence of a dry-jet wet-spinning process is that the spinning solution is extruded through a suitable spinneret into a gas medium (air-gap) for a relatively short distance and then passes through a coagulating bath liquid. Ordinarily, the gas between the spinneret and the coagulating bath is air, although any other gaseous medium that does not adversely affect the filaments may be used. The distance that the spinneret is positioned above the coagulating bath may be varied. During their brief passage through the space above the surface of the coagulating bath and below the face of the spinneret only a small amount of the solvent is believed to be removed by evaporation from the extruded streams of the polymer dope, with the result that little solidification takes place in this region. Then almost complete elimination of the solvent takes place in the coagulating bath by the normal solvent and non-solvent diffusion processes between the spinning solution and the coagulating liquid. These freshly formed filaments are then removed from the coagulating bath as undrawn and swollen thread-like filaments, and subjected to the same procedure for washing and drawing as in wet-spinning.

It is claimed that a spinning system of this type constitutes an improvement over the dry-spinning or the wet-spinning systems, since in the air-gap region, there are retained the advantages of dry-spinning, while in the subsequent passage through the coagulating bath, there is the advantage of obtaining coagulation under preferred conditions[47]. On the other hand, the coagulation of a filament in a liquid bath is a dynamic operation which occurs as the filament is being drawn along. The force required to draw the filament to the take-up roller is opposed by a number of tensions; surface tension, internal frictional tensions, and hydrodynamic and frictional drags[65]. In dry-jet wet-spinning, because of the high fluidity of the thread line of the spinning solution in the zone between the spinneret and the coagulating bath liquid, the longitudinal force applied to the coagulating filaments to pull them through and out of the coagulating bath is accepted by the extruded streams of the polymer dope, in the main, in this zone. Also dry-jet wet-spun filaments have smoother surfaces than wet-spun filament[8]. Apparently, the coagulating filaments, as a result, are passed through the coagulating bath under a minimum tension; that is, the tension exerted on the coagulating filaments would only be that tension required to overcome the forces within the thread like filaments and the drag forces in the coagulating bath.

The spinnerets which are used in this process can be of the type ordinarily used in the dry-spinning operation. However, it is necessary to consider, in selecting a spinneret, the distance between adjacent holes. Holes should not be too close to each other, otherwise this will disturb continuous spinning. An important variable in any spinning process is the hole diameter of the spinneret, and it is often desirable to employ the largest diameter consistent with good spinning. In the dry-jet wet-spinning system, one may employ holes having relatively large diameters due to the fact that the filaments may be given a considerable attenuation immediately after extrusion of the spinning solution. It is also claimed that spinnerets with holes of a non-circular cross-section can also be used in this system[51].

The coagulating bath liquid suitable for use in dry-jet wet-spinning normally consists of a mixture of a solvent and a non-solvent for the acrylonitrile polymer and co-polymers.

Whilst water is typically the non-solvent, the solvent used in the coagulating bath is preferably the same as the one used in preparing the polymer dope; however, such need not be the case[8]. Although good spinning can be accomplished while using a coagulating bath composed essentially of water, it is preferred that the bath contain either an aqueous solution of the organic solvent in a concentration of 20% to 70% or, an aqueous solution of the appropriate inorganic salt in a concentration of less than 20%. However, normal organic solvent concentrations for coagulating baths are 40% - 55%, though coagulating baths with concentrations of 78%[62], 75%[49], 70%[36,47,50,54] have been claimed. On the basis of available data, the temperature range for the coagulating bath is from -40°C to +80°C. It is preferred that the bath contain rather high percentages of the solvent at the lower bath temperature.

The filaments may be given a travel in coagulating baths for example, from 5 to 60 cm. or more by employment of at least two suitably spaced guides, the first of which is located vertically below the spinneret and at the maximum possible distance from the upper surface of the coagulating liquid, and the second one between the coagulating bath and take-up roller.

Since in the dry-jet wet-spinning system, the spinning solution extruded from the spinneret is not immediately coagulated as in an ordinary wet-spinning process, the obtained gel filaments may be more rapidly extruded into air or gas before they are dipped into the coagulating bath. Therefore, it is possible to set the rate of extrusion at much higher values than in the ordinary wet-spinning process. There has been considerable difficulty in the actual operation of higher spinning speeds, such as in the application of high take-up speeds due to the resistance caused by the static coagulating bath. The bath liquid restricts the movement of the bundle of filaments, particularly in the final sections of the bath, immediately before the emergence of the filaments, and hence can cause filament breakage. In addition, in the high speed spinning of filaments of less than 1 d tex, for example, when the unoriented filaments are stretched directly at a high stretching ratio in a static draw bath, the breaking phenomenon can again occur in such filaments of low tensile strength to such an extent that it becomes impossible to carry on the spinning. To overcome these limitations and drawbacks of the dry-jet wet-spinning process, some improved methods of dry-jet wet-spinning have been described in many patents[8,33,47,59]. These improvements are related to the coagulating bath, and to the subsequent stages of the spinning process, i.e. in the stretching bath. In some methods, the coagulating liquid is allowed to flow with the freshly extruded filaments. Such spinning is described as a "flowing bath type"[8]. In the flowing bath type, the coagulating liquid is made to flow in the same direction as the freshly extruded filaments are drawn, so that the contact resistance between the coagulating liquid and filaments is reduced and filament breakage is thereby reduced. It has been claimed[59] that making the coagulating liquid flow in the same direction as the direction of the advance of the filaments allows the take-up velocity to be greatly elevated to higher values than when using a static bath. The increase in the take-up velocity can be as high as a factor of two and at the same time makes it possible to produce filaments which have low counts.

When such flowing bath type spinning is used in the coagulating step, the solvent will be extracted from the gel filaments into just that portion of the coagulating liquid that flows with the filaments. As the coagulation of the filaments progresses, the concentration of the solvent in the coagulating liquid will become higher. Thus in the flowing bath type spinning unit, the filaments can be stretched while not fully coagulated. Therefore filaments which have finer counts can be produced under stable high speed conditions in which filament breaks are negligible.

The most preferred flowing bath type spinning uses a coagulating bath having a frustoconical tube, provided vertically at a fixed distance from the lower surface of the spinneret (Fig. 1.3). A spinning solution extruded out of the spinneret passes through the air-gap and then passes through the tube body filled with moving coagulating liquid, always kept at a constant liquid level. Here, the filaments and coagulating liquid advance in the same direction through the tube. Then the filaments are led out from the coagulating bath by a godet roller and subjected to other after treatments. Due to the frustoconical shape, the tube narrowing toward the bottom of the bath, the speed of the coagulating liquid increases as the diameter of the tube decreases. This increase helps to increase the jet stretch by reducing the resistance of the coagulating liquid. The coagulating liquid is fed through a pipe located about the tube, and the excess of the liquid in the coagulating bath is taken out through an outlet pipe provided on the side wall of the coagulating bath and is transferred to a recovery bath.

Another improved system claimed uses a "spinning shaft"[33], in which the spinning solution is extruded through spinneret holes into a spinning shaft (Fig. 1.4). The spinneret is in a gas-tight connection with the shaft, while the lower end of the shaft is placed under the level of the coagulating liquid in the coagulating bath. The upper part of the shaft can be filled with a preheated gas at a lower pressure, which is reduced by means of a suction pipe, and the lower part of the shaft is filled with the coagulating liquid up to a height determined by the pressure in the upper part of the shaft.

Fig. 1.3 Flowing type bath spinning

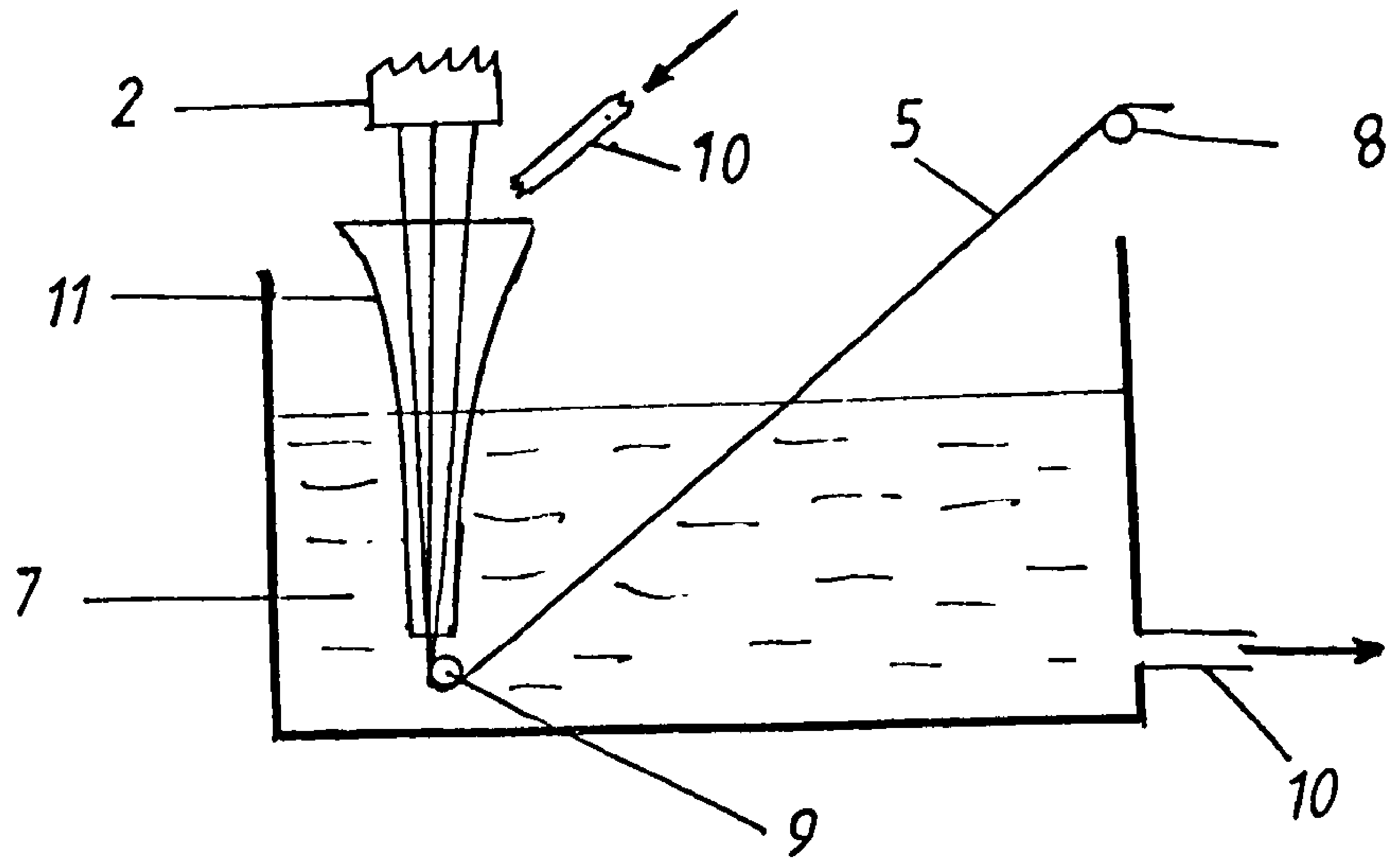
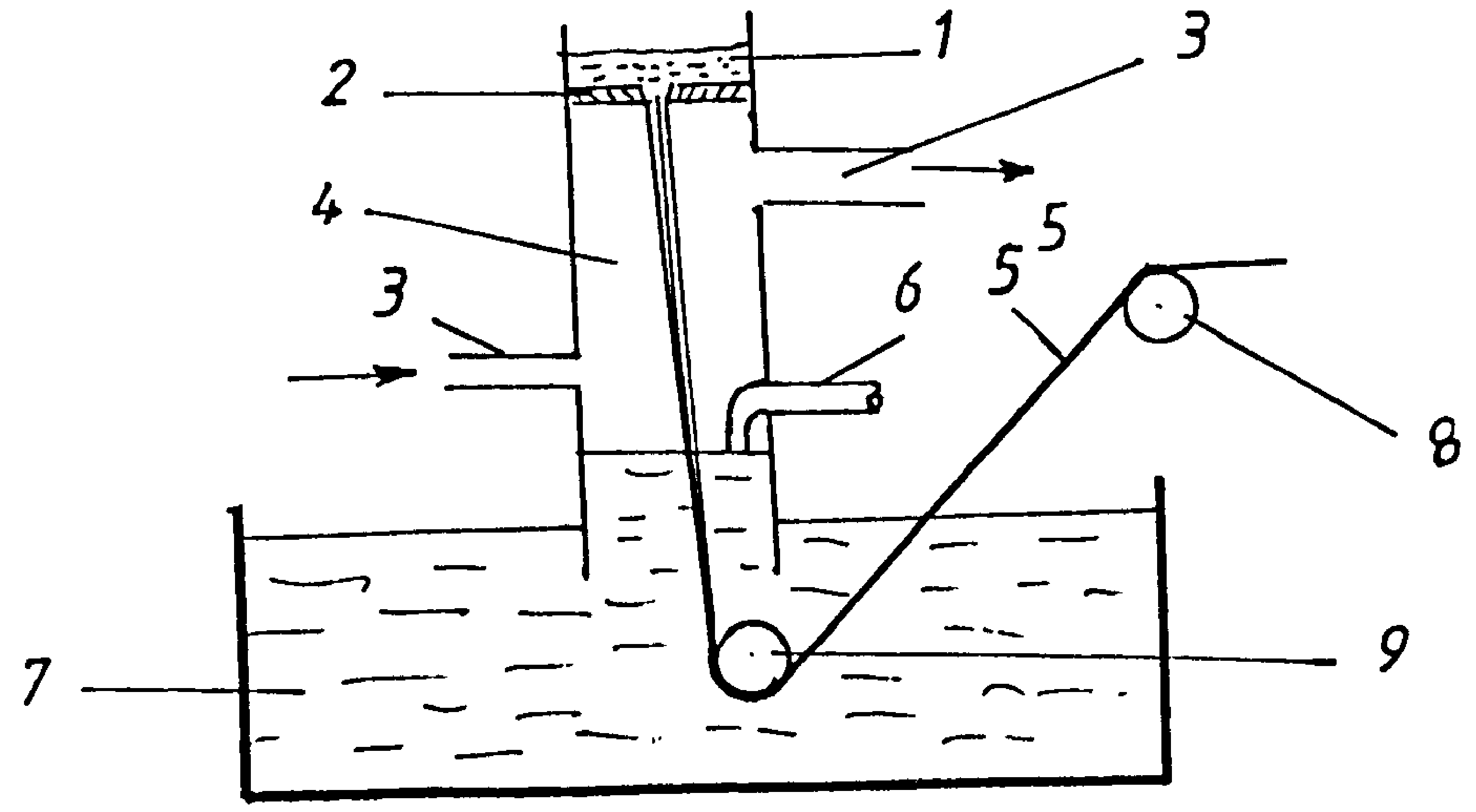


Fig. 1.4 Spinning shaft



1. Polymer dope
2. Spinneret
3. Hot air (gas) inlet and outlet
4. Spinning shaft
5. Filament
6. Pipe to vacuum pump
7. Spinning bath
8. Take up roller
9. Guide roller
10. Pipe for coagulation solution inlet and outlet
11. Funnel

1.3.3 The effect of the spinning conditions on the spinning process

The main feature of the dry-jet wet-spinning process in comparison with wet-spinning is the relatively high speed of the spinning process. However, some of the spinning conditions, such as polymer dope viscosity and concentration, the diameter of the spinneret holes, air-gap distance, and some other variables have an effect, to some extent, on the process.

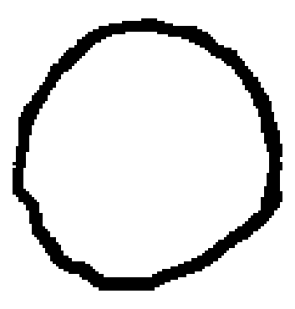
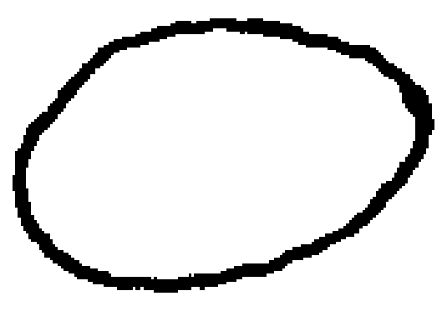
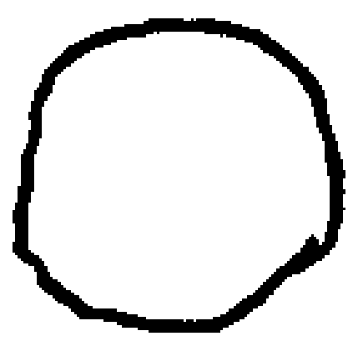
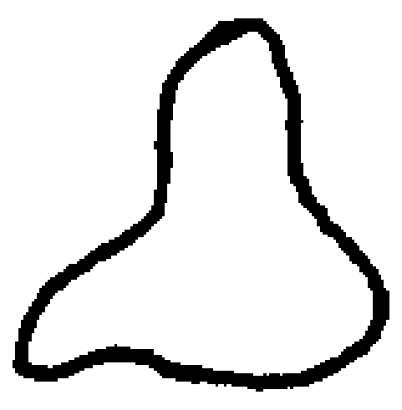
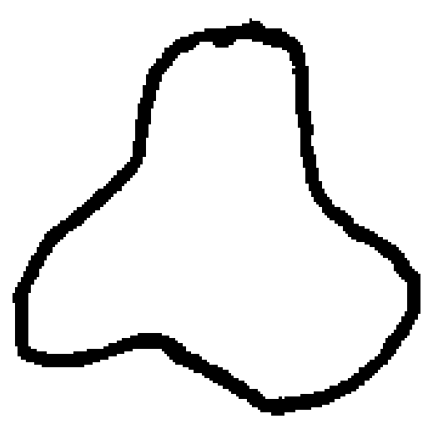
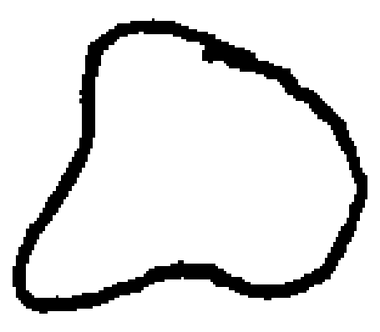
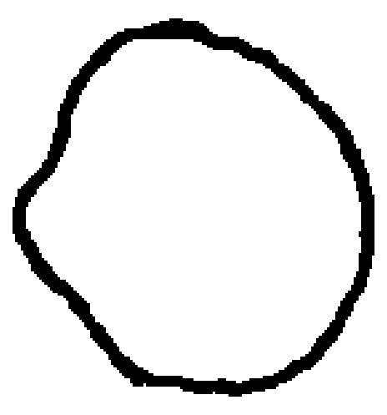
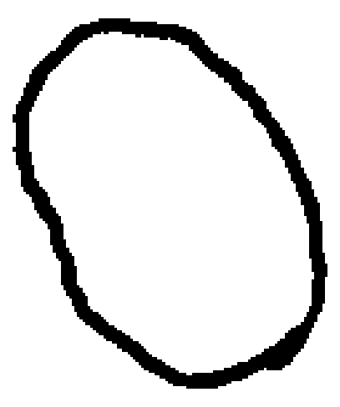
It seems that the effect of the polymer dope viscosity is more important than the other variables. Although dry-jet wet-spinning is a modified wet-spinning, a polymer dope prepared in an appropriate solvent, or, the polymer solution obtained directly in solution polymerisation can be used in a similar way to that used in wet-spinning. Because this process differs technically when compared with conventional wet-spinning, there is usually some limitations with respect to the spinning solution viscosity. The polymer dope concentration or the spinning solution viscosity depends upon the particular polymer or copolymer and solvent employed, as well as upon the temperature at which the spinning solution is to be extruded. It is desirable to use a solution containing rather a high percentage of polymer. It is recommended that the viscosity of the spinning solution to be used in the dry-jet wet-spinning process be in the range of 2×10^4 to 1×10^7 centipoise[59], or more preferably 4×10^4 to 2×10^6 centipoise at 30°C. In another patent[51] the preferred viscosity of the spinning solution at the time of extrusion through the spinneret was claimed to be in the range of 1.5×10^4 to 3×10^6 centipoise. In particular, when the polymer dope viscosity at 30°C is lower than the recommended value, the spinning solution extruding from the spinneret will cause problems, such as the breaking of the liquid thread lines of the dope on the surface of the spinneret or the bonding of the filaments to themselves and will disturb the continuous production of fibres with high uniformity. In the case when the spinning solution viscosity at 30°C is higher than 1×10^7 centipoise, in order to continue a favourable spinning operation, it is necessary to elevate the spinning solution temperature to above 100°C. In this case, such high temperatures applied to the spinning solution cause the acrylonitrile polymer and copolymers to become coloured. This limits the maximum polymer concentration in the polymer dope. On the other hand, if the spinning solution viscosity is larger than a certain value, the spinning characteristics are reduced so much that the breaking of the filaments at the time of spinning increases to such an extent that continuous operation becomes impossible.

Another factor which determines the spinning solution viscosity is the polymer molecular weight. The acrylonitrile polymers and copolymers used in dry-jet wet-spinning, so far, have had average molecular weights corresponding to an intrinsic viscosity, [η], of 0.1 to 4.0 dlg^{-1}, as measured in DMF at 30°C[38,8]. If the intrinsic viscosity, [η], is larger than 4.0, the spinning characteristics of the solution are claimed to be poor, the obtained filament is very brittle and the practical value of the filaments markedly reduced. On the other hand, if the intrinsic viscosity, [η], is smaller than 0.1, it is difficult to impart to the filaments a strength and elongation required for the purpose of textile fibres. However, it seems that acrylonitrile polymers and copolymers used in the dry-jet wet-spinning process mainly have average molecular weights coresponding to an intrinsic viscosity, [η] ranging from 1.0 to 2.0.

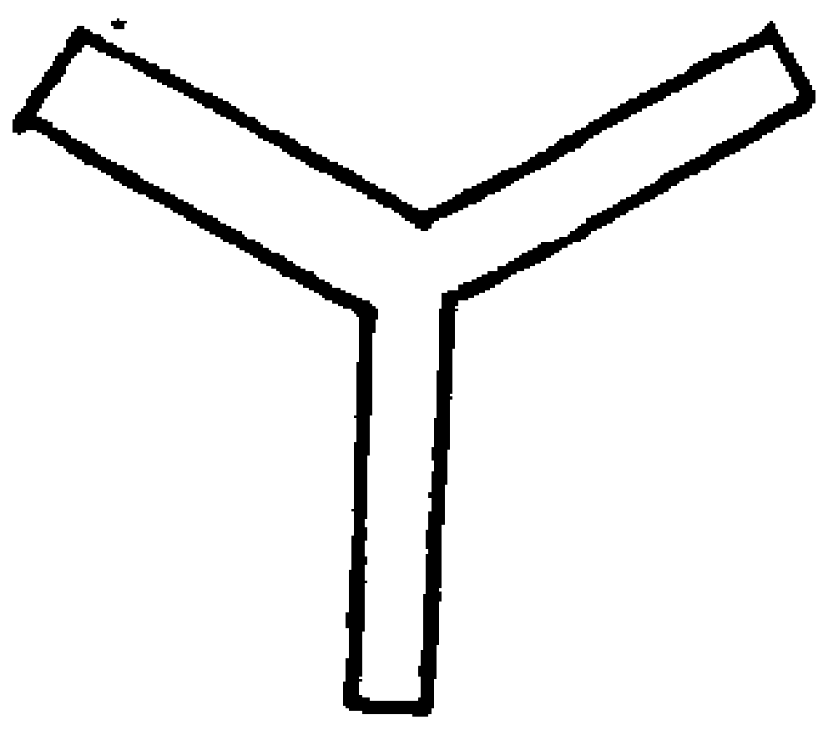
The usual air-gap distance in dry-jet wet-spinning is between 0.5 and 5 cm[38]. However, one can increase this range from 0.2 to 10 cm[47] by taking precautions that adjacent thread line of the dope do not come in contact with and cohere to each other, or by preventing the change of dry-jet wet-spinning to false dry-jet wet-spinning. It is also preferable that the air-gap distance should be more than 0.2 cm., otherwise, even the slightest vibration of the spinneret device or coagulant level may cause the spinneret to dip into the coagulating liquid and hence change the spinning system. However, for the best results, it is claimed that there should be a combination of some of the spinning variables such as flow rate, dope temperature, take-up speed, and air-gap distance, in such a way that less than one per cent of the solvent (based on the weight of the solution) is evaporated into the gaseous medium from the thread line of the dope[51]. When a spinneret with non-circular cross-section holes was used to produce filaments with cross-sections other than circular (using an aqueous solution of sodium thiocyanate as solvent), it was shown that with increasing air-gap distance, the cross section of the filament was increasingly deformed to a substantially circular cross-section shape. It was also claimed that if the spinning solution viscosity at the time of the extrusion is smaller than a certain value, the cross-section of the filaments will be deformed towards the circular[51]. However, it was shown that as the polymer dope viscosity at the time of extrusion was increased, the filament cross-section became closer to the shape of the spinneret hole, though on further increases, the spinning procedure was impossible. Table 1.5 shows the effect of the polymer viscosity on the cross-section.

Other variables in the dry-jet wet-spinning process are the diameter of the spinneret holes and the amount of solvent in the coagulating bath. The patent literature survey shows that any spinneret having hole diameters in the range of 75 to 650 microns can be used in the dry-jet wet-spinning process[38,47], although with spinnerets with hole diameters of less than 150 microns, it is difficult to have a proper spinning[63]. It was indicated that as the spinneret hole diameter increased, there

Table 1.5 Effect of dope viscosity and air-gap on fibre cross-section[51]

Dope viscosity at the time of extrusion (centipoise)	Air-gap (cm)					
	0.5	0.8	1	1.2	1.4	1.6
1×10^4						
23×10^4						
43×10^4						
350×10^4	spinning was impossible					

- spinneret shape



was an increase in the maximum amount of the jet stretch-ratio. On the other hand, a significant increase in the maximum jet stretch value occurred when the solvent content of the coagulating bath was about 50%. Jet stretch ratios about 10 were obtained. It was claimed that unlike conventional wet-spinning where the opposite relationship holds, the maximum jet-stretch in dry-jet wet-spinning decreased with increasing amounts of water in the coagulating bath[38].

1.3.4 The effect of the spinning conditions on the properties of the fibres

The amount of work published on dry-jet wet-spinning is, unfortunately, not large. However, by reference to papers and patents published so far, it was found that some of the spinning conditions such as air-gap distance, dope concentration, coagulating bath composition, and spinning jet stretch-ratio have an effect on the physical and mechanical properties of the final fibres.

Due to the air-gap distance between the lower surface of the spinneret and the upper surface of the coagulating liquid, initially the filaments behave differently than in wet-spinning. Therefore, this air-gap distance plays an important role in the dry-jet wet-spinning produced fibres. Yunitskii et al[62], using DMF as solvent and 78% DMF - water as spinning bath liquid, have found that, generally, as the air-gap distance was increased, the tenacity of the fibres first increased and then decreased. The optimum value for this air-gap distance, based on the tenacity of the final fibres, varied with the take-up speed, v_1, polymer molecular weight, $\overline{Mw}$, and the dope concentration. However, in their work, these optimum values were between 15 and 50 mm.

Apart from the air-gap distance effect, the tenacity of the fibres increased as the polymer molecular weight increased, and so, the viscosity of the spinning solution. But there was a decrease in the tenacity with increase in the spinning speed, i.e. take up velocity, v_1. They considered the possibility that in the dry-jet, wet-spinning process, the total force exerted by the take-up device is transmitted to a large extent to the thread line of the spinning solution above the coagulating bath liquid and this portion of the thread line is stretched correspondingly[62]. However, in a later study of the deformation of the extruded filaments in the air-gap distance and in the coagulating bath liquid, Yunitskii et al[62] showed that this is not quite correct, because they found that the diameter of the extruded filaments entering the coagulating bath is not equal to that of the filaments emerging from the bath. This they claimed suggested that the air-gap distance is less important than the time for which extruded filaments remain in the air or inert gas.

Patel[63] studied the effect of the spinneret hole diameter and jet stretch-ratio using 25% Courtelle polymer in DMF and 50% DMF - water as coagulating bath. He found that, by increasing the spinneret hole diameter and the jet stretch ratio, the tensile factor, $TE^{\frac{1}{2}}$, decreased. Also as the spinneret hole diameter increased, the initial Young's modulus and yield stress of the fibres decreased.

The effect of the bath concentration has also been studied by Yunitskiĭ et al, who showed that a decrease in the DMF concentration of the coagulating bath results in a considerable decrease in the regularity of the fibre cross-section. In addition, it was shown that as the amount of the DMF in the coagulating bath was increased, the maximum jet-stretch ratio increased as shown in Table 1.6.

The effect of the temperature of both the spinning solution and the coagulating bath has been studied[59], and it was shown that an increase in the spinning solution temperature from 25°C up to 120°C did not have any effect on the tenacity and the elongation of the fibres, while, a gradual reduction in the coagulating bath temperature from +50°C to -10°C resulted in corresponding increases in the tenacity and a significant change in the elongation (see Table 1.7).

Table 1.6 Effect of the bath concentration on the maximum jet-stretch ratio[59]

Bath composition DMF/Water	Maximum jet-stretch
70/30	15.4
60/40	9.6
40/60	8.0
20/80	7.3
0/100	6.6

Table 1.7 Effect of the coagulating bath temperature on the mechanical properties of the fibres[59]

Coagulating bath temperatures (T°C)	Tenacity (g/den)	Elongation (%)
- 10	4.4	13
0	4.4	15
+ 10	4.2	15
+ 50	3.6	18

The study also indicated a general improvement in abrasion resistance as coagulating bath temperature is decreased. Their results also showed that the relaxed samples had a significantly higher elongation as compared with the unrelaxed samples. However the filaments not permitted to relax have tenacities comparable to the filaments permitted to relax. Hence, while relaxation is important to obtain optimum properties when relatively high temperature coagulating baths are employed, the step of relaxing may be omitted with low temperature coagulating bath spinning without substantial sacrifice of tenacity. They also found that the elongation increased for a given draw stretch in a hot drawing bath as the temperature in the bath was decreased without an appreciable sacrifice in the tenacity (Table 1.8).

Table 1.8 Effect of the temperature of the hot-drawing bath on the mechanical properties of the fibres[59]

Hot drawing bath temperature (T°C)	Tenacity (g/den)	Elongation (%)
80	2.6	31.3
90	2.6	28.3
100	2.7	26.9

1.3.5 Advantages and disadvantages of the dry-jet wet-spinning process

The major advantage of dry-jet wet-spinning, if compared with wet-spinning, lies in the several times higher spinning velocity which has been claimed by many patents and papers[8,33,35-39,41,43,46,53,54,62]. Other advantages of dry-jet wet-spinning included the production of fibres with higher tenacities[8,33,35-37,39,42,63], smooth and void free fibres[35,36,38,63], improved dyeability[42,44,48,50,55], and improved lustre[33,38,39,50]. These advantages are derived by employing an air-gap, a polymer dope with a higher than ususal concentration, and using a spinneret with a larger than usual hole diameter, as well as improvements in the different spinning stages.

An advantage of the dry-jet wet-spinning process, due to the air-gap, is the fact that a spinning solution having a much higher temperature than the bath can be employed than ordinarily possible in wet-spinning. Hence a greater percentage of polymer in the solution can be used successfully. The spinning solution can be maintained prior to and at extrusion at temperatures from 20°C to 180°C[38]. Since the viscosity of acrylonitrile polymer and co-polymer solutions varies inversely with temperature, the advantage of employing a high dope spinning temperature is that it permits the use of low extrusion pressures for a given percentage of polymer. Normally, the polymer dope temperature for a successful wet-spinning should be closely correlated with the temperature of the bath[65]. In order to spin acrylonitrile polymer and copolymer solutions by the conventional wet-spinning method, it is necessary to avoid elevated coagulation bath temperatures, since such temperatures substantially accelerate the rate of coagulation to the point where the fibres produced are too brittle.

In dry-jet wet-spinning, as mentioned before, it is possible to employ spinnerets with relatively large hole diameters. The benefits derived by employing a large hole diameter are the higher spinning speeds as well as improvements in the physical properties by the attenuation of the filaments that can be attained. In conventional wet-spinning this is not possible because the maximum jet-stretch ratio that can be imparted to the freshly spun filaments is usually less than a factor of two, and in most cases is less than one[66], due to the coagulating behaviour of the normally spun filaments. On the other hand, it is possible to stretch the freshly spun filaments in dry-jet wet-spinning to the extent of as much as 15 times.[33] Moreover, filament counts below 1 d.tex can be spun readily without difficulty whereas 1 to 2 d.tex per filament is generally the least that can be spun in the ordinary wet-spinning process. Another advantage of the dry-jet wet-spinning process is that a wide range of filament counts can be spun from a single spinneret. For example, it is claimed that filament counts from 0.8 d tex to 22 d tex and higher, having satisfactory textile properties, may be spun from a single spinneret having a hole diameter of 125 microns. In other words, filaments having various counts may be spun conveniently without shut down being required to change from production of one diameter to another. The use of a spinneret with rather large holes is very convenient for production of bicomponent and biconstituent fibres, as in these cases it is necessary to use a split spinneret and to feed polymer solutions with different properties into each part of the hole. By increasing the diameter of the spinneret holes, the filtration of the spinning solution becomes less important, and the number of the spinneret changes due to blockage thereof will be reduced.

As mentioned before, most of the reported work that has been done in dry-jet wet-spinning relates to patents, and naturally, these emphasise only its advantages. However, there are some disadvantages in this system of spinning in comparison with wet-spinning. The first depends on the spinneret type. The minimum distance which can be maintained between two adjacent holes on the spinneret useable in dry-jet wet-spinning is higher than that in wet-spinning. This means a lower number of filaments per spinneret can be produced in dry-jet wet-spinning.

Another difficulty is due to the higher speed of this method, especially, in a hot water bath for hot drawing operations and other after-treatments. The hot drawing is difficult due to such troubles as frequent filament breaks where the filaments are hot drawn at speeds of about 300 m/min[59]. There has also been considerable difficulty in the actual operation in increasing the running speed of hot drawn filaments of finer counts (d tex), for example, in the high speed spinning of filaments of less than 1 d tex. If undrawn filaments are drawn directly at a high speed, the breaking of these filaments of low tensile strength will occur to such an extent that it will be impossible to carry on the spinning.

Another disadvantage is the difficulty of starting up the spinning in some cases, which is mainly due to the need to keep the spinneret surface clean. According to some workers[67,68] in dry spinning, the greatest difficulty is encountered in starting up, and the spinneret face must be wiped in a certain way to start spinning. In dry-spinning, circulating hot air and in wet-spinning coagulating liquid overcome the starting-up difficulty to some extent, while in dry-jet wet-spinning neither hot air nor coagulating liquid acts to keep the spinneret surface clean. There is also a difficulty of adhesion of adjacent filaments together before they enter the coagulating liquid. This difficulty appears when either the air-gap distance is rather long, or the distance between two neighbouring holes in the spinneret is too short.

In addition, it was noticed in the present study, that a polymer dope viscosity of less than a certain value of viscosity cannot be processed as the breakage of the thread line of the spinning solution at the air-gap occurred to such an extent that it was not possible to carry out the spinning, i.e. in the case of Courtelle acrylic polymer, a polymer dope with less than 20% concentration in DMF was not suitable in a dry-jet wet-spinning process, which means that spinning solution viscosities should be above 150 P. However in wet-spinning, polymer dopes of much less viscosity can be processed without any difficulty.

1.4 Aims of this study

The aims of the present study were to compare the wet-spinning and the dry-jet wet-spinning of acrylic fibres to clarify the basic reasons for the differences in fibre properties and furthermore to examine the full potential of dry-jet wet-spinning to produce acrylic fibres with enhanced properties.

CHAPTER 2. EXPERIMENTAL

2.1 The spinning equipment

A laboratory scale spinning apparatus which was suitable for wet-spinning processes, was used throughout the work. Fig. 2.1 shows schematically this versatile spinning equipment, that consisted of the extrusion unit, coagulation bath, stretching bath, drying rollers, and wind-up unit. Plate 2.1 shows a photograph of these units in a running condition.

2.1.1 Extrusion unit

Plate 2.2 shows the extrusion unit, together with the coagulation bath and the first pair of advancing reels. The extrusion unit consisted of the dope reservoir with lid and spinning block, together with the gear pump (meter pump), spinneret holder, and the spinneret assembly. The dope reservoir had a capacity of about 2 litres and was surrounded by a 1 kw. jacket-heater, which provided uniform heating. The dope reservoir lid was screwed down onto a teflon-washer, to make the whole reservoir airtight and the reservoir was screwed into the spinning block. The spinning block was fitted on two sides with two separate heating plates. Each plate was drilled with two pockets for two 150 watt cartridge heaters, and it was also drilled with one hole for a thermistor.

Fig. 2.1 - The spinning line

1. reservoir lid
2. dope reservoir
3. heater
4. spinning block **and pump**
5. spinneret holder
6. spinneret
7. coagulating bath
8. advancing reels
9. washing baths
10. hot bath (stretching)
11. stand (adjustable)
12. chrome rollers
13. heaters

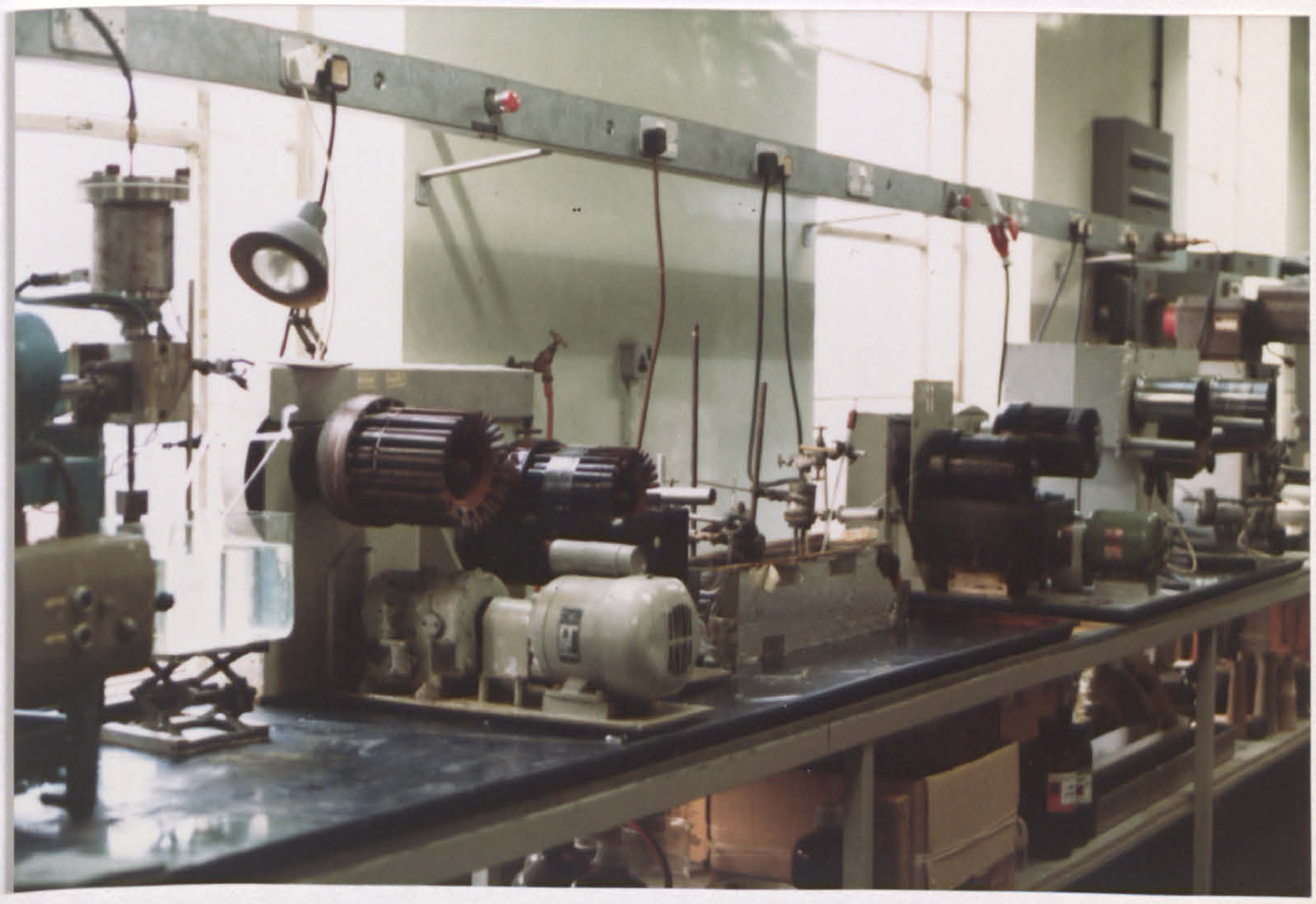


Plate 2.1

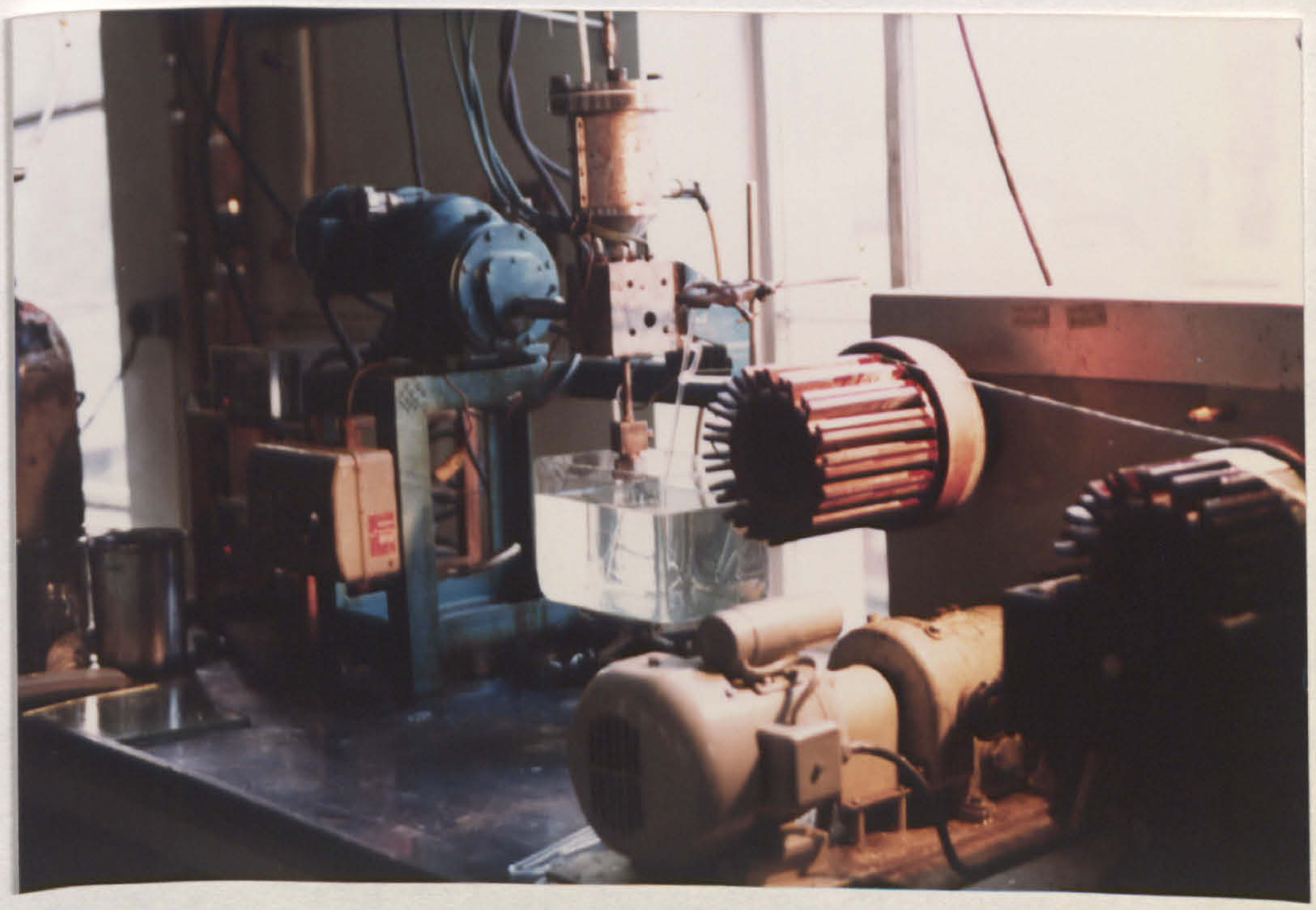


Plate 2.2

The temperature of the dope reservoir and the spinning block could be set and controlled individually by means of two separate temperature controllers, from 20°C up to 400°C.

The gear pump which was bolted to the spinning block, was driven by a three phase electromotor with a variable speed by means of a build-up Kopp rotary regulator between 3 and 27 r.p.m. The capacity of the gear pump which was used was 0.4 cc/rev., so the minimum feed of the polymer dope to the spinneret was 1.2 cc. per minute, and the maximum feed was 10.3 cc. per minute. For pushing the polymer dope from the reservoir to the gear pump, an arrangement was made to apply nitrogen pressure at the top of the spinning solution in the dope reservoir.

To attain a satisfactory run from a spinning unit, it was of the greatest importance to extrude a very homogeneous and regular dope free from any undissolved matter and any foreign impurities. It was therefore essential to filter the dope thoroughly; this was done by using wire gauze with different mesh sizes. In some cases, an additional filter such as gamgee tissue (cotton) and cheesecloth was used. To ensure efficient filtration during the spinning procedure, two types of filtration were used. One type of filter was used to improve the filtration process as well as to reduce the load on the main filtering system which was situated just above the spinneret. This filter consisted of three wire-gauzes. The first one was a 50 mesh/inch round wire-gauze filter with a diameter equal to the inner diameter of the dope reservoir. This filter was held firmly by two rings, and was placed inside the dope reservoir about 8 cm. from the top of the reservoir, supported on four stainless steel rods. The second filter was a 170 mesh/linear inch wire gauze, which was fixed between two teflon-washers, and situated between the lower end of the dope reservoir and the upper end of the spinning block. There was another filter of a 170 mesh/linear inch wire-gauze, which was placed between the lower end of the spinning block and the upper end of the spinneret holder. These filters were changed each time a newly prepared dope was to be spun.

The main filtration system was varied depending on the system being investigated. For fine spinneret holes, with diameters less than 150 micron, the system consisted of a teflon-washer, a 370 mesh/linear inch wire gauze, a layer of a half thickness of gamgee tissue (cotton) with the cheese cloth support downwards, two layers of a closely woven plain weave cotton fabric a 370 mesh/linear inch, wire-gauze, a 170 mesh/linear inch wire-gauze, a 50 mesh/linear inch wire gauze and finally a teflon-washer laid behind the spinneret in that order. This type of filter was found to give efficient removal of all residual foreign matter from the dope. The wire-gauzes acted as filter supports on both sides. For spinnerets with larger hole diameters (greater than 300μ), the filter consisted of a teflon-washer, two 370 mesh/linear inch wire-gauzes, a 170 mesh/linear inch wire-gauze, a 50 mesh/linear inch wire gauze, and finally a teflon-washer laid behind the spinneret in that order. This filter assembly was removed after any spinning operation, which could last between 20 minutes and 4 hours.

The spinning assembly acts as a mechanical support for the spinneret and the final filters. It was possible to heat the spinning assembly by a jacket heater, and the temperature could be regulated by means of the variac regulator. The type of spinnerets used during experiments were suitable either for wet-spinning or dry-spinning processes, ranging from 75 micron up to 500 micron, with the number of holes varied from 1-24 holes per spinneret. Of course, for the dry-jet wet-spinning, the distance between the individual holes must be such as to prevent coalescence between adjacent neighbouring filaments. In general therefore, spinnerets which were suitable in dry-spinning were used mostly in the dry-jet wet-spinning, though in some cases spinnerets designed for wet-spinning were used too. It is of the greatest importance that all holes of each spinneret be completely clean, otherwise, dope delivery will vary from one hole to another, and the filament count will be very variable. At the limit, some holes will deliver an insufficient flow of dope and spinning breakage will occur. For this reason all spinnerets were stored in chromic acid solution. Also every four months all spinnerets were cleaned in an ultrasonic bath in D.M.F.

2.1.2 The coagulation bath

A static coagulation bath, containing a mixture of DMF and water was used. A constant coagulating length (33± 2 cm) was maintained through most of the experiments, unless otherwise stated. The coagulating length was set by using two adjustable glass rods as thread-guides, one in the coagulating bath and one between the bath and the first roller of the advancing reels. It was also possible to adjust the height of the coagulation bath to fix the required clearance (air-gap) between the lower surface of the spinneret and the upper surface of the coagulating liquid level. The coagulating bath tank and both glass rod thread-guides were fixed on the adjustable stand, so that the filament length within the coagulating liquid did not change on raising or lowering the coagulation bath, and the distance between the two glass rods was kept constant (Plate 2.3).

2.1.3 The drawing unit (plate 2. 4)

A hot water bath fed with running water to maintain a constant level and with two extra heating elements to supplement the existing heater was fixed between the two pairs of advancing reels, and was used for hot drawing. There were two glass rod guides immersed in the hot water bath fixed at a constant separation (83 cm). The speed of the first pair of reels could be varied in the range of 0 to 30 r.p.m., and the speed of the second pair of reels could be varied between 0 and 90 r.p.m., with the aid of two rotary regulators separately. These operated by means of Carter Junior Hydraulic Controllers. There were two washing baths, one of them under the second roller of the first pair of the advancing reels, and the other one on the first roller of the second pair of the advancing reels. These two washing baths were filled with distilled water, and were changed at the beginning of each experiment.

By adjusting the speed of each pair of these two pairs of advancing reels, it was possible to adjust the jet stretch ratio (J.S.R.) and the draw ratio (D.R.). In some cases the jet stretch ratio was adjusted by means of changes in the speed of the gear pump

2.1.4 The drying unit

A set of drying rollers consisting of two chrome rollers, two idler rollers, and two radiant heaters, was used to carry out the drying of the drawn filaments. The drying rollers were positively driven, and their speeds could be controlled by means of a rotary regulator. The surface speed of these rollers was adjusted to equal that of the second pair of the drawing rollers in each experiment, so that no extension

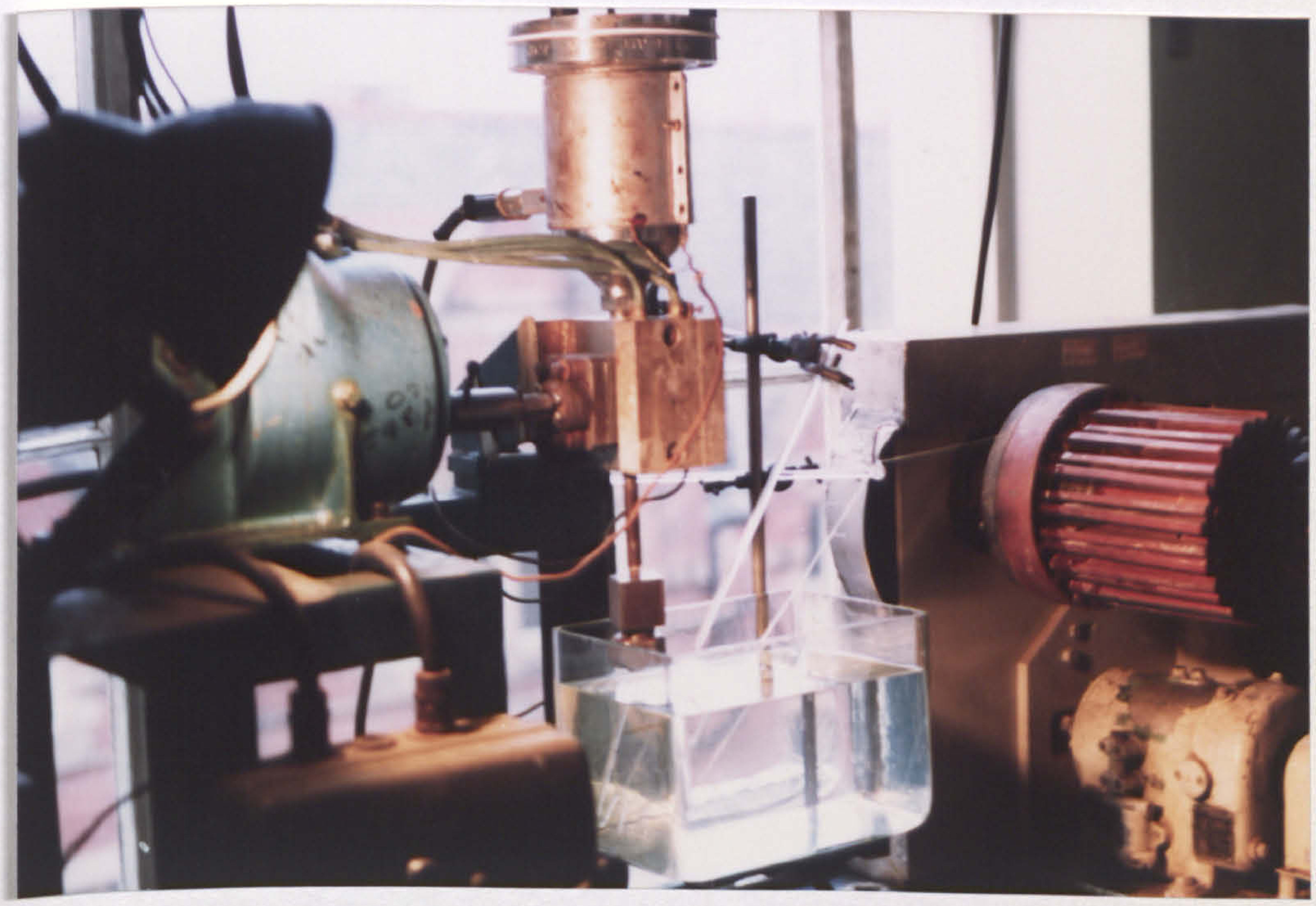


Plate 2.3

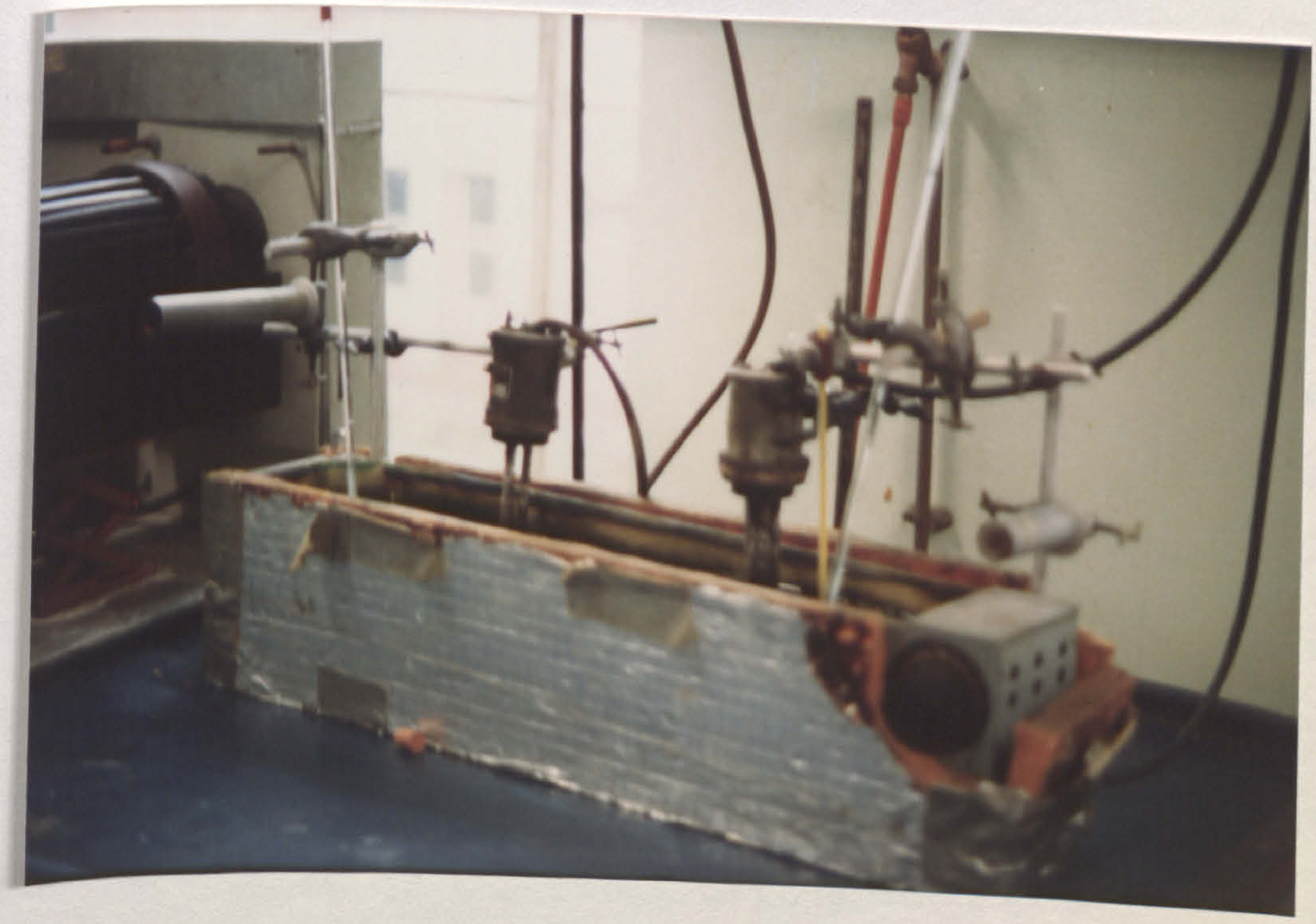


Plate 2.4

or relaxation took place at this stage. The temperature produced by the radiant heaters could be varied individually by means of two Variac controllers in the range from room temperature (R.T.) up around 200°C, as measured as the air temperature near the drying rollers (1 cm. distance) (Plate 2.5).

2.1.5 The winding-up unit

A Leesona (955S) precision cone winder unit was used for winding purposes. The winding-up unit was sensitive to the yarn tension and the speed varied automatically to compensate for the variation in yarn tension (Plate 2.6).

2.1.6 Additional drawing unit

In some experiments another drawing unit was used (Plate 2.7), which consisted of two godets with their attendant idlers. The speed of the first godet is fixed and constant, while the speed of the second godet and winding unit could be varied by means of a Kopp variator. There was a heated shoe between these two godets, approximately 10 cm long. The heated shoe was a brass cylinder with a flat surface milled along the length of the shoe, with a long groove cut into the middle of the surface along which the filaments were passed.

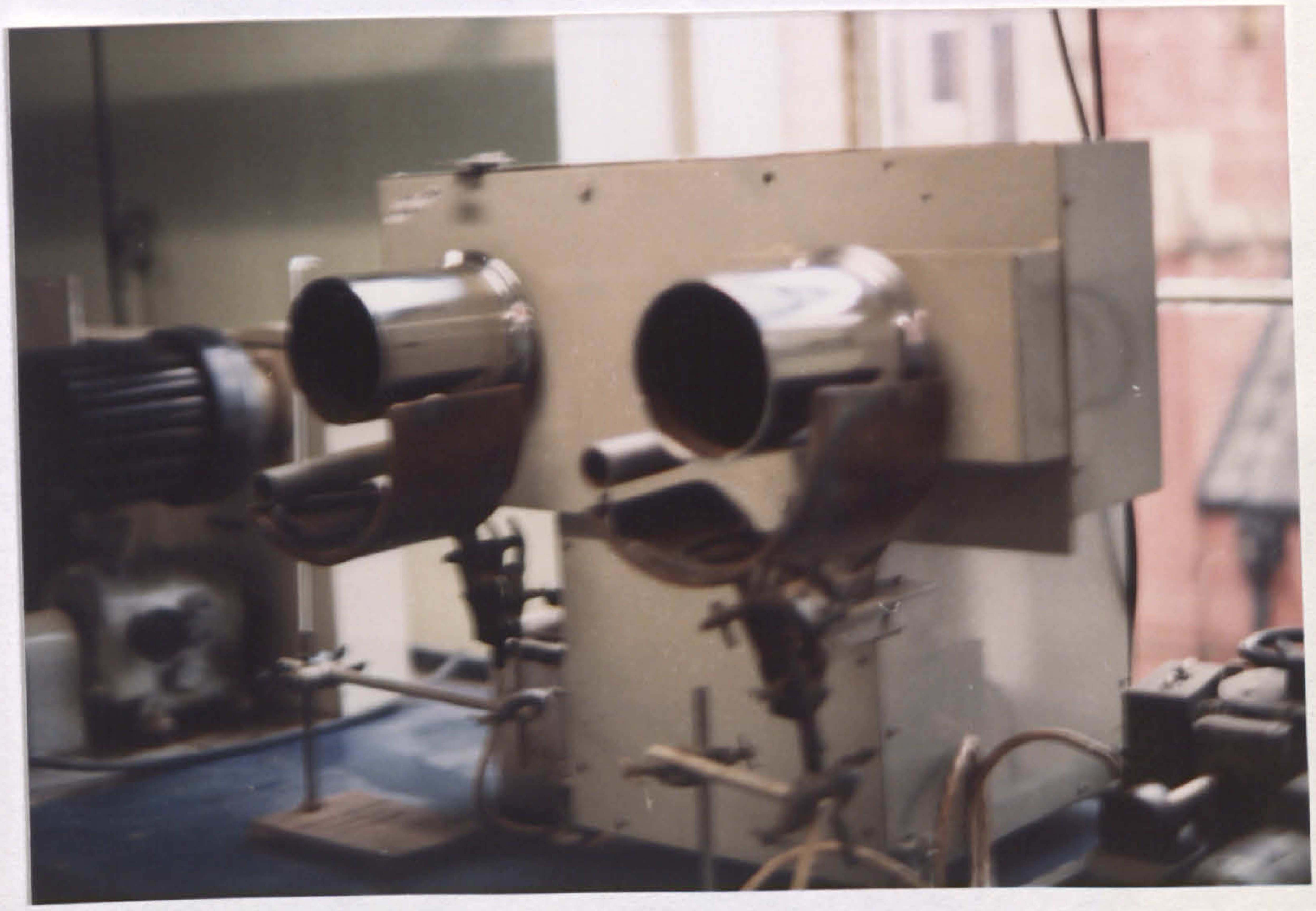


Plate 2.5

Plate 2.6

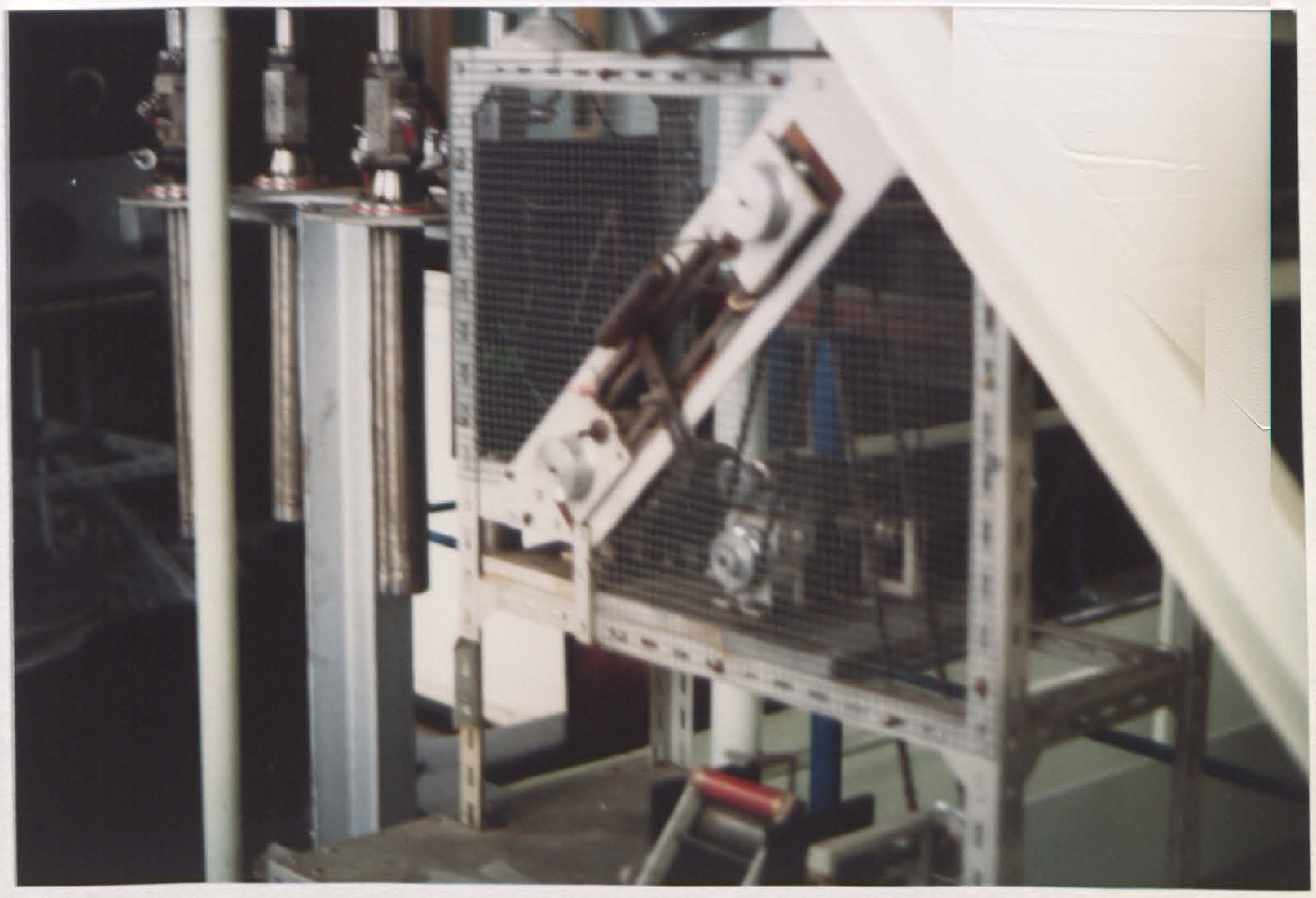


Plate 2.7

The shoe was drilled with two pockets, one for a 150 watt cartridge heater, and the other for a thermometer, to give a close estimate of the actual filament temperature. The temperature could be controlled and varied from room temperature up to 200°C by a variable controller.

The winding-up unit consisted of a rotating drum, whose surface speed was approximately 1% faster than the speed of the second godet. The filaments were wound onto a paper bobbin by means of a traverse mechanism composed of a slider, which travelled forwards and backwards as its base ran in a continuous peripheral groove cut on a roller. The bobbin itself was driven by friction as it rested on the rotating drum.

2.2 Fibre production

2.2.1 Materials

1. Polymer; "Courtelle" acrylic fibre in tow form, obtained from Courtaulds Ltd., was used as a source of polymer. It was bright, 3.3 d.tex fibre with an average density of 1.15 g/cc[69]. Before use, the samples were soxhlet extracted with methylene chloride to remove spin finish and other impurities.

2. Solvent; Dimethyl formamide, obtained from B.D.H. Ltd., was used, without any prior purification, both as the polymer solvent and as aqueous solutions in the coagulation bath.

2.2.2 Preparation of the spinning dope

The spinning dopes containing between 17% and 30% by weight of Courtelle in dimethyl formamide (D.M.F.) were prepared as follows:

xg (usually in the range of 30-100 g). Courtelle were soaked with y cc D.M.F. in a 500 cc glass jar, and mixed quite well with a glass rod. Then the glass jar was placed in the oven for 4 - 6 hours at 50 - 55°C without stirring. After this period almost all of the polymer had dissolved. This solution was then stirred with a stainless steel stirrer (120 r.p.m.) for 10-12 hours at room temperature and then transferred to the dope reservoir on the spinning unit.

The amount of the D.M.F. (y cc) was calculated by using the formula 2.1;

$$y = \frac{x.(100-c)}{c.p.} \qquad 2.1$$

where;

x = weight of the Courtelle polymer in g,
y = volume of the D.M.F. in cc,
c = the polymer content of the dope in %, and
p = density of the solvent (D.M.F) in g./cc (0.948)

2.2.3 Fibre extrusion

After transferring the homogeneous spinning solution (polymer dope) to the reservoir, it was heated to 60°C without applying any pressure and allowed to deaerate on standing for at least 3 hours. Thus the removal of the air bubbles was assisted by the lower viscosity at this temperature. Skin formation was prevented by pouring a few drops of the solvent onto the surface of the dope. The reservoir lid was then tightened down and the heater was reset to give the required dope temperature and the heater of the spinning block was switched on to give the required temperature. About one hour later, when all air bubbles had disappeared, and the dope had reached the desired temperature, pressure was applied above the dope and the gear pump was switched on. When bubble-free homogeneous dope emerged from the spinneret holder, and continued to do so for a few minutes, the gear pump was stopped. Then a spinneret assembly containing an appropriate filtering device was screwed on.

In the case of wet-spinning, as soon as the solution appeared on the surface of the spinneret, the latter was immersed in the coagulation liquid, and kept in this position for the whole period of the experiment. When the coagulation bath was lowered to convert the wet-spinning process into dry-jet wet-spinning, due to the surface tension, the coagulation liquid remained present between the spinneret surface and the coagulation liquid level. This condition was described as "false dry-jet wet-spinning" by Patel[63]. If the bath was lowered more than a certain amount, it was possible to overcome this difficulty, but as soon as this point was reached the thread-like spinning solution broke and continuous spinning was not possible, because the extruding solution spread over the spinneret face. After several attempts by trial and error, it was found that there were two different ways to establish a clear dry-jet wet-spinning operation (Plate 2.8).

The best method was by applying a certain value of the nitrogen pressure, determined by the dope concentration and the dope temperature, with a pre-determined distance between the

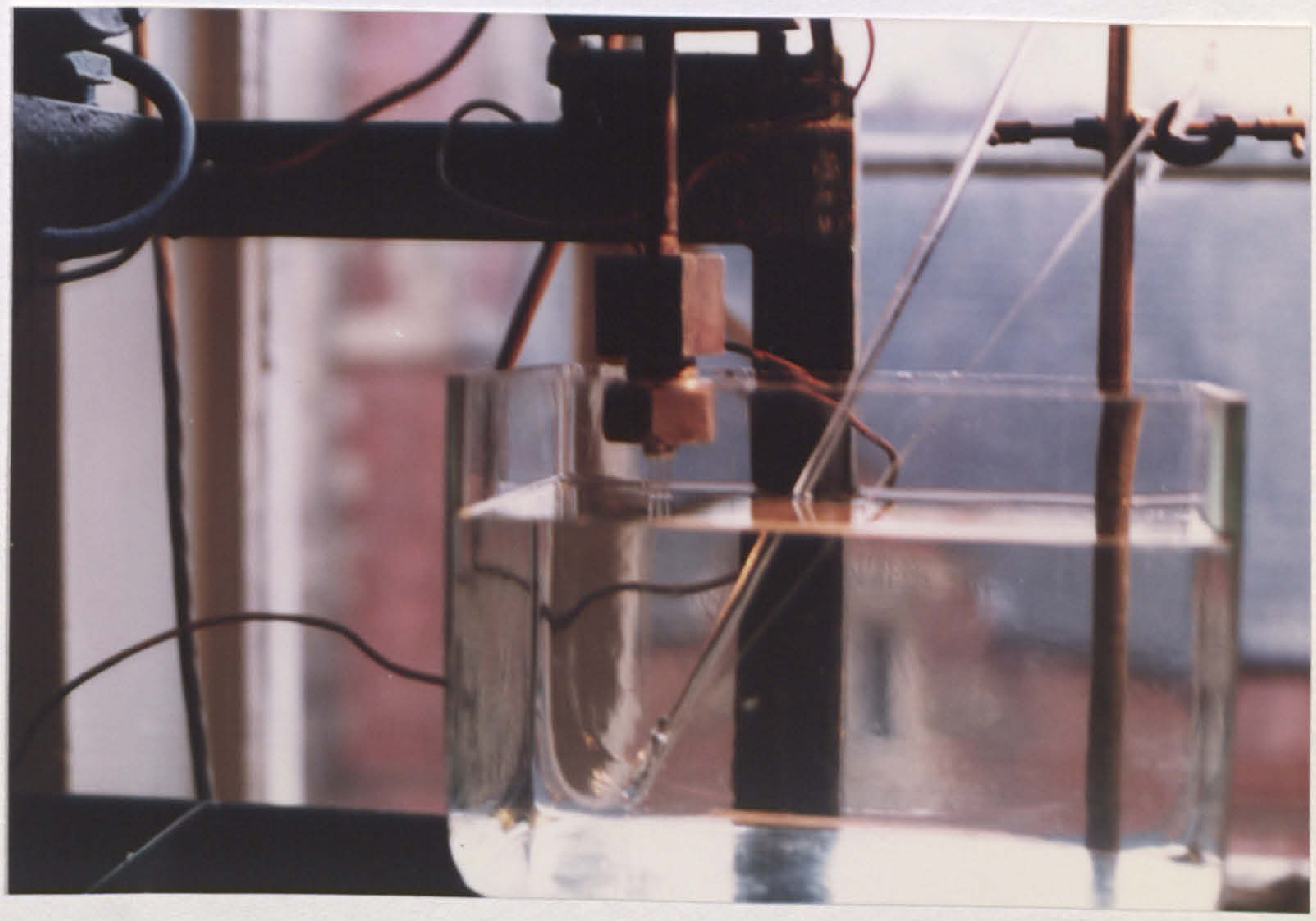


Plate 2.8 Dry-jet wet-spinning

spinneret surface and the coagulation liquid surface, so producing a jet of liquid thread-like filaments in the air at the start of spinning. Alternatively, it was possible to start the extrusion as a wet-spinning operation and to continue this for at least 10 minutes. Then it was possible to lower the coagulation bath very slowly to allow the dry-jet wet-spinning process to begin. A jet wiping technique with silicone oil, as described by Esfahani[68] was also useful in the first procedure.

The thread-like filaments were allowed to pass through the coagulation liquid. As the coagulating proceeded, the filaments were guided through glass-rod guides with the aid of a glass rod in the shape of a hook. Then the filaments were passed round the first pair of advancing reels, with two turns around the first roller and fifteen turns around the second roller. The filaments were washed on the second roller of the first pair of the advancing reels. Then the filaments passed into the hot-drawing bath at a temperature of 96±2°C, from where they were led around the second pair of the advancing reels, with twenty turns around the first roller, for washing, and five turns around the second roller. The drawn filaments were dried on the chrome rollers at an appropriate temperature and were finally wound on a paper cone.

On occasions, samples of the undrawn fibres were collected manually, either on a bobbin, after washing on the second roller of the first advancing reels, or in a beaker of distilled water into which they were guided from the first roller of the first advancing reels. The filaments were treated subsequently as necessary. In some cases, where it was necessary, yarns were transferred from the cone to a paper bobbin by means of the additional drawing and winding-up unit with appropriate treatments.

2.3 Testing procedures

2.3.1 Determination of linear density (filament count)

The count (tex or denier) of the filaments produced by solution spinning is dependent upon three controllable factors, namely the polymer content of the dope, the amount of the dope pumped through the spinneret orifices per minute, and the speed of the last take-up roller. So, the theoretical linear density of the filament yarns was calculated according to the formula 2.2;

$$\text{yarn count (in d tex)} = \frac{100.C.R.P.X}{G} \qquad 2.2$$

where;

X = pump capacity in cc/rev (= 0.4)
R = pump speed in r.p.m.
P = the density of the polymer dope in g/cc (1.15)
C = concentration of dope, % and
G = final wind-up speed in m/min.

Actual measurements were made on a torsion balance using a 10 metre length of the yarn. The sample length was measured off on a wrap-reel. The yarn count was expressed in d tex by taking the mean of ten measured values.

2.3.2 Determination of yarn tenacity and extensibility

The yarns were tested for strength (expressed in g/d tex), and extension (expressed in %). These properties were measured on the multifilament yarns, using an Instron tester model 1026, and the load cell used through all tests was cell no. 2511. Test samples were prepared by mounting on 2 cm x 2 cm paper frames. Each 2 cm sample was taken from a separate one metre length on the yarn. The samples were conditioned in a standard testing laboratory atmosphere (20±2°C and 65%±2%r.h.) for 24 hours before testing took place. For each batch of the yarn, 10 load-elongation curves were obtained, and the tenacity in g/d tex and extensibility in % were calculated for each sample according to the formulae 2.3 and 2.4 respectively:

$$\text{Tenacity (g/d tex)} = \frac{\text{maximum load in grams (mean)}}{\text{yarn count (d tex)}} \qquad (2.3)$$

$$\text{Extensibility (\%)} = \frac{\text{strain at the max load(mean) x sample speed x 100}}{\text{chart speed x sample size (2 cm)}} \qquad (2.4)$$

The stress-strain curve was obtained from the ten individual curves by extracting the value of the stress in gram/d tex at each 5% increment of extension from the Instron Chart. The mean values of the stress corresponding to 5% extension and so on for the extensions of 10%, 15%, 20% etc.

up to the largest extension value divisible by 5 shown by all the 10 curves were computed. The values of the tenacity and the extensibility quoted are the means of the final values of the curves.

The initial Young's modulus was calculated by extending the initial straight line of the Instron chart to find the load in grams for 5 or 10% extension for each of the individual curves and their mean was calculated.

2.3.3 X-ray diffraction pattern

Wide angle X-ray diffraction photographs were taken using a Hilger and Watts Y 90 constant output generator, with a water cooled copper target in a sealed tube.

2.3.4 Electron and optical microscopy

For the examination of the filament surfaces and cross-section, both scanning electron microscopy and optical microscopy were used. Microscope studies followed standard techniques for the preparation of the cross-sections. The scanning elctron microscope was a "Stereoscan" (Cambridge Instruments Ltd.) and the optical microscope was a "Projectina".

CHAPTER 3. DIFFERENCES BETWEEN DRY-JET WET-SPINNING AND WET-SPINNING

3.1 Introduction

As mentioned before, the dry-jet wet-spinning system is a modified form of wet-spinning. However, there are some obvious differences between these two systems. According to most papers published in this field, the main difference is the higher speed of operation, in the case of dry-jet wet-spinning. In any spinning system the speed of the operation depends on the viscoelastic characteristics of the fluid, i.e. the polymer dope, and also on the conditions of spinning. So when the same polymer dope is used in two different methods of spinning, the speed will be determined only by the spinning conditions.

It seems that in wet-spinning, the effect of the spinning conditions on the speed of the operation can be varied, either by changes in the coagulation bath or in the drawing units. There are two important factors which will determine the spinning conditions in the coagulating bath, namely (a) the free velocity (v_f), and (b) the spinnability as defined by (v_1, max). In the drawing unit, the most important factor for determining the spinning conditions is the maximum draw ratio which can be achieved either in one step, or in two or more separate steps.

3.1.1 Free velocity

In a typical wet-spinning operation, a polymer dope is pumped by a positive displacement pump to a spinneret with n holes. The rate of pumping is adjusted so that the flow rate per hole $q = \frac{Q}{n}$ cc/min. The spinneret is fully immersed in a bath that coagulates the filaments by mass transfer with the liquid coagulating bath[70-72], after they emerge from the spinneret holes. These filaments are removed from the bath by a rotating roller at a velocity v_1, m/min. These filaments are passed through a hot stretch bath and are removed from there by another rotating roller with a velocity v_2, m/min., which is usually higher than v_1. The value of v_2/v_1 is called the draw ratio or hot-stretch-ratio, and the value of $v_1/\bar{v}$ is the jet stretch ratio, when $\bar{v}$ is the average jet velocity.

The average velocity, $\bar{v}$, is the theoretical jet velocity, which can be calculated by assuming plug flow in the spinneret holes, according to formula 3.1:

$$\bar{v} = \frac{4.Q.(10^4)^2}{n \quad d^2.100} \qquad (3.1)$$

$$= \frac{4\ Q\ 10^6}{n \quad d^2}$$

where,

$\bar{v}$ = jet velocity (average in m/min)

Q = volumetric flow rate in cc/min

n = no. of holes in the spinneret, and

d = hole diameter in micron (μ)

If one observes the velocity at which the filament emerges from the hole under conditions of free extrusion, i.e. when no mechanical take-up of the freshly formed filament is employed, it will be seen that the filament is emerging with a velocity, v_f, which is in the case of wet-spinning, much lower than the average velocity, $\bar{v}$, of the solution in the holes. This is because the elasticity of the spinning solution permits it to store energy, arising from the non-Newtonian shear flow within the spinneret hole, and the deformation on entering the spinneret. As a result the fluid jet leaving the spinneret hole contracts axially, its diameter increases to some value, while the velocity decreases from the average extrusion value, $\bar{v}$, to some free jet velocity, v_f, due to the release of stored energy as the liquid emerges from the hole.

The importance of the free velocity, v_f, in the case of wet-spinning, in relation to the spinnability has been discussed by several workers[70,73-76]. The measurement of the free velocity, v_f, has been carried out either by extruding filaments for a known period of time and measuring the length of the filaments produced[70], or by calculation from the flow rate and the measurement of the maximum filament diameter on emergence from the jet.[73] During experiments, it was noticed that the free velocities of the wet-spinning process and the dry-jet wet-spinning process were not the same, and it was thought that the difference of the free velocities of these two spinning processes could be one of the reasons for the higher speed of dry-jet wet-spinning. Therefore, some measurements of free velocity were done. For this purpose, it was decided to calculate the free velocity from the length of the filaments extruded in a given length of time, but it was found that there were two main problems in the measurement of the free velocity as described by earlier workers[70]. Firstly, the problem of handling the freshly formed filaments, i.e. taking them out of the coagulating bath, washing, and length measurement as during these procedures a lot of disturbances were put on the filaments which could have caused changes in the length of the filaments since they were, at this time, very easily stretched. Secondly, in the case of dry-jet wet-spinning, it was not possible to cut off filaments below the spinneret in the air-gap zone, because of the relatively low viscosity and the sticky nature of the fluid thread lines which caused disruption of spinning. Therefore, another method of measurement (based on the measurement of the speed of the first pair of advancing reels) was employed, in which the speed of the take-up rollers was adjusted to the speed of the extruded filament. The variations in free velocity observed under a range of different spinning conditions are described in Section 3.3.

3.1.2 Spinnability

In general,the spinnability refers to the ability or the ease of making fibres or yarns from a given set of raw materials, and in practice in the textile and fibre industries, the word is used to describe everything from pulling out filaments from a polymer melt or solution to the production of yarns from staple fibres. However, the criterion of spinnability was defined by Ziabicki[77] as follows:

> "a fluid is spinnable under given deformation conditions if steady-state, continuous elongation of the fluid jet proceeds without a break of any kind",

and he believed this definition to reflect precisely the problem involved in technical fibre production. In the present work, the spinnability or spinning stability is used to mean the maximum thread length which could be pulled out under the wet-spinning and the dry-jet wet-spinning conditions by the first pair of the advancing reels with a constant flow rate, Q. In other words, for a given set of spinning conditions, and constant flow rate, Q, by increasing the speed of the first pair of the advancing reels, there will be a critical speed above which all the filaments begin to break near the face of the spinneret[70]. This critical speed defines the spinnability due to spinning conditions which, in fact, is the maximum take-up velocity, v_1 max.

The physical mechanisms of the breakage of fluid threads line which determine the maximum thread length can be divided into two groups[77]. The first process leading to the breakage of fluid threads is a cohesive, brittle fracture occurring when the tensile stress in a viscoelastic jet exceeds some critical limit (tensile strength), which depends on the spinning conditions (velocity, jet-stretch ratio, solidification rate) and the material itself. The elasticity of the fluid here plays a determining role, as in the viscoelastic material a part of the deformation energy is stored and on reaching some limiting value, which is a limit to the elastic energy the fluid can sustain[79,80], results in a cohesive, brittle fracture. The other possible process of breaking fluid threads line is associated with surface tension, considered to be a critical factor for spinnability[81], and the so-called "capillary wave" on the free surface of a liquid jet, which will grow spontaneously, leading to the break-up of the jet into drops. In principle the breakage or instability associated with capillary wave or cohesive failure, usually occurs in the initial part of the spinning line, i.e. that part close to the spinneret surface. Paul[70] suggested that the first type of breakage, cohesive failure, may be in part the operative mechanism in the instability in the wet-spinning process, as this instability due to cohesive fracture determines the upper limit of take-up velocity and the jet stretch ratio above which no spinning is possible. But it seems likely that in dry-jet wet-spinning, both mechanisms may be responsible under different conditions for the instability.

So,following the above descriptions of the free velocity and the spinnability it can be seen that in the wet-spinning system and in the dry-jet wet-spinning process, a stable spinning operation can exist anywhere within the limits of;

$$v_f < v_1 < v_{1\ max.} \qquad (3.2)$$

It was found by Paul[70] that both the free velocity and the spinnability of an acrylic copolymer solution were affected to some extent by spinning conditions such as temperature, coagulation bath composition, spinning solution concentration, and rheological properties of the spinning solution in the wet-spinning process. Measurements made of the variations in spinnability for dry-jet wet-spinning and wet-spinning are described in Section 3.3.

3.1.3 Maximum draw ratio

The other factor for increasing the speed of a spinning process, in relation to the spinning conditions, is the draw ratio. The drawing process consists of irreversible elongation of as-spun filaments in the solid state to extend the length of the filaments by several times the original and was carried out in the present part of the study in one step. The draw ratio, i.e. the ratio of drawing and feed velocities is usually used to describe the amount of drawing, and may be varied from zero per cent extension to the extension where filaments break. The upper limit of the draw ratio is called the "maximum draw ratio". The maximum draw ratio is strongly dependent on the structural characteristics of the original (undrawn) filament entering the drawing operation as well as other parameters of drawing, such as drawing temperature.

In the present work the maximum draw ratio was the ratio of the maximum velocity of the second pair of the advancing reels, $v_{2,max}$, to the velocity of the first pair of advancing reels, v_1. It was established for different samples as described below.

The freshly made filaments were drawn to three times their original length in a stretching bath as a continuous operation. Then to determine the maximum draw ratio, the speed of the second pair of the advancing reels was increased in very small increments successively by means of the variable regulator until the filaments finally broke. At this point the speed was lowered, and drawing started again. This procedure was repeated until the drawing was stable, but where any further increase in speed caused the filaments to break. In other words, the filaments were withdrawn from the bath at a speed such that the filaments were stretched just short of the point at which breaking occurred. This was taken as the maximum draw ratio. The results of such measurements are given in Section 3.3.

3.2 Experimental

25% (w/w) spinning solutionswere prepared by dissolving Courtelle fibre in D.M.F. as described in Section 2.2.2 and the dry-jet wet-spinning and the wet-spinning were carried out as described previously in Section 2.2.3 under conditions shown in Table 3.1. The free velocity, the maximum jet stretch ratio, and the maximum hot draw ratio were measured separately.

3.2.1 Measurement of the free velocity

To measure the free velocity the extrusion was started and the freshly formed filaments were guided to the take-up rollers, the speed of which was set to be slightly higher than the calculated average velocity, $\bar{v}$. Under these conditions the filaments were pulled out from the coagulating bath with tension. The system was allowed to come to a steady state for a few minutes, during which time the filaments were removed from the coagulating bath by the take-up roller at this speed. Then the speed of the take-up roller was slowly reduced until there was no tension on the filaments, and the filaments were just slack in the coagulating bath. If the decrease of the speed of the take-up roller was made slowly enough, the system responded and the spinning remained stable up to a certain well-defined speed. This velocity, designated

Table 3.1 Spinning conditions

Constant parameters		Variable parameters
Reservoir temperature	35°C	Spinneret size, n,d.
Spinning block temperature	30°C	Flow rate, Q.
Nitrogen pressure	0.5 atm. (7^{lb}/ ")	Take-up speed, V_1
Coagulating bath composition	50/50 H_2O/DMF (v/v)	Draw speed, V_2
Coagulating bath temperature	25 ± 2°C	
Filament length in coagulating bath	33 ± 1 cm	
Drawing bath temperature	96 ± 2°C	
Filament length in drawing bath	98 ± 1 cm.	

here v_f, was determined, the filaments continuing to be withdrawn from the coagulating bath. Spinning below this velocity was almost impossible, since the filaments became spread throughout the bath and some of them could not be removed. By operating slowly, it was possible to define accurately the transition speed from stable to unstable spinning within about 5%. As an example, Table 3.2 shows 10 measurements of the free velocity, using a 500 micron spinneret at constant pump speed of 8 r.p.m.

Table 3.2 Measurements of free velocity

Test No.	Free velocity (m/min)	
	DJWS	WS
1	2.12	0.97
2	1.96	0.99
3	2.15	0.99
4	2.17	1.04
5	2.07	1.01
6	2.08	1.06
7	2.23	1.07
8	2.10	1.00
9	1.99	0.99
10	1.98	1.10

3.3 Results

Tables 3.3 - 3.8 show the free velocity, v_f, of filaments in both the wet-spinning and the dry-jet wet-spinning systems using spinnerets with different sizes. For each spinneret size the free velocity of the filaments was measured with different spinning solution flow rates, Q, (i.e. at four different pump speeds). The average velocities, $\bar{v}$, under these conditions, were calculated, by using formula 3.1. The ratios of the free velocity to the average velocity, $v_f/\bar{v}$, for the different spinneret sizes and different spinning solution flow rates are also presented in the appropriate columns of these tables. Table 3.9 shows the log. average velocity, log $\bar{v}$, and the free velocity with different spinning solution flow rates for the three spinnerets with the larger hole diameters. Table 3.10 shows the relation between apparent shear rate, γ_ω , for these three spinnerets with different spinning solution flow rates. Tables 3.11 and 3.12 show the maximum take-up speed, $v_{1\,max}$, and maximum draw ratio, v_2, $_{max}$, for the spinnerets with different hole diameters.

Figs 3.1 and 3.2 show the free velocity as a function of the spinneret hole diameters, and the spinning solution flow rates of each hole respectively. Figure 3.3 shows the free velocity in relation to the log. average velocity, and figure 3.4 shows this parameter in respect to the log. apparent shear rate, log γ_ω. Finally figure 3.5 shows the variation of the ratio D_f/D with log γ_ω .

Table 3.3 Free velocity in both wet-spinning and dry-jet wet-spinning (spinneret size; 500/6)

Sample no.	Pump speed (rpm)	Flow rate per hole (q cc/min)	Average velocity ($\bar{v}$ m/min)	Free velocity (v_f m/min)		Ratio $v_f/\bar{v}$	
				DJWS	WS	DJWS	WS
3-1	8	0.53	2.72	2.09	1.02	0.77	0.37
3-2	6	0.40	2.04	1.61	0.94	0.79	0.46
3-3	4	0.27	1.36	1.10	0.70	0.81	0.51
3-4	3	0.20	1.02	0.83	0.58	0.79	0.57

Table 3.4 Free velocity in both wet-spinning and dry-jet wet-spinning

(spinneret size; 400/8)

Sample No.	Pump speed (rpm)	Flow rate per hole (q cc/min)	Average velocity ($\bar{v}$ m/min)	Free velocity (v_f m/min)		Ratio $v_f/\bar{v}$	
				DJWS	WS	DJWS	WS
3-5	8	0.40	3.20	2.18	1.05	0.68	0.33
3-6	6	0.30	2.40	1.82	0.99	0.76	0.41
3-7	4	0.20	1.60	1.25	0.76	0.78	0.48
3-8	3	0.15	1.20	0.96	0.59	0.80	0.49

Table 3.5 Free velocity in both wet-spinning and dry-jet wet-spinning (spinneret size: 300/10)

Sample No.	Pump speed (rpm)	Flow rate per hole (q cc/min)	Average velocity ($\bar{v}$ m/min)	Free velocity (v_f m/min)		Ratio $v_f/\bar{v}$	
				DJWS	WS	DJWS	WS
3-9	8	0.32	4.56	2.73	1.09	0.60	0.24
3-10	6	0.24	3.42	2.19	0.92	0.64	0.27
3-11	4	0.16	2.28	1.57	0.76	0.69	0.33
3-12	3	0.12	1.71	1.25	0.60	0.73	0.35

Table 3.6 Free velocity in both wet-spinning and dry-jet wet-spinning (spinneret size 125/24)

Sample No.	Pump Speed (rpm)	Flow rate per hole (q cc/min)	Average velocity ($\bar{v}$ m/min)	Free velocity (v_f m/min)		Ratio $v_f/\bar{v}$	
				DJWS*	WS	DJWS*	WS
3-13	8	0.13	10.88	-	1.20	-	0.11
3-14	6	0.10	8.16	-	1.06	-	0.13
3-15	4	0.07	5.44	-	0.76	-	0.14
3-16	3	0.05	4.08	-	0.69	-	0.17

* Dry-jet wet-spinning was not possible in this case

Table 3.7 Free velocity in both wet-spinning and dry-jet wet-spinning (spinneret size: 80/4)

Sample No.	Pump speed (rpm)	Flow rate per hole (q cc/min)	Average velocity ($\bar{v}$ m/min)	Free velocity (v_f m/min)		Ratio $v_f/\bar{v}$	
				DJWS	WS	DJWS	WS
3-17	8	0.8	159	12.75	1.93	0.08	0.01
3-18	6	0.6	120	9.98	1.19	0.08	0.01
3-19	4	0.4	80	8.76	1.39	0.11	0.02
3-20	3	0.3	60	6.57	1.16	0.11	0.02

Table 3.8 Free velocity in both wet-spinning and dry-jet wet-spinning (spinneret size 75/10)

Sample no.	Pump speed (rpm)	Flow rate per hole (q cc/min)	Average velocity ($\bar{v}$ m/min)	Free velocity (v_f m/min)		Ratio $v_f/\bar{v}$	
				DJWS	WS	DJWS	WS
3-21	8	0.32	72	13.05	2.17	0.18	0.03
3-22	6	0.24	54	11.96	1.79	0.22	0.03
3-23	4	0.16	36	11.32	1.29	0.31	0.04
3-24	3	0.12	27	8.69	2.17	0.24	0.08

Fig. 3.1 Variation of free velocity with spinneret hole diameter DJWS——— WS ---------

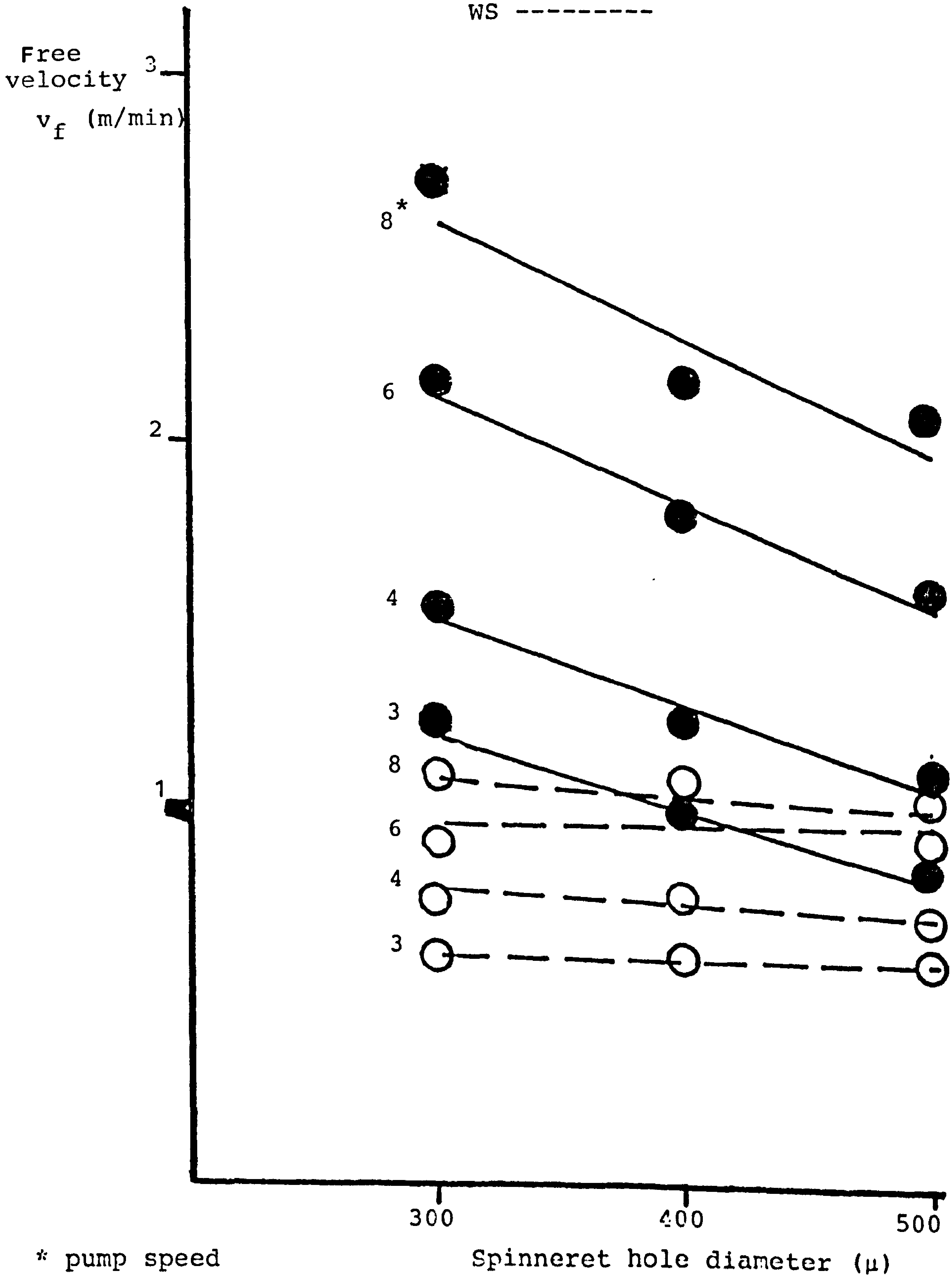


Fig. 3.2 Relation of the free velocity and flow rate per hole, DJWS ————, WS ------------

Table 3.9 Average velocity and free velocity data for spinneret sizes; 500/6, 400/8, and 300/10

Average velocity (m/min)		Free velocity (v_f m/min)	
$\bar{v}$	log. $\bar{v}$	DJWS	WS
1.02	0.009	0.83	0.58
1.20	0.079	0.96	0.59
1.36	0.134	1.10	0.70
1.60	0.204	1.25	0.76
1.72	0.235	1.25	0.60
2.04	0.310	1.61	0.94
2.28	0.358	1.57	0.76
2.40	0.380	1.82	0.99
2.72	0.435	2.09	1.02
3.20	0.505	2.18	1.05
3.42	0.534	2.19	0.92
4.56	0.659	2.73	1.09

Fig. 3.3 Relation between free velocity and average velocity, DJWS ———, WS ------------

Table 3.10 Apparent shear rates

(spinneret sizes: 500/6, 400/8, and 300/10)

Sample No.	$\gamma_\omega \times 10^4$ (sec $^{-1}$)	q (cc/min)	v_f (m/min)		D_f/D	
			DJWS	WS	DJWS	WS
3-4	1.63	0.20	0.83	0.58	1.12	1.33
3-3	2.20	0.27	1.10	0.70	1.11	1.39
3-8	2.39	0.15	0.96	0.59	1.15	1.43
3-7	3.18	0.20	1.25	0.76	1.13	1.45
3-2	3.26	0.40	1.61	0.94	1.13	1.47
3-1	4.32	0.53	2.09	1.02	1.14	1.63
3-12	4.53	0.12	1.25	0.60	1.17	1.68
3-6	4.78	0.30	1.82	0.99	1.15	1.56
3-11	6.04	0.16	1.57	0.76	1.21	1.73
3-5	6.37	0.40	2.18	1.05	1.24	1.75
3-10	9.06	0.24	2.19	0.92	1.25	1.92
3-9	12.08	0.32	2.73	1.09	1.29	2.05

Fig. 3.4 Free velocity as a function of apparent shear rate, DJWS ———, WS -------

Fig. 3.5 Ratio of die swell as a function of log shear rate, **DJWS** ———— , **WS** — — — —

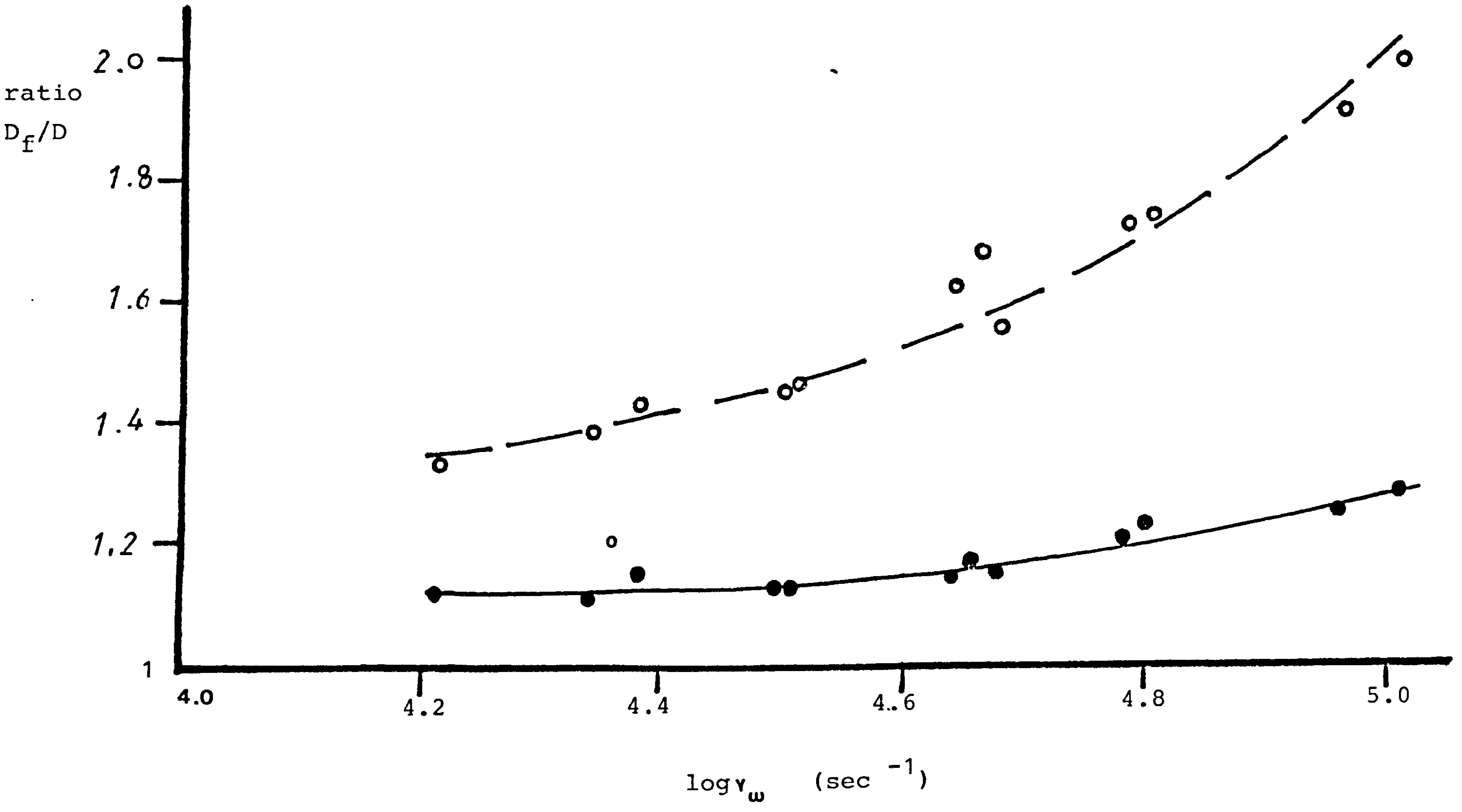


Table 3.11 Maximum jet stretch ratio and maximum free jet stretch ratio with three different spinnerets (minimum flow rate)

Sample No.	Spinneret size	q (cc/min)	$V_{1}'_{max}$ (m/min)		$\bar{v}$ (m/min)	$V_{1\,max}/\bar{v}$		v_f (m/min)		$V_{1\,max}/v_f$	
			DJWS	WS		DJWS	WS	DJWS	WS	DJWS	WS
3-4	500/6	0.20	8.70	4.67	1.02	8.53	4.59	0.83	0.58	10.48	8.05
3-8	400/8	0.15	9.44	5.11	1.20	7.87	4.25	0.96	0.59	9.83	8.66
3-12	300/10	0.12	11.68	6.35	1.71	6.83	3.74	1.25	0.60	9.34	10.58

Table 3.12 Maximum draw ratio for different spinneret sizes

Sample No.	Spinneret size	Draw ratio	
		DJWS	WS
3-4	500/6	12.50	6.12
3-8	400/8	11.09	6.92
3-12	300/10	10.34	7.33

3.4 Discussion

Table 3.13 shows a comparison of the free velocities measured in this work with those measured by other works, and it can be seen that they are of similar magnitude to those measured by other workers.[70,74]

Table 3.13 Free velocity in wet-spinning

I			II			III		
q	$\bar{v}$	v_f	q	$\bar{v}$	v_f	q	$\bar{v}$	v_f
0.06	5.31	1.88	0.1	7.89	1	0.05	4.08	0.69
0.09	7.61	1.97				0.07	5.44	0.76
0.12	10.15	2.25	0.2	15.78	1.65	0.10	8.16	1.06
0.19	12.46	2.34	0.3	23.63	2.15	0.13	10.88	1.20
0.25	20.30	3.28						

Spinneret diameters: I, II, 0.005 (127μ) and III, 125μ

I - Na SCN[74]

II - DMA[70]

III - (present work) DMF

Tables 3.3 - 3.8 show the variation of the free velocities of dry-jet wet-spinning and wet-spinning obtained by using spinnerets with different hole diameters and on using different polymer dope flow rates. Although the free velocity, v_f, of these two spinning systems was affected by the spinning solution flow rate and the spinneret hole diameters, it was apparent from the data that the spinning technique (dry-jet wet-spinning or wet-spinning) was the most important factor for determining the free velocity, as for the same spinning conditions, the values of the free velocities for the dry-jet wet-spinning were much higher than those in the wet-spinning. A detailed study showed that, in addition, the free velocity in dry-jet wet-spinning increased sharply as the spinneret hole diameter decreased, while in wet-spinning this increase was less pronounced and in fact, in this case, when the spinnerets with rather larger hole diameters were used, the change in the free velocity was almost negligible as shown in Fig. 3.1. On the other hand, as the polymer solution flow rate increased, the free velocity in both methods increased in a similar manner when spinnerets with large hole diameters were used (Fig. 3.2). This figure shows that in the case of the dry-jet wet-spinning process the increase in the free velocity with increase of the spinning solution flow rate was much more marked as the spinneret hole diameter decreased, but in the case of wet-spinning the increase of the free velocity was very small for all three spinnerets. On the other hand, for spinnerets with smaller hole diameters, a much more peculiar behaviour was observed in the case of wet-spinning. For example, initially, the values of the free velocity decreased with decreasing the spinning solution flow rate, and then increased in the case of the spinneret with a 75 micron hole diameter. But with a spinneret of 80 micron hole diameter, there were fluctuations of the free velocities as the solution flow rate decreased. Paul[70] also noticed the same behaviour for the free velocity at different flow rates using a spinneret with a 3.0 mil. (78μ) hole diameter. However, in the dry-jet wet-spinning process with the same spinnerets, there was a decrease in the free velocity as the spinning solution flow rate decreased, almost in the same pattern as observed for the spinnerets with larger hole diameters. With the spinneret hole diameter of 125 micron and 24 holes, the dry-jet wet-spinning process was not possible at all, due to the close positioning of the holes on the spinneret.

These data and figures suggest that, although the effect of the spinneret hole diameter is important in the processability in the dry-jet wet-spinning method, it is not the same for the wet-spinning system, especially, when the spinneret hole diameter becomes large. In addition, the spinning solution flow rate is another factor which determines the free velocity in both spinning systems.

The differences between the values of the free velocities in the dry-jet wet-spinning and in the wet-spinning systems, measured under the same spinning conditions up to the exit of the spinneret, suggested that one of the most important factors affecting free velocity was the system of spinning and hence the environment to which the polymer dope (as a thread line) is subjected when emerging from the spinneret hole. So, the factors affecting free velocity can be divided into two groups, i.e. the events inside the spinneret and those outside the spinneret. Thus it appears that, for given spinning conditions, the free velocity should be partially a function of the shear conditions inside the hole, and partially a function of the events outside the spinneret. The simple method of expressing those conditions inside the hole is to use the apparent shear rate, γ_{ω} , at the hole wall[70,73] as shown in formula 3.3 or average velocity, $\bar{v}$, (equation 3.1);

$$\gamma_{\omega} = \frac{4\,q}{\pi R^3} \tag{3.3}$$

where γ_{ω} = apparent shear rate at the hole wall,

q = flow rate per hole, and

R = radius of the spinneret hole = $\frac{1}{2}D$

Table 3.10 and Fig. 3.4 show that γ_{ω} adequately reduces the v_f, q , and D data in into a single curve for each spinning procedure. Although there is a certain amount of scatter, the data show that for any given shear rate the value of the free velocity in dry-jet wet-spinning is higher than that in wet-spinning. Also the variation in the free velocity with shear rate is more pronounced in the former system. The same results were obtained when the relation between average velocity and free velocity of both systems were considered as shown in Table 3.9 and Fig. 3.3. In this case it was possible to represent the data as a line and to derive an empirical equation for dry-jet wet-spinning as follows:

$$v_f = 3 \log \bar{v} + 0.7 \qquad (3.4)$$

On the other hand, it is known that the polymer dope is a viscoelastic fluid with non-Newtonian behaviour. When this kind of fluid is forced through a hole of diameter D at a flow rate q , the situation is more complex, because of the release of stored elastic energy as the fluid emerges from the capillary. This causes the stream of fluid to broaden or swell to a diameter D_f, which is larger than the capillary diameter, D, due to the well known Barus effect. This swelling causes the fluid jet or filament to slow down. The diameters and velocities are related by formula 3.5[75].

$$D_f/D = (\bar{v}/v_f)^{\frac{1}{2}} \qquad (3.5)$$

This elastic energy results from the deformation processes involved in entering the capillary plus those generated by the shear within the capillary. Thus D_f/D should depend on the spinneret hole design, the shear rate involved, the rheological properties of the spinning solution, etc. The amount of swelling in any given situation will depend on all of those factors (polymer and events inside the spinneret) plus the environment into which the filaments are extruded, depending on what restraints the environment can have on the swelling process.

The free velocity data in Tables 3.3 - 3.5 were converted into jet-swell ratios, D_f/D, via eq. 3.5 and Fig. 3.5 shows this relation. It is apparent from this figure that in the case of wet-spinning this ratio is more pronounced than in the case of dry-jet wet-spinning, where no significant change appears in this ratio at this range of shear rates.

Tables 3.3 - 3.8 also show the ratio between free velocity and average velocity for different solution flow rates, and for the spinnerets with different sizes.

It is apparent from these data that, for the three spinnerets with large hole diameters, in the dry-jet wet-spinning, the average ratio is about 80%, while with the wet-spinning this average ratio decreases to something about half that of the dry-jet wet-spinning.

From the data and the figures presented here, one can see that the main differences between these two processes are the values of the free velocities, and it seems that the free velocity of the dry-jet wet-spinning is one of the main factors allowing the high speed operation of this spinning process. Since this difference in the free velocity is due to the air-gap distance of the dry-jet wet-spinning, it is possible to conclude that, although in any spinning system the free velocity is essentially determined by the spinneret size and polymer dope flow rate, the behaviour of the spinning solution just after emerging from the spinneret affects the free velocity drastically. It seems that in the case of wet-spinning, the viscous drag pressure of the coagulating bath liquid around the spinneret face and the coagulating conditions in this zone are among those factors which are responsible for this phenomenon. It has been shown[82] that this pressure appears to be negligible in dry and melt spinning because of the comparatively low viscosity of air compared with liquids. Paul[70] pointed out that in wet-spinning, the free velocity is influenced mainly by events inside the spinneret hole; but as the L/D ratio for the spinnerets used here was much less than one (and less than that used by Paul), and as the spinneret hole diameters were relatively large, so it appears that, under the conditions examined, the major factor which is responsible for the difference in the free velocities in these two processes is the coagulation procedure. In other words, in wet-spinning the free velocity is affected by both conditions inside and outside the spinneret, and in fact the coagulation conditions and the media (liquid) become of overriding importance. On the other hand in dry-jet wet-spinning the free velocity is mainly determined by the extrusion behaviour (i.e. the events inside the spinneret).

Table 3.11 shows that the maximum take-up speed, $v_{1\,max}$, of the dry-jet wet-spinning is nearly twice that of the wet-spinning. But a closer examination of these data indicates that, although the average jet stretch ratios, $(v_{1\,max}/\bar{v})$ in dry-jet wet-spinning are nearly twice those in wet-spinning, the free jet stretch ratios, $v_{1\,max}/v_f$, of both processes are nearly the same. While, for the dry-jet wet-spinning process, the values of the free jet stretch ratio decrease as the spinneret hole diameter decreases, for the wet-spinning, the opposite relation exists, i.e. with decrease in the spinneret hole diameter, the free jet stretch ratio increases. One possible explanation of this behaviour could be as follows. In spinning through an air-gap the filament is not stretched in the coagulating bath liquid, the main jet stretch being applied in the air-gap, so that the finer the filament the less stretch it can accommodate. In the case of the wet-spinning process, as the diameter of the jet-stream decreases, the solidification process becomes more homogeneous, so the filament will have a more regular structure and hence can withstand more tension on it.

Thus, it could be concluded that in the coagulating region, the major factor controlling the processability of both types of wet-spinning is the free velocity, which will be determined by the spinning solution flow rate and the spinneret hole diameter, as well as the environment in which the fluid emerges. Other factors can be regarded as minor factors; for example the maximum take up speed itself is related to the free velocity of the spinning system.

The result of the maximum attainable draw ratio of the filaments produced both in dry-jet wet-spinning and wet-spinning are given in Table 3.12. The filaments as mentioned, were first drawn to three times their original length, and then the maximum drawing was established. The maximum draw ratio was then calculated. In the case of the dry-jet wet-spinning, the values of the maximum draw ratio decreased with a decrease in spinneret hole diameter, while for wet-spinning, there was an increase as the spinneret hole diameter decreased.

However, looking at the maximum draw ratios given in Table 3.12, it is obvious that the dry-jet wet-spinning process has produced a remarkable effect on these values. This could suggest that these filaments have a more homogeneous structure than the filaments which were produced in the wet-spinning, since the values for the maximum draw ratio are at least 30% higher in the dry-jet wet-spinning process. So the higher maximum draw ratio is also responsible for the higher speeds of the dry-jet wet-spinning. It is interesting that the opposite trends of maximum draw ratio vs. hole size noted in the two different types of spinning parallels that obtained in the maximum free jet stretch shown in Table 3.12.

CHAPTER 4: STRUCTURE AND PROPERTIES OF DRY-JET WET-SPUN AND WET-SPUN FIBRES

4.1 Introduction

The physical and chemical properties of fibres can be divided into two main groups. Some of these properties such as the basic chemical properties and dyeing characteristics are almost entirely dependent upon the chemical composition and molecular weight of the polymeric raw material from which the fibres were spun. These properties can be altered only slightly by changing the different factors in the fibre forming process. The second group, however, although influenced by the chemical composition of the polymer, can be controlled to a large extent by varying the details of the fibre forming process or spinning conditions. These properties, which are more important in yarn and fabric production and in the textile end-use, are those of the so-called "fundamental fibre properties" namely; tenacity, extensibility, lustre, cross-sectional shape, covering power, bulkiness, fibre count (d.tex or denier), etc. all of which belong to the second group of fibre properties.

In any solution spinning, the structure of the fibre produced is strongly influenced by the spinning conditions, and this structure, in turn, influences the extent to which desirable properties can be developed in the finished product.

So, it is a usual practice, for characterising any spinning systems, to produce fibres under a given spinning conditions and to measure some of these fundamental fibre properties, and to characterise the fibre physical structure. The most readily measured fundamental fibre properties useful for characterising finished fibres are tenacity, t, extensibility, E, and tensile factor, $tE^{\frac{1}{2}}$[83].

A wealth of literature references[70-76,84-86] can be cited in which various spinning conditions are employed for preparing acrylic fibres on the wet-spinning system. Unfortunately, it is not the same in the dry-jet wet-spinning area, where only a few references could be found.[61-64].

In order to study the effect of the different spinning conditions a series of spinnings were carried out using wet-spinning as well as dry-jet wet-spinning. In each experiment one of the spinning conditions, which has an effect on the fibre properties, was varied, while the other spinning conditions were held constant. Among the more important spinning conditions, which are common both to the wet-spinning and to the dry-jet wet-spinning systems, are polymer dope concentration, coagulating bath composition and temperature, jet stretch ratio and the hot draw ratio. The spinning solutions were prepared as described in the experimental section.

4.2 Experimental

4.2.1 Preparation of spinning solution

The polyacrylonitrile co-polymer used in this work was Courtelle acrylic fibre, with the specification described in Section 2.2.1. A series of experimental samples were prepared by wet-spinning and by dry-jet wet-spinning processes, using the laboratory wet-spinning equipment. The experimental conditions are listed in Table 4.1. The polymer dope concentration, coagulating bath temperature and its composition, the speed of the first advancing roller, and that of the second advancing reels were used as independent variables. The polymer dope of the above mentioned copolymer in DMF was spun, stretched and aftertreated.

4.2.2 Sample characterisation

After coagulation, the samples tend to collapse if dried in air. Consequently, a freeze-drying technique was used for some of the undrawn samples. Undrawn samples were immersed in liquid nitrogen and then dried in a vacuum oven at 50°C. Mechanical properties measurements were made, and a testing speed of 150% per minute was used on an Instron.

Table 4.1 Sample preparation conditions

Fixed conditions	
Pot temperature	40°C (±2)
Pump temperature	30°C (±2)
Nitrogen pressure	0.5 Atm.
Pump speed	4 r.p.m. unless stated otherwise
Spinneret sizes	a: 300 μ with 10 holes
	b: 100 μ with 21 holes
Hot draw bath temperature	90°C ± 2
Drying roller temperature	60°C ± 2
Variable conditions	
Polymer dope concentration:	17.5%-30% $(w/_w)$
Coagulating bath composition:	20/80 - 70/30 $(v/_v$, DMF/water)
Coagulating bath temperature:	20-45°C
First advancing reel speed	5-22 r.p.m.
Second advancing reel speed	19 - 86 r.p.m.

4.3 Resultsand discussion

4.3.1 General

In attempting to make a comparison between wet-spinning and dry-jet wet-spinning, a difficulty in choice of spinneret hole size was apparent since the typical hole size in the two types of spinning are so different. To allow for this, dry-jet wet-spinning was carried out using a 300 μ, 10 hole spinneret and wet spinning was performed both with this spinneret (ws_1) and also with a 21 hole spinneret of hole size 100 μ (ws_2), more typical of that usually used in wet spinning. Excepting the change in spinneret, all of the variable spinning conditions for these samples (summarised in Table 4.1) were identical.

Table 4.2 shows the mechanical properties for the three samples; one of them was produced by dry-jet wet-spinning, and the other two by wet-spinning. Table 4.3 shows the stress-strain data of these three samples together with Fig. 4.1 which shows the stress-strain curves. These results show that under the conditions examined, the dry-jet wet-spinning generally gives higher values for tenacity, extensibility, and therefore tensile factor, than the wet-spinning. However from the comparison of the stress-stain curves of the fibre produced in the dry-jet wet-spinning with those produced in the wet-spinning (using the spinneret with 100 micron hole diameter) it seems that the yield stress values of the latter

Table 4.2 Effect of spinning procedure on fibre properties

Sample No.	Spinning process	Spinneret size		Yarn count d.tex	Tenacity t g/d tex	Extensibility E%	Tensile factor $tE^{\frac{1}{2}}$
		Dia. µ	No of hole n				
4-1	DJWS	300	10	125	2.65	36.44	16.0
4-2	WS_1	300	10	140	2.13	23.00	10.2
4-3	WS_2	100	21	136	2.45	27.35	12.8

Conditions:

- Polymer dope concentration: 25% $w/_w$
- Coagulation bath composition: 50/50 $v/_v$
- Coagulation bath temperature: 25°C ±2
- Jet stretch ratio: a - 3.8 (300µ)
  b - 0.9 (100µ)
- Hot draw ratio 4

Fig. 4.1 Stress-strain curves of dry-jet wet-spun fibres, DJWS ———— ,WS$_1$ —·—·—·—· WS$_2$ — — — —

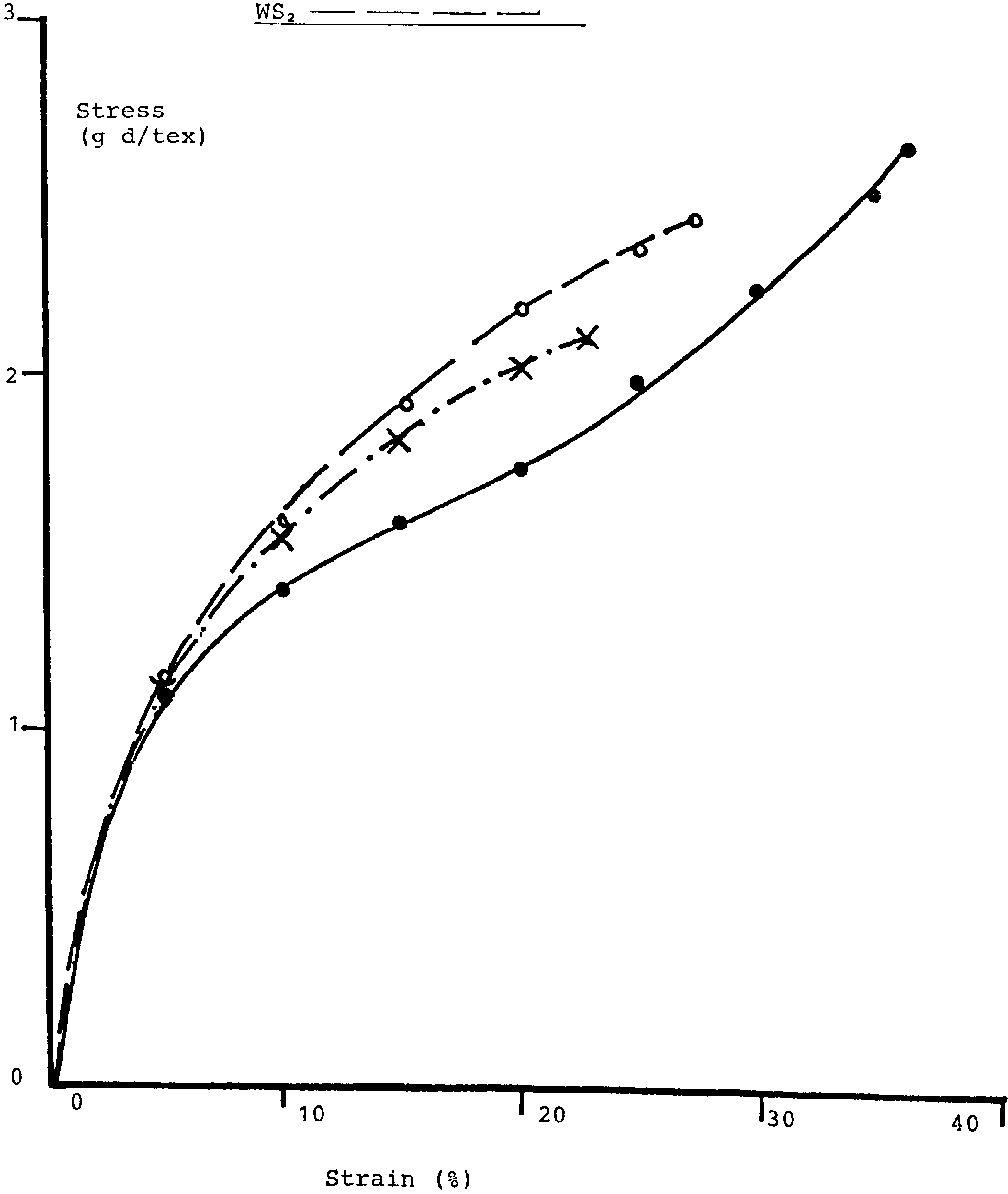


Table 4.3 Stress-strain data for fibres produced under different spinning procedures

Strain %	Stress g/d.tex		
	4.1	4.2	4.3
5	1.08	1.10	1.10
10	1.39	1.54	1.58
15	1.58	1.82	1.91
20	1.76	2.01	2.19
23	-	2.13	-
25	1.99	-	2.36
27.35	-	-	2.45
30	2.25	-	-
35	2.52	-	-
36.44	2.65	-	-

Spinning conditions: Under table 4.2

fibres are higher. It also shows that for any given value of the strain, the value of the stress of the fibres produced in the wet-spinning are higher than those of the dry-jet wet-spinning. But as the final extensibility of the dry-jet wet-spun fibres is much higher than for the wet-spun fibres, so their tenacity is also higher. In fact, as will be discussed later this higher extensibility is one of the main factors which allow the dry-jet wet-spun fibres to accept a higher draw ratio than the wet-spun fibres.

With a closer examination, another interesting feature of these curves is that, between the yield stress and the breaking load of these two differently spun fibres, the wet-spun fibres not only possess higher values of stress, but also it seems that the slope of the curve is decreasing regularly. Over the same range for the dry-jet wet-spun fibre, the initial decrease in slope is followed by a steepening of the curve, i.e. the curve shows a point of inflexion.

Apart from the differences in the mechanical properties of the dry-jet wet-spun fibres and the wet-spun samples, there were some differences in the microscopical and morphological structure of these two fibres. The most noticeable difference between fibres produced in dry-jet wet-spinning and those produced in wet-spinning was that the dry-jet wet-spun fibres were more lustrous than the corresponding wet-spun fibres, which may have been a function of the compactness of the filament structure as the former had fewer macrovoids than the latter (see later), or may be due to a difference in the surface smoothness. On the other hand the wet-spun fibres always gave higher count (d.tex) values (i.e. a thicker fibre) than the dry-jet wet-spinning, both in the undrawn state and in the oriented state (finished fibre). The increase in the fibre count (d. tex) and thickness was in the region of about 5% to 25% as is shown in Plate 4.1. This plate is an electromicrograph of freeze-dried undrawn samples produced in dry-jet wet-spinning and in wet-spinning. Patel[63] also noticed a higher decitex in wet-spun fibres than in equivalent dry-jet wet-spun fibres on drawn and dried fibre. Presumably the wet-spun fibres must be contracting after spinning, perhaps in an attempt to recover the diameter they possessed immediately on coagulation i.e. this might be an effect related to the die-swell.

The amounts of macrovoids or capillaries in these two different spun fibres are different too. Plates 4.2A and 4.2B show the light photomicrographs of two undrawn samples (prepared by the freeze-drying technique), one sample being dry-jet wet-spun and the other wet-spun fibre respectively. It is clear from these plates that the macrovoids, which are a feature of the wet-spun fibre are absent in the dry-jet wet-spun sample.

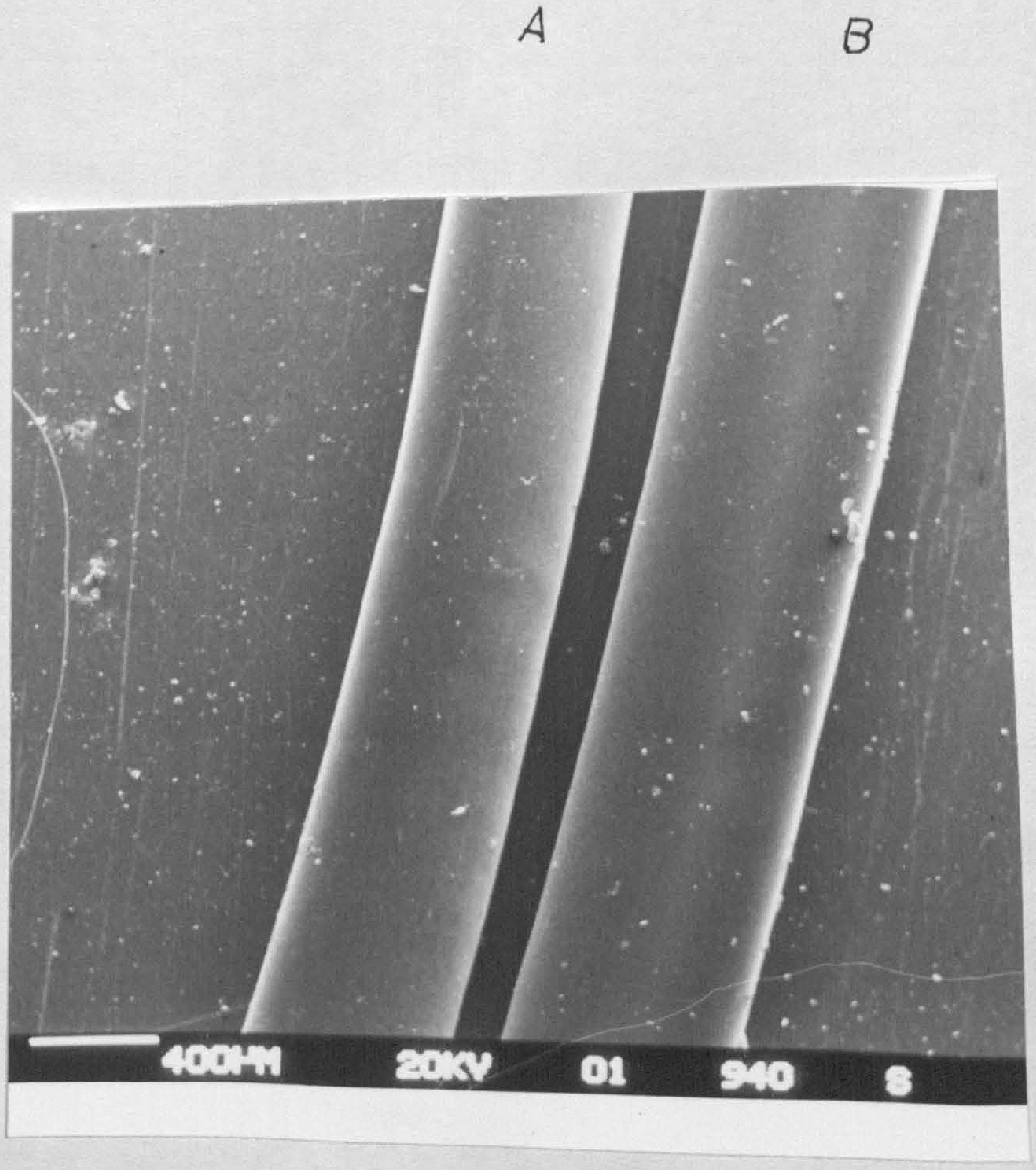
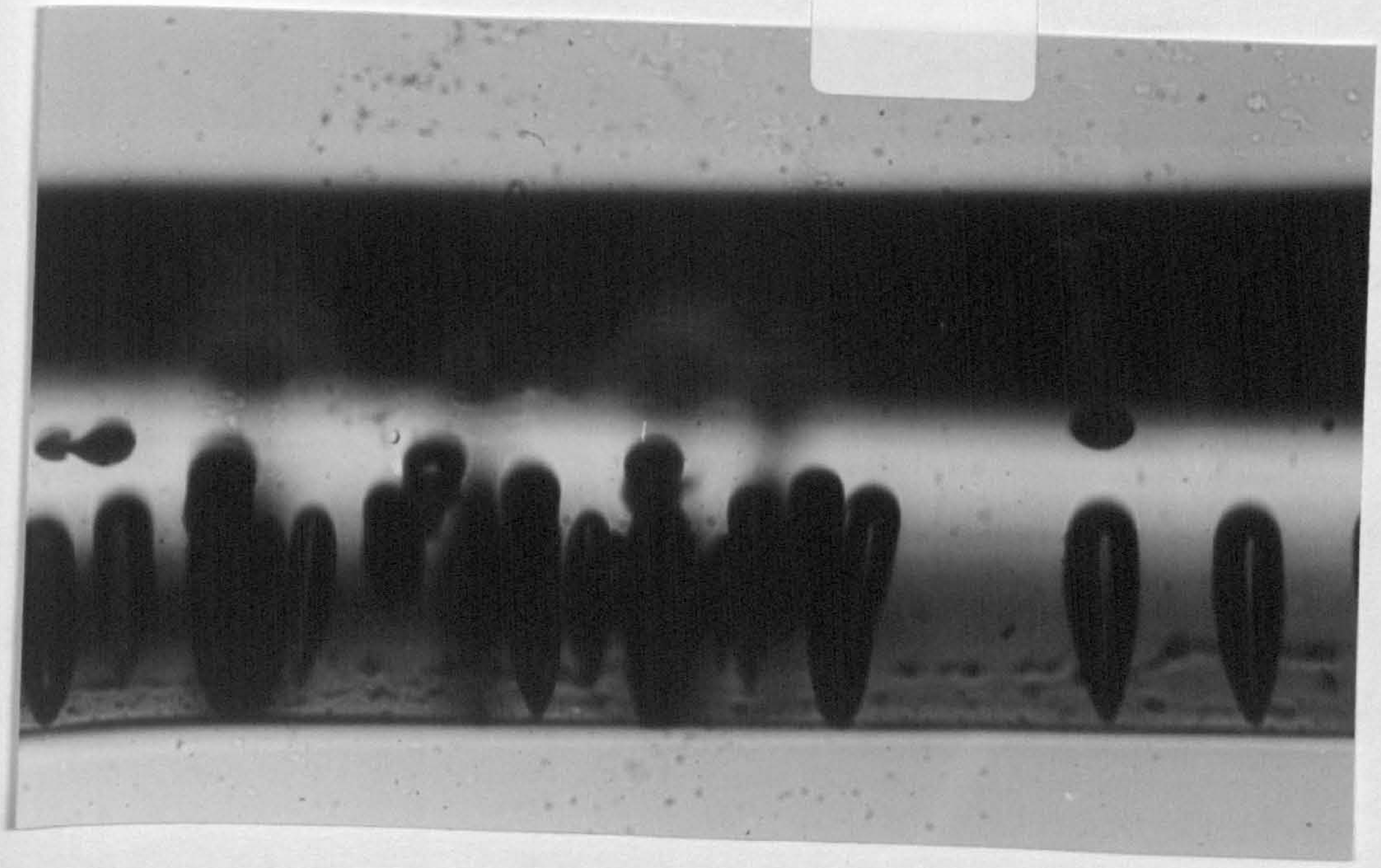
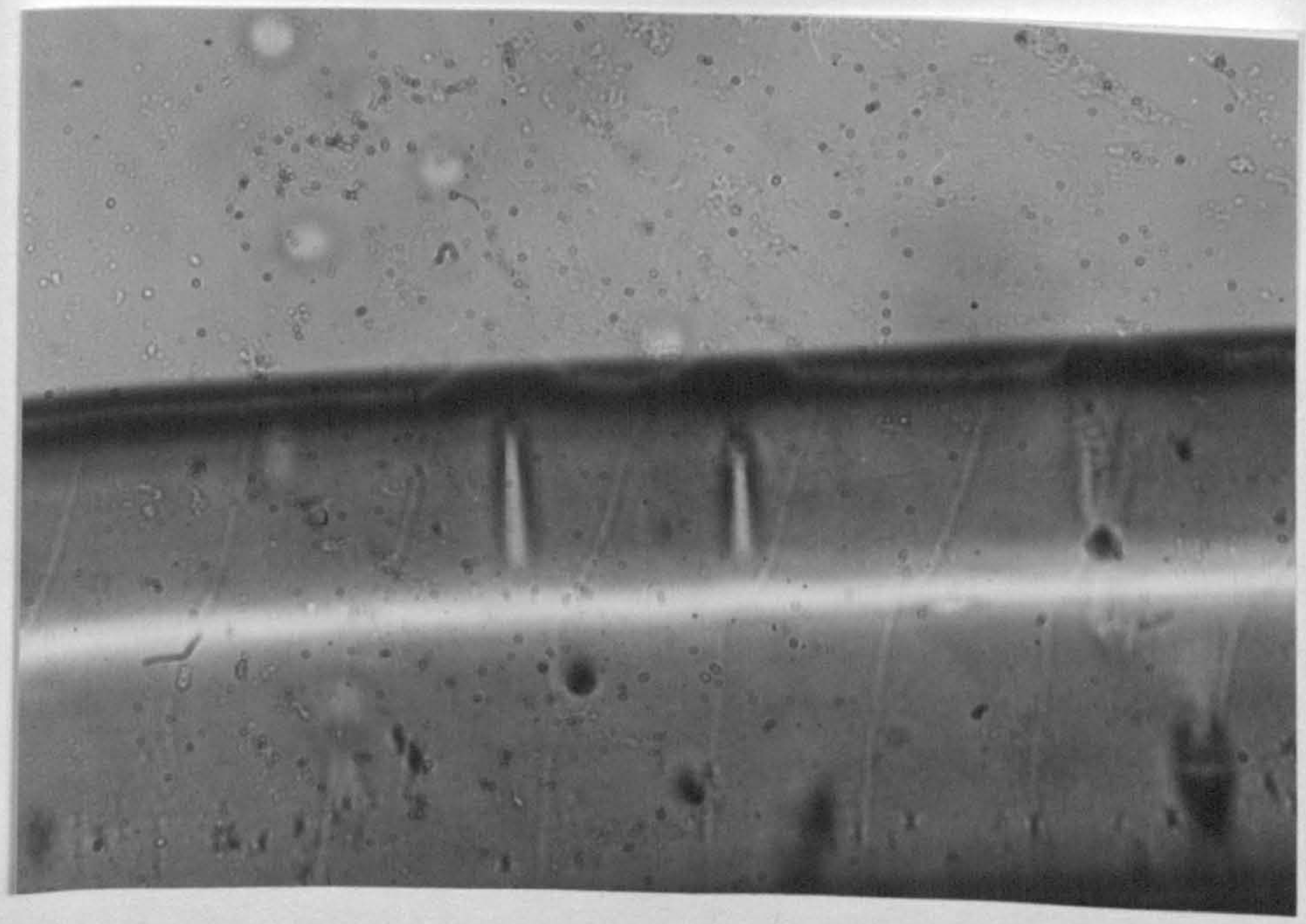


Plate 4.1 Comparison of fibre diameter (Undrawn filaments, 300μ spinneret), (A) DJWS (B) WS



A



B

Plate 4.2 Light micrograph of undrawn filaments,

(A) DJWS (B) WS

As mentioned in Section 1.2.2, normally, in wet-spinning during coagulation there is an inward diffusion of coagulating bath liquid into the filaments undergoing coagulation, as well as a corresponding outward movement of solvent into the coagulating bath. Several workers believe that the solvent and bath liquid can interchange in such a manner that the resulting filaments contain many macrovoids or cavities along their length, which can be seen clearly with an optical microscope[84]. Grobe[85] attributed the capillary formation to a rupture of the internal structure caused by a rigid skin and the subsequent pressure produced by the inward diffusion. Craig and co-workers[84] postulated that the voids are caused by the penetration of the coagulating bath into the fibre through surface faults. These faults they suggest are probably caused by minor imperfections in the spinneret holes. Knudsen[86] suggested that the formation of voids is related to the coagulating rate and counter diffusion of solvent and non-solvent. However, the absence of the macrovoids , the thinner and more lustrous fibre in dry-jet wet-spinning could be accounted for by the die-swell in this case occurring outside the bath as well as by changes in the mechanism of diffusion. In the dry-jet wet-spinning process most of the jet-stretch inserted into the freshly made filaments goes into the air-gap region[62]. The maximum die-swell occurs at a distance of only a few millimetres below the spinneret surface[87], and then the radius of the swollen filament reduces as this distance increases from the spinneret surface. So when the filament begins to solidify there is no longer any die-swell, or at least there is a minimum effect of die-swell in the freshly formed filament. This suggests that the speed of diffusion of the coagulating liquid into the polymer dope and the solvent into the spinning bath, and the mechanism of the skin formation in dry-jet wet-spinning process is different from wet-spinning. In wet-spinning the solidification of the fibre skin take place as soon as the spinning solution emerges from the spinneret hole into the coagulating liquid. So coagulation begins and the fibre cross-section will begin to take shape while it is in the swollen state, but in dry-jet wet-spinning, due to the air-gap between the spinneret surface and the coagulating liquid level, the solidification takes place almost entirely after the spinning solution enters into the coagulating bath liquid, and the inter-layer air distance between spinneret surface and liquid level allows the freshly formed filament (liquid thread-line) to relax some of its swelling before the solidification process. It seems likely that as the liquid thread line of spinning solution passes through the air-gap region, not only will the die-swell be relaxed, but also an extremely thin "skin" will form on the surface of the filament in this region. The formation of this skin could well regulate the rate of diffusion in subsequent stages to some extent. In other words the solidification process of the fibre skin in these two different methods is as shown below:

a - In wet-spinning

spinning solution $\xrightarrow{\text{spinneret hole}}$ coagulating bath

fluid (liquid state) $\longrightarrow$ skin (solid state)

b - In dry-jet wet-spinning

spinning solution $\xrightarrow{\text{spinneret hole}}$ air gap $\longrightarrow$ coagulating bat

fluid (liquid state) $\longrightarrow$ thin skin (gel) $\longrightarrow$ skin(solid state)

This suggestion is supported by the morphological structure of the dry-jet wet-spun fibre. The morphological structures of these two differently spun fibres are shown in plates 4.3A, 4.4A, 4.3B, and 4.4B. These plates show the electromicrograph of these two fibres at different magnifications. First of all, there appear to be very fine, almost parabolic ridges on the surface of the dry-jet wet-spun fibres, which are not present in the wet-spun fibres (Plates 4.3A and 4.3B). These ridges could be either due perhaps to the fluid running down on the surface of freshly formed filament, or due to the elastic behaviour of the polymer solution. However, it is almost certain that these ridges formed on the filament surface during its passage through the air-gap before entering into the coagulating liquid.

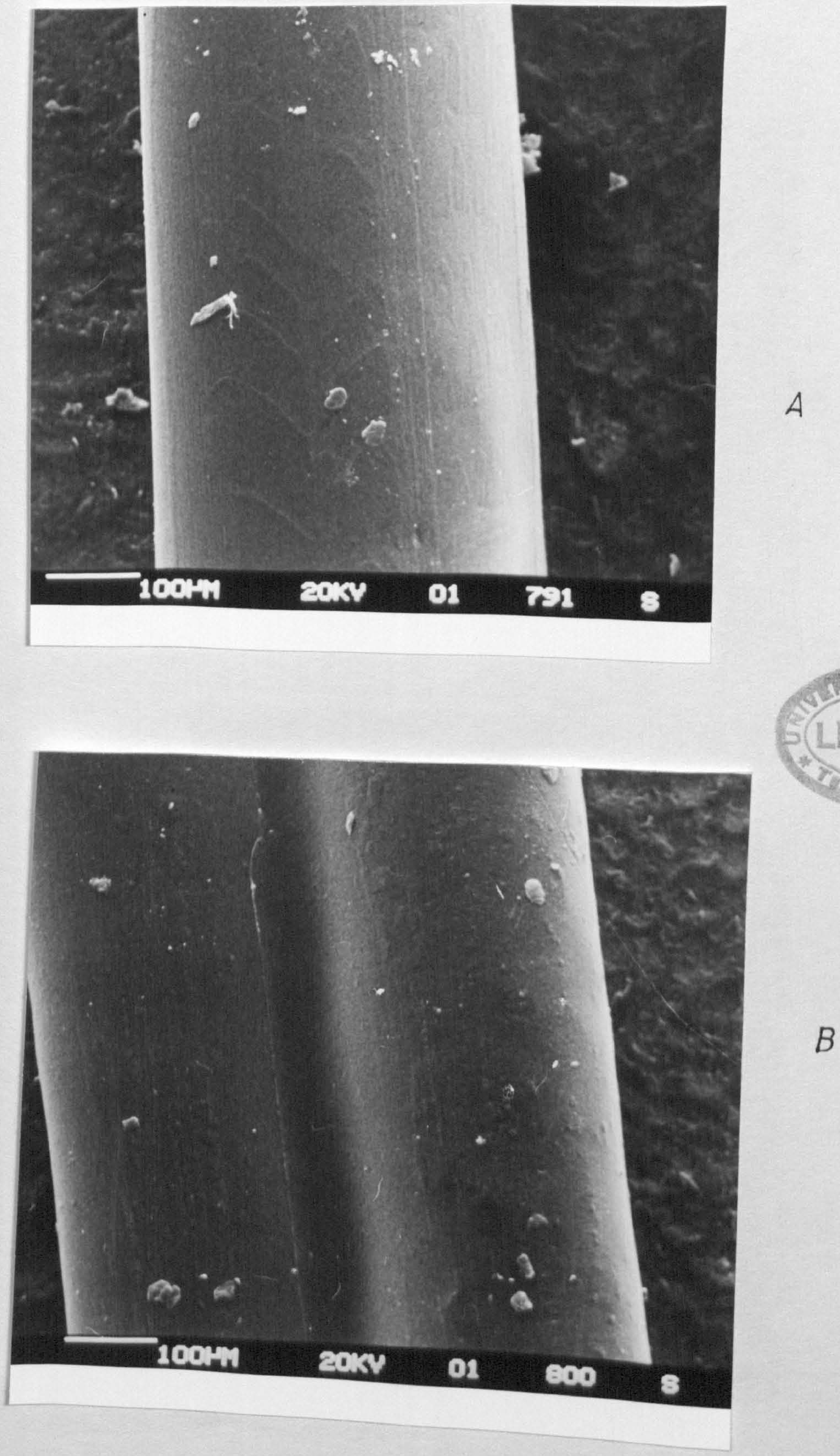


Plate 4.3 Electron micrograph of undrawn filaments,

(A) DJWS (B) WS

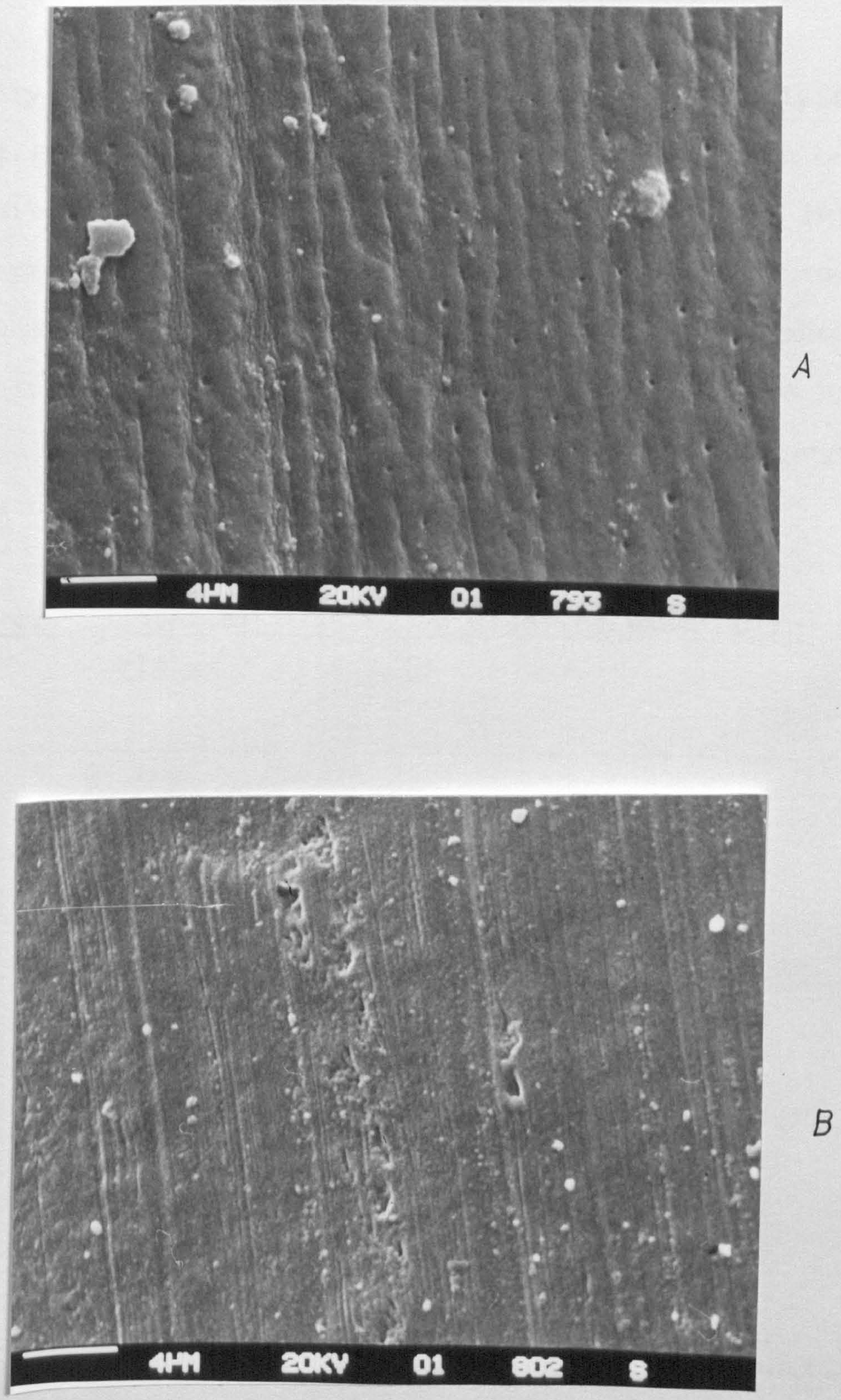


Plate 4.4 Surface texture of undrawn filaments,

(A) DJWS (B) WS

Secondly the surface textures of the two differently spun fibres (spun into the bath with no spinning stretch or drawing) are quite different. The dry-jet wet-spun sample (Plate 4.4A) shows pronounced ridges parallel to the fibre axis together with what appear to be small dones or depressions about 0.2µ in diameter. The wet-spun sample appears to have a flat surface texture, accompanied by longitudinally arranged surface cracks or cavities.

Table 4.4 Spinning conditions used for samples in Plates 4.5A - 4.7B

- Polymer dope concentration		25% w/w
- Pot and pump temperature		40°C (±2)
- Pump speed		5 r.p.m.
- Spinneret size		300 ,10 holes
- Hot draw bath temperature		85°C (±2)
- Jet stretch ratio		4
- Coagulation bath composition		50/50 $v/_v$
- Hot draw ratio:	(a) DJWS	4
	(b) WS	3.5

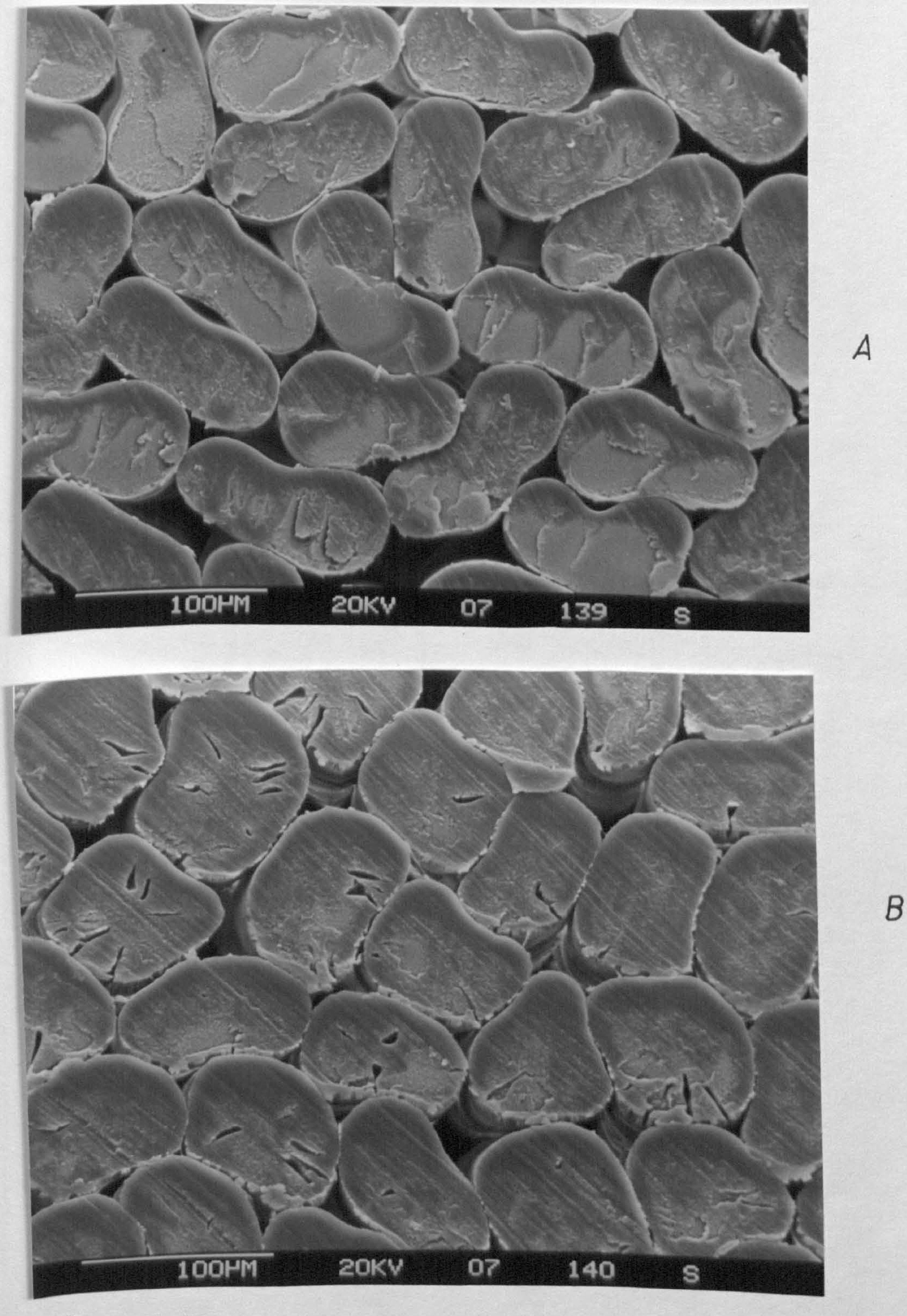


Plate 4.5 Cross-section of undrawn fibres,

(A) DJWS (B) WS

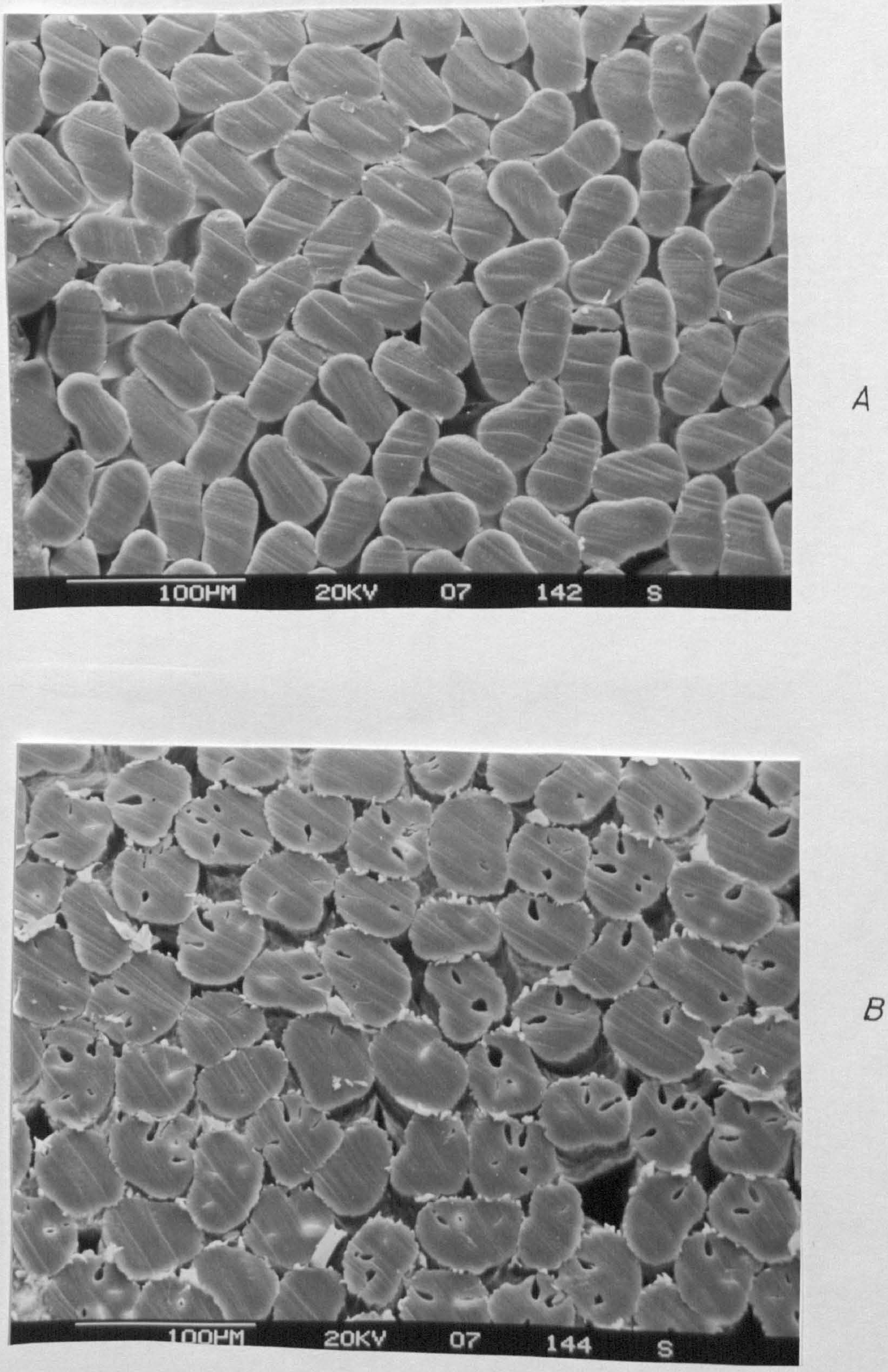


Plate 4.6 Cross-section of drawn fibres,

(A) DJWS (B) WS

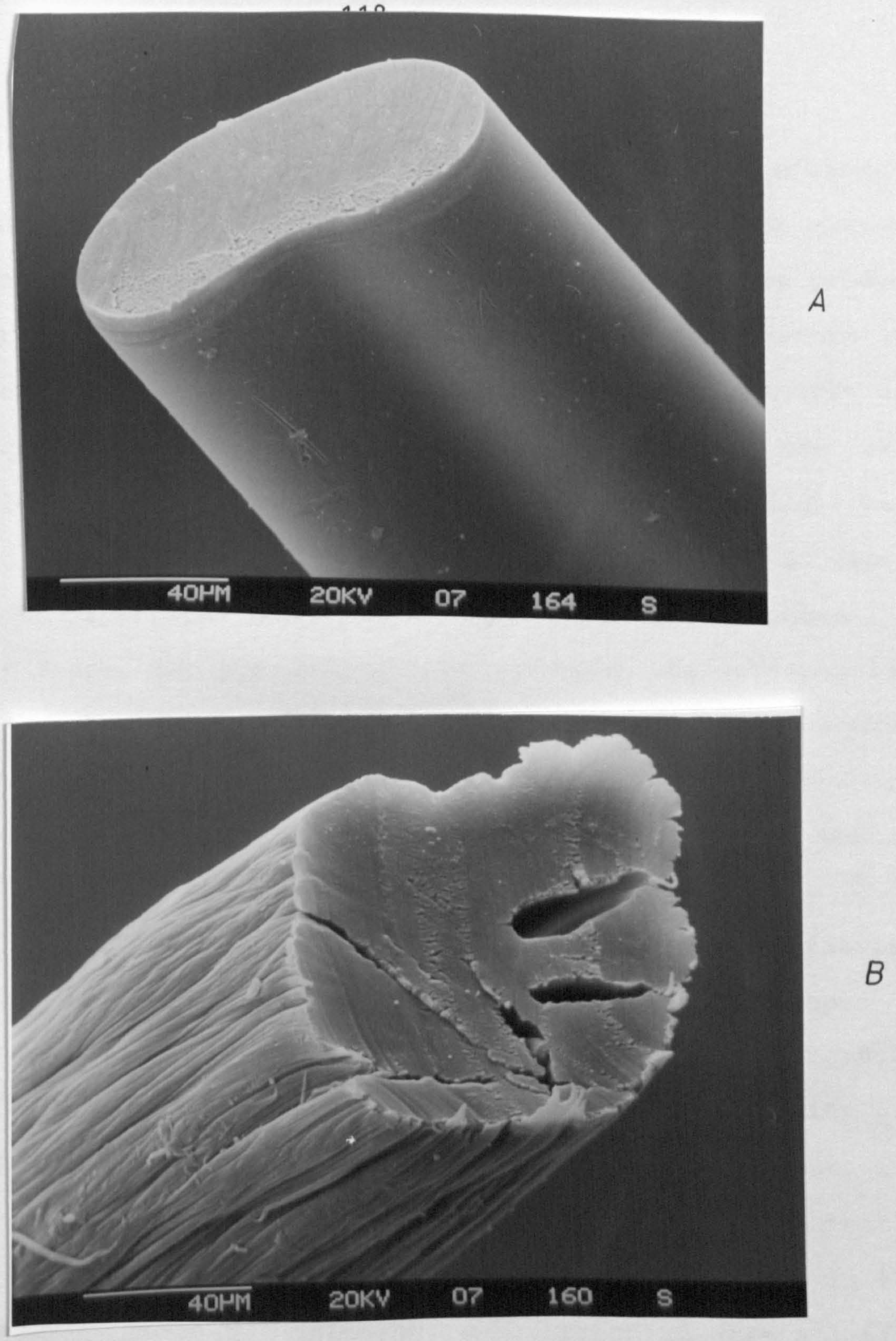


Plate 4.7 Cross-section and surface structure of fibres, (A) DJWS (B) WS

Plates 4.5A - 4.7B show further electron micrographs of these fibres as obtained on the scanning electron microscope at the magnification indicated. These samples were produced under the conditions shown in Table 4.4. The cross-section as well as the surface structure of the dry-jet wet-spun fibres are quite different to those of wet-spun fibres. The former samples have cross-sections usually dog-bone or kidney-shaped, while the latter samples look more nearly circular as expected from the spinneret hole shape. Beside the differences in their shape, the presence of macrovoids in the wet-spun fibres and the absence of them in the dry-jet wet-spun fibres are clearly noticeable. In the wet-spun samples both the undrawn filaments and the drawn fibres contained macrovoids, though the voids were rounder in shape in the drawn samples.

The surface structure in dry-jet wet-spun fibres, at this magnification, looks smooth, but in the wet-spun fibres it is different. Of course, these fibres were stretched 4 times in the spinning bath, so there is a possibility that this high jet stretch is responsible for this structure in the wet-spun samples in this particular case. It seems that, in dry-jet wet-spinning, jet stretching is taking place in the air-gap while in wet spinning, the stretching acts all along the thread line in the coagulation bath.

4.3.2 Effect of equipment variables

The most important equipment variables in dry-jet wet-spinning and in wet-spinning are the jet stretch ratio and the hot draw ratio. The range over which the jet stretch ratio can be varied depends essentially on many variables, e.g. polymer properties, dope concentration, type of spinning solvent, spinneret hole diameter, extrusion rate, and coagulating conditions. According to Knudsen[86], in the wet-spinning process, the jet stretch ratio is not a primary variable, but rather the range of us~~e~~able stretch is determined by the coagulation conditions. However, in wet-spinning, an increase in jet stretch ratio results in a decrease in density and cross-sectional surface area, and an increase in the number of voids. Knudsen believes that the increase in the number of voids is related to the rupturing of the fibre surface during coagulation as the stress imposed by stretching is increased.

Table 4.5 shows the effect of the jet stretch ratio on the mechanical properties of the fibres from dry-jet wet-spinning and from wet-spinning. Figs. 4.2 - 4.4 show the effect of jet stretch ratio on tenacity, extensibility, and tensile factor for both methods. These figures confirm Knudsen's data[86] indicating that as the jet stretch ratio increases, there is a decrease both in tenacity and extensibility of the wet-spun fibre, while in dry-jet wet-spinning as the jet stretch ratio is increased, the extensibility decreases and the tenacity of the dry-jet wet-spun fibre has a maximum value at the jet stretch ratio of 3.6. However in dry-jet wet-spinning, higher jet stretch ratios than 3.6 cause the mechanical properties of the fibres to deteriorate. It has been pointed out for wet-spinning that although stretching in the coagulating bath can cause orientation[72], it does not contribute any measurable orientation to the fibre[71], while in dry-jet wet-spinning, according to the x-ray patterns (Plates 4.8A and 4.8B), there might be some very slight orientation in the fibre structure. It is very clear that the dry-jet wet-spun fibre can accept more jet stretch than the wet-spun fibres as was shown in Chapter 3. It is interesting that, as expected, better fibre properties were obtained on wet-spinning from the smaller hole diameter spinneret of the two used. In addition, there was an optimum jet stretch ratio close to 1 in this system.

Another interesting and unusual feature of the effect of jet stretch was noted on measuring the extensibility of the undrawn samples. Table 4.6 shows the mechanical properties of undrawn samples of dry-jet wet spun fibres at different jet-stretch ratios. A close look at this table shows that the amount of jet stretch did not have any significant effect on the tenacity of the fibres but the extensibility of the fibres was increased very sharply as the amount of jet

Table 4.5 Mechanical properties of dry-jet wet-spun fibres and wet-spun fibres as a function of jet-stretch

Sample No.	Jet stretch ratio	Fibre count d tex			Tenacity (t) g/d tex			Extensibility (E) %			Tensile factor $tE^{\frac{1}{2}}$		
		DJWS	WS_1	WS_2	DJWS	WS_1	WS_2	DJWS	WS_1	WS_2	DJWS	WS_1	WS_2
4-4	0.66	-	-	190	-	-	2.32	-	-	30.2	-	-	12.7
4-5	1.01	-	-	126	-	-	2.70	-	-	27.7	-	-	14.2
4-6	1.29	-	-	97	-	-	2.56	-	-	23.0	-	-	12.3
4-7	1.30	400	430	-	2.37	2.26	-	36.0	26.3	-	14.3	11.6	-
4-8	1.58	338	358	-	2.35	2.20	-	36.0	24.1	-	14.1	10.8	-
4-9	1.71	306	321	-	2.56	2.12	-	33.4	23.9	-	14.8	10.9	-
4-10	2.42	218	232	-	2.87	2.16	-	34.2	18.4	-	16.8	9.3	-
4-11	3.63	140	152	-	3.05	2.02	-	33.5	12.1	-	17.7	7.0	-
4-12	4.25	123	-	-	2.74	-	-	32.8	-	-	15.7	-	-
4-13	5.80	91	-	-	2.67	-	-	24.8	-	-	13.4	-	-

Spinning conditions:

- Polymer dope concentration: 25% w/w
- Coagulation bath composition and temperature 50/50 v/v, 25°C
- Hot draw ratio: 3.8

Fig. 4.2 Effect of jet stretch on tenacities, DJWS ———, WS$_1$ —.—.— WS$_2$ ------

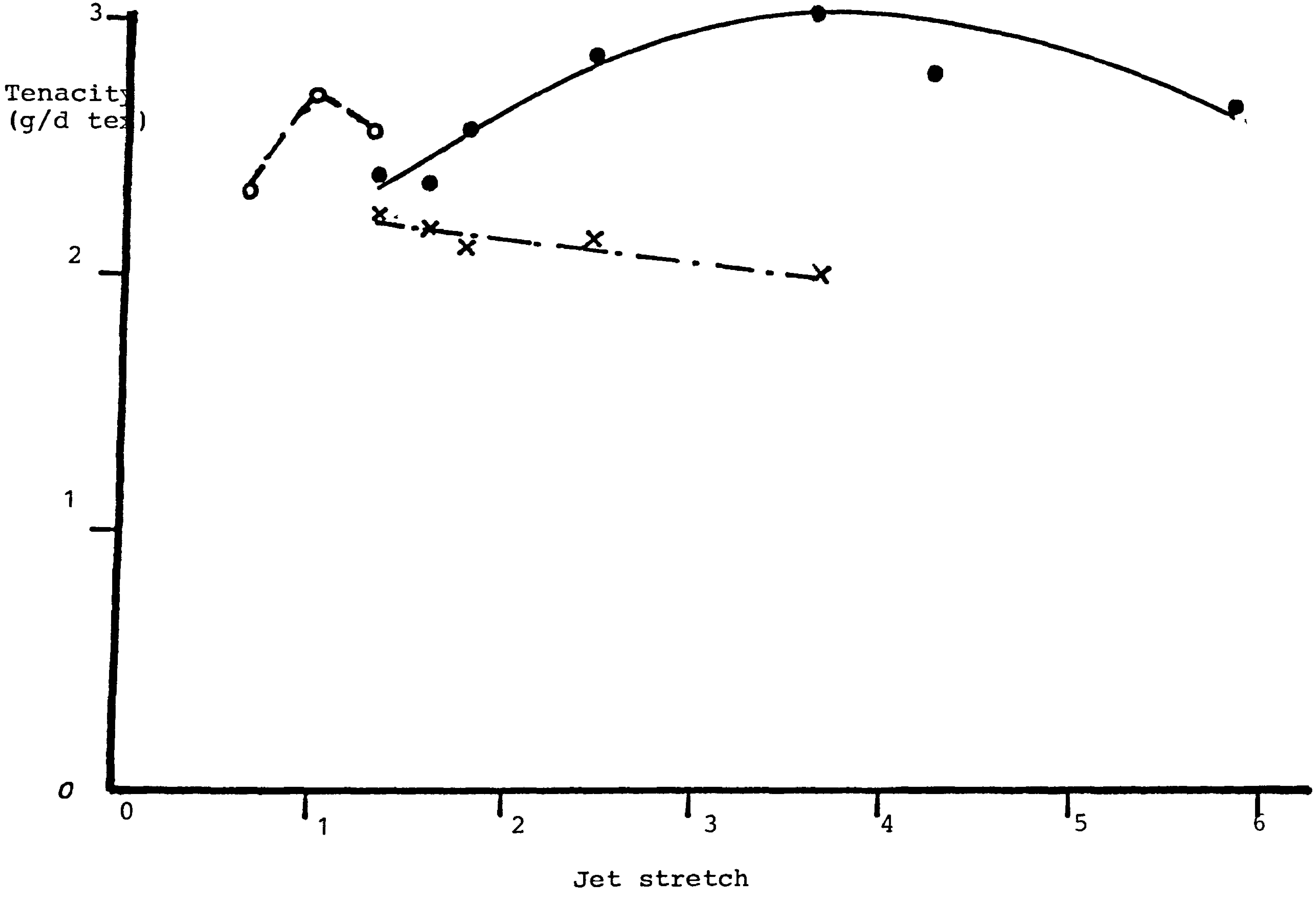
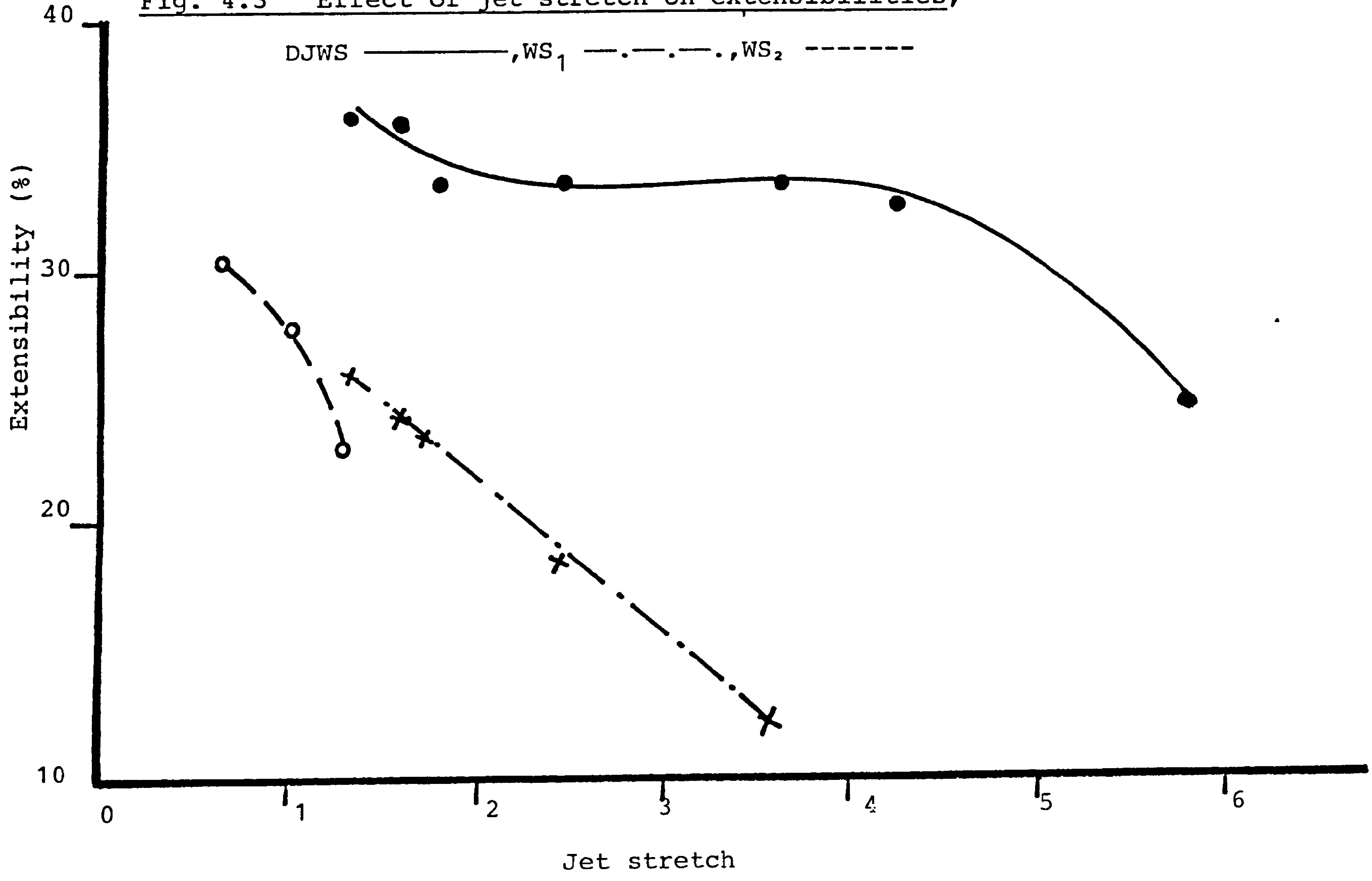


Fig. 4.3 Effect of jet stretch on extensibilities,

DJWS ————, WS_1 —.—.—., WS_2 -------



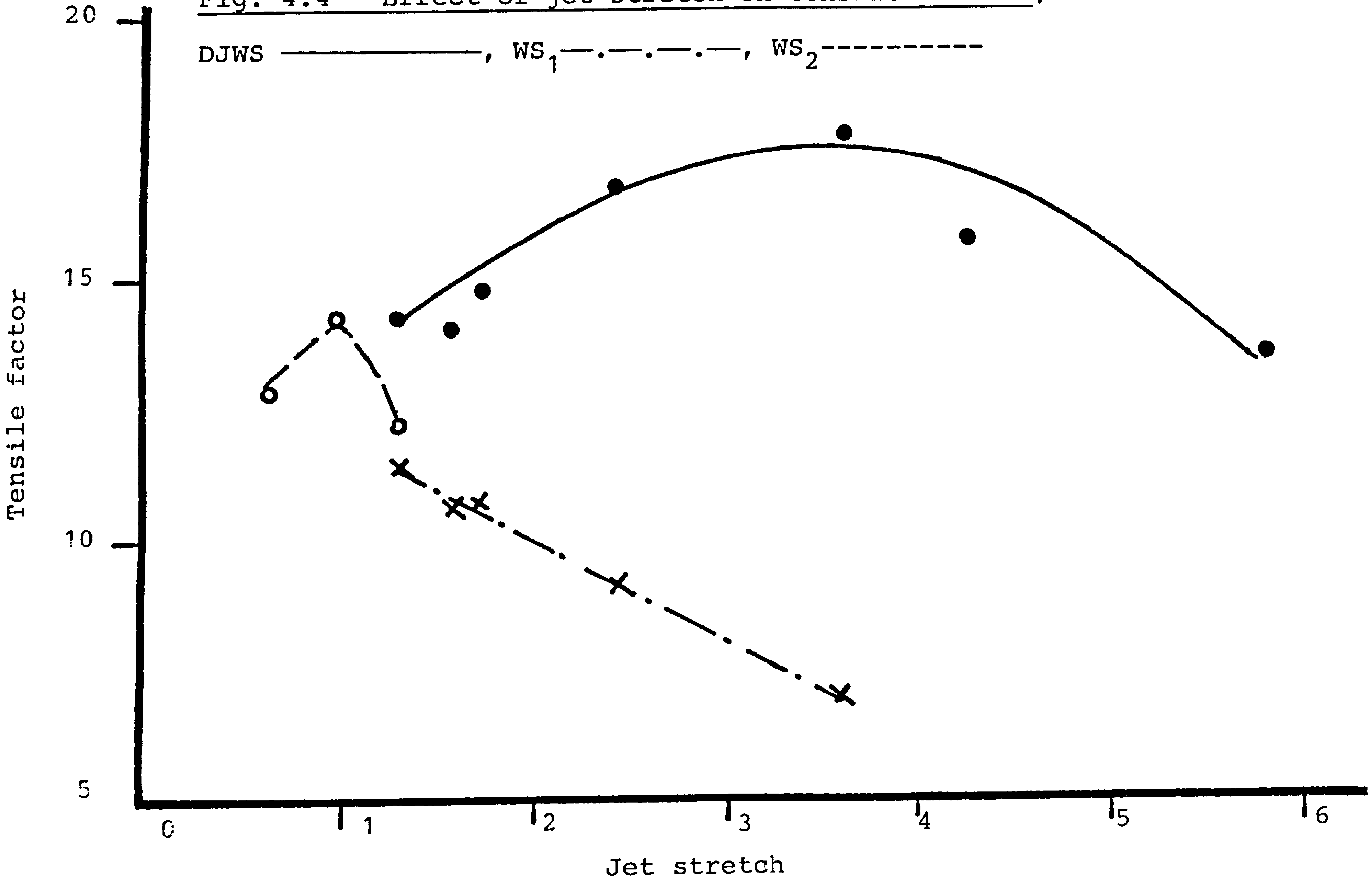


Fig. 4.4 Effect of jet stretch on tensile factors,

DJWS ————, WS_1 —.—.—.—, WS_2 ----------

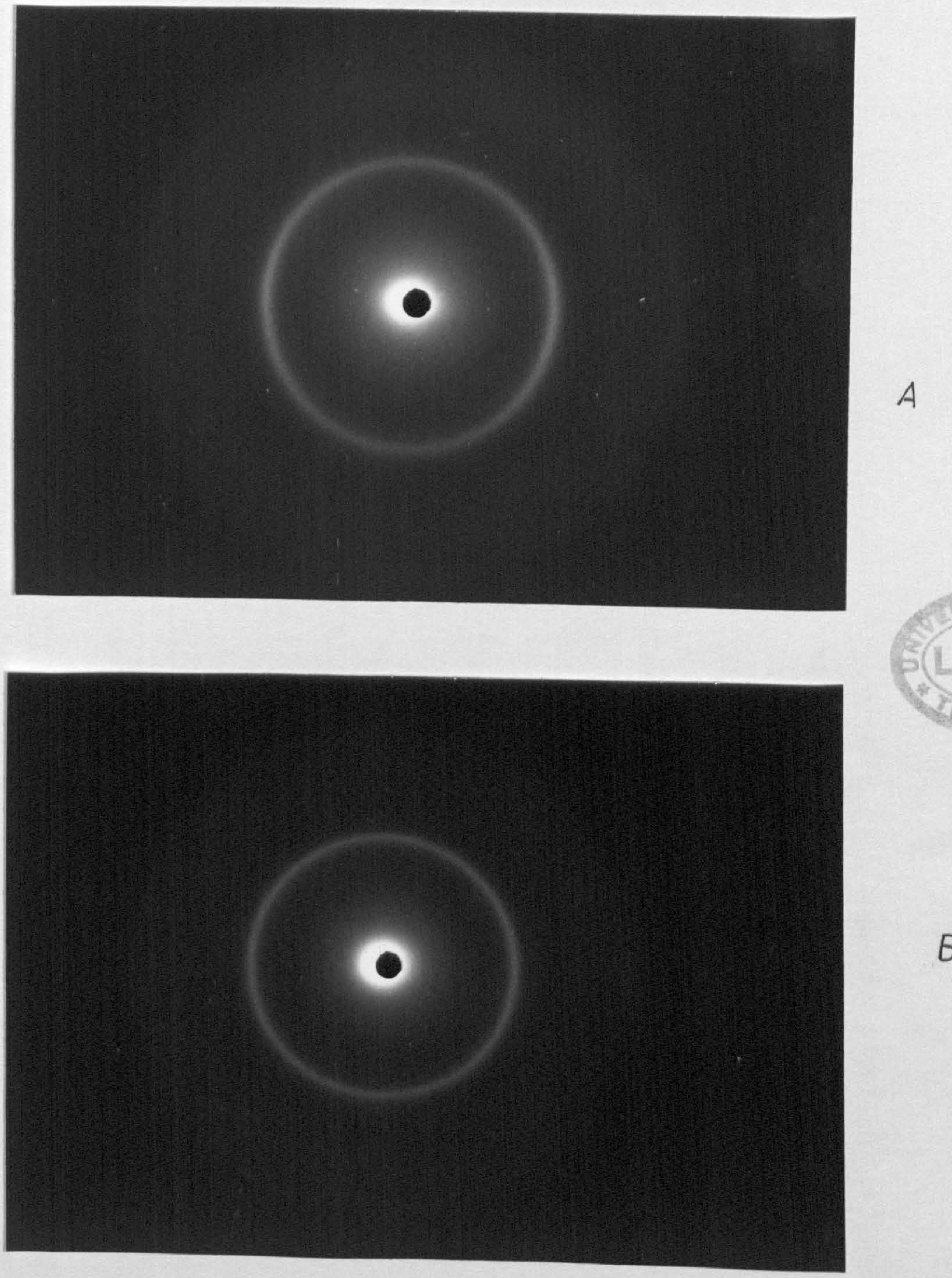


Plate 4.8 X-Ray diffraction patterns of undrawn filaments, (A) DJWS (at high jet stretch ratio), (B) WS

Table 4.6 Properties of undrawn fibre prepared by dry-jet wet-spinning

Sample No.	Pump speed r.p.m.	Jet stretch ratio	Tenacity t(g/d tex)	Extensibility E %
4-U1	11	1.57	0.50	175
4-U2	7	2.47	0.52	600
4-U3	4	4.32	0.53	725
4-U4	3	5.77	0.56	925

Spinning conditions:

- Polymer dope concentration 25% w/w
- Coagulation bath composition and temperature 50/50, $v/_{v}$, and 25°C
- First advancing reels speed 17 r.p.m.

stretch increased. It suggests that, while increasing the jet-stretch did not cause much more orientation in the fibre, it caused some sort of structural change, which increased the extensibility of the undrawn fibres remarkably. The structural changes associated with this increase in extensibility are clearly very important but the origin of the effect is not at all clear.

Table 4.7 shows the experimental conditions used and the mechanical properties of dry-jet wet-spun fibres as well as wet-spun fibres at different draw ratios (different hot stretching), and Figs. 4.5, 4.6 and 4.7 show the tenacities, the extensibilities, and the tensile factors for different draw ratios from 2 to 4. For those series of experiments wet-spinning was performed using the 100 μ hole spinneret. Conditions were chosen to give the same total yarn decitex by using, for both spinning, the same pump speed and identical first and second advancing reels (godet) speeds. As usual the tenacity increased and the extensibility decreased, in both fibres, as the draw ratio was increased, but dry-jet wet-spun fibres responded more strongly to the change of draw ratio than wet-spun fibres. For wet-spun fibres, the increase in the value of the tenacity and the decrease of the value of the extensibility is almost linear and small, while for the dry-jet wet-spun fibres at low draw ratios the changes in tenacity and extensibility are negligible, but at higher draw ratios, these changes are pronounced. However, the more interesting behaviour appeared in their tensile factors, where, as the draw ratio increased, the value of the tensile factor for wet-spun fibre decreased slightly, but for the dry-jet wet-spun fibre, these values increased. This behaviour suggests that the mechanical properties of dry-jet wet-spun fibre will be better at higher draw ratios than those at lower draw ratios, and it is possible to put more draw into this fibre. (This effect will be discussed in the next section).

4.3.3 The effect of coagulation variables

Among the more obvious variables related directly to the coagulation process are dope concentration, coagulation bath composition, and coagulant temperature. Observation of the effect of spinning bath temperatures on fibre structure in wet-spinning have been made before for a variety of different coagulating bath systems. Knudsen[86], Halbig[88], Grishina[89] and several other workers[71,84,90,91] observed improvements in fibre structure, such as reduction in the number of large voids, and a change in cross-sectional shape, and also improvements in some of the physical and mechanical properties, such as lustre, density, internal surface, tenacity, abrasion resistance, and initial modulus, if coagulating bath

Table 4.7 Comparison of effect of draw ratio on properties of dry-jet wet-spun and wet-spun yarn

Sample No.	Draw ratio	Filament count d tex		Tenacity (t) g/d tex		Extens. (E) %		Tensile factor	
		DJWS	WS	DJWS	WS	DJWS	WS	DJWS	WS
4-14	2.0	328	338	1.30	2.00	75	52.1	11.3	14.4
4-15	2.5	252	270	1.42	2.15	74	46.9	12.2	14.7
4-16	3.0	210	226	1.80	2.17	62	40.7	14.2	13.8
4-17	3.5	178	189	2.28	2.32	49	32.2	16.0	13.2
4-18	4.0	159	170	3.00	2.45	34	26.2	17.5	12.5

Spinning conditions:

- Polymer dope concentration: 25% w/w
- Coagulation bath composition: 50/50 v/v
- Jet stretch ratio: a - Dry-jet wet-spinning = 3.05 (300 μ ,10 hole)
  b - Wet-spinning = 0.71 (100 μ ,21 hole)

Fig. 4.5 Effect of draw ratio on the fibres tenacities,

DJWS ————————, WS ----------------

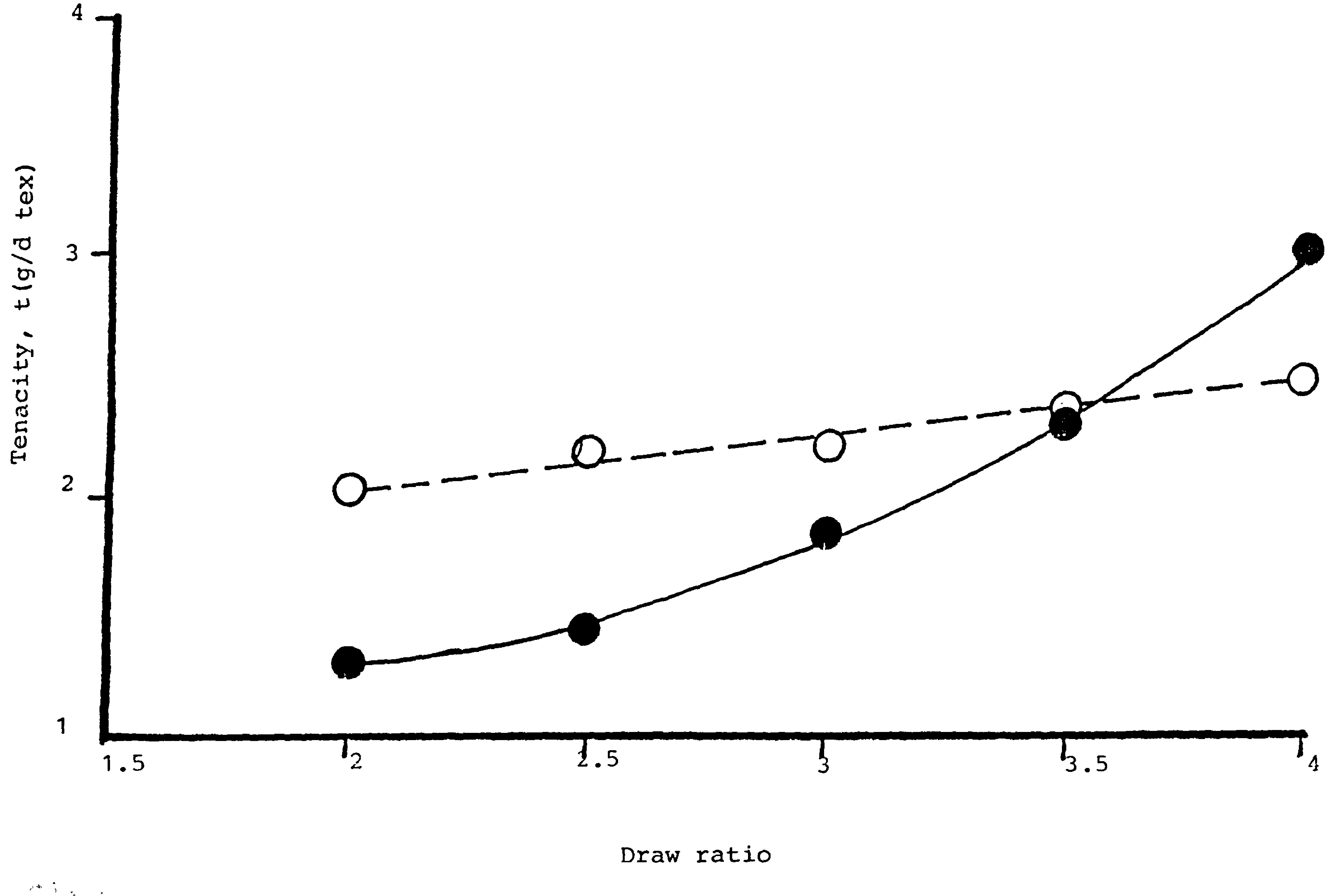


Fig. 4.6 Effect of draw ratio on the fibres extensibility, DJWS ———,WS -------

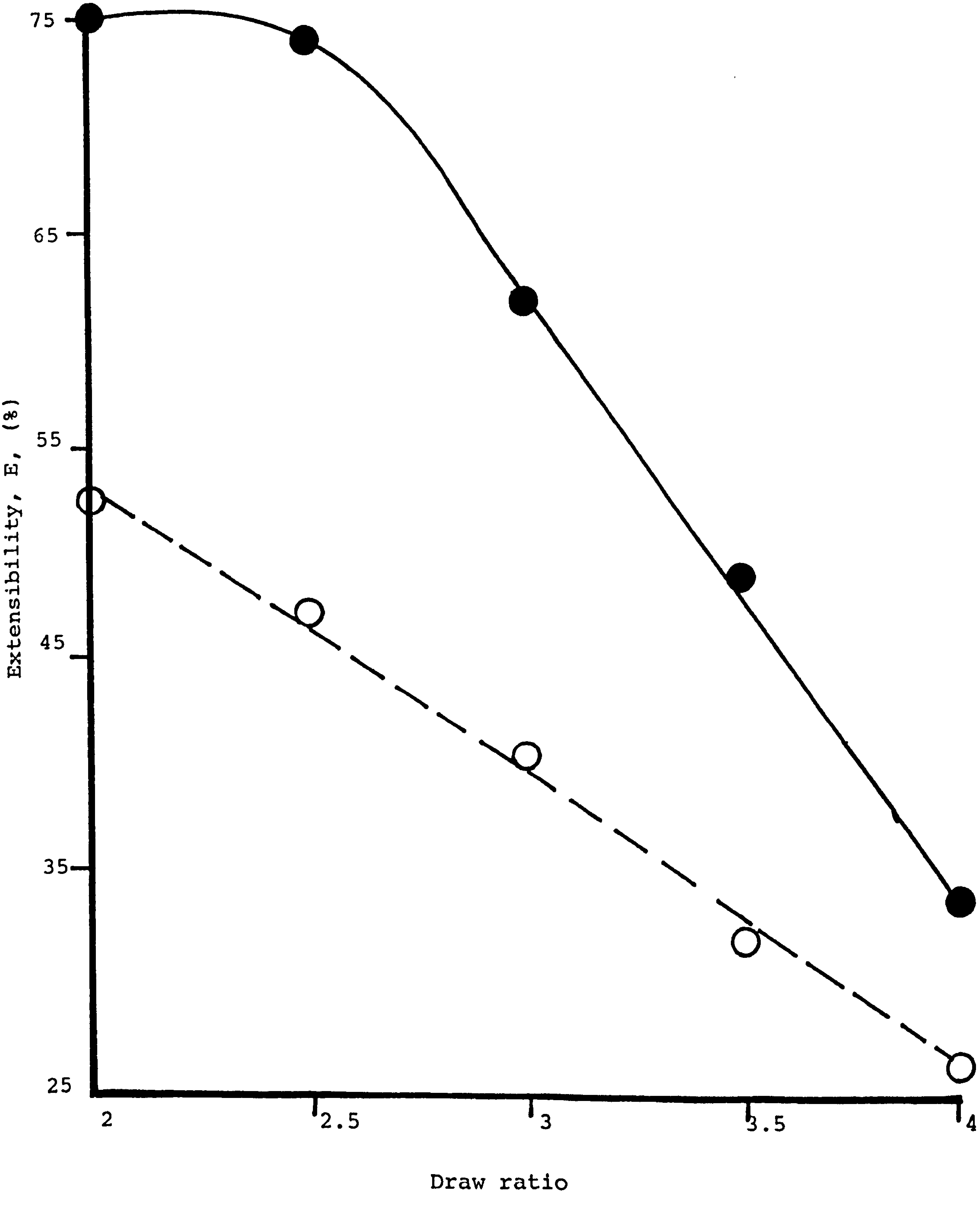
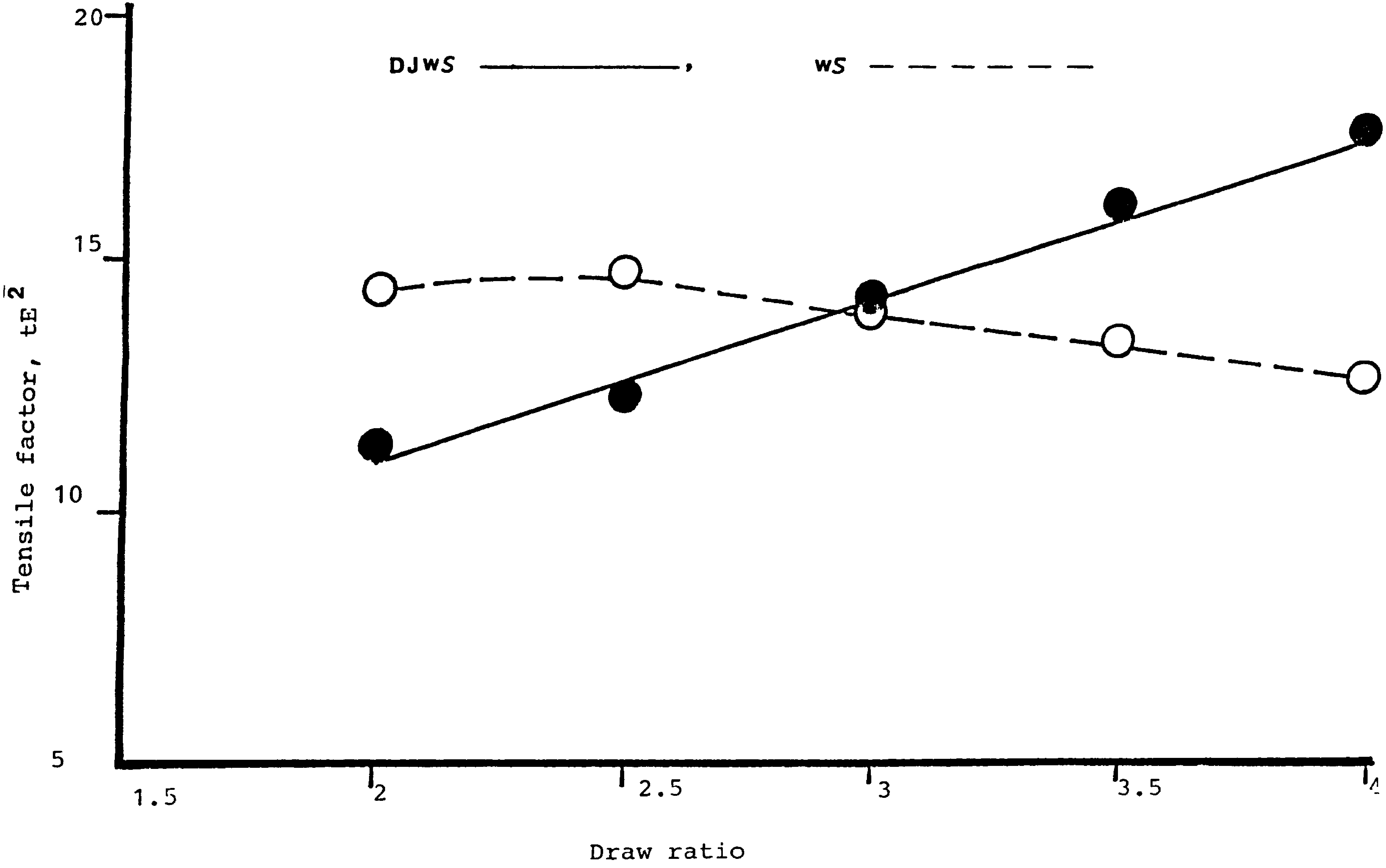


Fig. 4.7 Effect of draw ratio on the fibre tensile factor



temperatures were lowered. Craig and his colleagues[84] also confirmed some of these improvements for organic as well as for aqueous inorganic salt spinning solvents. They showed that the fibres coagulated at lower coagulating bath temperatures, in both types of coagulating baths (organic solvent/water and aqueous based solvent/water) have a smaller void size. Knudsen[86] suggested that, at lower temperatures the coagulation rate is low, which allows more time for internal adjustment of osmotic stresses, resulting in a denser fibre. In addition, slower coagulation results in less skin formation and this leads to fewer voids. But, Ovitigala[92], in his work observed different results than those of the previous workers. In his study Courtelle acrylic fibre was redissolved in DMF and spun into a DMF/water bath. As the coagulating bath temperature was raised from about 7°C to 20°C there was an increase in the value of the work of rupture of the fibres. It should be noted that the temperature range, the temperature intervals used (as shown in Table 4.8), and the polymer type used were different in the different studies.

In the present study, with a coagulating bath composition of 50/50, v/v, DMF/water, and bath temperatures varied between 20°C and 45°C, at 5°C intervals for each experiment, a progressive improvement in the mechanical properties with decreasing coagulating bath temperature was clearly apparent in dry-jet wet-spinning. (Table 4.9)

Table 4.8 Summary of different conditions used to examine effect of coagulation bath temperature on fibre properties

Temperature intervals	Coagulation bath temperature (°C)								
	10	3	0	30	0	20	30	30	7
	40	40	30	50	20	40	40	40	10
	55	70	50	70	40	60	60	60	15
	70	80	-	90	-	80	-	-	20
References	84	71	86	90	75	94	95	96	92

In wet-spinning (see Table 4.9 and Figs. 4.8 - 4.10) on the contrary the tenacity and the tensile factor gave an optimum value at a coagulating bath temperature around 30°C and then decreased at temperatures above this. A close examination of the spinning conditions in Table 4.1 and Table 4.9 indicate that the optimum values of the tenacity and the tensile factor in wet-spinning occur in the temperature range close to the pump temperature, which will be the temperature of the spinning solution as it emerges from the spinneret holes. It has been noticed that in wet-spinning, the polymer dope temperature (extrusion temperature) has a strong influence on the fibres produced. It affects the coefficient of diffusivity, which together with the power of the coagulating bath, particularly at the point of contact with the spinneret, determines how severe the skin-core effect will be in the fibre produced[97], and quite naturally, the coagulating bath temperature cannot deviate much from the extrusion temperature[98]. It suggests that, normally, the temperature of the coagulating bath for successful wet-spinning should be closely correlated with the spinning solution temperature, since the effect of temperature on the dope viscosity appears to be more important than its effect on coagulation rate, but in dry-jet wet-spinning this correlation is not necessary as the coagulating bath temperature acts independently of polymer dope temperature due to the air-gap. This behaviour allows spinning to be carried out at a

Table 4.9 Effect of coagulation bath temperature on fibre properties for dry-jet wet-spinning and wet-spinning

Sample No.	Bath Temp. T °C	t g/d tex		E %		$tE^{\frac{1}{2}}$	
		DJWS	WS	DJWS	WS	DJWS	WS
4-19	20	2.94	2.54	35.2	28.1	17.4	13.4
4-20	25	2.89	2.56	36.0	29.4	17.3	13.9
4-21	30	2.89	2.63	35.1	31.2	17.1	14.7
4-22	35	2.72	2.46	35.6	31.4	16.2	13.8
4-23	40	2.63	2.17	34.3	33.2	15.4	12.0
4.24	45	2.45	2.02	36.0	34.5	14.7	11.0

Spinning conditions:

- Average yarn count - a: dry-jet wet-spun 160 d tex
  b: wet-spun 173 d tex
- Jet stretch ratio - a: Dry-jet wet spinning 3.05
  b: Wet-spinning 0.71
- Draw ratio: 4

Fig. 4.8 Effect of coagulation bath temperature on tenacities

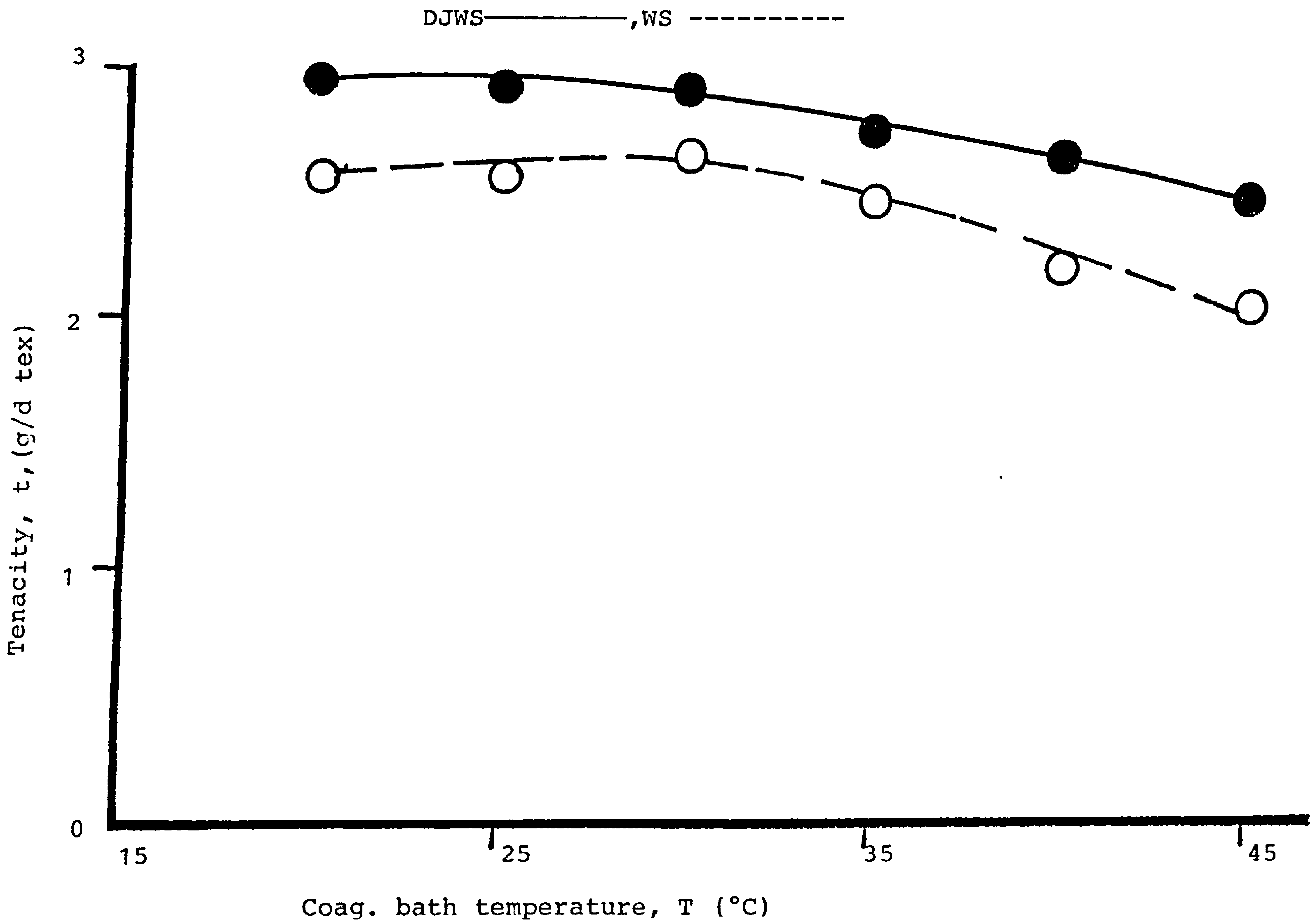
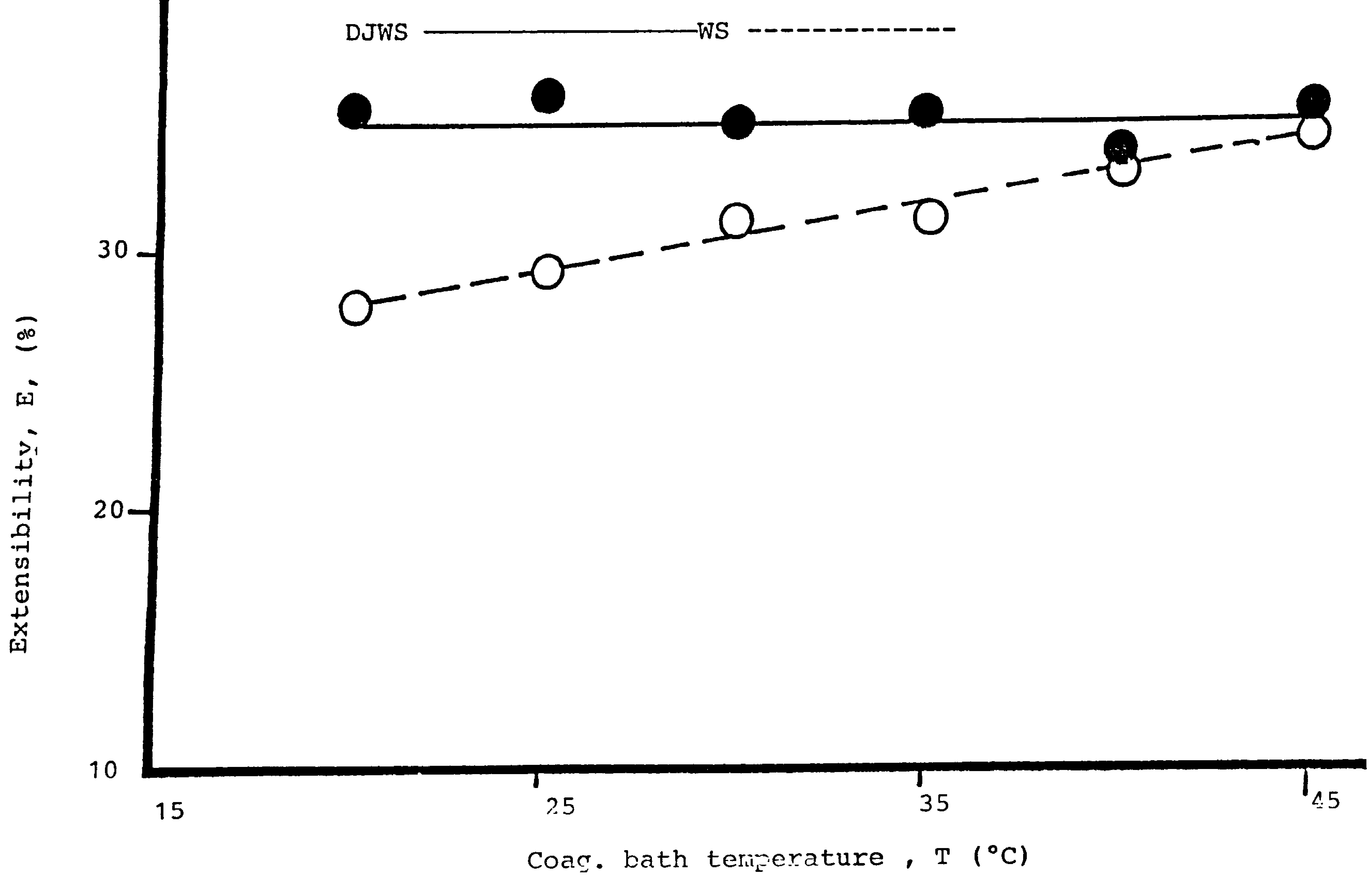


Fig. 4.9 Effect of coagulation bath temperature on extensibilities



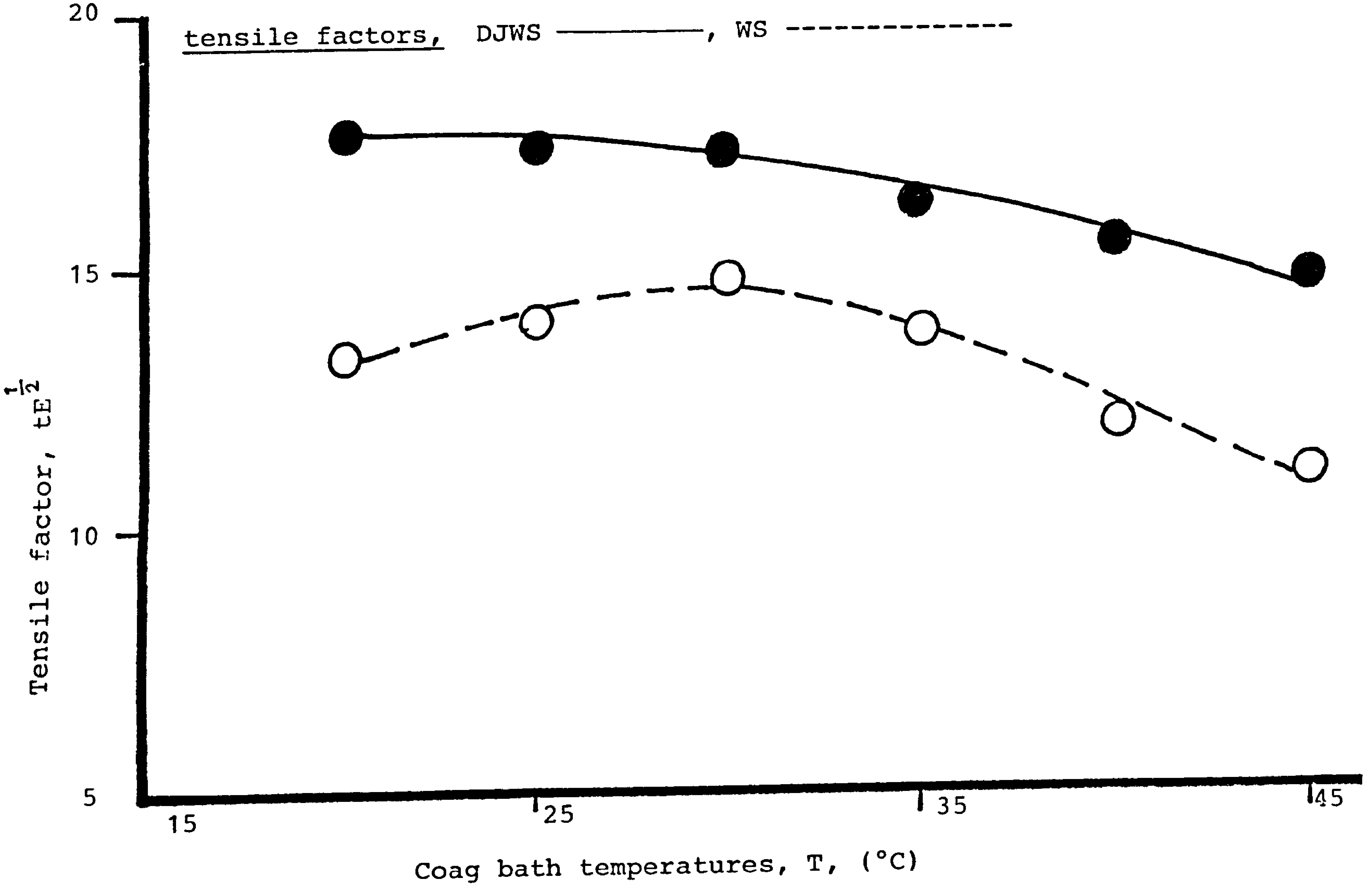


Fig. 4.10 Effect of coagulation bath temperature on tensile factors, DJWS ———, WS - - - - - - - - - - - - -

higher solids content in dry-jet wet-spinning than would be possible in wet-spinning. Interestingly, when the data (Table 4.8) of certain workers on the effect of bath temperature is examined, so large are the temperature intervals in many studies that it is possible that maxima in the relation of fibre properties to bath temperature might well have been missed. Further comparisons with earlier work are difficult since dope temperatures are rarely quoted.

Paul[78] has studied the reversible gelation of concentrated solutions of acrylic copolymers and found that the gelation tendency, as measured by gel melting point, increased as the polymer concentration increased and the co-monomer content of the polymer decreased. His observations on the effect of polymer concentration parallel those made on the influence of polymer concentration on the coagulation behaviour and hence final polyacrylonitrile fibre properties as studied by Knudsen[86]. Grobe and Meyer[85] have studied diffusion rates in DMF/water systems and found that diffusion coefficients of both solvent (DMF) and non-solvent (water) increase with decreased solid content and decreased co-monomer content.

Table 4.10 shows the effect of the polymer dope concentration on the mechanical properties of the final fibres produced by dry-jet wet-spinning and wet-spinning. Figs 4.11 - 4.13 show the effect of the polymer dope concentration on the tenacity, extensibility, and tensile factor of the fibres.

Table 4.10 Effect of dope concentration

Sample No.	Dope conc. %	Yarn count		Tenacity (t)g/d tex		Exten. (E) %		Tensile factor	
		DJWS	WS	DJWS	WS	DJWS	WS	DJWS	WS
4-25	17.5	-	122	-	1.50	-	12	-	5.2
4-26	20	131	140	1.82	2.32	31.1	17.8	10.1	9.8
4-27	22	146	148	2.15	2.64	31.0	21.9	12.0	12.4
4-28	25	154	170	2.99	2.54	30.0	20.2	16.4	11.4
4-29	28	186	195	3.03	2.11	31.9	17.2	17.1	8.8
4-30	30	193	219	2.89	2.00	32.6	16.0	16.5	8.0

Spinning conditions

- Jet stretch ratio: a - dry-jet wet-spinning 3.05 (300 μ , 10 hole)
  b - wet-spinning 0.71 (100 μ , 21 hole)
- Draw ratio: 4
- Bath composition and temperature 50/50 $v/_v$ DMF/water and 25°C±2

Fig. 4.11 Effect of polymer dope concentration on tenacities,

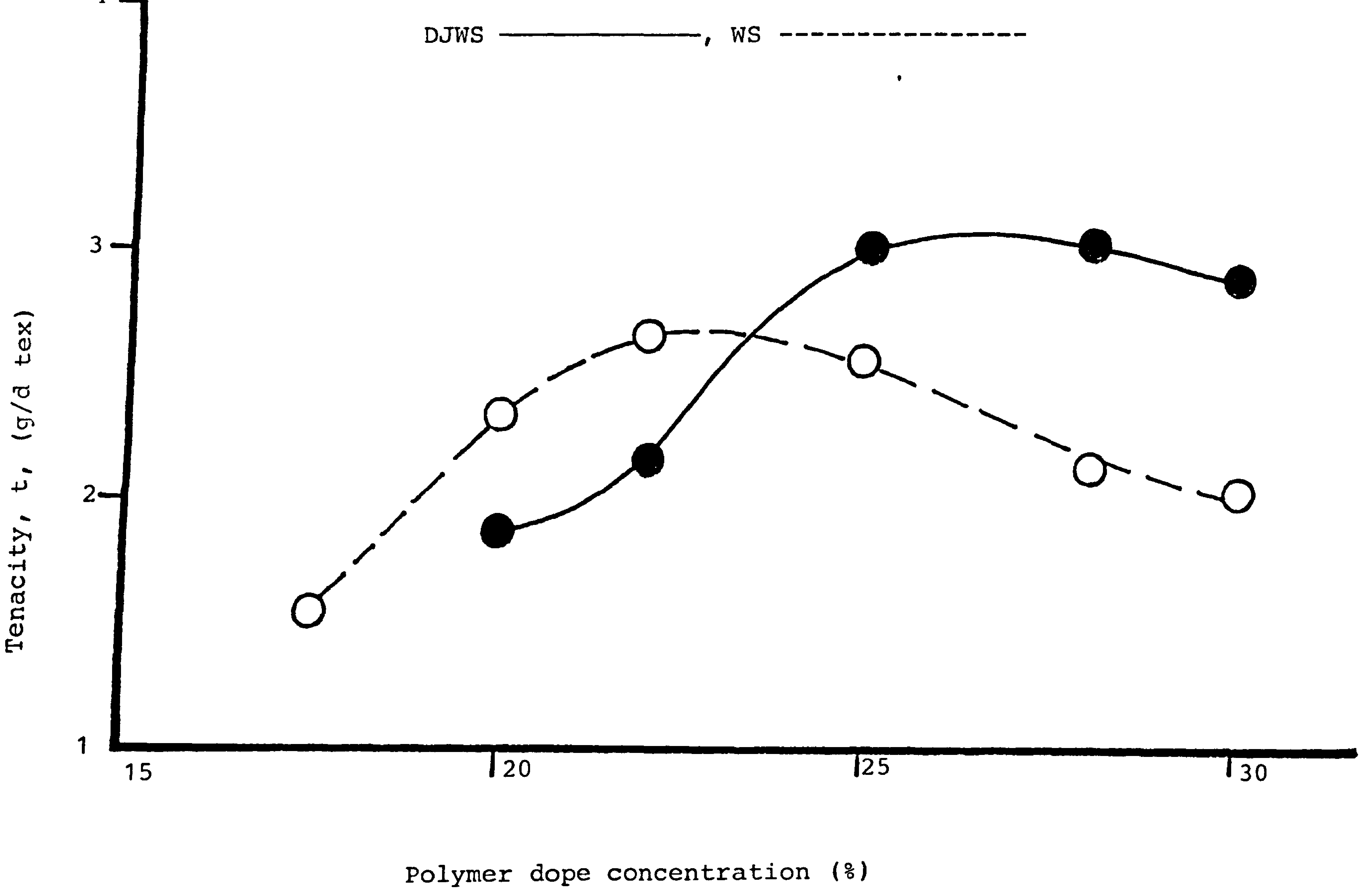


Fig. 4.12 Effect of dope concentration on extensibilities

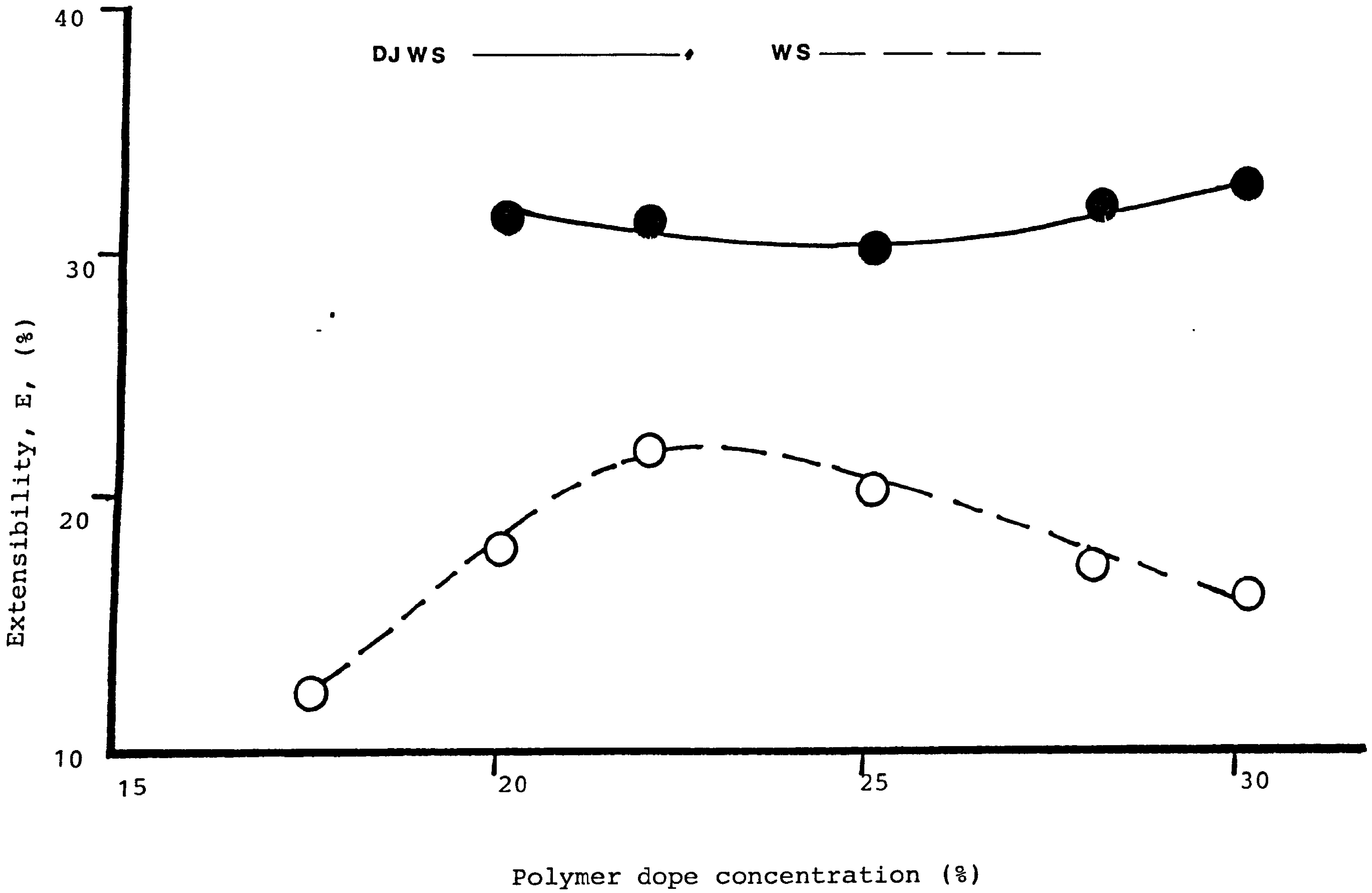
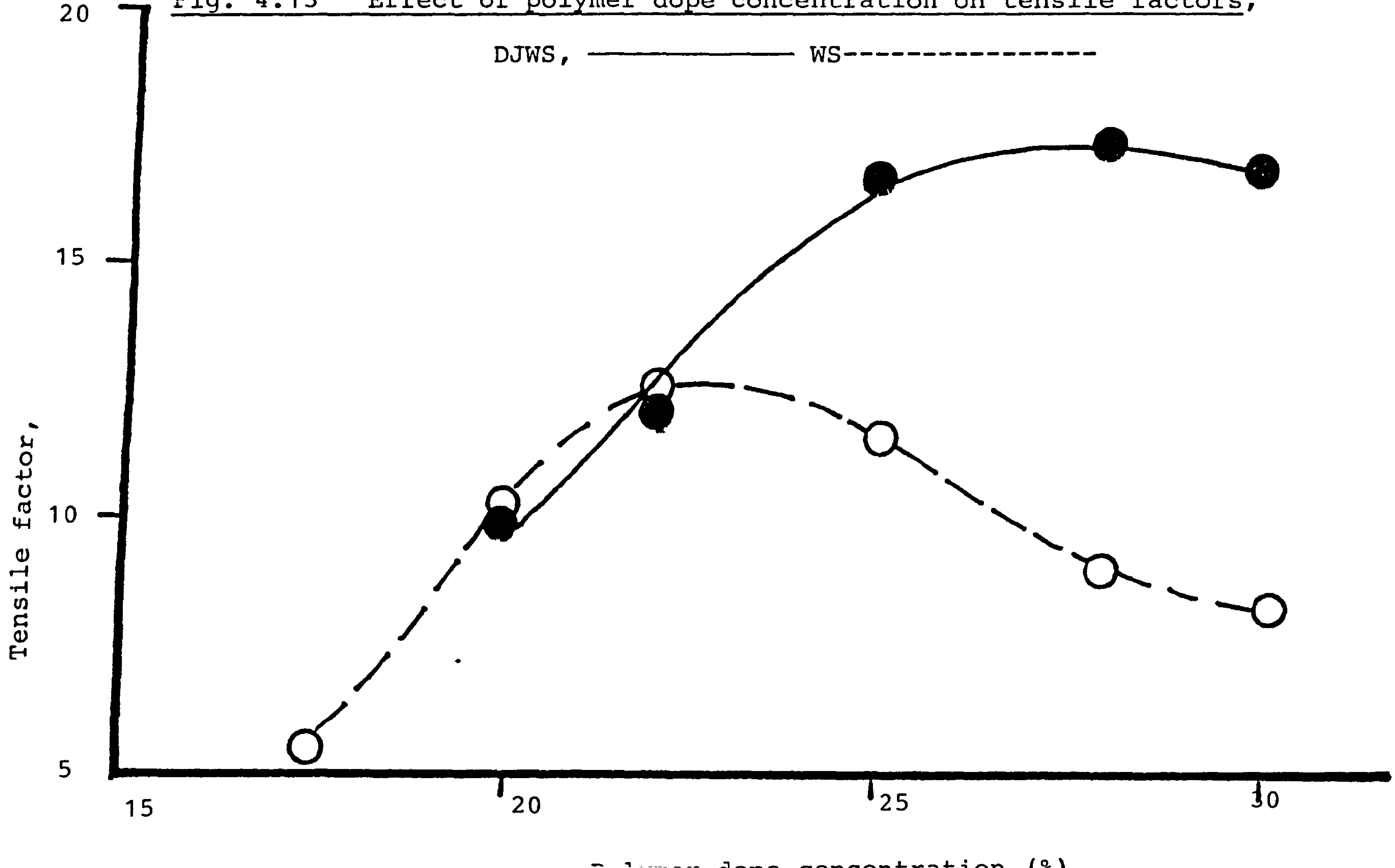


Fig. 4.13 Effect of polymer dope concentration on tensile factors,



The polymer dope concentrations were between 17.5% and 30%, w/w, though with as low a polymer dope concentration as 17.5%, because of the low viscosity of the spinning solution, it was not possible to carry on dry-jet wet-spinning. However, in studying the mechanical properties as a function of dope concentration, a consistent improvement in tenacity with increasing dope concentration was found, and almost no effect on extensibility was evident in dry-jet wet-spinning. In the case of wet-spinning the values of tenacity and extensibility became optimum around a polymer dope concentration of 23% although the effect on tenacity was more pronounced.

Table 4.11 shows the effect of spinning bath composition on the mechanical properties of the final fibres produced in dry-jet wet-spinning and in wet-spinning and Figs 4.14 - 4.16 show the mechanical properties of these fibres in relation to the spinning bath composition. These data show that the spinning bath composition was found to be a relatively inactive variable for tenacity, though it did effect the extensibility of both fibres. The tensile factor of wet-spun fibres increased with the increase of solvent in the bath and the tensile factor of dry-jet wet-spun fibre was at an optimum around 30/70 DMF/water; above 30% DMF under these conditions both the tenacity and extensibility were reduced as the DMF content increased. The improvement in the extensibility of the wet-spun fibres with increasing solvent in the coagulating bath can be regarded as due to the presumably lower coagulation rate. By slowing down coagulation, more time is allowed for the viscoelastic effects to relax before significant solidification occurs. In effect this allows a better separation of the relaxation of the die-swell and the coagulation. Not so easily explained is the particular noticeable decline in yarn extensibility in the dry-jet wet-spun samples when the solvent content in the bath exceeds 30%. One possibility is that the slower coagulation leaves the filaments in the bath with little greater resistance to deformation than the liquid thread-line. Under these conditions, it can be imagined that some of the jet-stretch may take place in the bath rather than, as before, in the air-gap. Such stretching in the bath, accompanied by the coagulation process would probably cause some impairment of fibre structure, relative to that obtained at lower bath solvent concentrations. In other words, in dry-jet wet-spinning, if this view is correct, it is important that sufficiently rapid coagulation occurs on entering the bath to raise the viscosity of the coagulating filament to such a value that only in the air-gap can attenuation of the filaments occur.

Table 4.11 Effect of bath composition on mechanical properties

Sample No.	bath comp. DMF/water v/v	t g/d tex		E %		$t E^{\frac{1}{2}}$	
		DJWS	WS	DJWS	WS	DJWS	WS
4-14	20/80	3.05	2.43	27.87	15.12	16.10	9.45
4-15	30/70	3.04	2.44	31.15	18.22	16.97	10.42
4-16	40/60	2.89	2.41	29.55	22.70	15.71	11.48
4-17	50/50	2.81	2.41	26.85	27.34	14.56	12.60
4-18	60/40	2.59	2.37	22.75	28.17	12.35	12.57

Spinning conditions

- Average yarn count - a: dry-jet wet-spun 158 d tex
  b: wet-spun 170 d tex
- Other conditions chosen as described under Table 4.9

Fig. 4.14 Effect of bath composition on tenacities, DJWS ——— WS ----------

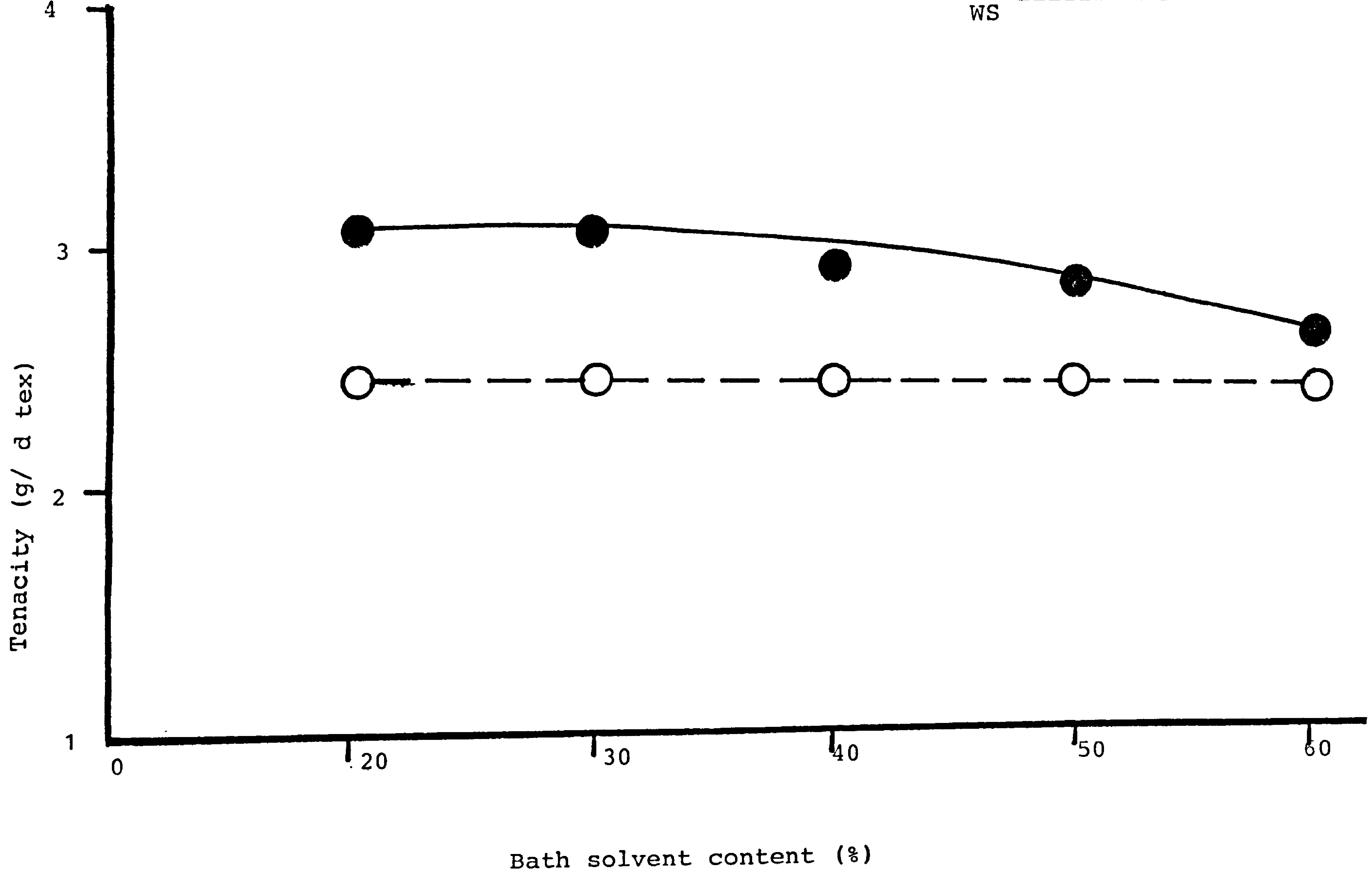


Fig. 4.15 Effect of bath concentration on extensibilities, DJWS ——————
WS ----------

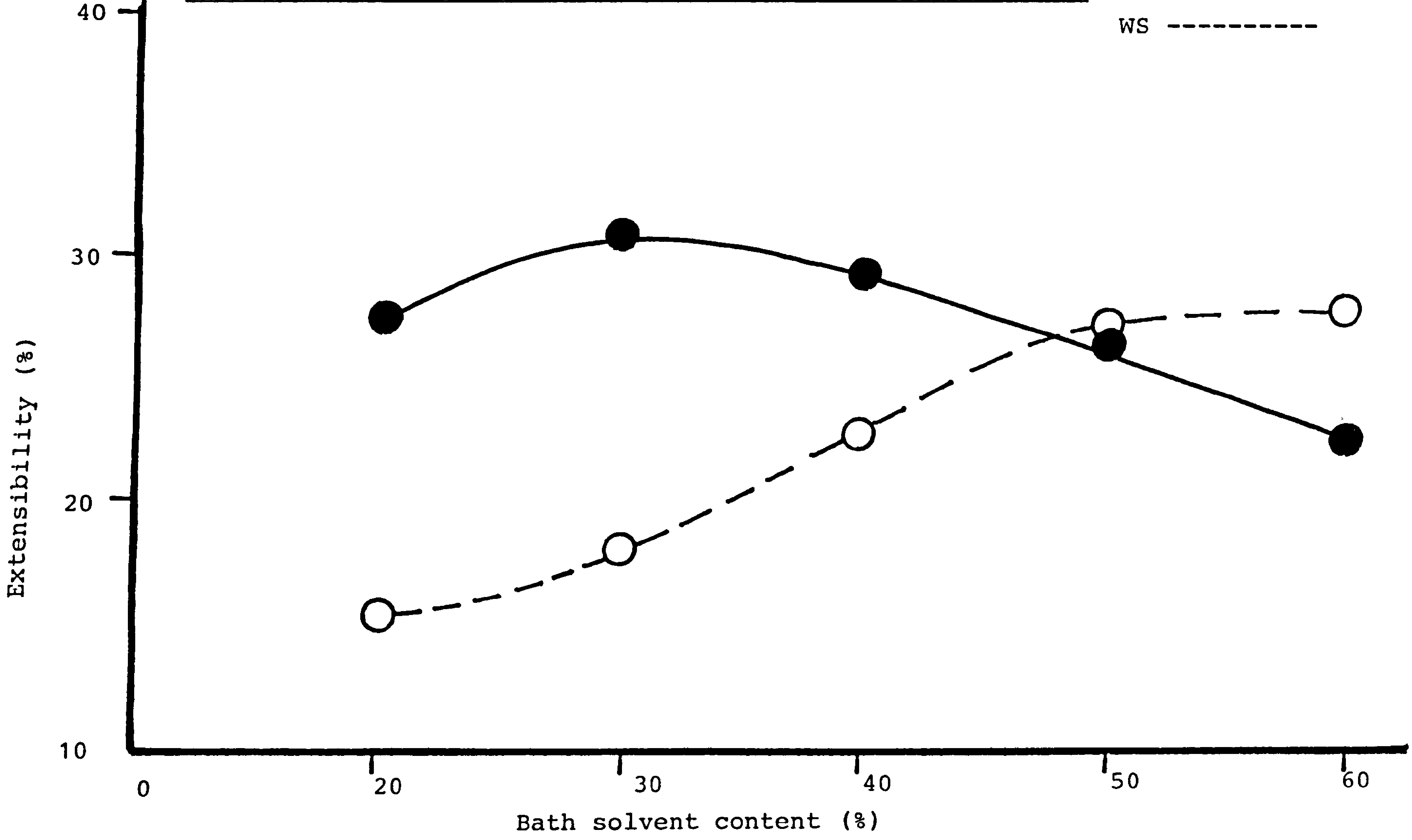
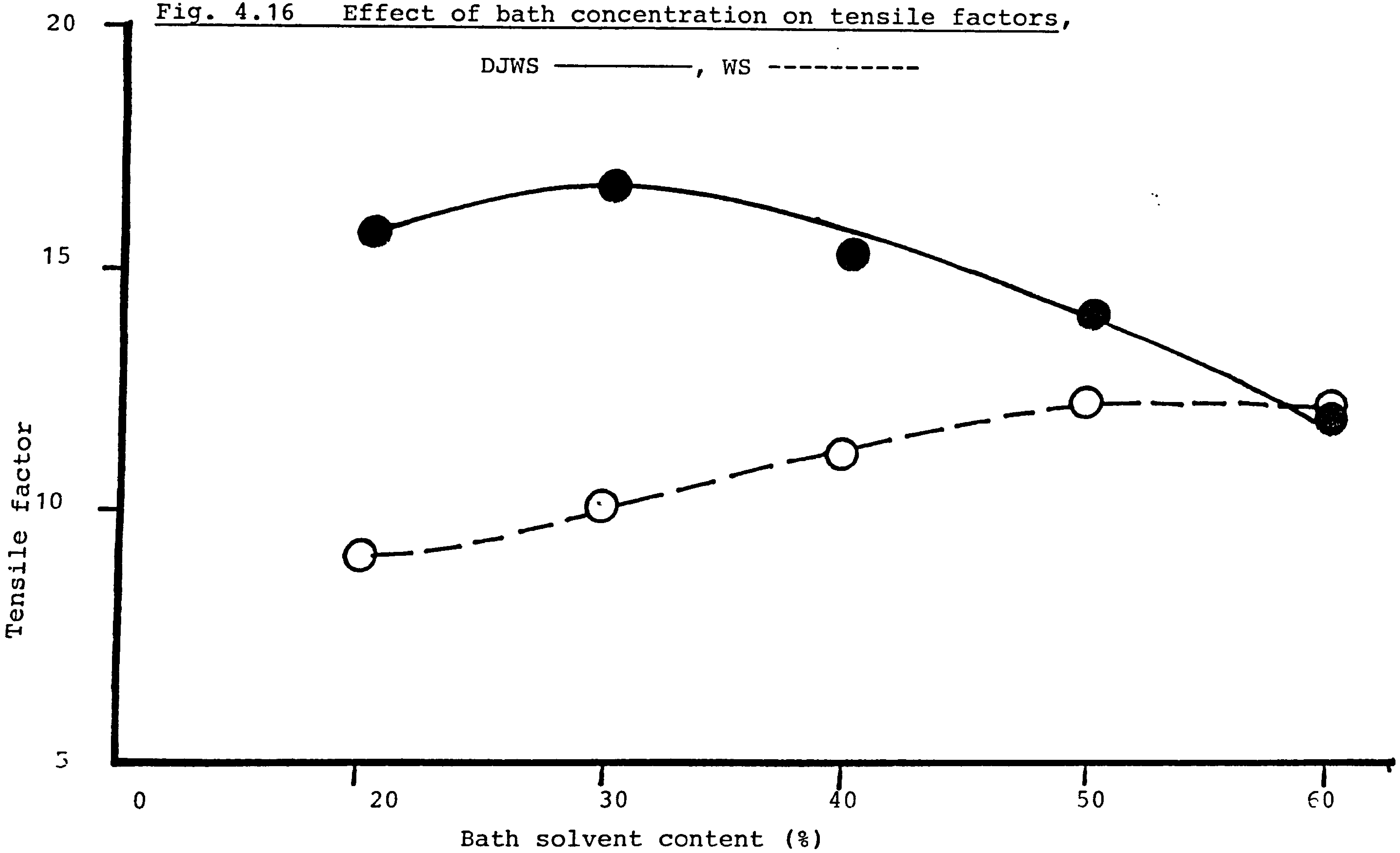


Fig. 4.16 Effect of bath concentration on tensile factors,



CHAPTER 5. DRY-JET WET-SPINNING STUDIES AT HIGHER SPEEDS

5.1 Introduction

The properties of the final fibre depend strongly on the processing methods and the specific conditions. Sometimes the processing conditions have an even stronger influence on the final product properties than do the changes in polymer characteristics. It has been shown in the previous section that the dry-jet wet-spinning process has a pronounced influence on the fibre properties and structural features. Its influences are mainly due to equipment variables rather than coagulating variables, and it was shown that the fibre properties became much improved as the speed of the operation was increased. The operational speed could be increased either in the coagulating bath, by increasing the jet stretch, or in the subsequent stages during hot drawing.

The effect of jet stretch was discussed, and it was found that as the jet stretch ratio increased, the extensibility of the drawn fibre increased up to a maximum value and then decreased. The effect of hot draw ratio was discussed only up to a certain value as above that value it was almost impossible to draw wet-spun fibres. On the other hand, whatever type of fibre one aims for, the fibre should be drawn to its practical maximum; this means drawing only as much below the breaking draw ratio as is necessary to secure a reasonable process continuity

For these reasons, it was decided to study the dry-jet wet-spinning process at high spinning speeds. Of course, in this series of experiments, the wet-spinning process was omitted as it was not possible to carry out wet-spinning at this speed. In these experiments attempts were made to produce dry-jet wet-spun fibres under spinning conditions which were more suitable for this process, so many of the factors were different from those in the previous section.

The factors which were examined in these series of experiments were; air-gap distance between spinneret surface and coagulation liquid level, hot draw ratio at high draw ratios, drying temperature, and drawing at high temperatures in air. After these series of experiments were done, the capability of the dry-jet wet-spinning process for the production of high tenacity acrylic fibre was examined.

5.2 Experimental

5.2.1 Preparation of fibre samples

The acrylonitrile copolymer used in this study was Courtelle acrylic fibre with the specification mentioned in Section 2.2.1. The polymer was dissolved in DMF to give a solution containing 23% polymer by weight. The methods of dope preparation and fibre production were essentially the same as those described in Section 2.2. The air-gap distance between the bottom surface of the spinneret and coagulation liquid level, the temperature of the dryer rolls (chrome rollers and hot plate), and the speed of the second advancing reels were used as independent variables. The spinning and testing conditions are listed in Table 5.1.

Table 5.1 Spinning and testing conditions

Fixed conditions	
Polymer dope concentration	23% w/w
Pot temperature	25°C(±1)
Pump temperature	22°C(±1)
Nitrogen pressure	0.5 Atm
Pump speed	3 r.p.m.
*Spinneret size	500 micron with 6 holes
Coagulation bath temperature	22°C(±1)
Hot draw bath temperature	95°C(±2)
First advancing reel speed	6 r.p.m.
Jet stretch ratio	3.4
Coagulation bath composition	30/70 v/v,DMF/water
Test conditions	
Sample length	20 m m
Sample speed	2 cm/min = 100%/min
Variable conditions	
Air-gap distance	1 cm - 8 cm
**Drying temperature	25°C,106°C,138°C
Second advancing reel speed	24 r.p.m. - 72 r.p.m.

* For samples given a subsequent drying in air the 300μ spinneret was used.

** In some cases, yarn was further drawn at 185°C

5.3 Results and discussion

5.3.1 Effect of the air-gap (interlayer air distance)

Table 5.2 shows the effect of the interlayer air distance on final fibre properties in the dry-jet wet-spinning and Figs. 5.1,5.2 and 5.3 show tenacity, extensibility, and tensile factor for different air gaps from 1 cm up to 8 cm. Beyond 8 cm, it was not possible to carry out the spinning process, because of occasional breakage of some of the liquid thread-lines and also because of adhesion of some neighbouring filaments to each other in the interlayer air region before reaching the liquid level of the coagulating bath. Both the tenacity and the extensibility curves gave optimum values at an interlayer air distance of 4 cm, and then both values decreased as the air gap increased. However the increase in the tenacity value up to a 4 cm air-gap was much bigger than the decrease in its value beyond 4 cm., but the extensibility curve was quite different. The extensibility of fibres produced at interlayer air distances between 1 cm. and 4 cm was almost unchanged and after that decreased sharply. This behaviour could indicate that due to the increasing air-gap, the die-swell effect is increasingly removed from the filaments up to a certain distance and this change improves fibre properties. But as the air-gap is increased, this benefit could be suppressed by other factors such as the slightly more irregular flow observed in the liquid

Table 5.2 Effect of air-gap on fibre properties

Sample No	Air-gap cm	Tenacity t g/d tex	Extensibility E %	Tensile factor $tE^{\frac{1}{2}}$
5-1	1	4.41	15.8	17.53
5-2	2	4.36	15.9	17.39
5-3	3	4.67	16.1	18.62
5-4	4	4.77	16.2	19.02
5-5	5	4.71	15.9	18.78
5-6	6	4.65	14.6	17.77
5-7	8	4.62	13.9	17.22

Spinning conditions:

Hot draw ratio = 7
Drying temperature = 90°C(±4)
Average yarn count = 131 d tex

Fig. 5.1 Effect of the air-gap on tenacity

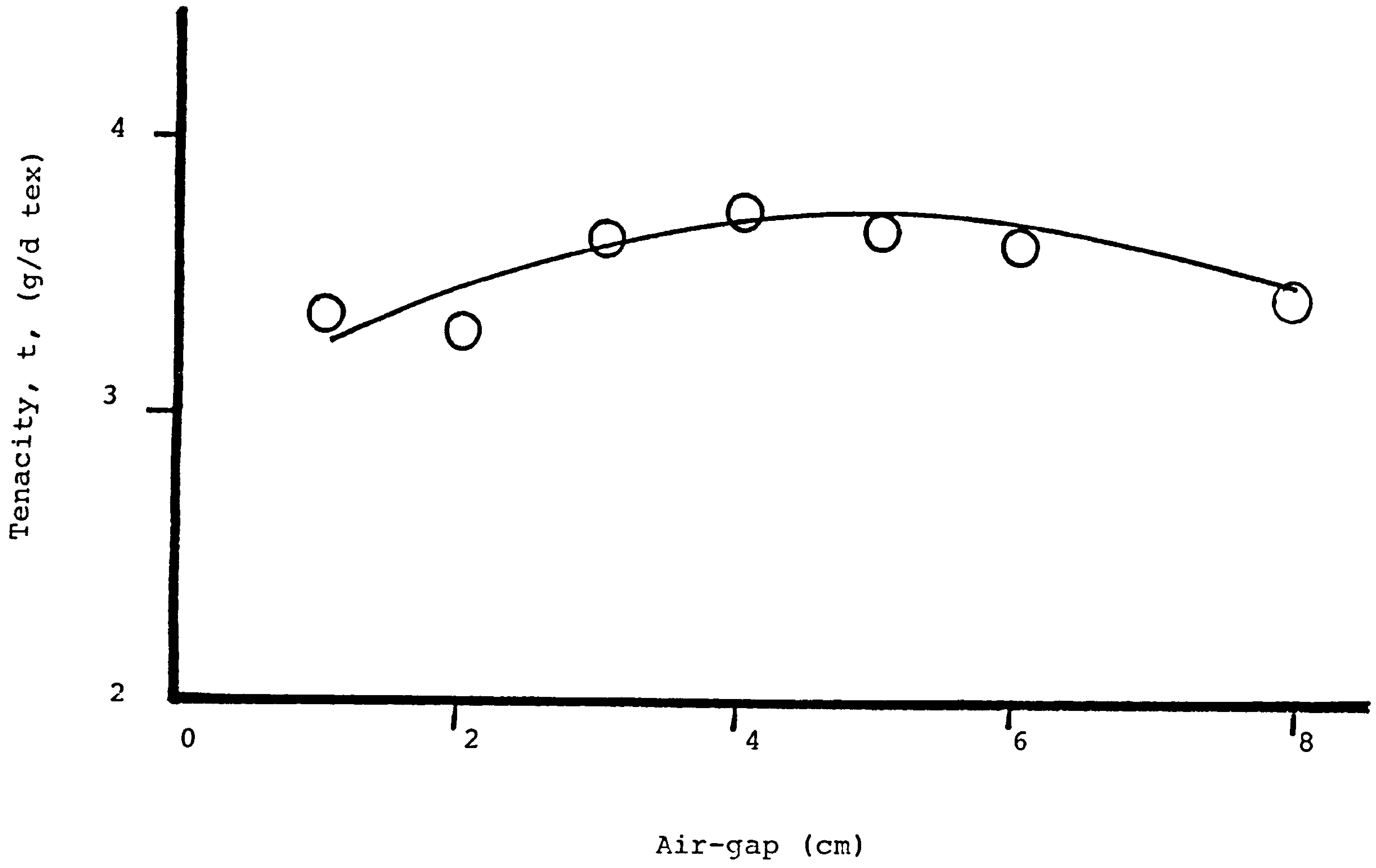


Fig. 5.3 Effect of the air-gap on extensibility

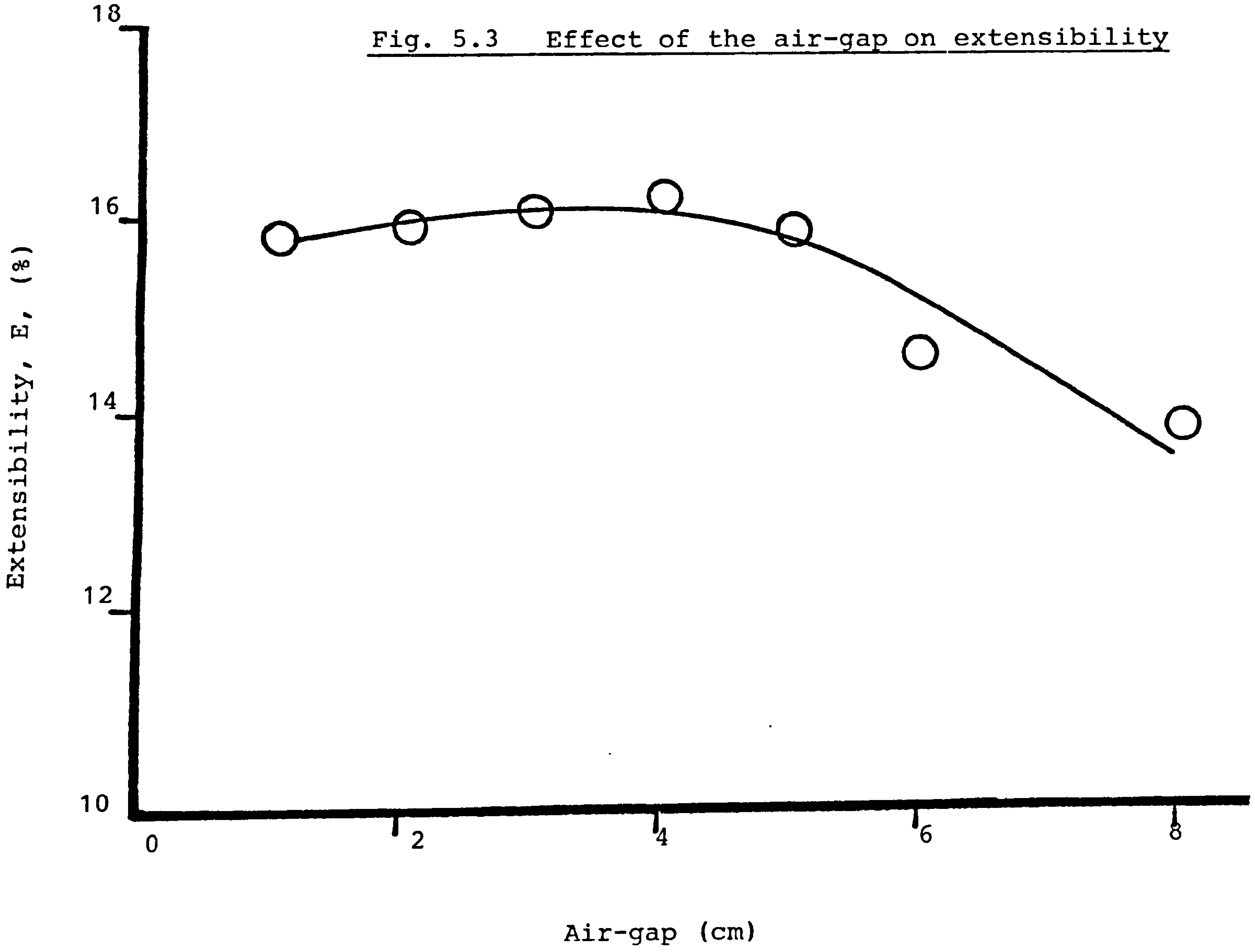
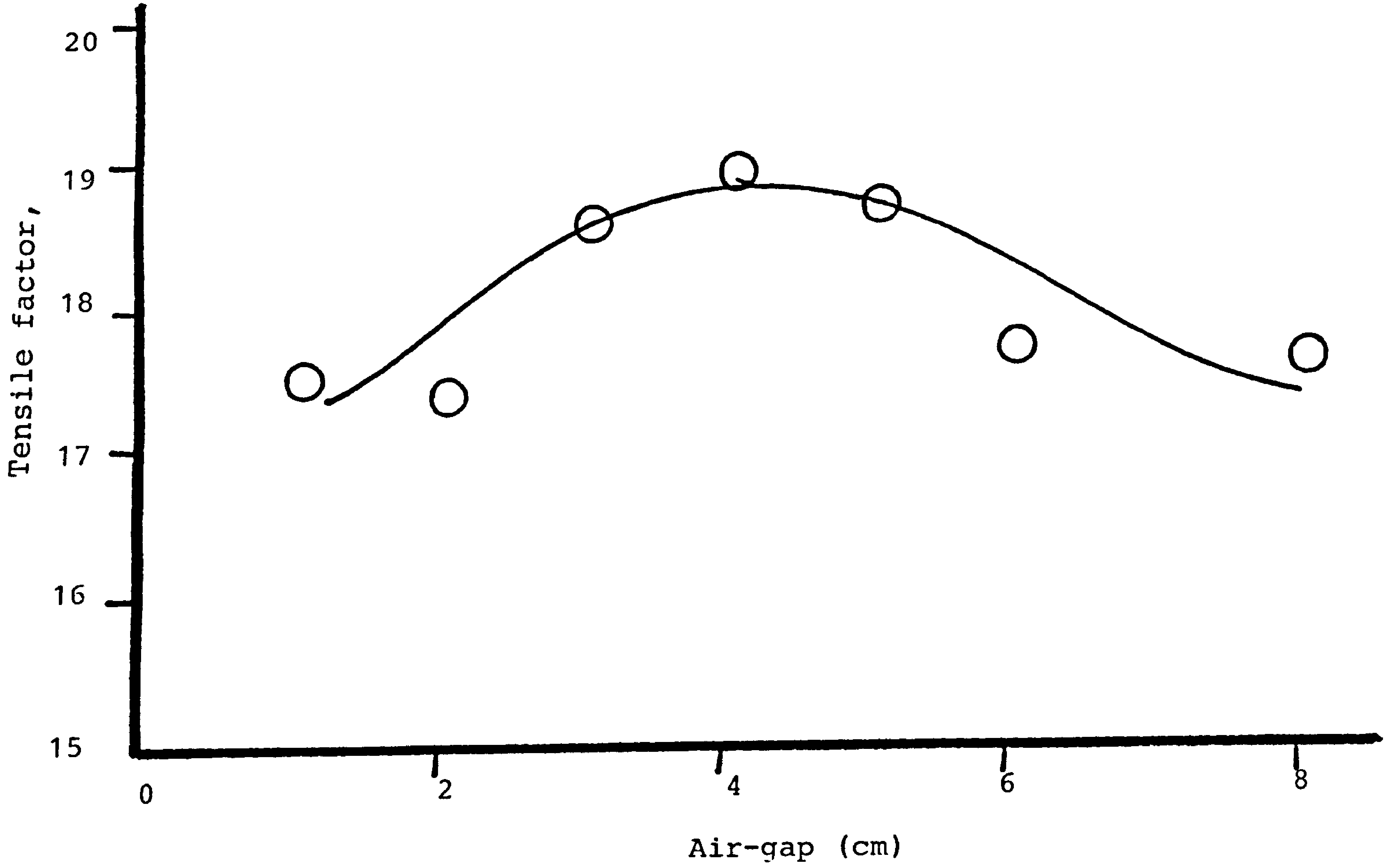


Fig. 5.2 Effect of the air-gap on the tensile factor



threadlines and the greater vibration, and these factors now cause some defects in fibre properties and structure. It seems that this optimum occurs at a distance where the die-swell has been completely relaxed. There is also the possibility that at the larger air-gaps the outer skin of the freshly formed filament could become thicker which could cause irregularity in the solidification process of the whole filament in the coagulating bath. Another explanation could be an uneveness in the distribution of the stretch force in this zone and subsequently the filament structure would be more irregular. It was noticeable that the c.v.% calculation for filament count (d tex) above and below the 4 cm air-gap indicated that those fibres produced with interlayer air distance larger than 4 cm had the more irregular counts (d tex). (See Table 5.3)

Table 5.3 Filament irregularity at different air-gaps

Sample No.	Air-gap cm.	Average d tex	S.D.	C.V.%
5-1	1	131.6	2.02	1.53
5-2	2	132.4	4.33	3.27
5-3	3	131.2	1.48	1.13
5-4	4	130.7	2.05	1.57
5-5	5	131.6	4.76	3.62
5-6	6	131.4	8.00	6.08
5-7	8	130.3	6.98	5.35

Spinning conditions: As shown under Table 5.2

5.3.2 The effect of draw ratio

It has been claimed in several patents[8,38,59] that, dry-jet wet-spun fibres are capable of accepting a greater draw ratio than wet-spun fibres. Also, as discussed in the previous section, there is a direct relation between amount of draw ratio and the value of the tensile factor. To study this relation at the higher draw ratios, a series of experiments were carried out with the dry-jet wet-spinning process and six samples were prepared at different draw ratios from 3 to 8. Table 5.4 shows the effect of draw ratio on the mechanical properties of the final fibres in dry-jet wet-spinning and Figs. 5.4, 5.5 and 5.6 show the tenacity, extensibility and tensile factor in relation to draw ratio. It is obvious that as the draw ratio was increased the value of the extensibility decreased and the values of tenacity and tensile factor increased. However, between 3 and 5 times draw ratio, the change in the tenacity and extensibility are significant but, beyond this draw ratio, the tenacity increases very slowly and the change of extensibility is almost negligible. This indicates that a dry-jet wet-spun fibre will develop its mechanical properties at a medium draw ratio and the orientation of polymer molecules in the fibre takes place mainly, in this region of draw ratio. On the other hand as a higher draw ratio has less effect on the extensibility, it makes it possible to put more draw into the fibre without any significant effect on its mechanical properties.

Table 5.4 Effect of draw ratio on properties of dry-jet wet-spun filaments

Sample No	Draw ratio	Yarn count d tex	Tenacity t g/d tex	Extensibility E %	Tensile factor $tE^{\frac{1}{2}}$
5-8	3	305	2.62	33.5	15.2
5-9	4	228	3.32	22.1	15.6
5-10	5	189	3.80	18.2	16.2
5-11	6	150	4.14	16.8	17.0
5-12	7	129	4.41	16.1	17.7
5-13	8	111	4.70	16.2	18.9

Spinning conditions:

Air-gap = 2.5 cm ± 0.2
Drying temperature = 100°C ± 4

Fig. 5.4 Effect of drawing on tenacity

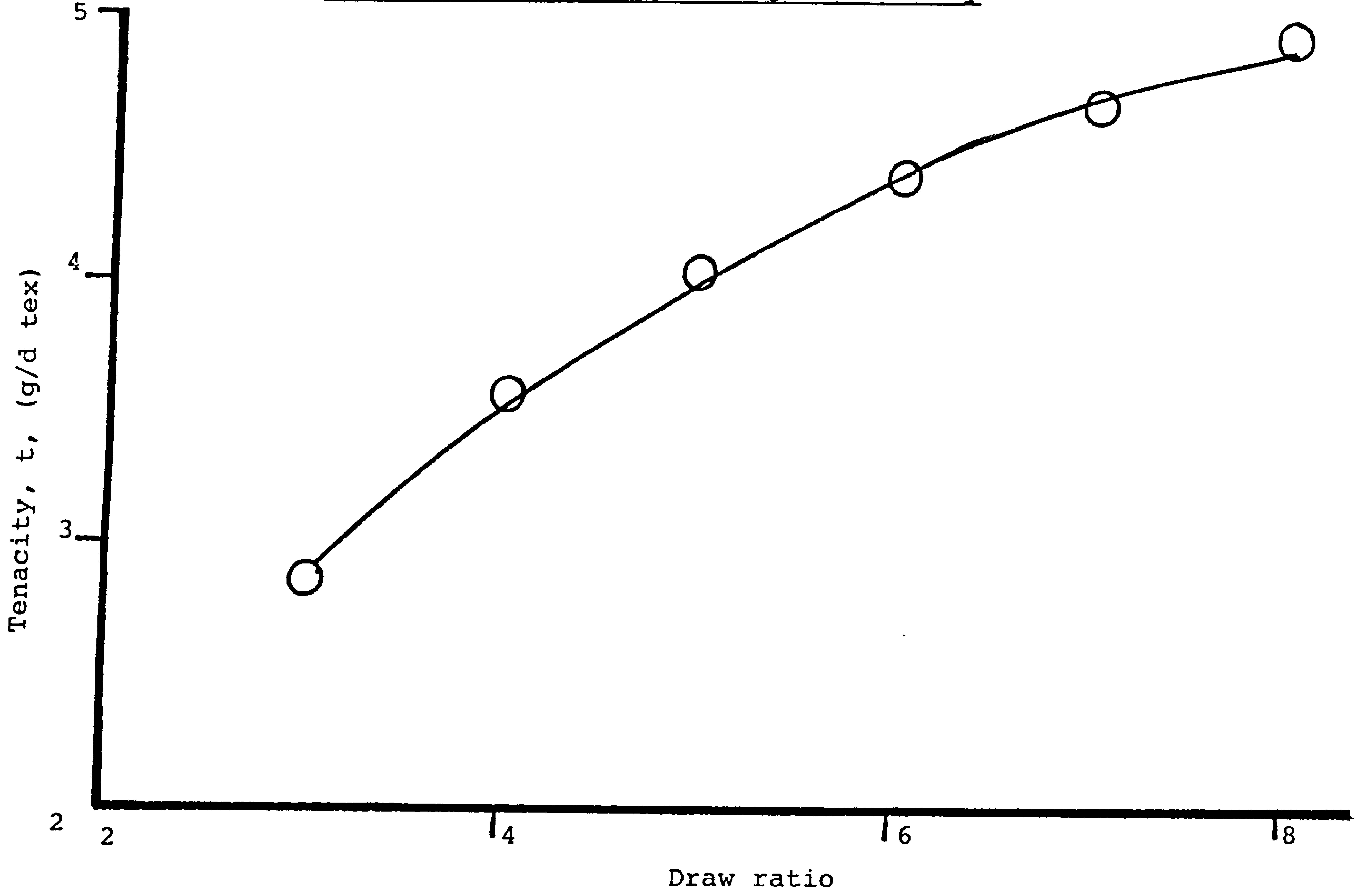


Fig. 5.5 Effect of drawing on extensibility

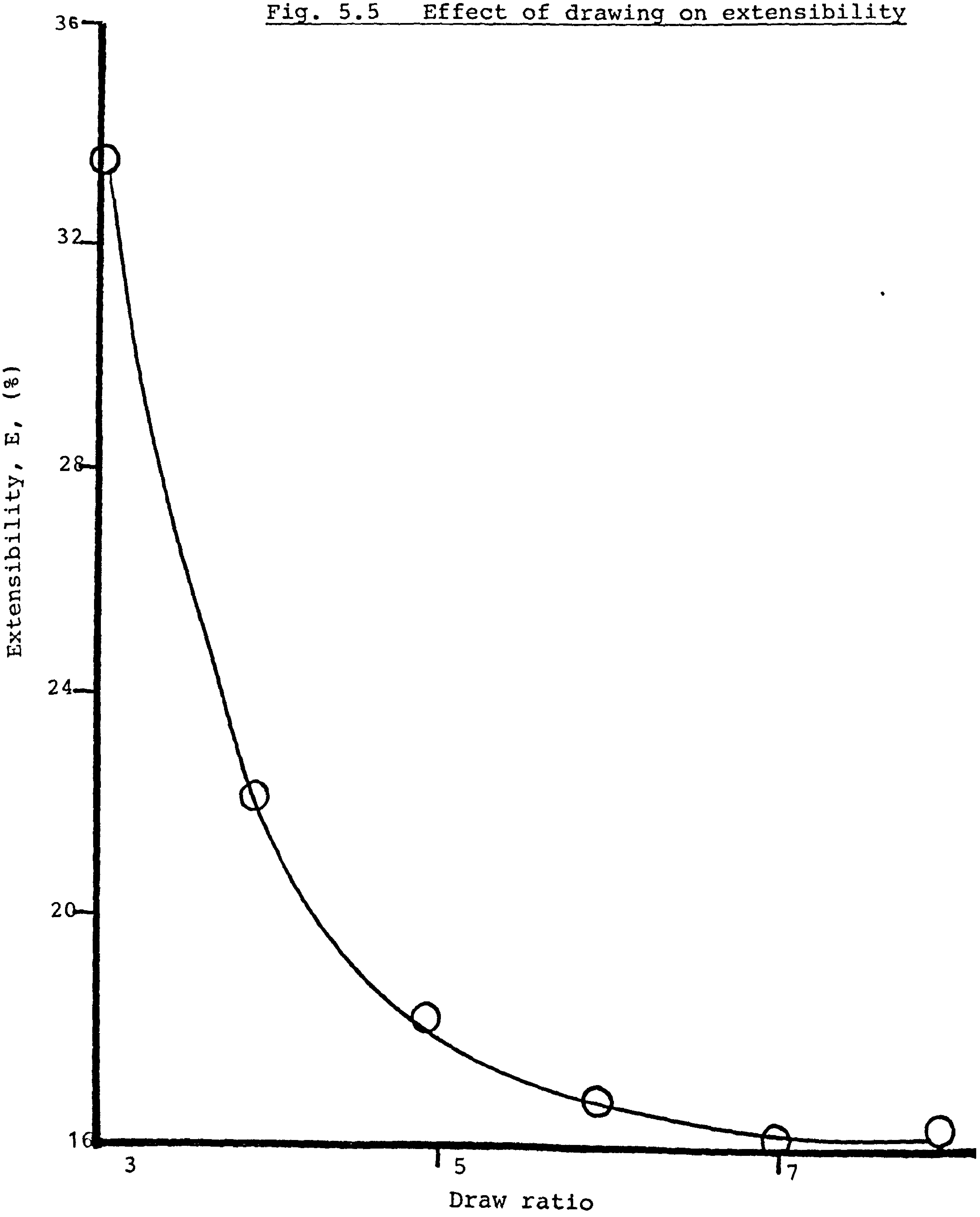
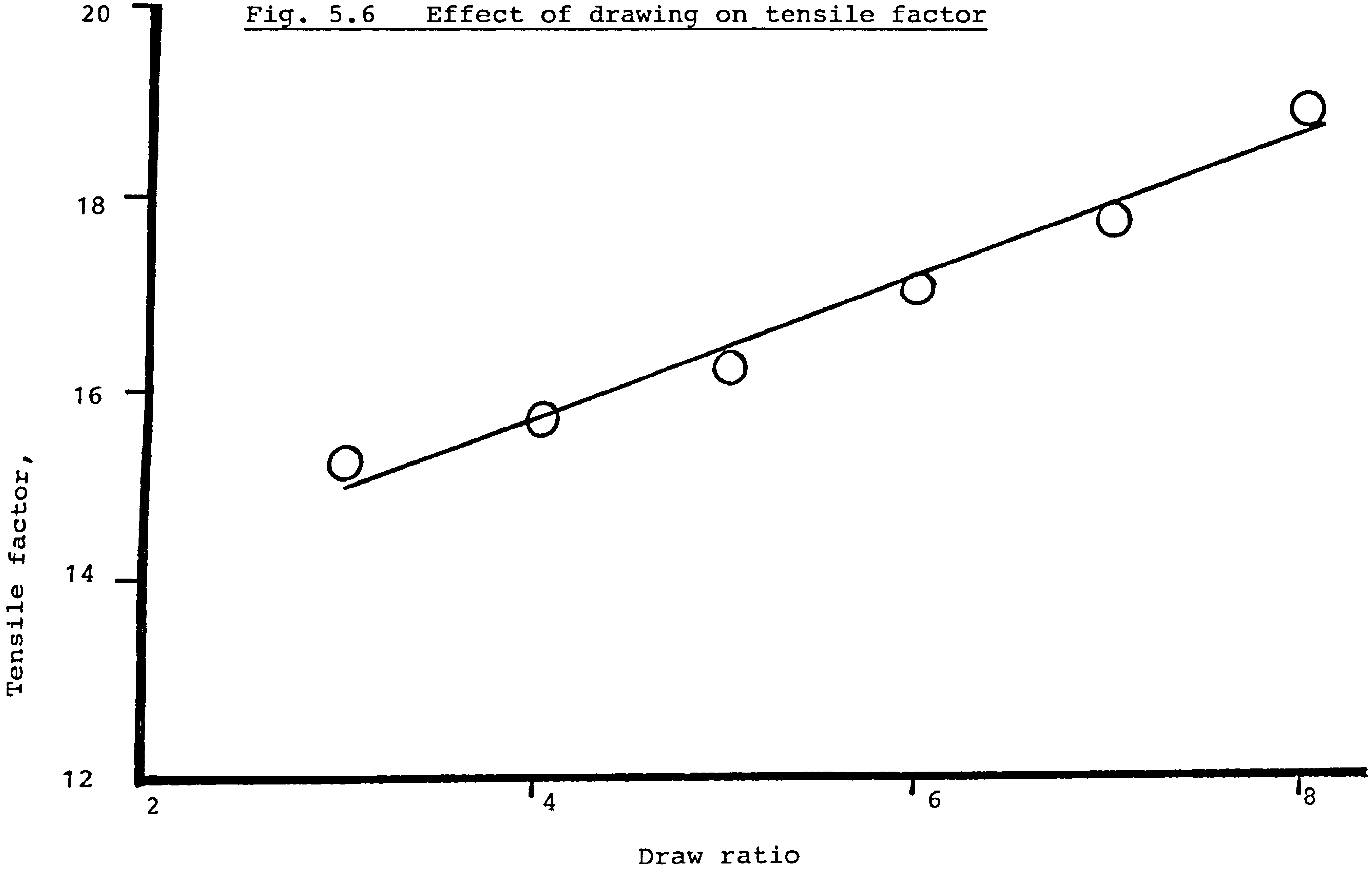


Fig. 5.6 Effect of drawing on tensile factor



This behaviour is important from the technological and processing point of view in that the productivity of the spinning system could be increased without sacrificing the properties of the fibres to any significant extent.

5.3.3 The effect of the drying temperature

Polyacrylonitrile fibres are unique in structure and in the effect that temperature has on their structure; they differ radically in these respects from other synthetic fibres such as polyamides, polyesters, or polyolefins. Underlying this uniqueness in structure and temperature sensitivity is the strong dipolar bonding that exists between chains due to the nitrile side groups. However, in wet-spinning, it has been found that if a coagulated, stretched fibre is heated above Tg, either at constant length or in a relaxed state, the fibre exhibits radial contraction and becomes transparent[84]. This phenomenon is frequently termed "collapse". Craig and co-workers[84] have shown that the change in structure of the filament during the drying and collapsing operation involved an outside-to-centre coalescing of the polymer portion of the drying fibre. Takahashi[90] found that heat treatment of dried samples in the dry state did not exert a strong influence on the microstructure, but heat treatments in the wet state even affected the microstructure of dried samples whose structures had been fixed by previous drying, so that their voids became elongated as a result of treatments. Bell and Dumbleton[71] believe that the moisture content of the fibre, time, and temperature are important factors in determining the amount of collapse during drying, and they believe that, in addition to elimination of voids and reformation of a network, some retraction of the molecular chains occurs during drying, which is either a return to a preferred (helix) conformation (in the relaxed state) or a certain amount of molecular retraction occurs by means of slip.

Whilst it might be expected that some change would occur at temperatures around the glass transition, it has been suggested that there are several transition temperatures in polyacrylonitrile polymers and copolymers. A considerable interest also has been the investigation and interpretation of transitional phenomena in polyacrylonitrile. At least two transitions are generally recognised in the temperature range from 70°C to 150°C. These are:[100]

(1) a transition in the 80°C - 105°C range which is usually referred to as a glass transition, although several authors denote this as the β-transition and,

(2) a transition above the β-transition in the region of 140°C which is sometimes denoted the α-transition. These transitions were detected usually by dynamic mechanical loss peaks (101-103). Further, the birefringence studies of

Kimmel and Andrew[104] and dielectric studies of Van Beek[105] lend support to the existence of two transitions in polyacrylonitrile above room temperatures. Finally, IR spectroscopic studies[106] and reciprocal chromatography studies[107] indicate the existence of three or more transitions in the 50°C to 150°C range. The transition around 140°C has been attributed to intermolecular bonding associated with the nitrile groups, and the lower transition (around 95°C), to the onset of backbone mobility[108]. In the spinning process, the collapsing action usually occurs as the fibres, which are still wet after stretching, are heated. The Tg of the wet fibre is approximately 75°C and collapse occurs in that general temperature region also. Takeda and co-workers showed as the drying temperature became higher, the homogeneity of the internal structure of the filament as well as the compactness of the polymer in the filament was increased.[109]

In order to study the effect of drying temperature on the properties of the final fibre, three different samples (Nos. 5-13, 5-14, and 5-15) were prepared under the same spinning conditions, but after a final washing on the second advancing reel, they were dried at three different temperatures on the chrome rollers. Table 5.5 shows the effect of the drying temperature on the final fibre properties in dry-jet wet-spinning and Figs. 5.7, 5.8 and 5.9 show tenacity, extensibility and tensile factor at these three temperatures. It is clear from

Table 5.5 Effect of drying temperature on properties of dry-jet wet-spun filaments

Sample No.	Drying temp. + °C	Tenacity t gr/d tex	Extensibility E %	Tensile factor $tE^{\frac{1}{2}}$
5-14	(R.T.) 25±2	4.29	13.47	15.75
5-15	106 ± 2	4.33	14.43	16.45
5-16	138 ± 4	4.48	15.83	17.82

Spinning conditions:

Hot draw ratio = 6
Air gap = 3 cm ± 0.2

Fig. 5.7 Effect of drying temperature on tenacity

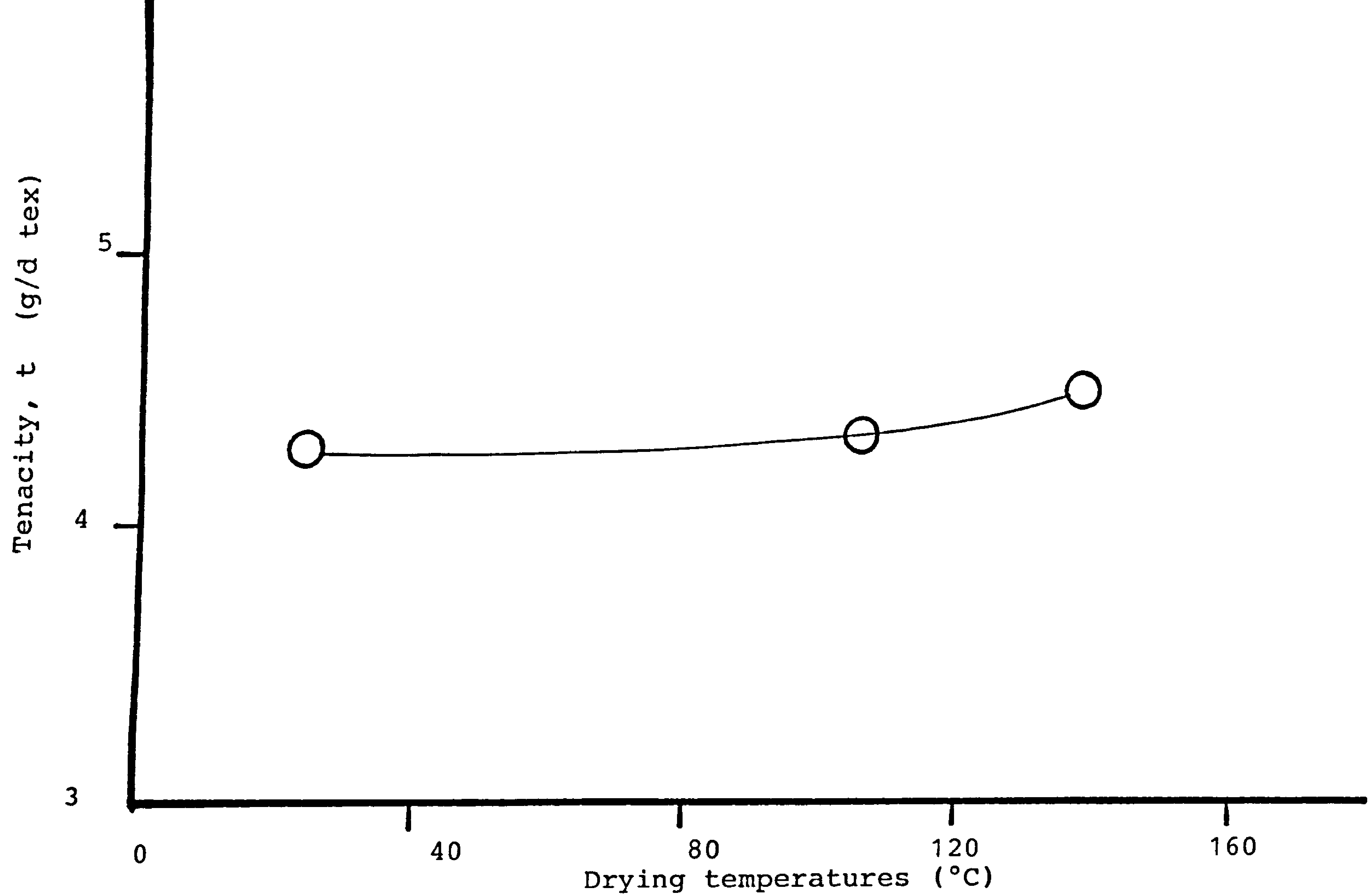
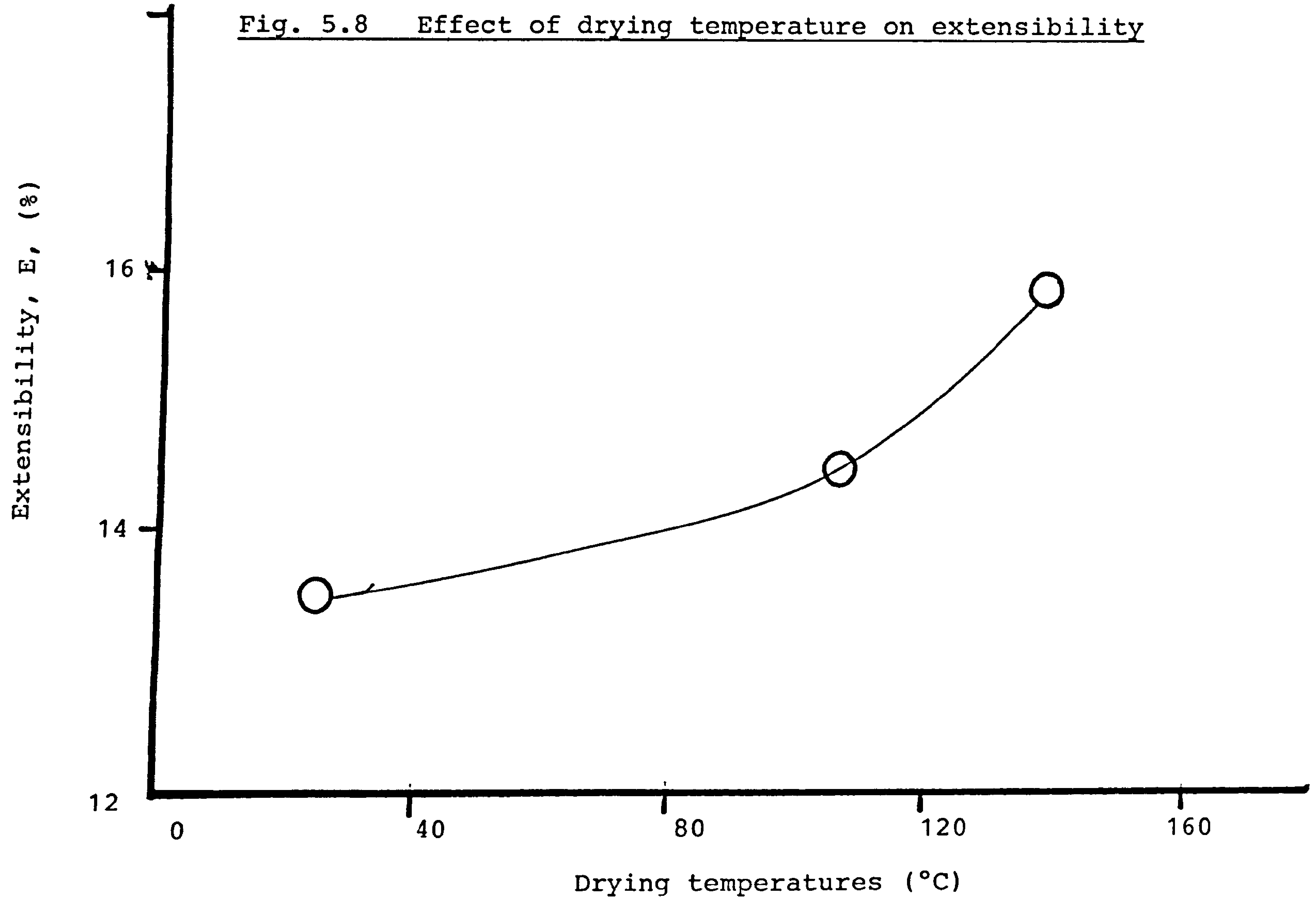


Fig. 5.8 Effect of drying temperature on extensibility



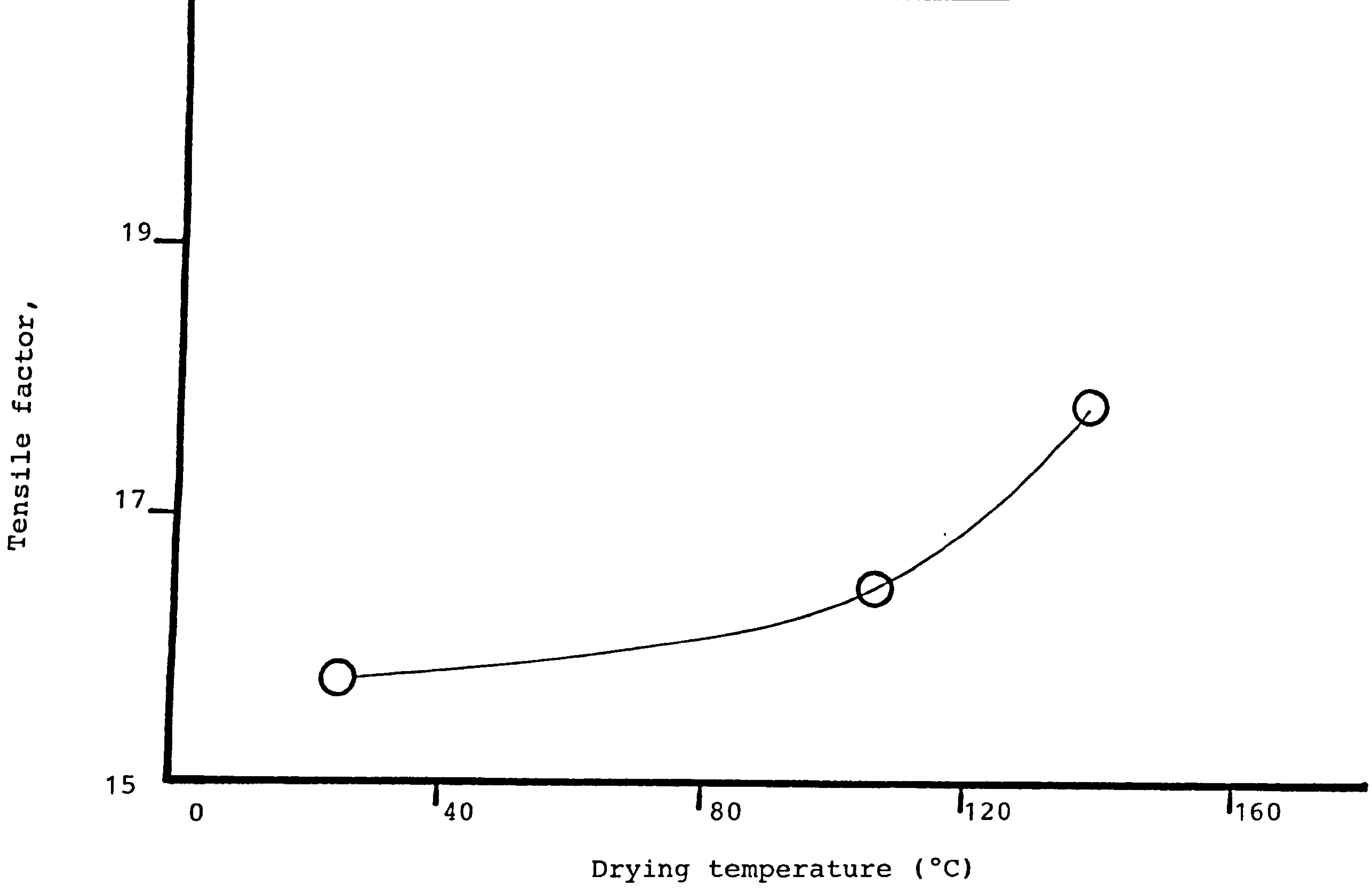


Fig. 5.9 Effect of drawing on tensile factor

these figures, that as the drying temperature was increased, both the tenacity and the extensibility of the fibres increased too. These changes in the mechanical properties of the fibres suggest that the fibres had been undergoing structural change during the drying process of the two higher temperatures. A closer examination of these data revealed that the effect of the drying temperature on the extensibility was more pronounced than on the tenacity, especially between those samples dried at 25°C and 106°C, where the change in the tenacity value is less than 1% but the change in the extensibility value was more than 7%. Although the most effective change in the fibre structure, due to the increased drying temperature, is probably the removal of voids in the fibre, the rearrangement of the molecules or the fibrillar structure must have taken place without any further orientation or otherwise the extensibility would have decreased. For comparison the effect of drying temperature on the mechanical properties of wet-spun fibre, some of the published data are shown in Table 5.6[71].

5.3.4 The effect of drawing at high temperatures

It has been suggested in some patents that when dry-jet wet-spun acrylic fibres are additionally drawn at high temperature, usually above 170°C, their mechanical properties are improved. According to the published work in this area,

Table 5.6 The effect of the drying temperature on the mechanical properties of wet-spun acrylic fibres[71]

Tenacity g/ den			Extensibility		
I	II	III	1	II	III
3.06	3.35	3.08	11.3	17.1	17.9
2.60	3.44	3.10	11.4	21.1	21.5
2.30	3.31	3.18	9.3	20.1	21.2

I - After drawing

II - After drying at 110°C

III - After drying at 140°C

there is some evidence that polyacrylonitrile polymer and copolymers show a transition around this temperature; e.g. a transition region is reported by Andrews and Kimmel[110] between 170°C - 240°C. Also Chiang et al[111] described 175°C as a characteristic constant, (T_m) . Okajima et al[112] found a transition temperature at 160°C when an acrylic sample was heated with high temperature steam, and the activation energy of the transition at 160°C was twice that observed at the glass transition. Colvin and co-workers[113] prepared acrylic fibres using an extra stretching at 170°C, and the x-ray diffraction of the resulting fibre showed an orthorhombic unit cell with cell dimensions quite different from others. Koboyashi et al[114] designated 175°C as the softening temperature, i.e. that temperature at which melting or decomposition of the crystalline phase begins. The temperature around 170°C has also been designated as the "plastisising temperature"[8]. So an attempt was made to investigate the effect of drawing at this high temperature, and two samples, Nos. 5-16 and 5-17, were prepared using a two stage drawing procedure. At the first stage both samples were drawn to 4 times their original length in the hot bath and were dried at 60°C on the chrome rollers as the spinning was carried out. Then both samples were subjected to another 1.5 times drawing on the hot plate, at different temperatures as described in Section 2.1.

Table 5.7 Effect of drawing at higher temperature

Sample No.	Temp. T °C	Tenacity t (g /d tex)	Extensibility E (%)	I.Y.M. g/dtex	Tensile factor $tE^{\frac{1}{2}}$
5-17	138±4	3.79	18.11	78	16.13
5-18	185±4	4.12	17.47	94	17.22

Spinning conditions:

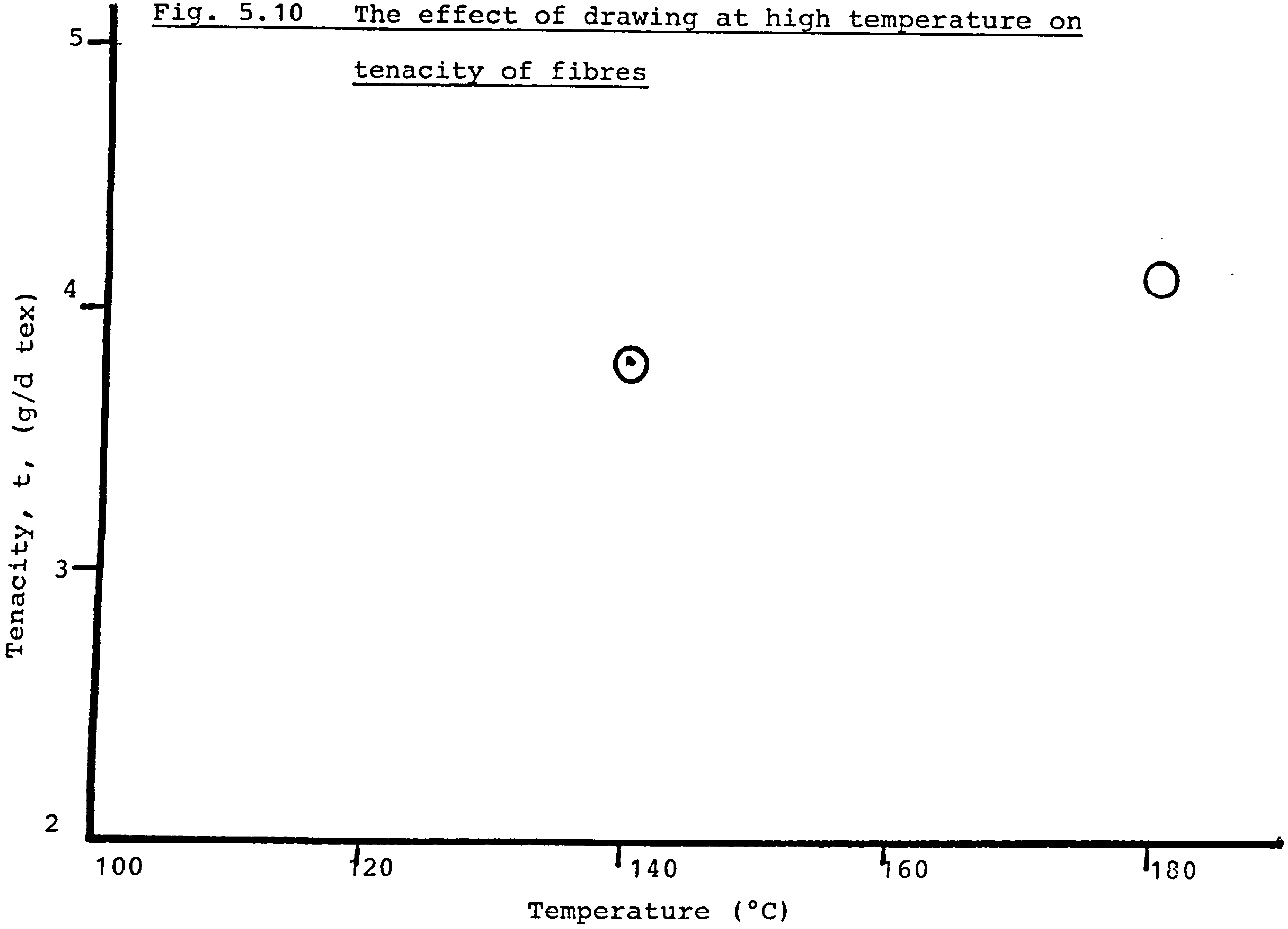
1st hot draw ratio in water	4
2nd hot draw ratio on hotplate	1.5

Total D.R. 6
Spinneret size 300/10

Table 5.8 Stress (g/d tex) at 9% extension, repeated extensions

Sample No.	No. of cycles				
	1	2	3	4	5
5-17	2.66	2.50	2.39	2.36	2.30
5-18	3.17	2.98	2.88	2.82	2.77

Fig. 5.10 The effect of drawing at high temperature on tenacity of fibres



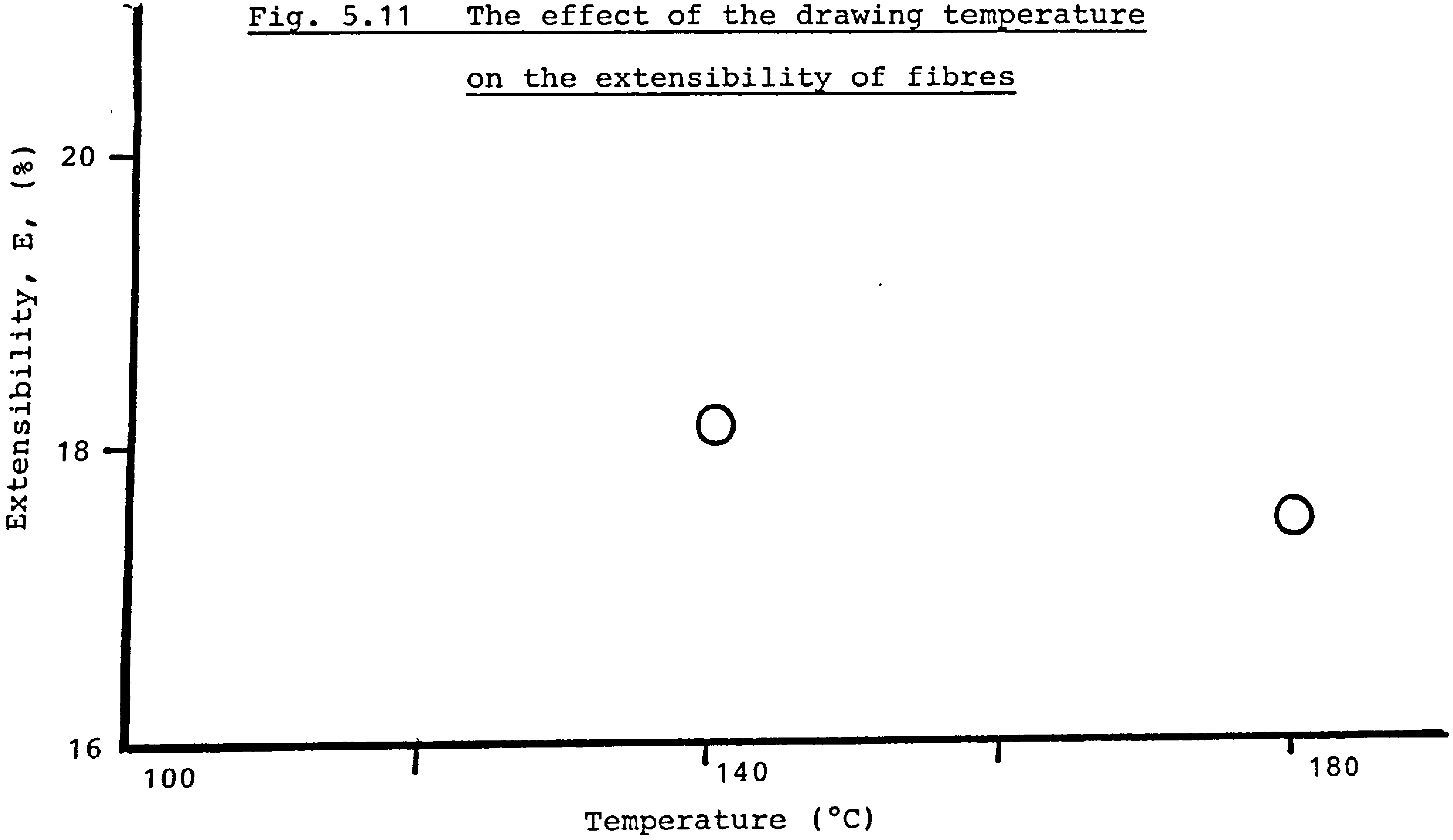


Fig. 5.11 The effect of the drawing temperature on the extensibility of fibres

Fig. 5.12 The effect of the drawing temperature on the tensile factor of the fibres

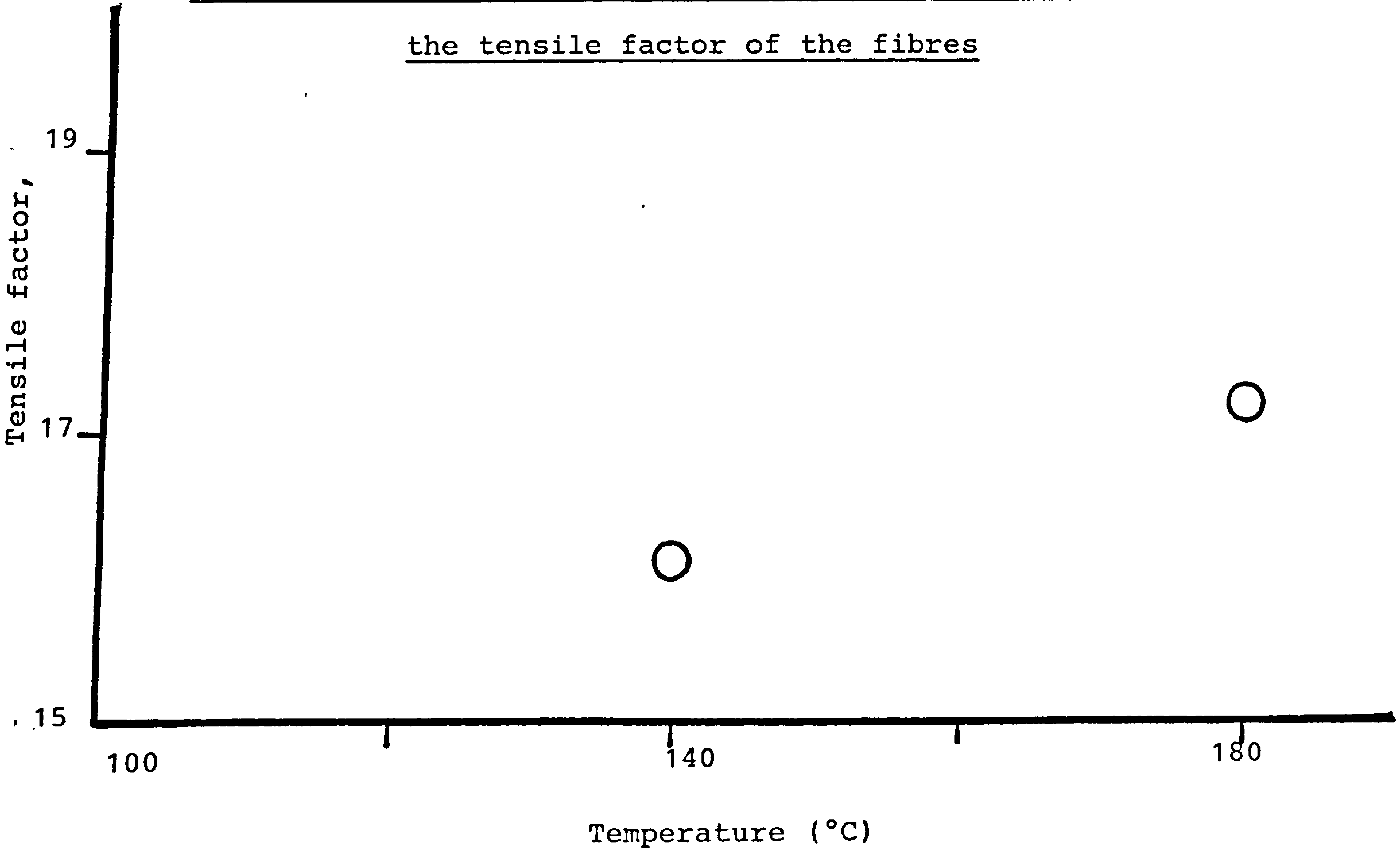
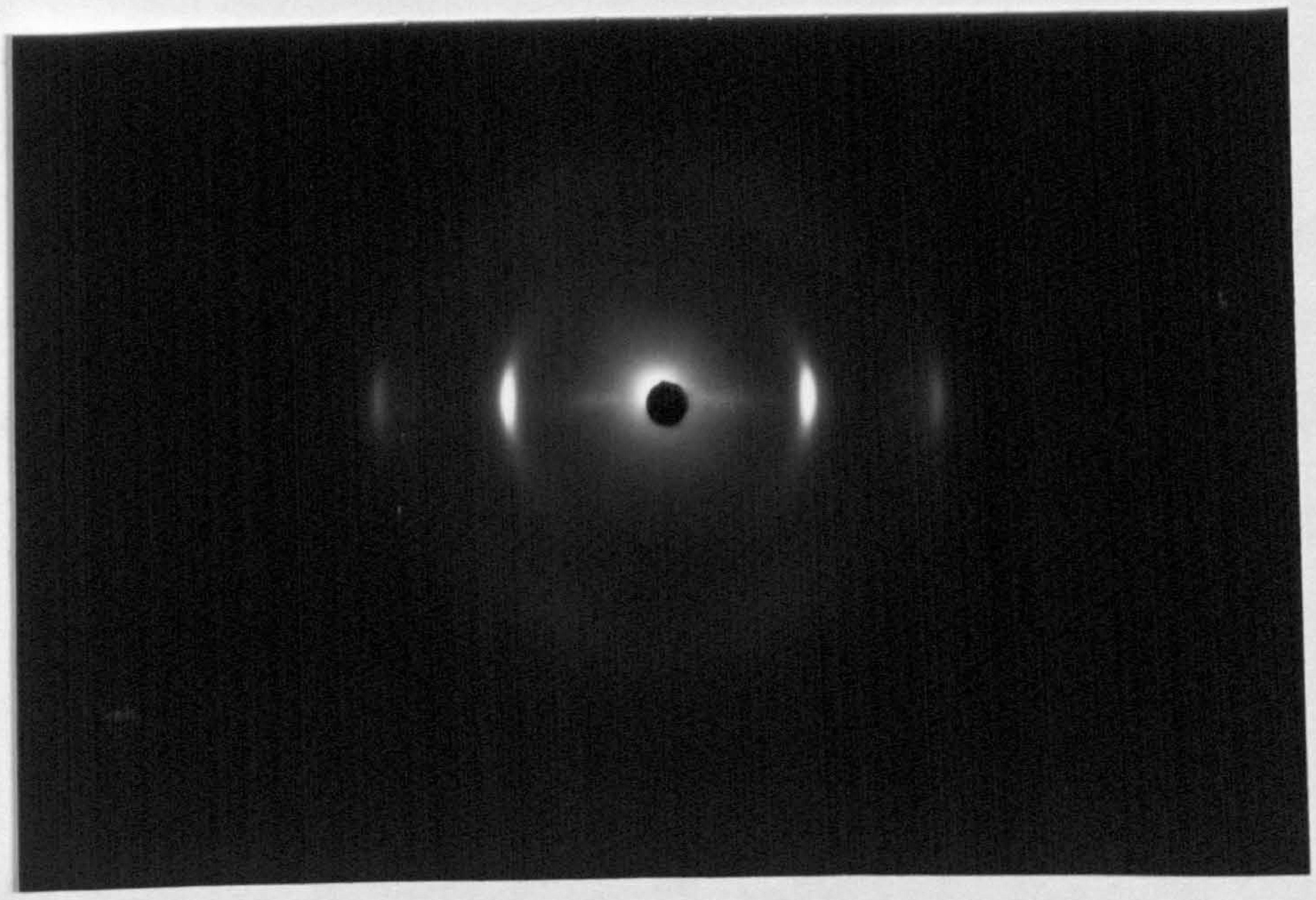


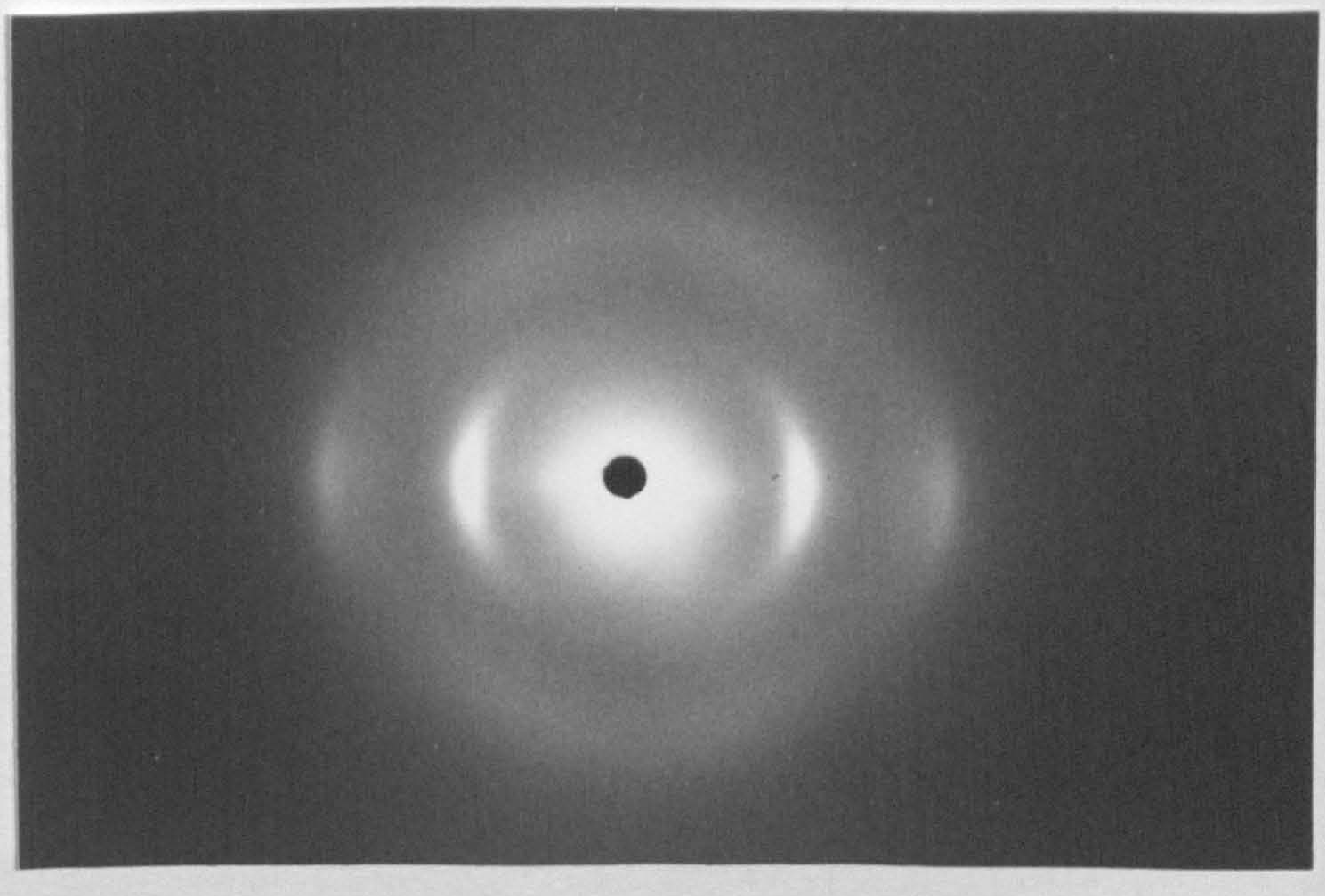
Table 5.7 shows the effect of the second drawing step at these high temperatures on the tenacity, the extensibility, the initial Young's modulus, and the tensile factor. Table 5.8 shows the recovery results of these two samples at a constant rate of extension of 9%. It is quite clear from these data that the sample drawn at the higher temperature had a higher tenacity and tensile factor but a lower extensibility than the sample drawn at the lower temperature, which indicated that sample No. 5-18 was more oriented than sample No. 5-17. The extra orientation of the former sample is also shown in the x-ray diffraction patterns (Plates 5.1A and 5.1B).

These data suggest that the change in the mechanical properties is not simply due to a higher orientation of the sample drawn at the higher temperature, as the increase of the tenacity is about 9%, while the decrease in the extensibility is around 3.5%. Also the initial Young's modulus of the former sample is much bigger than the latter one (See Table 5.7). In addition, a close examination of the x-ray patterns reveals that some change in the crystalline structure of sample No. 5-18 has taken place due to the higher temperature of drawing.

There are many references dealing with the structure of polyacrylonitrile polymers and copolymers[9,115-126], but very few conclusions have been reached as to the crystal structure of this polymer, and it is still impossible to obtain a complete picture for a model for polyacrylonitrile with the available data.



A



B

Plate 5.1 X-Ray diffraction patterns of drawn fibres; (A) drawn at 170°C, (B) drawn at 140°C

For a better understanding of this complexity a summary of the different interpretations is given below;

The usual fibre diagram of polyacrylonitrile polymers and copolymers usually consists of two relatively sharp equatorial diff raction lines and occasionally a third very weak line may be distinguished, but the off-equatorial reflections are diffuse. This result has been interpreted by some workers as indicating that a definite repeat distance along the polymer chain does not exist. The structure has been considered by some as that of a single-phase laterally ordered polymer[121]; it has been described in terms of a planar unit cell and called a two dimensional crystal by others[118,124,127]; and it has been described as a paracrystalline, liquid crystal texture by still others[128]. Other authors take the position that three-dimensional crystallinity does exist in polyacrylonitrile and have defined a hexagonal unit cell[129,130], or an orthorhombic unit cell when diffraction is observed from either carefully annealed polymer or from single crystals or fibres that have been stretched at high temperatures[113,120,122,126]. The situation is further confused because under certain conditions the polymer can assume a spherulitic morphology[124] or even a "single crystal" plate like texture[125,126]. The latest model for the structure of oriented acrylic fibres consists of two distinct regions within a fibril; amorphous and partially ordered as suggested by Warner and Uhlmann[131].

A further indication of the formation of ordered regions is the development of lamella-like structures when acrylic fibres or film are hot-stretched[126]. The scale of the structure ranges from 80 to 120 Å and increases with annealing time or temperature[125,126], so it has been accepted that a variation in shape and size of individual lamellae with temperature is not uncommon for this polymer; also the variation of thickness with temperature is a strong function of the polymerisation conditions of the polyacrylonitrile. Finally, it was reported recently[132] that polyacrylonitrile fibres can have different structures depending upon the spinning conditions, type of co-monomer and the stretch ratio, etc.

With regard to the literature cited above and the data and x-ray diffraction patterns of the samples, it is tempting to suggest that drawing of fibres at high temperature, (above 170°C) causes a change in the crystalline structure of the fibre as well as better orientation. If this were so, then temperatures around 170°C may be regarded as the region where a crystalline-crystalline transition occurs in acrylonitrile polymers. This sort of transition has already been found in some other semicrystalline polymers such as polyamides[133-136], where it is due to rotation of the chains in the crystalline regions of the polymer structure.

5.4 High tenacity fibres

The tensile properties of acrylic fibres like other synthetic fibres depend to a considerable extent on the polymer characteristics, such as molecular weight, as well as on the amount of drawing. The drawing conditions together with the structure and properties of the resulting fibre also depend strongly on the characteristics of the original (undrawn) fibre which is determined, in turn, by the spinning conditions. The general tendency in acrylic fibre production, with regard to mechanical properties, is for moderate strength to be combined with moderately high breaking extension (extensibility) resulting in a fairly tough fibre. This is open to modification through the amount of drawing, i.e. the earliest produced acrylic fibre had a tenacity between 1 and 4 g/denier with an extensibility ranging from 13% up to 38%.[9] Although some experimentally prepared acrylic fibres with a tenacity up to 5 g/denier or higher values have been reported[137], todays acrylic fibres are still produced with almost the same moderate mechanical properties, with a lower limit of the tenacity increased to about 2 g/denier and an upper limit of extensibility increased to 40% — 50%[138].

It seems that there are two factors in the spinning process that prevent the production of acrylic fibres with a higher tenacity. These are the draw ratio limit, and the rapid reduction in the extensibility of the fibre with increasing draw ratio. As the draw ratio increases in the spinning operation, the fibre becomes so brittle that the rate of breakage will increase dramatically so that a continuous process becomes impossible, and also the resulting fibre would have a very low extensibility (less than 7%) which makes it unsuitable for textile purposes.

It was shown in a previous section (Section 3.3) that in the dry-jet wet-spinning process the maximum draw ratio is about twice that possible in the conventional wet-spinning process and the extensibility of dry-jet wet-spun fibre can be almost 50% higher than the wet-spun fibre. In addition, it was found that the reduction of extensibility at higher draw ratios is almost negligible. In view of these characteristics of dry-jet wet-spinning, it was decided to attempt to produce some fibre at high draw ratios. Table 5.9 shows the stress-strain values and Fig. 5.13 shows the stress-strain curve of such a fibre. Both the tenacity and the extensibility are at least 50% more than the same values of the conventional wet-spun fibre produced with a high draw ratio. On the other hand the estimated work of rupture from the product [tE] is about the same as for a conventional wet-spun fibre with a moderate draw ratio, but the value of the initial Young's modulus is somewhat lower than that for a wet-spun fibre as the stress-strain curve is like a neck-type deformation,C,[139], which means there is still the capacity for further drawing of the fibre (in this experiment the limitations of the equipment did not allow greater drawing). The data for the strongest acrylic fibres that have been reported in the literature are tabulated in Table 5.10.

Table 5.9 Properties of high tenacity acrylic fibre

Strain	Stress t		Tensile factor $t\,E^{\frac{1}{2}}$	
E %	g / d tex	g/den	g/d tex	g/den
5	2.21	2.46	4.94	5.5
10	3.47	3.86	10.97	12.21
15	5.51	6.12	21.34	23.7
15.87	5.80	6.45	23.11	25.69

Spinning conditions:

- Coagulation bath composition	50/50 v/v
- Air-gap distance	4 cm
- Jet stretch ratio	2.27
- Draw ratio	12.5
- Yarn count	106 d tex

Fig. 5.13 Stress-strain curve of high tenacity acrylic fibre

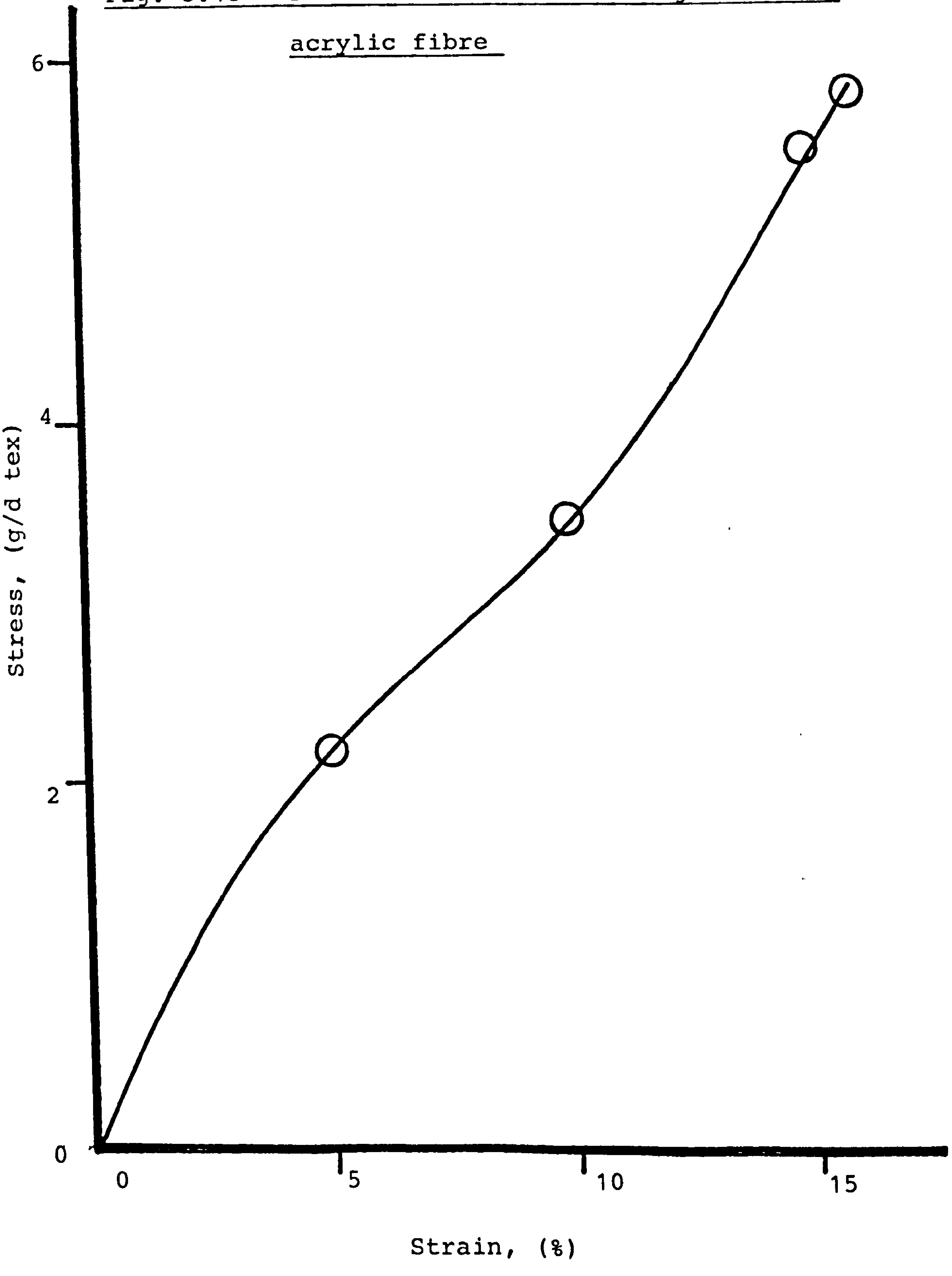


Table 5.10 The tenacity and the extensibility of some acrylic fibres

Tenacity g/d tex	Extensibility %	Draw ratio	Reference
7.56	17.1	30	137
3.10	21.1	8	71
4.13	14.0	15	183
3.60	15.0	-	9
5.80	15.87	12.5	*

* present work

CHAPTER 6. COPOLYMERISATION OF ACRYLONITRILE AND BICYCLO [2,2,1] HEPTA-2, 5-DIENE

6.1 Introduction

Acrylic polymers have a chemical structure consisting essentially of the repeating unit, $[CH_2CH(CN)]_n$, but there are at least two main problems in using polyacrylonitrile homopolymer as a textile fibre. The first is that the homopolymer itself is so difficultly soluble and its solutions are so unstable that spinning is very inconvenient. The next problem is related to the difficulty of dyeing fibres made from homopolymer. Therefore it is necessary to modify the homopolymer in some way, and there are different ways for these modifications.

The modifications that are at present being used include chemical modification, mainly carried out during the polymerisation process, physical modifications which are done during spinning and subsequent processes, and physico-chemical modification such as bicomponent systems. Among these modification systems the most general type is chemical modification, which can be done in two different ways. The first is, the molecular weight, and molecular weight distribution, which can easily be modified during polymerisation, by the temperature, and by the use of appropriate initiator, accelerators and chain transfer agents. Another is copolymerisation in order to obtain certain favourable properties.

The greatest and most valuable advantage of the addition polymers such as polyacrylonitrile, is the almost limitless possibility for modifying their behaviour by copolymerisation. In fact the entire technology of acrylic fibres is based on the systematic use of copolymerisation. So most of today's commercial acrylic fibres are made from copolymers, with up to 15% by weight of the copolymer consisting of units other than acrylonitrile. One type of comonomer is introduced into the polyacrylonitrile chain to improve the solubility without serious disadvantageous effects on other properties, such as softening temperature, rigidity, and resistance to swelling in water and organic solvent, even at elevated temperatures. The most commonly employed co-monomers of this kind include vinyl acetate, methyl acrylate, and methyl methacrylate[140]. The control of the dyeing properties is accomplished by introducing of acidic or basic comonomers, such as vinyl and allyl sulphonic acids[141-143], vinyl pyridine, allyl amines[144], imines[145-146] or less basic compounds such as N,N-disubstituted hydrazide derivatives of unsaturated carboxylic acids[147], and oxalimides[148]. Finally it is possible to introduce active centres for crosslinking reactions by the introduction of suitable comonomers.

In addition to the two above mentioned problems which are involved mainly in the production stage, there are some other problems for acrylic materials with regard to its end-uses.

In this field some modifications and improvements have been made. These modifications have dealt with, for example, flame-resistance, whiteness, soiling behaviour, handle and static properties of the fibres. For each of these improvements, there are a lot of papers and patents. For example, additives to spinning solutions have been widely used to improve the flame resistance of acrylic fibres[149-153], or to produce whiter fibres[154-156]. Permanent improvements in the soiling behaviour of acrylic fibres have been claimed by copolymerisation of acrylonitrile with fluorinated acrylates or methacrylates[157], as well as with fluorinated acrylamides or methacrylamides[158]. Improvements in the fibre softness and surface friction have been claimed by peeling off the fibre surface with solvents[159], by partial dissolution in DMF[160], by core-sheath spinning[161], and by grafting copolymer containing longchain esters onto an already formed fibre[162]. Antistatic properties have been claimed for copolymers derived from polyalkylene ether derivatives[163,164], or by the metallising with nickel and copper, of fibre sensitised with tin salts and tannic acid[165]. Some other modifications have also been done to improve tensile properties[166-168], and hydrophilic properties[169-17

However, the mechanical properties of acrylic fibres are extremely sensitive to temperature. This sensitivity increases when they are wet. Since the majority of acrylic fibres in the textile industry are wet processed at some stage, i.e. scoured, dyed, finished, etc., this behaviour is a drawback in the usage of these fibres and in some cases it imposes some limitation on its processability. Usually above 85°C (around Tg), the values of the initial Young's modulus of wet acrylic fibres are low and at these temperatures these fibres have little resistance to stretch. Their tenacities fall with temperature and extensibilities increase by factors of as much as 4 times. Guthrie[173] in his work, found that, at 95°C (in water) Acrilan, Orlon 42 and X54 have extensibilities of over 100% whereas the tenacities fall by a factor of about three over the temperature range 22 - 95°C, and the initial Young's modulus falls by factors in the region of twenty. Similar results have been reported by others[174,175].

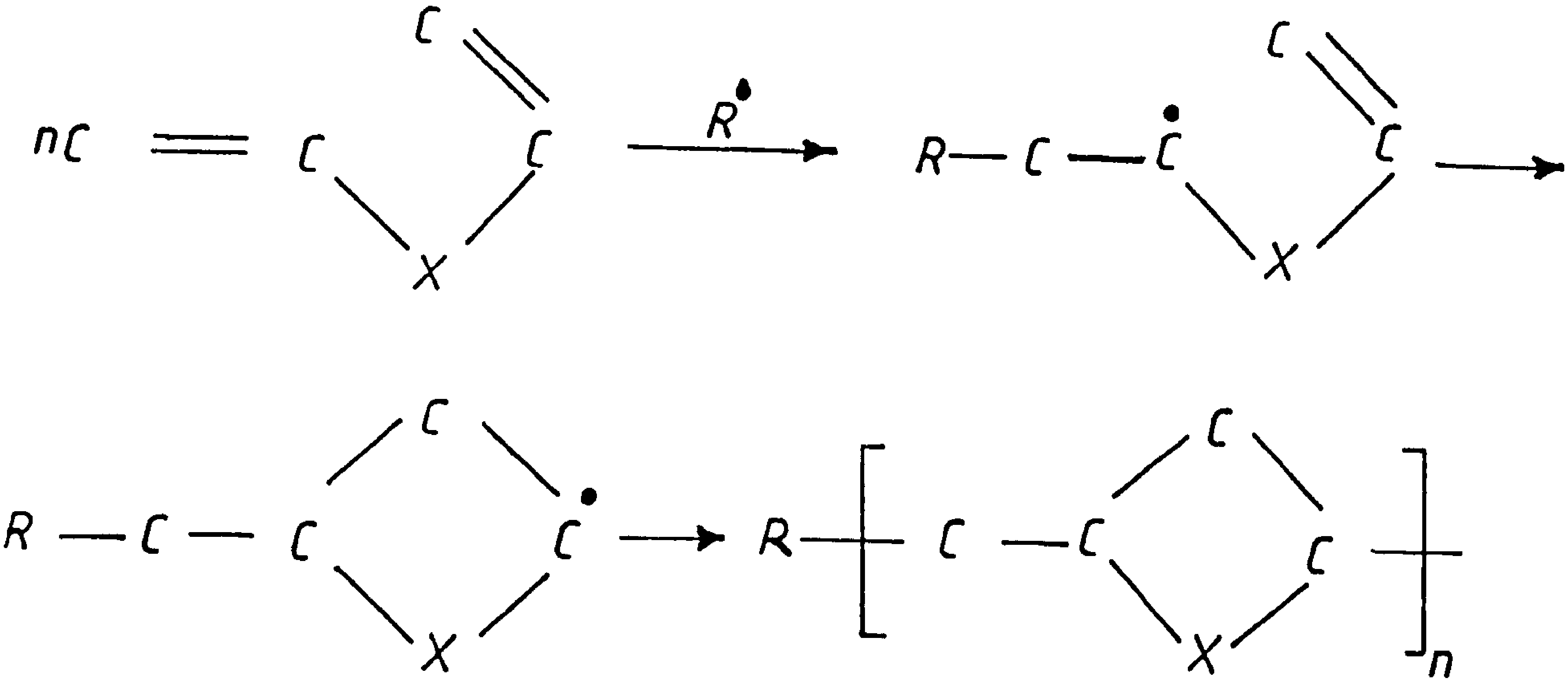
Some attempts have been made to overcome these drawbacks. These have been either by crosslinking or by graft copolymerisation. In these cases, the control of the operation is rather difficult and the final products are sometimes too rigid for textile purposes. One potential method for improving the wet mechanical properties of the fibre not explored in the literature, would be the introduction of cyclic units in the polymer backbone since these would be expected to make the chains more rigid. Whereas this is a relatively easy process in condensation polymers (e.g. using terephthalic acid in polyesters or polyamides), the equivalent structures in addition polymers are not apparently easily synthesised.

A literature survey showed that there were studies of the copolymerisation of some vinyl monomers with some cyclic and bi-cyclic compounds such as 1-substituted cyclobutenes[176], bi-cyclo butanes[176-179] and bi-cyclo[2,2,1]-hepta-2,5-diene[180-183]. From this group of compounds, it was noted that the bicyclo [2,2,1]-hepta-2,5-diene was easily available at a price comparable to acrylonitrile. Hence it was decided to use this monomer to prepare acrylic copolymer for spinning.

6.2 Cyclopolymerisation

6.2.1 Introduction

In 1951[84], it was found that some diallyl quaternary ammonium salts polymerised with free-radical initiators to yield water-soluble, noncrosslinked polymers. On the other hand, the monoallyl quaternary ammonium salts would not polymerise and the triallyl homologues polymerised to yield crosslinked products. In an attempt to account for these unexpected results, a polymerisation mechanism was proposed[185]. The principal on which it operates is shown in the following equations.



(6.1)

This mechanism can be defined most accurately as an alternating intramolecular-intermolecular chain propagation. This type of polymerisation illustrates a phenomenon observed with some dienes in which a polymer is formed having cyclic recurring units. Thus it is a cyclopolymerisation. The cyclopolymerisation can be brought about, using typical free-radical initiators like peroxides, peracids, azobis isobutyronitrile (AIBN), oxygen, ferrous ion/hydrogen peroxide, and persulphate. The polymerisation can be performed in bulk, solution or emulsion. Several types of solvents can be used, and heat or radiation (UV, γ ray) were also successfully employed. In addition to the free radical polymerisation, other methods of initiation, such as cationic initiation can be used. Beside homopolymerisation, numerous examples of co-polymerisation of some dienes with common vinyl monomers and other comonomers such as sulphur dioxide have been recorded in the literature[180,183,197,207 In most cases, the predominant role of the diene was that of cyclization.

A special case of cyclopolymerisation or intra-intermolecula polymerisation is transannular polymerisation. Bicyclo[2,2,1] -hepta-2,5-dienes[180], 1,4-dimethylenecyclohexane[186],1-vinyl-4-methylenecyclohexane[187],2-carbethoxybicyclo[2,2,1]-hepta2,5-diene[188], and cis-cis-1, 5 cyclooctadiene[189] are monomers which have been shown to undergo transannular polymerisation.

6.2.2 Bicyclo[2,2,1] hepta-2, 5-diene polymer and copolymers

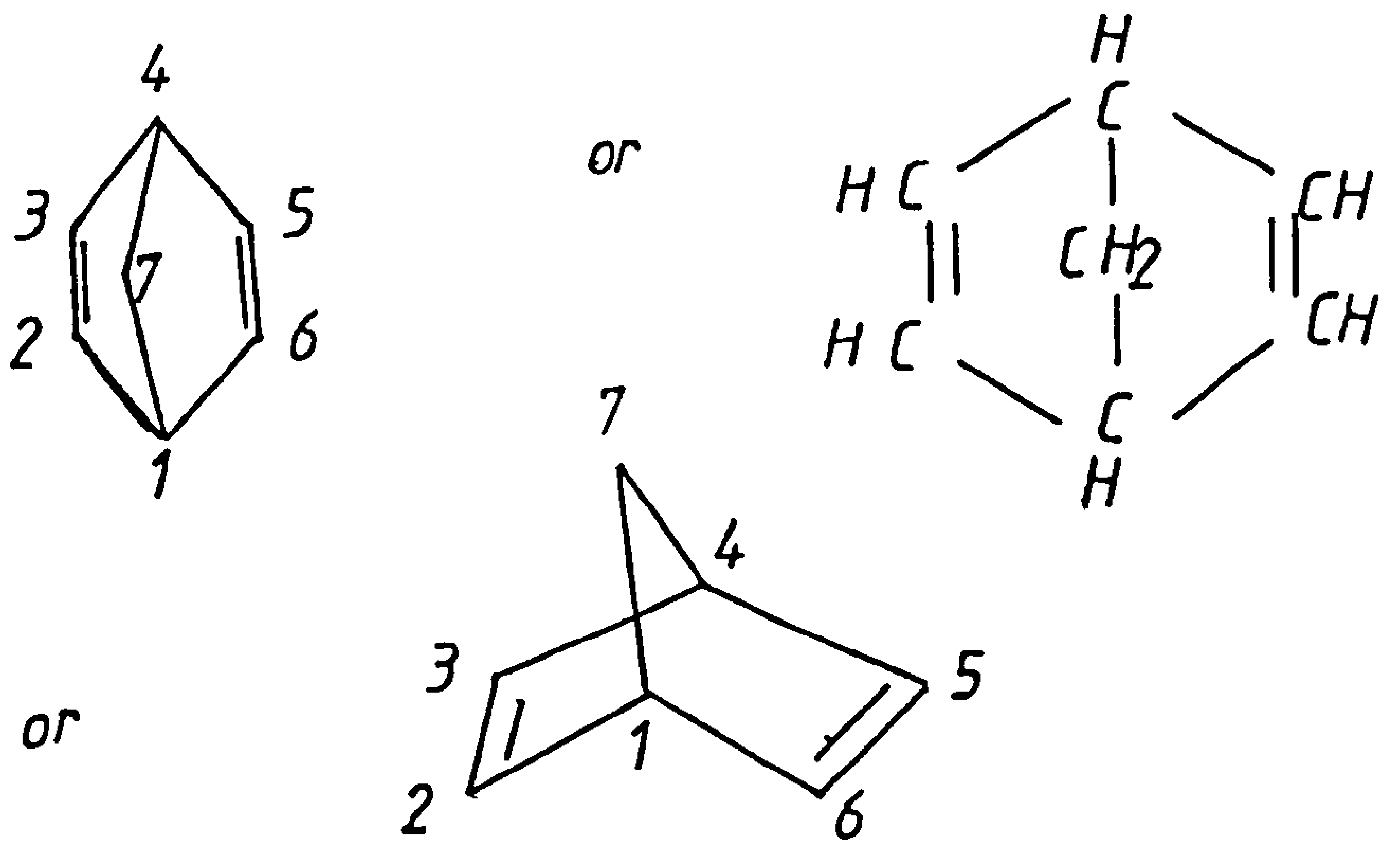
Bicyclo [2,2,1] hepta-2, 5-diene or norbornadiene, which is the reaction product of cyclopentadiene and acetylene, has the formula C_7H_8 and its properties are shown in Table 6.1

Table 6.1 Some physical properties of bicyclo [2,2,1] hepta-2, 5-diene

Molecular weight	92.15
Melting point	-19.1°C
Boiling point	+89.5°C
Density	0.9064 g/cc
R. index	1.4702

It is prepared by a Diels-Alder reaction between cyclopentadiene and acetylene[190]. It has also been prepared by dehalogenation of 5,6-dichlorobicyclo [2,2,1] - hepta-2-ene and by the dehydrohalogenation of the 5-chloro-compound[191]. It is a very versatile diene and can react with other chemicals such as cyclopentadiene[192], maleic anhydride[193] and acrylonitrile[194].

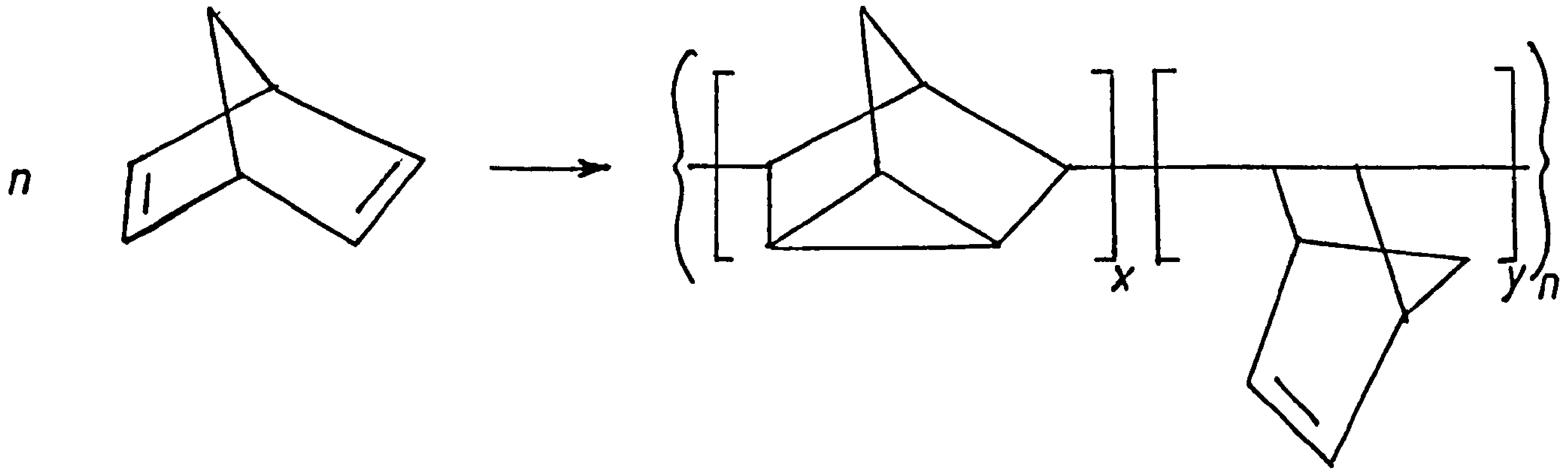
It has the structual formula:



(6.2)

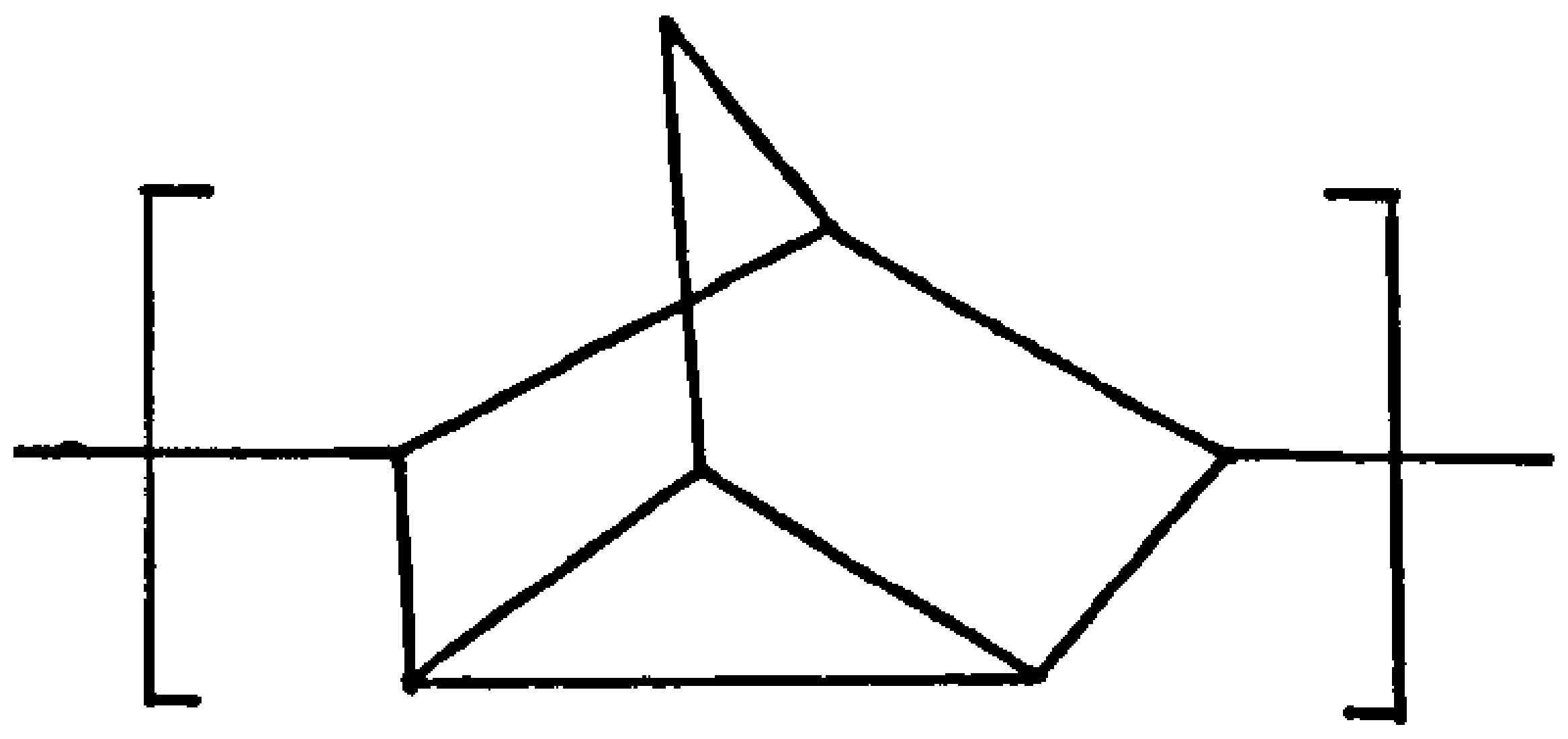
The distance between the 2,6 and 3,5 atoms in bicyclo [2,2,1] hepta-2, 5-diene has been calculated from electron diffraction data and found to be 2.37Å , or about 1.58 times the normal carbon-carbon single bond in polyacrylonitrile[195].

The transannular homopolymerisation of bicyclo [2,2,1] hepta-2, 5-diene yield a polymer containing nortricyclene units and bicyclo [2,2,1] hept-2-ene units[179-181] (Equation 6.3).



(6.3)

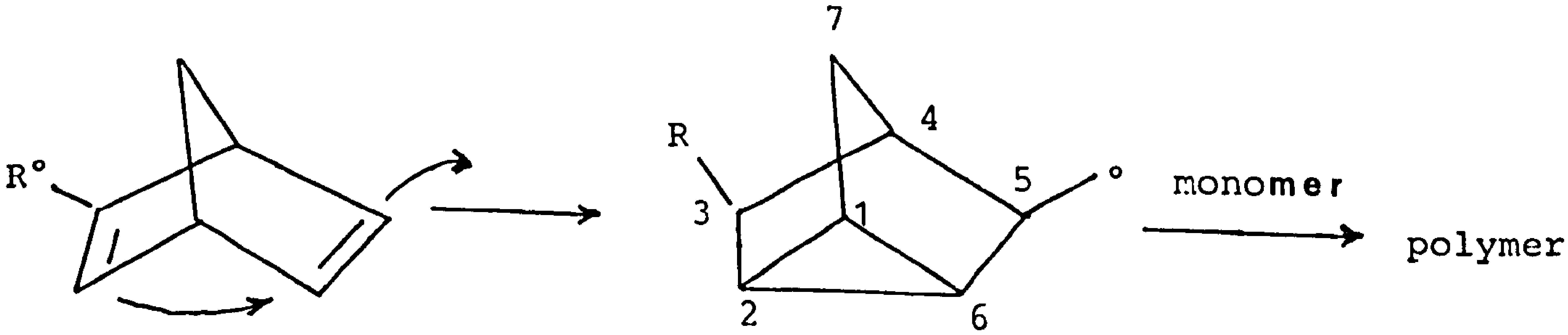
Dibutylperoxide[188] and AIBN in bulk or benzene solution were initiators. The same polymer was obtained by initiation with γ-irradiation[181] for 17 days. The molecular weight of the resulting polymer was approximately 1500, and the product was probably a mixture of polymer molecules of different chain lengths, averaging a 16-unit chain. The infra-red (IR) absorption spectrum and the NMR spectrum of this homopolymer showed the presence of the tricyclo [2,2,1,0] heptane structure as the principal structural unit in the polymer. (6.4)



(6.4)

tricyclo [2,2,1,0] heptane unit

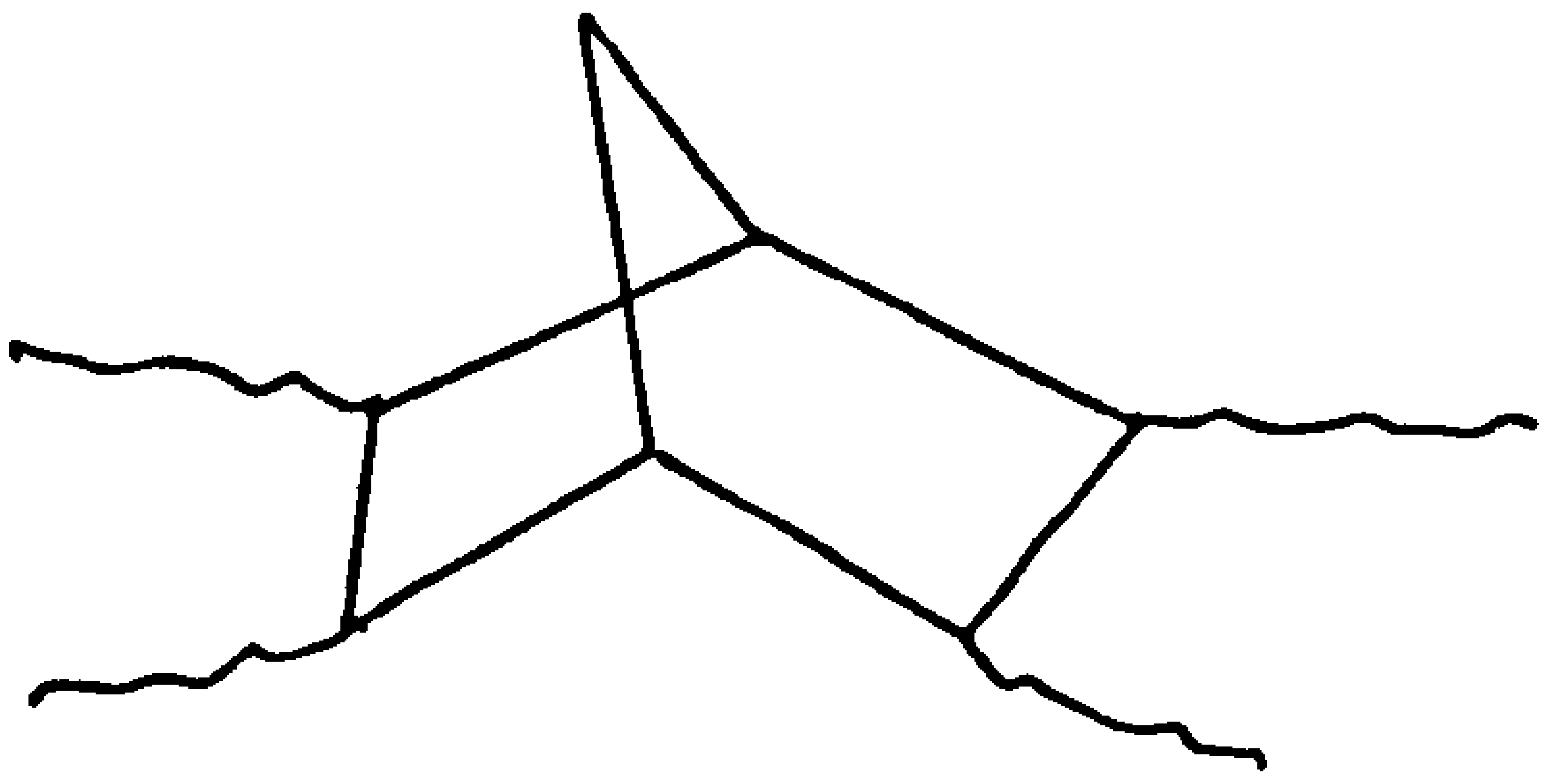
Zutty[180] observed that under mild homopolymerisation conditions low yields of low molecular weight, soluble polymer were found. He concluded that the homopolymerisation appeared to involve an intramolecular addition followed by an intermolecular addition (6.5). Thus:



(6.5)

That just such a mechanism was in operation was based on data from the IR spectrum. The IR spectrum of the homopolymer showed three strong bands at 6.4μ, 12.4μ, and 14.1μ. The strong band in the homopolymer at 14.1μ coupled with the band at 6.4μ indicated the presence of a cis strained double bond. From such data polybicyclo [2,2,1] hepta-2, 5-diene was thought to be essentially a copolymer containing both 3,5 disubsituted nortricyclene and 5,6 disubstituted bicyclo [2,2,1] hepta-2-ene units (6.3).

On the other hand, the cationic polymerisation of bicyclo [2,2,1] hepta-2, 5-diene yields poly (nortricyclene)[182]. Polymerisations using aluminium chloride catalyst in ethyl chloride and methylene chloride were carried out at -123°C, -78°C, 0°C and +40°C. The molecular weight of the polymer was determined by osmometry and was 8400. Its solubility in solvents such as carbon tetrachloride, benzene, and toluene was in agreement with a linear structure. However, only the product synthesised at -123°C was completely soluble, the rest contained some cross-linked, insoluble polymer that presumably possessed structures such as shown in (6.6)



(6.6)

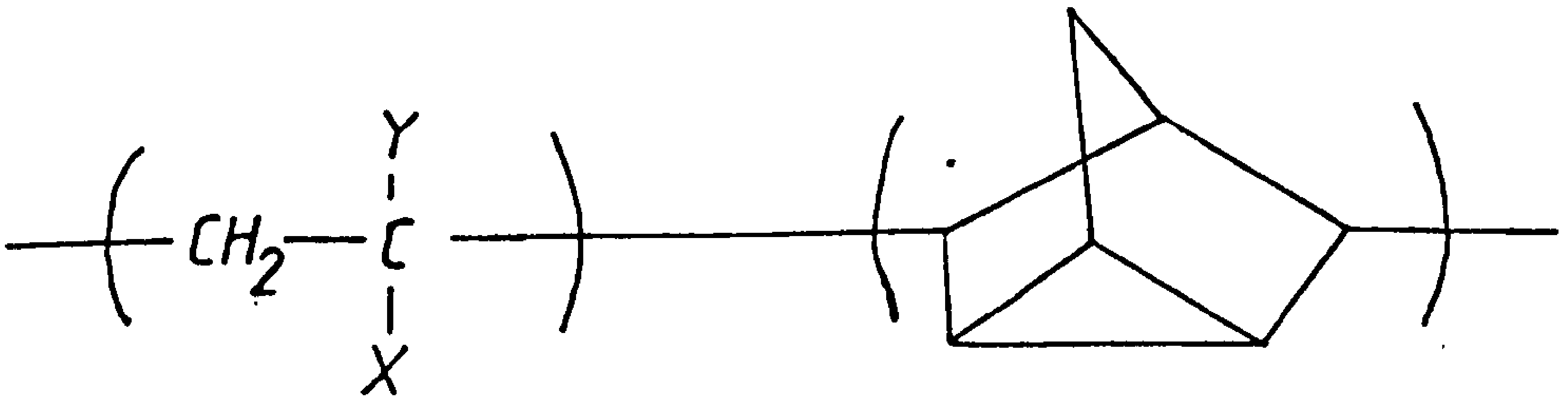
The structure of the soluble product was determined by IR and NMR spectroscopy and the repeat unit of the polymer was identified as a 2,6-disubstituted nortricyclene. Also a catalyst was prepared by the interaction of molybdenum with bicyclo [2,2,1] hepta-2, 5 diene[196]. It was described as being effective for the cyclopolymerisation. The reaction was performed in bulk or inert solvents such as benzene or xylene. Temperatures ranging from 25°C to 140°C were employed. The presence of nortricyclene units in the polymer was indicated by its IR spectrum. The molecular weight of the material was not reported.

An extensive study of the copolymerisation of bicyclo [2,2,1] hepta-2, 5-diene with vinyl monomers has been described[183]. Different radical initiators such as, tri-n-butylboron, AIBN, isopropyl peroxydicarbonate, and diacetyl peroxide were employed. The polymerisations were carried out in either solution or bulk and products well into the useful molecular weight range were obtained. On the basis of IR evidence, all of the bicyclo [2,2,1] hepta-2, 5-diene was stated to be present in the polymers as nortricyclene units. Although vinyl chloride copolymers were studied most extensively, most of the other commercial vinyl monomers were also examined. The reactivity of the monomer toward free-radical co-polymerisation is good, reaction occurring under normal mild conditions (Table 6.2)

Table 6.2 Monomer reactivity ratio, and Q and e values for the copolymerisation of the bicyclo [2,2,1] hepta-2, 5-diene and some vinyl monomers

M_2	r_2	r_1	Q_1	e_1	poly. temp. °C	Reference
Acry lonitrile	0.67	0.08	0.13	-0.60	50	180
Acrylonitrile	0.65	0.47	0.27	0.03	60	198
Vinyl chloride	0.74	0.35	-	-	50	180
Vinylidene chloride	1.41	0.08	-	-	50	180
Ethyl acrylate	3.05	0.01	-	-	50	180
Methyl methacrylate	10.00	0.00	-	-	50	180
Vinyl acetate	0.82	1.28	-	-	70	197
P-chlorostyrene	85.00	0.01	-	-	70	197

Zutty[180] believed that when the bicyclo [2,2,1] hepta-2, 5-diene was copolymerised with vinyl chloride, vinylidene chloride, acrylonitrile, ethyl acrylate, and methyl methacrylate, only the transannular product, the 3,5-disubstituted nortricyclene unit,was found in the high molecular weight copolymers.. These copolymers contained very little, if any, unsaturation and had evidently formed via reaction of the bicyclo [2,2,1] hepta-2, 5-diene almost solely through the nortricyclene route. These data were based upon infra red spectra which in all cases showed almost complete absence of the double band (detectable at 6.4μ and 14.1μ) and the appearance, when not masked, by bands due to comonomer, of a strong band at 12.4μ due to the 3,5-disubstituted nortricyclene. The bicyclo [2,2,1] hepta-2, 5-diene radical attacks vinyl monomers and relatively easily copolymerises to give polymers having the following schematic structure;



(6.7)

Reactivity ratios for the copolymerisation with acrylonitrile at 50°C and 60°C are shown in Table 6.2.

The copolymerisation was carried out in the bulk using AIBN as initiator. Thus, the bicyclo [2,2,1] hepta-2, 5-diene enters the copolymer essentially as a substituted nortricyclene. The copolymers tend to be alternating in character as indicated by the "S" shape of the monomer-polymer composition curve[198]. It is believed that the copolymerised bicyclo [2,2,1] hepta-2,5-diene increases the copolymer glasstransition temperature[183,197,199] due to the rigid nortricyclene group in the carbon backbone in the amorphous phase of the copolymer. It has been claimed[197] that the properties of the copolymers of vinyl monomers and bicyclo [2,2,1] hepta-2, 5 diene were usually an average of the monomer pairs. For example a copolymer of vinyl acetate and bicyclo [2,2,1] hepta-2, 5-diene containing 3 moles of bicyclo to 10 of vinyl acetate started to soften at 50°C, while the copolymer containing 6.5 moles of bicyclo to 1 mole of vinyl acetate did not soften until 230°C[197], which is around the glass transition temperature of the homopolymer (The Tg of the homopolymer has been reported as from >200 up to 240°C[183,188,197]).

In addition the homopolymer is stiff and some of its mechanical properties such as impact strength, flexural strength, and flexural modulus are 12.5%, 21.7%, and 22.5% less than polymethyl methacrylate respectively[197]. The extensibility of the polymer of 2-carbethoxybicyclo [2,2,1] hepta-2, 5-diene was only 6%[188].

6.3 Experimental

6.3.1 Materials

All materials were obtained from B.D.H. or from Aldrich Ltd. as indicated. The chemicals were analytical grade or first grade general laboratory reagents, as follows:

(A) Monomers

Acrylonitrile was obtained from B.D.H., and was re-distilled before use.

Itaconic acid was supplied by B.D.H.

Bicyclo [2,2,1] hepta-2, 5-diene was obtained from Aldrich, and was re-distilled before use.

(B) Solvents

Dimethyl sulphoxide (DMSO), (Analar)
Dimethyl acetamide (DMA,(Analar)
Dimethyl formamide (DMF)

All solvents were supplied by B.D.H. and were used without further purification.

(C) Initiators

Azo-bis-isobutyronitrile (AIBN) was supplied by B.D.H. and was recrystallised from warm methanol.

Ceric ammonium nitrate was technical grade, from B.D.H.

Ammonium persulphate and sodium metabisulphite, (analar grades) supplied by B.D.H., were used without further purification.

Table 6.3 Some physical properties of the raw materials

Materials	Supp.	M.W.	Density	n_D	Remarks
Monomers					
Acrylonitrile $CH_2:CHCN$	B.D.H.	53.06	0.806	1.391	redistilled
Itaconic acid $CH_2:C(COOH)CH_2COOH$	B.D.H.	130.10	1.632	-	
Bicyclo [2,2,1] hepta-2,5-diene	Ald.	92.14	0.9064	1.4702	redistilled
Solvents					
DMSO	B.D.H.	78.13	1.10	1.478	
DMA	B.D.H.	82.12	0.94	1.438	
DMF	B.D.H.	73.09	0.948	1.430	
Initiators					
AIBN	B.D.H.				recrystallised

The main physical properties of the monomers and the solvents are shown in Table 6.3

6.3.2 Polymerisation

Three general methods of polymerisation are used commercially, namely the solution method, the suspension method, and the emulson method[200]. It has been claimed that, of these, the solution method and the suspension method are the most frequently employed for acrylic fibre manufacture[201]. In solution polymerisation, the polymer is retained in solution by addition of a suitable solvent, while in the suspension method, polymerisation is carried out in aqueous media and the polymer precipitates as it is formed. The former method is particularly convenient for fibre manufacture since, under favourable conditions, the polymer solution can be spun directly, so that the troublesome processes of isolation and redissolving of the polymer are avoided[202]. It was decided to prepare copolymers using bicyclo [2,2,1] hepta-2, 5-diene as comonomer , using suspension polymerisation as the most convenient procedure.

6.3.2.1 Suspension polymerisation

A 1 litre 3 neck flask equipped with a stirrer, reflux condenser and a gas inlet tube, was placed in a constant temperatures bath which was maintained at 50°C. To the flask was added 700cc distilled water and 0.0 275 g H_2SO_4 (1% H_2SO_4 solution was prepared and 2.75 g of the solution was used). A rapid stream of nitrogen was passed through the solution for 30 minutes. The nitrogen flow was then reduced to about one bubble per second and 50g of acrylonitrile and 2g bicyclo [2,2,1] hepta-2, 5-diene were added to the flask. The reduction-oxidation catalyst, consisting of ammonium persulphate and sodium metabisulphite, 1.66g and 0.67g respectively, each dissolved in 50cc of deaerated water were then added consecutively with a 30 second interval between additions. The polymerisation was stopped after 4 hours. The polymer was filtered off and washed several times with distilled water and finally washed with methanol, filtered and dried in a vacuum oven at 50°C overnight. The overall product was weighed and then stored in an evacuated desiccator over P_2O_5.

Suspension copolymerisation of acrylonitrile and bicyclo [2,2,1] hepta-2, 5-diene was also carried out using ceric ammonium nitrate as initiator, as follows:

25g acrylonitrile, 160 CC distilled water , 1g bicyclo [2,2,1] hepta-2, 5-diene, 12.64g concentrated HNO_3, and 1.25g ceric ammonium nitrate were placed in a 300 cc screw cap dyeing bottle, with an airtight cap. It was capped and placed in a rotary dyeing bath at room temperature. Polymerisation seemed to begin after about one hour and decoloration of the solution occurred after about three hours. The polymerisation was stopped after 3½ hours, and the polymer was washed and dried as described above.

6.3.3.2 Solution polymerisation

A 300cc screw cap dyeing bottle, with an airtight cap, was charged with solvent, in the range 100-130ml (See Table 6.5 for precise amounts). A rapid stream of nitrogen was passed through the solvent for 30 minutes. The nitrogen flow was then shut-off and a calculated amount of acrylonitrile and other comonomer (or co-monomers) were added to the bottle. The bottle cap was tightened and the bottle was shaken by hand until all ingredients were mixed thoroughly (In the case where itaconic acid is present, it should be allowed to dissolve completely). Then the bottle was opened and a calculated weight of recrystallised AIBN, which was dissolved in a small volume of solvent, was added. Nitrogen was then passed through the bottle for 10 minutes, after which it was capped and placed in a rotary dyeing bath, maintained at the desired temperature, and rotated for the necessary time at constant temperature. The resulting reaction mixture was collected from the tube, and poured into methanol, and the copolymer was recovered in the form of solid lumps which precipitated in the methanol. The solid lumps were ground into finer particles with the aid of a liquidiser. The copolymer was collected on a sintered glass crucible of porosity No. 1 and washed several times with a mixture of methanol/distilled water, and several times with distilled water and finally with methanol. The product was dried in a vacuum oven at 50°C for 24 hours. The overall product was weighed and then stored in an evacuated desiccator over P_2O_5.

6.3.3 Polymer characterisation

6.3.3.1 Viscosity molecular weight

The $\bar{M}w$ of the samples was calculated from viscosity measurements of the polymer solutions. The viscosity measurements were carried out in an Ubbelohde suspended level dilution type viscometer. Solutions (1% w/v) were made up by dissolving 1g of sample in 100ml of DMF. The solution was filtered through a sintered glass filter, porosity No. 1, into another flask. The required amount of filtered solution was transferred into the viscometer in a thermostat bath (maintained at 30°C) using a long narrow pipette and the flow time was determined. Three flow times checking within 0.2 seconds were obtained before diluting the polymer solution with the solvent, again using a long narrow pipette. After each dilution, nitrogen from a cylinder was bubbled through the solution to assure proper mixing.

From the flow times of the solvent and the solutions with different concentrations the relative viscosity, the specific viscosity and the viscosity number were calculated by using the following formulae:

relative viscosity, $\eta_r = \frac{ts}{to} = \frac{\eta_\$}{\eta_o}$ (6.8)

Specific viscosity, $\eta_{\$p} = \eta_r - 1$ (6.9)

viscosity number, $\eta_{\$p}/c$ (6.10)

where,

t_o and t_s are the flow times of solvent and of dilute solution of polymer in the same solvent respectively.

c, is the concentration of polymer solution in g/100cc (g/dl),

$\eta_\$$ is the viscosity of solution, and

η_o is the viscosity of solvent.

The viscosity number was plotted against concentration and the limiting viscosity number, [η], (or intrinsic viscosity) determined from the intercept at the ordinate.

$$[\ \eta\ ] = (\ ^{\eta}sp/c)_{c \rightarrow o} \qquad (6.11)$$

This technique is based on the equation of Huggins.[204]

$$^{\eta}sp/c = [\ \eta\ ] + K\ [\ \eta\ ]^2 c \qquad (6.12)$$

where K is the Huggins constant, and $[\eta]$ is the limiting viscosity number. The average molecular weights of the polymer were determined according to the equation (6.13)[203]

$$[\eta] = 3.46 \times 10^{-4}\ \bar{M}w^{0.733} \qquad (6.13)$$

6.3.3.2 IR spectroscopy

Infra-red spectroscopy was done on samples as KBr discs.

6.3.4 Spinning and testing

6.3.4.1 Fibre production

Dope containing 23% by weight of polymer and copolymers were prepared as follows:

For 30-40g of polymer the amount of solvent was calculated by using formula (2.1). The solvent was poured into a glass bottle and placed in a bath cooled with a mixture of water and ice for 10-20 minutes. Then the polymer was added to the bottle with gentle mixing. The mixing was continued for at least 5 minutes, and then the mixture was left to stand for 2 hours. The bottle was then transferred to an oven at 60°C for 4 hours. The solution was then mixed with a stainless steel stirrer (120 r.p.m.) for 12-16 hours at room temperature. The dope was poured into the spinning reservoir and allowed to stand for 2-3 hours at 60°C. Other procedures were described in Chapter 2, under conditions shown in Table 6.6. On one occasion the dope used was the polymer solution obtained by polymerisation (Samples Nos. 6-12-5 and 6-12-6).

For comparison a dope containing 23% Courtelle fibre was prepared as described in Section 2.2.2.

6.3.4.2 Mechanical testing

Mechanical testing under standard conditions was carried out as described in Section 2.3.2. For testing under hot/wet conditions a special stainless-steel reservoir, 30cm in length and 15 cm in diameter, which was equipped with a tap at the bottom was used. The bottom end of the reservoir was conical, and it could be fixed to the rack of the Instron testing machine, where usually the lower jaw is held. Inside the reservoir, was placed a jaw, which was used as the lower jaw. A 1 kw jacket heater was fixed around the outside of the reservoir and was insulated with glass-wool and aluminium foil. The heater was connected to the mains through a rotary regulator and a thermometer was maintained in the reservoir during the test. The temperature fluctuation was around ±2°C. For each test, the reservoir was filled with water (up to 1 cm of its edge), and heated up to 90°C. Then the sample was fixed to the jaws in such a manner that the whole sample, including that part of the upper jaw which held the sample, was covered by the water. The sample remained in the hot water for 60 secs. Then the machine was switched on for the testing operation. For each fibre ten samples were tested. The speed of testing was the same as that of the standard conditions. It was noticed that, for those fibre produced with hot draw-ratios less than 4, this test, under the conditions described above, was not suitable as the results were not reliable because of the very high extensibility of the fibres. To avoid this, testing was carried out only for those samples that were drawn with high draw ratios (4 times and more).

6.4 Results and discussion

It should be mentioned that although about a hundred polymerisations were carried out, only those copolymers which were capable of producing fibres with reasonable properties were characterised, as the aim of the experiments was to produce copolymers suitable as fibre forming materials.

With regard to this, after each polymerisation, the product was tested for solubility in DMF, DMA, or DMSO. If the result was satisfactory, then a polymer dope with concentration between 15% and 25% was prepared, and the spinning of such a dope was carried out. If it was possible to produce fibre without too much difficulty, and spinning and drawing operations were maintained for a reasonable time, then the copolymers were studied in some detail. In other words, no attempts were made to characterise all copolymers which were produced, because this would have been too time consuming, and there would not have been enough time for the fibre-spinning.

Solubility tests were carried out on 1g samples of copolymer obtained from suspension polymerisation, using ammonium persulphate and sodium metabisulphite as initiators. The copolymer was treated with 100cc DMF. After one hour it was noticed that there were some very small insoluble particles in the solution. The solution was shaken for a few minutes and left for another four hours in the oven at 50°C. The insoluble material was still present. The solution was heated at 80°C for 2 hours, while stirring with a magnetic stirrer, but the insoluble particles did not dissolve. The same procedure was carried out with copolymer prepared by using ceric ammonium nitrate, and the result was the same. It thus appeared that the polymer product was not homogeneous. Attempts to make more concentrated solutions for spinning were also characterised by insoluble material remaining. The results suggested that there might be two different polymers present. It was thought this had happened because the acrylonitrile is much more soluble in water than bicyclo [2,2,1] hepta-2, 5-diene, so that polymerisation of each monomer took place in two different phases. In other words, the acrylonitrile polymerised in the water to essentially homopolyacrylonitrile and the bicyclo [2,2,1] hepta-2, 5 diene polymerised, if at all, in a separate phase. (The low density and limited solubility of the bicyclo [2,2,1] hepta-2,5-diene compound were illustrated by its presence as a separate surface layer). With this assumption, the suspension polymerisation was abandoned, and solution polymerisation was carried out as both monomers are soluble in such solvents as DMF, DMA and DMSO.

The copolymers produced by solution polymerisation, on the other hand dissolved completely in DMF, although the viscosities of such solutions became excessively high with a jelly-like consistency as the concentration of the copolymers in the solvent exceeded 15% w/w. Attempts were made to spin the solutions into 50/50 DMF/water at room temperature, but problems were encountered particularly at the extrusion and coagulation stages, and it was impossible to carry on a reasonable drawing as the undrawn fibre appeared to be too inextensible. Faced with this problem it was decided to use itaconic acid as a third monomer and to produce terpolymers by solution polymerisation. It was mentioned[92] that, when acrylonitrile is copolymerised with itaconic acid, the copolymers so formed give fibres whose mechanical properties, especially the extensibility, are improved substantially. The amount of itaconic acid in comonomers in any case was around 6% in the feed.

Table 6.4 shows the solution polymerisation conditions examined using different solvents, together with the polymer yields and the calculated weight percentage and mole percentage of each monomer in the copolymer feeds. It is clear from these results that among different parameters of the polymerisation, the effect of the solvent is the most important factor for the polymer yield. The highest yields were obtained when DMSO was used as a solvent. It was also noticeable that at the end of the polymerisation period the DMSO solutions were much clearer than the polymer solutions prepared using the two other solvents. In the case of DMA, the first attempts to produce polymer yielded opaque gel type polymer solutions.

Table 6.4 Solution polymerisations

NO.	Solvent DMSO (cc)	AIBN g	time h	temp °C	Monomers g				wt % of mon. in pol.			Mole % of mon.in pol			Polymers yield	
					AN	IA	bi.c.	Total	AN	IA	bi.c.	AN	IA	bi.c.	wt g	Con-version %
6-1	150	1	18	55	60.5	3.5	2.71	66.66	90.7	5.25	4.07	95.3	2.26	2.43	60.0	82.5
6-2	150	1	18	55	60.5	3.5	0.67	64.62	93.5	5.42	1.04	97.1	2.29	0.63	53.9	83.5
6-3	150	1	18	55	60.5	0	2.71	63.16	95.7	0	4.29	97.5	0	2.52	45.5	72.1
6-4	150	0.7	16	55	40.3	3	0	43.3	93.1	6.93	0	97.1	2.94	0	41.5	95.8
6-5	150	0.7	16	55	40.3	3	0.45	43.75	92.1	6.86	1.03	96.4	2.92	0.64	37.4	85.4
6-6	150	0.7	16	55	40.3	3	1.81	45.11	89.1	6.83	4.12	94.6	2.87	2.49	28.5	63.2
6-7*	100 +2.5	0.7	36	52	40.3	2.7	0.91	43.91	91.8	6.15	2.07	96.1	2.66	1.26	25.0	56.9
6-8*	100 +2.5	0.7	36	52	40.3	2.7	0	43.0	93.7	6.28	0	97.3	2.69	0	38.12	88.7
6-9*	100 +0.5	0.5	30	52	40.3	3	0.72	44.02	91.0	7.26	1.74	96.1	2.91	1.01	28.0	63.3
6-10*	180	1	23	55	60.5	3.5	3.63	67.58	89.5	5.18	5.37	94.5	2.24	3.24	56.1	83.0
6-11**	75	0.2	40	60	13.7	1	1.81	16.51	83.0	6.06	10.97	90.8	2.82	6.34	8.1	49.2
6-12	100	1	18	55	60.5	3.5	1.5	65.5	-	-	-	-	-	-	-	-

* = DMAC + conc. H_2SO4

** = DMF

It was thought that this might be due to cross-linking, since it has been mentioned[205] that acidifying the solvent, before initiating the polymerisation, by adding an organic or inorganic acid can prevent gelling of the polymerisation system. When DMA was acidified by addition of 2% sulphuric acid (by weight, based upon the weight of DMA), before polymerisation, the resulting polymer solution was clear. However the presence of H_2SO_4 decreased the yield of the polymer. Another factor which affected the yield was the bicyclo [2,2,]] hepta-2,5-diene content. An increase in the amount of this monomer in the terpolymer decreased the yield, and this decrease was very pronounced as shown in Fig. 6.1. Other factors, such as amount of initiator, time, and temperature were not investigated except to find by trial and error the conditions which gave polymer with [η] values in the range 1.5-2.0 .

Viscosity measurements were carried out for some of the copolymer samples and Table 6.5 and Fig. 6.2 show the results of such measurements. The viscosity measurement of a Courtelle sample is also shown for comparison. It is clear from these results that for otherwise identical polymerisation conditions, the molecular weight of the terpolymer not only varied with the amount of bicyclo [2,2,1] hepta-2, 5-diene, but the slope of the viscosity number-concentration line was also changed. The slope of Sample 6-4, which is a copolymer with no bicyclo [2,2,1] hepta-2, 5-diene, is more or less similar to the slope of that of the Courtelle sample. But the slopes for the two other samples, where bicyclo [2,2,1] hepta-2,5-diene was incorporated, are detectably steeper. Another interesting feature of the effect of this co-monomer was on molecular weight, in that the addition of 0.64 mole % of the bicyclo [2,2,1] hepta-2,5-diene caused an increase of the limiting viscosity number, [η], (and hence the molecular weight of the terpolymer), while the further increase of this monomer in the system reduced the limiting viscosity number as shown in Fig. 6.3

Table 6.5 Solution viscosity measurements

Sample No.	Mole % bi.c.h.d. (feed)	$\eta_{SP/C}$			[η]	$\overline{MW} \times 10^{-4}$
		C(%)				
		1	0.78	0.64		
6-4	0	2.70	2.49	2.30	1.60	10.00
6-5	0.64	3.60	3.12	2.91	1.73	11.13
6-6	2.49	3.24	2.80	2.62	1.51	9.24
6-C (Courtelle)	--	2.91	2.65	2.48	1.72	11.04

Fig. 6.1 Effect of bicyclo [2,2,1] hepta-2,5-diene on polymer yield

(See Table 6.4 for experiments conditions), in DMSO ○

in DMAC ●

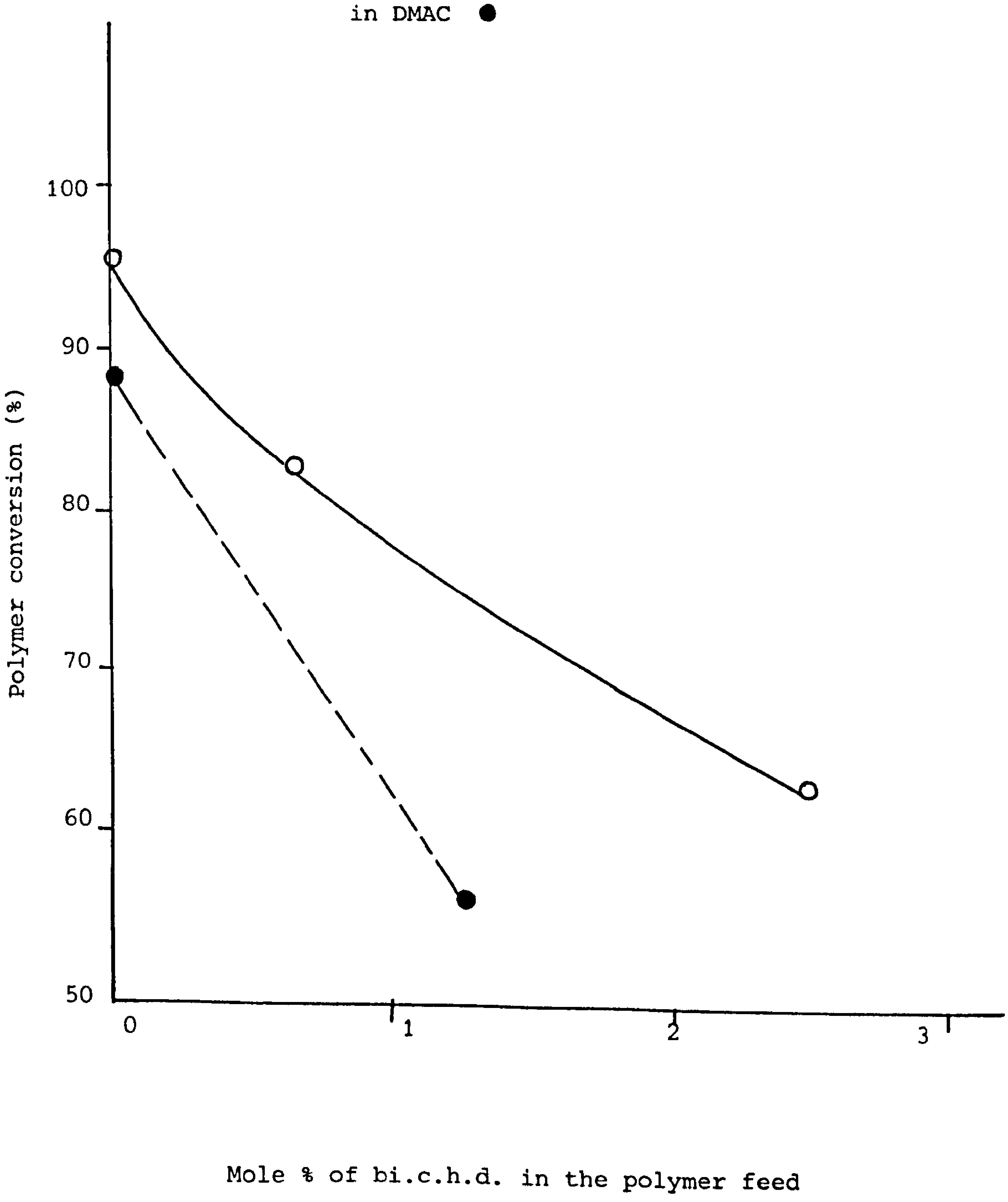


Fig. 6.2 Solution viscosity measurements of some polymers,

6-5, ◒ , 6-6 ● , 6-C ○ , 6-4 ◓

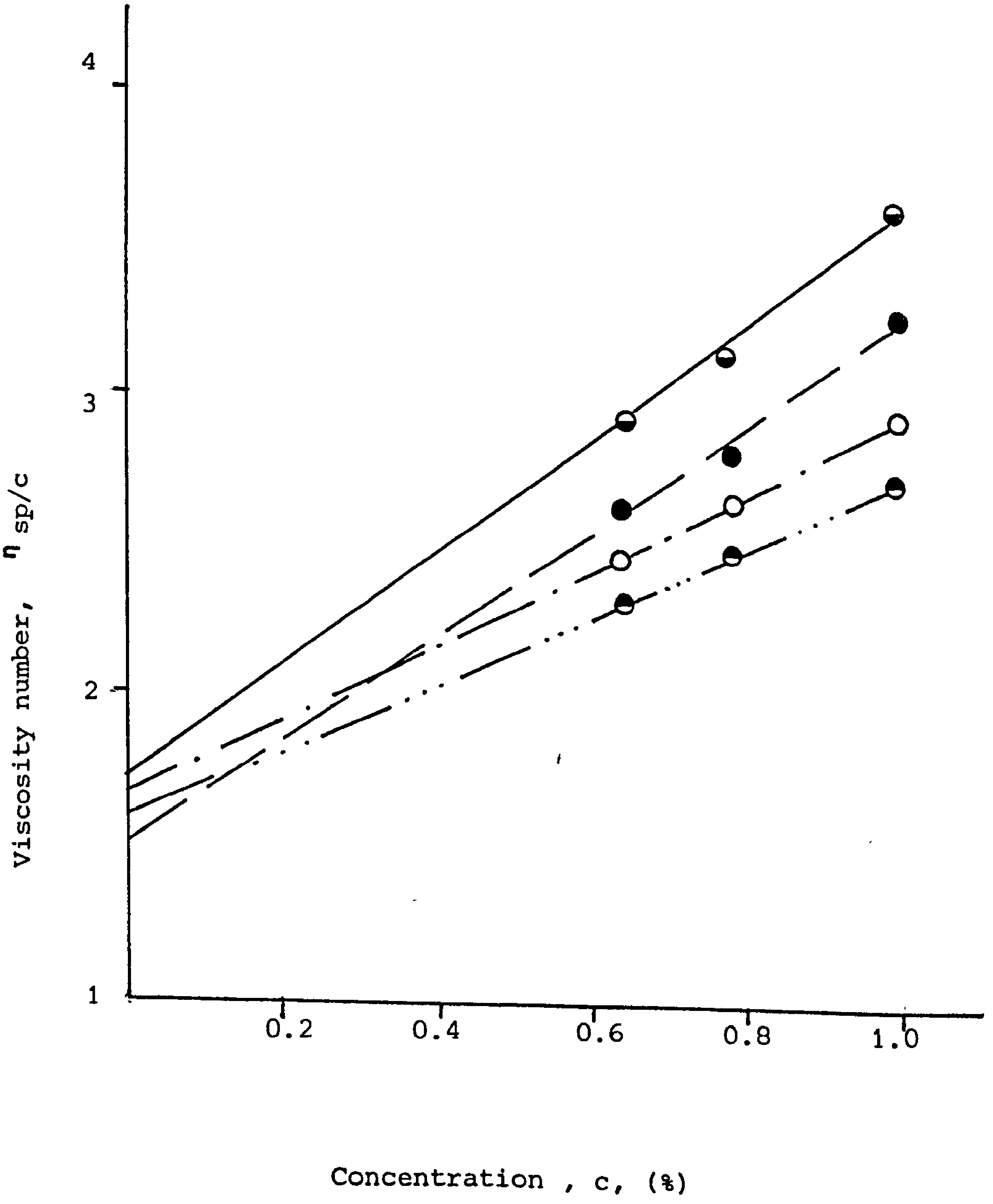
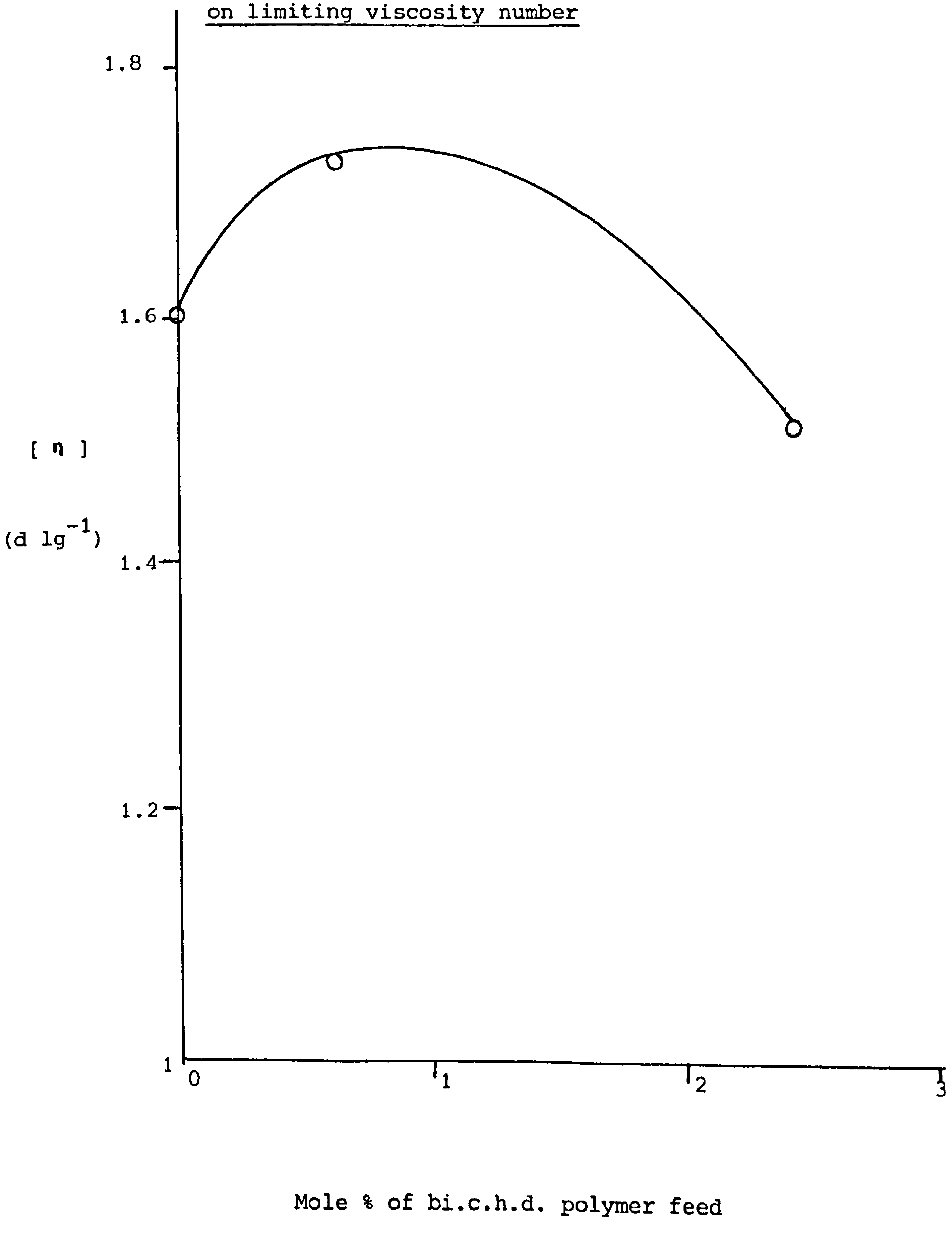


Fig. 6.3 Effect of bicyclo [2,2,1] hepta-2, 5-diene on limiting viscosity number



One of the most powerful methods to study the polymerisation reaction of bicyclo [2,2,1] hepta-2, 5-diene is IR spectroscopy, which has been used extensively for this purpose. According to the literature, the IR spectrum of a homopolymer of bicyclo [2,2,1] hepta-2, 5-diene usually shows three absorption bands at 6.4μ, 12.4μ and 14.1μ. However, copolymers of this monomer with different vinyl monomers showed only the absorption band at 12.4μ, when it is not masked by others, and the two other bands were not observed[180]. Accordingly, IR spectra of some terpolymer samples were obtained, and Fig. 6.4 shows such spectra for samples 6-6, 6-9, and 6-11. All three spectra show an absorption band at 12.4μ and the absence of the two other bands at 6.4μ, and 14.1μ. This data confirmed that the bicyclo [2,2,1]hepta-2,5-diene was copolymerised essentially to give nortricyclene units in the copolymers, and hence such units exist in the copolymer backbone. No other units, such as the unsaturated unit, which is present when bicyclo [2,2,1] hepta-2,5-diene is homopolymerised, were detected.

On the other hand, it was found[206] that the IR spectrum of the copolymer of acrylonitrile and itaconic acid showed a similar weak absorption band around 12.8μ as shown in Fig. 6.5a for a sample made from a 94:6 AN:ICA feed. To confirm that 12.4μ band was due to the nortricyclene unit, sample 6-3 which was only of a copolymer of acrylonitrile and bicyclo [2,2,1]hepta-2,5-diene (with no itaconic acid) was prepared

Fig. 6.4 IR spectra of terpolymers,

(a) sample 6-6
(b) sample 6-9, and
(c) sample 6-11

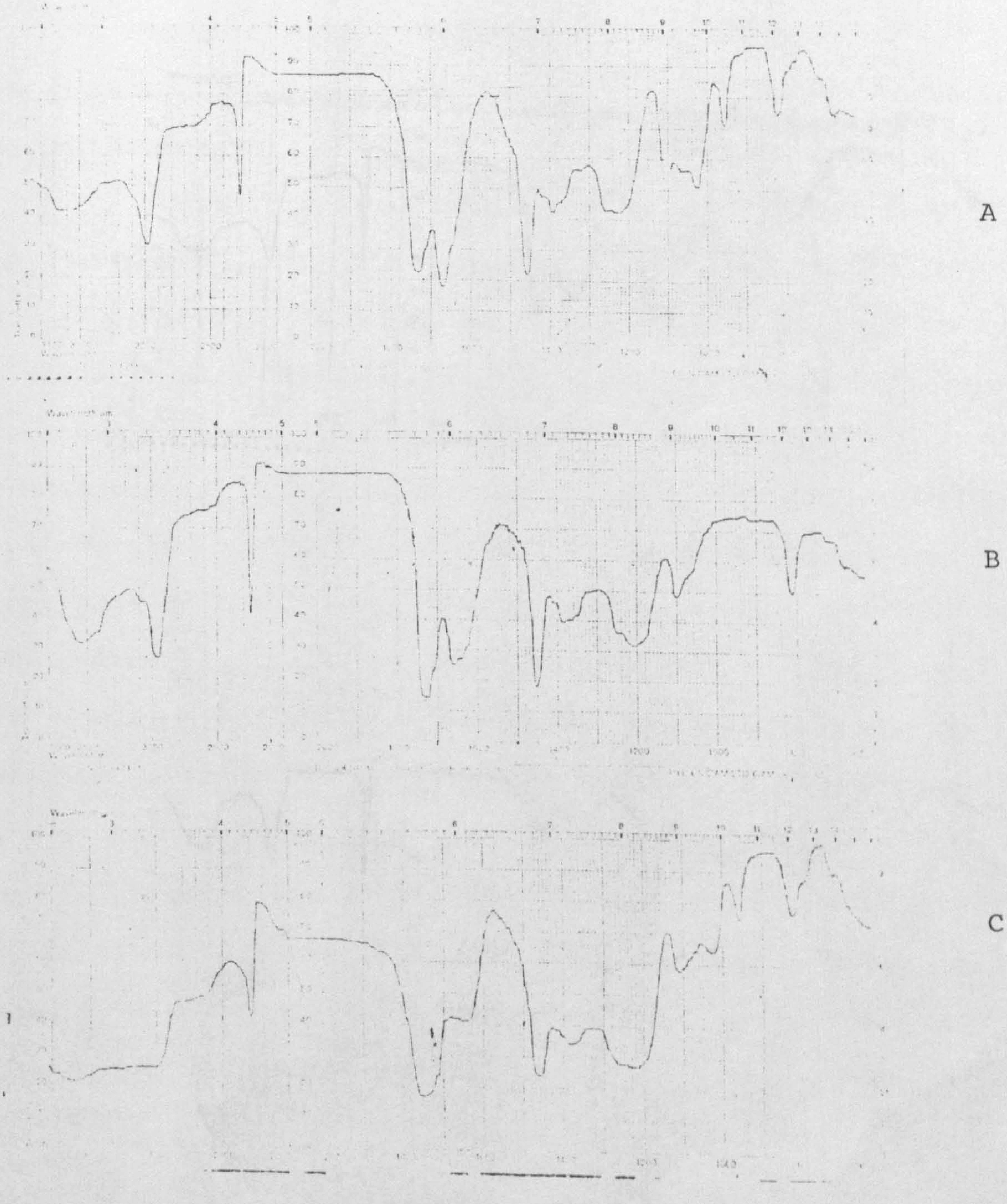
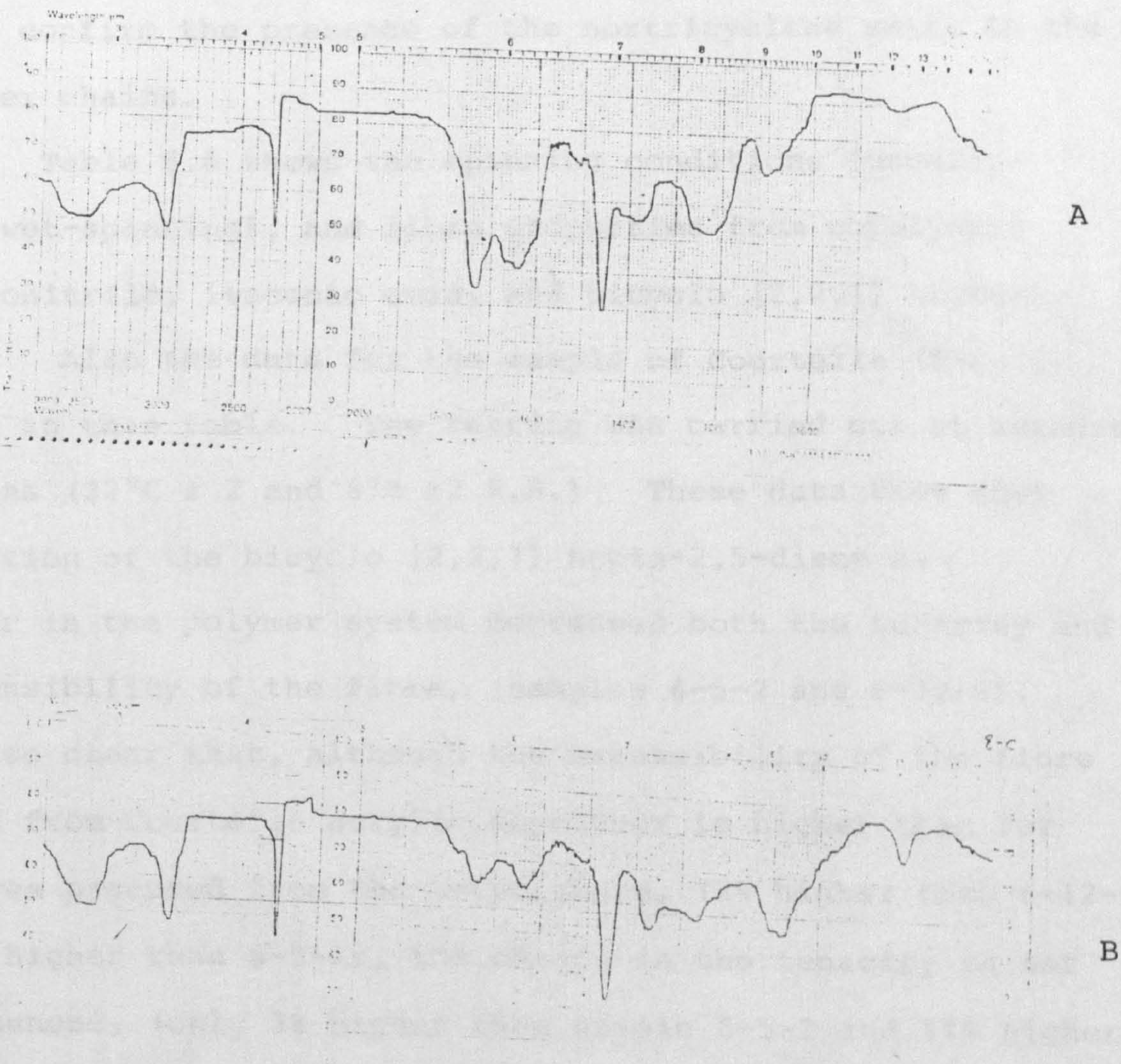


Fig. 6.5 IR spectra of copolymer and terpolymer,

(a) sample 6-4 (b) sample 6-3



and Fig. 6.5b is the IR spectrum obtained. It shows again the absorption band at 12.4μ. In addition, the comparison of Fig. 6.5a with Fig. 6.5b, clearly show that the intensity of the absorption band for the copolymer without bicyclo[2,2,1] hepta-2,5-diene, is quite different than that of the copolymer without itaconic acid. These spectra could therefore be taken to confirm the presence of the nortricyclene units in the terpolymer chains.

Table 6.6 shows the spinning conditions (usually dry-jet wet-spinning), and fibre properties from copolymers of acrylonitrile, itaconic acid, and bicyclo [2,2,1] hepta-2,5-diene. Also the data for the sample of Courtelle (6-C-1) is shown in this table. The testing was carried out at standard conditions (22°C ± 2 and 67% ±2 R.H.) These data show that the addition of the bicyclo [2,2,1] hepta-2,5-diene as comonomer in the polymer system decreased both the tenacity and the extensibility of the fibre, (samples 6-5-2 and 6-12-6). It is also clear that, although the extensibility of the fibre produced from Courtelle acrylic copolymer is higher than for the fibres produced from the terpolymers, (2% higher than 6-12-6 and 25% higher than 6-5-2), the change in the tenacity is not so pronounced, (only 3% higher than sample 6-5-2 and 11% higher than sample 6-12-6). On the other hand, the initial stress of the latter two fibres are higher than for the former (by about 7%)

Table 6.6 Spinning conditions and filaments properties

Sample No.	Dope conc. %	Spinneret size	Pot		Pump		Coag.		Draw ratio		Yarn count	t	E	I.S.	$tE^{\frac{1}{2}}$
			T °C	P	T °C	R rpm	T °C	Comp.	Jet	Hot	dtex	g/d. tex	%	g/d. tex	
6-5-2	18.5	400/8	27	8	25	4	25	70/30	2.8	7.5	100	4.11	12.5	1.85	14.5
6-5-3**	18.5	400/8	27	8	25	6	25	70/30	1.5	3	370	1.04	9.6	0.65	3.2
6-C-1	23	400/8	25	5	25	4	25	50/50	2.8	7.5	125	4.24	16.7	1.72	17.3
6-6-4	20	300/10	30	10	27	4	25	50/50	2.2	4.4	155	2.21	22.2	1.14	9.03
6-12-5*	-	300/10	35	14	30	3	25	60/40	1.6	5	175	2.90	16.1	1.13	11.06
6-12-6*	-	300/10	35	14	30	3	25	60/40	1.6	6.3	125	3.77	16.4	1.83	15.2

Remarks: * Samples 6-12-5 and 6-12-6 were spun directly from polymerisation solution into DMSO/water bath.

** Sample 6-5-3 was wet-spun, and spinning continued for 5 minutes only. I.S. stress at 3.94% strain.

This data suggest that the fibres produced from the terpolymers were more brittle compared with the fibre produced from the Courtelle copolymer. This brittleness is seriously affecting the properties of the wet-spun fibre (sample 6-5-3), where its extensibility and tenacity are very low. In addition the wet-spinning process could not be carried on for more than above five minutes as the filament breakage was so frequent.

Table 6.7 shows the mechanical properties and spinning conditions of filaments produced from terpolymers in standard conditions and in hot/wet conditions. The data show that with a moderate draw ratio (4.4 times) these fibres in hot/wet conditions lost about half of their tenacity while their extensibility increased less than a factor of 2. On the other hand, their strengths at 2% extension were decreased by a factor of about four times. For a better comparison of these results, the data of patent work[205] for high hot water resistance acrylic copolymers are shown in Table 6.8.

Table 6.9 and Fig. 6.6 show stress-strain data for two different samples, one the terpolymer con taining bicyclo [2,2,1] hepta-2,5-diene and itaconic acid as comonomers and the other the Courtelle polymer. The testing was carried out in standard conditions (22°C ± 2 and 67% ± 1 RH) and in addition in hot/wet conditions (90°C ± 2 in water). It is clear from these results that the value of the tenacity for the fibre produced from the Courtelle polymer in the hot/wet conditions falls by a factor of about 2.5, while the tenacity of the fibre produced from the terpolymer falls by a factor of about 3. But the value of the extensibility of the former sample in the hot/wet conditions increased by about 228% compared to the extensibility in the standard conditions, whilst the increase for the terpolymer sample was only 18.4%. In addition, at low extension (3.94%), the stress value of the sample No. 6-5-2 reduced from 1.8g/d tex to 0.30 g/d tex, which is about 6 times lower, and for the sample 6-C-1 reduced from 1.76 g/d tex to 0.165 g/d tex or about 10.6 times lower. In other words, although the tenacity of the terpolymer in the hot/wet conditions was reduced much more than the tenacity of the Courtelle fibre in the same conditions, it seems that the value of the initial Young's modulus of the terpolymer fibre in the hot/wet conditions improved substantially in comparison with Courtelle fibre. Also, the dimensional stability of the fibre produced from the terpolymer, under hot/wet conditions was much better than the Courtelle fibre, as the increase of the extensibility of the former fibres are minimised.

Table 6.7, Mechanical properties in standard and hot/wet conditions

Sample No.	Spinning conditions			Count d tex	Tenacity g/d tex		Extensibility %		Strength at 2% elongation	
	Pump speed r.p.m.	Jet-stretch ratio	Spinneret size		ST	HW	ST	HW	ST	HW
6-6-4	4	2.2	300/10	155	2.21	1.02	22.2	35.52	0.82	0.17
6-6-7	6.5	1.9	400/8	250	2.47	1.45	27.7	34.6	0.89	0.23
6-6-8	3.5	4.2	500/6	135	2.79	1.49	27.0	37.2	0.88	0.30
6-6-9	3	4.9	500/6	120	2.49	1.33	24.3	41.2	0.87	0.21

Remarks:

Draw ratio = 4.4

Dope concentration 20%

Coagulation bath composition 50/50 v/v DMF/water

ST - Standard condition

HW - Hot water condition

Table 6.8 Strength and elongation of high hot water resistance acrylic copolymers [205]

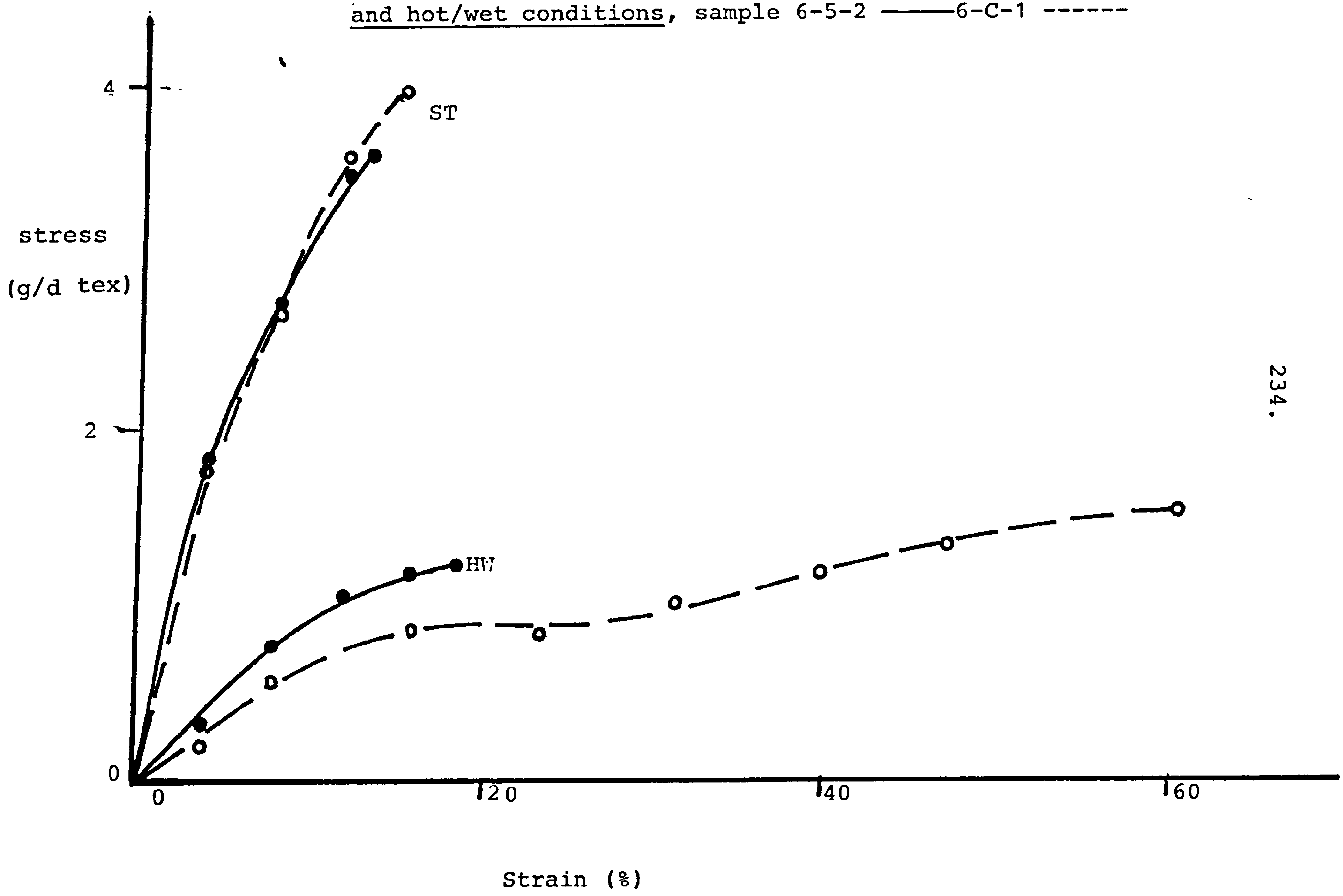
Sample	Strength g/denier		Elongation %	
	Dry	hot water*	Dry	hot water
1	4.41	1.7	14.8	36
2	4.59	2.4	14.0	32
3	4.14	1.7	16.3	34.9
6-5-2	4	1.36	13.2	18.58

* Hot water temperature = 90°C

Table 6.9 Stress/strain relation of Courtelle filament and terpolymer

Stress g/d tex / Strain %	Standard condition		Wet/hot condition	
	6-5-2	6-C-1	6-5-2	6-C-1
1.18	0.94	0.91	-	-
3.94	1.84	1.79	0.31	0.17
7.88	2.73	2.68	0.74	0.54
11.82	3.47	3.59	1.04	-
13.20	3.60	-	-	-
15.17		3.99	-	-
15.76			1.19	0.83
18.52			1.22	-
23.64				0.81
31.52				1.01
39.40				1.20
47.28				1.36
60.68				1.58

Fig. 6.6 Stress-strain curve of two filaments in standard (ST), and hot/wet conditions, sample 6-5-2 ——— 6-C-1 ------



CHAPTER 7. CONCLUSIONS

7.1 Dry-jet wet-spinning

The dry-jet wet-spinning and wet-spinning processes were studied in some detail. First of all, the speed of operation may be much higher in the former as mentioned in several papers and patents. To find the cause of this, the free velocity, maximum jet stretch, and maximum hot draw ratio were analysed in both systems. It was found that although all three factors were higher in dry-jet wet-spinning, the detailed study, as discussed in Chapter 3, showed that the higher free velocity together with the higher hot draw ratios were responsible for the higher operational speed in dry-jet wet-spinning. The maximum jet stretch or what has been termed the spinnability in both systems remained almost the same when the free jet stretch rather than the average jet stretch was discussed.

It was shown that the free velocity (v_f) not only depends on the apparent shear rate but also depends on the environment the spinning solution enters after emerging from the spinneret hole. In fact the effect of this factor on the free velocity appears to be more pronounced than the events inside the spinneret. The presence of the air-gap in dry-jet wet-spinning provides a completely different environment than that in wet-spinning, causing the different free velocities in the two spinning systems. Relative to dry-jet wet-spinning the established free velocity in wet-spinning was reduced considerably. In a spinning system, the free velocity should be established mainly through pump speed (dope flow rate), and spinneret size (hole diameter and its number), though its magnitude will be affected by both dope and coagulation conditions. On the other hand, the coagulation conditions determine to a large extent the solidification process and hence the structural features and physical properties of the filaments. So it is reasonable to conclude that both the solidification process and the spinning solution behaviour just below the spinneret (up to some certain distance) are the most important factors in the processability of these spinning systems and the properties of the fibres produced by them.

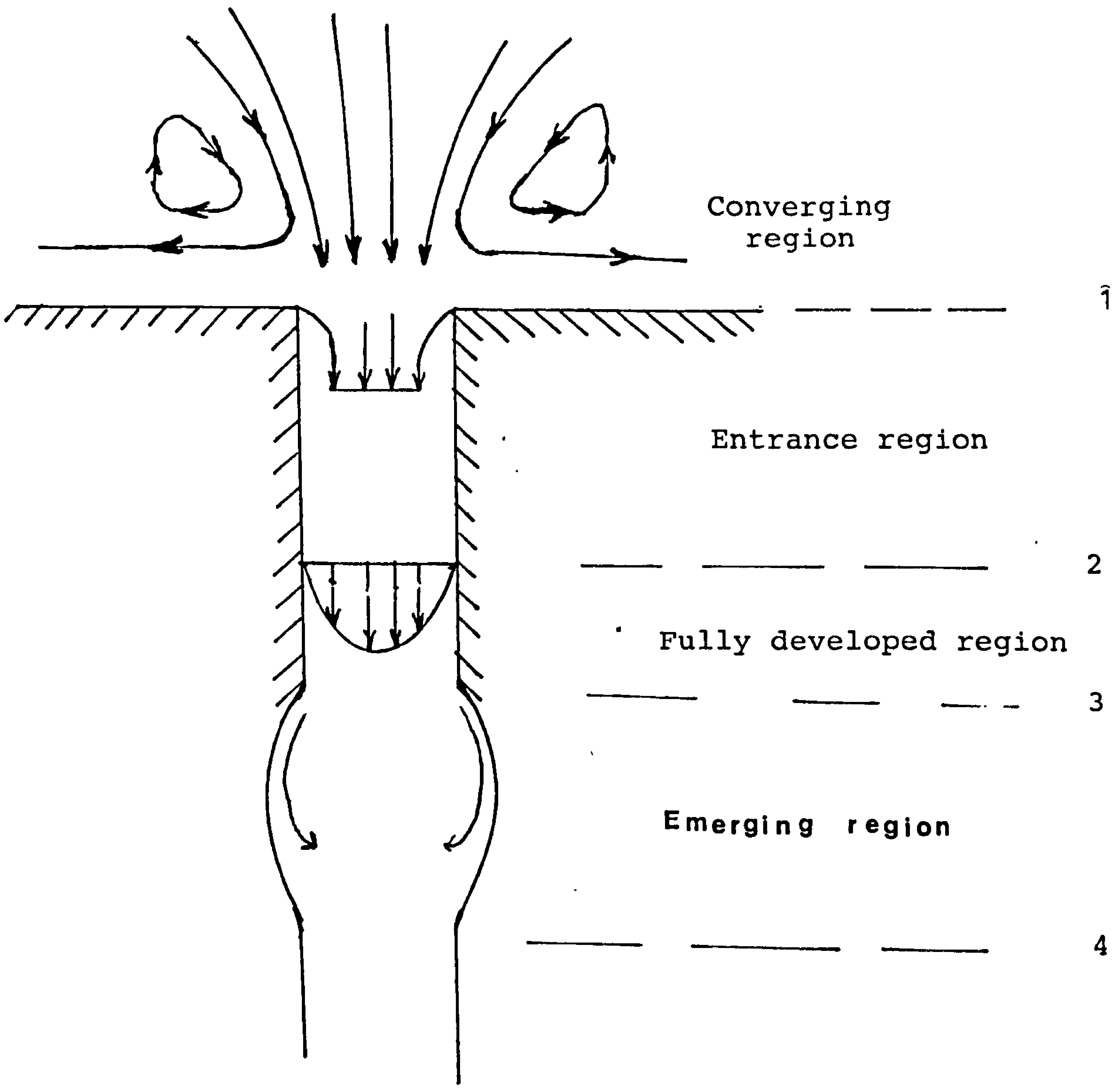
The amount of published work dealing with the characteristics of the actual extrusion process in wet-spinning of acrylonitrile polymers and copolymers may be divided into two categories, as shown below.

(a) The hydrodynamics and rheology of the flow of a viscoelastic fluid through a fine hole. This work is confined in the main to an examination of the spinning line and to defining the effect of the coagulating variables on the hydrodynamics.

(b) Thermodynamic and diffusional considerations with respect to the physical and structual properties of undrawn and drawn fibres. These studies, in the main, are concerned with the effect of the coagulating variables on the physical properties and structural features. It seems that the rheological behaviour of the spinning solution just after its emergence from the spinneret hole, and the resulting effect on hydrodynamic and diffusional processes have not been studied so far.

In the fibre spinning process, the viscoelastic properties of polymer melts and solutions affect the fluid flow inside and outside the spinneret and this flow pattern outside the spinneret, together with the forces acting on the filament, produces a velocity profile which is different from the average velocity. For viscoelastic fluids, the flow into the spinneret hole does not take place in the same manner as with other fluids such as time-independent fluids. The elastic properties of the fluid influence the flow pattern. The flow of a viscoelastic fluid into the entrance of a tube has been shown to follow the streamline pattern shown in Fig. 7.1.[208] In the converging flow region upstream of the tube entrance, only part of the fluid approaching the inlet enters the tube. The fluid which enters the tube forms a central conical region. Fluid outside this conical region is diverted away from the inlet to

Fig. 7.1 Flow Pattern of a viscoelastic fluid.[208]



form a torroid vortex[208]. This sort of flow pattern has been shown photographically for a polymer melt[209] and a polymer solution[208] when they were extruded from a reservoir through a capillary. It was also found that this flow pattern could cause some irregularity in the shape of the extruded filament cross-section[210-212] at and above the critical flow rate which is believed to be due to melt fracture[212]. There does not appear to be a discussion of flow lines in the emerging fluid though in view of the die-swell, it seems clear that the flow lines will not be simple. The obvious possibility of the flow lines leading to a vortex has been added to Fig. 7.1, though it must be admitted that these are, at this stage, purely speculative.

In the light of the above discussion, it is acceptable to suppose that, in these two spinning systems when the extruded fluid leaves the spinneret holes, although some part of it (particularly close to the centre of the cross-section) will move in the direction of the applied force, the other part of the fluid will tend to snap-back (hence the die-swell), due to the viscoelastic characteristics of the dope, and the movement will be more or less the same as exhibited before entering the spinneret holes. In wet-spinning, while the fluid jet still possesses the complex flow profile, that part of the fluid which comes to the surface of the thread-line will precipitate due to contact with the coagulating liquid. It means that, just below the spinneret face the solidification process at the outer section of the emerging thread-line will take place in such a manner that the snap-back motion of the fluid will tend to be frozen and the filament will eventually reflect this profile. This happens because the solidification process and the visco-elastic relaxation, at least for some part of the fluid, will occur simultaneously. On the other hand, in dry-jet wet-spinning, due to the air-gap, almost all the viscoelastic behaviour of the polymer dope will relax and disappear before the thread line enters the coagulating liquid, and therefore, the solidification process will not occur simultaneously with the relaxation of the die-swell.

This account could explain the nature of the differences of the free velocities in these two spinning systems in that there is a strong dependence of the free velocity on the rate of coagulation immediately at the spinneret face. In the former process, the effect of the rheological behaviour of the polymer dope on the solidification process and on the rate of diffusion is almost negligible due to the air-gap, but in the wet-spinning process this effect cannot be ignored, though it can be changed to some extent by the changes in the spinning conditions and nature of the polymer and the dope composition. For example, it seems that in the commercial production of acrylic fibres these effects are minimised in two important but separate ways; one is related to the polymer characteristics and another related to the spinning conditions. Usually acrylic polymers and copolymers which are used industrially for fibres have molecular weights lower than the maximum value that could be easily obtained during polymerisation. Another way is to introduce such comonomers into the copolymer which perhaps reduce the viscoelasticity of the polymer solution for a given concentration as well as reducing the rate of coagulation, e.g. the use of itaconic acid as comonomer, which produces better processability[92]. The polymer dope is always prepared with a relatively low polymer concentration (compared with dry-spinning), which is again the minimum concentration to achieve satisfactory properties in the fibre. In addition, the spinning conditions in the coagulation bath are usually chosen in a manner that the rate of diffusion is not too rapid.

However, with regard to the effect of the air-gap on the free velocity and viscoelastic properties of the polymer dope as discussed above, it is possible to propose that there are two distinguishable zones in the wet-spinning process in the coagulating bath, and that the solidification process takes place differently in these two zones; the first is immediately below the spinneret face extending a short distance into the bath where the filaments are still in a swollen state, because of the die-swell effect as well as other possible rheological effects in the polymer dope, and the second is beyond that, in the main part of the coagulating bath through which the filaments travel. It seems likely that the solidification process and the rate of diffusion in the first zone will be affected to a large extent by the viscoelastic properties of the polymer dope, and in the second zone only by the coagulating conditions. In wet-spinning, the coagulating process in the first zone produces a structure which will limit the extent of attenuation of the filament both in the undrawn state (coagulation bath) and in the drawn state (hot-drawing). This means that in wet-spinning, the solidification process not only forms the filament, but also causes some damage to the fibre structure such as micro cracks on the surface of the fibres. These defects will prevent the application of drawing to its full extent and the aftertreatment operation such as heat treatment is an essential part of the spinning process for repairing some of these defects and developing the fibre properties.

On the other hand, in dry-jet wet-spinning, the solidification process only takes place after the spinning fluid is almost free from the rheological effects as the coagulation only takes place in the second zone. This means that solidification causes minimal damage to the fibre structure and the properties of the fibre are maintained at this stage. So higher draw ratios can be applied and the aftertreatment operation will improve only slightly the fibre properties so that this stage may be used only for higher productivity and increasing the speed of the spinning process. In dry-jet wet-spinning, during their brief passage through the air-gap only a small amount of the solvent, if any, is removed from the extruded filaments with the result that little or no coagulation takes place when the filaments are being attenuated. Because of the high fluidity of the spinning solution in the zone between the spinneret and the coagulating bath, the longitudinal force applied to the coagulating filaments to pull them through and out of the coagulating bath is accepted by the freshly formed filaments, in the main, in this zone. Apparently, the coagulating filaments as a result are passed through the coagulating bath under a minimum tension: that is, the tension exerted on the coagulating filament would be only that tension required to overcome the viscoelastic forces within the filaments and the drag forces in the coagulating bath. Under these conditions, there is also the possibility that the filament exhibits only an extremely thin outer skin and a reduced susceptibility to skin rupture. On the other hand, in wet-spinning a much thicker skin is formed from the very beginning of filament formation, and the longitudinal force necessary to impart a moderate jet stretch in the filaments undergoing coagulation can be sufficient to cause rupture or cracks of the filament skin as shown in plates 4.4A and 4.4B.

If the idea of two separate zones in which solidification occurs is accepted, then it also offers an explanation for the occurrence of macrovoids in the fibre. There is a common belief that in solution spinning, whether dry-spinning or wet-spinning, the mechanisms involved in fibre formation are, mainly, diffusion and mass transfer of solvent and non-solvent (in the case of wet-spinning). Because of these mechanisms all fibres produced by solution spinning contain some amount of voids (in general). However, some factors such as the elastic properties of the polymer solution can significantly affect the fibre structure and its properties under certain conditions . Another important factor, which is associated with the elastic properties of the polymer solution and the jet stretch ratio, is "die-swell". The phenomenon, in solution spinning plays a very important role[70,73,75,213]. The importance of this factor has been discussed in relation to the spinnability of polymer dopes, but appears to have been disregarded in its effect on the physical properties and structure of the fibres with respect to both wet and dry spinning systems.

As mentioned before, there are two types of defect in wet-spun fibres, namely microvoids and macrovoids or capillaries. The presence of microvoids is generally believed to be the result of solvent diffusion which occurs in all fibres produced from solution . Apart from these microvoids,there are some macrovoids, in the micron size range, in the fibres produced by wet-spinning. In this case, unfortunately, there is no agreement on the mechanism of formation of such voids.

The presence of the macrovoids or capillaries in wet-spun fibres and their absence in dry-jet wet-spun fibres suggests strongly that such voids are mainly due to the rheological behaviour of the polymer dope inside and outside the spinneret holes. A close look at the macrovoids in Plate 4.2B shows that the pattern of these voids is more or less similar to the profile of the fluid movement shown in Fig. 7.1. The formation of these voids, certainly, takes place below the spinneret, where the polymer dope could still be affected by its viscoelastic characteristics. So it seems that neither the interpretation of Grobe[85], i.e. the rupture of the internal structure caused by a rigid skin and the subsequent pressure produced by the inward diffusion, nor the postulate of Knudsen et al[86], i.e. that voids are caused by the penetration of the coagulation bath into the fibre throygh surface faults which are probably caused by minor imperfections in the spinneret, are necessarily the only satisfactory explanations for the radial formation of capillaries.

Another noticeable feature is that, generally, the mechanical properties of the fibres produced in dry-jet wet-spinning are better than those prepared from wet-spinning, which is mainly due to the better structural feature of the fibres produced in the former method. However, the mechanical properties of the dry-jet wet-spun fibre are more sensitive toward equipment variablessuch as jet stretch ratio and hot draw ratio. Presumably, this sensitivity is mainly due to the higher extensibility of the fibres produced in this spinning system. It was shown that as the amount of jet stretch increased, the value of the extensibility of undrawn dry-jet wet-spun fibre increased very much (in the range of several hundred percent), and this increase of extensibility allows the application of a much higher hot draw ratio to the fibre. So it could be postulated that increasing the jet stretch causes some sort of structural change in the liquid thread line by reducing the time the liquid thread line has to form some sort of surface structure. This more perfect structure is largely maintained as the soldification process takes place. As this solidification occurs more evenly, it will give rise to a more regular and homogeneous structure in this fibre. Hence it seems very likely that some skin region will exist in the dry-jet wet-spun fibre but it will be finer than in wet-spinning and its formation will be different in this process, and possibly occurs over a longer time.

With regard to the coagulating variables, it seems that these variables have more effect on wet-spun fibres than dry-jet wet-spun. It is, probably, in the main, due to the solidification process, especially in the first zone of the coagulating bath. These variables control the rate of solidification to a large extent. So any change of these factors could have an effect on the rate of solidification and hence the relation between this rate and the viscoelastic relaxation of the thread-line filament below the spinneret face. This behaviour could also be related to the skin formation mechanism as well as the effect of jet stretch on the wet-spun fibres. It is well known that a jet stretch ratio, even less than one, causes microcracks on the surface of the wet-spun fibres; also the rate of skin formation depends on the diffusion coefficients, which are altered by changes in spinning conditions.

Consequently in dry-jet wet-spinning, the coagulating variables could be chosen over a wider range without any significant effect on fibre properties, i.e. polymer dope concentrations of 20% to 30%, or coagulating bath temperatures between 20°C and 30°C, or coagulating bath compositions from 20% to 40% DMF had only a minimal effect on the mechanical properties of the final fibres. In wet-spinning the situation was different and these ranges were much more narrow. This illustrates why controlling the coagulating conditions during wet-spinning is so important.

When the mechanical properties of the dry-jet wet-spun fibres were investigated, it was shown (Section 5) that the variation in interlayer air distance has a small effect on the fibre properties, and in fact for a range of air-gap lengths the changes in mechanical properties are so minimal that they could be ignored. The drawing operation increased the tenacity as well as the tensile factor of the fibre, but the rate of increase in the tenacity for draw ratios up to six times is greater than that beyond that draw ratio. But as the extensibility of the fibre after a 5 times draw ratio remained almost constant, so the tensile factor increased steadily as the amount of draw ratio was increased, and this was in sharp contrast with the wet-spun fibre (Sections 4 and 5). The effect of the drying temperature on the mechanical properties as well as the effect of drawing at higher temperature was referred to earlier. In the wet-spinning the heat treatment markedly affected the structure and consequently the properties of the acrylic fibre[84,71,1] while in dry-jet wet-spinning, although heat treatment affected the mechanical properties of the fibre, the effect was not as pronounced as in the case of the wet-spun fibres. It seems that this is mainly due to the absence of the macrovoids in the latter fibre as drying above the glass transition temperature causes the collapse of the fibre structure, which results in the macro voids being removed in this operation. In the case of the dry-jet wet-spinning, these macrovoids have been reduced to a minimum number in the first stage through the effect of the air-gap. The combination of this factor together with the relaxation of the die-swell in the air-gap zone are believed to be responsible for the net improvement of the dry-jet wet spun fibres.

Another factor which seems important in the dry-jet wet-spinning and which may be responsible for the better mechanical properties of the fibres, is the formation of an outer layer or thin skin in the interlayer air-gap, which regulates the diffusion process in the coagulation bath liquid to some extent. The presence of this outer skin may well reduce the effect of such spinning conditions as bath temperature or bath concentration. In practical terms it means that the dry-jet wet-spinning operation can be carried out over a wider range of spinning conditions than the wet-spinning process, and the adjustment of different variables is not so important in the former process (as discussed earlier).

Finally, the differences between fibre formation in dry-jet wet-spinning and in wet-spinning can be summarised as follows:

(a) In dry-jet wet-spinning, the rheological effects on the thread-line close to the spinneret will be almost absent by the time the filaments enter the bath due to the air-gap, while in wet-spinning they will have an effect on the solidification mechanism and hence the physical properties and structural features of the fibre.

(b) In dry-jet wet-spinning, most of the jet-stretch takes place in the air-gap zone and at high jet stretches cause some sort of structural changes in the fibres. In wet-spinning the jet stretch acts along the length of the solidifying fibre in the coagulating bath, so it causes some damage to the fibre surface (micro-cracks).

(c) In dry-jet wet-spinning the skin formation is less rapid than in wet-spinning, and presumably, in the air-gap zone the very outer part of the liquid thread-line changes to some very thin skin (gel), which is perhaps maintained during passage through the bath.

The consequences of these differences are that;

(a) In dry-jet wet-spinning, the speed of the spinning operation can be much faster than in wet-spinning.

(b) In dry-jet wet-spinning, the control of the spinning conditions is less important than in wet-spinning.

(c) The structure of dry-jet wet-spun fibres are likely to be more homogeneous than wet-spun fibres.

(d) The skin of dry-jet wet-spun fibres are more smooth than the wet-spun fibres.

(e) The mechanical properties of dry-jet wet-spun fibre, in most cases, are better than wet-spun fibres.

7.2 Polymer modification

It is clear that incorporating the nortricyclene ring into the acrylic polymer has resulted in differences in fibre mechanical properties when the fibre is tested in hot-wet conditions. The initial modulus (i.e. the stress at 4.0% extension) is almost a factor of two greater than with Courtelle polymer whilst the extensibility is less by a factor of three. The significance of these results depends on understanding which of these two parameters is the more important in determining the behaviour of the fibres when subjected to the hot-wet conditions. If a modulus is the most important factor, then fibres containing the nortricyclene ring should show better resistance to deformation in the hot-wet state than, for example Courtelle. If fibre extensibility is the more important factor, i.e. if the high extensibility of normal acrylic fibres in the hot-wet state is the major drawback in their properties, then the nortricyclene containing polymer does give a satisfactory low hot-wet extensibility. The problem may be that with such a low hot-wet extensibility, there may well be easier fibre breakage in the hot-wet state.

It should be pointed out that strictly speaking it is difficult to define the initial modulus for an acrylic fibre above Tg since such fibres do not show a Hookean region under these conditions. Rosenbaum[98] pointed out that, below the Tg, acrylic fibres show stress-strain curves which can be divided into three parts, the first of which is the Hookean region. As the temperature is increased, the ratio of the slope of this region to the slope of the next part of the curve decreases until the initial Hookean region disappears at Tg and above.

The disappearance of the Hookean region is also reported when viscose rayon is wetted although the wet modulus of viscose fibres is still reported as an important fibre characteristic.

It could be argued that the difficulty of wet processing acrylic materials is not due to a low value of the initial Young's modulus in this state, but that the maximum care should be taken during wet processing of these materials, because of their very high elongations in hot/wet conditions (above some hundred percent). This elongation is so high that the fibre cannot recover its original length. Further evidence for this suggestion comes from comparing the behaviour of acrylic fibres with some cellulosic man-made fibres in hot/wet conditions. In these conditions, although the tenacities of some cellulosic man-made fibres are less than those of acrylics and their initial Young's moduli are more or less the same as for acrylic fibres, wet processing is much easier than for acrylic fibres and fewer precautions are needed. In other words, if this comparison is valid, it would appear that the amount of elongation under hot/wet conditions is the most important parameter.

7.3 Suggestions for further work

In the present studies, the dry-jet wet-spinning and the wet-spinning of an acrylic copolymer were compared. A great drawback of this work was the lack of methods for the characterisation of the acrylic fibre structure as these fibres are amongst the most difficult to characterise in detail. So for a better understanding of the effect of the spinning technique (dry-jet wet-spinning versus wet-spinning) on the fibre structure, it would be much more convenient to choose a polymer which gave a fibre with a more easily characterised structure. It seems that, although dry-jet wet-spinning is a modified wet-spinning, it is necessary to compare this method with dry-spinning and wet-spinning simultaneously for a better understanding of the effect of the air-gap on the viscoelastic behaviour of the polymer dope, as this part is related more to dry-spinning than to wet-spinning.

However, the main aim of the present studies was to determine the processability of the dry-jet wet-spinning system and the capability of this for producing acrylic fibres with some modification. It is obvious that, the spinning operation, as a whole, is a very complicated process which involves several stages, i.e. dope preparation and extrusion,coagulation stage, drawing, and aftertreatment, and hence in each stage several parameters are affecting the processability and the final product. Due to lack of time it was found difficult to investigate the effect of the parameters at each stage in detail, and the effect of some other factors has not been studied at all (for example, the effect of drawing bath temperature). Experience gained during this work allows some suggestions for future work in this field. In wet-spinning considerable progress has been reported in the theory of diffusion and rates of solidification as well as the mechanics of wet-spinning. But, because this is a most complex and difficult process, where multicomponent heat and mass transfer is accompanied by phase transition, it is insufficient to allow the drawing of any general conclusions or formulating a quantitative theory of wet-spinning. The most important problems seem to be the thermodynamic and kinetics of phase transitions as controlling factors both in the rate of solidification and in determining the structure and properties of the resulting fibres. By regarding dry-jet wet-spinning as an extreme case of wet-spinning, where the effect of viscoelastic factors of the polymer dope can be isolated from the solidification process due to the air-gap, it may be possible to overcome some of the difficulties at present encountered in studies of wet-spinning.

With regard to the above discussion, it is worth studying the effect of variations in polymer dope and the shear in the spinneret hole in more detail, i.e. over a wider range of shear rates, and a wider range of dope viscosity (polymer molecular weight, dope concentration, different L/D ratios, flow rates, and temperatures, etc.). These studies should deal both with processability and with the structure and properties of undrawn fibres as well as final product. Another group of variables which could be studied relate to the hot drawing bath. It has been claimed that by reducing the drawing bath temperature from 95°C to 85°C fibres with better mechanical properties can be produced[38]. Also the rate of drawing can affect the properties of fibre. These variables should be studied not only in relation to each other but also as a function of the variables in previous stages, i.e. spinneret hole diameter, jet stretch ratio, and flow rate, etc. Finally, the structural features of the final fibre such as crystallinity, void density and size, and fibrillar structure should be carefully analysed in relation to other spinning parameters and in comparison with the structure of the undrawn fibres.

Whilst there are earlier reports[180,182,183,197,198,214-216], of copolymerising acrylonitrile with comonomers giving cyclic units in the polymer backbone, it is believed that hitherto the production of fibres from such copolymers has not been investigated. The present study suggests that further work in this area could be useful in studies directed towards producing acrylic fibres with better properties in the hot-water condition. In particular it could be an advantage if the bicyclo [2,2,1] hepta-2,5-diene used here were replaced by a similar monomer containing carboxyl or sulphonic acid groups since this should improve the properties of the fibre and the ease of spinning without recourse to second comonomer such as itaconic acid. The great difficulty in this work, however, is to establish which characteristics of the fibres are important in, for example, the dimensional stability of acrylic garments when subjected to hot-wet conditions. The only satisfactory criteria would be to study the properties of fabrics and this would necessarily involve fibre production on a larger scale than possible on the presently available equipment in the Department.

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