Low Temperature Dyeing of Polyester Fibres through *In-situ* Dye Synthesis

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The candidate confirms that the work submitted is her own and that appropriate credit has been given where reference has been made to the work of others.

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Abstract

Polyester fibres are the mostly used synthetic fibres in textile industry. As the majority of polyester in commercial terms, polyethylene terephthalate (PET) is generally dyed at 130℃. High-pressurised dyeing equipment and excessive energy are required to achieve the high temperature for dyeing. The high temperature also limits the dyeing of blend fabrics with fibres unstable to high temperature, such as wool. Polylactic acid (PLA) fibres show strength loss after high temperature dyeing due to the hydrolysis of the fibre. Low temperature dyeing for polyester was carried out with carriers or additional process, which increases the production costs. Therefore, it is beneficial to carry out low temperature dyeing of polyester fibres without additional surfactant of process.

In this project, a low temperature dyeing method through *in-situ* dye synthesis was developed. The diazoamines synthesised from 4-chloro-2-methylaniline and N-phenyl-p-phenylenediamine were used for the dyeing of polyester fibres. Aqueous dyeing through *in-situ* dye synthesis can be carried out on polyester fabrics at 100℃ and achieve similar or better dyeing behaviour than the conventional high temperature dyeing at 130℃ with the corresponding disperse dyes. For the dyeing with the precursors in supercritical CO_2 ($scCO_2$), uniform dyeing was only achieved on PET fabrics. The dyeing behaviour and the optimum dyeing conditions depend on the reaction efficiency of the precursors in $scCO_2$.

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Chapter 1
Introduction

Polyesters, as their name indicates, are made by joining monomeric units by ester linkage (-O-CO-). By far the vast majority of polyester in commercial terms is polyethylene terephthalate (PET). Other polyester fibres including polybutylene terephthalate (PBT), polycyclohexanedimethylene terephthalate (PCT), polytrimethylene terephthalate (PTT), polyethylene naphthalate (PEN) and polylactic acid (PLA) also have some commercial impact (Figure 1.1), although they are miniscule in volume in comparison (Mather and Wardman, 2011). The polyester fibres used in this project include PET and PLA fibres.

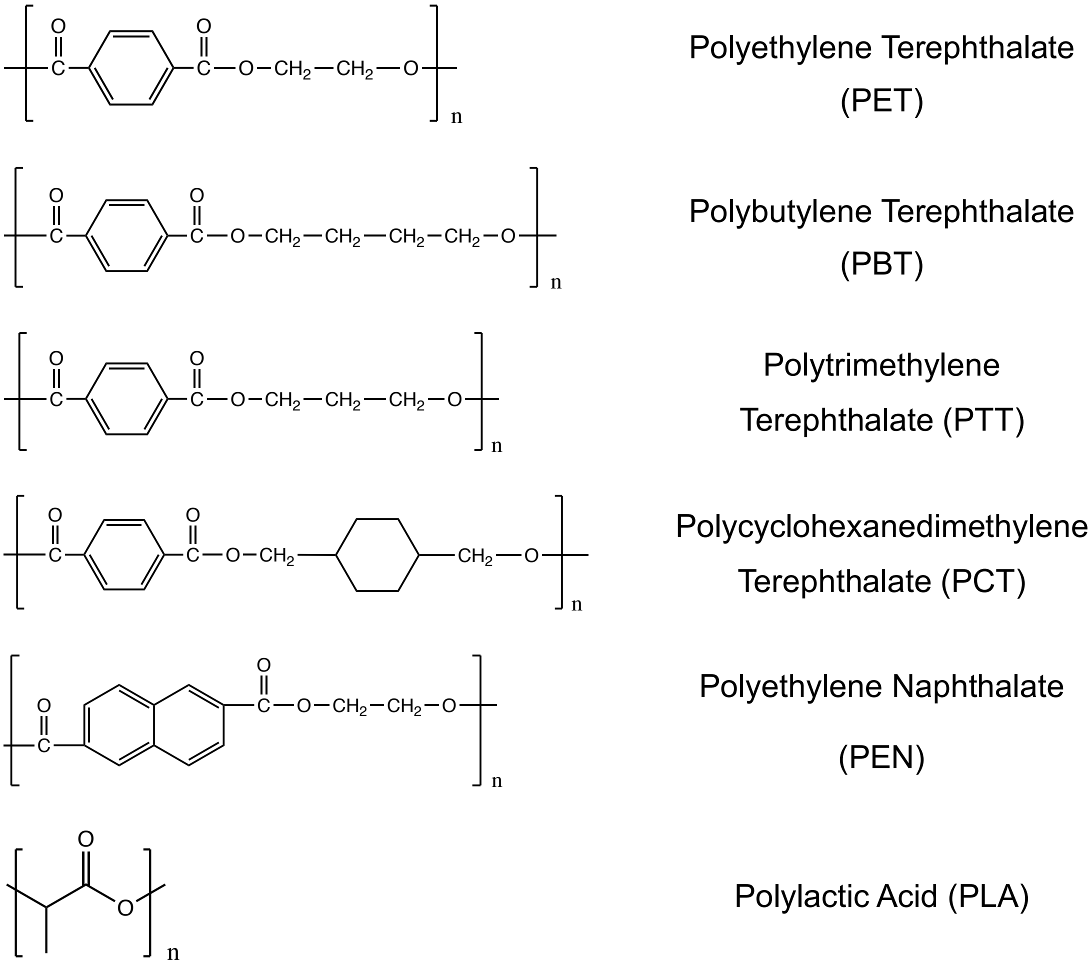


Figure 1.1 Structures of Polyester

Polyester fibres have achieved a dominant share in synthetic fibre market since it was first produced in 1940s (Textiles Intelligence, 2018). Polyester fibres are hydrophobic and hence are dyed with disperse dyes with very low water solubility (Datyner, 1978). Due to the high glass transition temperature (T_g) of PET fibres, the dyeing needs to be carried out at high temperature, normally at 130℃. This high temperature requires the use of high-pressurised dyeing equipment and excessive energy, which increases the production costs. The high temperature also limits the dyeing of blend fabrics with fibres unstable to high temperature, such as wool (Murray and Mortimer, 1971b). The dyeing of PLA fibres has also been a problem due to the significant strength loss of PLA at high temperature. The use of carriers is not recommended for the dyeing of PLA (Hussain *et al*., 2015). Therefore, it would be beneficial to achieve the dyeing of polyester fibres at low temperature without additional auxiliaries or process.

This project aims to investigate the use of dye precursors (azoic combinations) for the low temperature dyeing of polyester fabrics, including PET and PLA fabrics, through *in-situ* dye synthesis without the use of carrier or other additional process. The dyeing behaviours of the dyes formed *in-situ* were examined and compared with corresponding pre-formed dyes.

1.1 Polyethylene Terephthalate (PET)

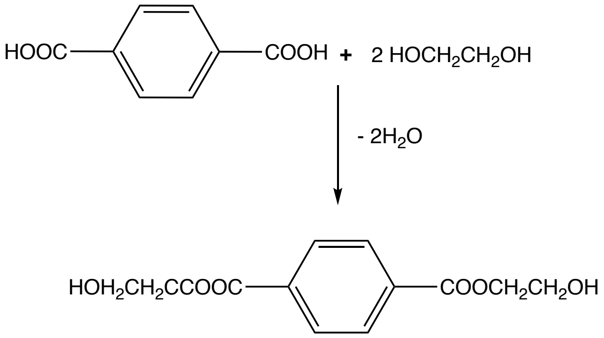
Condensation polymer chemistry was first undertaken by Dr Wallace H. Carothers of DuPont Company in the early 1930s (Carothers, 1929). His research was the foundation for the development of polyester. His group was able to produce uniform polyester fibres from aliphatic co-monomers both by dry spinning and by melt extrusion through a spinneret. However, the melting points (80-100℃) of these fibres were too low for practical use in textile production (Carothers, 1929; Craig, 1993).

The publications of Carothers gave inspiration to Whinfield, who worked at the CPA Central Research Laboratories in UK. He started a research programme on the formation of polyester fibres with Dickson. In 1941, they succeeded in producing ‘Terylene’ as a dirty brown resin from which fibres could be drawn from ethane-1,2-diol (ethylene glycol; $HO-CH_2-CH_2-OH$) and terephthalic acid. This polyester was PET (Whinfield, 1946; Brunnschweiler, 1993).

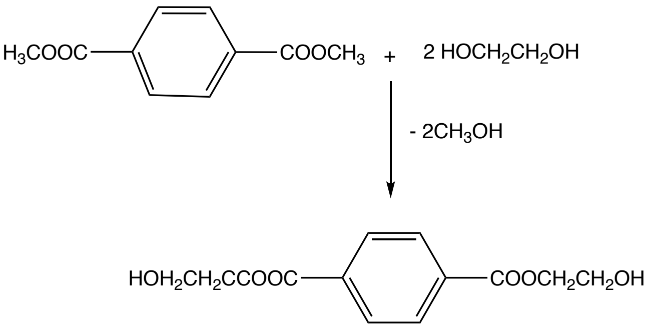
Further developments were carried out by Imperial Chemical Industries (ICI) in UK from 1943 and by DuPont in America from 1944. After the war, DuPont got the production rights in America and ICI in the rest of the world (Burkinshaw, 1995). From 1970s, PET fibres overtook polyamide fibres and have dominated the synthetic fibre industry ever since (Textile Intelligence, 2018).

1.1.1 Chemistry of PET

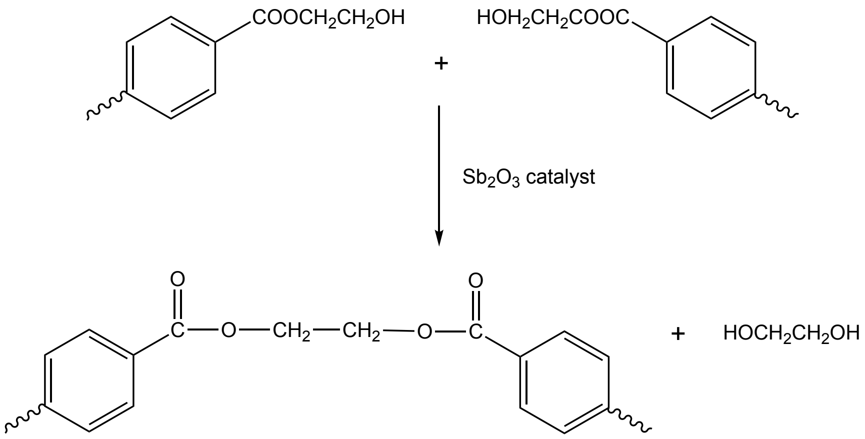
PET is produced by esterification from monoethylene glycol (MEG) and purified terephthalic acid (PTA) or dimethyl terephthalate (DMT). PTA is preferred for process economic reasons, while DMT is favoured in polyester film applications due to its adhesion addition quality (ICIS, 2007). It is important that the same number of two comonomers must be present in order to obtain a long molecular chain. An initial reaction is introduced to produce bishydroxyethyl terephthalate (BHET) (Scheme 1.1 and Scheme 1.2) to ensure the stoichiometry. Then follows the polymerisation of bishydroxyethyl terephthalate. Two BHET molecules condense to eliminate one glycol molecule and form a PET dimer (Scheme 1.3). The chains grow by adding on monomer units and eliminating more glycol units (Broughton, 1972). The catalyst is generally antimony trioxide or less harmful germanium dioxide. Polymerisations can be carried out in a batch process or a continuous process (East, 2009).



Scheme 1.1 Production of BHET from PTA and MEG



Scheme 1.2 Production of BHET from DMT and MEG

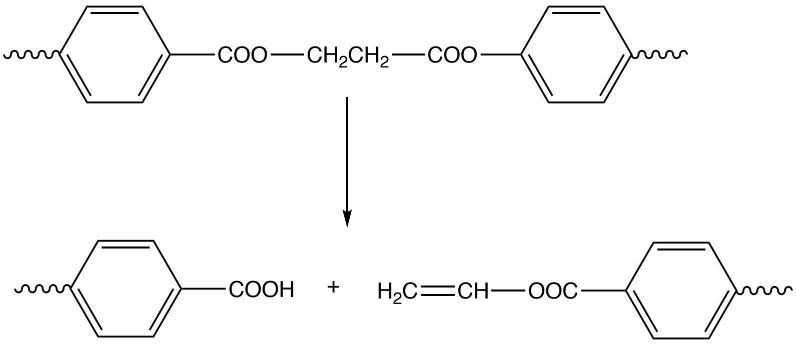


Scheme 1.3 Polymerisation of PET from BHET Monomer

All the groups in the PET molecule are nonpolar groups except for the terminal hydroxyl. Therefore, PET fibres are hydrophobic. The hydrocarbon chain in the glycol residue gives some flexibility to the PET molecules. However, the molecule is rigid due to the benzene ring and tends to maintain linear (Davison and Corish, 1955). Therefore, the molecules are relatively easy to crystallise. As a result, the crystallinity and orientation of PET are relatively high (Hindeleh and Johnson, 1978). Therefore, the glass transition temperature (T_g) is relatively high.

One of the advantages of PET fibres is the outstanding resistance to a wide range of chemicals. Considering the chemical structure of PET fibres, the benzene nucleus and two methylene groups are slow to react and the ester groups react more readily (East, 2009). Therefore, the chemical properties of PET are largely determined by the ester groups. The high crystallinity also contributes to the high resistance. PET is resistant to acids unless in strong acids at high temperature. Hydrolysis happens when PET fibres are treated with alkali, such as caustic soda, but without serious fall in quality (Mather and Wardman, 2011).

Thermal degradation is slow without oxygen below the melting point, but becomes substantial above 300℃ (Mather and Wardman, 2011). Pohl (1951) suggested that the degradation happens at the β-methylene group producing free carboxylic acid and vinyl ester end-groups (Scheme 1.4).



Scheme 1.4 Thermal Degradation of PET (Pohl, 1951)

1.1.2 Dyeing of PET with Disperse Dyes

PET fibres are generally dyed with hydrophobic disperse dyes. As the dye precursors used in this project are also hydrophobic, the absorption of the precursors onto the fibres and diffusion inside the fibres are expected to proceed in a manner identical to that of disperse dyes. Furthermore, when dyeing with the precursors, the dyes formed inside the fibres have the features of disperse dyes, and hence any diffusion and molecular interactions is expected to be related to those found with disperse dyes. It is therefore relevant to review the process of dyeing PET with disperse dyes.

The disperse dye is defined as “a substantially water-insoluble dye having substantivity for one or more hydrophobic fibres, e.g. cellulose acetate, and usually applied from fine aqueous dispersion” (Colour Terms and Definitions,1988, p.7). Disperse dyes were first developed in the 1920s for the dyeing of hydrophobic cellulose acetate fibres (Green and Saunders, 1923). Disperse dyes have become the most important class of dyes used for the dyeing of polyester fibres.

Disperse dyes generally exhibit good yield and very good fastness on PET fibres (Dawson, 1984). The diffusion rate of disperse dyes within the PET fibres is very low due to the compact and highly crystalline structure of the fibres (Giles *et al.*, 1982). The dyeing rate increases to a commercially acceptable level at high temperature (generally 130℃) or by the use of carriers (Murray and Mortimer, 1971a; Burkinshaw, 1995).

1.1.2.1 Principle of Disperse Dyeing

In the application of disperse dyes, the substrates are immersed in an aqueous dispersion of the dyes. Clavel (1923; 1924, cited in Burkinshaw, 1995, p.9) proposed the aqueous solution theory without experimental evidence. Burns and Wood (1929) also suggested that the disperse dyes were adsorbed onto the fibres from aqueous solution and proposed that the adsorption occurred within the fibres. Nowadays, Clavel's theory is accepted, and the dyeing of polyester is known to proceed via the aqueous phase transfer of disperse dyes to fibres. A small amount of disperse dyes forms an aqueous solution while the greater amount of dyes remains in bulk dispersion in the dyebath. The monomolecular dyes are adsorbed onto the surface of the fibres from the solution at the fibre surface. As the dyes diffuse in the fibres, the solution is depleted allowing dye particles in dispersion to dissolve in the solution. The aqueous solution is thus replenished with monomolecular dyes that can be further adsorbed onto the fibres. This process (Figure 1.2) continues until the fibres are saturated with dyes or the dyebath is exhausted.

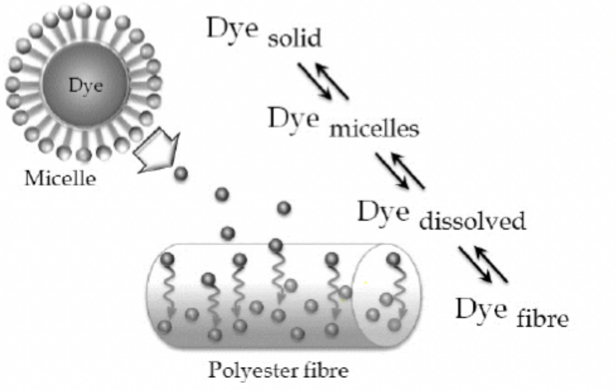


Figure 1.2 Mechanism of Aqueous Phase Transfer of Disperse Dyes to Polyester Fibres

(Koh, 2011)

The second view was put forward by Kartaschoff (1925) and supported by material evidence. Kartaschoff observed crystalline dye particles adhering to the surface of acetate fibres and the particles disappeared by adsorption at 60℃. He proposed that the solid dye particles, which are positively charged, were attracted to the negatively charged fibres and formed a surface layer on the fibres. The solid dyes then dissolved or diffused within the fibres by a solid-state mechanism.

Works have been done to repeat Kartaschoff's experiment and detect the attraction of dye particles to the fibres but all failed (Vickerstaff and Waters, 1942; Millson and Turl, 1951). It was even shown that the dye particles were normally negatively charged and therefore could not be attracted to the fibres (Iyer, 1974; Peters, 1975). Later works confirmed that disperse dyes had appreciable solubility (Bird, 1954) so that the theory of Clavel was viable.

It was observed that the uptake of disperse dyes on polyester fibres follows a mechanism obeying (Schuler and Remington, 1954):

$$K = D_f/D_s = S_f/S_s$$

Wherein K = the partition coefficient

D_f and D_s = the concentration of dye in the fibre and solution respectively

S_f and S_s = the saturation values of the dye in the fibre and solution respectively

Schuler and Remington (1954) also suggested that in a mixture of two dyes, the behaviour of the dyes was related to the similarity of the structures between the dyes. For the dyes with completely different structures, they behaved independently of the other. The isotherm for each dye was linear up to the saturation of the fibre. On the other hand, when the dyes have similar structures, interference was noted. With the presence of a large amount of the other, the solubility of each dye was decreased by about 20%, both in the fibre and in the dyebath.

It was demonstrated that the substantivity of disperse dyes towards polyester fibres is mainly attributed to hydrogen bonding between an azo-nitrogen atom and a hydrogen of the methyl ester group, while the contribution of dispersion forces and possibly dipole-dipole and dipole-induced dipole forces depend on the structure of the dyes (Allingham *et al*, 1954). Nonpolar forces between aromatic molecules in the dyes and the fibres also play an important role through charge transfer and electron donor-acceptor effects (Hunter,1994; Lewis, 1998).

It was proposed that the proper hydrophilic-hydrophobic property of a dye was a key factor to achieve good dyeability. The dyes containing hydrogen donating groups showed better dyeing performance than those without these groups or containing hydrogen accepting groups. For the azo dyes, the dyeability increased with increasing contribution of the ionic form (Kuroki and Konishi, 1956).

1.1.2.2 High-temperature Dyeing

The dyeing of PET fibres with disperse dyes is normally carried out at high temperature (130℃). In this research, the dyeing with the precursors at low temperature will be compared with the conventional high temperature dyeing with corresponding disperse dyes. Therefore, it is relevant to consider the high temperature dyeing process, which is reviewed here.

As mentioned previously, the diffusion rate of disperse dyes in PET is low at the boil. The rate can be increased to a commercially acceptable level in high temperature dyeing (normally at 125-135℃). The dyeing rate increases about six times as temperature increases 10℃ above the polymer T_g (Bird *et al.*, 1959; Burkinshaw, 1995).

It is commonly considered that high-temperature dyeing without carrier at 125-135℃ offers several benefits, including shorter dyeing time, higher colour yield, excellent penetration and fastness properties. The superior dye migration compared to dyeing at the boil can be considered as the result of higher kinetic energy of dye molecules and better solubility of the dye at high temperatures. On the other hand, the use of carriers in high-temperature dyeing also offers several advantages, such as excellent coverage of barré effects and better levelling. The handle and bulk of texturized polyester can be less impaired as the use of carriers enables high temperature dyeing to be carried out at a relatively low temperature (commonly 110-125℃) (Burkinshaw, 1995).

The exhaustion of disperse dyes on PET increases significantly with increasing temperature up to 130℃ (Fern, 1955). It has been demonstrated that the exhaustion rate of the dye is determined by the temperature, duration of dyeing and the concentration of dye in the dyebath (Beckmann, 1970). The levelling property of the dyes also improves with increasing temperature up to 140℃ and depends on the diffusional behaviour of the dyes. Dyes with faster diffusional behaviour exhibit better levelling property at all temperatures (Hadfield and Broadhurst, 1958).

Due to the limited water solubility, disperse dye molecules are deposited on the surface of the fibres as large particles as the dyebath is cooled down. These surface deposits of ‘unfixed’ dyes can cause a reduction in fastness and dulling of the shade. Surfactants and carrier residues may also be present on the surface (Broadhurst, 1979). The removal of surface-deposited dyes, as well as auxiliaries, by treatment with a detergent or reductive or oxidative treatment, improves the fastness of the dyeing and the brightness of the shade. Therefore, a reduction-clearing process is generally applied to polyester fibres after dyeing. Reduction clearing of the dyed PET fibres is usually carried out with sodium hydrosulfite and sodium hydroxide at 60-80℃ for 10-20 minutes (Aspland, 1992).

1.1.2.3 Surfactants in the Application of Disperse Dyes

Surfactants are employed in the dyeing with disperse dyes in order to achieve good dyeing properties. The surfactants used are relatively complex and contain hydrophilic and hydrophobic groups within the same molecule (Murray and Mortimer, 1971b). The internal pressure of water on hydrophobic groups tends to squeeze them out of solution while the hydrophilic groups prevent the complete insolubility of the molecule. There are three main types of surfactants: anionic, cationic and non-ionic (Murray and Mortimer, 1971b). They are used for various purposes in the dyeing process for polyester fibres, and notably as dispersing and levelling agents. As the dyeing with the precursors is thought to be similar to disperse dyeing, same surfactants could be employed in the dyeing with the precursors.

Disperse agents are used for promoting the milling of dyes and maintaining dispersion stability during dyeing. The hydrophobic groups are adsorbed on the dye particle surface and the hydrophilic groups are orientated outwards in the water (Murray and Mortimer, 1971b). The possibility of dispersion failure is the greatest in high-temperature dyeing and additional dispersing agents can be used in the dyebath (Carbonell, 1962; Derbyshire *et al*., 1972). Dispersing agents perform two main functions in the dyeing process. The first is to keep the dye particles apart in order to prevent agglomeration during dyeing, while the second is to increase the aqueous solubility of the dyes (Murray and Mortimer, 1971b; Datyner, 1993). It was observed that with the presence of the dispersing agents, the solubility of disperse dyes increased to an extent which depends on the solubility of the dye and the dispersing agents used (Bird, 1954). Dispersing agents also have an effect on the dyeing rate and uptake of disperse dyes on polyester fibres. The dispersing agents increase the solubility of the dyes and the affinity of the dyes for the aqueous phase. Therefore, the uptake rate of the disperse dyes increase with increasing concentration of dispersing agents. However, for some more soluble disperse dyes, the uptake rate decreases with increasing concentration of dispersing agents (Bird *et al*. 1955; Bird and Manchester, 1955). The small amount of dyes dissolved in water forms a saturated film of dyes on the surface of the fibres. The solution maintains saturated by almost instant dissolution of the suspended dyes. As long as the solution is saturated, the concentration of the solution and hence the uptake rate of the dye does not change. However, with the presence of an appreciable number of dispersing agents, all dyes can be dissolved in water at an early stage of the dyeing. After the dyes diffuse into the fibres, the solution is no longer saturated. As the result, the concentration of the solution becomes lower and hence the diffusion rate also decreases.

Levelling agents are non-ionic surfactants added to the dyebath during exhaust dyeing in order to improve the migration and levelling of disperse dyes on polyester fibres (Murray and Mortimer, 1971b). The levelling agents increase the solubility of disperse dyes and hence decrease the initial strike and uptake rate of the dyes. They may also cause a loss in colour yield (Derbyshire *et al.*, 1972; Beckmann and Hamacher-Brieden, 1973; Thakore *et al.*, 1987). The solubility of non-ionic levelling agents decreases as temperature goes up. If the temperature of the dyebath is higher than the agents' cloud point, the dispersion breaks down which results in dye aggregation and unlevel dyeing. Anionic dispersing agents can be added to increase the cloud point of non-ionic agents (Murray and Mortimer, 1971b).

1.1.3 Low Temperature Dyeing of PET Fibres

Low temperature dyeing of polyester fibres would be of benefit for two salient reasons: the cost saving in machinery and energy and the elimination of production restrictions with blend fibres (Murray and Mortimer, 1971a). Many researches have been carried out in order to improve the disperse dyeing of polyester fibres and its fastness properties at low temperature. Low temperature dyeing of polyester fibres has been achieved with various techniques.

1.1.3.1 Carrier Dyeing

Carrier is described as "a type of accelerant particularly used in the dyeing or printing of hydrophobic fibres with disperse dyes" (Colour Terms and Definitions, 1988, p.4). The use of carriers became widespread in order to achieve a comprehensive shade range on PET until high-temperature dyeing was available (Murray and Mortimer, 1971a). Carriers are generally aromatic compounds with small molecular sizes. They are added to the dyebath as solution or emulsion (Burkinshaw, 1995). Carriers can be either hydrophobic or hydrophilic, working in different uptake mechanisms. It is suggested that hydrophobic carriers are more effective than hydrophilic ones for the dyeing of PET (Murray and Mortimer, 1971a).

The uptake of hydrophobic carriers onto PET fibres follows the same mechanism as that of disperse dyes. Interactions between fibre and carriers involve dispersive forces between aromatic parts of carriers and polyester (Murray and Mortimer, 1971a; Ingamells and Yabani, 1977). As the carriers are smaller than the dye molecules, they diffuse more readily into the amorphous regions of the fibres at lower temperature. The swelling of the fibre creates more spaces between polyester macromolecular chains (Ingamells and Yabani, 1977). The fibres then become more easily accessible for the larger dye molecules. This swelling also causes a plasticisation of polyester and decreases the glass transition temperature (Murray and Mortimer, 1971a; Burkinshaw, 1995). Therefore, the carriers can accelerate the dye diffusion inside the fibres. The carriers can also reduce the intermolecular forces of fibre-fibre bonds and replace with weaker fibre-carrier bonds. With the effect of thermal agitation, increased vibration gives more space for the diffusion of dyes (Fortess and Salvin, 1958). Another theory is that the carriers work as molecular lubricants, which attach to the polymer molecules and destroy cross-linkages. The polymer chains can slide more easily over one another and hence increase the diffusion of the dye molecules (Schuler, 1957). For the hydrophobic carriers with hydrophilic groups, the aromatic groups of the carriers are attracted to the hydrophobic fibre by Van der Waals’ forces while the hydrophilic groups attract water. The increased attraction of water creates a more hydrophilic environment where the dyes can move more rapidly and hence increases the diffusion rate of the dyes (Vickerstaff, 1954).

On the other hand, the hydrophilic carriers have a different mode of uptake. They increase the solubility of the disperse dyes in water, resulting in the increased concentration of the dilute aqueous solution and hence the increased diffusion rate of the dyes. However, the increased solubility of the dyes in water may reduce the affinity to the fibres (Arcoria *et al*., 1989).

Although carrier dyeing was once widely used and enabled a commercially acceptable dyeing rate to be achieved at the boil, most compounds used as carriers possess hazards for humans and aquatic organisms (Murray and Mortimer, 1971a; Tavanaie *et al*., 2010). During dyeing, a large amount of carriers is released into wastewater, while some remain in the fibres (Vigo, 1994) and are likely to be released into air during drying, thermo-fixation and later use. Many carriers also cause reduction on light fastness of the dyeing (Broadhurst, 1979).

Some ‘environmentally friendly’ carriers have been investigated (Wei *et al*., 2009; Xiang *et al*., 2009; Song *et al*., 2011; Pasquet *et al*., 2013). For some of the carriers, the dyeing needs to be carried out above 100℃, which still requires high-pressurised equipment. Dyeing can be carried out at or below 100℃ with some carriers, but for a longer time (80-90 minutes). The most importantly, some toxicity data were missing in the assessment, which cannot completely eliminate the environmental and toxicity risks of these compounds.

1.1.3.2 Dyeing with Gemini Surfactants

The hydrophobic part of conventional dispersing agents is mostly single hydrocarbon chains and can aggregate with themselves in water to form bilayer structures. It was found that some synthetic double tailed surfactants improved the exhaustion of disperse dyes and the dyeing rate (Kim *et al.*, 1997a; Kim *et* al., 1997b).

Low temperature dyeing of polyester was achieved with didodecyldimethylammonium bromide (DDDMAB) as dispersing agent at

110℃ (Kim *et al.*, 1997a; Kim *et* al., 1997b). The amount of adsorbed DDDMAB onto polyester fibres was considerably higher than conventional dispersing agents. The bilayer structure accommodated more dye molecules. Therefore, a concentrated layer of monometric dye molecules was constructed on the fibre surface, which improved the dyeing rate and the equilibrium exhaustion. The colour fastness and dye uptake of the dyeing with DDDMAB were similar to those with conventional dispersing agents. The colour of the dyeing with DDDMAB was brighter, which was probably due to the interactions of DDDMAB with fibres and dyes.

1.1.3.3 Dyeing with Ultrasound

Ultrasound refers to the sound of high frequency, above the range of human hearing. The ultrasonic waves can be focused, reflected and refracted through a medium for propagation. When they are propagated through the medium, the particles of the medium oscillate and transfer energy in the direction of propagation. The combination effects of cavitation and microsteaming cause intermolecular tearing and surface scrubbing (Thakore *et al*., 1990).

Ultrasound was found to improve dye uptake on different substrates (Saligram *et al*., 1993). It was observed that the activation energy of the dyes decreased when treated with ultrasound. No permanent damage of fibre structure or morphological changes occurred after ultrasonic treatment (Thakore *et al*., 1990). It was suggested that the influence of ultrasound on dyeing included breaking the aggregation of the dye molecules, increasing the pressure and temperature at the microscopic level in the dye bath through the formation and collapse of tiny bubbles and increasing the diffusion rate of the dye (Saligram *et al*., 1993).

Dyeing of PET fibres can be achieved with ultrasound at 40-50℃ (Saligram *et al*., 1993; Carrion Fite, 1995; Ahmad and Lomas, 1996). As the electrical energy used to produce the ultrasonic effect is low, the dyeing method is relatively energy efficient. However, the colour yield was not as high as in high-temperature dyeing. The dyeing performance also depended on the energy levels of the dyes. The results of the dyes with higher energy level were not commercially acceptable. The ultrasonic dyeing can be improved with a pre-swelling process. However, the process was expensive and difficult to carry out commercially.

1.1.3.4 Dyeing with Nano TiO_2 Pre-treatment

The major application of Nano TiO_2 on polyester fibres was to impart multi-functional properties, such as self-cleaning, antimicrobial and UV protection (Mihailovic *et al.*, 2009; Dastjerdi and Montazer, 2010). It was found that Nano TiO_2 pre-treatment could also positively affect the dyeing of polyester fibres (Harifi and Montazer, 2013).

The aqueous dispersion of Nano TiO_2 particles was prepared in an ultrasonic bath. The polyester fabrics were pre-treated with the dispersion through one-minute immersion following by padding. Dyeing was carried out at the boil. The amount of dyes absorbed by the fibres was almost equal to the one dyed with carriers. No significant change in fastness properties was observed. Furthermore, the pre-treated fabrics also benefit from multi-properties obtained by Nano TiO_2 application (Harifi and Montazer, 2013). However, the preparation and application of Nano TiO_2 is relatively expensive and complicated.

1.1.3.5 Azoic Dyeing

Polyester is not generally dyed with azoic dyes. However, heavy shades such as black, maroon and red can be obtained on PET materials with azoic dyes. Polyester is firstly boiled in a dispersion of coupling component and the base. The coupling is carried out by addition of hot nitrous acid. A “reversed azoic process" can also be used, in which the diazonium component is applied to polyester followed by naphtholation and coupling (Wilcock and Ashworth, 1964).

A method of dyeing PET fibres at 100℃ with dye precursors was attempted (Rigout *et al*., 2005). Dyebaths were prepared with both diazoamine derivative and coupling component. These components were more readily absorbed by the fibres at low temperature due to their small molecular sizes. The PET fabrics dyed with precursors exhibited significantly higher colour yield than the corresponding disperse dyes at 100℃. The washing fastness and rubbing fastness were good, but the light fastness was poor. This project is to carry out further research on the low temperature dyeing of polyester fibres through *in-situ* dye synthesis.

1.2 Polylactic Acid (PLA)

Polylactic acid (PLA) is a highly versatile, biodegradable, aliphatic polyester that can be derived from 100% renewable resources (Drumright *et al*., 2000). It is the first melt-processable natural-based fibre (Sawyer, 2003). It is a synthetic polymer based on lactic acid ($C_3H_6O_3$) and produced from agricultural resources, such as corn and sugar beets. It degrades easily by simple hydrolysis under the appropriate conditions (Drumright *et al*., 2000). PLA was first discovered in 1932 by Carothers (Dupont) who produced a low molecular weight product by heating lactic acid under vacuum (Farrington *et al*., 2005). In spite of its excellent balance of properties, the initial uses were limited to medical pharmaceutical applications due to its high cost and low molecular weight (Lipinsky and Sinclair, 1986). The formation of a new company, Cargill Dow LLC, in 1997 brought two large companies together to focus on the production of PLA with the intention of reducing the cost of manufacture (Naitove, 1998). Cargill Dow LLC has developed a patented, low-cost continuous process for the production of lactic acid-based polymers

(Gruber *et al.*, 1992; 1993; 1994; 1996). The advancement in the fermentation of dextrose obtained from corn has further reduced the cost to make the lactic acid monomer, which is the precursor to PLA production (Dartee *et al.*, 2000).

A wide variety of forms from staple fibres to composite materials can be produced from PLA. The use of PLA can be found in many areas, from medical and pharmaceutical applications to environmentally friendly film and fibres for packaging, houseware and clothing (Lunt and Shafer, 2000; Gupta *et al.*, 2007; Avinc and Khoddami, 2009).

1.2.1 Chemistry of PLA

Lactic acid is the starting material for the production of PLA. Lactic acid is a simple chiral molecule and has two optically active stereoisomers, the dextro- (D-) and levo- (L-) forms (Figure 1.3), differing in their effect on polarised light. The L- isomer rotates the plane of polarised light clockwise, while the D- isomer rotates it counter-clockwise (Linnemann *et al.*, 2003).

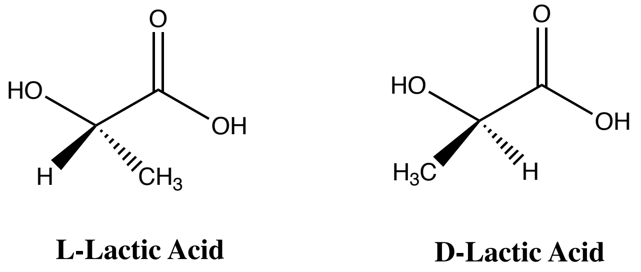


Figure 1.3 The Two Stereoisomers of Lactic Acid

Lactic acid can be easily produced by the extraction of starch from plants such as corn or the extraction of sugar from plants such as sugar beets (Sawyer, 2003). The starches are converted to fermentable sugars (e.g. glucose and dextrose) by enzymatic hydrolysis. The sugar is then converted into lactic acid through bacterial fermentation (Sawyer, 2003; Farrington *et al.*, 2005) (Figure 1.4). The lactic acid produced in the Cargill Dow LLC process is exclusively

(>99.5%) the L-isomer (Lunt and Shafer, 2000).

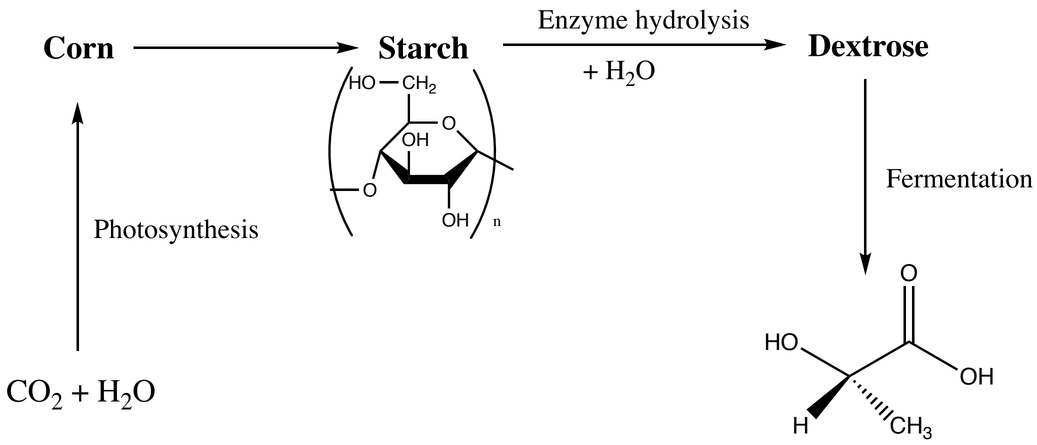


Figure 1.4 Production of Lactic Acid from Renewable Resources

PLA can be synthesised from the lactic acid monomer in two ways (Figure 1.5). The conventional process is by the direct condensation of lactic acid. The process is carried out under high vacuum and high temperature. A solvent is used in addition to the vacuum to extract the water produced in the reaction (Dartee *et al.*, 2000). This was the same method used by Carothers to produce PLA polymer. The polymer produced with this approach tends to have low to intermediate molecular weight due to the difficulties to remove water and impurities (Zhong *et al.*, 1999; Farrington *et al.*, 2005).

The other method is ring-opening polymerisation of a cyclic dimer of lactic acid, commonly referred to as lactide. This method is solvent-free. The product is purified by distillation. PLA with controlled molecular weight can be produced with this approach (Kricheldorf *et al.*, 1996; Radano *et al.*, 2000). Production of lactide from lactic acid potentially creates three different stereoisomeric forms: L-lactide, D-lactide and meso-lactide (Figure 1.6). L-lactide and D-lactide are optically active. Meso-lactide is dimerised from D- and L- lactic acids. It is optically inactive and exhibits a lower melting point than the other two forms (Dartee *et al.*, 2000). It is possible to control the ratio and sequence of the polymer backbone by controlling residence time and temperature, as well as the catalyst type and concentration (Fambri *et al.*, 1997; Lunt and Shafer, 2000). The ratio of D- and L-isomers and their distribution along the polymer backbone influence the molecular weight, crystallinity and melting point of the PLA (Linnemann *et al.*, 2003; Farrington *et al.*, 2005). This process completely eliminates the use of costly and environmentally unfriendly solvents. The remaining monomer is recycled back to the beginning of the process (Drumright *et al.*, 2000; Farrington *et al.*, 2005).

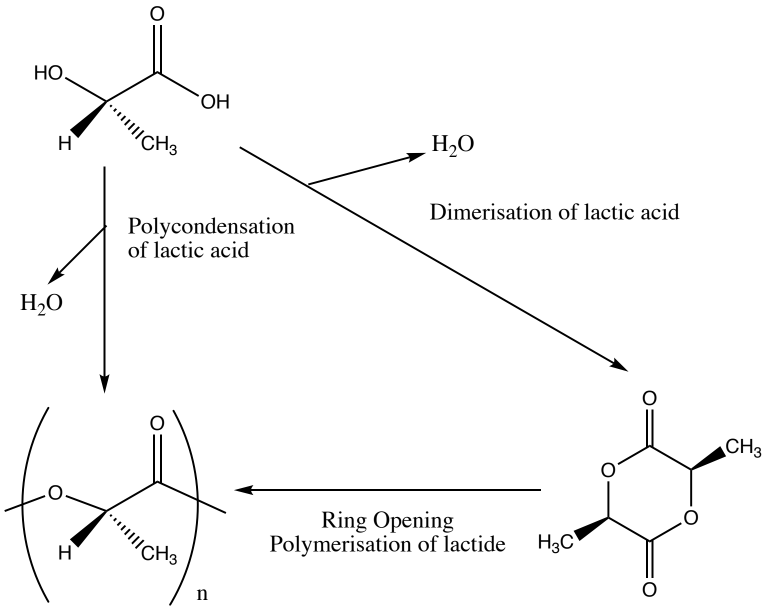


Figure 1.5 Polymerisation routes to PLA (Avinc and Khoddami, 2009)

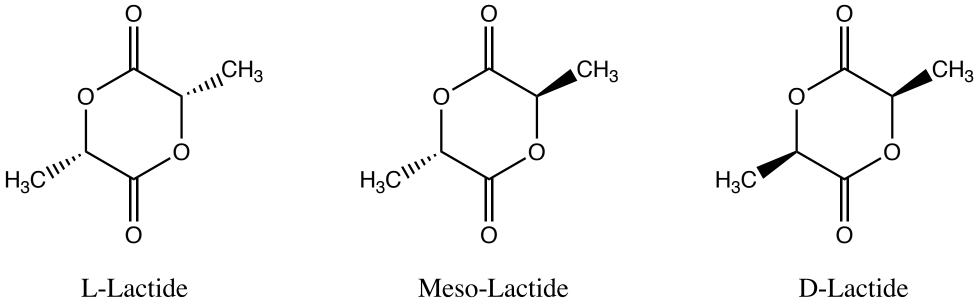


Figure 1.6 The Different Lactide Isomers

Although PLA fibres are stable enough under normal use, they are completely compostable under specific composting conditions, generally around 60℃, with 90-95% relative humidity (Drumright *et al.*, 2000; Farrington *et al.*, 2005).

PLA degrades by hydrolysis, followed by microbial action, to carbon dioxide, water and humus, which are the basic necessities for new growth (Papong *et al*., 2014). However, the hydrolysis of the PLA can cause strength loss of the PLA fibres during wet processing at high temperature. The recycling of PLA can be carried out with water at a wide range of temperatures from 100℃ to 250℃ (Farrington *et al*., 2005). The produced lactic acid can be reused as the monomer for the production of new PLA.

PLA is more sensitive to alkali than PET. Loss of fibre strength during wet processing is observed if care is not taken in dyeing and finishing (Avinc and Khoddami, 2009).

1.2.2 Performance and Properties of PLA

PLA combines ecological advantages with very good technical performance in textiles. It has high mechanical strength, compostability and biocompatibility (Sawyer, 2003). The mechanical properties of PLA are broadly similar to those of PET (Drumright *et al*., 2000). PLA is a relatively stiff polymer at room temperature, but its glass transition temperature (T_g) is rather low (normally 55-65℃) (Farrington *et al*., 2005). The melting temperature (T_m) of PLA is between 160-180℃, while the melting point of stereocomplex PLA is 220℃ (Perepelkin, 2002; Farrington *et al*., 2005). The low melting point leads to limitation for end use. A clear decrease in molecular weight occurs on heat treatment above 190℃, at which the thermal degradation of PLA takes place (Jamshidi *et al*., 1988).

PLA exhibits good moisture management and comfort properties. The moisture regain and wicking property of PLA is superior to PET (Dartee *et al*., 2001). Its lower contact angle compared to PET results in improved wicking with water. PLA fibres wick moisture well without absorbing large amounts of water, which is particularly important in respect of applications such as sportswear and performance apparel.

1.2.3 Dyeing of PLA

PLA is commonly dyed with disperse dyes as PET. However, the high temperature (130℃) used for the aqueous dyeing of PET is not suitable for PLA due to its hydrolytic sensitivity and low melting temperature (T_m). The temperature, time and pH must be controlled in order to avoid significant reduction in molecular weight and therefore the tensile strength of the PLA fibres (Kameoka *et al.*, 1997). The highest strength and elongation of PLA were observed with a weakly acid dyebath. A more acidic or more alkaline dyebath caused significant loss of fibre elongation and strength (Yang and Huda, 2003b).

The critical temperature range over which disperse dyes exhaust onto PLA is 70-100℃ (Lunt and Bone, 2001). The dyeing condition recommended by DyStar is 15-30 minutes at 110-115℃ at pH 4.5-5.0 (DyStar, 2004). Holding the dyeing temperature at 90-95℃ for 5 minutes can increase the levelness of the dyeing (Yang and Huda, 2003b). At the end of the dyeing process, the temperature should be decreased to 50℃ before removing the fabric from the dyebath in order to prevent fabric crease (Yang and Huda, 2003b). The recommended disperse dyeing cycle for PLA is shown in Figure 1.7.

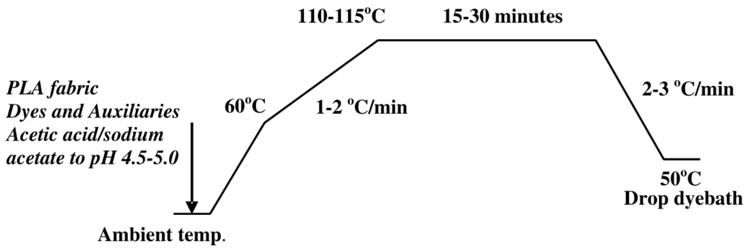


Figure 1.7 Disperse Dyeing Procedure for PLA Fabrics

Dye selection for dyeing PLA is crucial. Dyes that have very good exhaustion on PET can show great variation in exhaustion levels on PLA, which is generally lower than that on PET (Lunt and Bone, 2001; Scheyer and

Chiweshe, 2001; Yang and Huda, 2003a). Small linear dyes were found to show good exhaustion on PLA because the high crystallinity of PLA inhibits dye diffusion (Scheyer and Chiweshe, 2001). It is also proposed that medium energy azo dyes are suitable for the dyeing of PLA (Lunt and Bone, 2001). Disperse dyes with multiple carbonyl groups and anthraquinone dyes should be avoided (Scheyer and Chiweshe, 2001). Attempts have been made to develop new dyes with good affinity for PLA fibres as an alternative to the commercial disperse dyes. Good exhaustion and light fastness were achieved with the new yellow dyes, while the washing fastness is moderate to good (He *et al*., 2007; 2009; 2010).

Since PLA is alkali sensitive, milder sodium carbonate is preferred to sodium hydroxide for after-clearing treatment. The optimum condition for the clearing of PLA is 15 minutes at 60℃ with 2g/L sodium carbonate and 2g/L sodium dithionite (Avinc *et al*., 2006), which can avoid significant change of shade and maximise washing fastness.

The individual dye behaviour on PLA is different from dyeing on PET. Shades obtained on PLA are different tone, hypsochromic (maximum absorption at a shorter wavelength) and brighter than those on PET (Avinc and Khoddamine, 2010). The colour yield of dyed PLA is higher than that of PET with the same dye due to the lower reflectance index of PLA (Yang and Huda, 2003a). The orange and red dyes tend to be yellower on PLA than PET, while the blue dyes tend to be redder on PLA (Choi and Seo, 2006; Choi *et al*., 2007).

The colour fastness of dyed PLA is overall slightly lower than that of PET at the similar depths of shade. Most disperse dyes on PLA fibres would have acceptable washing fastness, either similar or up to 1 point lower than that of PET (Choi and Seo, 2006). The difference in light fastness between dyes on PLA and PET is small (Yang and Huda, 2003a).

1.3 Azoic Dyeing

The azoic dyes have mainly been used for the dyeing of cellulosic fibres. The following text is mostly about the azoic dyeing of cellulosic fibres unless otherwise stated. The reactions of azoic dyeing in polyester fibres is presumed to be similar to that of cellulosic fibres. The dyeing process employed in this project was also modified according to that of cellulosic fibres. Therefore, the azoic dyeing of cellulosic fibres was reviewed here.

1.3.1 Introduction

Azo compounds account for 60-70% of dyes (Zollinger, 2003). They contain an azo group, -N=N-, with two sp^2 hybridised carbon atoms on both sides of the azo group. These carbon atoms are usually part of aromatic systems. Most azo dyes contain one azo group, but some may contain two (diazo), three (trisazo) or more (Zollinger, 2003). While azo dyes are ready-made dyes, azoic dyes are produced inside the textile materials by the reaction of two compounds called coupling components and diazo components or fast bases (Ghosh, 2004). The first azoic dye was produced by Caro and Witt in 1875 at BASF (Morris and Travis, 1992). The first patent for the application of azoic dyes on cotton was granted in 1880 to Thomas and Robert Holliday of Read, Holliday&Co., for the coupling of 2-naphthol with diazotised naphthylamines to produce red shades (Wallwork, 1939). Currently, azoic compounds are mostly used on cellulosic materials.

The main advantages of the azoic dyes include (Shore, 1995; Roy Choudhury, 2006):

1. Azoic dyes can be used on different forms of textile materials in different machines or even in short batches with domestic utensils.
2. Shades including orange, red, bordeaux, black and navy blue can be obtained economically.

3. The fastness properties are generally good.
4. The dyeing procedures have excellent reproducibility.
5. The components are mostly dischargeable.

However, there are several limitations of the azoic components, as follows:

1. The application processes are complicated and time-consuming.
2. The rubbing fastness is generally poor. The excess naphthol has to be removed efficiently from the surface of the dyed materials in order to obtain good rubbing fastness. The use of coupling component with high substantivity and thorough soaping after development will also be helpful.
3. Only limited shades can be produced.
4. Different chemicals need to be used and stored. Difficulties of handling the chemicals may occur under certain conditions, especially during the diazotisation process of fast bases.
5. Compound shades, which are produced with other classes of dyes by mixing three or four dyes, are difficult to produce with azoic dyes as there would be cross coupling between different naphthols and diazonium salts. Also, the shades are unpredictable and non-reproducible.
6. Since the shade is only visible after coupling, the unevenness caused during naphtholation cannot be detected. Shade correction is difficult after coupling.

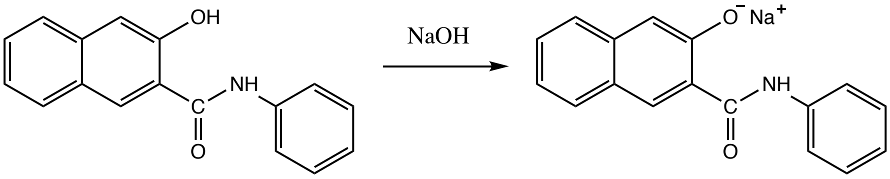
In 1994, the German government banned the use of some azo dyes that produce any of a list of the twenty arylamines, including benzidine and its disubstituted congeners, on reduction. Other European countries introduced similar regulations later. Nowadays, 22 amines are banned according to EU Directive 2002/61/EC. Many amines used for diazotisation are under eco-pressure. These environmental issues limit the use of azoic dyes to a great extent (Anliker *et al*., 1988; Chattopadhyay and Kumar, 2001; Hallas, 2002).

1.3.2 Chemistry of Azoic Dyeing

1.3.2.1 Coupling Component

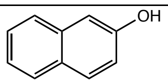
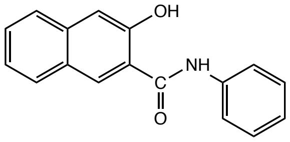
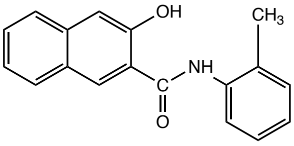
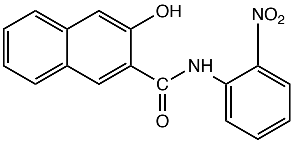
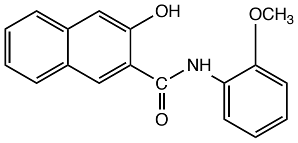
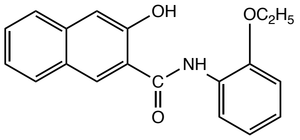
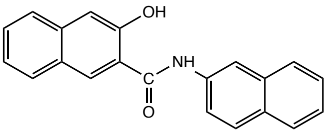
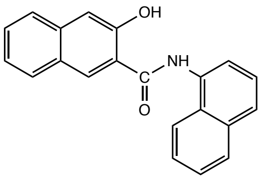
The first coupling component employed in the commercial production of azoic dyes was β-naphthol (2-hydroxy-naphthalene) (Morris and Travis, 1992). The decisive step in the development of azoic colourant was the discovery of Naphthol AS (3-hydroxy-N-phenylnaphthalene-2-carbox-amide) in 1911 in Germany (Zollinger, 2003). Its negatively charged, water soluble form, exhibits high affinity for cellulosic fibres (Hueckel, 1969). Other coupling components were subsequently developed with different substitutions on the basic structure, which were named after the Naphthol AS series (Table 1.1) (Chattopadhyay, 2011). The most commonly used coupling components are phenols, naphthols and aromatic amines (primary, secondary or tertiary). A β-ketoacid derivative, in which the coupling takes place at a methylene group, can also be used as coupling component (Christie, 2015).

The coupling components are insoluble in water but are converted to the corresponding sodium salts and are soluble under strong alkaline condition. Scheme 1.5 refers to the reaction of converting a naphthol (Naphthol AS) into its naphtholate ion. The naphtholate ions are coplanar and have elongated molecular structures. The relatively small molecules have low to moderate substantivity for cotton (Shenai, 1993).



Scheme 1.5 Conversion of Naphthol into Naphtholation Ion

Table 1.1 Examples of Some Coupling Components

Naphthol	Substantivity on Cellulose	Structure	C.I.constn. No.	C.I.ACC No.
β-Naphthol	--		--	--
Naphthol AS	Low		37505	2
Naphthol ASD	Low		37520	18
Naphthol AS-BG	Medium		--	19
Naphthol AS-OL	Low		37530	20
Naphthol AS-PH	Low		37558	14
Naphthol AS-SW	Higher		37565	7
Naphthol AS-BO	Higher		37560	4

The coupling components with higher substantivity generally lead to dyeing that exhibit better rubbing fastness as less azo dye forms on the fibre surface. The substantivity increases with the increase of the molecular size of the coupling components, but the diffusion rate and the solubility in dilute alkali decrease. Addition of salt would promote the exhaustion of the naphtholate in the bath, particularly needed for the naphthols with lower substantivity. Caustic soda solution is usually used for the dissolution of the coupling components (Dăescu and Hădă Rugă, 1999).

A correlation between the chemical structure of the coupling components and their affinity for cotton has been attempted. The correlation of the affinity with theoretically computed hydrophobicity, van der Waals surface and molecular size indicates that the hydrophobic-hydrophobic interaction displays greater importance than hydrophilic-hydrophilic interaction in the adsorption of coupling component to cellulose materials (Dăescu and Hădărugă, 1999)

Reversing the position of amide groups in the naphthols of AS series can enhance the brightness of the shades achieved, however, the advantage is not significant (Hall *et al*., 1980)

1.3.2.2 Diazo Component (Fast Base)

In order to produce azoic colourants on the textile materials, the naphtholated material has to be developed in a bath containing a diazo component, which is also called a fast base. The components may be free bases ($R\text{-}NH_2$), hydrochlorides of the bases ($R\text{-}NH_2 \cdot HCl$) or sometimes hydrogen sulphates ($R\text{-}NH_2 \cdot HSO_4$). The mostly used amines are simple substituted aniline derivatives. The fast base needs diazotisation for coupling with the coupling components. This is usually the reaction of primary aromatic amine under acidic condition or in dispersion with sodium nitrite, at relatively low temperature. The diazotisation reaction is difficult and the diazonium ions produced are unstable. The storage of diazonium ions is not usually possible (Chattopadhyay, 2011).

1.3.3 Dyeing Process

The azoic dyes are synthesised *in-situ* in the textile materials in four steps. Firstly, the insoluble coupling components are converted to their corresponding water-soluble sodium salts or prepared as a stable dispersion. Secondly, the coupling components are applied on the textile materials, which is called naphtholation. Thirdly, the fast bases are diazotised by the reaction called diazotisation. Finally, the naphtholated materials are treated with the diazotised component and the dyes are formed inside the substrates. The final stage is called coupling or development (Shore, 1995; Chattopadhyay, 2011).

1.3.3.1 Dissolution of Coupling Component

The coupling components are insoluble in water and needs to be converted to the water soluble naphtholate form before applying to the textile materials. Therefore, the dissolution of the coupling component is the first step for the production of azoic dyes on textile materials. Two methods can be used for the dissolution of coupling component.

In the hot dissolution method, a hot solution of dispersing agent is poured over the coupling component. After a short period at the boil, the required amount of hot caustic soda solution is added. The mixture is heated until a clear solution is achieved and ready for use (Trotman, 1984). The hot method is preferred for padding processes at high temperature near the boil.

In the cold dissolution method, naphthol is pasted with ethanol and warm water. The coupling components are converted to the naphtholate form by the addition of caustic soda. Instead, a mixture of caustic soda, methanol and water can be poured over the coupling components and become a solution by stirring. Dark brown to olive green solutions with high concentration are obtained. The cold method is normally used for batchwise application at room temperature (Shore, 1995).

1.3.3.2 Naphtholation

Naphtholation refers to the treatment of textile materials with the solution of coupling components. Naphtholation can be carried out either by exhaustion or by padding application. It is generally applied on yarn or fabric. The exhaustion rate depends on the substantivity of the naphtholate anion (Hodgson and Norris, 1949).

Coupling components of high substantivity are preferred for batch application while low substantivity ones are usually used for continuous dyeing (Shore, 1995; Chattopadhyay, 2011). The affinity of most coupling components decreases as the application temperature increases (Shenai, 1993). It is important to prepare the solution just before application since the stability of the solution is limited.

The depth of the shade depends on the amount of coupling components applied. The depth of shade in batch application is controlled by the liquor ratio, the form of textile material, the concentration of the solution and electrolyte, if added. In padding application, the concentration of coupling component can be calculated from the required depth (Chaven, 1999).

The solution is absorbed inside the textile material as well as held on the surface. All the coupling components can react with the diazonium salt during development. The dyes formed by the properly absorbed ones are firmly bound in the material while those formed by the superficially held ones are only on the surface and easy to be removed hence affect fastness performance, particularly the rubbing fastness. The poor rubbing fastness is a general problem for azoic dyeing. To minimise the poor fastness, unabsorbed coupling components need to be removed from the material by a suitable technique, such as rinsing, wringing or hydro-extraction. The use of coupling components of high substantivity can also be helpful. Another method is through a treatment at the boil with a solution of detergent and sodium carbonate (Wiltshire, 1954)

1.3.3.3 Diazotisation

Diazotisation is the process to convert primary aromatic amines into their reactive diazonium salt form with nitrous acid (Hodgson and Norris, 1949). This reaction is important not only in the application of azoic dyes, but also in the synthesis of dyestuffs with azo group. Since nitrous acid is rather unstable, sodium nitrite, which reacts with strong acid to produce nitrous acid, is usually used. The mineral acid used for diazotisation is usually concentrated hydrochloric acid (Christie, 2015). The diazotisation reaction proceeds as Scheme 1.6 (Hodgson and Norris, 1949; Ridd, 1959).

$$R-NH_2 + 2HCl + NaNO_2 \longrightarrow R-\overset{+}{N}\equiv N\overset{-}{Cl} + H_2O$$

Scheme 1.6 Diazotisation Reaction

The temperature needs to be controlled critically during the diazotisation. The reaction is usually carried out at 0-5℃ (Fierz-David and Blangey, 1949). This is achieved by adding ice into the bath. The main reason for the need of low temperature is that the diazonium salts are unstable. They react with water and decompose. The other reason is that higher temperature favours the decomposition of nitrous acid (Christie, 2015).

Excess acid is usually used. One reason is that highly acidic conditions promote the generation of reactive nitrosating species from nitrous acid. The other reason is that acidic conditions prevent the formation of triazine as a side product, which is formed by the reaction of the diazonium salt with the aromatic amine (Zollinger, 2003). There is an optimum amount of acid used for the diazotisation for a certain aromatic amine, depending on the basicity of the amine. Higher level of acidity is generally required for lower basicity amines (Christie, 2015).

The required amount or a slight excess of sodium nitrite is generally used in diazotisation. A large excess of sodium nitrite is avoided due to the instability of nitrous acid. The high concentration can also promote the decomposition of the diazonium salt. The amount of sodium nitrite can be easily monitored with the use of starch/potassium iodide paper, which turns blue when it contacts nitrous acid (Zollinger, 2003; Christie, 2015).

Two methods, namely direct and indirect methods, are available for diazotisation (Fierz-David, 1949; Zollinger, 2003; Chattopadhyay, 2011). In the direct method, the aromatic amine, which is soluble in dilute hydrochloric acid, is dissolved with a small amount of water and required quantity of acid. The mixture is heated for complete dissolution of the amine if needed. After the amine is completely dissolved, the solution is cooled to 0-5℃ by addition of ice. When the optimum temperature is achieved, the required amount of sodium nitrite dissolved in a little water is added into the solution dropwise with stirring. The mixture is then left for some time until the completion of diazotisation, which usually takes 20-30 minutes. In the indirect method, the amine, which is insoluble in dilute hydrochloric acid, is pasted with a little water. Sodium nitrite is added into the solution with stirring until it is completely dissolved. The acid is prepared in another bath with ice. The mixture of the amine and nitrite is then added slowly into the acid with stirring.

A clear solution and the absence of foam indicate successful completion of diazotisation. At the end of diazotisation, the excess nitrous acid must be destroyed before coupling by adding sulfamic acid (Scheme 1.7) (Christie, 2015). Urea can also be used to destroy the excess nitrous acid (Zollinger, 2003).

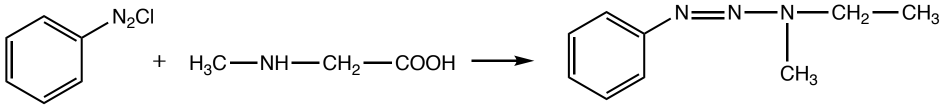
$$NH_2SO_3H + HNO_2 \longrightarrow N_2 + H_2SO_4 + H_2O$$

Scheme 1.7 Reaction of Nitrous Acid and Sulfamic Acid

Diazotisation is a time-consuming process. In order to save time in practical use, stabilising the diazonium salt is necessary so that the dyers or the printers are spared the trouble of diazotising the amines. The stabilisation methods for diazonium salts include active stabilisation and passive stabilisation (Von Glahn and Bergstrom, 1952; Saunders and Allen, 1985).

Active stabilised products are converted into diazonium salts when dissolved in water or alcohol and couple immediately when mixed with the coupling components. The diazonium salts can be stabilised by conversion into corresponding sulphates or chlorides. The acidic solution of the diazonium salt is evaporated under vacuum at 45℃ and treated with anhydrous sodium sulphate in order to obtain the sulphates of the diazonium salts. Another method is to form the complex salts of diazonium salts. The basicity of the diazonium salt is used to form double salts of metals. Zinc chloride double salts are the mostly used for the stabilisation of diazonium compounds.

Passive stabilised products, on the other hand, do not form diazonium salt when dissolved in water and hence stay inert when mixed with the coupling component. Therefore, the products can be mixed with the coupling component in dry state and are mainly used for printing. The activation of the products can be achieved by either acid treatment or steam. The most commonly used method is to treat the diazonium salt with a suitable amino compound to form the diazoamino compounds (Scheme 1.8). They do not have coupling power and are stable in neutral and alkaline conditions. The diazoamino compounds are also called triazenes. The mixture of diazoamino and coupling component is dissolved in alkaline solution. On acidification, the diazoamino compound is converted into the active diazonium salt and couples immediately. Other methods including converting the diazonium salts into antidiazotates, aminosulphonic acids or diazosulphonates can also be used for the stabilisation of diazonium salts.



Scheme 1.8 Conversion of Diazonium Salt into Diazoamino Compound

1.3.3.4 Coupling

When the naphtholated material comes into contact with the bath containing diazonium salt, the formation of azoic dyes begins. The reaction is called coupling (Christie, 2015). Some time is required for the completion of the reaction.

To ensure the azoic dyes are obtained in high yield, careful control of the reaction conditions is important to prevent the formation of side-products. Unlike the case of diazotisation, temperature control is less important in coupling reaction. Coupling reaction is commonly carried out at or just below room temperature. Raising the temperature is not necessary, since it may increase the rate of decomposition of the diazonium salt more than the rate of coupling (Christie, 2015).

The factor that needs the most careful control in coupling reaction is pH. The rate of coupling can be controlled by pH (Chattopadhyay, 2011). The optimum pH may vary for a specific coupling component. The phenols and naphthols are generally treated under alkaline conditions and mainly converted into anion. The first reason is that the anion is more soluble than phenol or naphthol itself. The other more important reason is that the $–O^-$ group is considered more powerful in electron-releasing than –OH group. Very high pH must be avoided as it may promote the decomposition of diazonium salt. When using aromatic amines as coupling components, weakly acidic condition is preferred. The amines are converted into the more soluble protonated form (Christie, 2015).

After coupling, the textile materials need to go through after-treatment process including rinsing, acidification, after-development and alkaline soaping. Following acidification, the material is treated in a bath containing alkaline soap and sodium carbonate at 70-80℃ for 10-15 minutes (Chattopadhyay, 2011). During the alkaline soaping, the dyes formed within the fibre undergo reorganisation and crystallisation (Shore, 1995). The intermolecular interaction of the azoic dyes increases and hence the fastness properties improve (Zollinger, 2003).

1.4 Supercritical CO_2 Dyeing of Polyester Fibre

Supercritical fluid dyeing (SFD) is a waterless dyeing process that makes use of the unique properties of supercritical fluids. It was first established by Professor Schneider in 1989. Although several substances can be used as supercritical fluids, carbon dioxide (CO_2) is generally used as it is cheap, non-flammable, nontoxic, recyclable, and chemically inert under most conditions (Bach *et al.*, 2002).

Above the critical point (T_c = 31.1℃, P_c =73.7bar), carbon dioxide has the properties of both a liquid and a gas. Its density is near that of a liquid, which is advantageous for dissolving hydrophobic dyes, and its viscosity and diffusion properties are gas-like, which lead to shorter dyeing time. The dissolving power of the supercritical carbon dioxide towards disperse dyes and the swelling and plasticisation action towards hydrophobic polymers make it suitable for the dyeing of polyester fibres. Compared to conventional water based dyeing, dyeing with supercritical carbon dioxide has many advantages (Knittle *et al.*, 1993; Saus *et al.*, 1993; Knittle and Schollmeyer, 1995; Bach *et al.*, 2002; Banchero, 2012):

1. The process is environmentally friendly in relation to water consumption and pollution.
2. No auxiliary is required.
3. The dyeing and the removal of excess dye can be carried out in one plant in the carbon dioxide dyeing process.
4. Drying step is not required because the carbon dioxide is released in the state of gas at the end of the dyeing process.
5. The carbon dioxide and the dyes can be recycled after dyeing.

1.4.1 Interaction between Supercritical CO_2 and Polyester Fibres

When the polyester fibres are in contact with the supercritical dyeing bath, the small CO_2 molecules can easily penetrate inside the free volume of the amorphous parts of the polyester. The plasticisation of the amorphous phase in the polymers increases the mobility of the polymer chains which leads to the reduction of the glass transition temperature and swelling of the polymer (Park *et al.*, 2010). A lowering of T_g by at least 20-30℃ was observed (Saus *et al.*, 1993; Beltrame *et al.*, 1998), indicating the carrier effect of the supercritical fluid.

The sorption of the carbon dioxide results in the changes of thermo-mechanical properties of the polymer after the dyeing process. Lower glass transition temperature and melting point were observed after carbon dioxide dyeing (Bach *et al.*, 1998; Zhong *et al.*, 1999). These depend on the treatment temperature up to 160℃ (Drews and Jordan, 1998).

During dyeing, the polymer chains are rearranged into more ordered configurations, leading to increased crystallinity. It is thought that temperature is mainly responsible for the morphological changes of the polymer (Smole and Zipper, 2002). Generally speaking, the structure of polyester fibres does not change significantly in supercritical carbon dioxide under optimum dyeing condition. Significant changes of structure only occur when the material is not heat-set or the treatment temperature is above the heat-set temperature (Drews and Jordan, 1998). As a result, heat-set fibres must be used for the dyeing in carbon dioxide and the heat-set temperature should be 30℃ higher than the treatment temperature (Bach *et al.*, 2002).

Migration of oligomers is another consequence of the plasticisation of polyester (Drews and Jordan, 1998). This phenomenon occurs above 100℃ (Hou *et al.*, 2004) and depends on many technological factors such as flow rates and liquor ratio (Montero *et al.*, 2000). Oligomer migration can affect the quality of the dyed product and requires specific cleaning steps of the plant as extracted fine particles would build up on the interior surface of the dyeing machine.

1.4.2 Dye Distribution between Fibre and CO_2

Generally, dye partition between the fibre and CO_2 mainly depends on the time and the dyeing conditions, such as temperature, pressure and CO_2 density, which would influence the solubility, the affinity for polyester and the dye diffusion coefficient (Kazarian *et al.,* 1998; Montero *et al*., 2000). While the amount of dye sorption increases almost linearly with temperature at a certain pressure, the dye uptake reaches a limited value with increasing pressure at constant temperature. It indicates that the polymer is saturated with dyes at high pressure (Ferri *et al*., 2006; Park *et al*., 2010). The influence of temperature on the dye uptake is due to the significant increase in chain mobility and free volume above the glass transition temperature (Ferri *et al.,* 2006).

The partition coefficient is the ratio between the dye concentration in the polymer and the corresponding concentration in the supercritical fluid. The values of the partition coefficients are typically in the range of 10^2-10^4 (Bach *et al*., 2002). The coefficient decreases as the pressure or density increases when the temperature is fixed. This indicates that the affinity of the dyes decreases because when the dye solubility increases with pressure, the dye uptake shows levelling-off effect. Under certain pressure, the coefficient decreases as the temperature increase because the CO_2 dyeing process is exothermic (Ferri *et al.*, 2006).

The equilibrium partition coefficient (K_{eq}) is defined by the adsorption rate constant divided by the desorption rate constant and depends on the equilibrium concentration of dye in solution. Dyeing in the CO_2 should be carried out under the condition with the highest K_{eq}, resulting in the highest exhaustion. K_{eq} decreases if the dye solubility in CO_2 increases. Therefore, dyeing under condition of the highest solubility does not give the highest colour yield (Montero *et al.*, 2000).

1.4.3 Supercritical Fluid Dyeing Technology of Polyester Fibres

A typical SFD plant consists of a CO_2 tank, a compression pump, a heated dyeing vessel, a dye container and a circulation pump (Hou *et al.*, 2010). The yarns or fabrics to be dyed are put into the dyeing vessel. Then the system is pressurised and heated at the required condition. The dyeing step is performed by circulating the supercritical bath from the dye container and the dyeing vessel through the circulation pump. At the end of the dyeing step, the system is gradually depressurised and washed with clean CO_2 to remove the unfixed dyes.

The fluid circulation has significant influence on the dyeing process, including levelness, dye exhaustion and dye partition. It takes up to 2-3 days to obtain dyeing equilibrium without circulation (Tabata *et al.*, 2001). The same dyeing can only be obtained in static system by adding co-solvents, such as acetone (Bach *et al.*, 2002). The action of co-solvents works in two ways. Firstly, they increase the swelling of the fibres, resulting in increased mass transport into the polymer (Kazarian *et al.*, 1999). On the other hand, co-solvents can increase the solubility of the dyes in CO_2. A higher concentration of the dye on the fibre surface can promote the dye uptake.

In trichromatic dyeing, it was found that changes in the temperature and pressure lead to significant colour differences including the colour yield and the hue. Since the auxiliaries would affect the dyeing, the hues and the colour yield would vary significantly in CO_2 and in water (Bach *et al.*, 2002). The uptake and the colour yield of individual dyes show different trends compared to those observed during single-dye coloration. During dyeing, the dyes seems to compete for accessible locations. The dye with the lowest molecular weight has the highest mobility, therefore, has the highest dye uptake (Tušek *et al.*, 2000). Therefore, the conventional colour prediction method is not suitable for carbon dioxide dyeing.

1.5 Aims and Objectives

The main aim of this project is to synthesise and apply dye precursors in the form of stabilised diazonium compounds (diazoamines) and coupling components with good substantivity and diffusion characteristics on polyester, including PET and PLA fabrics, at 100℃.

The key objectives are as follows:

1. Synthesis of diazoamines with good substantivity to polyester fibres.
2. Application of the azoic combinations on PET fabrics in aqueous dyebath
   a. Investigation of the colour yield and fastness properties of the dyeing on PET with azoic combinations
   b. Investigation of the colour gamut achieved with mixture of the azoic dyes on PET.
   c. Investigation the dyeing behaviour of the azoic dyes in PET/wool competitive dyeing.
3. Application of the azoic combinations on PLA fabrics in aqueous dyebath
   a. Investigation of the colour yield and fastness properties of the dyeing on PLA with azoic dyes
   b. Investigation of the colour gamut achieved with mixture of the azoic dyes on PLA.
   c. Comparison of the dyeing with azoic dyes on PET and PLA fabrics
4. Application of the azoic dyes on polyester fabrics in supercritical CO_2 ($scCO_2$).
   a. Investigation of the influence of temperature on dyeing.
   b. Investigation of the colour yield and fastness properties of the dyeing in $scCO_2$.

c. Comparison of the dyeing in $scCO_2$ and aqueous dyeing with azoic dyes.

Chapter 2

Experimental

2.1 Materials

The PET fabrics (150g/m^2) used in this project were knitted single jersey fabrics (scoured and heat set). The PLA fabrics (205g/m^2) were knitted double jersey fabrics (scoured and set) purchased from Valuable Enterprise, Taiwan. The woven wool fabric (295g/m^2, 2/2 twill, scoured and heat set) was purchased from Whaley's Ltd with 36 ends per inch and 24 picks per inch.

4-chloro-2-methylaniline, Naphthol AS, 2-naphthol, hydrochloric acid (reagent grade), diethanolamine and sodium carbonate were purchased from Sigma Aldrich. N-phenyl-p-phenylenediamine, sodium nitrite and sulfamic acid were purchased from Alfa Aesar. Potassium iodide paper was purchased from Sigma Aldrich. Ufoxane 2 (anionic dispersing agent) was purchased from Borregaard Lignotech. Citric acid, Sandozin NIE (non-ionic wetting agent), sodium hydroxide, sodium hydrosulphite and acetone (HPLC grade) were purchased from Sigma Aldrich. Disodium hydrogen phosphate was purchased from Lancaster Synthesis. Distilled water and HPLC grade water were obtained from on-site apparatus.

2.2 Synthesis of the Pre-formed Dyes and Diazoamine

2.2.1 Preparation of the diazonium salt

Aniline derivatives (4-chloro-2-methyaniline or N-phenyl-p-phenylenediamine) (0.2M) and concentrated hydrochloric acid (36.5% w/v, 40ml) were added to de-ionised water (100ml). The solution was cooled to 0-5℃ with a bath of ice. A solution of sodium nitrite (0.2M) in water (50ml) was gradually added to the ice-cold solution over 30 minutes. The mixture needed a further stirring at 0-5℃ for 30 minutes until the diazonium salt was formed. At the end of the reaction, the presence of excess nitrous acid was confirmed with starch potassium iodide paper, which turns blue when contacts nitrous acid. The excess nitrous acid was then destroyed by adding a 10% w/v aqueous sulphamic acid until the potassium iodide paper did not turn blue.

2.2.2 Synthesis of Pre-formed Dyes

Coupling component (2-naphthol or Naphthol AS) (0.2M) was dissolved in sodium hydroxide (10% w/v, 50ml) and cooled to 0-5℃. The solution of the coupling component was then added to the diazonium salt solution over 30 minutes and stirred at 0-5℃ for a further 60 minutes. The formed dyes were vacuum filtered and washed with alkaline solution until the filtered solution is not coloured. The purified dyes were dried in a vacuum desiccator for 48 hours.

2.2.3 Synthesis of Diazoamine

The diazoamine derivatives were synthesised as described by Adam *et al*. (2004). The solution of diethanolamine (0.25M) and sodium carbonate (70g) in de-ionised water (300ml) was prepared and cooled to 0-5℃. The diazonium salt solution obtained in previous step was gradually added to the diethanolamine solution with stirring over 15 minutes. The mixture was then stirred at 0-5℃ for a further 30 minutes. The formed diazoamine was vacuum filtered and washed with water until the filtered solution is neutral. The purified diazoamine was dried in a vacuum desiccator for 48 hours.

2.3 Characterisation of the Synthesised Components

2.3.1 HPLC-MS Method

HPLC-MS was used as an analytical tool for verifying the purity of the synthesised pre-formed dyes and diazoamine. The analysis was carried out with Kinetex 100 C18(2.1×150mm, 2.6μm) chromatographic column. The injector volume was 20μL. Chromatography was carried out using two solvents: (A) water and 0.1% formic acid solution and (B) acetonitrile and 0.1% formic acid solution. For the first 3 minutes, the eluent system included 60% B and 40% A and for 3-10 minutes, the gradients were changed to 90% B and 10% A. The eluent flow rate was 0.5ml/min. The detector was set at 270nm and the temperature was 40℃. The method was carried out on an Agilent 1200 HPLC using a Bruker HCT Ultra Ion Trap for the MS detection and a Diode Array Detector. The ESI (electronspray ionisation) parameters in the NI (negative ion) mode were as follows: spray voltage 4000V, dry gas 10 dm^3/min, dry temperature 365℃, capillary 60 nA, nebulizer 65 psi, nebulising gas N_2.

2.3.2 UV-Visible Spectrophotometry

UV-Visible Spectrophotometry was used to measure the λ_{max} (wavelength of the maximum absorption) and molar attenuation coefficient (ε) of the pre-formed dyes. The pre-formed dyes were dissolved in acetone at four different concentrations. The analysis was carried out with a *Jasco V630* UV-Visible/NIR spectrophotometer in the visible region of the spectrum (400-700 nm), at 1 nm intervals.

The molar absorptivity (ε)was calculated according to Beer-Lambert law:

$$\mathrm{A} = \varepsilon \times \mathrm{l} \times \mathrm{c}$$

Where A= the absorbance at a specific wavelength

l = the distance that the light travels through the solution (the depth of the cuvette)

c = the concentration of the solution

With the values obtained from the spectrophotometer, the concentration of the solution was plotted on X-axis and the absorbance at a specific wavelength (λ_{max} was used here) was plotted on the Y-axis. The points should form a straight line as the absorbance is proportional to the concentration according to the Beer-Lambert law. The molar absorptivity can be calculated by dividing the slope of the line by the path length (depth of the cuvette).

2.4 Exhaustion of the Pre-formed Dyes on PET Fabrics

The dyebath was prepared at 2% o.m.f. of 10g PET fabrics without any auxiliary or buffer. The dyeing process was carried out at 130℃ for 90 minutes. Samples of the dyebath were taken before and after dyeing and diluted with the same amount of acetone until all the dye particles were dissolved. The prepared dye solution was measured using a *Jasco V630* UV-Visible/NIR spectrophotometer in the visible region of the spectrum (400-700 nm), at 1 nm intervals. Absorbance of the diluted dye solution was measured at λ_{max} and exhaustion (E%) calculated using the equation

$$\mathrm{E\%} = (1 - \frac{A_1}{A_0}) \times 100$$

where A_0 and A_1 represent absorbance of dye solution at λ_{max} before and after dyeing, respectively.

2.5 Aqueous Dyeing Procedures for Polyester Fabric

Dyeings of polyester fabrics were carried out with *Pyrotech* 2000 series Infrared dyeing machine.

2.5.1 Preparation of Dyeing Liquor

The dyeing liquor was prepared for 3.5g fabric samples at a liquor ratio of 20:1 at different concentration.

For the precursors, a solution containing 0.1g Ufoxane 2 (anionic dispersing agent), 50ml de-ionised water and 20ml buffer (Table 2.1) was prepared. The pH 6 buffer was used for the dyeing liquor with precursors. The diazoamine derivative and coupling component were respectively dissolved in a minimum amount of acetone until the particles were completely dissolved. They were then added dropwise to the solution while stirring. The precursor liquor was applied immediately after preparation.

For the dyeing liquor with pre-formed dyes, the same method was used for the preparation of the dyeing liquor. The pH 5 buffer was used for the dyeing liquor with pre-formed dyes.

Table 2.1 Buffers Employed to Set the Required Dyebath pH (Pearse, 1980)

pH	Buffering System
5.0	0.1M Citric acid (9.70ml) and 0.2M disodium hydrogen phosphate (10.30ml)
6.0	0.1M Citric acid (7.37ml) and 0.2M disodium hydrogen phosphate (12.63ml)

2.5.2 Dyeing Process of PET Fabrics

The PET fabrics were dyed with the preformed dyes at 100℃ and 130℃ for 45 minutes, and with precursors at 100℃ for 60 minutes. After dyeing, the fabrics were rinsed with cold water and reduction cleared at 60℃ for 20 minutes with a solution containing 2g/L Sandozin NIE (non-ionic wetting agent), 2g/L sodium hydrosulfite and 2g/L sodium hydroxide. Then the fabrics were rinsed thoroughly in cold water and dried at room temperature. The process is presented in Figure 2.1.

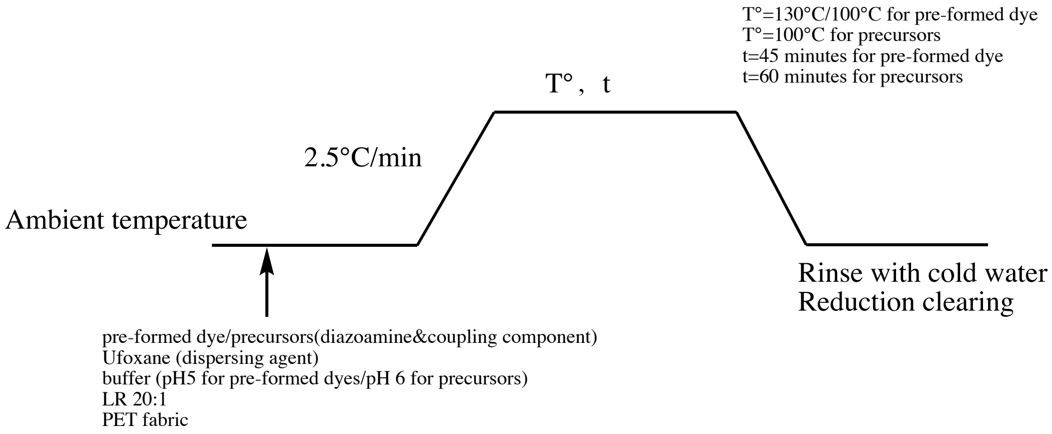


Figure 2.1 Dyeing Process of PET Fabrics

2.5.3 Dyeing Process of PLA Fabrics

The dyeing of PLA fabrics with pre-formed dyes was carried out at 110℃ for 30 minutes and cooled down to 50℃. The dyeing with precursors was carried out at 100℃ for 30 minutes and cooled down to 50℃. The dyeing temperature was held at 90℃ for 5 minutes in order to increase the levelness. The dyed fabrics were rinsed with cold water and reduction cleared at 60℃ for 15 minutes with a solution containing 2g/L Sandozin NIE (non-ionic wetting agent), 2g/L sodium hydrosulfite and 2g/L sodium carbonate. Then the fabrics were rinsed thoroughly in cold water and dried at room temperature. The process is presented in Figure 2.2.

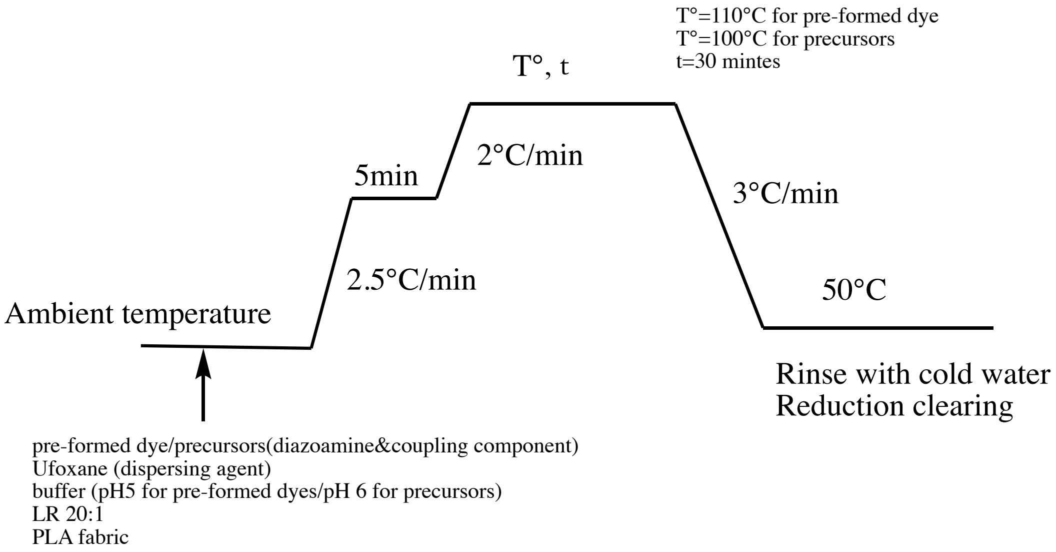


Figure 2.2 Dyeing Process of PLA Fabrics

2.5.4 Dyeing Process with Mixture Components

According to the colour coordinates of the fabrics dyed with individual dyes, the concentration with the highest L* value is set as 100% for each dye. The concentration as 25%, 50% and 75% is calculated accordingly and used to determine the concentration of each dye when dyeing with mixtures. In the following part, the ratio of the mixtures is represented with the percentage of L* value. For example: the ratio 100/25 of orange/red mixtures means the concentration at which the highest L* value is achieved for the orange dye and the concentration at which the 25% of the highest L* value is achieved for the red dye were used when dyeing with the mixtures. The dyeing with mixtures was carried out in one bath with all the components added at the same time. The dyeing procedure for the mixtures is the same as the individual dyes.

2.6 Supercritical CO_2 dyeing of Polyester Fabrics

The vessel used for scCO_2 dyeing is shown in Figure 2.3. The precursors (2% o.m.f.) were added into the vessel. The fabrics were wrapped around a net in order to allow the CO_2 to have even contact with the fabric. Eight steel balls were added to increase the circulation. After screwing the lid tight, the vessel was cooled in freezer for 20 minutes and filled with 150g CO_2. The dyeing process was carried out at 90℃ and 100℃ for 90 minutes in a *Roaches WashTec-P* dyeing machine. After dyeing, the CO_2 was released from the vessel and the fabrics were washed with acetone as clearing process.

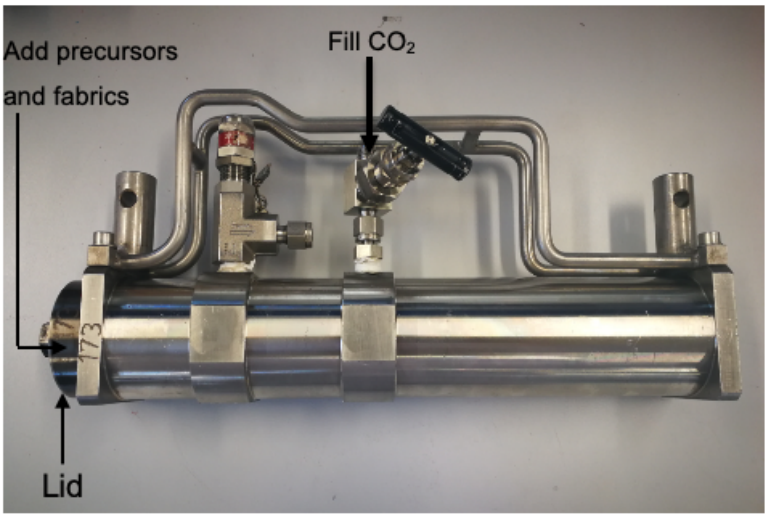


Figure 2.3 Vessel for Supercritical CO_2 Dyeing

2.7 Colour Measurement

The dyed fabric samples were measured using a *Datacolor SF600 Spectraflash* colour spectrophotometer connected to a computer using *DCI Colour Tools* software. At a specified wavelength, the colour yield (K/S) of the sample was calculated from the reflectance values (R) using the Kubelka-Munk equation:

$$\mathrm{K/S} = \frac{(1-R)^2}{2R}$$

2.8 Fastness Properties Test

2.8.1 Rubbing Fastness Test

Rubbing fastness test was carried out according to BS EN ISO 105-X12:2016 with *James Heal CrockMaster* colour fastness to rubbing tester.

Four pieces of samples (50mm*140mm) of each dyed fabric were prepared and conditioned in standard atmosphere (a temperature of 20±2℃ and a relative humidity of 65±4%) for at least four hours. Conditioned rubbing cloth (purchased from James Heal) was placed flat over the end of the finger with the weave parallel to the direction of rubbing finger. At a rate of one cycle per second, rub to and fro in a straight line 20 times, 10 times to and 10 times fro, along a track (104 ± 3) mm long on the dry specimen, with downward force of (9 ± 0.2) N. For the wet rubbing fastness, the rubbing cloth was soaked in distilled water with take-up of 95%-100% before the test.

The staining of the rubbing cloths was assessed with the grey scale for staining (purchased from James Heal) under D65 (artificial daylight) illuminate. The rubbing cloths for wet rubbing fastness tests were air dried before assessment of the staining.

2.8.2 Washing fastness Test

Washing fastness test was carried out according to BS EN ISO 105-C06:2010 with *James Heal GyroWash* colour fastness tester.

Samples (100mm*40mm) of the dyed fabric and multifibre adjacent fabric DW complying with BS EN ISO 105-F10:1989 (purchased from James Heal) were prepared and sewed together along the short edge. The wash liquor was prepared with 4g/L ECE phosphate reference detergent (B) (purchased from SDC Enterprises Limited) and 1g/L sodium carbonated in water. 50ml of the wash liquor and 25 steel balls were used for each sample. The test was carried out at 60℃ for 30 minutes. After washing, the fabrics were rinsed with cold water and dried at room temperature.

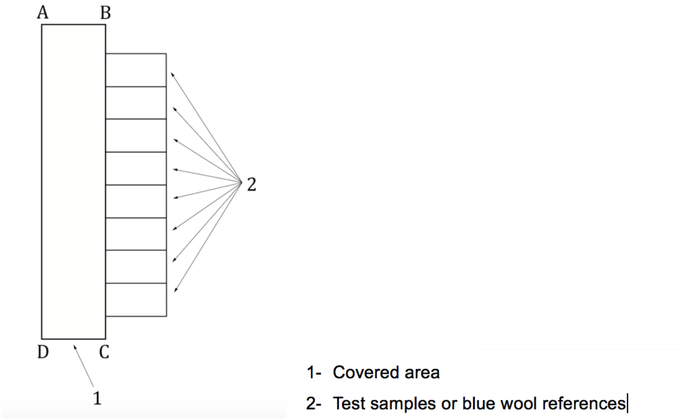
The staining of the multifibre adjacent fabrics and the colour change of the dyed fabrics were assessed with *Datacolor SF600 Spectraflash* colour spectrophotometer.

2.8.3 Light Fastness Test

Light fastness test was carried out according to BS EN ISO 105-B02:2014 with *James Heal TruFade* Xenon arc light (1.34$\mathrm{W \cdot cm^{-2}}$) fastness tester.

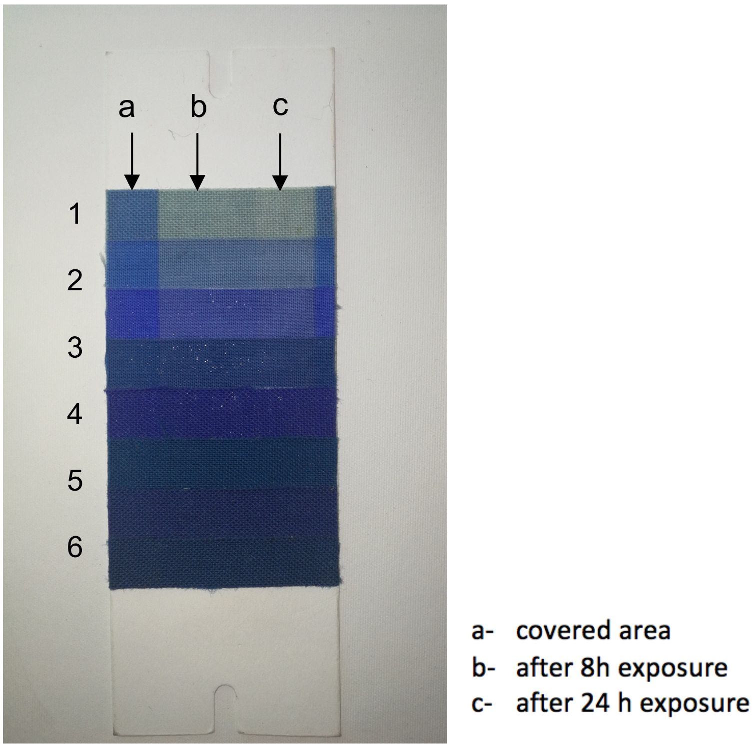
Samples were cut into strips and fastened on a white card. An opaque cover was used to cover two third of the samples from exposure for the first 8 hours and one third of the samples for the remaining 16 hours, as shown in Figure 2.4. Blue wool references 1-8 complying with ISO 105-B08:1999 (purchased from James Heal) was exposed together with the samples. The test was carried out at 36℃ with a relative humidity of 45%.

After 24 hours exposure, the colour changes of the samples were compared with the changes of the blue wool references (Figure 2.5) under D65 (artificial daylight) illuminate. The light fastness of the sample is the number of the blue wool reference which shows similar colour change.



1- Covered area
2- Test samples or blue wool references

Figure 2.4 Mounting of Test Samples/Blue Wool References



a- covered area
b- after 8h exposure
c- after 24 h exposure

Figure 2.5 Blue Wool References

2.8.4 Dry Heat Fastness

Dry heat fastness test was carried out according to BS EN ISO 105-P01:1995.

The samples (100mm*40mm) of the dyed fabrics were prepared and attached to a piece of the undyed fabric with the same size. The PET samples were heated at 210℃ ± 2℃ and the PLA samples were treated at 150℃ ± 2℃ for 30s with a pressure of 4kPa ± 1kPa.

The colour change of the dyed fabrics were assessed with *Datacolor SF600 Spectraflash* colour spectrophotometer.

2.9 Colour Prediction

The colour prediction of the dyeing with mixtures was carried out with MATLAB. The code was as below.

```
function varargout = myfig(varargin)
% MYFIG MATLAB code for myfig.fig
%      MYFIG, by itself, creates a new MYFIG or raises the existing
%      singleton*.
%
%      H = MYFIG returns the handle to a new MYFIG or the handle to
%      the existing singleton*.
%
%      MYFIG('CALLBACK',hObject,eventData,handles,...) calls the local
%      function named CALLBACK in MYFIG.M with the given input arguments.
%
%      MYFIG('Property','Value',...) creates a new MYFIG or raises the
%      existing singleton*.  Starting from the left, property value pairs are
%      applied to the GUI before myfig_OpeningFcn gets called.  An
%      unrecognized property name or invalid value makes property application
%      stop.  All inputs are passed to myfig_OpeningFcn via varargin.
%
%      *See GUI Options on GUIDE's Tools menu.  Choose "GUI allows only one
%      instance to run (singleton)".
%
% See also: GUIDE, GUIDATA, GUIHANDLES

% Edit the above text to modify the response to help myfig

% Last Modified by GUIDE v2.5 08-Sep-2017 16:04:07

% Begin initialization code - DO NOT EDIT
gui_Singleton = 1;
gui_State = struct('gui_Name',       mfilename, ...
                   'gui_Singleton',  gui_Singleton, ...
                   'gui_OpeningFcn', @myfig_OpeningFcn, ...
                   'gui_OutputFcn',  @myfig_OutputFcn, ...
                   'gui_LayoutFcn',  [] , ...
                   'gui_Callback',   []);
```

```
if nargin && ischar(varargin{1})
   gui_State.gui_Callback = str2func(varargin{1});
end

if nargout
   [varargout{1:nargout}] = gui_mainfcn(gui_State, varargin{:});
else
   gui_mainfcn(gui_State, varargin{:});
end
% End initialization code - DO NOT EDIT


% --- Executes just before myfig is made visible.
function myfig_OpeningFcn(hObject, eventdata, handles, varargin)
% This function has no output args, see OutputFcn.
% hObject    handle to figure
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)
% varargin   command line arguments to myfig (see VARARGIN)

% Choose default command line output for myfig
handles.output = hObject;

% Update handles structure
guidata(hObject, handles);

% UIWAIT makes myfig wait for user response (see UIRESUME)
% uiwait(handles.figure1);

s = imread('spectrum.jpg');
axes(handles.axes11);
imshow(s);

load data.mat
handles.orange100 = orange100;
handles.orange130 = orange130;
handles.dullred100 = dullred100;
handles.dullred130 = dullred130;
handles.dullredac = dullredac;
handles.orangeac = orangeac;
handles.sub = sub;
handles.w = w;
handles.conc = conc;
handles.col = 1;
set(handles.listbox1,'Value',handles.col);

guidata(hObject, handles);
handles.p1 = orange130';
handles.p2 = orange100';
handles.p3 = dullred130';
handles.p4 = dullred100';
handles.p5 = dullredac';
handles.p6 = orangeac';

handles.ks1 = ((1-handles.p1).^2)./(2*handles.p1);
handles.ks2 = ((1-handles.p2).^2)./(2*handles.p2);
handles.ks3 = ((1-handles.p3).^2)./(2*handles.p3);
handles.ks4 = ((1-handles.p4).^2)./(2*handles.p4);
handles.ks5 = ((1-handles.p5).^2)./(2*handles.p5);
```

```
handles.ks6 = ((1-handles.p6).^2)./(2*handles.p6);
handles.kssub = ((1-handles.sub).^2)./(2*handles.sub);
for i=1:31
   handles.ks1(:,i) = handles.ks1(:,i) - handles.kssub(i);
   handles.ks2(:,i) = handles.ks2(:,i) - handles.kssub(i);
   handles.ks3(:,i) = handles.ks3(:,i) - handles.kssub(i);
   handles.ks4(:,i) = handles.ks4(:,i) - handles.kssub(i);
   handles.ks5(:,i) = handles.ks5(:,i) - handles.kssub(i);
   handles.ks6(:,i) = handles.ks6(:,i) - handles.kssub(i);
end



guidata(hObject, handles);

[handles] = update(handles);
[handles] = predict(handles);

guidata(hObject, handles);

% --- Outputs from this function are returned to the command line.
function varargout = myfig_OutputFcn(hObject, eventdata, handles)
% varargout  cell array for returning output args (see VARARGOUT);
% hObject    handle to figure
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Get default command line output from handles structure
varargout{1} = handles.output;


function [handles] = update(handles)


switch handles.col
   case 1
      data = handles.orange130;
      lmax = 13;
      conc = handles.conc;
   case 2
      data = handles.orange100;
      lmax = 13;
      conc = handles.conc;
   case 3
      data = handles.dullred130;
      lmax = 13;
      conc = handles.conc;
   case 4
      data = handles.dullred100;
      lmax = 13;
      conc = handles.conc;
   case 5
      data = handles.dullredac;
      lmax = 13;
      conc = handles.conc;
   case 6
      data = handles.orangeac;
      lmax = 13;
      conc = handles.conc(1:end-1);
   otherwise
```

```
        beep
end
sub = handles.sub;

axes(handles.axes1);
hold off
plot(handles.w,handles.sub,'r-');
hold on
plot(handles.w,data,'b-');
axis([400 700 0 1])

im = ones(1,1,3);
dataRGB = xyz2srgb(r2xyz(data',400,700,'d65_64')/100);
axes(handles.axes2);
im(1,1,1) = dataRGB(1,1);
im(1,1,2) = dataRGB(1,2);
im(1,1,3) = dataRGB(1,3);
imshow(uint8(im));

axes(handles.axes3);
im(1,1,1) = dataRGB(2,1);
im(1,1,2) = dataRGB(2,2);
im(1,1,3) = dataRGB(2,3);
imshow(uint8(im));

axes(handles.axes4);
im(1,1,1) = dataRGB(3,1);
im(1,1,2) = dataRGB(3,2);
im(1,1,3) = dataRGB(3,3);
imshow(uint8(im));

axes(handles.axes5);
im(1,1,1) = dataRGB(4,1);
im(1,1,2) = dataRGB(4,2);
im(1,1,3) = dataRGB(4,3);
imshow(uint8(im));

axes(handles.axes6);
im(1,1,1) = dataRGB(5,1);
im(1,1,2) = dataRGB(5,2);
im(1,1,3) = dataRGB(5,3);
imshow(uint8(im));

axes(handles.axes7);
if handles.col<6
   im(1,1,1) = dataRGB(6,1);
   im(1,1,2) = dataRGB(6,2);
   im(1,1,3) = dataRGB(6,3);
else
   im(1,1,1) = 240;
   im(1,1,2) = 240;
   im(1,1,3) = 240;
end
imshow(uint8(im));


ks = ((1-data).^2)./(2*data);
axes(handles.axes8);
hold off
plot(conc,ks,'b-');
```

```
axis([0 8 0 30])

axes(handles.axes9);
hold off
plot([0 conc],[0 ks(lmax,:)],'bo');
axis([0 8 0 30])



% --- Executes on selection change in listbox1.
function listbox1_Callback(hObject, eventdata, handles)
% hObject    handle to listbox1 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: contents = cellstr(get(hObject,'String')) returns listbox1 contents as cell array
%        contents{get(hObject,'Value')} returns selected item from listbox1

handles.col = get(hObject,'Value');
guidata(hObject, handles);
[handles] = update(handles);

% --- Executes during object creation, after setting all properties.
function listbox1_CreateFcn(hObject, eventdata, handles)
% hObject    handle to listbox1 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: listbox controls usually have a white background on Windows.
%       See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'), get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor','white');
end



function [handles] = predict(handles)
c1 = get(handles.slider1,'Value')*8;
c2 = get(handles.slider2,'Value')*8;
c3 = get(handles.slider3,'Value')*8;
c4 = get(handles.slider4,'Value')*8;
c5 = get(handles.slider5,'Value')*8;
c6 = get(handles.slider6,'Value')*6;

set(handles.text6,'String',sprintf('%.2f',c1));
set(handles.text7,'String',sprintf('%.2f',c2));
set(handles.text8,'String',sprintf('%.2f',c3));
set(handles.text9,'String',sprintf('%.2f',c4));
set(handles.text11,'String',sprintf('%.2f',c5));
set(handles.text13,'String',sprintf('%.2f',c6));

ks = zeros(1,31);
for w=1:31
    if (c1>0)
        c = handles.conc;
        ks1 = handles.ks1(:,w);
        ks(w) = ks(w) + interp1([0 c],[0; ks1],c1);
    end
    if (c2>0)
        c = handles.conc;
```

```
        ks2 = handles.ks2(:,w);
        ks(w) = ks(w) + interp1([0 c],[0; ks2],c2);
    end
    if (c3>0)
        c = handles.conc;
        ks3 = handles.ks3(:,w);
        ks(w) = ks(w) + interp1([0 c],[0; ks3],c3);
    end
    if (c4>0)
        c = handles.conc;
        ks4 = handles.ks4(:,w);
        ks(w) = ks(w) + interp1([0 c],[0; ks4],c4);
    end
    if (c5>0)
        c = handles.conc;
        ks5 = handles.ks5(:,w);
        ks(w) = ks(w) + interp1([0 c],[0; ks5],c5);
    end
    if (c6>0)
        c = handles.conc(1:end-1);
        ks6 = handles.ks6(:,w);
        ks(w) = ks(w) + interp1([0 c],[0; ks6],c6);
    end
end
ks = ks + handles.kssub;
p = 1 + ks - sqrt(ks.*ks + 2*ks);
w = linspace(400,700,31);
axes(handles.axes10);
plot(w,p,'r-');
axis([400 700 0 1]);

if (get(handles.checkbox1,'Value'))p = 1 + ks - sqrt(ks.*ks + 2*ks);
    disp(p')
end

% --- Executes on slider movement.
function slider1_Callback(hObject, eventdata, handles)
% hObject    handle to slider1 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'Value') returns position of slider
%        get(hObject,'Min') and get(hObject,'Max') to determine range of slider
[handles] = predict(handles);

% --- Executes during object creation, after setting all properties.
function slider1_CreateFcn(hObject, eventdata, handles)
% hObject    handle to slider1 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: slider controls usually have a light gray background.
if isequal(get(hObject,'BackgroundColor'), get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor',[.9 .9 .9]);
end


% --- Executes on slider movement.
function slider2_Callback(hObject, eventdata, handles)
% hObject    handle to slider2 (see GCBO)
```

```
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'Value') returns position of slider
%        get(hObject,'Min') and get(hObject,'Max') to determine range of slider
[handles] = predict(handles);

% --- Executes during object creation, after setting all properties.
function slider2_CreateFcn(hObject, eventdata, handles)
% hObject    handle to slider2 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: slider controls usually have a light gray background.
if isequal(get(hObject,'BackgroundColor'), get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor',[.9 .9 .9]);
end



% --- Executes on slider movement.
function slider3_Callback(hObject, eventdata, handles)
% hObject    handle to slider3 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'Value') returns position of slider
%        get(hObject,'Min') and get(hObject,'Max') to determine range of slider
[handles] = predict(handles);

% --- Executes during object creation, after setting all properties.
function slider3_CreateFcn(hObject, eventdata, handles)
% hObject    handle to slider3 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: slider controls usually have a light gray background.
if isequal(get(hObject,'BackgroundColor'), get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor',[.9 .9 .9]);
end



% --- Executes on slider movement.
function slider4_Callback(hObject, eventdata, handles)
% hObject    handle to slider4 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'Value') returns position of slider
%        get(hObject,'Min') and get(hObject,'Max') to determine range of slider
[handles] = predict(handles);

% --- Executes during object creation, after setting all properties.
function slider4_CreateFcn(hObject, eventdata, handles)
% hObject    handle to slider4 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: slider controls usually have a light gray background.
if isequal(get(hObject,'BackgroundColor'), get(0,'defaultUicontrolBackgroundColor'))
```

```
   set(hObject,'BackgroundColor',[.9 .9 .9]);
end



% --- Executes on button press in checkbox1.
function checkbox1_Callback(hObject, eventdata, handles)
% hObject    handle to checkbox1 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hint: get(hObject,'Value') returns toggle state of checkbox1
[handles] = predict(handles);



% --- Executes on slider movement.
function slider5_Callback(hObject, eventdata, handles)
% hObject    handle to slider5 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'Value') returns position of slider
%        get(hObject,'Min') and get(hObject,'Max') to determine range of slider
[handles] = predict(handles);

% --- Executes during object creation, after setting all properties.
function slider5_CreateFcn(hObject, eventdata, handles)
% hObject    handle to slider5 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: slider controls usually have a light gray background.
if isequal(get(hObject,'BackgroundColor'), get(0,'defaultUicontrolBackgroundColor'))
   set(hObject,'BackgroundColor',[.9 .9 .9]);
end



% --- Executes on slider movement.
function slider6_Callback(hObject, eventdata, handles)
% hObject    handle to slider6 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'Value') returns position of slider
%        get(hObject,'Min') and get(hObject,'Max') to determine range of slider
[handles] = predict(handles);

% --- Executes during object creation, after setting all properties.
function slider6_CreateFcn(hObject, eventdata, handles)
% hObject    handle to slider6 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: slider controls usually have a light gray background.
if isequal(get(hObject,'BackgroundColor'), get(0,'defaultUicontrolBackgroundColor'))
   set(hObject,'BackgroundColor',[.9 .9 .9]);
end
```

2.10 Compatitive Dyeing Studies for PET/Wool Fabrics

2.10.1 Dyeing Process for Competitive Dyeing of PET/Wool Fabrics

The dyeing liquor was prepared so as to give a 2% o.m.f. shade on 20g fabric samples (10g PET and 10g wool) at a liquor ratio of 30:1.

The dyeing liquor was prepared with the same method as that for polyester fibres with precursors as described in Section 2.5.1 and the dyeing was carried out with precursors using the same method as the PET fabrics without reduction clearing. After dyeing, the fabrics were washed with cold water and dried at room temperature.

2.10.2 Wash-off of the Wool Fabrics

The wool fabrics after dyeing were washed with non-ionic detergent at 50℃ for 20 minutes. After washing, the absorbance of the wash liquor was measured with a *Jasco V630* UV-Visible/NIR spectrophotometer. The colour of the wool fabrics before and after dyeing was measured using *Datacolor SF600 Spectraflash* colour spectrophotometer.

2.10.3 Mechanical Properties of the Wool Fabrics

2.10.3.1 Wet Bursting Strength Test

The wet burst strength test was carried out according to BS EN ISO 13938-2:1999 with *James Heal TruBurst* pneumatic bursting strength tester. The fabrics were soaked in distilled water for 1 hour and placed on blotting paper to remove excess water before testing. The test was carried out at 23℃ with a relative humidity of 55%. The test area was 50cm^2 (φ79.8 mm).

2.10.3.2 Abrasion Resistance

The abrasion resistance test was carried out according to BS EN ISO 12947-2:1998 with *James Heal Martindale* abrasion and pilling tester. The samples were conditioned in standard atmosphere overnight before the test. After 10,000 rubs, the mass loss of the fabrics was measured according to BS EN ISO12947-3:1998.

2.11 Tearing Strength Test

The tearing strength test was carried out according to BS EN ISO13937-1:2000 with *James Heal ElmaTear Tester.* The samples were conditioned in standard atmosphere overnight before the test.

2.12 Bending Property Test

Bending property of the fabrics were measured with FAST-2 Bending Meter. The bending length (c) of a 50mm wide strip of fabric was measured. The samples were conditioned in standard atmosphere overnight before the test. The bending rigidity (B) was calculated as below:

$$\mathrm{B} = \mathrm{W} \times c^3 \times 9.81 \times 10^{-6}$$

Where W is the mass per unit area in g/m^2

2.13 Fabric Thickness Test

Fabric thickness test was carried out with FAST-1 Compression Meter. The thicknesses of the fabric were measured at 2 gf/cm^2 and 100 gf/cm^2. Surface thickness was used to comparatively study the changes in the handle of the fabric. The surface thickness (ST) was calculated as below:

$$ST = T2 - T100$$

Where T2 is the thickness at 2 gf/cm^2,

T100 is the thickness at 100 gf/cm^2

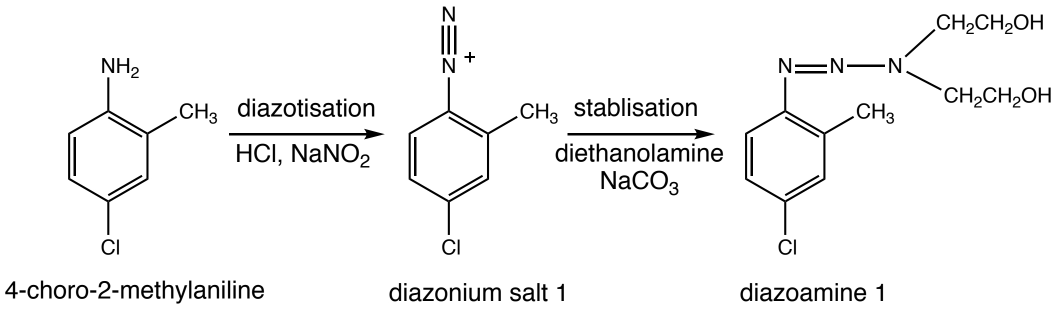
Chapter 3

Synthesis and Characterisation of Diazoamines and Pre-formed Dyes

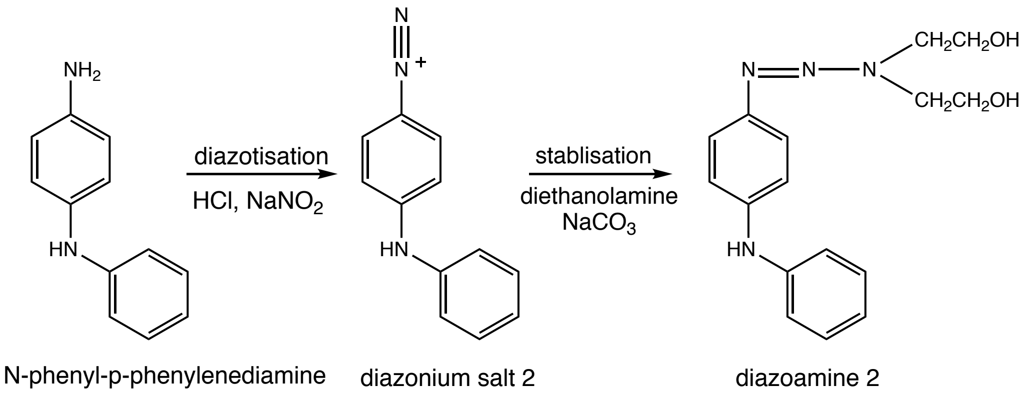
As azoic dyes are mainly used for the dyeing of cellulosic fibres, the azoic components on the market are mostly for cellulosic fibres and not suitable for polyester fibres. Therefore, the azoic components used for the *in-situ* dyeing of polyester fibres and the corresponding pre-formed dyes were synthesised.

3.1 Synthesis of the Diazoamines and Pre-formed Dyes

The diazoamines used for the *in-situ* dyeing of polyester fibres and corresponding pre-formed dyes were synthesised with the method described in Section 2.2. 4-chloro-2-methylaniline and N-phenyl-p-phenylenediamine were used for the synthesis of the diazonium salts through diazotisation reaction and stabilised by reacting with diethonolamine into diazoamine derivatives, as shown in Scheme 3.1 and Scheme 3.2. The coupling components used for *in-situ* dyeing are 2-naphthol and Naphthol AS (Figure 3.1). The corresponding pre-formed dyes were synthesised with coupling reaction of the diazonium salts and the coupling components. The structures of the synthesised dyes were shown in Table 3.1.



Scheme 3.1 Synthesis of Diazoamine from 4-chloro-2-methylaniline



Scheme 3.2 Synthesis of Diazoamine from N-phenyl-p-phenylenediamine

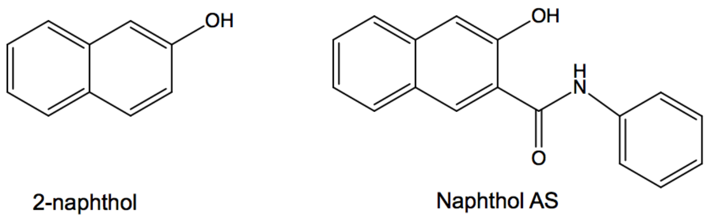
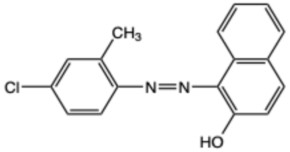
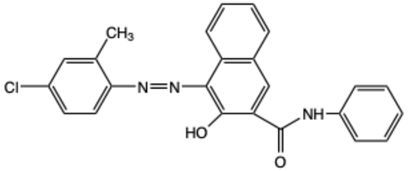
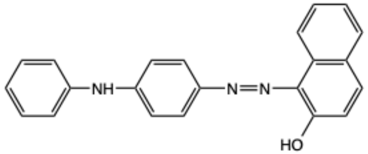
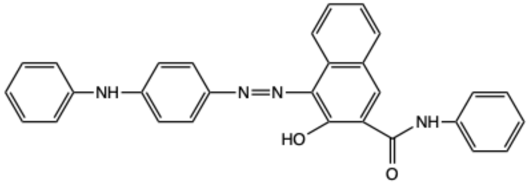


Figure 3.1 Structure of the Coupling Components

3.2 Characterisation of the Pre-formed Dyes

The properties of the synthesised pre-formed dyes are summarised in Table 3.1. The absorbance of the dyes was measured in acetone solution. The blue dye gives the highest λ_{max}. This may be attributed to the bathochromic effect caused by the hydrogen bonding between the amine group and the carbonyl group (Christie, 2015). With the similar structure, the red dye has lower $\lambda_{max.}$ This may be due to the presence of the methyl group, which clashes sterically with the lone pair of electrons on one of the azo nitrogen atoms and thus forced to rotate out of a planar conformation. The less planar structure of the red dye leads to a hypochromic shift compared with the blue dye (Christie, 2015). This is also the case for the orange dye, which gives the lowest λ_{max}.

Table 3.1 Structure and Physicochemical Properties of the Pre-formed Dyes

Colour	Azoic Combination	Dye Structure	M_w	λ_{max} (nm) in acetone	ε at λ_{max} ($M^{-1}cm^{-1}$)	Exhaustion at 2% o.m.f. (%)
Orange	Diazoamine 1 2-naphthol		298	482	42 950	98
Red	Diazoamine 1 Naphthol AS		417	502	8 420	96
Dull Red	Diazoamine 2 2-naphthol		340	490	23 490	96
Blue	Diazoamine 2 Naphthol AS		459	529	6 260	94

The exhaustion of the pre-formed dyes on PET fabrics was carried out according to the method described in Section 2.4. The results are shown in Figure 3.2. The orange dye has the highest exhaustion (98%). The red and dull red dyes give lower exhaustion of 96%. The blue dye shows the lowest exhaustion, which is only 94%. The exhaustion rates of most of the dyes are relatively high. The exhaustion is already close to equilibrium after 10 minutes. Only the dull red dye has a lower exhaustion rate, which reaches the equilibrium after 50 minutes.

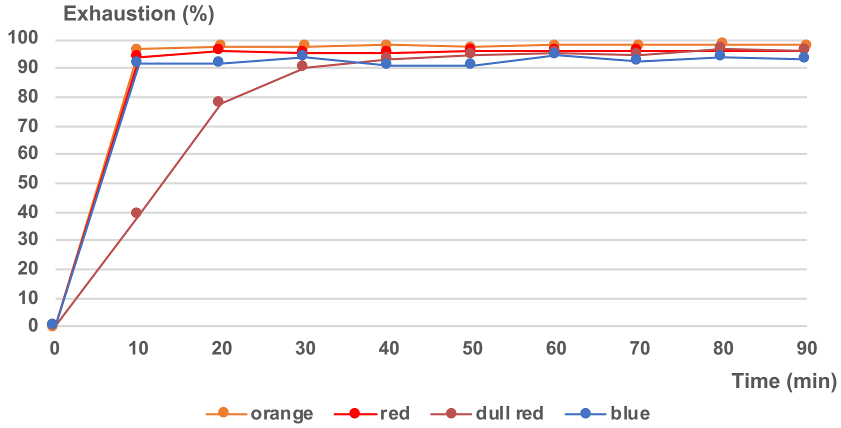


Figure 3.2 Exhaustion of the Pre-formed Dyes on PET Fabrics at 130℃ (2% o.m.f.)

HPLC-MS analysis was carried out as described in Section 2.3.1 with the synthesised pre-formed dyes in order to verify the structure of the components and work as a reference for later analysis of the dyeing. Only the results related to the synthesised dyes are presented here. The entire result is shown in Appendix A.

In Figure 3.3, the peak for the orange dye (No.7) occurs at 0.9 min with the molecular weight of 297.13. In Figure 3.4, the peak for the red dye (No.7) occurs at 1.0 min with the molecular weight of 414.27. In Figure 3.5, the dull red dye gives a peak (No.8) at 0.9 min with the molecular weight of 340.29. In Figure 3.6, the blue dye gives a peak (No.10) at 0.9 min with the molecular weight of 459.34. Although other peaks were observed, these peaks were detected with the same molecular weight for all the dyes. Moreover, the result of the blank test (Appendix A.5) also detects peaks. This indicates that these peaks may be the interference from the equipment. It is reasonable to presume that the synthesised dyes are the expected structures.

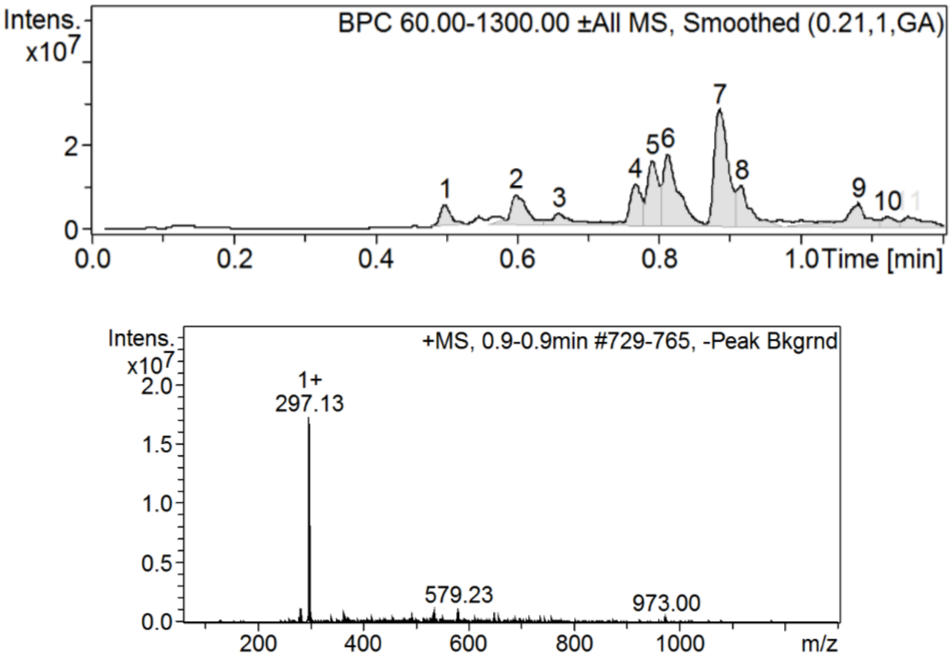


Figure 3.3 HPLC-MS of the Pre-formed Orange Dye

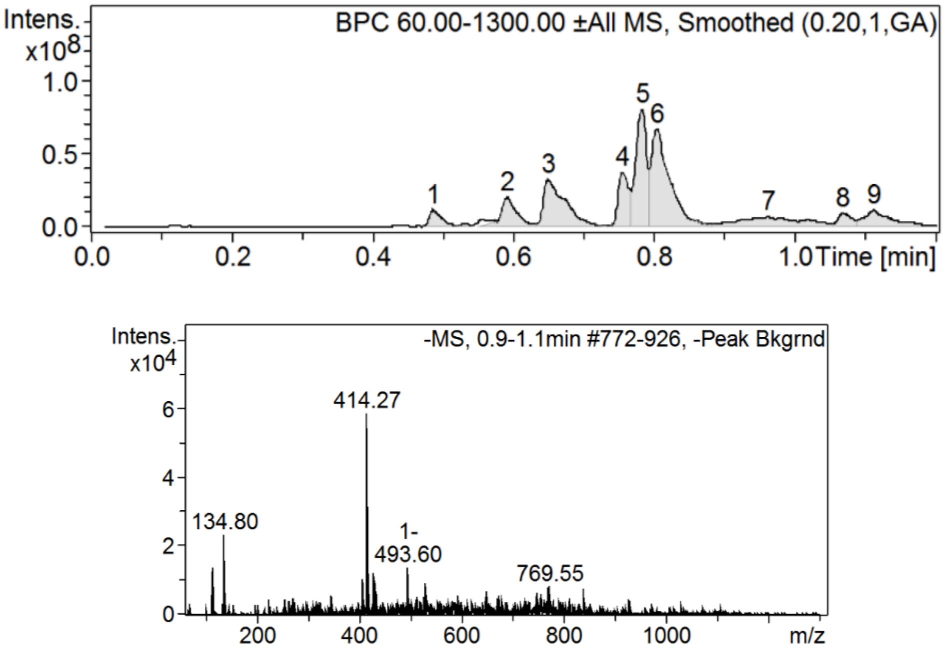


Figure 3.4 HPLC-MS of the Pre-formed Red Dye

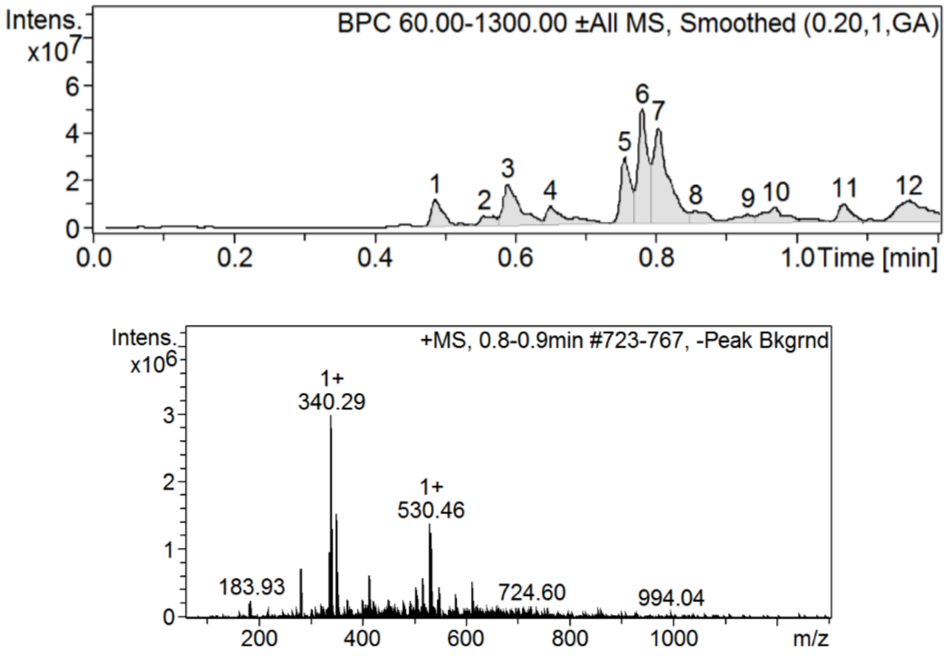


Figure 3.5 HPLC-MS of the Pre-formed Dull Red Dye

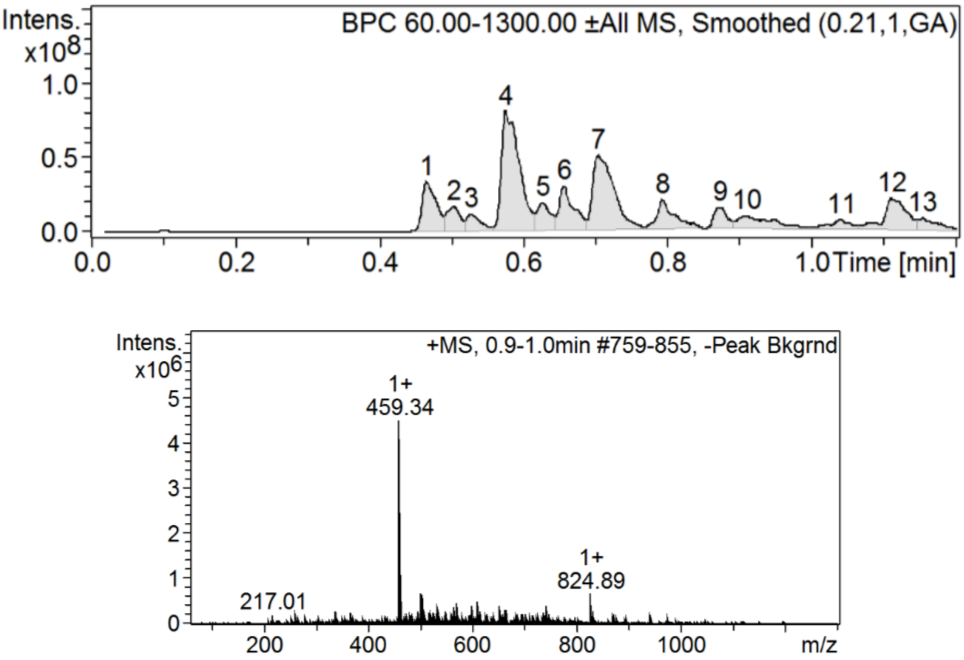


Figure 3.6 HPLC-MS of the Pre-formed Blue Dye

3.3 FT-IR Analysis of the Synthesised Components

The structures of the synthesised components were confirmed with FT-IR analysis. In order to facilitate analysis, the spectra of the raw materials used for the synthesis are also included.

Figure 3.7 shows the FT-IR spectrum of 4-chloro-2-methylaniline, which is used to synthesise diazoamine 1. For the aromatic ring, the strong bands due to the C-H in plane bending vibrations are observed at 1147,1086,1032 and 995 cm^{-1}. The C-H in plane bending of aromatic ring is combined with C-N stretching vibration, which is observed at 1086 cm^{-1}. This confirms the substitution of NH_2 in the aromatic ring. The peaks at 1575, 1492 and 1445 cm^{-1} are due to quadrant and semi-circle stretching of C=C bonds. For the methyl group, the strong asymmetric stretching bands of the CH_3 group are observed around 2912. The intense vibrations at 882 and 806 cm^{-1} are assigned to CH_3 rocking modes. The N-H stretching occurs at 3454 and 3371 cm^{-1}. The N-H in plane bending is observed at 1620 cm^{-1} and the out of plane bending is assigned at 1311 and 1271 cm^{-1}. The C-Cl stretching vibrations are observed at 648 and 620 cm^{-1} (Arjunan and Mohan, 2008; Ramalingam *et al.*, 2010).

Figure 3.8 shows the spectrum of diazoamine 1. Compared with the spectrum of 4-chloro-2-methylaniline, the peaks at 3454, 3371 and 1620 cm^{-1}, which are due to the NH_2 group do not exist in the spectrum of diazoamine 1. The peaks at 1395 cm^{-1} is observed for N=N vibration (Zimmermann *et al.*, 1993). This indicates that the NH_2 group in 4-chloro-2-methylaniline is reacted into N=N in diazoamine. Other peaks due to the aromatic ring and the substitute groups are also observed in the spectrum of diazoamine 1 with minor shift. The increased peaks in the region 600-1100 cm^{-1} are assigned to the $-CH_2$ groups. The O-H stretching occurs at 3280 cm^{-1}. The C-O bending occurs at 1339 cm^{-1} (Kurtaran *et al.*, 2008). These peaks confirm the structures change due to the stabilisation reaction with diethanolamine.

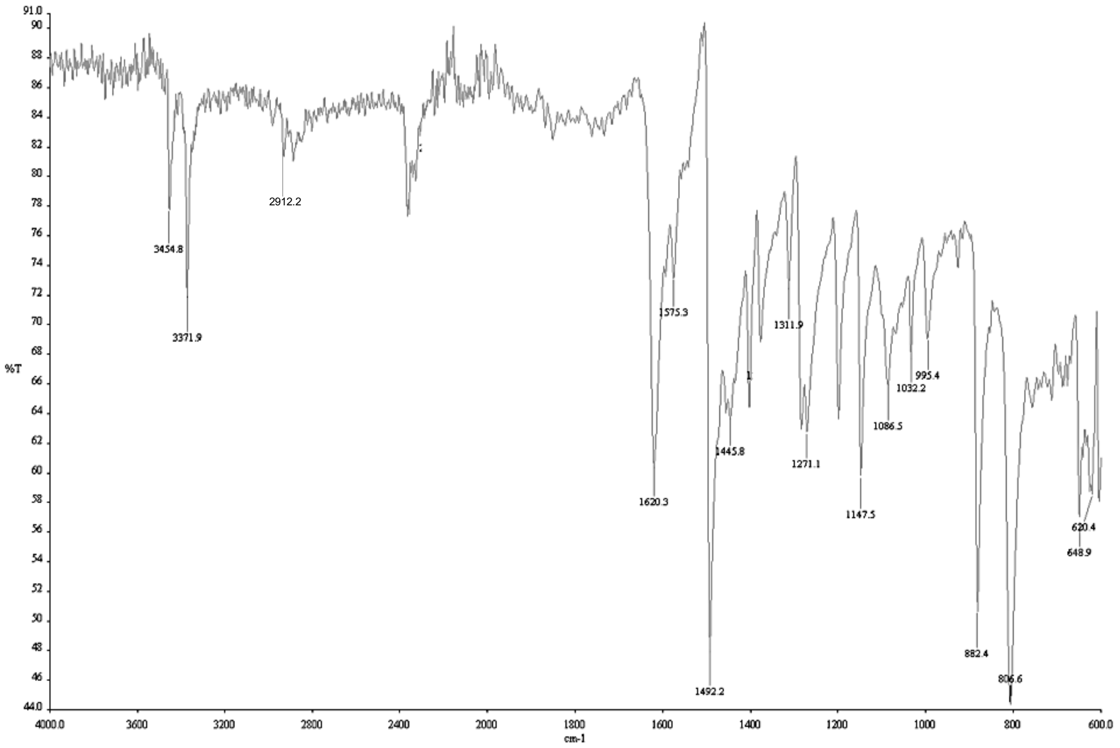


Figure 3.7 FT-IR Spectrum of 4-chloro-2-methylaniline

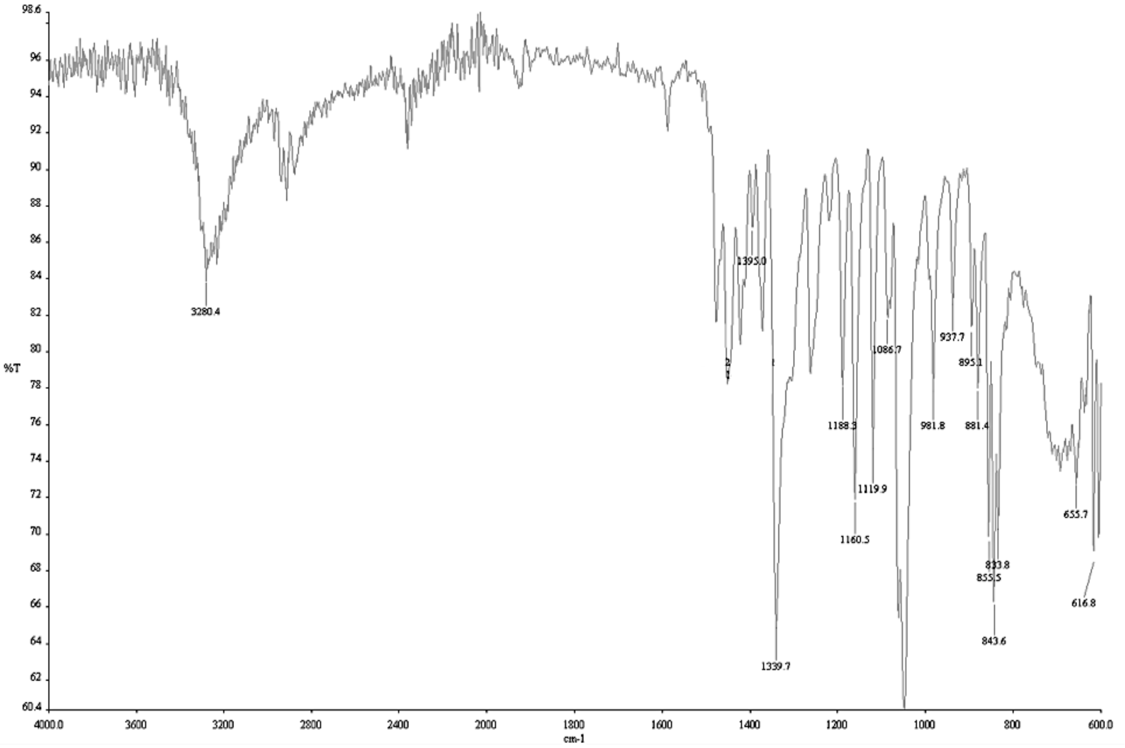


Figure 3.8 FT-IR Spectrum of Diazoamine 1

Comparing the spectrum of the orange dye (Figure 3.11) and diazoamine 1 (Figure 3.8), the peak due to the -OH group in diazoamine 1 becomes weaker in the orange dye. This is caused by the reduction of -OH group after the coupling reaction. The peak for C-O bending in diazoamine 1 also disappears in the spectrum of orange dye. The peak at 1280 cm^{-1} due to C-O stretching occurs in the spectrum of the orange dye, which is introduced by the coupling reaction with 2-naphthol (Figure 3.9) (Pei *et al.*, 2013).

For the red dye (Figure 3.12), the peak for -OH group also becomes weaker and the peak for C-O bending disappears compared to that in diazoamine 1. The peak around 1600 cm^{-1} for C=O stretching and the peak at 1540 cm^{-1} for N-H bending in the red dye are introduced by the coupling reaction with Naphthol AS (Figure 3.10) (Crasmareanu *et al.*, 2013).

According to Figure 3.13 and Figure 3.14, the peaks at 3393, 3327 and 3291 cm^{-1} due to the -NH$_2$ group in N-phenyl-p-phenylenediamine (Cibulková *et al.*, 2005) disappear in diazoamine 2, while the peak at 1490 cm^{-1} is observed for N=N vibration in diazoamine 2 (Zimmermann *et al.*, 1993). These changes are due to the diazotisation reaction. The peak at 3350 cm^{-1} due to -OH group and the peak at 1301 cm^{-1} due to C-O bending are introduced into diazoamine 2 by the stabilisation reaction (Kurtaran *et al.*, 2008).

For the dull red and blue dyes (Figure 3.15 and Figure 3.16), similar changes are observed as the orange and red dye. The peak due to the -OH group becomes weaker for both dyes compared to diazoamine 2. The peak at 1301 cm^{-1} for C-O bending in diazoamine 2 disappears in the spectra of the dyes. The peak at 1316 cm^{-1} for C-O stretching is observed in dull red dye introduced by the reaction with 2-naphthol (Pei *et al.*, 2013). For the blue dye, the peak at 1313 cm^{-1} for C-O stretching and the peak around 1600 for C=O stretching are observed in blue dye as the result of the reaction with Naphthol AS (Crasmareanu *et al.*, 2013).

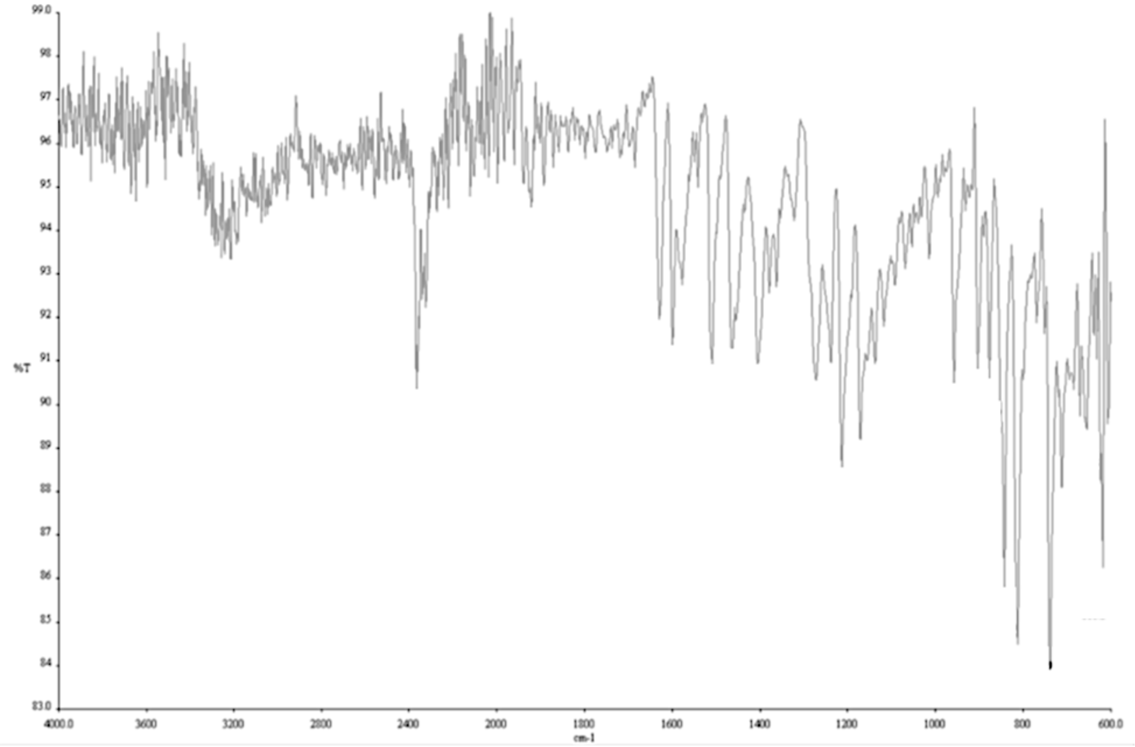


Figure 3.9 FT-IR Spectrum of 2-naphthol

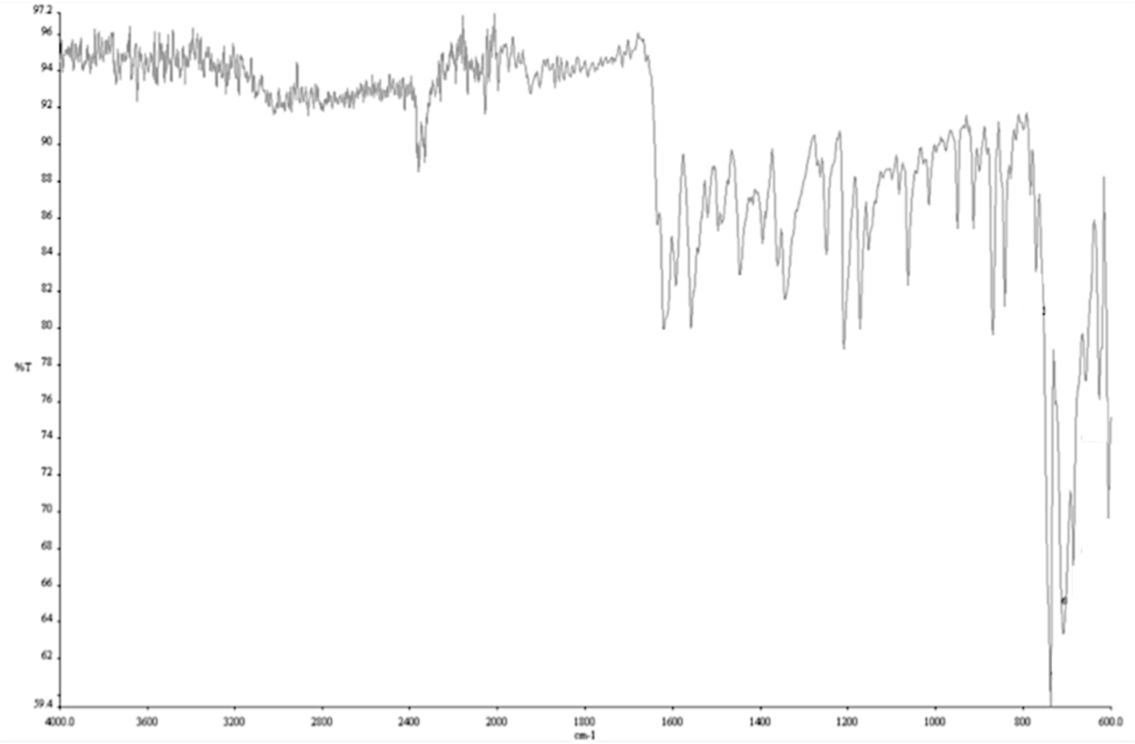


Figure 3.10 FT-IR Spectrum of Naphthol AS

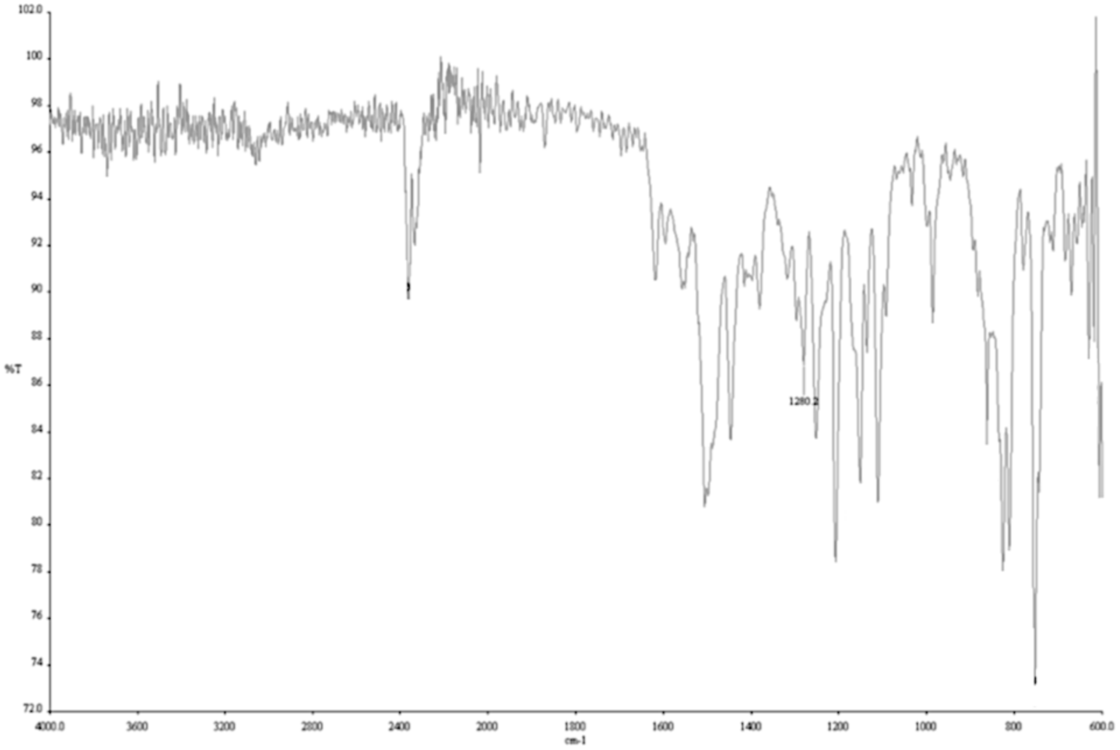


Figure 3.11 FT-IR Spectrum of Orange Dye

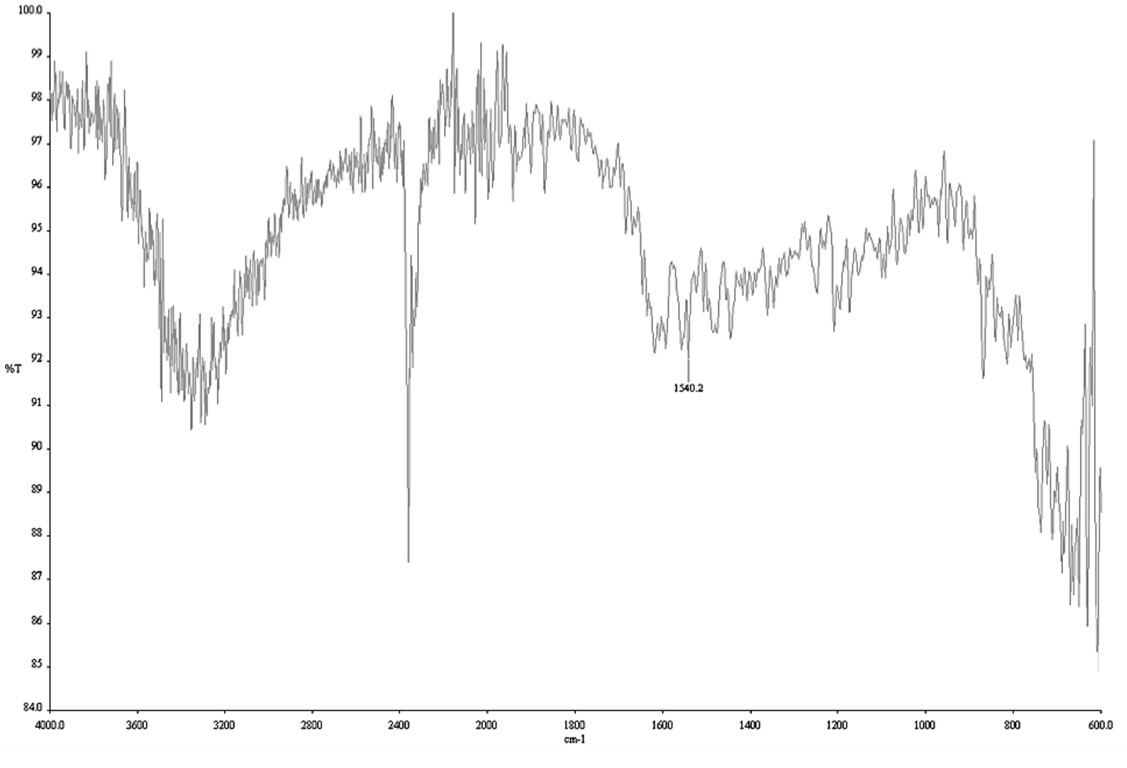


Figure 3.12 FT-IR Spectrum of Red Dye

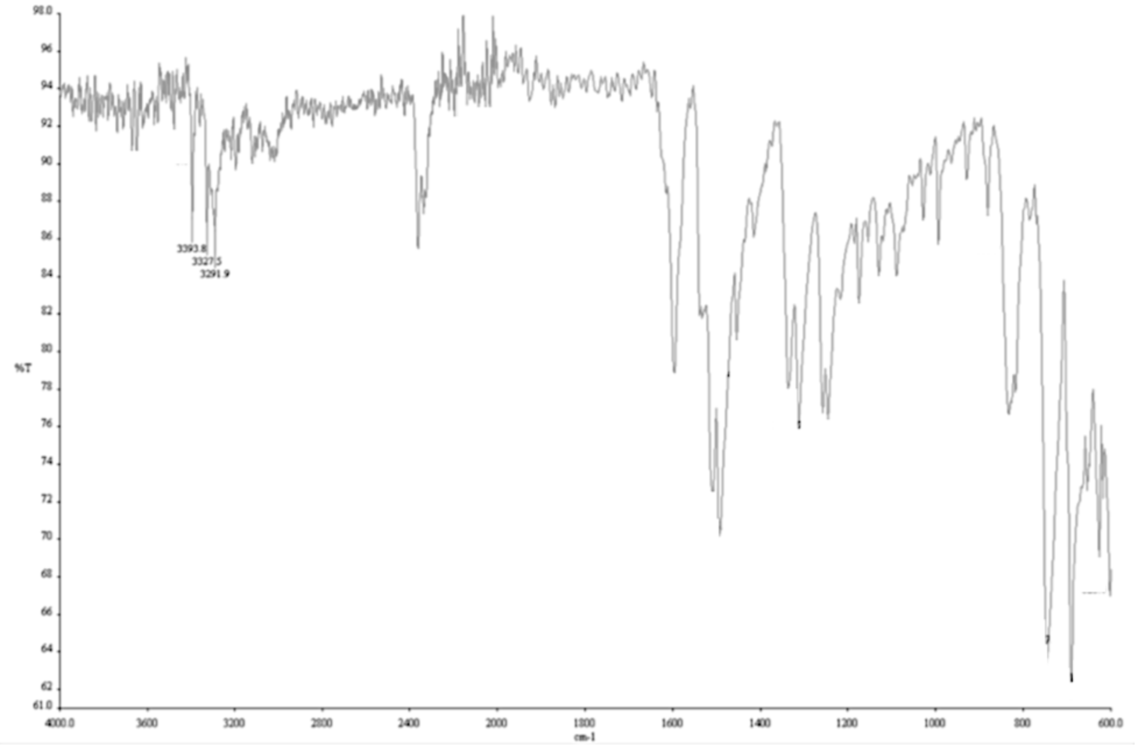


Figure 3.13 FT-IR Spectrum of N-phenyl-p-phenylenediamine

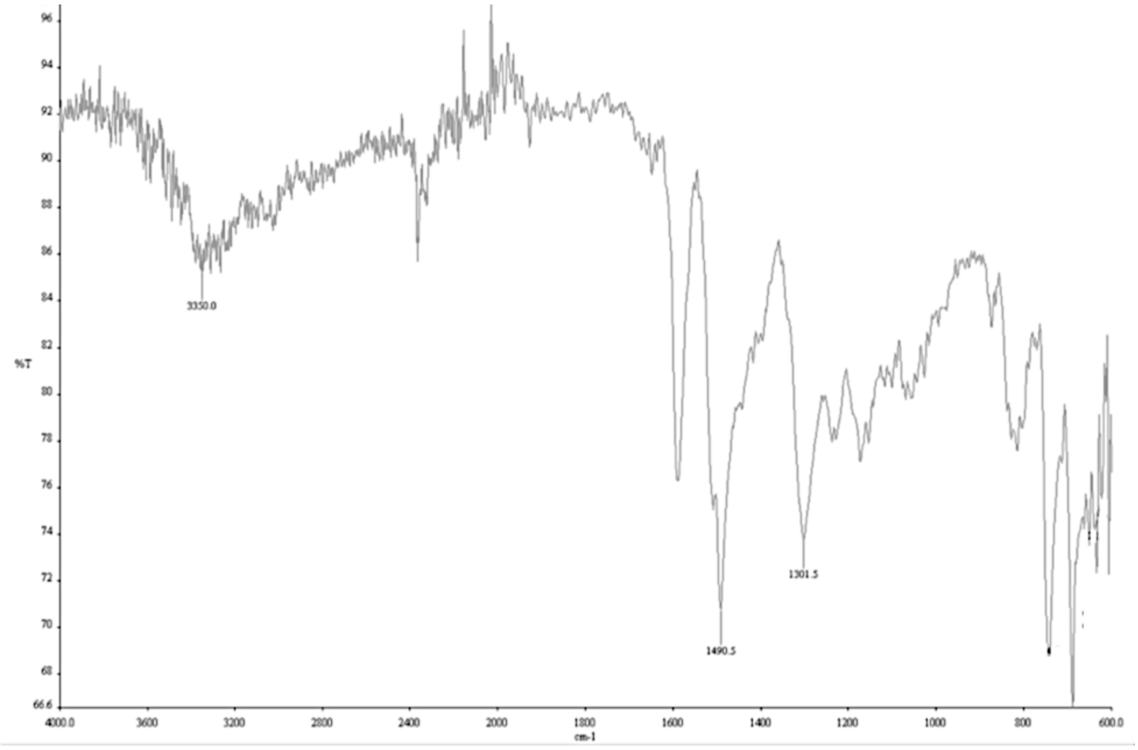


Figure 3.14 FT-IR Spectrum of Diazoamine 2

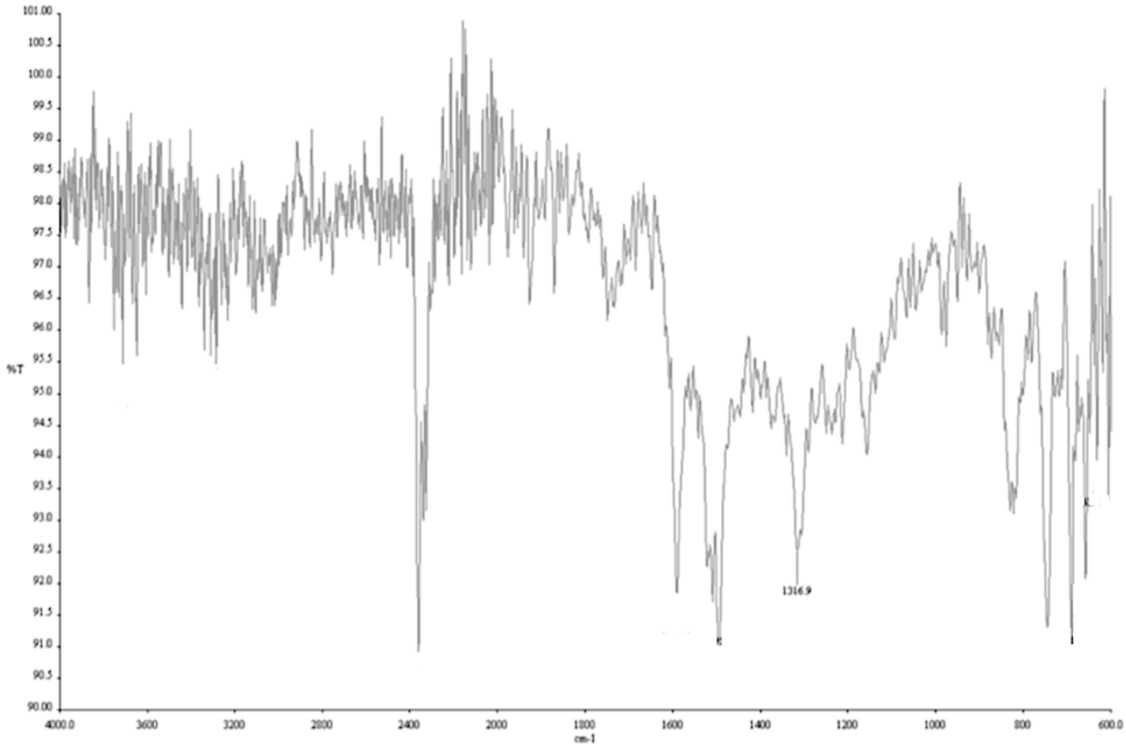


Figure 3.15 FT-IR Spectrum of Dull Red Dye

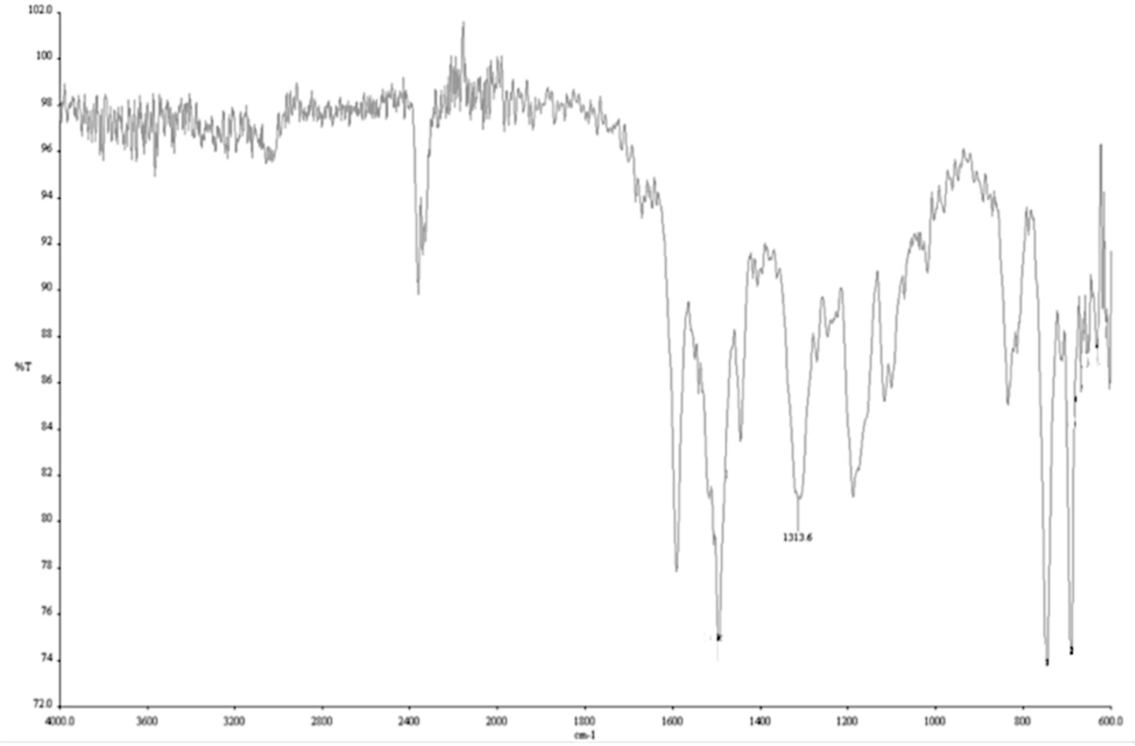


Figure 3.16 FT-IR Spectrum of Blue Dye

Chapter 4

Aqueous Dyeing of PET Fabrics

PET fabrics were dyed with both pre-formed dyes and *in-situ* dye formation with the method described in Section 2.5.2. The *in-situ* dyeing was carried out at 100℃. The dyeing with pre-formed dyes was carried out at 130℃, which is the conventional temperature for PET dyeing, and 100℃ in order to facilitate a direct comparison with the *in-situ* dyeing. As the precursors are smaller than the dyes, it is presumed that the precursors can penetrate inside the PET fabrics at 100℃ while the dyes cannot.

4.1 Dyeing with Individual Dye

The four synthesised pre-formed dyes and the corresponding azoic combinations were used for the dyeing of PET fabrics. The colour yield and the fastness properties were measured to compare the dyeing behaviour of the pre-formed dyes and *in-situ* formed dyes on PET fabrics.

4.1.1 Shade Build-up of Pre-formed Dyes and *In-situ* Dyeing

The fabrics were dyed at different concentrations with both pre-formed dyes and precursors. The colour of the dyed fabrics was measured with spectrophotometer and the K/S values at λ_{max} (Figure 4.1) calculated from the reflectance of the dyed fabrics were used to present the colour yield of the dyed fabrics. The average of three replicates was used for the analysis.

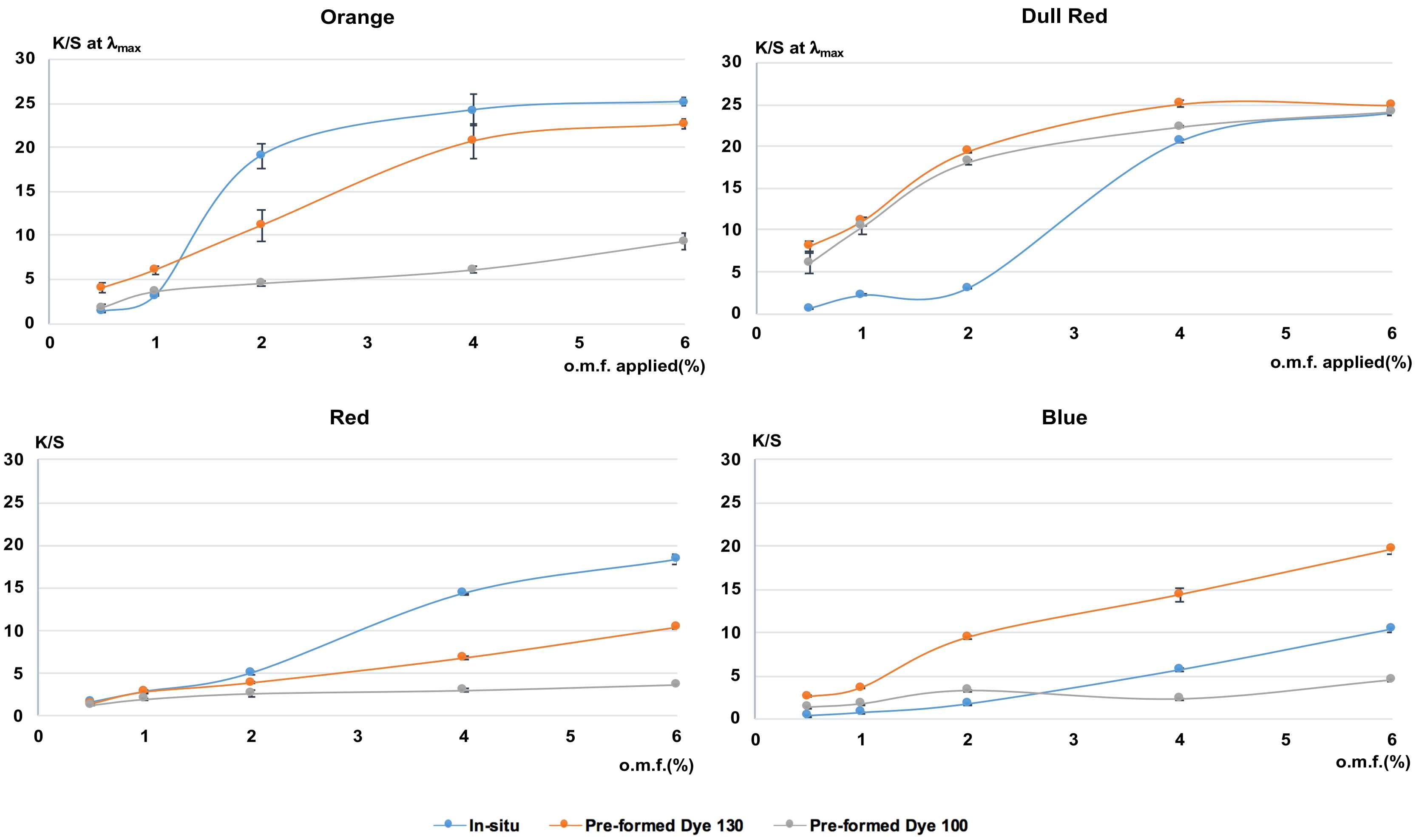


Figure 4.1 Build-up of Pre-formed Dyeing and *In-situ* Dyeing on PET Fabrics

The orange and red dyes show similar trend. At low concentration (below 2% o.m.f.), the colour yield of the dyes with the three dyeing methods are quite close. As the concentration increased, the colour yield of the *in-situ* dyeing becomes higher than that of the pre-formed dyes at 130℃. And the colour yield of the pre-formed dye at 100℃ is much lower than the other two.

The low colour yield obtained when dyeing PET with the pre-formed dyes at 100℃ is expected since while above the polymer T_g, segmental mobility is expected to remain too low for molecules of this size to diffuse significantly in the duration of the dyeing procedure (Giles *et al.*, 1982). The colour yield of the dyeing achieved with the pre-formed dyes at 130℃ may be regarded as a likely optimal colour yield as the dyeing profile adheres to the generally optimised dyeing profile for disperse dyes on PET (Burkinshaw, 1995).

It is to be noted that the synthesised dyes conform to the properties of typical disperse dyes. The majority of azo disperse dyes have relatively low molecular weights, which are normally below 600, and contain no ionic solubilising groups (Aspland, 1993; Koh, 2011). The molecular weights of the pre-formed dyes are in the range of 290-460. The chemical structure also fits the typical structure of disperse dyes. Therefore, it is reasonable to take the dyeing of these pre-formed dyes as a reference point for the conventional disperse dyeing.

The good colour yield obtained with the dyes formed *in-situ* indicates that both the synthesised diazoamine and the coupling components can adsorb and migrate within the polymeric structure at 100℃. The intended coupling reaction occurs within the fibre instead of in the liquor as the dye cannot penetrate inside the fibres at 100℃. It can also be presumed that the diffusion of dyes out of the fibre is impaired. It is found that the diffusion of the dyes from liquor to fibre is low at 100℃, thus the reverse direction is very likely to be subject to similar diffusion effects. The analysis of the spent liquor of the *in-situ* dyeing further corroborates these findings. The absorbance of the dyeing liquor after dyeing, as shown in Figure 4.2, is relatively low. A small amount of orange dyes is observed in the dyeing liquor at the end of the dyeing cycle. This indicates either that some dyes form outside of the fibre, or that dyes formed in the fibre desorbs during the dyeing process. Dyeing at 100℃ of pre-formed dyes indicates that little dyes can penetrate the fibre at this temperature. Hence it is unlikely that dyes formed in the fibre would desorb. It is presumed that the pH of the dyeing liquor and the relative reactivities of diazoamine and coupling component lead to some dyes formed in the liquor. As they cannot penetrate inside the fibres at 100℃, they are left in the dyeing liquor. For the red dye, no absorbance is shown, which implies there is no dye in the liquor. The fact that the colour yield achieved with the dye formed *in-situ* is higher than the colour yield achieved with pre-formed dyes at 130℃ illustrates that the dyeing with *in-situ* dyeing synthesis at 100℃ does not follow the usual dyeing equilibrium.

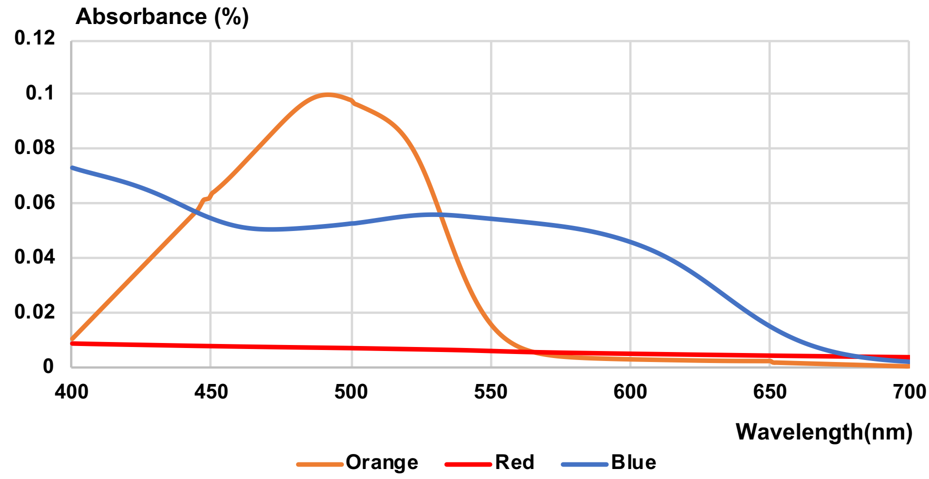


Figure 4.2 Absorbance of the Residue Dyeing Liquor with *In-situ* Dyeing after Dyeing

In addition, it is noted that the colour yield achieved for the red dye (diazoamine 1+Naphthol AS) formed *in-situ* is higher than that for the pre-formed dye applied at 130℃, while the difference is smaller for the orange dye (diazoamine 1+2-naphthol). This could be caused by a number of reasons. Firstly, as seen in Figure 4.2, more orange dyes were formed in the liquor than the red dye, leading to more red dyes formed in the fibre. However, the amount of the orange dyes formed in the liquor is very small, which suggests that it is not a huge contribution to this phenomenon. Another reason may be that the rate of reaction between diazoamine 1 and Naphthol AS is higher than that between diazoamine 1 and 2-naphthol, thus a larger amount of red dyes is formed than the orange dye. While Naphthol AS is a bulkier molecule than 2-naphthol, it also possesses an amide link which is capable of forming hydrogen bonding. Furthermore, this group can be considered as deactivating the naphthol ring through withdrawing π electron density through resonance towards the carbonyl oxygen. Therefore, it is unlikely that an increased rate of reaction between Naphthol AS and the diazoamine is responsible for the increased colour yield. The most possible reason is that Naphthol AS exhaust better than 2-naphthol on PET, leading to an increased concentration of dye in the fibre for the red dye than the orange dye. The high exhaustion of Naphthol AS would also explain why there is no red dye formed in the dyeing liquor.

With regards to the dull red dye (diazoamine 2+2-naphthol), the colour yield obtained with the pre-formed dye at both 100℃ and 130℃ are similar throughout. This may be due to either the diffusion of the dye in the fibre is sufficient at 100℃ or the substantivity of the dye for the fibre is low so that the equilibrium between dye in fibre and dye in solution is in favour of dye in solution at 130℃. However, considering the high K/S values achieved, the latter is not likely. As the dull red dye (M_w = 340) is heavier and bulkier than the orange dye (M_w = 298) (diazoamine 1 and 2-naphthol) due to the additional aromatic ring, it is expected that the orange dye should diffuse more readily than the dull red dye. However, it is observed that the orange dye does not give good colour yield at 100℃ while the dull red dye does. It may be that the aryl substituent which is expected to be in the plane of the dye molecule (resonance stabilisation) does diffuse through the polymer segments more readily than the orange dye, for which the *o*-methyl group clashes sterically with the lone pair of electrons on one of the azo nitrogen atoms and is thus forced to rotate out of a planar conformation (Christie, 2015). The increase of the aromatic interaction with the extra aromatic ring, although negligible compared to hydrogen bonding, may also play a part to improve the affinity between the dull red dye and the fibre (Lewis, 1998).

As for the *in-situ* dyeing for the dull red dye, at high concentration, all colour yields are within expected experimental variations of one another, possibly supporting the fact that the dye once formed may diffuse in and out of the fibre and hence colour yield in all cases (pre-formed dye at 100℃, 130℃ and *in-situ* dye formation) are equivalent. At low levels of application (2% o.m.f. and lower), however, the colour yield of the *in-situ* dyeing is substantially lower than that of the pre-formed dye. This is possibly due to the low concentration leading to a low reaction rate between the diazoamine 2 and 2-naphthol, thus not as many dyes were formed within the duration of the dyeing procedure.

In the case of the blue dye (diazoamine 2+Naphthol AS), as expected, the colour yield obtained with the pre-formed dye at 130℃ is higher than that at 100℃, which again supports the fact that the dyes are too bulky to penetrate the polymer structure at 100℃ since segmental mobility is limited. At 130℃, the dye shows good exhaustion and thus diffuses in the fibre appropriately. The colour yield achieved with *in-situ* dyeing remains lower than that achieved with the pre-formed dye at 130℃. This could be caused by either the low exhaustion of the components in PET or the low rate of reaction between these two components. Since the red dye, which is formed with Naphthol AS, and the dull red dye, which is formed with diazoamine 2, both show good colour yield of the *in-situ* dyeing. It can be presumed that these two components have appropriate levels of adsorption and migration within the polymeric structure at 100℃. Therefore, the low exhaustion is not likely to be the reason for the low colour yield of the blue dye with *in-situ* formation. It must thus be presumed that the low rate of reaction between diazoamine 2 and Naphthol AS is the problem. Indeed, it is already stated that the arylamide substituent of Naphthol AS will deactivate the naphthol ring towards nucleophilic substitution. Concurrently, the aryl amine substituent in diazoamine 2 will increase the electron density in the diazoamine functionality through resonance, which also deactivates it towards nucleophilic attach. This effect is not observed in the *in-situ* dyeing with dull red dye because 2-

naphthol is sufficiently nucleophilic. According to the absorbance of the dyeing liquor after dyeing (Figure 4.2), the small amount of dyes formed both in the dyeing liquor and in the fabrics further proves that the low reaction rate is the reason for the low colour yield.

4.1.2 Fastness Properties

Fastness testing, including rubbing, washing, light and dry heat fastness, was carried out with the fabrics after reduction clearing with the method described in Section 2.8. The data of 2% and 6% o.m.f. was used for analysis because the colour yield generally has a significant increase above 2% and the maximum colour yield occurs at 6%. Three replicates were carried out for each test.

4.1.2.1 Rubbing Fastness

Wet and dry rubbing fastness properties of the dyed fabrics in both warp and weft directions were measured. The average of the two directions were used for the analysis. The rubbing fastness results of the dyed fabrics are shown in Table 4.1 (2% o.m.f.) and Table 4.2 (6% o.m.f.).

Table 4.1 Rubbing Fastness of the PET Fabrics Dyed at 2% o.m.f.

Colour	Pre-formed Dye 130℃		Pre-formed Dye 100℃		*In-situ* Dyeing	
	Dry	Wet	Dry	Wet	Dry	Wet
Orange	4/5	5	4	5	3/4	3/4
Red	4/5	4/5	4	4	3/4	3/4
Dull Red	4	4/5	3/4	4/5	4/5	4/5
Blue	4	4/5	2/3	2/3	4/5	4/5

For the orange and red dye, the dyeing with the pre-formed dyes at 100℃ and

130℃ both show good rubbing fastness, with the dyeing at 100℃ slightly lower than the dyeing at 130℃. This is expected as the dyes cannot penetrate inside the fibre at 100℃ and stay at sub-surface, leading to a lower fastness. For most fibres, wet rubbing fastness is generally lower than dry rubbing fastness because wet rubbing fastness does not just include the dyes that was rubbed off but also the dyes dissolved in water (Suganuma, 2013). Moreover, the standard cotton cloth used for rubbing fastness swell under wet condition and the fibre array is disordered, which causes higher friction and thus lower wet rubbing fastness (Suganuma, 2015). However, for the pre-formed dyes and *in-situ* dyeing here, the wet fastness is equal to or higher than the dry fastness. The T_g of PET is not affected by water, hence the dyes remain trapped in the fibres. Also, the solubility of the dyes is very low at room temperature, which means no dissolving is expected. The rubbing fastness of the *in-situ* dyeing is lower than the dyeing with pre-formed dyes. This may be because some dyes were formed in the dyeing liquor and were loosely deposited on the fibre surface. Although reduction clearing can help to remove the dye particles on the surface, the *in-situ* dyeing still shows lower rubbing fastness than the dyeing with pre-formed dyes. Furthermore, the colour yield of the orange and red dye achieved with *in-situ* dyeing is higher than that with pre-formed dyes, which may be responsible for the lower rubbing fastness.

In the case of the dull red and blue dyes, the dyeing with pre-formed dyes at 100℃ also shows lower rubbing fastness than the dyeing at 130℃. Unlike the orange and red dye, the *in-situ* dyeing of the dull red and blue dyes shows better rubbing fastness than the pre-formed dyes. One reason is the lower colour yield of the *in-situ* dyeing with blue and dull red dye compared with the dyeing with pre-formed dyes at 130℃. The structures of the dyes may also play a part to improve the rubbing fastness. It is known that the influence of the chemical structure on rubbing fastness is complicated (Giles *et al*., 1982). Based on the results, the rubbing fastness of the *in-situ* dyeing is not simply related to the molecular size, since the dull red has a smaller molecular weight than the red dye but shows better rubbing fastness. The *in-situ* dyeing of the dull red and blue dyes, which are formed with diazoamine 2 exhibit better rubbing fastness than the orange and red dyes formed with diazoamine 1.

Meanwhile, the dyes formed with the same diazoamine and different coupling component do not show significant difference on rubbing fastness. Therefore, it is presumed that the structure of diazoamine has more effect on rubbing fastness than the coupling component. Rubbing fastness is related to the substantivity of the dyes to a certain extent, which increases with the length of the conjugated chain in the dye (Maradiya and Patel, 2001). The blue and dull red dye has a longer conjugated chain due to the extra aromatic ring in diazoamine 2, thus show better rubbing fastness. The increased aromatic interaction due to the extra aromatic ring in diazoamine 2 may also play a part to help improve the substantivity of the dye and thus the rubbing fastness.

Table 4.2 Rubbing fastness of the PET Fabrics Dyed at 6% o.m.f.

Colour	Pre-formed Dye 130℃		Pre-formed Dye 100℃		*In-situ* Dyeing	
	Dry	Wet	Dry	Wet	Dry	Wet
Orange	3/4	4/5	3/4	4/5	2	2/3
Red	4	4	3/4	4	3	3/4
Dull Red	3	4/5	2	4	3	3/4
Blue	3	3/4	2	2	3/4	3/4

A very similar trend is observed for the dyeing at 6% o.m.f. All the dyeing shows lower rubbing fastness than the dyeing at 2% o.m.f. This is within expectation as more staining would occur with higher concentration. The type of diazoamine still has the most significant influence on the rubbing fastness results. However, as the concentration increases, the molecular size also starts to show influence on the rubbing fastness. For the dyes formed with the same diazoamine, the dyes with larger molecular weight (blue and red) show higher rubbing fastness.

Overall, the *in-situ* dyeing shows moderate rubbing fastness and is lower than commercial disperse dyes, which normally gives moderate to good rubbing fastness (Broadbent, 2001). This may be due to the relatively small molecular size of these dyes, leading to fewer and weaker fibre-dye interaction. Also, the structure of the dyes may not be optimised for rubbing fastness. The number of conjugated bonds in these dyes is limited and the substantivity of the dyes for PET may not be good.

4.1.2.2 Washing fastness

The washing fastness tests were carried out with the fabrics dyed with pre-formed dyes and *in-situ* dyeing. The staining results of the multifibre adjacent fabrics and the shade change of the dyed fabrics were measured. Table 4.3 gives the washing fastness results from the dyeing at 2% o.m.f. and Table 4.4 gives the washing fastness results from the dyeing at 6% o.m.f.

Table 4.3 Washing fastness of the PET Fabrics Dyed at 2% o.m.f.

		Diacetate	Bleached Cotton	Polyamide	Polyester	Acrylic	Wool	Shade Change
Orange	PD* 130℃	4/5	5	4	4/5	5	5	4/5
	PD 100℃	3/4	4/5	3	4	4/5	4/5	4
	In-situ	2	3/4	2	2/3	4	2/3	4
Red	PD 130℃	4/5	5	4/5	4/5	5	4/5	4/5
	PD 100℃	4/5	5	3/4	4/5	5	4/5	4/5
	In-situ	4	4/5	3	4	4/5	4/5	4
Dull Red	PD 130℃	4/5	4/5	3/4	4/5	4/5	5	4/5
	PD 100℃	3	4/5	2	4	4/5	4/5	4
	In-situ	5	5	4/5	5	5	5	4/5
Blue	PD 130℃	4/5	5	4	4/5	4/5	5	4/5
	PD 100℃	4	4/5	2/3	4/5	4/5	4/5	4/5
	In-situ	4/5	5	4	4/5	4/5	4/5	4/5

*PD – Dyeing with Pre-formed Dyes

According to Table 4.3, all the dyeing achieved with the pre-formed dyes at 130℃ shows relatively good washing fastness. The fading (shade change) results are all rated as 4/5. The staining results are also relatively good, with most of the results above 4. The fabrics dyed with the pre-formed dyes at 100℃ show considerably lower staining results, while the shade change is only slightly lower than those dyed at 130℃. For the *in-situ* dyeing, both shade change and staining results of the orange and red dyes are slightly lower than that with the pre-formed dyes at 130℃. This small difference is probably due to the higher colour yield of the *in-situ* dyeing with orange and red dye. The *in-situ* dyeing with the dull red and blue dyes gives the same shade change results as the pre-formed dyes at 130℃. The *in-situ* dyeing of dull red dye shows better staining results than the dyeing with pre-formed dye at 130℃.

The washing fastness of disperse dyes generally increases with molecular weight (Giles *et al.*, 1982). However, these dyes do not conform to this rule. The dull red dye has a lower molecular weight than the red dye, but shows higher washing fastness. The structure of the diazoamine appears to have the most significant influence to the washing fastness, as was found for the rubbing fastness. The longer conjugated chain and the increased aromatic interaction due to the extra aromatic ring for the dyes formed with diazoamine 2 help to increase the substantivity of the dye on PET, and hence improve the washing fastness.

As seen in Table 4.4, the washing fastness results of the dyeing at 6% o.m.f. shows the same trend as the dyeing at 2%. The dyeing with the pre-formed dyes at 130℃ gives higher fastness results than the dyeing at 100℃. Most of the shade change results of the dyeing at 130℃ do not change with increasing concentration, while the staining results tends to be lower at 6% than at 2%. This is as expected as more dyes were washed off and caused more staining for the dyeing at high concentration without significant difference in shade change. For the *in-situ* dyeing, the washing fastness results are very similar at different concentrations.

Table 4.4 Washing fastness of the PET Fabrics Dyed at 6% o.m.f.

Colour		Diacetate	Bleached Cotton	Polyamide	Polyester	Acrylic	Wool	Shade Change
Orange	PD 130℃	3/4	4/5	3	4	4/5	4/5	4/5
	PD 100℃	3	4/5	2/3	3/4	4/5	4/5	4
	In-situ	2/3	4	2/3	3	4	3	4
Red	PD 130℃	4/5	5	4	4/5	5	5	4/5
	PD 100℃	4	4/5	3	4	4/5	4/5	4
	In-situ	4/5	5	3/4	4/5	4/5	4/5	4
Dull Red	PD 130℃	2/3	4/5	2	3/4	4/5	4/5	4
	PD 100℃	2/3	4	1/2	3	4	3/4	4
	In-situ	4/5	4/5	4	4/5	4/5	4/5	4/5
Blue	PD 130℃	4/5	4/5	3	4/5	4/5	4/5	4/5
	PD 100℃	4	4/5	2	4	4/5	4	4
	In-situ	4/5	4/5	4	4/5	4/5	4/5	4/5

Overall, the washing fastness of *in-situ* dyeing is relatively good and shows similar or slightly lower results compared to the commercial disperse dyes (Broadbent, 2001). The reason for the slightly lower washing fastness is probably the same as that described for the rubbing fastness, which is due to the small molecular size of these dyes and the structures not optimised for washing fastness.

4.1.2.3 Light Fastness

The dyed fabrics and the blue wool standard were exposed to light from a Xenon lamp for 24h. The shade change of the dyed fabrics is compared with the blue wool standard and rated accordingly. The light fastness results are shown in Table 4.5.

Table 4.5 Light Fastness of the Dyed PET Fabrics

Colour		PD 130℃	PD 100℃	*In-situ* Dyeing
Orange	2%	2	2	3
	6%	3	2	4
Red	2%	3	2	4
	6%	4	3	5
Dull Red	2%	2	2	2
	6%	3	3	3
Blue	2%	2	1	2
	6%	3	2	3

The light fastness of all the dyeing with pre-formed dyes is low. This is because all these dye molecules are relatively small and greater surface of the dyes are exposed to light and air, leading to low light fastness (Giles and Walsh, 1977). Only the red dye gives fair light fastness at 6% o.m.f. It is attributed to the methyl group, which favours to form compact aggregates of dye and improves the light fastness, and the intermolecular hydrogen bonds between the carbonyl group and the amine group, which generally help to increase the light fastness (Giles *et* al., 1982). The dyeing with the pre-formed dyes at 130℃ generally shows higher light fastness than the dyeing at 100℃. This is because the dyes can penetrate deeper inside the fibres at 130℃ while the dyes are mostly at the sub-surface of the fibres at 100℃, resulting in higher light fastness for the dyeing at 130℃. The light fastness improves with increasing concentration as a result of aggregation in the fibres (Giles and McKay, 1963).

For the *in-situ* dyeing, the orange and red dyes show much higher light fastness than the pre-formed dyes. This may be because the dye precursors have lower molecular weights and can penetrate deeper inside the fibres than the pre-formed dyes even at a lower temperature, hence give higher light fastness. However, the *in-situ* dyeing of the blue and dull red dyes give similar results as the pre-formed dyes. This is probably due to the presence of the electron-attracting *p*-Cl substituent in the diazoamine 1, which is used to form orange and red dyes. On polyester, the fading is mainly caused by the oxidation of the dyes (Cumming *et al*., 1956). In azoic dyeing, the presence of electron-attracting substituents in the diazo component of azo dyes can reduce the electron density at the azo-nitrogen atoms and make them less susceptible to oxidation. It is also suggested that the electron-attracting groups can improve the stability of the azo form of dyes. As the oxidation was supposed to occur by attack on the hydrazine form, a higher portion of azo form means a reduced oxidation, which leads to higher light fastness (Desai and Giles, 1949). On the other hand, the dull red and blue dyes, which do not have electron-attracting groups in the diazo component (diazoamine 2), shows similar results as the dyeing with pre-formed dyes. The light fastness of *in-situ* dyeing also increases with increasing concentration.

The *in-situ* dyeing shows better light fastness than the corresponding pre-formed dyes. However, compared to commercial disperse dyes, which normally give good light fastness, the *in-situ* dyeing shows lower fastness. This is mainly due to the relatively small molecular size of these dyes. Moreover, the structures of the dyes used are not optimised for light fastness. The diazo components, particularly diazoamine 2, do not have enough electron-attracting substituents to achieve good light fastness results.

4.1.2.4 Dry Heat Fastness

The dry heat fastness is generally important for disperse dyes, as they are small non-ionic molecules and tend to melt and vaporise when heated (Gordon and Gregory, 1987). The dry heat fastness of the dyed fabrics was measured at 210℃.

Table 4.6 Dry Heat Fastness of the Dyed PET Fabrics

Colour		PD 130℃	PD 100℃	*In-situ* Dyeing
Orange	2%	2/3	2	2/3
	6%	2/3	2	2/3
Red	2%	3	3	3
	6%	3	3	3
Dull Red	2%	3	3	3
	6%	3	3	3
Blue	2%	3	3	4
	6%	3	3	3

As seen in Table 4.6, the dry heat fastness of the dyeing with pre-formed dyes at 130℃ is the same or slightly higher than the dyeing at 100℃. The *in-situ* dyeing gives similar results as the pre-formed dyes. Very similar results are observed at 2% and 6% o.m.f., which indicates that the concentration of the dyes does not have significant influence on the dry heat fastness.

The dry heat fastness is largely dependent on the molecular size and polarity of the dyes, which determine the diffusion rate of dyes out of the fibre and the volatility of the dyes (Schroeder and Boyd, 1957). Both the pre-formed dyes and *in-situ* dyeing corroborate this rule. The orange dye with the smallest molecular weight shows the lowest dry heat fastness, while the largest blue dye shows the highest dry heat fastness.

The dry heat fastness of commercial disperse dyes vary from poor to excellent according to their molecular size and polarity. The *in-situ* dyeing gives acceptable dry heat fastness, considering the small molecular size of the dyes used here.

4.2 Dyeing with Mixtures

The mixtures of dyes were used to create a larger range of colours. However, when dyeing with mixtures of *in-situ* formed dyes, it is necessary to ensure there is one common component for the two colours as it is not possible to avoid cross reaction. According to the components used to produce these four dyes, only four combinations (orange/red, orange/dull red, blue/red, blue/dull red) are available for the dyeing with mixtures. As the blue and orange dyes share no common component, they cannot be used together for the dyeing. The dyeing process with the mixtures was described in Section 2.5.4.

4.2.1 Colour Gamut of the Dyeing

In 1976, the CIE recommended CIELAB (or CIE L*a*b*) colour space for surface colour industry (CIE, 2004). The colour space describes all colours in three dimensions (Figure 4.3). The L* (lightness) value of 100 and 0 represent a reference white and black respectively. The a* and b* values represent colour components green-red and yellow-blue. CIELAB colour space is used here to show the colour gamut achieved with the pre-formed dyes and *in-situ* dyeing, including individual colour and mixtures.

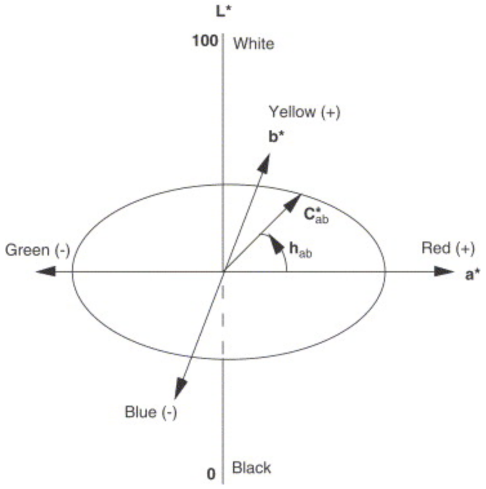


Figure 4.3 Three-dimensional Representation of CIELAB Colour Space (Luo, 2006)

Figure 4.4 and Figure 4.5 show the colour gamut obtained with the pre-formed dyes at 130℃ and *in-situ* dyeing, including individual colour and the four possible combinations of mixtures. No a* value below 0, which means no green colour, is obtained. This is because the blue and orange cannot be mixed for *in-situ* dyeing as they are formed with different diazoamine and coupling component. Only a small range of blue colour (b* value below 0) can be obtained. This is due to the limitation of the structures that can be used for the *in-situ* dyeing. Some colours, such as blue and greenish-yellow, are not typical for simple azo dyes (Broadbent, 2001). Since only the precursors of azo compounds can be used for *in-situ* dyeing, the colour is limited. The *in-situ* dyeing gives a wider range of shades than that using the pre-formed dyes. This is because the colour yield of *in-situ* dyeing is lower than the pre-formed dyes at low concentration but higher at high concentration, which leads to a larger range of both a* and b* values. The range of the lightness (L* value) of the dyeing with pre-formed dyes and *in-situ* dyeing is similar.

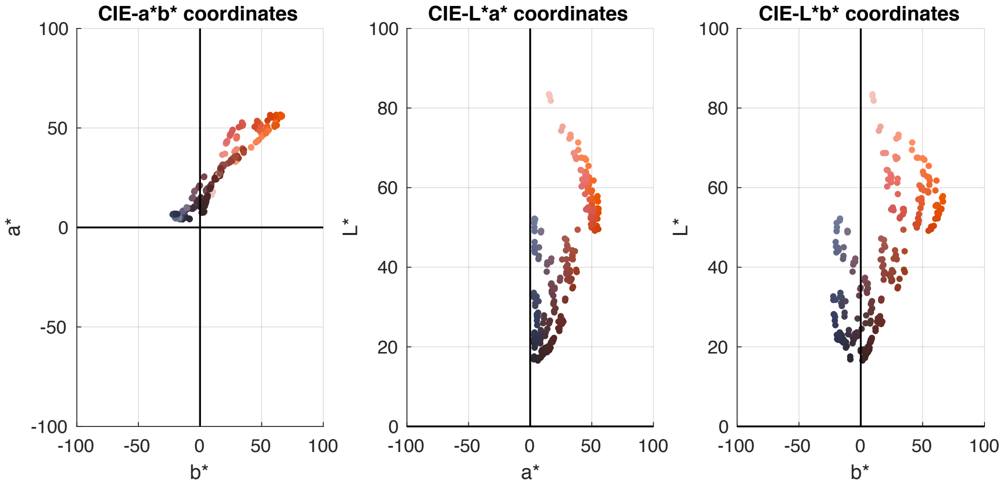


Figure 4.4 Colour Gamut of the Dyeing with All Combinations of the Pre-formed Dyes at 130℃

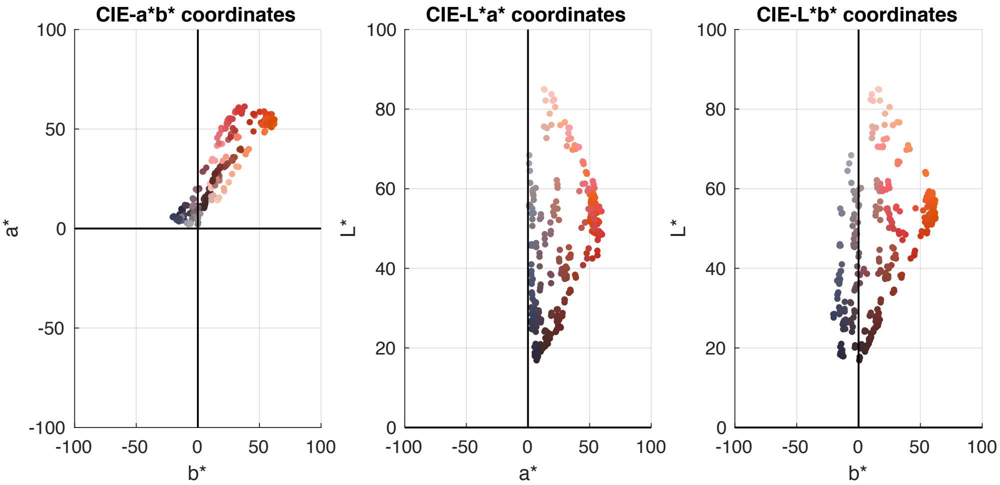


Figure 4.5 Colour Gamut of the Dyeing with All Combinations of the Azoic Dyes through *In-situ* Dyeing at 100℃

4.2.2 Colour Prediction

Colour prediction is carried out based on the K-M theory developed by Kubelka and Munk (Kubelka, 1948). As the reflectance is non-linearly related to the concentration of dye, K/S value, which is linear to the concentration of the dye, was introduced for colour prediction. K represents the absorption coefficient and S represents the scattering coefficient. The K/S value can be calculated from the reflectance (R) for each wavelength:

$$K/S=(1-R)^2/2R$$

In the theory, it is assumed that the total absorption and scattering is the summation of those from each individual colourant. Therefore, the absorption and scattering coefficients of the mixture can be further represented using absorption and scattering coefficients of the individual dyes:

$$(K/S)_{\text{mixture}} = (K/S)_1 + \ldots + (K/S)_n$$

$$= K_1/K_{\text{sub}} + \ldots + K_n/S_{\text{sub}} + K_{\text{sub}}/S_{\text{sub}}$$

where K_1 to K_n are the absorption coefficients of the dyes, K_{sub} and S_{sub} are the absorption and scattering coefficients of the substrate. The various K/S_{sub} ratios may be considered as a single constant, which is called 'absorption coefficients'. The absorption coefficient is related to the concentration. A range of concentrations are used to obtain a calibration database by dyeing and the absorption coefficient at a certain concentration can be calculated accordingly.

The colour prediction was carried out with MATLAB, as described in Section 2.9, with the help of Prof. Stephen Westland, where the predicted K/S values of the dyeing with mixtures were calculated from the reflectance data of the dyeing with individual colour and then converted back to reflectance and L*a*b* values. The a* and b* values of the prediction and the measurements from the dyeing with mixtures are compared in order to see the colour difference, as shown in Figure 4.6-Figure 4.8.

As shown in Figure 4.6, the shades obtained with the mixtures of pre-formed dyes at 130℃ are overall close to the prediction. The dyeing with the mixtures of orange/dull red and orange/red pre-formed dye mixtures gives slightly higher a* value, which means that the obtained colour is redder than the prediction. For the dyeing with blue/dull red and blue/red dyes, the a* and b* values are overall slightly higher than prediction, which means that the obtained colour is less blue and redder than the prediction. When dyeing with the mixtures of disperse dyes with similar structures, changes in the solubility of the dyes in the fibres and in the dyebath were observed (Schuler and Remington, 1954). The pre-formed dyes used together for dyeing here all have similar structures. Therefore, the obtained colour is slightly different from the prediction.

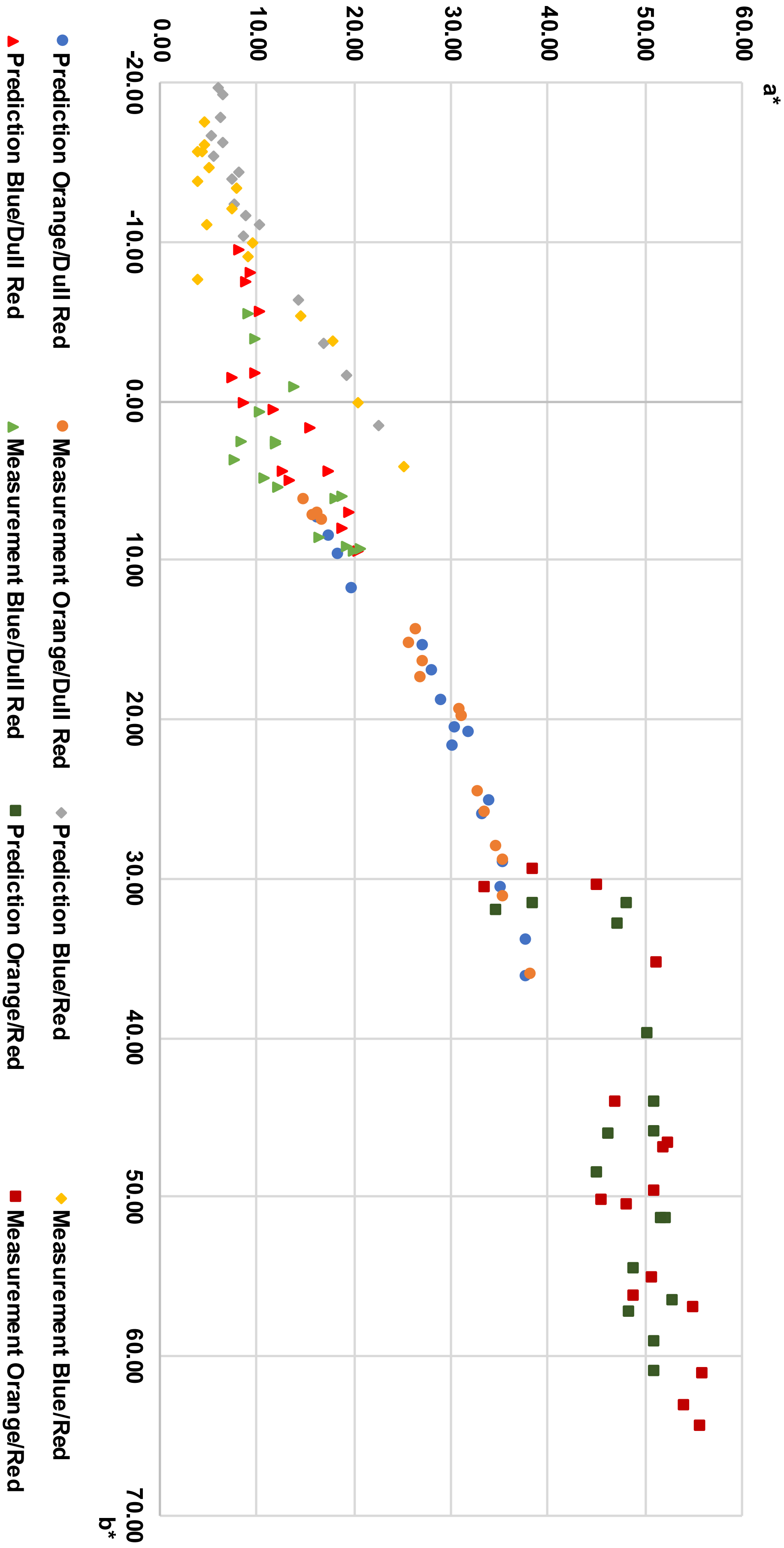


Figure 4.6 Colour Prediction and Measurement of the Dyeing with the Mixtures of Preformed Dyes at 130°C

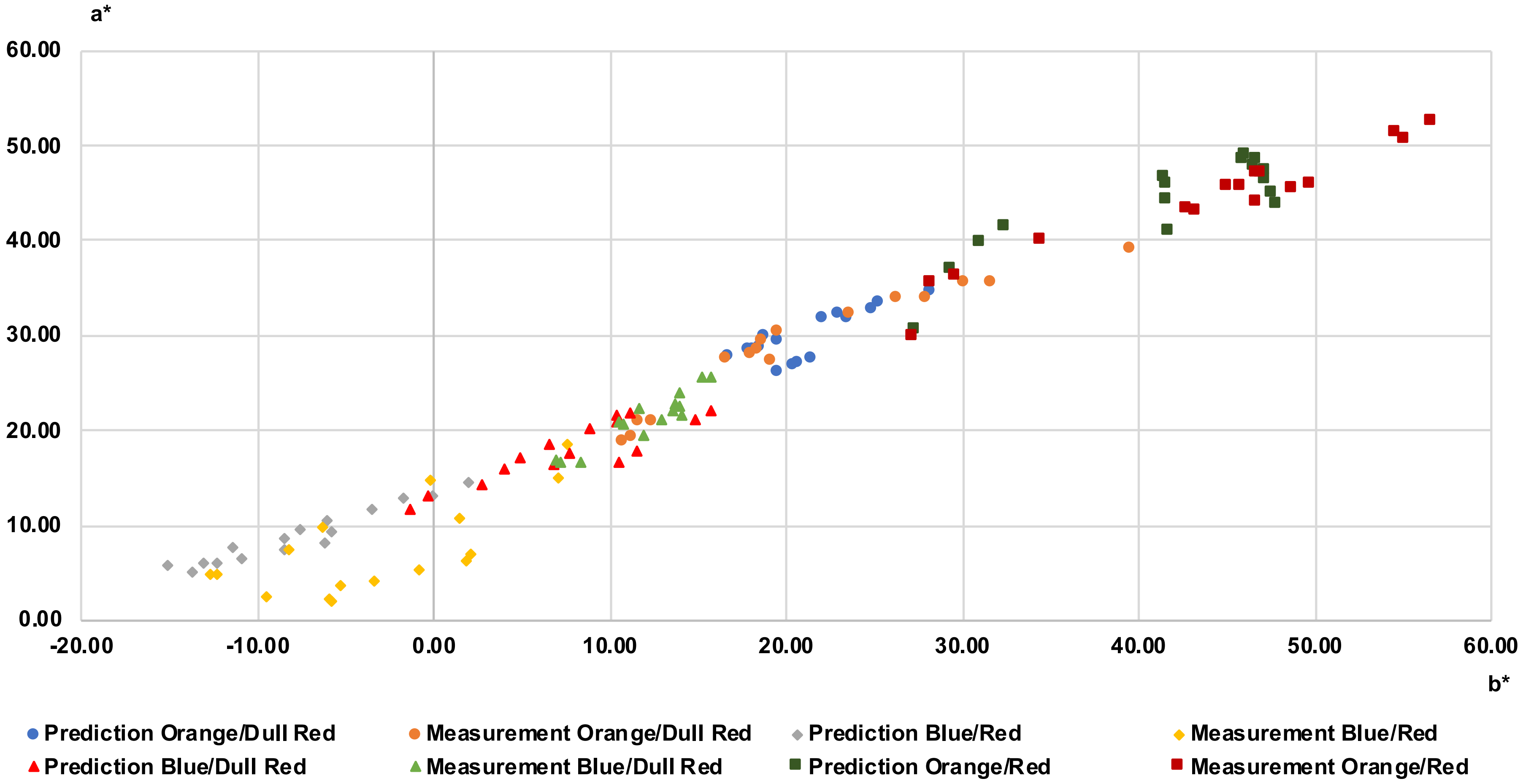


Figure 4.7 Colour Prediction and Measurement of the Dyeing with the Mixtures of Preformed Dyes at 100℃

Figure 4.7 shows that the colour difference between prediction and measurements of the dyeing with pre-formed dyes at 100℃ is more significant than that at 130℃. The dyeing with the mixtures of orange/dull red and orange/red dyes both show higher a* and b* values than the prediction, which means that the absorption of both the dyes are higher than prediction. It is presumed that the orange dye might be acting as a carrier for the red and dull red dyes when dyeing with the mixtures, which help to increase the exhaustion of the dyes at 100℃ and hence increase the colour yield. As for the blue/red dyes, unlike the dyeing at 130℃, the a* value is lower than the prediction, which means fewer red dyes were absorbed onto the fabrics. This indicates that the exhaustion of the red dye reduces considerably at 100℃ in the presence of the blue dye. The dyeing with blue/dull red dyes gives higher a* and b* values, which means that the obtained colour is redder and less blue. As mentioned in Section 4.1.1, the dull red dye has similar colour yield at 100℃ and 130℃, which indicates that the exhaustion of the dull red dye does not change significantly with decreasing temperature. This is not the case for the blue dye. Therefore, when dyeing with mixtures, similar results, with more dull red absorbed in the fibres than the blue dye, are observed for the dyeing at both 100℃ and 130℃.

As seen in Figure 4.8, obvious colour difference between the *in-situ* dyeing and the prediction can be observed. The dyeing with orange/dull red mixtures shows lower a* and b* values than predicted. As the dull red dye has lower a* and b* value, it is assumed that more dull red dyes and fewer orange dyes were formed during the dyeing with mixtures. These two dyes were both formed with 2-napthol. One possible reason for the colour difference is that the diazoamines used for form these two dyes have different exhaustion rate in PET fibres. As explained in Section 4.1.1, the *o*-methyl group in diazoamine 1, which was used to form the orange dye, clashes sterically with the lone pair of electrons on one of the azo nitrogen atoms and is forced to rotate out of a planar conformation (Christie, 2015), causing the diazoamine to diffuse less readily into the fibres. The other possible reason is that the diazoamines have different reactivity towards the coupling component. Diazoamine 2, which is used to form the dull red dye, may be more reactive with the 2-naphthol and

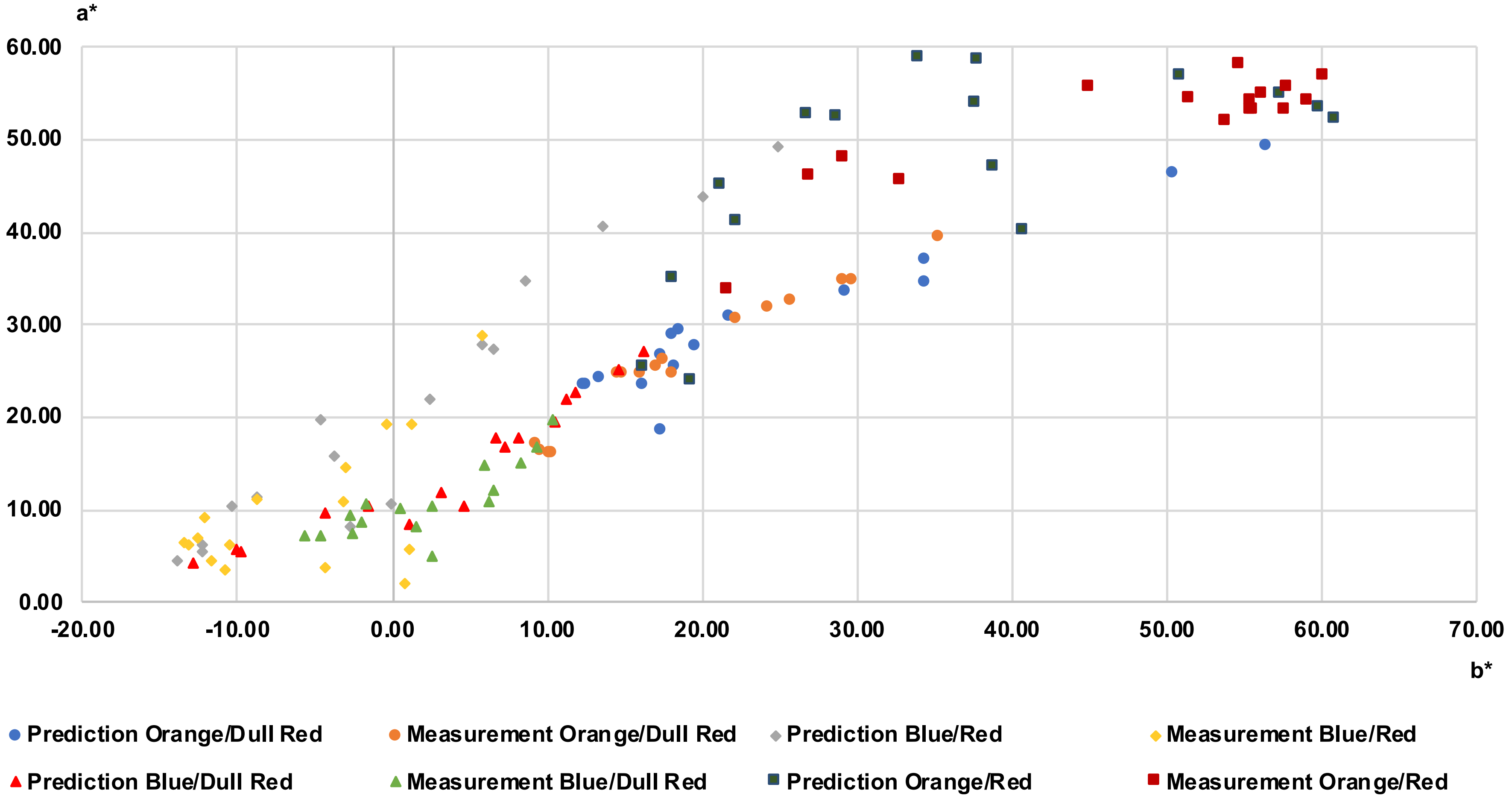


Figure 4.8 Colour Prediction and Measurement of *In-situ* Dyeing with the Mixtures

thus formed more dull red dyes. For the dyeing with blue/red and blue/dull red dyes, both a* and b* values are lower than prediction, which means more blue dyes were formed. For the blue/red dye mixtures, these two dyes are formed with the same coupling component (Naphthol AS). The reason for the colour difference may be the same as that for the orange/dull red dyes. In the case of the blue/dull red dyes, they are both formed with diazoamine 2. Therefore, the possible reason would be the higher reactivity of Naphthol AS, which is used to form the blue dyes, towards the diazoamine or the higher exhaustion rate of Naphthol AS in PET. However, the dyeing with orange/red mixtures, which shares the same diazoamine (diazoamine 1), gives lower a* values and higher b* values than prediction and indicates that more orange dyes were formed. The orange dye was formed with 2-naphthol. It is not likely that the exhaustion rate of the coupling component is responsible for the colour difference as the dyeing of the orange/red mixtures and the blue/dull red mixtures show opposite results. Therefore, the different reactivity between the components used for dyeing is more possible to be the reason for the colour difference between the dyeing and the prediction.

The colour difference between the colour obtained through *in-situ* dyeing and the prediction is relatively large due to the different reactivity of the azoic components used to form the dyes. As one of the combinations is more reactive, more of the corresponding dye would be formed during dyeing. Therefore, the CIE values of the obtained colour would be more shifted towards that particular dye, which would be different from the prediction. A new colour prediction method, which considers the reactivity of different components, is required for the colour prediction of *in-situ* dyeing.

4.2.3 Fastness Properties of the Dyeing with Mixtures

The fastness tests were carried out with the fabrics dyed with mixtures of both pre-formed dyes and *in-situ* dyeing with the same methods used for the individual dyes.

4.2.3.1 Rubbing fastness

The rubbing fastness results of the dyeing with mixtures of pre-formed dyes at 130℃ and *in-situ* dyeing are shown in Table 4.7. The rubbing fastness of the dyeing with mixtures follows similar trend with the dyeing with individual dyes. The wet rubbing fastness is generally better than the dry rubbing fastness. The *in-situ* dyeing tends to give lower rubbing fastness than the dyeing with the pre-formed dyes. The rubbing fastness decreases with increasing concentration. The rubbing fastness of the dyeing with mixtures are generally lower than that of individual dyes due to the increased concentration of the dyes applied.

For the dyeing with orange/dull red mixtures, the rubbing fastness is only acceptable, which is within expected, as the rubbing fastness of dull red dye is not good. The rubbing fastness of *in-situ* dyeing is lower than the dyeing with pre-formed dyes. When dyeing with the individual dyes, the fastness of the dull red dye changes more significantly with the increasing concentration than the orange dye. Therefore, when dyeing with mixture, the concentration of the dull red dye shows more influence on the fastness properties.

The dyeing with orange/red mixtures shows overall good rubbing fastness properties. The results of the dry rubbing fastness and wet rubbing fastness are very close. The difference of the fastness between the dyeing with pre-formed dyes and *in-situ* dyeing is small. When dyeing with individual dyes, the difference between the pre-formed dyes and *in-situ* dyeing is quite noticeable for both these dyes, while the difference becomes smaller when dyeing with mixtures. This indicates that the interactions between these two dyes, including hydrogen bonding formed between the carbonyl group in the red dye and the hydroxyl group in the orange dye and aromatic interactions, may help to increase the aggregation between the dyes and hence improve the rubbing fastness. The changes of the fastness with the concentration of orange and red dye are similar, so they have almost the same influence on

Table 4.7 Rubbing fastness of the Dyeing with Mixtures

	Orange/Dull Red				Orange/Red				Blue/Red				Blue/Dull Red			
	PD130		*In-situ*		PD130		*In-situ*		PD130		*In-situ*		PD130		*In-situ*	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
100/25	4	4/5	2/3	3	4	4/5	4	4	3	3	2	2	2/3	3/4	2/3	2/3
100/50	3/4	4/5	2	2/3	3/4	4	3/4	3/4	3	3	2	2	2	2/3	1/2	1/2
100/75	3	3/4	3	2/3	3/4	3/4	3	3	3	3	2	2	1/2	2	1/2	1/2
100/100	1/2	3	2	2/3	2/3	3	2/3	2/3	3	3	2	2	1	1/2	1/2	1/2
75/25	4	5	3/4	4	4	4/5	4/5	4/5	3/4	3/4	2	2/3	2/3	3/4	2/3	2
75/50	4/5	4/5	3/4	3/4	4	4	4/5	4/5	3/4	3/4	2	2/3	2/3	3/4	2	2
75/75	4	4/5	3	3	4	4	4	4	3	3	2	2	2	2/3	1/2	1/2
75/100	1/2	3/4	1/2	2	3/4	3/4	2/3	2/3	3	3	2	2	1	1/2	1/2	1/2
50/25	4/5	5	3	4	4/5	4/5	4/5	5	4/5	4/5	4	4/5	4	3/4	4	3/4
50/50	4	4/5	3/4	4	4	4	4/5	4/5	4/5	4/5	4	4/5	3/4	3/4	3	3
50/75	3/4	4	3	3/4	4	4	4	4	4	4	3	4	3	2	2/3	2
50/100	2/3	3	2	2/3	3/4	3/4	3	3	4	4	2	2/3	1	1/2	2	1/2
25/25	4	5	4	4	4/5	4/5	5	5	4/5	5	4/5	4/5	4/5	3/4	4/5	4/5
25/50	3/4	4/5	3/4	4	4	4	5	5	4/5	5	4	4/5	3/4	3/4	3/4	4
25/75	3	4/5	3	3	4	4	4	4	4/5	4/5	3/4	3/4	3	3	3/4	3/4
25/100	2	4	2	1/2	3/4	3/4	3	3	4/5	4/5	2	2/3	1/2	2/3	2/3	2/3

the change of fastness properties when dyeing with mixtures.

For the dyeing with the blue/red mixtures, the dyeing with the pre-formed dyes at 130℃ shows relatively good rubbing fastness results, with minor difference between dry and wet rubbing fastness. The results of the *in-situ* dyeing are lower than that of the dyeing with the pre-formed dyes. The concentration of the red dye has very little influence on the fastness of the dyeing with mixtures, particularly when the ratio of the blue dye is high, because the fastness of the red dye only changes slightly with the increasing concentration.

The fabrics dyed with the mixtures of blue/dull red dyes exhibit relatively poor rubbing fastness, particularly at high concentration, which is also caused by the low rubbing fastness of the dull red dye. The rubbing fastness of *in-situ* dyeing is lower than the dyeing with pre-formed dyes when the concentration is high, while the difference becomes smaller with decreasing concentration. This trend was also observed when dyeing with individual colour. The change of the rubbing fastness with increasing concentration is relatively large when dyeing with mixtures because these two dyes both show relatively significant fastness change with concentration. The influence of the concentration of these two dyes on the fastness of the dyeing with mixtures is similar.

4.2.3.2 Washing fastness

Both the staining and colour change results were assessed in the experiments. Only the shade change results of the dyeing with the mixtures of pre-formed dyes at 130℃ and *in-situ* dyeing are used for analysis here, as shown in Table 4.8, as all staining results were in line with those expected from the below.

The washing fastness of the dyeing with the mixtures of orange and dull red pre-formed dyes are relatively good. The rating is above 4/5 in most cases.

Table 4.8 Washing fastness of the Dyeing with Mixtures

	Orange/Dull Red		Orange/Red		Blue/Red		Blue/Dull Red	
	PD130	*In-situ*	PD130	*In-situ*	PD130	*In-situ*	PD130	*In-situ*
100/25	4/5	4	5	3/4	4	4/5	4/5	4/5
100/50	4/5	4	4/5	3/4	3/4	4/5	4	4/5
100/75	4/5	4	4/5	3/4	3/4	4/5	4	4
100/100	4/5	3/4	4/5	3/4	3/4	4/5	4	3/4
75/25	4/5	4/5	5	3/4	4	4/5	4/5	4
75/50	4/5	4/5	5	4	4	4/5	4/5	4
75/75	4/5	4	4/5	4	4	4/5	4	4
75/100	4	3/4	4/5	4	4	4/5	3/4	3/4
50/25	4/5	4/5	5	4	4/5	5	4/5	5
50/50	4/5	4/5	5	4	4/5	5	4/5	4/5
50/75	4/5	4	4/5	4	4/5	4/5	4	4
50/100	4	3/4	4/5	4	4/5	4/5	3/4	3/4
25/25	5	5	5	4/5	5	5	4/5	5
25/50	4/5	4/5	5	4/5	5	5	4	5
25/75	4/5	4/5	4/5	4/5	5	4/5	4	4/5
25/100	4	4	4/5	4/5	4/5	4/5	4	4

The *in-situ* dyeing shows slightly lower fastness results than the pre-formed dyes. This is mostly because the fastness of *in-situ* dyeing with orange dye is lower than the dyeing with the pre-formed dye. The fastness decreases slightly with increasing concentration. The concentration of the dull red dye shows more influence on the fastness when dyeing with mixtures.

The dyeing with mixtures of orange/red pre-formed dyes shows good washing fastness results, which is rated above 4/5 at all concentration. The results of *in-situ* dyeing are lower than that with the pre-formed dyes. The difference is relatively large compared with the other combinations. This is because the *in-situ* dyeing with both the orange and red dye gives lower washing fastness than the fastness than the pre-formed dyes. The change of washing fastness with increasing concentration is small.

The washing fastness of the dyeing with blue/red dye mixtures is not good when the concentration is high. As the concentration decreases, the colour change increases. The *in-situ* dyeing, unexpectedly, shows better fastness than the dyeing with pre-formed dyes. When dyeing with individual dyes, the *in-situ* dyeing with the red dye shows lower washing fastness than the pre-formed dye and the blue dye provides the same degree of washing fastness. It is presumed that the interactions between these two dyes when dyeing improves the fastness when dyeing with mixtures. Both the dyes have carbonyl groups that can form hydrogen bonding with the hydroxyl groups and the amine groups in the other dye. These interactions increase the aggregation of the dyes inside the fibre and make it more difficult for these dyes to diffuse out of the fibre during washing, hence improve the washing fastness. The increasing concentration has very small influence on the washing fastness of the dyeing.

The dyeing with blue/dull red pre-formed dye mixtures shows acceptable washing fastness. When dyeing with individual colour, both the blue and red dyes give the same washing fastness results with the pre-formed dyes and *in-situ* dyeing. As expected, when dyeing with mixtures, the difference between the fastness of *in-situ* dyeing and pre-formed dyes is also small. The concentration of the dull red dye has more influence on the change of fastness of the mixtures. This also happens when dyeing with orange/dull red dyes. Although the fastness of dull red dye does not change with concentration, it has a larger influence on the fastness results when dyeing with mixtures.

4.2.3.3 Light Fastness

The light fastness results of the fabrics dyed with the mixtures of pre-formed dyes and *in-situ* dyeing are shown in Table 4.9. Similar to the individual dyes, the light fastness of the dyeing with mixtures is relatively poor. However, the dyeing with the mixtures tends to exhibit higher light fastness than individual dyes presumably due to the higher concentration of dyes applied.

For the dyeing with the orange/dull red pre-formed dyes, the light fastness is relatively poor. This is as expected because both the dyes give poor light fastness. The *in-situ* dyeing shows better light fastness results than the pre-formed dyes. This is mainly attributed to the higher light fastness of the *in-situ* dyeing with orange dye.

In the case of the orange/red dyes, the pre-formed dye mixtures also show poor light fastness as expected. However, although the *in-situ* dyeing of these two dyes gives higher light fastness than the pre-formed dyes when dyeing alone, the *in-situ* dyeing with the mixtures gives same results as the dyeing with the pre-formed dyes.

The dyeing with the mixtures of blue/red pre-formed dyes also gives poor light fastness, while the *in-situ* dyeing with the mixtures gives better light fastness results. This is mainly due to the higher light fastness of the *in-situ* dyeing with the red dye, which is the contribution of the presence of the electron-attracting group (*p*-Cl) in the diazo component. The intermolecular hydrogen bonds may

Table 4.9 Light Fastness of the Dyeing with Mixtures

	Orange/Dull Red		Orange/Red		Blue/Red		Blue/Dull Red	
	PD 130	*In-situ*	PD 130	*In-situ*	PD 130	*In-situ*	PD 130	*In-situ*
100/25	2	3	3	3	2	4	2	3
100/50	2	3	3	3	2	4	2	4
100/75	3	4	3	3	2	5	3	4
100/100	4	5	4	4	3	5	4	4
75/25	2	2	2	2	2	3	2	3
75/50	2	2	2	2	2	3	2	3
75/75	3	3	2	2	2	4	3	4
75/100	3	4	3	3	2	4	4	4
50/25	2	2	2	2	2	2	2	2
50/50	2	2	2	2	2	2	2	3
50/75	2	2	2	2	2	2	3	3
50/100	3	3	3	3	2	3	4	4
25/25	2	2	2	2	2	2	2	2
25/50	2	2	2	2	2	2	2	2
25/75	2	2	2	2	2	2	3	3
25/100	3	3	3	3	2	3	4	4

also play a part.

As expected, the light fastness of the dyeing with blue/dull red pre-formed dyes is also relatively poor. The *in-situ* dyeing with individual colour gives similar results as the pre-formed dyes, while the *in-situ* dyeing with mixtures shows slightly higher results. This is probably due to the hydrogen bonds formed between the carboxyl group in the blue dye and the amino group and the hydroxyl group in the dull red dye.

4.2.3.4 Dry Heat Fastness

The dry heat fastness of the fabrics dyed with the mixtures were measured with the same method as those dyed with individual dyes at 210℃ results of the dyeing with mixtures are shown in Table 4.10.

The dry heat fastness of the dyeing with the pre-formed dyes is rated from poor to fair. Most of the dyeing with mixtures gives slightly higher dry heat fastness than the individual colour. This is mainly attributed to the hydrogen bonds formed between the dyes, which increases the aggregates and reduces the diffusion out of the fibre and thus increase dry heat fastness (Salvin, 1966).

As for the *in-situ* dyeing, the dry heat fastness is generally higher than the pre-formed dyes, except for the mixtures of orange/red dye. It is presumed that the higher dry fastness of the *in-situ* dyeing is because the components used for dyeing is smaller than the according disperse dye and can penetrate into deeper layer of the fibre and formed dyes, which have larger molecular size and are not readily to diffuse out of the fibres. The lower dry heat fastness of the dyeing with the mixtures of orange/red dyes may be due to the presence of the *o*-methyl group in diazoamine 1, which was mentioned before to clash sterically with the lone pair of electrons on one of the azo nitrogen atoms and is forced to rotate out of a planar conformation (Christie, 2015). Therefore, it

Table 4.10 Dry Heat Fastness of the Dyeing with Mixtures

	Orange/Dull Red		Orange/Red		Blue/Red		Blue/Dull Red	
	PD130	*In-situ*	PD130	*In-situ*	PD130	*In-situ*	PD130	*In-situ*
100/25	2/3	4	3/4	2	3	3	3/4	3
100/50	2/3	4	3/4	3	2/3	4	3	3/4
100/75	2/3	3/4	3/4	3	2	4	2/3	3/4
100/100	2/3	2/3	3/4	3/4	2/3	4	2	2
75/25	3	4/5	2/3	2/3	2/3	3/4	3/4	3/4
75/50	3	4	2/3	2/3	3	4	3/4	3
75/75	2/3	2/3	3	2/3	3/4	4	4	2/3
75/100	2/3	3/4	4	3	3/4	4	3	3/4
50/25	2/3	4	2/3	2	3	4	2/3	4
50/50	2/3	3/4	2/3	2	3	4/5	3/4	4
50/75	2/3	3/4	2/3	2	3	3/4	2/3	2/3
50/100	2/3	3	2/3	3	3	2	2/3	2/3
25/25	3	4/5	2	1/2	3	4/5	3/4	3/4
25/50	2/3	4	2/3	1/2	3	4/5	3	3/4
25/75	2/3	4	3	3	3	3	3	4
25/100	2/3	3/4	3	3	2/3	2	2/3	4

cannot penetrate inside deeper layer of the fibre like the other azoic components and thus gives lower dry heat fastness.

4.3 Competitive Dyeing of PET/Wool Fabrics through *In-situ* Dye Synthesis

When dyeing with PET/Wool blend fabrics, the high temperature (above 110℃) required for good dyeability on PET fabrics would cause chemical and physical changes to the wool component in the blend, leading to reduced strength and abrasion resistance (Lewis, 1989). In order to achieve a good colour yield on PET and minimise the damage to the wool fibres, carriers or reagents for wool protection must be used for the dyeing of the blend (Doughty, 1986). The use of *in-situ* dye synthesis on PET/wool blend would be beneficial as it does not need any extra auxiliaries other than dispersing agents and can achieve good colour yield on PET at 100℃.

In order to allow the assessment to be made of the dyeing behaviour of the dyes on each component fibre of the blend, one piece of wool fabric and one piece of PET fabric with the same weight in close contact is dyed in the same dyebath to simulate a 50:50 blend. The fabrics were dyed with the precursors (2% o.m.f.) at 100℃ with the method described in Section 2.10.1. The colour of the wool and PET fabrics was measured after dyeing. The mechanical properties of the wool fabrics were assessed before and after dyeing to investigate the wool damage during dyeing.

4.3.1 Assessment of the Staining on Wool Fabrics

4.3.1.1 Difference of the Colour on Wool and PET

When dyeing PET/wool blend fabrics with disperse dyes at 100℃, the staining on wool may be greater than that on PET due to the slow diffusion rate of disperse dyes into PET and cannot produce good colour on PET fabrics (Fern and Hadfield, 1955). In order to investigate if the components used for the *in-situ* dyeing process can produce good colour on the blend fabrics, the colour of the dyed wool and PET was assessed after dyeing without soaping.

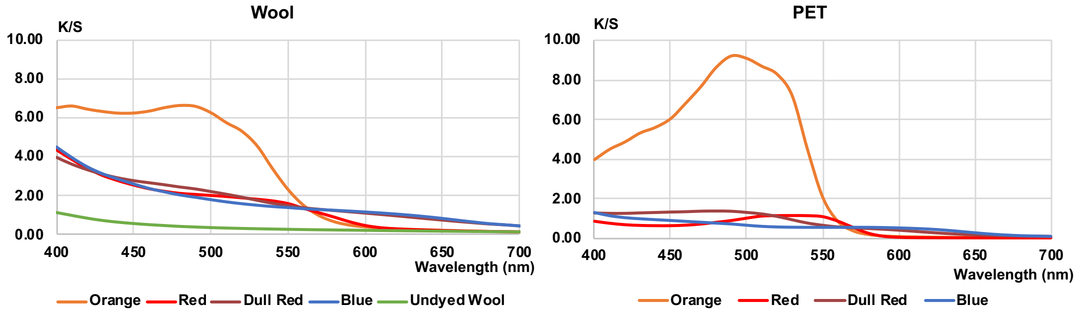


Figure 4.9 K/S Curves of the Dyed PET/Wool Fabrics in Competitive Dyeing (2% o.m.f.)

As shown in Figure 4.9, the colour achieved on these two substrates have different hues. The colour on wool fabrics shows increasing K/S values at the wavelength of 400-500nm due to the slightly yellow colour of the wool fabrics. Good colour yield is achieved on PET. This indicates that the components have sufficient affinity and diffusion rate on PET in order to achieve good colour yield when dyeing blend fabrics. Slightly deeper shades are achieved on PET than wool but the difference is relatively small. If the staining on wool is not just on the surface and cannot be easily washed off, it is possible to carry out the dyeing of the blends with the same dye through *in-situ* dye synthesis. The orange dye has the highest colour yield on both the substrates. This is probably due to the small molecular size of the components used to form orange dye, which makes them diffuse more readily inside the fibres. The red dye also gives a relatively deep staining on wool while the other two dyes only gives very pale shades on wool. It is presumed that Diazoamine 1 (M_w=258), which forms the orange and red dyes, has higher affinity to wool than Diazoamine 2 (M_w=300). With the same diazoamine, the dyes formed with 2-naphthol (M_w=144) give higher colour yield than the dyes formed with

Naphthol AS (M_w=263). It is presumed that the staining on wool fabrics is mainly dependent on the molecular size of the components used for dyeing. The diffusion of the dyes into wool and PET both follow the same rule.

4.3.1.2 Characterisation of Staining on Wool

In most cases, wool is only surface stained by the insoluble disperse dyes and can be easily washed off after soaping (Doughty, 1986). It was found that some disperse dyes can be applied on both fibres of the blend and achieve adequate fastness properties (Stapleton and Waters, 1981; Afifi and Sayed, 1997; Chao and Lin, 1998). In order to characterise the staining on wool, the dyed wool fabrics were washed with non-ionic detergent, as described in Section 2.10.2. The colour of the dyed wool fabrics before and after soaping and the absorbance of the wash-off liquor were measured in order to confirm if the staining on wool fabrics can be easily washed off.

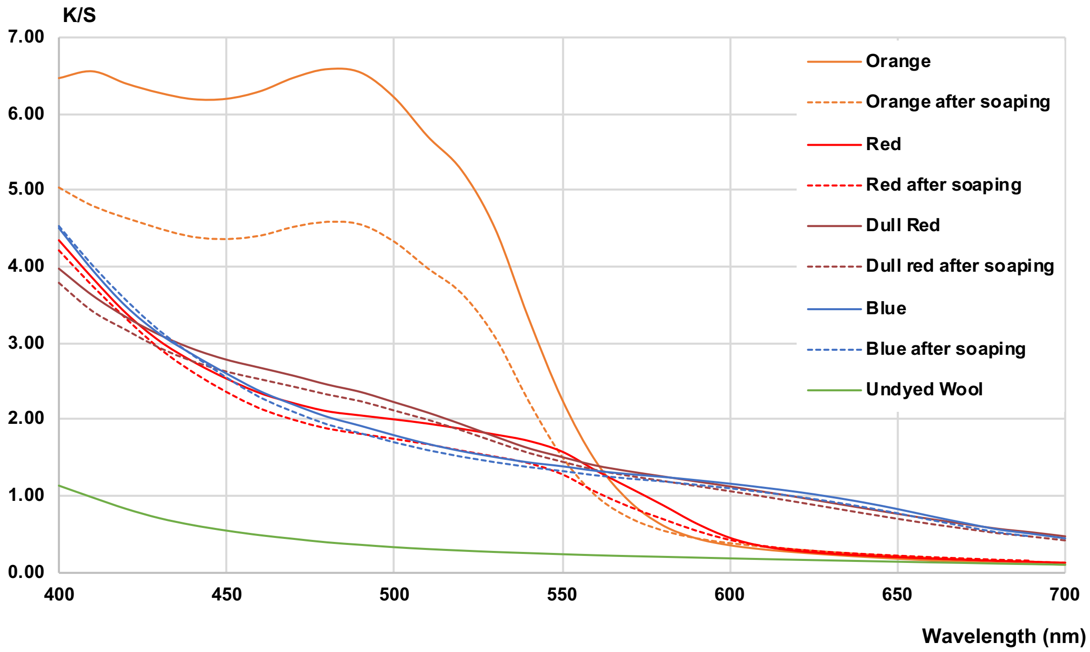


Figure 4.10 K/S Curves of the Wool Fabrics before and after Soaping

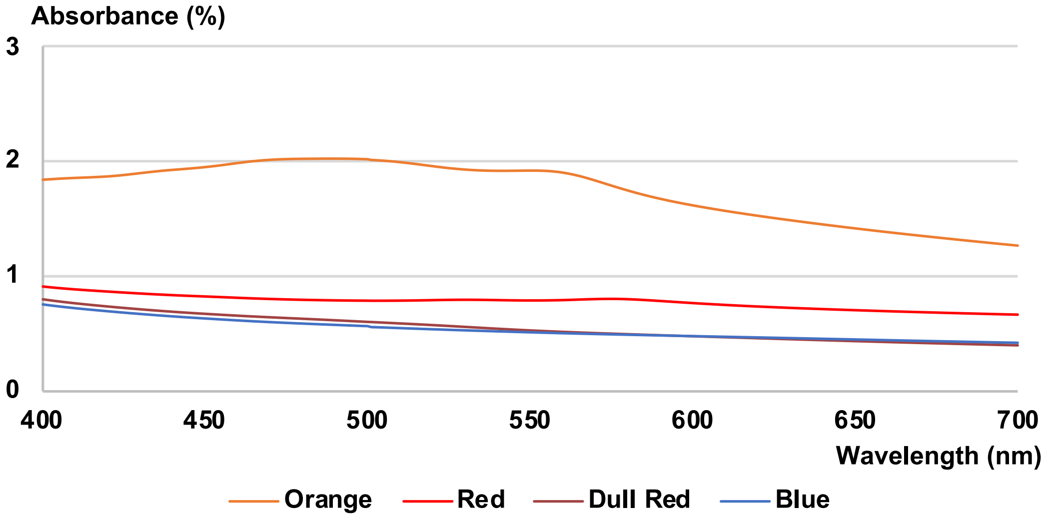


Figure 4.11 Absorbance of the Wash-off Liquor for Dyed Wool Fabrics

Figure 4.10 shows the colour difference of the dyed wool fabrics after soaping with detergent. The fabrics dyed with the orange dye shows more significant difference than the other dyes due to its initial higher colour yield. The colour change of the fabrics dyed with the blue and dull red dyes is very small because the colour is already quite pale before soaping. The absorbance of the wash-off liquor (Figure 4.11) shows the same results. A larger amount of orange dye was washed off during soaping, giving higher absorbance results. The liquor of the red fabric only gives a small peak, which indicates that only a small amount of red dye was washed off. The liquor of the blue and dull red fabrics does not give any peak, which means almost no dye was washed off.

Based on the wash-off results of the dyed wool fabrics, it is possible that the wool fabric can be dyed with *in-situ* dye formation to a certain extent. However, the colour on the wool fabrics after soaping is lower than that on PET. Further works could be carried out to investigate if different dyeing conditions or the addition of auxiliaries can help to improve the colour yield on wool fabrics to get a similar colour as the PET component so that the dyeing of the PET/wool blend fabrics can be carried out with the same dye.

4.3.2 Wool Damage after Dyeing

The keratins in wool fibres normally show extraordinary resistance to hydrolysis. However, during the high temperature dyeing process, the keratin proteins are hydrolysed due to the cleavage of the amide bonds and disulphide bonds depending on the pH of the dyebath, as shown in Figure 4.12 (Lewis, 1989). These changes cause reductions in strength and abrasion resistance, increases in alkali and urea/bi-sulphite solubility and yellowing (Doughty, 1986). Wool damage during dyeing was assessed with the change of mechanical properties, including wet abrasion strength and abrasion resistance before and after dyeing.

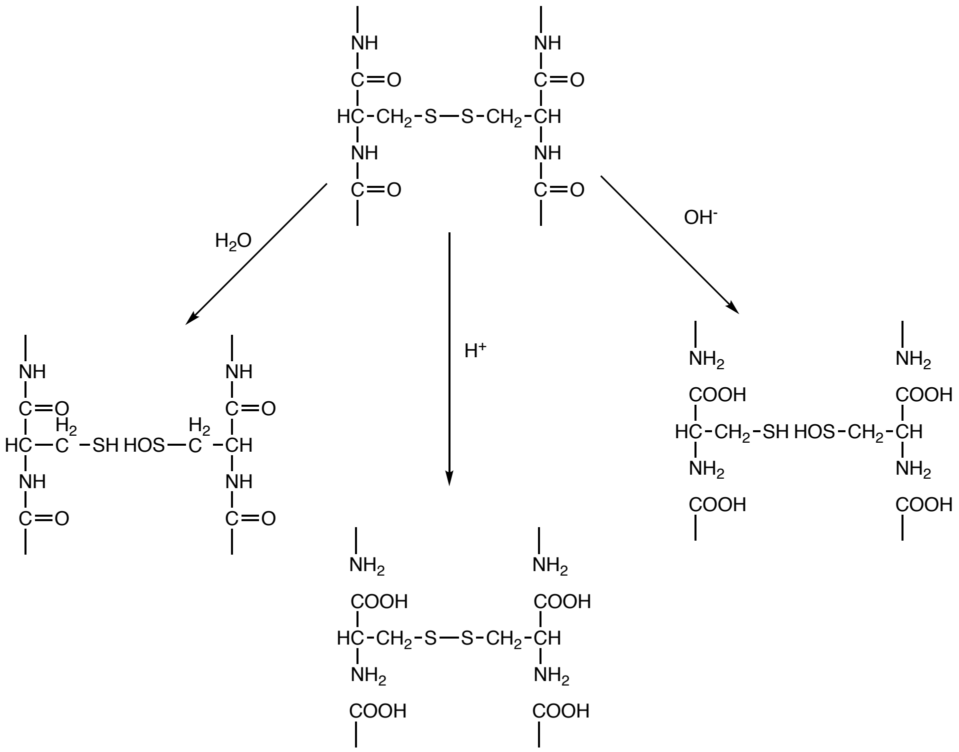


Figure 4.12 Keratin Hydrolysis

The wet burst strength test is proved to be extremely reliable and reproducible with an acceptable standard deviation for the assessment of wool damage (Liechti, 1982; Lewis,1989). The wet state can eliminate the influence of the hydrogen bonding to the strength test. As the wet burst strength of the wool fabrics dyed with different dyes does not show significant difference, the average of all the dyeing is used for the analysis. As shown in Figure 4.13, the wool fabrics dyed with *in-situ* dyeing at 100℃ only shows minor strength loss after dyeing. It is observed that the wool is seriously damaged after dyeing above 110℃ with more than 40% strength loss. It was reported that the strength loss is still more than 20% with the use of wool protection agents (Liechti, 1982; Lewis, 1989). Therefore, the *in-situ* dyeing at 100℃ provides a large improvement on strength loss of the wool component compared to high temperature dyeing.

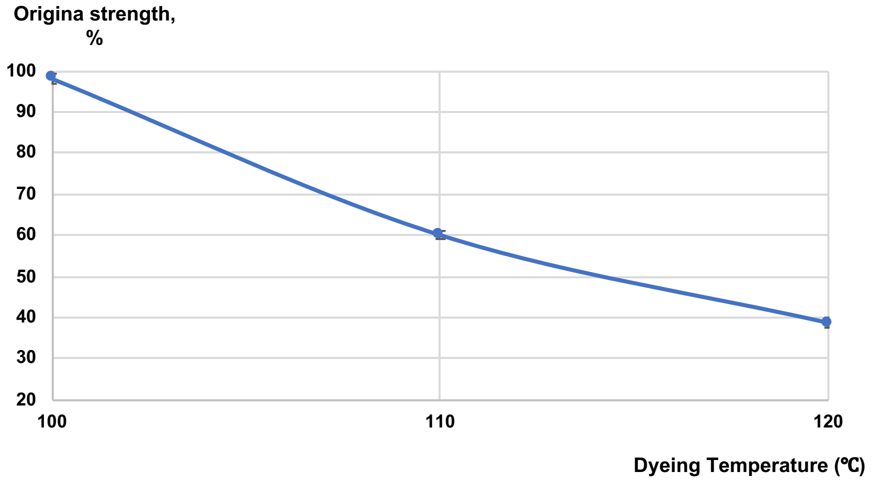
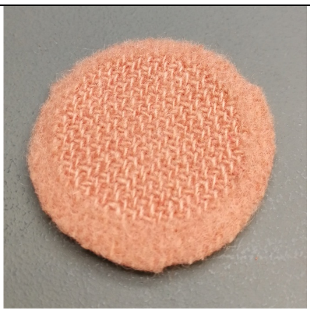


Figure 4.13 Strength Loss of Dyed Wool Fabrics at Different Dyeing Temperature

The abrasive resistance is another main aspect in the assessment for wool damage after dyeing. The wool fabrics were rubbed for 10,000 cycles. The appearance change and weight loss of the fabrics were compared, as shown in Table 4.11. The loose fibres on the surface are removed after abrasion and the weave pattern can be clearly seen. The weave pattern of the dyed wool fabrics after abrasion is more clearly than the undyed fabric. This indicates that more fibres of the dyed fabrics are removed during abrasion. However, the colour may also play a role on the perception. The weight loss can further prove this. The weight loss of the dyed fabrics is larger than the undyed wool fabric. The weight loss of the orange and red dyed fabrics is slightly higher than the other two.

Table 4.11 Appearance Change of the Wool Fabrics after Abrasion

	Before abrasion	After abrasion	Weight loss after 10000 cycles (mg)
Undyed Wool			78.7
Dyed Wool (Orange)			93.8
Dyed Wool (Red)			91.9
Dyed Wool (Dull Red)			83.2
Dyed Wool (Blue)			82.7

4.3.3 Colour of PET in Competitive Dyeing

The colour of the dye PET component in competitive dyeing was compared with the PET fabrics dyed with *in-situ* dye synthesis at the same concentration (2% o.m.f.), as shown in Figure 4.14.

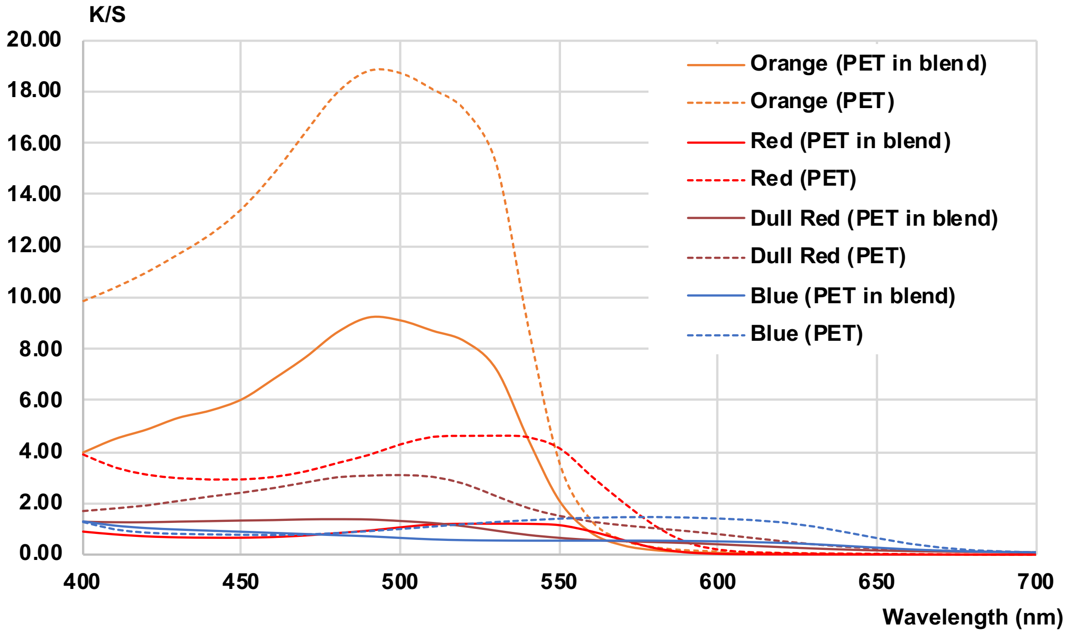


Figure 4.14 K/S Curves of the Dyed PET and PET in Competitive Dyeing (2% o.m.f., 130℃)

It is seen that similar K/S curves with the same λ_{max} are obtained for the PET dyed in competitive dyeing and dyed alone. This means the presence of wool does not affect the shades of the dyes on PET. The PET in competitive dyeing gives lower colour yield than the PET dyed alone at the same concentration. This means that the presence of the wool fabrics influences the uptake of the dyes on PET fibres. When dyeing PET/wool blend with disperse dyes, more dyes are absorbed by the wool component than PET at low temperature. The uptake of the dye by wool reaches the maximum at 90℃ and then the dyes are rapidly desorbed into the bath and absorbed by the PET component with increasing temperature (Cheetham, 1967; Stapleton and Waters, 1981). The precursors may follow the same mechanism. The precursors are absorbed by the wool fabrics and formed dyes inside at low temperature. As the temperature rises, some of the unreacted precursors and the formed dyes are desorbed from the wool fabrics. The precursors are then absorbed by the PET and formed dyes inside. However, the formed dyes are too large to diffuse inside the PET at 100℃ and are left in the dyebath. As the result, the PET component has higher colour yield than wool but lower than the PET fabrics dyed alone. This can be proved by the absorbance of the dyebath after dyeing. As shown in Figure 4.15, all four dyes have remain dyes in the dyebath after dyeing. Approximate 0.8g orange and dull red dyes were left in the dyebath, while more red (0.8g) and blue dye (0.7g) were left in the dyebath. This also conform to the fact that higher K/S values were achieved with orange and dull red dye on the PET component in competitive dyeing. This is probably due to the higher molecular weight of the red and blue dyes. Once the precursors react and form dyes, it is more difficult for them to diffuse inside PET fibres.

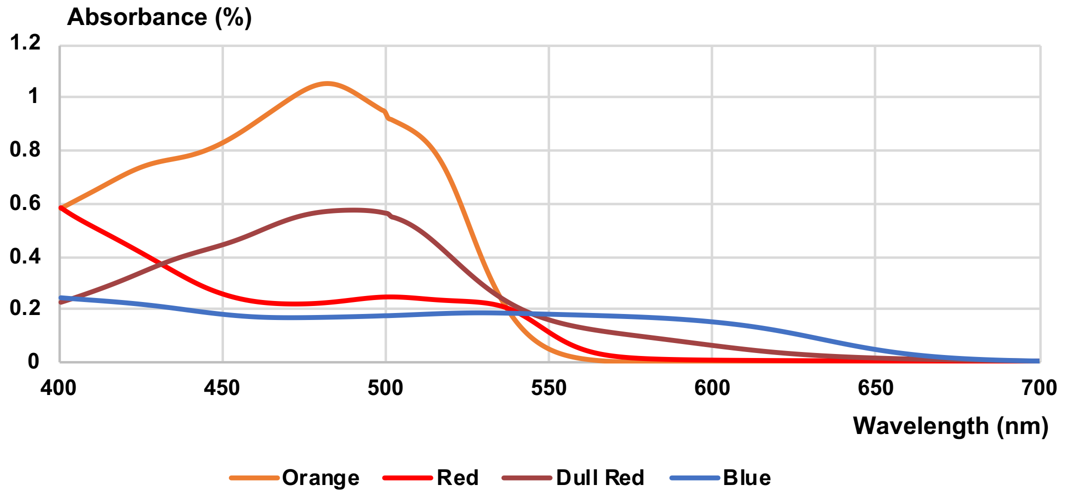


Figure 4.15 Absorbance of the Residue Dyebath of PET/Wool Competitive Dyeing after Dyeing

4.4 Conclusions

The aim of this chapter was to investigate the dyeing behaviour, including the colour yield and the fastness properties, of *in-situ* dyeing on PET fabrics compared with conventional dyeing with disperse dyes. The colour gamut that can be obtained through *in-situ* dyeing, with both individual colour and the mixtures, was also investigated. The application of dye precursors for the dyeing of PET/wool blend fabrics was investigated.

In general, the colour yield of *in-situ* dyeing at 100℃ is lower than conventional high temperature dyeing at low concentration (normally below 2% o.m.f.) and becomes higher at high concentration. The dyeing with pre-formed dyes at 100℃ does not have good colour yield, which proves that, in *in-situ* dyeing, the dyes are formed inside the fabrics, not in the liquor and then penetrate inside the fabrics.

The rubbing and washing fastness of the *in-situ* dyeing at 100℃ is slightly lower than the high temperature dyeing with the corresponding pre-formed dyes, while the light and dry heat fastness is the same or slightly higher. Compared to the commercial disperse dyes on market, the fastness properties of the *in-situ* dyeing are generally lower. This is mainly due to the small molecular size of the components used here, which leads to fewer and weaker dye-fibre interactions. The structures can also be improved to achieve better fastness properties.

The colour gamut obtained with *in-situ* dyeing does not have any green colour (a* value below 0) because the blue and orange dyes were formed with different diazoamine and coupling components and cannot be mixed for *in-situ* dyeing. The range of the shades obtained from *in-situ* dyeing is slightly larger than the pre-formed dyes.

When dyeing with mixtures, the colour prediction method that works well for the pre-formed dyes does not match the dyeing obtained with *in-situ* dyeing. This is due to the different reactivity between the components. A new method considering the reactivity of difference components is required for the colour prediction of *in-situ* dyeing.

Good colour yield on both PET and wool components was achieved with the dyeing through *in-situ* dye synthesis. Some of the dyes on wool are washed off during soaping but still an appreciable amount of dyes stays on the wool fabrics to give a good colour yield. Deeper shade is obtained on PET than wool with small difference. The colour yield on wool component could be improved by changing the dyeing condition in order to carry out the dyeing of both components in the blend fabrics with the same dye through *in-situ* dye synthesis. The damage of the wool fabric after *in-situ* dyeing at 100℃ is very small. The wet burst strength only reduced by 2% after dyeing. The abrasion resistance of the wool does not show significant difference before and after dyeing. With the same initial concentration of the precursors in dyebath, the PET component in competitive dyeing gains lower colour yield than the PET fabrics dyed alone.

Chapter 5

Aqueous Dyeing of PLA Fabrics

One of the biggest concerns about the dyeing of PLA is the loss of mechanical properties of the fibres during dyeing due to the hydrolysis of PLA. PLA fabrics can normally be dyed with disperse dyes. However, disperse dyes with good dyeing properties on PET do not always give good dyeability on PLA. Therefore, the dyeing with *in-situ* dye formation is also investigated for the dyeing on PLA fabrics. As the *in-situ* dyeing can be carried out at lower temperature, it would benefit for the dyeing of PLA with less strength loss of the fibres.

PLA fabrics were dyed with the same pre-formed dyes and precursors used for PET dyeing. The dyeing with the pre-formed dyes was carried out at 110℃ for 30 minutes, which is the conventional temperature for PLA dyeing. The optimum temperature for the *in-situ* dyeing on PLA fabrics was investigated and the dyeing behaviours including the colour yield and fastness properties of the *in-situ* dyeing at the optimum temperature were assessed and compared with the dyeing on PET.

5.1 Dyeing with Individual Dye

The dyeing was carried out with the synthesised pre-formed dyes and azoic components with the method described in Section 2.5.3. The colour yield and the fastness properties were assessed in order to compare the dyeing behaviour of the pre-formed dyes and *in-situ* dyeing on PLA fabrics. In addition, the difference between the dyeing behaviour on PLA fabrics and PET fabrics is also reviewed.

5.1.1 Investigation of the Optimum Temperature of *In-situ* Dyeing on PLA Fabrics

As the glass transition temperature (T_g) of PLA fibres is 55-65℃ and very little dye uptake is observed during dyeing below 80℃ (Yang and Huda, 2003b), three temperatures (80℃, 90℃, 100℃) are selected to investigate the optimum temperature. The colour yield at 2% o.m.f. of the dyed PLA fabrics was measured. Since the PLA fibres experience substantial strength loss at high dyeing temperature, the strength loss of the dyed fabrics was also measured in order to decide the optimum temperature, at which the dyed fabrics give good colour yield without affecting the physical properties. The strength loss is calculated according to:

$$\text{Strength loss (\%)} = (1-S_1/S_0) *100$$

where S_0 and S_1 are the tearing strength values (N) of the fabrics before and after dyeing, respectively.

It is presented in Figure 5.1 that the highest colour yield is achieved at 100℃ due to higher dye exhaustion at higher temperatures. At higher temperature, the fibres have higher chain mobility and thus create more accessible spaces for the dyes. The dye particles in the dyebath are also smaller at higher temperature and creates higher effective dye surface area in the dyebath (Yang and Huda, 2003b). Although the strength loss also increases with increasing dyeing temperature, as shown in Figure 5.2, the difference between the dyeing at 90℃ and 100℃ is relatively small. Therefore, it is suitable to carry out the *in-situ* dyeing at 100℃, which gives the highest colour yield with reduced strength loss. It also shows that the type of the dyes does not have significant influence on the strength loss of the dyed fabrics. Therefore, the average of all the dyed fabrics at a certain dyeing temperature were used for analysis below.

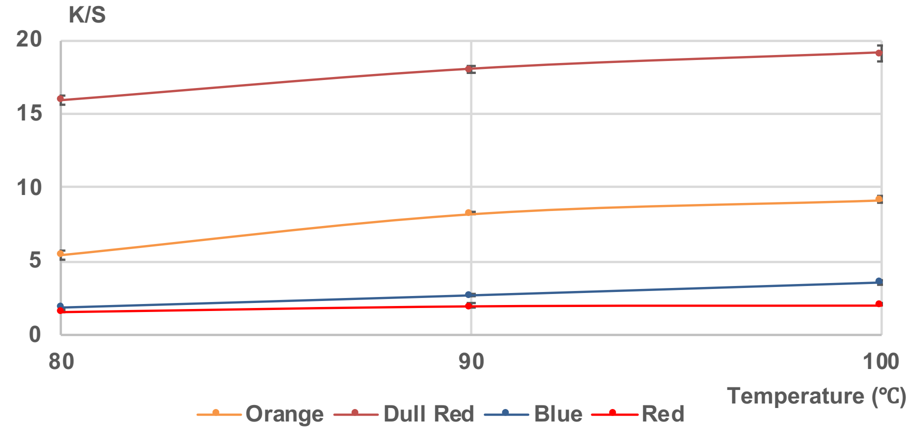


Figure 5.1 Influence of Temperature on Dyeing Behaviours of *In-situ* Dyeing at 2% o.m.f. on PLA Fabrics

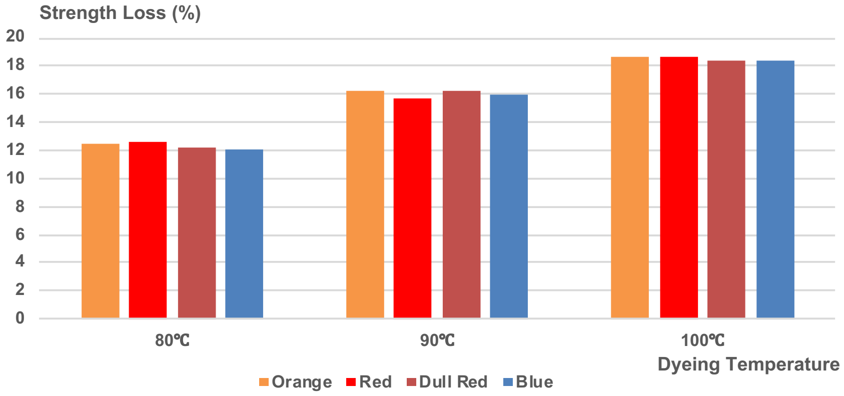


Figure 5.2 Strength Loss of the PLA Fabrics Dyed with *In-situ* Dyeing at 2% o.m.f.

5.1.2 Shade Build-up *vs* Concentration of Pre-formed Dyes and *In-situ* Dyeing on PLA Fabrics

The PET fabrics were dyed at different concentrations with both pre-formed dyes and *in-situ* dyeing. The colour of the dyed fabrics was measured with spectrophotometer and the K/S values calculated from the reflectance of the dyed fabrics at the wavelength of maximum absorption (λ_{max}) were used to present the colour yield of the dyed fabrics.

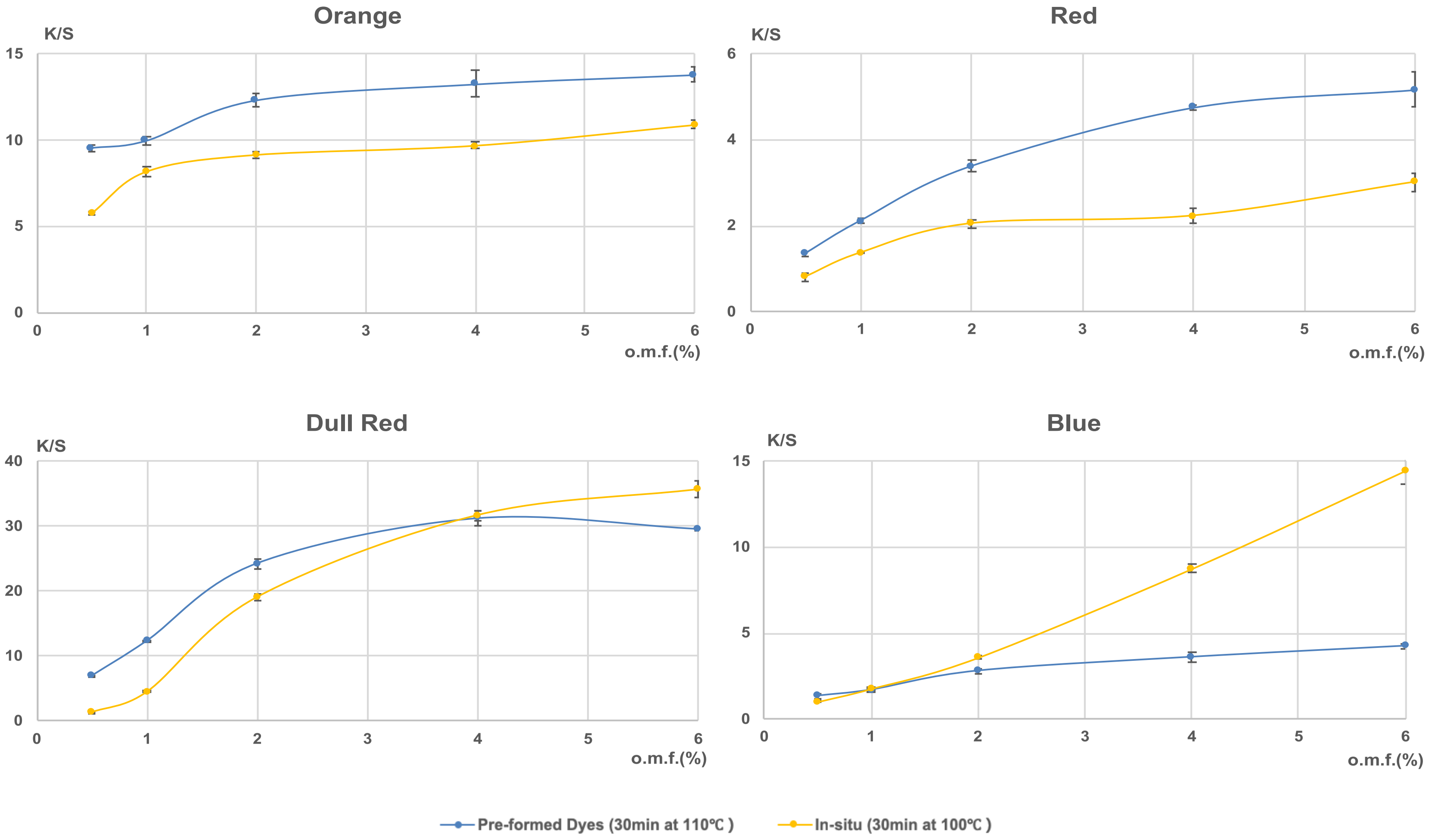


Figure 5.3 Shade Build-up of Pre-formed Dyes and *In-situ* Dyeing on PLA Fabrics

As illustrated in Figure 5.3, the orange and red pre-formed dyes applied at 110℃ give slightly higher colour yield than *in-situ* dyeing at 100℃ for all depths of applicant. The difference is relatively small for the orange dye. As for the red dye, the difference is small at low concentration but becomes larger as concentration goes up. On the other hand, the colour yield of the *in-situ* dyeing with dull red and blue dyes is lower than that of pre-formed dyes at lower concentration, but becomes higher with increasing concentration.

For the pre-formed dyes, the obtained shades are generally pale comparing with the dyeing on PET. This is within expected as the PLA only has moderate affinity for disperse dyes, which is high enough to create good colours but a considerable amount of dyes still remains in the dyebath (Scheyer and Chiweshe, 2001). The dull red dye gives the highest K/S values, while the blue dyes gives the lowest, which indicates that the dull red dye has the highest exhaustion on PLA fabrics and the blue dye has the lowest. Although many researches about the exhaustion of disperse dyes on PLA fabrics have been carried out, the relationship between dye structure classes and exhaustion values is still not conclusive. It is presumed that the low exhaustion of the blue and red dye is due to the relatively large molecular weight, which causes the low diffusion rate of the dyes inside the fabrics. The orange dye has the lowest molecular weight and is supposed to diffuse more readily than the dull red dye. However, the colour yield of the dull red dye is higher than the orange dye. This is presumably due to the same reason as discussed in 2.2.1. that the dull red dye molecule is more planar than the orange dye as the *o*-methyl group in the orange dye clashes sterically with the lone pair of electrons on one of the azo nitrogen atoms and is thus forced to rotate out of a planar conformation (Christie, 2015).

The *in-situ* dyeing with orange and dull red dyes give lower colour yield than the pre-formed dyes. One of the possible reasons is that the reaction rate of the precursors is low and fewer dyes may be formed during the dyeing cycle. The *in-situ* dyeing of the orange and red dyes gives good colour yield on PET. Since the coupling reaction rate is mainly dependent on pH (Chattopadhyay, 2011), the different internal pH of PET and PLA may cause different reaction rates of the dye precursors. The other possible reason is the low exhaustion of the precursors on PLA fabrics. As the *in-situ* dyeing of the blue and dull red dye works well, the coupling components should have good exhaustion on PLA. It is more likely to be the diazoamine 1, which is used to form orange and red dye, that has low exhaustion on PLA fabrics. The *o*-methyl group in the diazoamine 1 clashes sterically with the lone pair of electrons on one of the azo nitrogen atoms and is thus forced to rotate out of a planar conformation, and thus limits the exhaustion on PLA fabrics.

For the *in-situ* dyeing with the blue and dull red dye, the lower colour yield at low concentration (below 4% for dull red dye and 2% for blue dye) is probably due to the low reaction rate at low concentration. As the concentration increases, the reaction rate is high enough to achieve higher colour yield than the pre-formed dyes. Moreover, as the molecular weight of the precursors is smaller, they diffuse more readily inside the fibres than the larger pre-formed dyes and thus give higher colour yield.

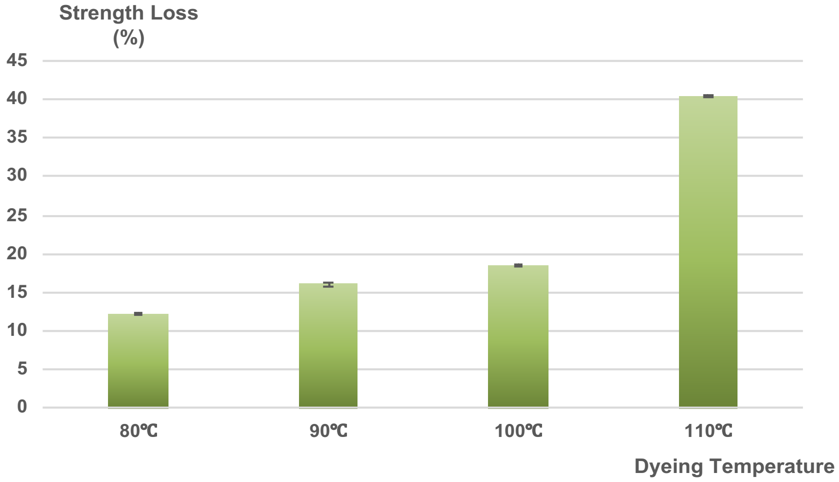


Figure 5.4 Influence of Temperature on Strength Loss of PLA fabrics dyed at 2% o.m.f.

As one of the largest problems in PLA dyeing, strength loss of the dyed fabrics is also considered. As shown in Figure 5.4, the strength loss of the fabrics dyed with the pre-formed dyes at 110℃ is much more substantial than that of *in-situ* dyeing at 100℃ due to hydrolytic cleavage at higher temperature.

Overall, the *in-situ* dyeing on PLA fabrics gives a slightly lower or similar colour yield compared with the dyeing with the pre-formed dyes but causes much lower strength loss of the dyed fabrics.

5.1.3 Comparison of the Colour Properties of PET and PLA Dyeing

Dyed PET and PLA fabrics with similar colour yield (K/S at λ_{max}) are selected to compare the colour properties of the dyeing on PET and PLA fabrics. The reason to use the fabrics with similar colour yield instead of the same initial dye concentration in the dyebath is due to the different exhaustion and potentially level of dye synthesis on these two substrates. With the same initial dye concentration, in all cases more dyes would diffuse into the PET fabrics than PLA as a deeper shade is obtained.

The colour properties including the CIE L*a*b* data and the reflectance spectra of the dyeing on PLA and PET fabrics are compared to investigate the difference of the dye shades on different substrates, as shown in Figure 5.5 and Table 5.1.

For the orange dye, both the pre-formed dyes and *in-situ* dyeing have very similar shades on these two substrates, with the same λ_{max} and similar L*a*b* values. All the other dyes show hypsochromic (maximum absorption at a shorter wavelength) shades on PLA fabrics, with both pre-formed dyes and *in-situ* dyeing. It is proposed that the dyeing on PLA normally gives a different tone on PLA, which is hypsochromic and brighter compared to PET due to the lower refractive index of PLA (Yang and Huda, 2003a; Avinc and Khoddami, 2010). Another reason for the hypsochromic shift is the solvatochromic effect

(Suesat *et al*., 2011). The fibre is considered as a solvent with the dye molecules dissolving in. As PLA is less polar, poorer stabilisation of the dye's excited electronic state creates a higher energy gap between the excited state and the ground state of the dye molecules and hence causes a hypsochromic shift comparing with PET.

It is also observed that the dyeing is lighter (greater L* value) on PLA fabrics than PET (Choi and Seo, 2006). The red dyes tend to be yellower (greater b* value) on PLA than PET, while the blue dyes are redder (greater a* value) (Choi and Seo, 2006; Choi *et al*., 2007). Most of the pre-formed dyes, with exception of the orange dye, conforms to the same rules. For the *in-situ* dyeing, the red dye and blue dyes gives darker shades (lower L* values) on PLA then PET, particularly the red dye. The L*a*b* values are similar to the trend of the pre-formed dyes, with yellower hue for the red dye and redder for the blue dye on PLA fabrics then PET.

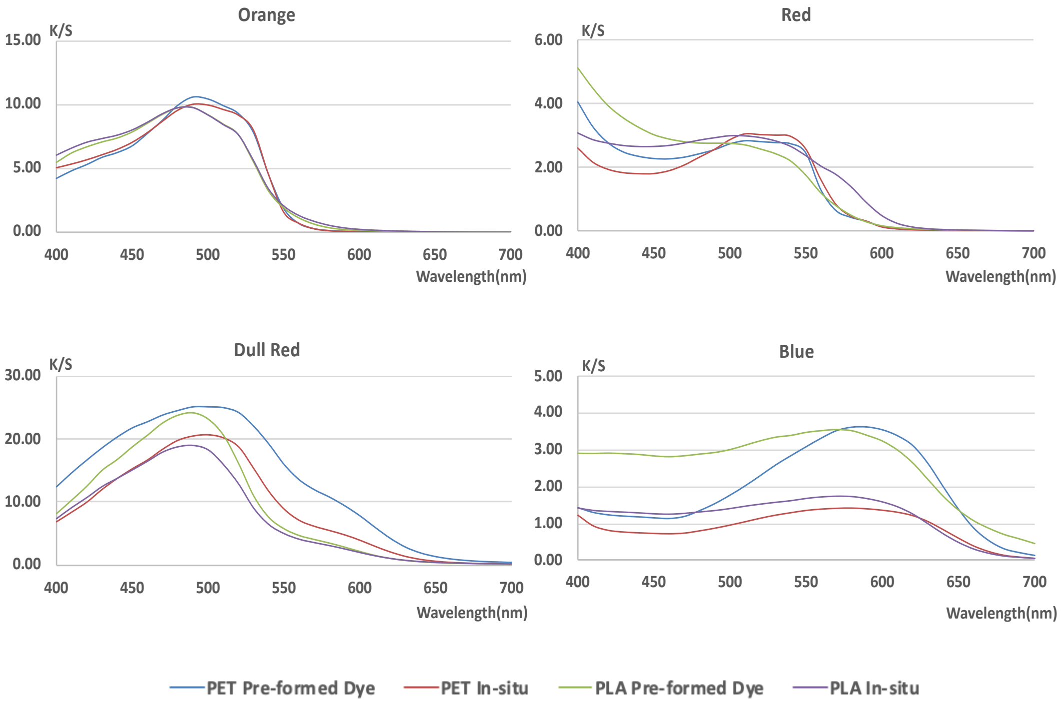


Figure 5.5 K/S Curves of the Dyeing on PET and PLA Fabrics

Table 5.1 Colour Properties of the Dyeing on PET and PLA Fabrics

Dye	Fabric	L*	a*	b*	λ_{max} (nm)
Orange (Pre-formed Dye)	PET	63.11	49.04	57.31	490
	PLA	62.06	45.82	59.49	490
Orange (*In-situ*)	PET	63.78	48.21	54.98	490
	PLA	60.44	41.59	53.28	490
Red (Pre-formed Dye)	PET	62.47	44.86	24.46	530
	PLA	64.35	34.69	27.40	500
Red (*In-situ*)	PET	60.40	44.86	17.53	530
	PLA	54.58	36.71	18.67	510
Dull Red (Pre-formed Dye)	PET	24.20	24.15	12.67	500
	PLA	37.30	33.99	32.35	490
Dull Red (*In-situ*)	PET	31.68	30.47	18.71	500
	PLA	38.03	30.17	29.74	490
Blue (Pre-formed Dye)	PET	44.85	4.38	-19.27	580
	PLA	45.70	6.18	-5.42	570
Blue (*In-situ*)	PET	53.99	4.43	-13.17	580
	PLA	52.70	6.38	-3.56	570

5.1.4Fastness Properties

The fastness test, including rub, wash, light and dry heat fastness, was carried out with the fabrics after clearing. The data of 2% o.m.f. was used for analysis. Three replicates were carried out for each test.

5.1.4.1 Rubbing fastness

Wet and dry rubbing fastness properties of the dyed fabrics in both warp and weft directions were measured. The average of the two directions were used for the analysis. The rubbing fastness results of the fabrics dyed at 2% o.m.f. are shown in Table 5.2.

Table 5.2 Rubbing fastness of the PLA Fabrics Dyed at 2% o.m.f.

Colour	Pre-formed Dye		*In-situ* Dyeing	
	Dry	Wet	Dry	Wet
Orange	3	3	3	3
Red	3	3	3	3
Dull Red	4/5	4	4/5	4
Blue	3	3/4	3/4	4

The rubbing fastness of the dyed PLA fabrics is moderate to good. For the orange and red dyes, the pre-formed dyes and the *in-situ* dyeing gives the same levels of rubbing fastness, with the dry and wet rubbing fastness all rated as 3. The dull red dye gives good rubbing fastness. The wet rubbing fastness is lower than the dry rubbing fastness. As stated in 3.2.2.1, the wet rubbing fastness is generally lower than the dry rubbing fastness due to the dissolving of the dyes in the water and the increasing friction caused by the swelling of the cotton cloth. The *in-situ* dyeing of the dull red dye has identical rubbing fastness as the pre-formed dye. For the blue dye, the rubbing fastness is only moderate. Like the dyeing on PET, the wet rubbing fastness is higher than the dry rubbing fastness. The *in-situ* dyeing of the blue dye is higher than the pre-formed dyes. This is probably because the blue dye has relatively large molecular size. The precursors with smaller molecular sizes diffuse more readily into the deeper layer of the fabrics compared with the larger pre-formed dye. Once the dye is formed in the deeper layer of the fabric, it is not easily rubbed off the fabrics and hence exhibits better rubbing fastness.

Compared with PET fabrics dyed at 2% o.m.f., the rubbing fastness of the dyeing on PLA fabrics is lower. This is expected as the dyeing on PLA normally exhibits lower rubbing fastness than PET (Yang and Huda, 2003b). The difference between the rubbing fastness with *in-situ* dyeing on these two substrates is smaller than with the pre-formed dyes. This is because the precursors can diffuse into deeper layer of the fibres due to their smaller molecular sizes and hence shows less decrease in the rubbing fastness.

As with PET, the rubbing fastness of the dyeing on PLA is not simply related to the molecular size of the dyes. The dull red dye has a small molecular size but exhibit the highest rubbing fastness. The dull red and the blue dye shows better rubbing fastness because of the longer conjugated chain with the presence of the extra aromatic ring in diazoamine 2, which is proposed to increase the substantivity of the dye and hence increase the rubbing fastness (Maradiya and Patel, 2001).

5.1.4.2 Washing fastness

The washing fastness tests were carried out with the fabrics dyed with pre-formed dyes and *in-situ* dyeing. The staining results of the multifibre adjacent fabrics and the shade change of the dyed fabrics were measured. Table 5.3 shows the results of the dyed fabrics at 2% o.m.f.

The orange and dull red dyes give acceptable fading results, with the same colour change results for the dyeing with pre-formed dyes and *in-situ* dyeing. For the red dye, the staining results are acceptable while the shade change results are not good. The *in-situ* dyeing gives slightly lower fastness than the pre-formed dye. For the blue dye, the *in-situ* dyeing gives better shade change results than the pre-formed dyes while the staining results are the same. This is probably because the higher colour yield of the *in-situ* dyeing. With the same amount of dyes washed off, the fading of the dyeing with pre-formed dyes is more obvious.

Table 5.3 Washing fastness of the PLA Fabrics Dyed at 2% o.m.f.

Colour		Diacetate	Bleached Cotton	Polyamide	Polyester	Acrylic	Wool	Shade Change
Orange	Pre-formed Dye	2	3	1/2	2/3	4	2/3	4
	In-situ Dyeing	2	3	1/2	2/3	4	2/3	4
Red	Pre-formed Dye	3/4	4/5	2/3	4	4/5	4/5	3/4
	In-situ Dyeing	3/4	4/5	2/3	3/4	4/5	4/5	3
Dull Red	Pre-formed Dye	2	4	1/2	3	4	3	4
	In-situ Dyeing	2/3	4	1/2	3/4	4	3/4	4
Blue	Pre-formed Dye	3/4	4/5	2	4	4	4/5	2/3
	In-situ Dyeing	3/4	4/5	2	4	4	4/5	3/4

The washing fastness of most of the dyeing on PLA is 1/2 or 1 point lower than the equivalent dyeing on PET, which is the normal case for PLA dyeing (Yang and Huda, 2003b). Only the blue pre-formed dyes show notably lower washing fastness on PLA than PET. This may be due to the low affinity of the blue dye to the PLA fabrics. The dyes are more easily washed off and hence give low washing fastness.

The washing fastness of disperse dyes generally increases with molecular weight (Giles *et al*., 1982). However, the dyeing on PLA shows opposite results. The orange and dull red dyes with lower molecular weight gives better washing fastness while the red and blue dyes with higher molecular weight gives lower results. This is probably because the dyeing of PLA is carried out at a relatively low temperature (110℃ for the pre-formed dyes and 100℃ for the *in-situ* dyeing) and the dyes with larger molecular size cannot penetrate into the deeper layer of the fabrics at such low temperature and can only stay at the sub-surface, resulting in lower washing fastness.

5.1.4.3 Light Fastness

The dyed PLA fabrics were exposed to light from a Xenon lamp for 24 hours. The shade change of the dyed fabrics is compared with the blue wool standard and rated accordingly. Table 5.4 shows the light fastness results of the dyed PLA fabrics.

Table 5.4 Light Fastness of the PLA Fabrics Dyed at 2% o.m.f.

Colour	Pre-formed Dye	*In-situ* Dyeing
Orange	2	3
Red	3	4
Dull Red	2	2
Blue	2	2

The light fastness of the dyeing on PLA is poor due to the small molecular size of the dyes. The light fastness of the dyeing on PLA is the same as that on PET. This indicates that the interaction between the dyes and fibres and the agglomeration of the dyes are similar on these two substrates, leading to the same light fastness results even though the shades are different on different substrates. The red dye gives the highest light fastness due to the presence of the methyl group, which favours to form compact aggregates of dyes, and the intermolecular hydrogen bonds, which helps to increase the light fastness (Giles *et al*, 1982). The *in-situ* dyeing of the orange and red dyes give higher light fastness than the pre-formed dyes, while the dull red and blue dyes give the same results for the *in-situ* dyeing and pre-formed dyes. This is due to the presence of the electron-attracting *p*-Cl substituent in diazoamine 1 used to form orange and red dye, which is proved to increase the light fastness in azoic dyeing (Desai and Giles, 1949).

5.1.4.4 Dry Heat Fastness

Since the PLA fibre would degrade at high temperature, the dry heat fastness was measured at 150℃. As illustrated in Table 5.5, the dry heat fastness of the dyeing on PLA is relatively low due to the small molecular size of the dyes used. The *in-situ* dyeing gives very similar dry heat fastness as the pre-formed dyes. Only the *in-situ* dyeing of the blue dye gives a higher dry heat fastness than the pre-formed dye.

Table 5.5 Dry Heat Fastness of the PLA Fabrics Dyed at 2% o.m.f.

Colour	Pre-formed Dye	*In-situ* Dyeing
Orange	2/3	2/3
Red	3	3
Dull Red	3	3
Blue	3	4

The dry heat fastness of the dyeing on PLA fabrics is mainly dependent on the molecular size of the dyes. The smallest orange dye gives the lowest dry heat fastness, while the largest blue dye shows the highest. The fact that the *in-situ* dyeing of the blue dye shows better dry heat fastness than the pre-formed dye indicates that the physical position of the dyes can also affect the dry heat fastness.

The dry heat fastness of the dyed PLA fabrics is the same as the results of the PET fabrics. This further proves that the molecular size is the main factor that determines the dry heat fastness. The substrate does not have significant influence on dry heat fastness.

5.2 Dyeing with Mixtures

The *in-situ* dyeing was carried out with the mixtures of the synthesised azoic components on PLA fabrics. The dyeing behaviour is assessed and compared with that on PET fabrics.

5.2.1 Colour Gamut of the Dyeing with Mixtures

The colour gamut of the *in-situ* dyeing, including individual colour and the four possible mixtures, on PLA fabrics is shown in Figure 5.6. As with PET, the dyeing on PLA does not include any green colour (a* value below 0) and only a limited range of blue colour (b* value below 0) is obtained. The dyeing on PLA fabrics gives a slightly smaller range of colours comparing to PET. The maximum a* and b* value obtained on PLA is lower than PET. This is mainly due to the low dye uptake of the red and orange dyes on PLA. The minimum b* value obtained on PLA is higher than PET, which is due to the higher colour yield of the blue dye on PLA. The minimum a* value is similar on PET and PLA. The lightness (L*) range of the dyed PLA and PET fabrics is also very close.

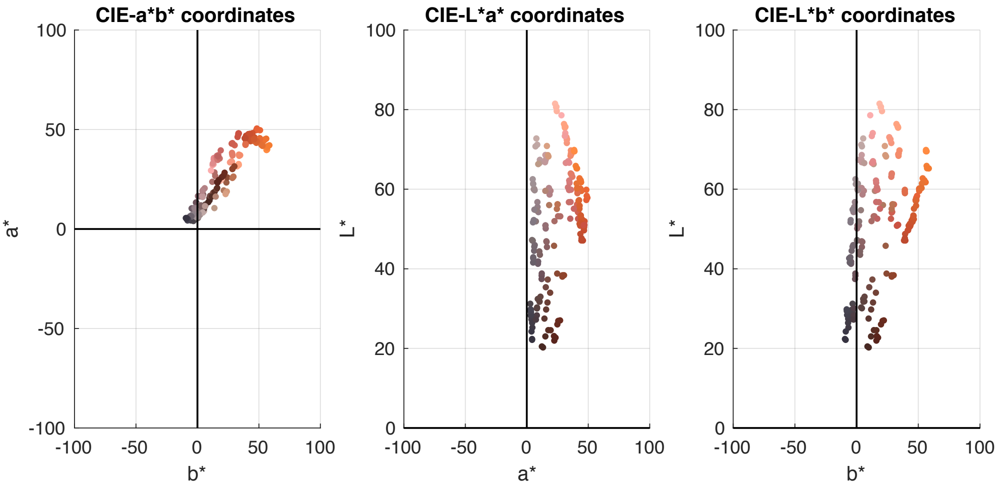


Figure 5.6 Colour Gamut of *In-situ* Dyeing on PLA Fabrics

5.2.2 Colour Prediction

The colour prediction of the dyeing on PLA fabrics was carried out with the same method as that on PET. As the colour prediction of the dyeing with pre-formed dyes mixtures is relatively accurate on PET fabrics, only one of each combination with pre-formed dyes was carried out for the dyeing on PLA. As shown in Table 5.6, the difference between the prediction and measurements of the dyeing on PLA fabrics is also quite small. Therefore, the colour prediction method can also be used for the dyeing with pre-formed dyes on PLA fabrics.

Table 5.6 Colour Prediction and Measurements of the Dyeing with the Mixtures of Pre-formed Dye

	Prediction			Measurement		
	L*	a*	b*	L*	a*	b*
O/DR*	23.44	24.53	21.75	25.57	25.78	22.04
B/R	50.89	15.01	3.63	49.77	12.87	2.59
B/DR	29.24	22.18	20.36	28.96	21.64	18.44
O/R	74.53	31.90	40.60	75.91	33.50	43.30

* O: orange; DR: dull red; B: blue; R: red

The results of the prediction and measurements of the *in-situ* dyeing on PLA fabrics were compared in Figure 5.7. The prediction does not work well for the *in-situ* dyeing on PET due to the different reactivity between the components and the different exhaustion rates of the components. However, the difference between the prediction and measurements on PLA is relatively small. The shades obtained with orange/dull red and orange/red mixtures are very close to the prediction. For the dyeing with blue/red and blue/dull red mixtures, the a* values are close to prediction while the b* values are slightly lower, which indicates that more blue dyes were formed during the dyeing. This is the same case on PET. Therefore, it is presumed that the diazoamine 2 and naphthol AS, which are used to form the blue dye, have higher reactivity than the other

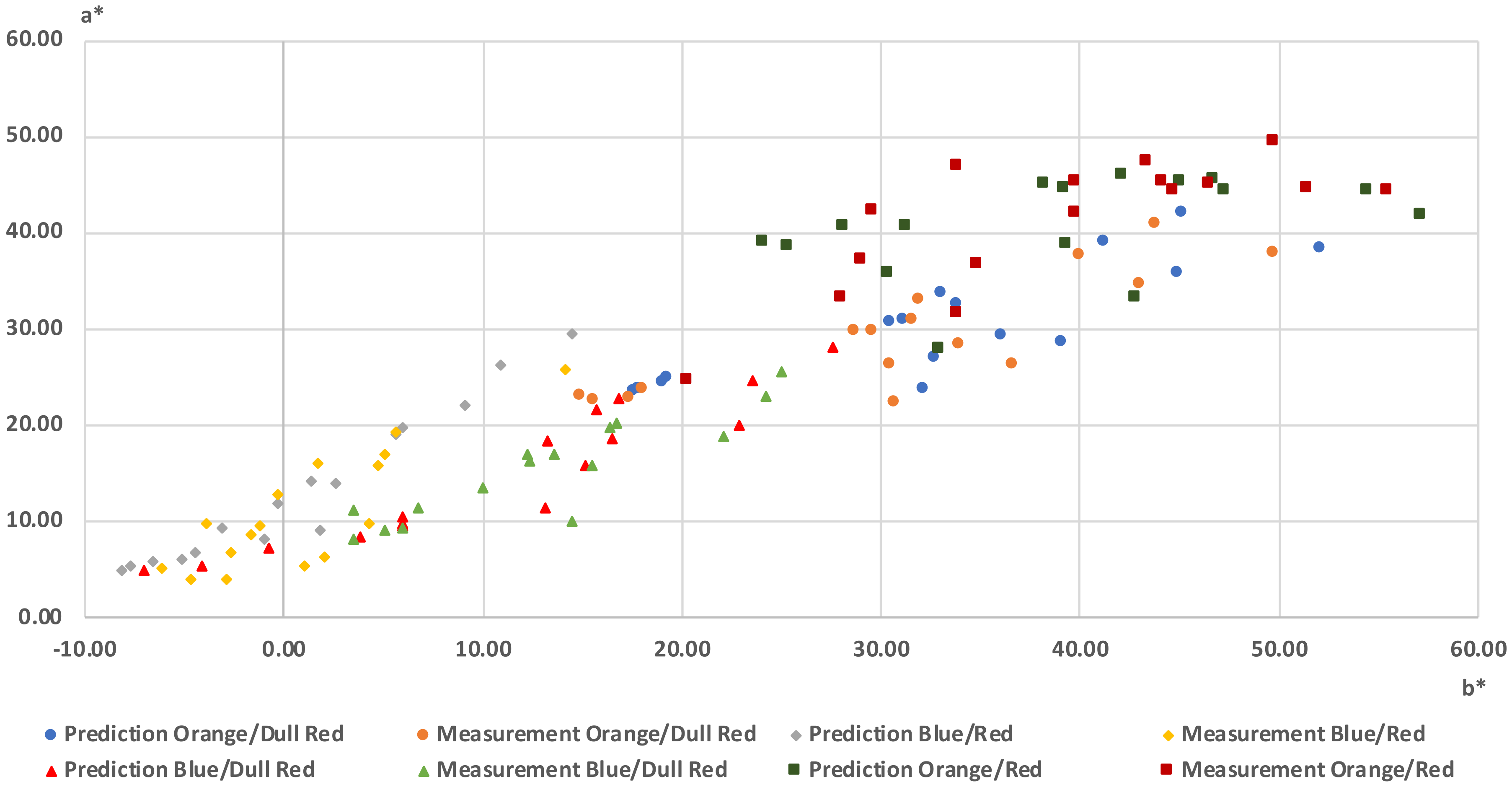


Figure 5.7 Colour Prediction and Measurements of the *In-situ* Dyeing with Mixtures

combinations.

The colour prediction method works better for the dyeing on PLA than PET. However, there is still deviation for some combinations due to the different reaction rate and exhaustion rate. A new colour prediction method is also needed for the *in-situ* dyeing on PLA fabrics.

5.2.3 Fastness Properties

The fastness properties of the *in-situ* dyeing with mixtures on PLA fabrics was assessed and compared with that on PET fabrics in order to investigate the different dyeing behaviour on different substrates.

5.2.3.1 Rubbing fastness

Both dry and wet rubbing fastness of the dyed PLA fabrics were measured. The results are shown in Table 5.7.

For the dyeing with orange/dull red and blue/red mixtures, the rubbing fastness is moderate to good and is similar to the corresponding individual dyes. The wet rubbing fastness is the same or higher than the dry rubbing fastness.

For the orange/red mixtures, the rubbing fastness of the dyeing with the mixtures is higher than the individual dyes. This indicates that the interactions between the two dyes, including the hydrogen bonds formed between the carbonyl group in the red dye and the hydroxyl group in the orange dye and the aromatic interactions, help to increase the aggregation between the dyes and hence improve the rubbing fastness.

Table 5.7 Rubbing fastness of the *In-situ* Dyeing with Mixtures on PLA

Ratio	Orange/Dull Red		Orange/Red		Blue/Red		Blue/Dull Red	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
100/25	2/3	2/3	3	3/4	2/3	2/3	3	3
100/50	2	2/3	3	3/4	2/3	2/3	1/2	2
100/75	2	2/3	3	3/4	2/3	2/3	1/2	1/2
100/100	2	2	3	3	2/3	2/3	1/2	1/2
75/25	3/4	4	3/4	4	3	3/4	2/3	3
75/50	3/4	3/4	4	4	3/4	3/4	2	2/3
75/75	3	3	3	3	4	4/5	1/2	2
75/100	2	2	3/4	3/4	2/3	3	1/2	1/2
50/25	3	3/4	4/5	4/5	4/5	4/5	4	4
50/50	3	3/4	4/5	4/5	4/5	4/5	3	3/4
50/75	3	3	4	4	4	4	2/3	3
50/100	2	2/3	3	3/4	2/3	3	2	2/3
25/25	4	4	5	5	4/5	5	4/5	4/5
25/50	3/4	4	4/5	4/5	4/5	5	3/4	4
25/75	3	3/4	4	4	4/5	4/5	3/4	3/4
25/100	2	2/3	3/4	3	3	3/4	2/3	3

On the other hand, the blue and the dull red dyes both give relatively good rubbing fastness when dyeing alone. However, the rubbing fastness of the dyeing with mixtures is poor, particularly when the concentration is high. This is probably due to the high colour yield of the *in-situ* dyeing with these two dyes at high concentration. With more dyes formed in the fabrics during dyeing, the possibility of more dyes coming off during rubbing is increased and hence causing poor rubbing fastness at high concentration.

The *in-situ* dyeing with individual dyes gives lower rubbing fastness on PLA than PET. When dyeing mixtures, the difference between the rubbing fastness on PLA and PET is small. Most of the dyeing gives very similar results on different substrates. This is probably due to the higher concentration of the dyes when dyeing with mixtures, leading to more dye-fibre interactions and hence increase the rubbing fastness on PLA.

5.2.3.2 Washing fastness

The washing fastness was assessed with both staining and fading results. Only the fading results are used here for analysis of the washing fastness properties of the *in-situ* dyeing with mixtures on PLA fabrics as all staining results were in line with those expected from the below. The results are show in Table 5.8.

The washing fastness on PLA fabrics is relatively poor and is generally lower than that with the individual dyes due to the increasing dye concentration in the fabric. The colour change results are all rated below or equal to 4. The dyeing with all the combinations gives similar washing fastness results. The washing fastness decreases as the concentration increases. The orange and dull red dyes give the highest washing fastness as individual dyes. However, the dyeing with the mixture of orange/dull red dyes give the lowest washing fastness, particularly when the concentration of the dull red dye is high. This is probably due to the increase in colour yield of the dull red dye at high concentration (above 4% o.m.f.) which causes decrease in washing fastness.

The washing fastness of the *in-situ* dyeing with individual dyes on PLA is 1/2 to 1 point lower than that on PET. The difference is more significant for the *in-situ* dyeing with mixtures. This is due to the lower affinity of the components and the formed dyes to PLA than PET.

Table 5.8 Washing fastness of the *In-situ* Dyeing with Mixtures on PLA

Ratio	Orange/Dull Red	Orange/Red	Blue/Red	Blue/Dull Red
100/25	2/3	2/3	2/3	2/3
100/50	2/3	2/3	2/3	2/3
100/75	2	2/3	2/3	2/3
100/100	2	2	2/3	2
75/25	4	4	3/4	4
75/50	3	3	4	4
75/75	2	2	4	4
75/100	1	1/2	3	3/4
50/25	4	4	4	4
50/50	3/4	3/4	4	4
50/75	2	2	3/4	3/4
50/100	2	1/2	2/3	2/3
25/25	3/4	3/4	4	4
25/50	3	3/4	4	4
25/75	2	2	3/4	3/4
25/100	1/2	1/2	2	2

5.2.3.3 Light Fastness

The PLA fabrics dyed with mixtures are exposed to light from a Xenon lamp for 24 hours. The fading is compared with the blue wool standard and rated accordingly, as shown in Table 5.9.

Table 5.9 Light Fastness of the *In-situ* Dyeing with Mixtures on PLA

Ratio	Orange/Dull Red	Orange/Red	Blue/Red	Blue/Dull Red
100/25	4	2	5	3
100/50	4	2	5	4
100/75	5	3	4	4
100/100	6	3	4	4
75/25	3	2	4	4
75/50	3	2	4	4
75/75	4	2	4	4
75/100	4	2	4	5
50/25	3	2	3	2
50/50	3	2	2	3
50/75	3	2	2	3
50/100	4	2	3	4
25/25	3	2	2	2
25/50	3	2	2	2
25/75	3	3	2	3
25/100	4	4	4	4

As expected, the light fastness of the *in-situ* dyeing with mixtures on PLA fabrics is overall poor due to the relatively small molecular size of the dyes. The dyeing with the mixtures generally gives higher light fastness than individual dyes presumably due to the higher concentration of dyes applied. The only exception is the dyeing with the mixtures of orange/red dyes, which gives lower light fastness than the individual dyes. This is also observed for the *in-situ* dyeing with the mixtures of orange/red dyes on PET. The light fastness of the *in-situ* dyeing with mixtures does not show significant difference on these two substrates.

5.2.3.4 Dry Heat Fastness

The dry heat fastness of the dyed PLA fabrics treated at 150℃ is shown in Table 5.10.

Table 5.10 Dry Heat Fastness of the *In-situ* Dyeing with Mixtures on PLA

Ratio	Orange/Dull Red	Orange/Red	Blue/Red	Blue/Dull Red
100/25	4	3	4	3/4
100/50	4	3	4	3/4
100/75	3/4	3	4	3/4
100/100	2/3	3/4	4	2
75/25	4/5	2/3	4	3/4
75/50	4	2/3	4	3
75/75	3/4	2/3	4	2/3
75/100	3/4	3	4	2/3
50/25	4	2	4/5	4
50/50	3/4	2	4/5	4
50/75	3/4	2	3/4	2/3
50/100	3	3	2	2/3
25/25	4/5	1/2	4/5	3/4
25/50	4	1/2	4/5	3/4
25/75	4	3	3	4
25/100	3/4	3	2	4

Most of the dyeing with mixtures gives slightly higher dry heat fastness than the individual dye. It is mainly due to the hydrogen bonds formed between dyes and increases the aggregates and reduces the diffusion out of the fibre, hence increase the dry heat fastness (Salvin, 1966). However, when dyeing with the mixtures, only the orange/red mixtures show increasing fastness as the concentration goes up. The other combinations all give opposite results. This indicates that the increased aggregation between the dyes can only improve the dry heat fastness to a certain extend. With higher concentration, the possibility of more dyes coming out of the fibre increases and hence leading to decreased dry heat fastness.

As with the individual dyes, the dry heat fastness of the *in-situ* dyeing with mixtures on PLA is similar to that on PET.

5.3 Conclusions

The aim of this chapter was to investigate the dyeing behaviour of the *in-situ* dyeing on PLA fabrics compared with conventional dyeing and the optimum condition for the dyeing process. The difference between the dyeing behaviour on PLA and PET substrates was also investigated.

It has been demonstrated that the optimum temperature for *in-situ* dyeing on PLA is 100℃, at which the colour yield is relatively high and the strength loss of the dyed fabrics is not substantial. At 100℃, the *in-situ* dyeing gives a relatively good colour yield compared with the conventional dyeing with the pre-formed dyes at 110℃, and causes much lower strength loss of the fabrics during dyeing. The fastness properties of the *in-situ* dyeing are the same or higher than that with the pre-formed dyes.

Compared with the *in-situ* dyeing on PET fabrics with the same dye concentration, the dyeing on PLA gives a lower colour yield. Most of the shades on PLA are hypsochromic and darker than those on PET. The rubbing fastness and washing fastness of the *in-situ* dyeing on PLA is generally 1/2 or

1 point lower than that on PET. The light fastness and dry heat fastness do not show great difference on different substrates. The colour gamut obtained with *in-situ* dyeing on PLA is smaller than that on PET.

When dyeing with mixtures, the colour prediction method works well for the dyeing on PLA with pre-formed dyes. The prediction for the *in-situ* dyeing on PLA works better than PET but still needs improvement with consideration of the different reactivity and the exhaustion rate of the components.

Chapter 6

Supercritical CO_2 Dyeing of Polyester Fabrics with *In-situ* Dye Synthesis

Compared with conventional aqueous dyeing, supercritical CO_2 ($scCO_2$) dyeing has many advantages, such as environmental impact related to water consumption and pollution, simpler dye formulation, short dyeing time, elimination of drying process, etc (Bach *et al*., 2002). The dissolving power of $scCO_2$ towards disperse dyes due to its low polarity and the swelling and plasticisation action towards hydrophobic polymers makes it suitable for the coloration of polyester (Banchero, 2012). As the precursors used for *in-situ* dye synthesis possess similar properties as disperse dyes, it is assumed that the precursors have appropriate solubility in $scCO_2$ and the dyeing of polyester fabrics *through in-situ* dye synthesis can also be carried out in $scCO_2$. Therefore, the dyeing behaviour, including colour yield and fastness properties, of the *in-situ* dyeing in $scCO_2$ is investigated and compared with the results of the *in-situ* dyeing in water in this chapter.

6.1 Supercritical CO_2 Dyeing of PET

The dyeing of PET fabrics with disperse dyes in $scCO_2$ can be carried out at lower temperature than conventional high temperature dyeing in water and achieve similar colour and fastness properties (Rita De Giorgi *et al*., 2000; Hou *et al*., 2010). This is due to the plasticisation effect leading to the decrease of the glass transition temperature (T_g) of PET (Von Schnitzler and Eggers, 1999; Park *et* al., 2010). The dyeing of PET with *in-situ* dye synthesis in $scCO_2$ was carried out with synthesised precursors (2% o.m.f.) at 90℃ and 100℃ for 90 minutes. No auxiliaries were added. The cleaning process after $scCO_2$ dyeing is normally carried out with clean CO_2 at temperature lower than 70℃ (Hou *et al*., 2010). However, due to the limitation of the equipment, the dyed PET fabrics were rinsed with acetone to remove the excess dyes on the surface of the fabrics. The colour of the dyed fabrics was then measured and compared with the PET fabrics dyed through *in-situ* dye synthesis at 100℃ in water with the same concentration.

6.1.1 Colour Difference between the Dyeing in Supercritical CO_2 and in Water

The reflectance spectra of the dyeing in $scCO_2$ and in water are shown in Figure 6.1.

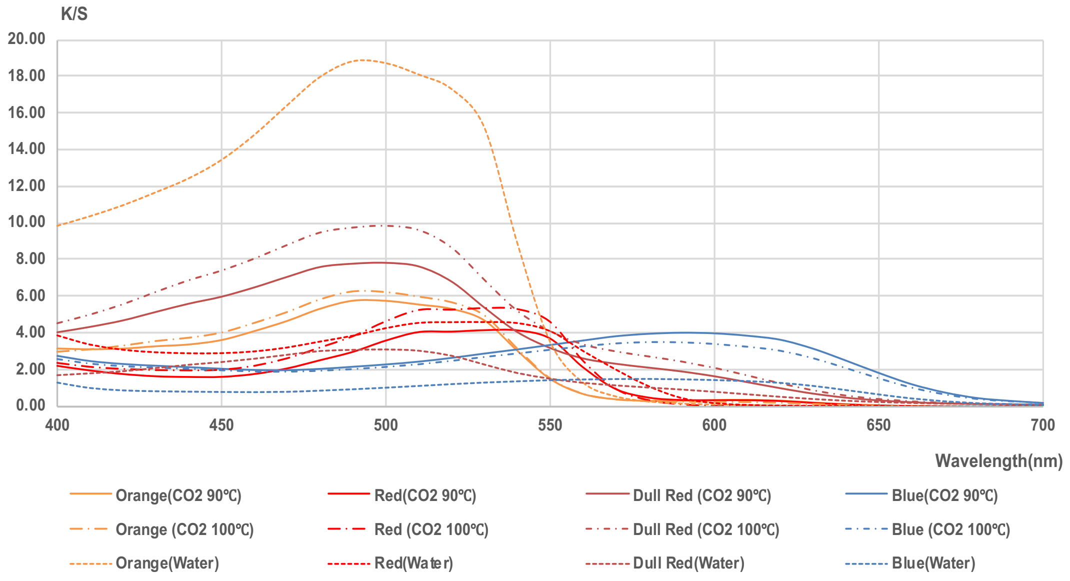


Figure 6.1 K/S Curves of the Dyeing of PET in Supercritical CO_2 and in Water (2% o.m.f.)

For the orange dye, the colour yield of the dyeing in $scCO_2$ is lower than that in water. In $scCO_2$ dyeing, due to plasticisation effect, the T_g of PET is normally shifted down by 20-30℃ (Von Schnitzler and Eggers, 1999; Park *et* al., 2010) leading to increase in the free volume of PET. This promotes the diffusion of the molecules of the precursors and probably also the dyes formed outside the fibres. It is expected that similar colour yield as conventional aqueous dyeing can be achieved at a lower temperature in $scCO_2$. Moreover, the components used to form the orange dye have the lowest molecular weight and are supposed to have the highest diffusion rate. However, the orange dye shows lower colour yield even for the dyeing at 100℃. This can be due to a number of reasons. One possible reason is that the precursors used to form the orange dye have low solubility in $scCO_2$ and hence have limited exhaustion in PET fibres in these dyeing conditions. However, the red and the blue dyes, which are formed with the same components, give good colour yield. Moreover, it was proposed that the presence of -Cl substituent on aromatic compounds can increase the solubility in $scCO_2$ (Draper *et al*., 2000). Therefore, it is presumed that these components should have appropriate solubility in $scCO_2$ and is not responsible for the low colour yield. Another possible reason is the low reaction rate of the components. As the dyebath in aqueous dyeing is slightly acid with the presence of buffer while the $scCO_2$ dyebath does not have any buffer solution. The internal pH of the PET fibres might be different and hence affect the reaction rate. Nevertheless, all the other dyes have good colour yield, which means the reaction rates of these components are not considerably affected. It is presumed that the internal pH of the PET fibre does not change significantly. Therefore, the low reaction rate may not be responsible for the low colour yield of the orange dye. The most possible reason is that the reactivity of the components used to form orange dye is low. It was found that some azoic combinations that have proper reaction efficiency in water may have limited reaction efficiency due to the combined effect of a number of factors, such as solubility in $scCO_2$, basicity of the amine used for the diazotisation reaction and the position of the substituents (Punrattanasin, 2006). This may also be the case for the components used to form the orange dye. Only a small amount of dyes was formed in PET due to the low reactivity, resulting in low colour yield. According to Punrattanasin (2006), the reaction efficiency can be improved by the addition of co-solvent.

For the red dye, the dyeing in $scCO_2$ at 100℃ gives higher colour yield than aqueous dyeing while the $scCO_2$ at 90℃ gives slightly lower colour yield than aqueous dyeing. This indicates that at the same temperature, the diffusion of the components in $scCO_2$ dyeing is higher than that in aqueous dyeing. As the T_g of the PET decreases in $scCO_2$, it is expected that the dyeing in $scCO_2$ at

90℃ should also have a higher colour yield or at least the same colour yield as the aqueous dyeing. The fact that the colour yield of the dyeing in $scCO_2$ at 90℃ is lower indicates that the reactivity of the precursors used to form the red dye is also reduced to a certain extend in $scCO_2$.

As for the dull red and blue dyes, the colour yield of the dyeing in $scCO_2$ is considerably higher than the aqueous dyeing, particularly the dull red dye. This is expected as the diffusion is promoted due to the plasticisation effect and more dyes are formed in PET resulting in higher colour yield. This indicates the possibility to carry out the dyeing at lower temperature and shorter dyeing time. The higher colour yield achieved with the dyeing in $scCO_2$ than in water means that the dyeing equilibrium or the reaction equilibrium is different.

The results show that the *in-situ* dye synthesis is applicable in $scCO_2$. For most dyes, the dyeing in $scCO_2$ can achieve similar colour yield as aqueous dyeing at a lower temperature. However, the results may differ considerably for different components used for the dyeing. The reactivity of the component is an important issue that needs to be considered. In future research, the relationship between the structure of the components and their reactivity will be considered to investigate the components suitable for *in-situ* dyeing in $scCO_2$. Furthermore, the results show the possibility of lower dyeing temperature and shorter dyeing time. The optimum dyeing condition will also be examined in future work.

6.1.2 Comparison of the Fastness Properties of the Dyeing in Supercritical CO_2 and in Water

The fastness properties of the PET fabrics dyed in $scCO_2$ at 90℃ and 100℃ were measured after rinsing with acetone with the same method as the aqueous dyeing. The results are shown in Table 6.1.

The rubbing fastness of the PET fabrics dyed in $scCO_2$ at both 90℃ and 100℃ is excellent. Most of the dyeing is rated as 5 for both dry and wet rubbing fastness. Only the blue dyes are slightly rubbed off and gives a rating of 4/5. The orange and red dyes give better rubbing fastness results in $scCO_2$ than in water. The difference is smaller for the dull red and blue dyes. This is probably because the colour yield of the dull red and blue dyes in $scCO_2$ is higher.

The washing fastness results differ for different dyes. For the orange and red dye, the dyeing in $scCO_2$ at 100℃ gives same or higher results than the dyeing at 90℃. The dyeing in $scCO_2$ gives 1/2 to 1 point higher washing fastness than the equivalent aqueous dyeing. For the blue and dull red dye, the dyeing in $scCO_2$ at 90℃ gives identical results as aqueous dyeing, while the dyeing in $scCO_2$ at 100℃ gives lower results. The higher colour yield of the dull red dye at 100℃ may be the reason that causes the slightly lower washing fastness. However, the blue dye gives lower colour yield and considerably lower washing fastness at 100℃ than that at 90℃. This may be because the rate of the coupling reaction in $scCO_2$ is higher at 100℃ than that at 90℃. Therefore, more precursors formed dyes in the fluid before they diffuse into the fibres at 100℃ and leading to lower colour yield. As the T_g of PET reduces in $scCO_2$, some of the dyes formed in the fluid can diffuse into the fibres at 100℃ and stays in the sub-surface, which causes the lower washing fastness. This is not observed with the orange and red dyes because the reactivity of the precursors used to form orange and red dyes ae limited in $scCO_2$ and only a small amount of dyes was formed in the fluid and diffuse into the sub-surface of the fibres, which does not significantly affect the colour yield and the washing fastness of the dyeing in $scCO_2$ at different temperatures.

The dry heat fastness shows similar trend as the washing fastness. The orange and red dye gives higher dry heat fastness in $scCO_2$ dyeing than in aqueous dyeing. This is presumably due to the lower colour yield of the dyeing with orange and red dyes in $scCO_2$ than that in water. The $scCO_2$ dyeing of the dull red and blue dyes gives similar results as the aqueous dyeing.

Table 6.1 Fastness Properties of the PET Fabrics Dyed through *In-situ* Dye Synthesis in $scCO_2$ and in Water

Dye		Rubbing fastness		Washing fastness (Colour Change)	Dry Heat Fastness	Light Fastness
		Dry	Wet			
Orange	$scCO_2$ 90℃	5	5	4/5	4	3
	$scCO_2$ 100℃	5	5	4/5	4/5	3
	Aqueous dyeing	3/4	3/4	4	2/3	3
Red	$scCO_2$ 90℃	5	5	4/5	3/4	4
	$scCO_2$ 100℃	5	5	5	4/5	4
	Aqueous dyeing	3/4	3/4	4	3	4
Dull Red	$scCO_2$ 90℃	5	5	4/5	3	2
	$scCO_2$ 100℃	5	5	4	2/3	2
	Aqueous dyeing	4/5	4/5	4/5	3	2
Blue	$scCO_2$ 90℃	4/5	5	4/5	3/4	2
	$scCO_2$ 100℃	4/5	5	3/4	3/4	2
	Aqueous dyeing	4/5	4/5	4/5	4	2

For the light fastness, all the dyeing in $scCO_2$ gives the identical results as the aqueous dyeing. It was also found in previous researches that the light fastness of the dyeing does not change significantly in $scCO_2$ and in water (Rita De Giorgi *et al.*, 2000).

Overall, most of the dyeing in $scCO_2$ gives higher fastness results than aqueous dyeing. When dyeing PET fabrics with disperse dyes in $scCO_2$, identical results as conventional high temperature dyeing in water are normally achieved for wash and light fastness (Rita De Giorgi *et al.*, 2000; Hou *et al.*, 2010). The rubbing fastness is generally 1/2 point lower in $scCO_2$ dyeing than aqueous dyeing, particularly the wet rubbing fastness (Hou *et al.*, 2010). Compared with the $scCO_2$ dyeing with disperse dyes, the dyeing in $scCO_2$ with *in-situ* dye synthesis shows higher fastness results. Most of the fastness are higher in $scCO_2$ dyeing than aqueous dyeing.

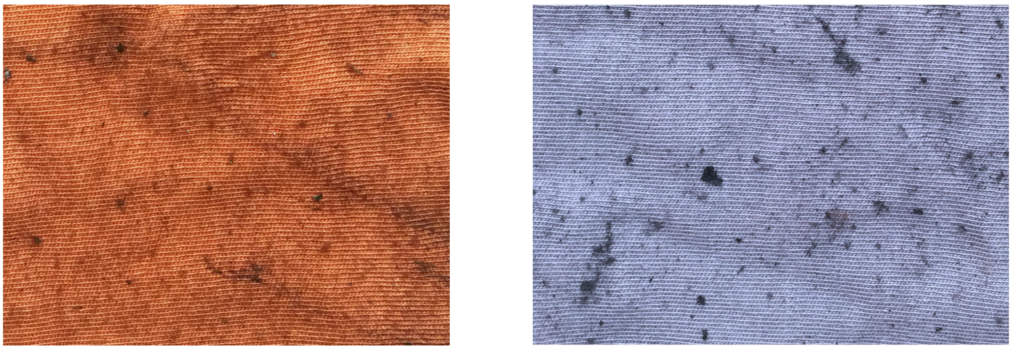
6.2 Supercritical CO_2 Dyeing of PLA

Many of the disperse dyes that have high exhaustion on PET do not show ideal exhaustion on PLA fibres and have reduced dye uptake (Yang and Huda, 2003b). Such condition causes problems for the wastewater treatment of PLA dyeing. Moreover, the strength loss of PLA fibre during aqueous dyeing is mainly due to the hydrolysis of the polymer (Kameoka *et al.*, 1997). Therefore, the dyeing of PLA in $scCO_2$ should be of benefit for the environment and the control of PLA degradation compared with conventional aqueous dyeing. The $scCO_2$ dyeing of PLA fibres with *in-situ* dye synthesis was carried out with the synthesised precursors at 90℃ and 100℃ for 90 minutes. No auxiliaries were added.

6.2.1 Dyeing Behaviour of the *In-situ* Dyeing of PLA Fabrics in Supercritical CO_2

The *in-situ* dyeing of PLA fabrics carried out at 90℃ shows uneven colour. Spots are observed on the dyed fabrics, as shown in Figure 6.2. The reason for the formation of the spots is presumably the low diffusion rate of the precursors in PLA, leading to dye aggregation. Only a few spots were formed for the orange and red dyes, while a larger amount of spots were formed for the blue and dull red dye. This indicates that the low diffusion rate of the diazoamine 2, which is used to form blue and dull red dye, may be mainly responsible for the spots formed during dyeing.

Orange Red



Dull Red Blue*

*The colour of the figure (blue) was adjusted with software in order to show the actual colour of the dyed fabric in the printed copy.

Figure 6.2 PLA Fabrics Dyed with *In-situ* Dye Synthesis in $scCO_2$ at 90℃

The PLA fabrics dyed at 100℃ are found to become stiff, particularly the orange one. Similar results were observed in previous research, where some of the PLA fabrics become hard and crumpling after 95℃ dyeing in $scCO_2$ while no change was found for the dyeing at 90℃ (Bach *et al*., 2006). Dye spots are also observed on the fabrics dyed at 100℃.

The change in the fabric quality at 100℃ limits the dyeing temperature. Therefore, it is not possible to improve the dyeing by increasing the dyeing temperature. Many other approaches can be employed to improve the levelness of the dyeing, such as increasing the pressure, increasing the CO_2 flow rate, prolonging the duration of the depressurisation step and the use of co-solvent (Banchero, 2012). Attempts will be made in future work in order to improve the levelness of the dyeing of PLA fabrics in $scCO_2$.

6.2.2 Analysis of the Stiffness of the Fabrics after Dyeing

The stiffness of the PLA fabrics dyed at temperature above 95℃ was observed before (Bach *et al*., 2006). However, the reason for this situation was not stated. Some analysis was carried out here attempting to figure out the reason for the hardening of the fabrics after dyeing in $scCO_2$.

The PLA fabrics were treated with $scCO_2$ under the same condition as the dyeing process without the precursors. The bending rigidity and the thickness of the fabrics before and after the treatment in $scCO_2$ were measured according to the method described in Section 2.12 and 2.13. The results are shown in Table 6.2.

Table 6.2 Mechanical Properties of PLA Fabrics before and after $scCO_2$ Treatment

	Untreated PLA	PLA after Treatment
Bending Rigidity	19.51±0.01	21.67±0.01
Surface Thickness (mm)	0.170±0.003	0.115±0.018

It is found that the PLA fabrics becomes slightly stiffer and thinner after the treatment. However, the difference is relatively small and not enough to cause the serious hardening of the dyed fabrics. Therefore, it is presumed that the reason for the hardening of the dyed fabrics is the dye or other components formed during dyeing. Extraction of the orange dyed PLA fabric was carried out with acetone at room temperature. After extraction, the fabric becomes less stiff. This further proves that the interaction between the formed components and the fibre is the reason for the hardening of the fabric. The UV-Vis spectrum of the solution is measured and compared with that of the pre-formed orange dye dissolved in acetone (Figure 6.3).

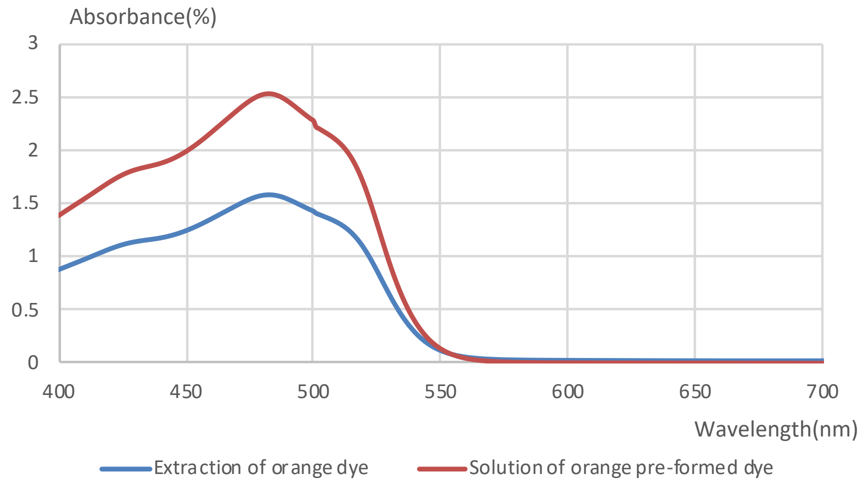


Figure 6.3 Absorbance Curves of the Orange Dye Extracted from dyed PLA and Orange Pre-formed Dye Solution in Acetone

The colour of the solution extracted from the PLA fabrics dyed in $scCO_2$ is the same as the pre-formed orange dye. This indicates that no other coloured component is formed in the PLA fabrics during dyeing process. In order to further confirm if there is any other component formed in the fabric, the solution is also analysed with HPLC. As shown in Figure 6.4 and Figure 6.5, a weak peak (No.4) for the orange dye at 0.9 min was observed in the extraction. The significant peaks at 0.4 min (No.1) and 1.1 min (No.6) were not observed in the pre-formed orange dye. This indicates that there may be some components other than the orange dye were formed during the dyeing process and may be responsible for the change in the fabric quality. However, further work is needed to identify the components and the interaction between these components and the fibres.

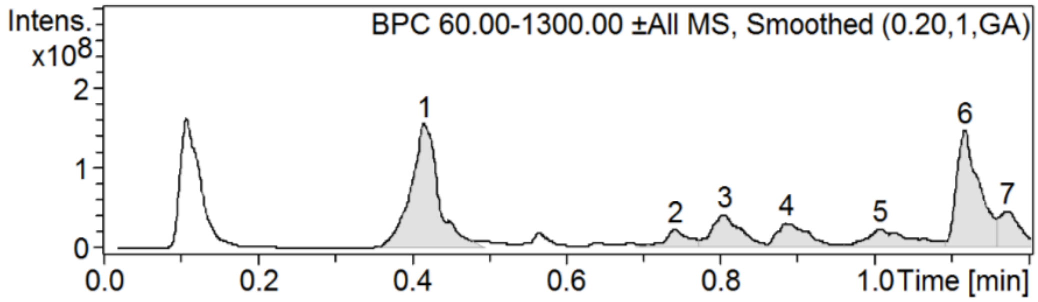


Figure 6.4 HPLC of the Extraction from the PLA Fabric Dyed with Orange *In-situ* Dyeing in $scCO_2$

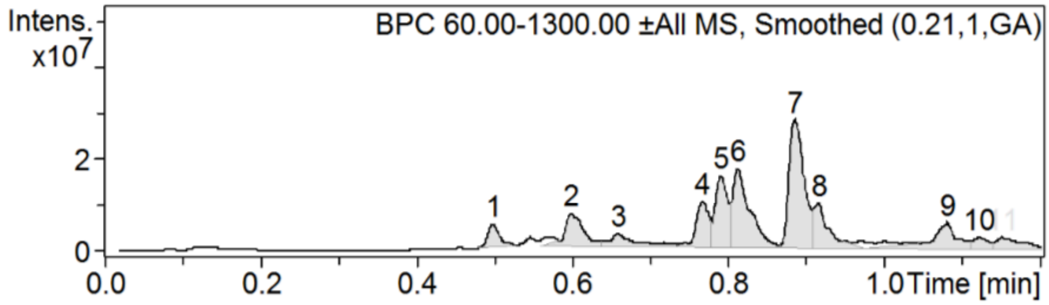


Figure 6.5 HPLC of Pre-formed Orange Dye

6.3 Conclusions

The aim of this chapter was to investigate the feasibility of dyeing polyester fabrics through *in-situ* dye synthesis in $scCO_2$. Dyeing behaviours at different temperatures were examined. The *in-situ* dyeing in $scCO_2$ was compared with that in water in the aspects of reflectance spectra and fastness properties.

The *in-situ* dyeing with orange and red dye show lower colour yield in $scCO_2$ than in water. This is presumably due to the reduced reactivity of the precursors in $scCO_2$. On the other hand, the colour yield of the blue and dull red dyes in $scCO_2$ is higher than that in water, even at a lower dyeing temperature. However, the optimum dyeing condition for different combinations are different, which depends on the reaction efficiency of the precursors in $scCO_2$. The fastness properties are similar for the dyeing in $scCO_2$ and in water. The results indicate that the dyeing of PET fabrics with *in-situ* dye synthesis is applicable in $scCO_2$. However, appropriate combinations with adequate reactivity in $scCO_2$ should be selected. The factors that may influence the reaction efficiency of the components in $scCO_2$ needs to be further investigated. With the appropriate precursors, it is possible to carry out the dyeing of PET fabrics though *in-situ* dye synthesis at lower temperature in $scCO_2$ than in water.

Unlike PET, the *in-situ* dyeing on PLA fabrics in $scCO_2$ does not work well. The dyeing is uneven, particularly for the blue and dull red dyes. Dye spots are observed on the dyed fabrics. The dyeing at 100℃ also causes reduce in fabric quality with hardening and crumpling. Therefore, the dyeing of PLA in $scCO_2$ needs to be carried out below 90℃. Improvements on the levelness of the dyeing on PLA may be achieved with different dyeing conditions and the addition of co-solvent.

Chapter 7

Conclusions and Future Work

7.1 Conclusions

The primary aim of this project was to investigate the application of dye precursors (azoic combinations) for the low temperature dyeing of polyester fibres (PET and PLA) through *in-situ* dye synthesis. Additionally, the possibility to use the precursors in $scCO_2$ for the dyeing of polyester fibres was also studied.

The two diazoamines used for the dyeing were synthesised from 4-chloro-2-methylaniline and N-phenyl-p-phenylenediamine, respectively, through diazotisation reaction and stabilisation reaction with diethanolamine. The structures of the synthesised components were confirmed with HPLC and FT-IR. The combinations were selected in order to obtain the three primary colours that can be used together to create a larger colour gamut. With the coupling components (2-naphthol and Naphthol AS), four colours can be achieved with the combinations, including red, orange, dull red and blue. The dyeing with mixtures can be carried out with two colours that share a common component used to form the dyes. As the orange and the blue dyes do not share any common component, no green colour was achieved.

For PET fabrics, the colour yield of the *in-situ* dyeing at 100℃ is lower than that with the corresponding pre-formed dyes at 130℃ at low concentration (normally below 2% o.m.f.) but becomes higher as the concentration increases. The rubbing and washing fastness of the *in-situ* dyeing is slightly lower than that of the high temperature dyeing with the corresponding pre-formed dye, while the light and dry heat fastness of the *in-situ* dyeing is the same or higher than the pre-formed dyes. However, compared with the commercial disperse dyes, the fastness properties of the *in-situ* dyeing are generally lower. This is mainly due to the small molecular size of the components used here.

The use of the precursors for the dyeing of PET/wool blend fabrics was also investigated. Good colour yield was achieved on both PET and wool component in the blend fabrics. Although some of the dyes were washed off from the wool fabrics during the soaping process, an appreciable amount of dyes was still left on the wool fabrics to give a good colour yield. Slightly deeper shades were achieved on the PET component than wool. The damage of the wool fabrics after the *in-situ* dyeing at 100℃ is very small, with only 2% strength loss. These results preliminarily showed the potential to carry out the dyeing of PET/wool blend fabrics with the precursors in one bath at low temperature.

In the case of PLA fabrics, the optimum dyeing temperature for *in-situ* dyeing is 100℃, at which high colour yield can be achieved with no significant strength loss of the fabrics. The *in-situ* dyeing at 100℃ gives similar colour yield compared with the conventional dyeing with pre-formed dyes at 110℃ with much lower strength loss of the dyed fabrics. The fastness properties of the *in-situ* dyeing are similar to that of the conventional dyeing at 110℃ with the corresponding pre-formed dye. Compared with the *in-situ* dyeing on PET fabrics, the shades on PLA are hypsochromic and darker. With the same dye concentration, the colour yield achieved on PLA is generally lower than that on PET. The rubbing and washing fastness of the dyed PLA is generally lower than that of the PET, while the light and dry heat fastness does not show significant difference on these two substrates.

When dyeing PET fabrics with the precursors in scCO2, different combinations show different dyeing behaviour. The orange and red dyes give significantly lower colour yield in $scCO_2$ than in water, while the blue and dull red dyes give higher colour yield in $scCO_2$ even at lower temperature. This is because the reaction efficiency of some of the precursors are limited in $scCO_2$ and only a small amount of dyes was formed during the dyeing cycle. The optimum dyeing condition also varies for different combinations relating to the reaction efficiency of the components in $scCO_2$. The blue dye shows the highest colour yield and fastness properties at 90℃ while the dull red dye gives the optimum dyeing behaviour at 100℃. On the other hand, the dyeing of PLA fabrics with the precursors in $scCO_2$ are not ideal. The levelness of the dyeing is poor, particularly with the blue and dull red dyes. Dye spots were observed on the dyed fabrics. Moreover, the PLA fabrics dyed at 100℃ became hard and crumpling. The reason for the quality loss of the dyed fabrics is assumed to be the interaction between the dye and the fibre.

Overall, the results gathered here indicate that the aqueous dyeing through *in-situ* dye synthesis can be carried out on PET and PLA fabrics at 100℃ and achieve similar or better dyeing behaviour than the conventional high temperature dyeing at 130℃ with the corresponding disperse dyes. The dyeing with the precursors in $scCO_2$ can only be carried out on PET at present. The azoic combinations with appropriate reaction efficiency in $scCO_2$ need to be selected. The optimum dyeing condition may also vary according to the reaction efficiency of the precursors.

7.2 Future Work

The work undertaken has fulfilled the use of the precursors for the low temperature dyeing of PET and PLA fabrics in water and the dyeing of PET in $scCO_2$. However, there are several areas where further research could be carried out related to the low temperature dyeing of polyester fibres through *in-situ* dye synthesis.

The components used in this project is only one possible combination that can be used for the *in-situ* dyeing of polyester fibres. There are opportunities to use a wide range of amines to synthesise the diazoamine through the same method and apply for the low temperature dyeing of polyester fibres in order to create larger colour gamut. Moreover, the structure of the components used in this project is not optimum for the fastness properties. The use of other structures with larger molecular size can also improve the fastness properties.

The prediction method that works well for the dyeing with the preformed dyes does not work for the *in-situ* dyeing. The different reactivity between the different components influence the amount of dyes formed when dyeing with the mixtures. Therefore, a new prediction method with the consideration of the reactivity between the components is needed to get an accurate prediction and formulation for the *in-situ* dyeing with mixtures.

The dyeing of PET/Wool blend fabric used a piece of PET fabric and a piece of wool fabric to simulate the blend fabric. It gives an idea about the dyeing behaviour of the *in-situ* dyeing on these two components and shows the possibility to dye the two components of the blend fabric with the same dye. However, the colour difference between PET and wool was observed. This may be improved by changing the dyeing conditions. The *in-situ* dyeing also needs to be carried out on blend fabrics in order to investigate the fastness properties of the dyeing.

For the dyeing in $scCO_2$, it was observed that the reaction efficiency of some precursors was low in $scCO_2$. In order to achieve good colour yield from the dyeing in $scCO_2$, it is necessary to select the azoic combinations with appropriate reactivity in $scCO_2$. Further research is needed to understand the factors that influence the reaction efficiency of the azoic combinations in $scCO_2$. The optimum dyeing condition also depends on the reaction efficiency of the precursors.

In this project, the dyeing with the precursors in $scCO_2$ can only achieve good dyeing on PET fabrics. Dye spots were observed on the dyed PLA fabrics.

The levelness of the dyeing PLA fabrics may be improved by changing the dyeing condition or the addition of co-solvent.

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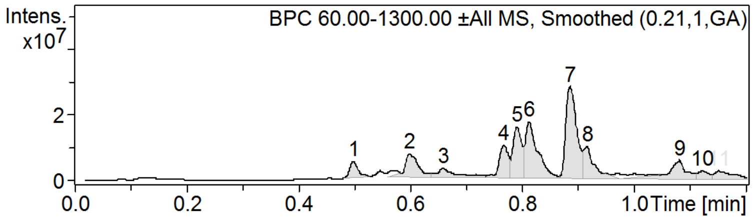
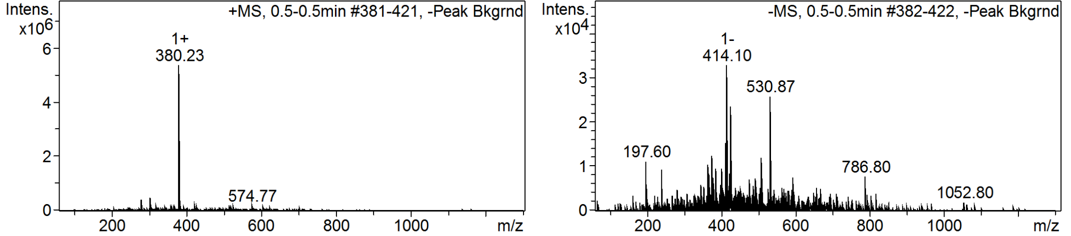
Appendix A

HPLC Results of the Preformed Dyes

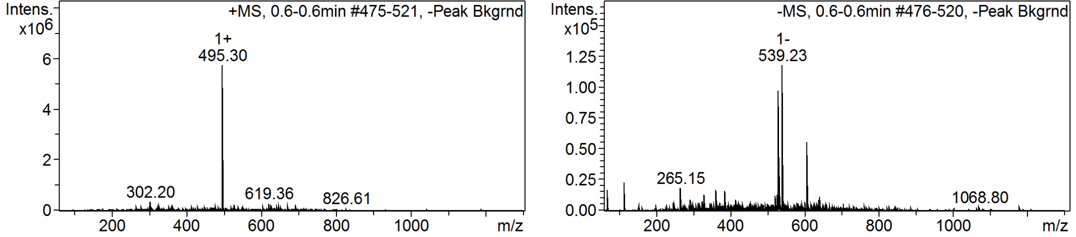
A.1 HPLC Results of Orange Dye



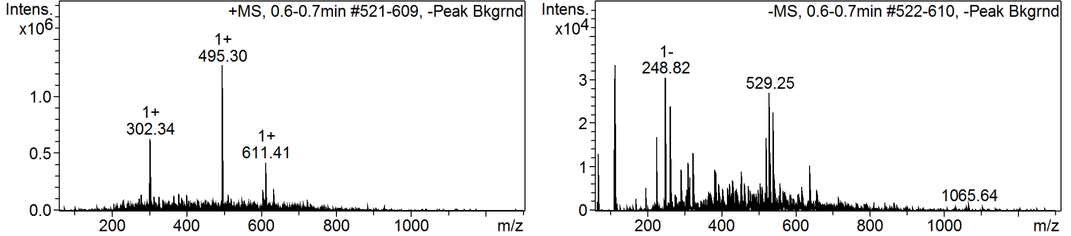
Cmpd 1, 0.5 min



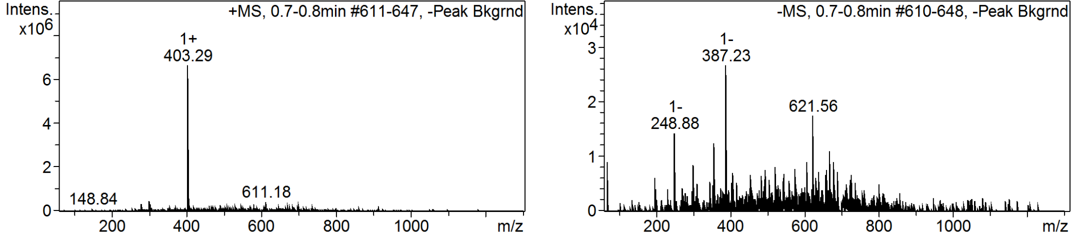
Cmpd 2, 0.6 min



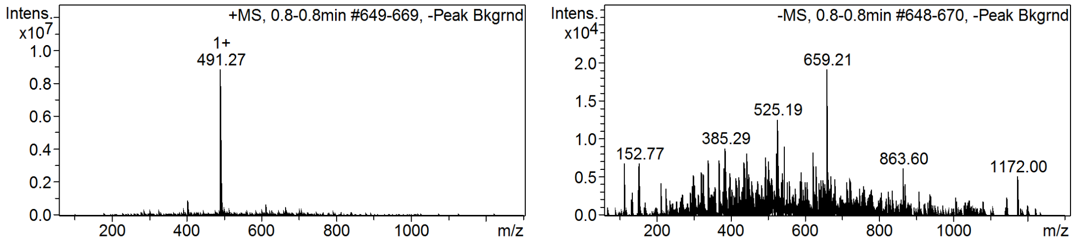
Cmpd 3, 0.7 min



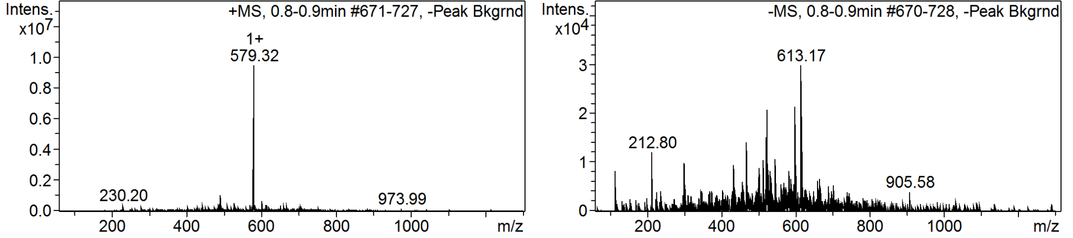
Cmpd 4, 0.8 min



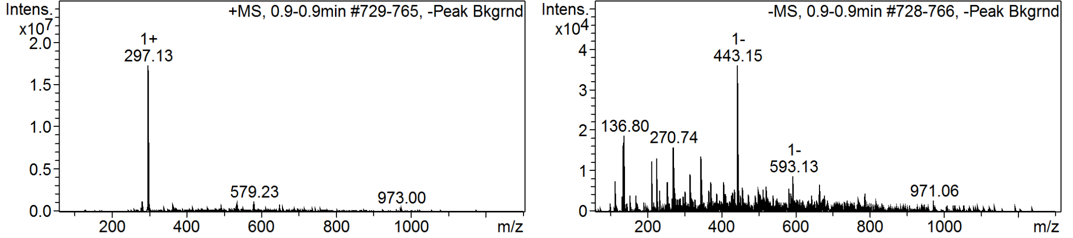
Cmpd 5, 0.8 min



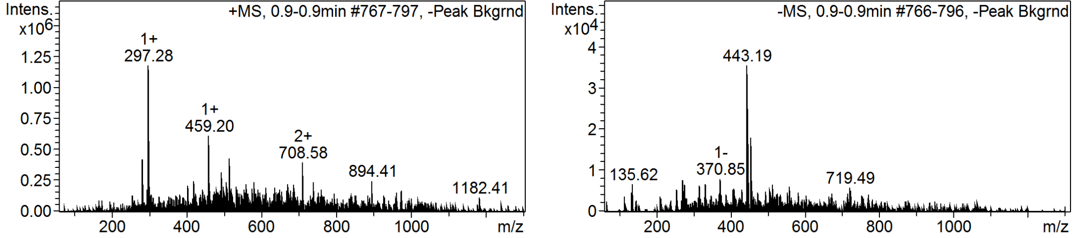
Cmpd 6, 0.8 min



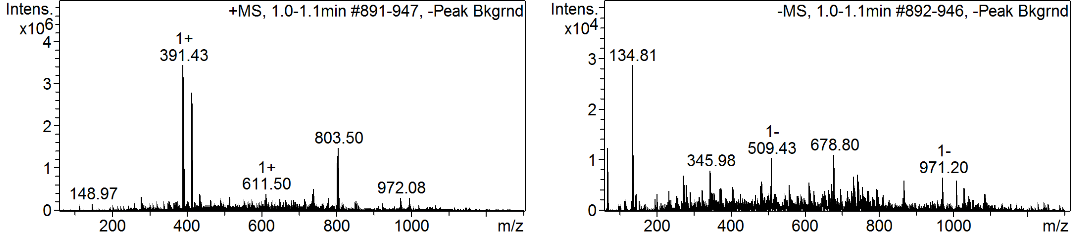
Cmpd 7, 0.9 min



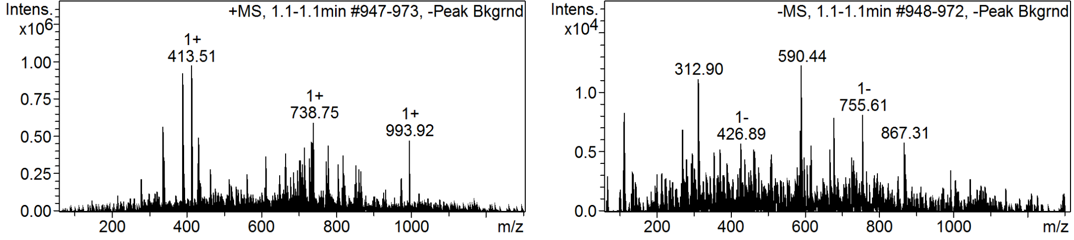
Cmpd 8, 0.9 min



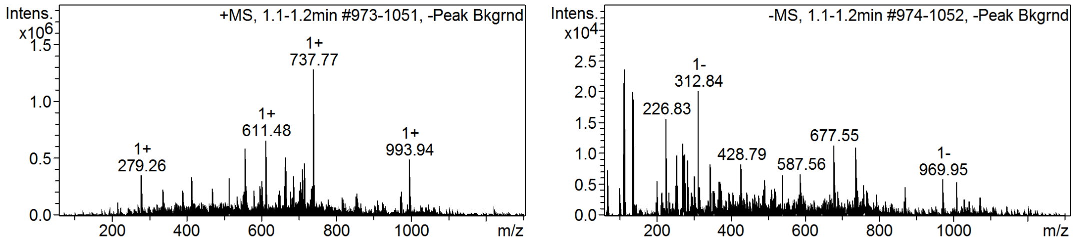
Cmpd 9, 1.1 min



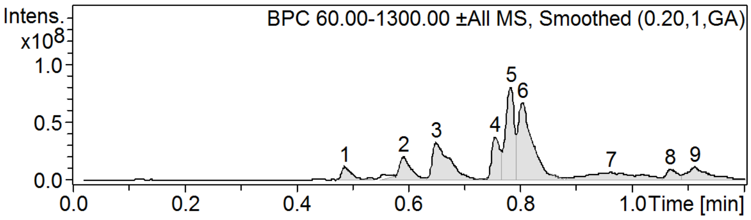
Cmpd 10, 1.1 min



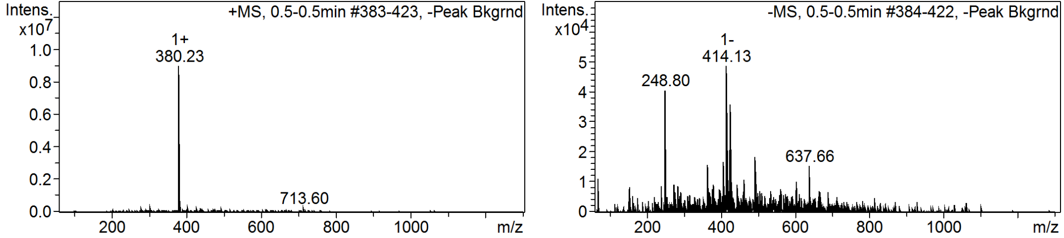
Cmpd 11, 1.2 min



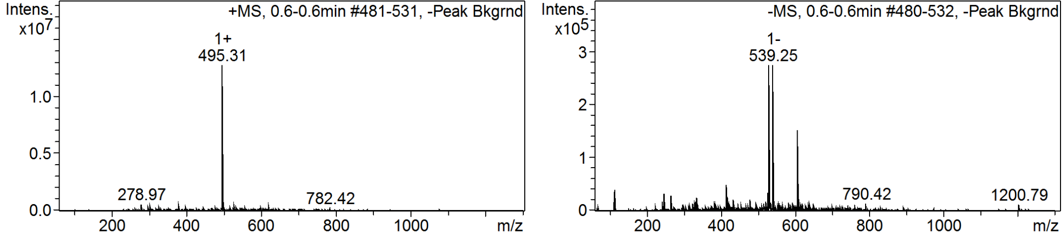
A.2 HPLC Results of Red Dye



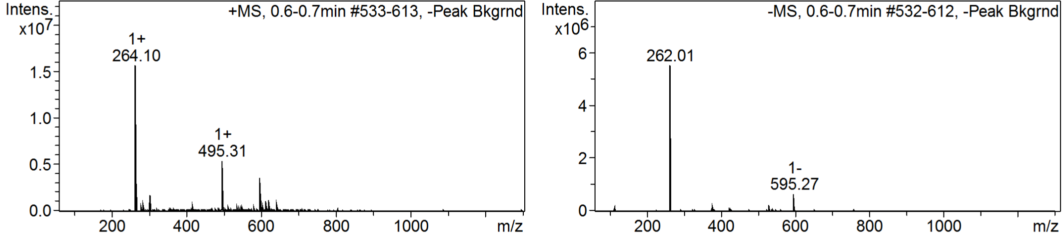
Cmpd 1, 0.5 min



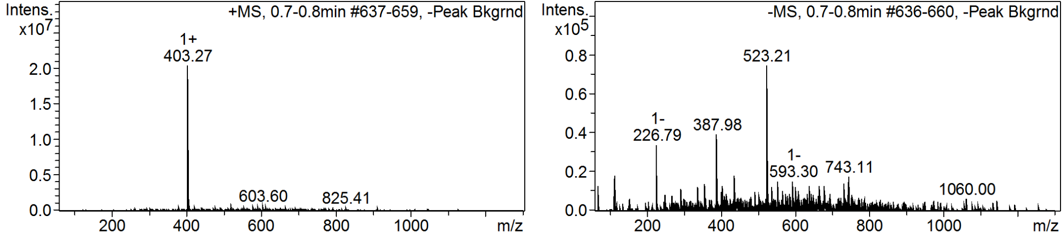
Cmpd 2, 0.6 min



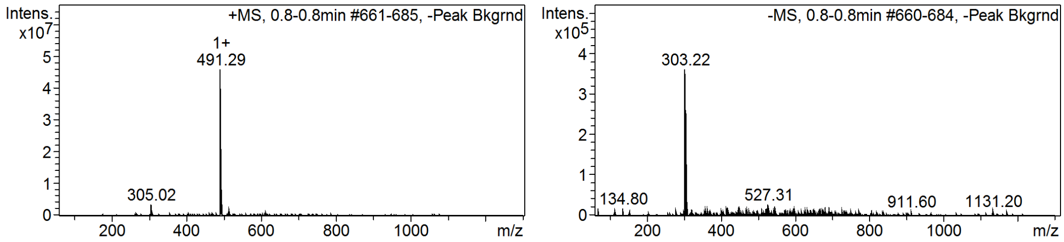
Cmpd 3, 0.6 min



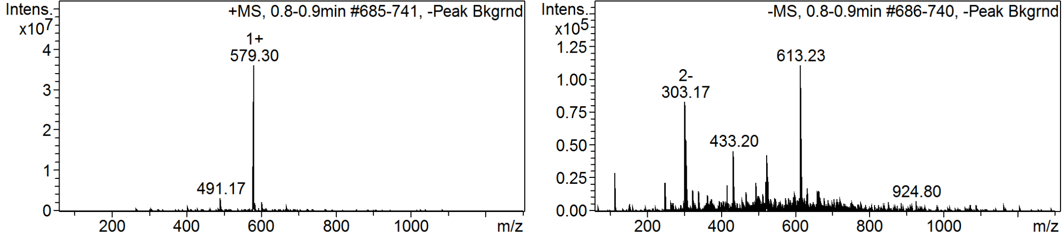
Cmpd 4, 0.8 min



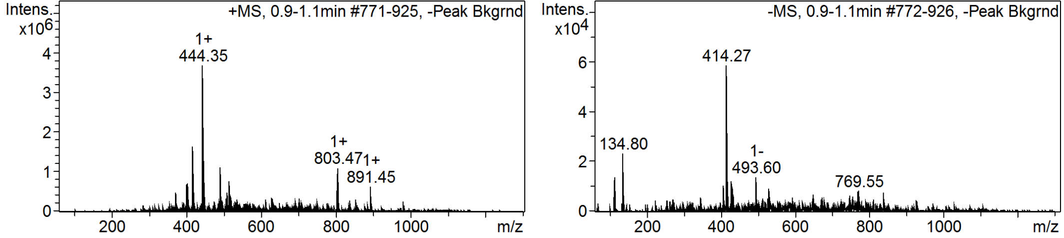
Cmpd 5, 0.8 min



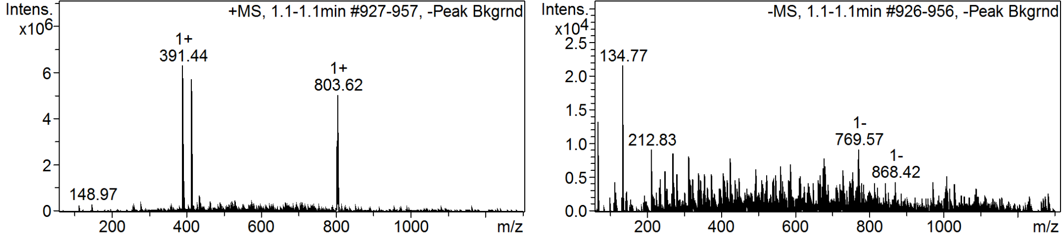
Cmpd 6, 0.8 min



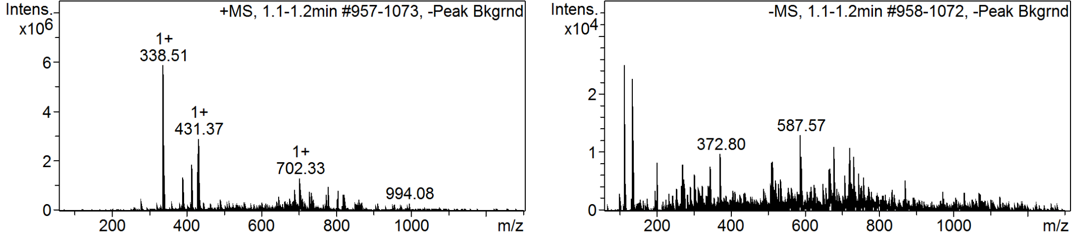
Cmpd 7, 1.0 min



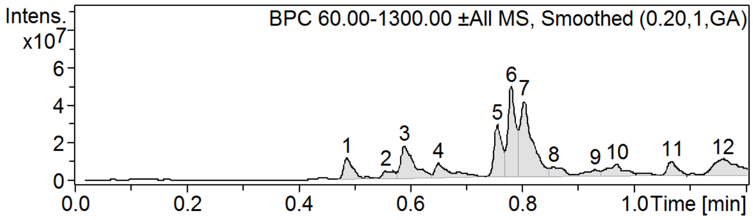
Cmpd 8, 1.1 min



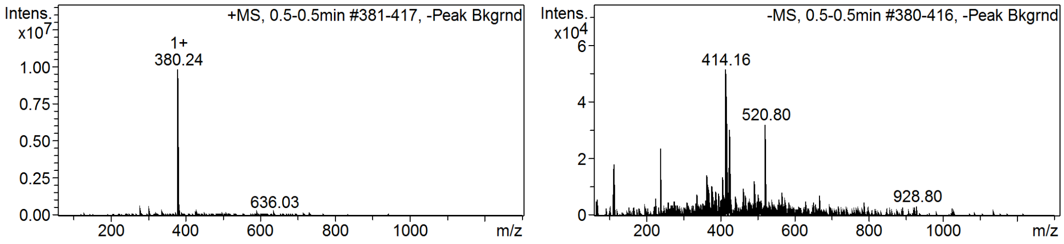
Cmpd 9, 1.1 min



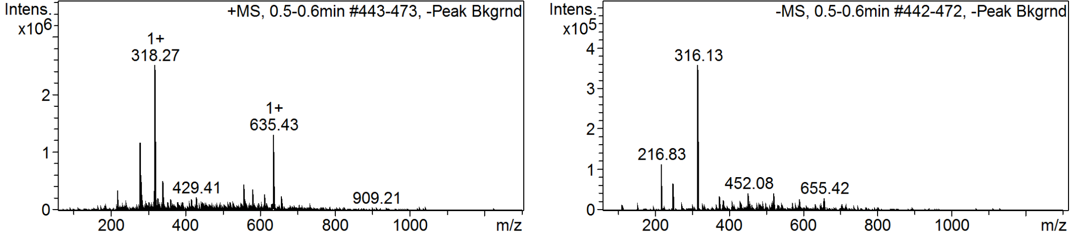
A.3 HPLC Results of Dull Red Dye



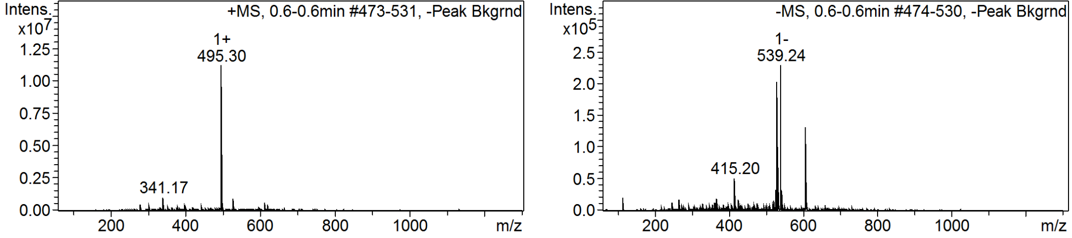
Cmpd 1, 0.5 min



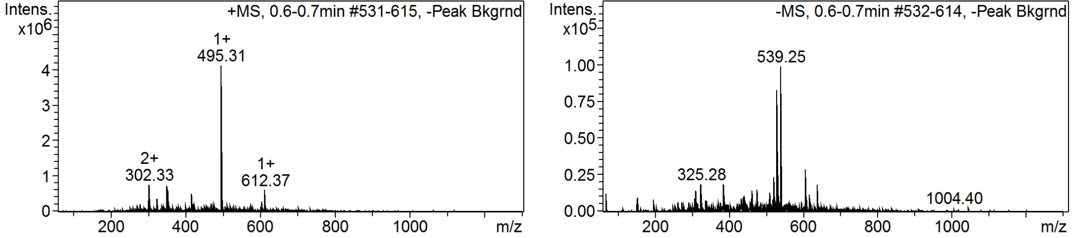
Cmpd 2, 0.6 min



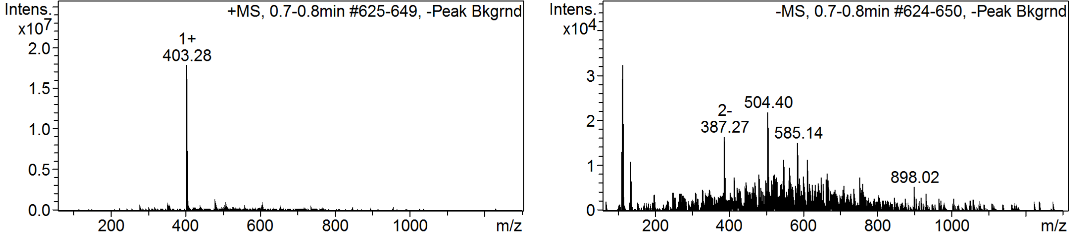
Cmpd 3, 0.6 min



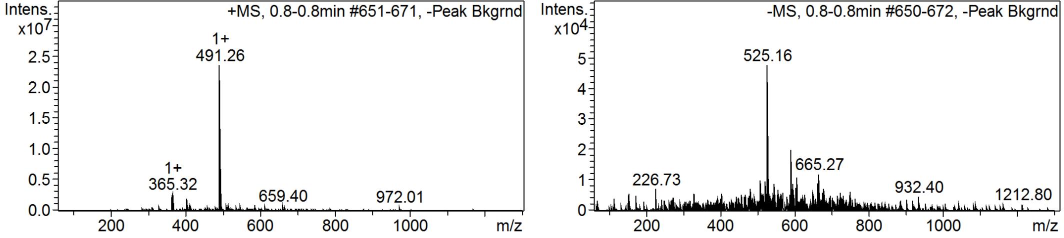
Cmpd 4, 0.6 min



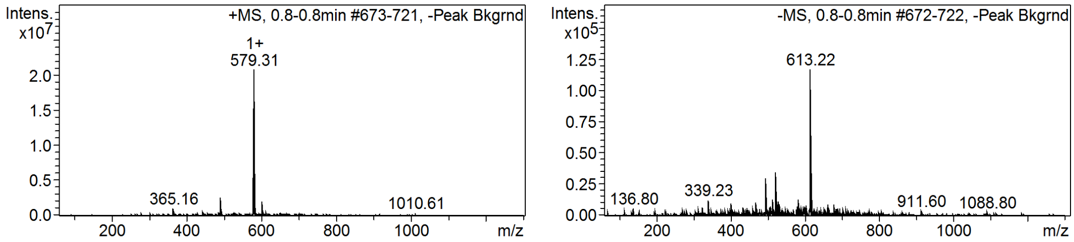
Cmpd 5, 0.8 min



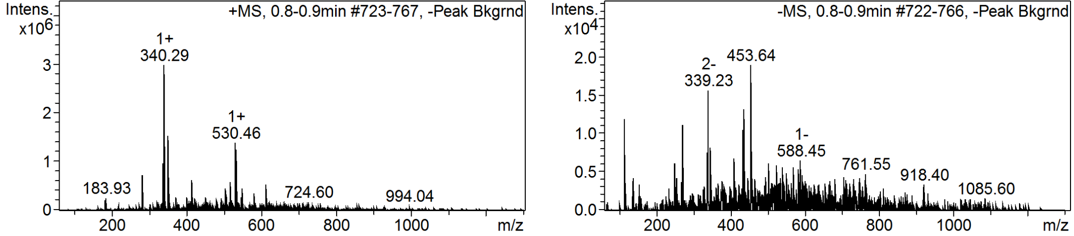
Cmpd 6, 0.8 min



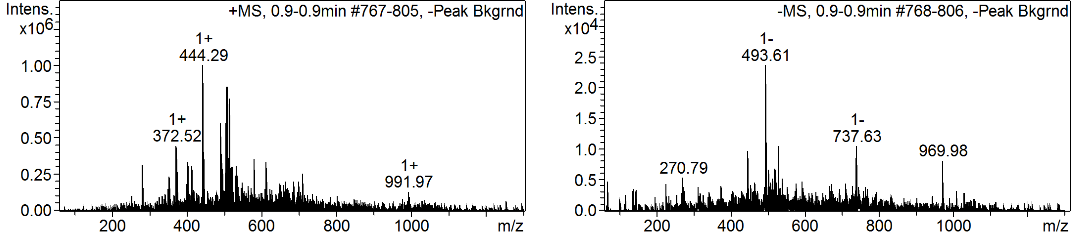
Cmpd 7, 0.8 min



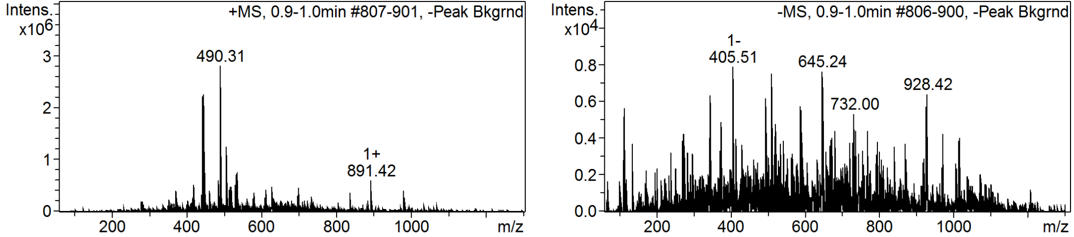
Cmpd 8, 0.9 min



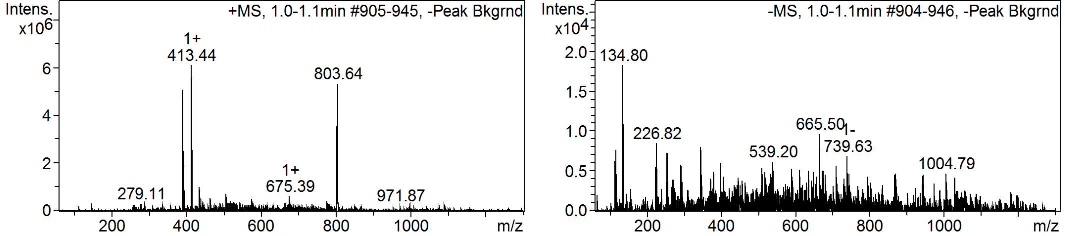
Cmpd 9, 0.9 min



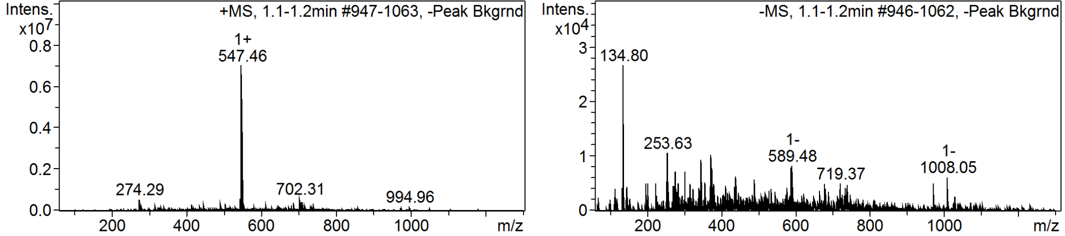
Cmpd 10, 1.0 min



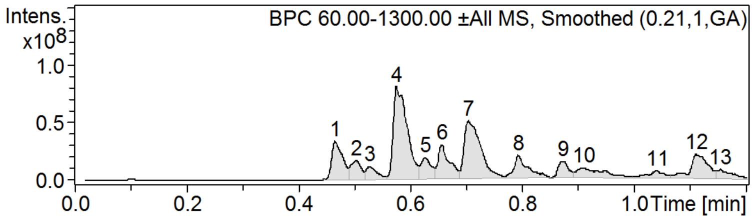
Cmpd 11, 1.1 min



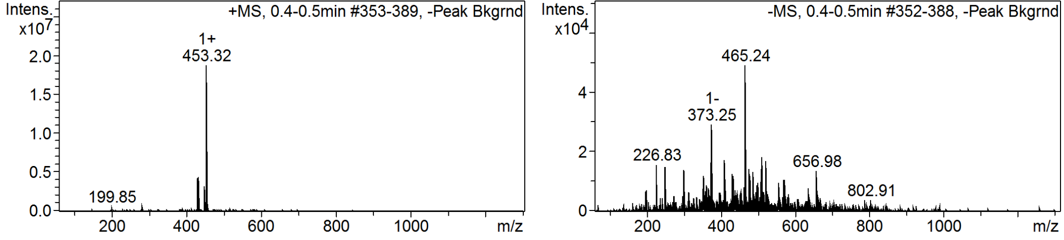
Cmpd 12, 1.2 min



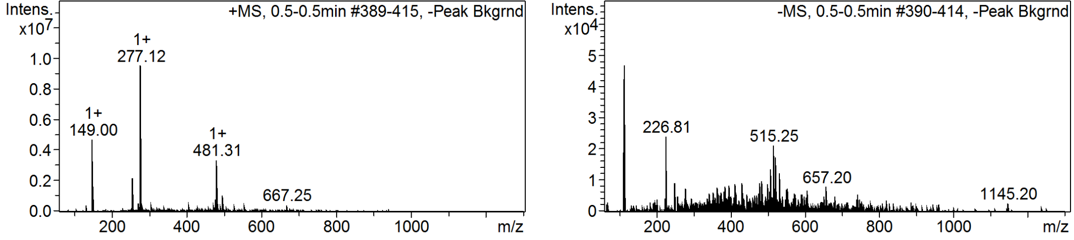
A.4 HPLC Results of Blue Dye



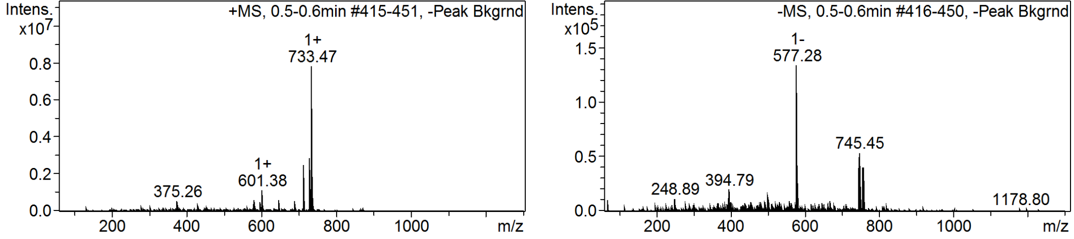
Cmpd 1, 0.5 min



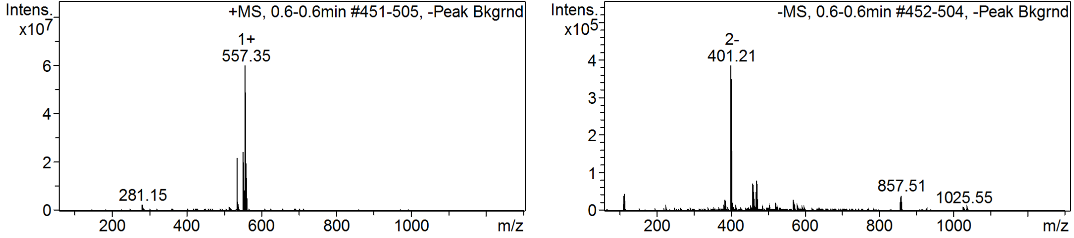
Cmpd 2, 0.5 min



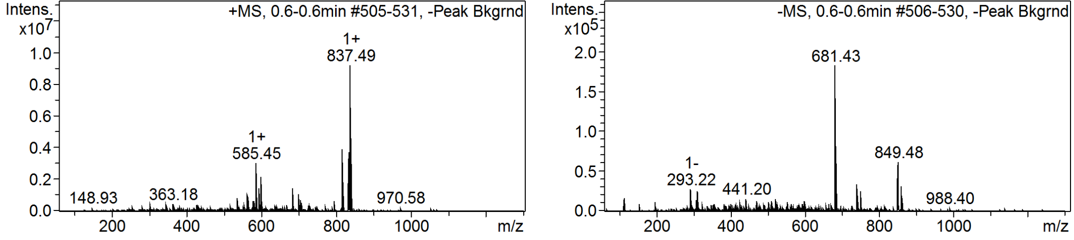
Cmpd 3, 0.5 min



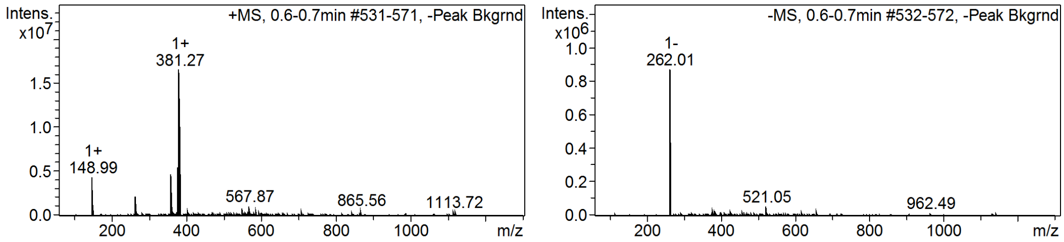
Cmpd 4, 0.6 min



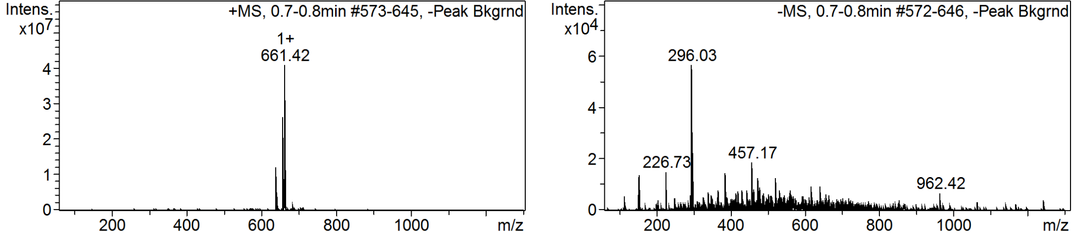
Cmpd 5, 0.6 min



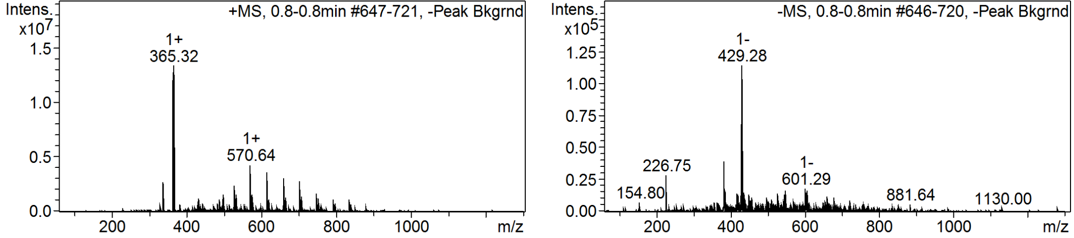
Cmpd 6, 0.7 min



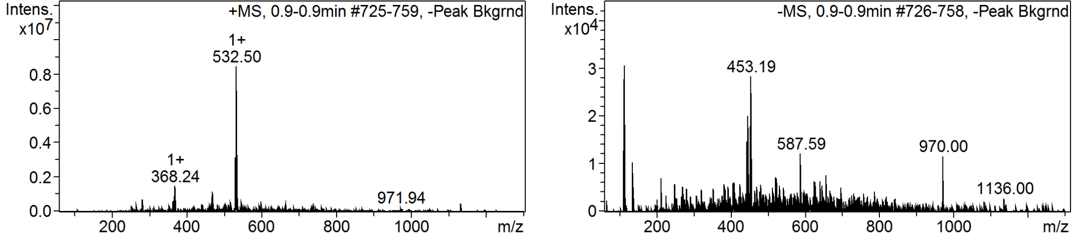
Cmpd 7, 0.7 min



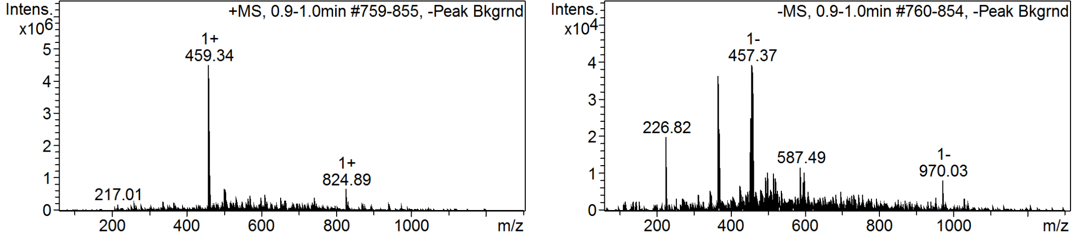
Cmpd 8, 0.8 min



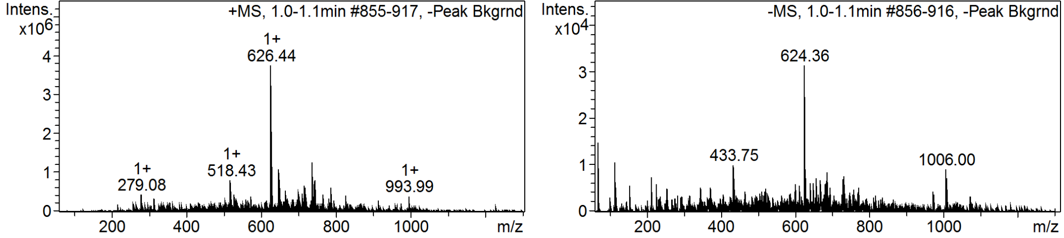
Cmpd 9, 0.9 min



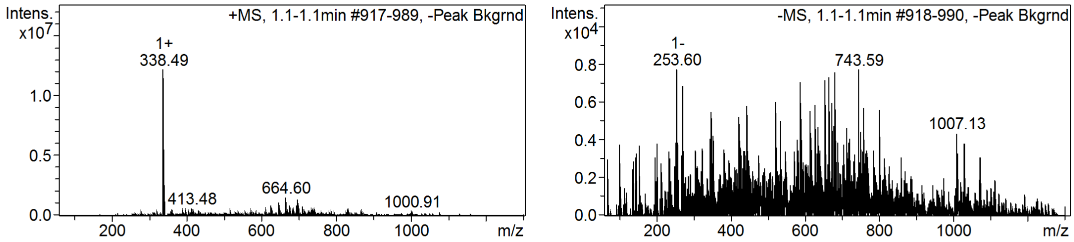
Cmpd 10, 0.9 min



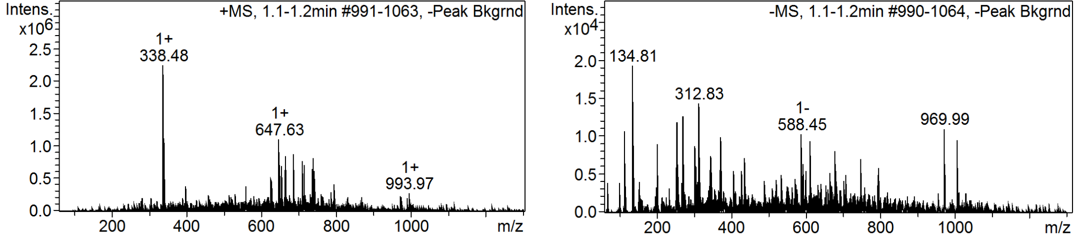
Cmpd 11, 1.0 min



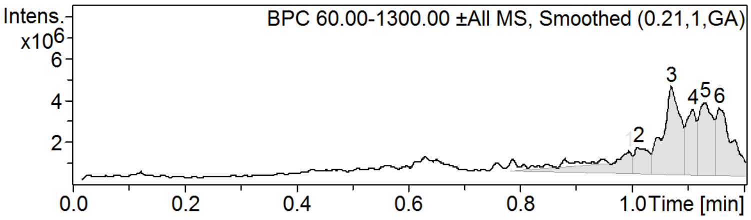
Cmpd 12, 1.1 min



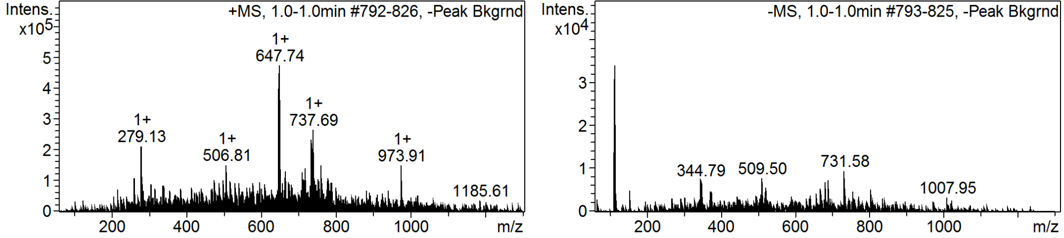
Cmpd 13, 1.2 min



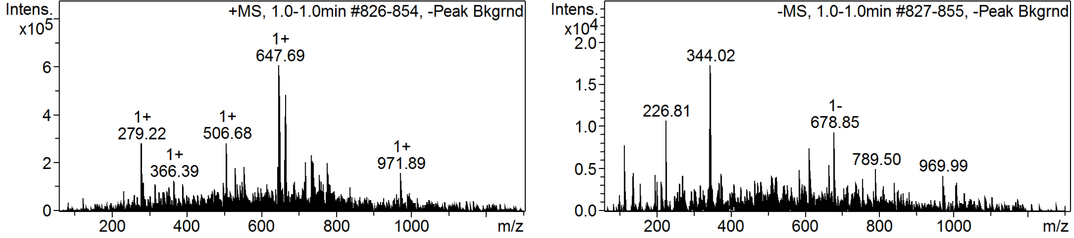
A.5 HPLC of the Blank Test



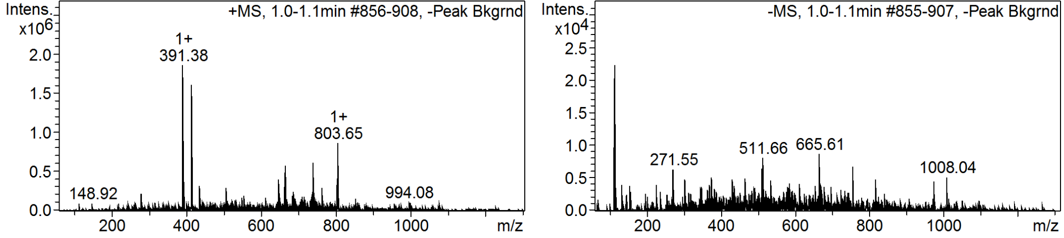
Cmpd 1, 1.0 min



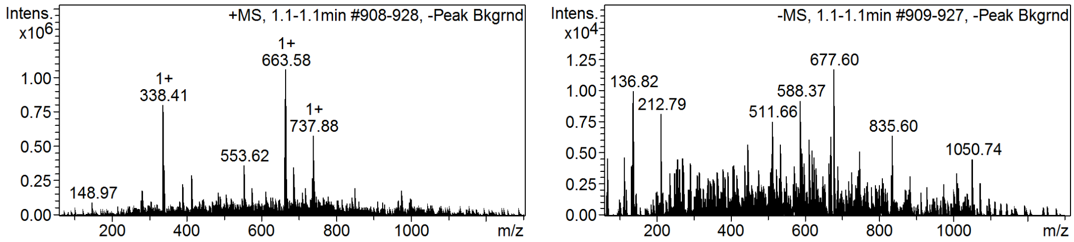
Cmpd 2, 1.0 min



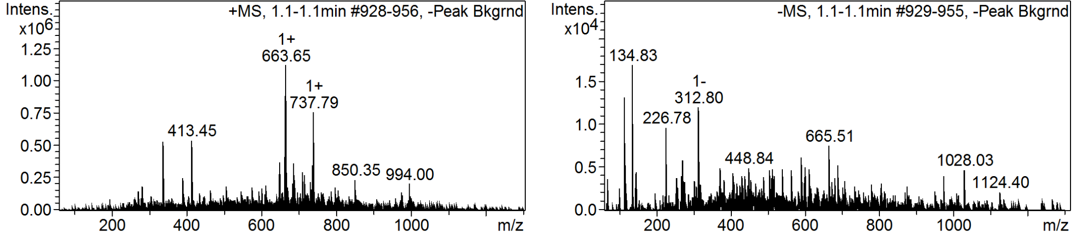
Cmpd 3, 1.1 min



Cmpd 4, 1.1 min



Cmpd 5, 1.1 min



Cmpd 6, 1.2 min