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INVESTIGATION OF NEW BIONIC MATERIALS FOR SUBSTRATE-INDEPENDENT COLOURATION OF TEXTILE MATERIALS

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INSTITUTE OF TEXTILES AND CLOTHING

INVESTIGATION OF NEW BIONIC MATERIALS FOR SUBSTRATE-INDEPENDENT COLOURATION OF TEXTILE MATERIALS

SO LAI LAI

A thesis submitted

in partial fulfilment of the requirements

for the degree of Doctor of Philosophy

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Abstract

Bio-inspired by the remarkable adhesion of marine mussels' adhesive proteins (MAPs) to almost any surface in a tidal environment, a novel bio-adhesive based method was developed for colouration of various textile materials. The colouration of various materials was easily achieved at room temperature through a simple dip-coating procedure. This method showed the characteristics of substrate-independence and room temperature colouration. Compared to the traditional colouration, it has the advantages of easy to application and low energy consumption.

3,4-dihydroxy-L-phenylalanine (DOPA), was found to be one of the amino acid responsible for the adhesion of the marine mussels. Due to the structural similarity to DOPA, dopamine was chosen as a biomimetic precursor for the adhesive colouration. On the one hand, dopamine-induced colouration was successfully developed through its *in situ* polymerization for various textile materials, organic and inorganic materials, and even materials resistant to colouration. The colour appearance of the dyed materials could be tuned in a controllable way through the incorporation of different nucleophilic species such as amino acid, aromatic and heterocyclic components. The properties of the dyed materials including colours, fastness, surface morphology, composition and wettability were studied using colorimetric analysis, fastness evaluation, scanning electron microscopy, X-ray photoelectron spectroscopy and water contact angle measurement, respectively. The results indicated that the various textile materials were successfully coloured.

In order to achieve a wider range of colour on textiles materials, commercially available dyes, being natural or synthetic, were also incorporated in the colouration process, in addition to the above-mentioned nucleophilic compounds. The dyed fabrics were evaluated by colorimetric analysis, scanning electron microscopy optical microscopic analysis and colour fastness tests. The obtained results showed that the fabrics were also successfully dyed with good colouration property.

Furthermore, a novel kind of cateholamine dye was designed and synthesized for textile material colouration as an approach to enhance the versatility of the dyes and further enrich the colour gamut produced on textiles. In this approach, a commercially available dye of Acid Yellow 11 was exampled as a model of chromophore, and dopamine was introduced as an adhesive antenna to enhance the dye fixation on textile materials. The chemical structure of the synthesized dye was confirmed from the analyses of high resolution mass spectrometry, proton and carbon nuclear magnetic resonance spectroscopy, the absorption spectra was tested by UV-visible spectroscopy. The UV-visible results showed that the introduction of the catechol group did not significantly change the absorption of the parent chromophore. The colouration results revealed that at room temperature the synthesized catechol dye had good colour yield on various textile fabrics, and the dyed fabrics had good fastness properties.

This developed method showed the substrate-independence to some extent and was especially suitable for those textile materials difficult to be dyed with traditional method, such as polylactic acid and polypropylene. In addition, less energy consumption and

colouration auxiliaries were needed by this colouration method. The biomimetic concept and its successful application represent a new step forward in textile material colouration and it is a promising alterative to the traditional process, which is substrate-dependent and high energy consumption.

Publications

Academic Journal Papers

1. **Vicky Lai Lai So,** Liang He, Bin Fei, Kevin K. L. Cheuk and John H. Xin, Bio-inspired colouration on various textile materials using a novel catechol colorant, RSC Advances, 2014, 4, 41081-41086.
2. **L. L. So,** Liang He, Bin Fei, K. K. L. Cheuk and John H. Xin, Bio-inspired coloration for wool fabrics at room temperature, Key Engineering Materials, 2016, 671, 25-31.
3. Liang He, **Vicky Lai Lai So** and John H. Xin, Dopamine polymerization –induced surface colouration of various materials, RSC Advances, 2014, 4, 20317-20322.
4. Liang He, **Vicky Lai Lai So** and John H. Xin, A new rhodamine-thiourea/Al^{3+} complex sensor for the fast visual detection of arginine in aqueous media, Sensors and Actuators B: Chemical, 2014, 192, 496-502.
5. **Vicky Lai Lai So,** Liang He and John H. Xin, Natural dyeing of various textile materials using a bio-inspired colouration method. (under preparation)

Conference Papers

1. **L. L. So,** Liang He, John H. Xin, Bin Fei, K. K. L. Cheuk, Bio-inspired coloration for wool fabrics at room temperature, The 13th International Wool Research Conference (IWRC-13) AATCC Sustainability Symposium (AATCC-SS), Hangzhou, China, 10-14 June 2015.

2. **L.L. So,** Liang He and John H. Xin, Bio-inspired coloration for textile materials, Proceedings, 14th Autex World Textile Conference, Bursa, Turkey, 26-28 May 2014.
3. **L.L. So,** Liang He and John H. Xin, Biomimetic melanin dyestuffs for textile *in situ* coloration, The Fibre Society Spring 2013 Technical Conference, Victoria, Australia, 22-24 May 2013.
4. **Vicky L.L. So**, Liang He, John H. Xin, Bin Fei and Kevin K.L. Cheuk, Bio-base coloration process for textile materials, Third International Conference on Multifunctional, Hybrid and Nanomaterials, Sorrento, Italy, 3-7 March 2013.

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List of Abbreviations

Abbreviations	Notes
DOPA	3,4-dihydroxy-L-phenylalanine
MAPs	Mussel adhesive proteins
PP	Polypropylene
PLA	Polylactic acid
PET	Polyethylene terephthalate
PBI	Polybenzimidazole
SEM	Scanning electron microscopy
UV-vis	Ultraviolet –visible
^{1}NMR and ^{13}C NMR	Proton and carbon nuclear magnetic resonance spectroscopy
AATCC	American Association of Textile Chemists and Colorists
CIE	Commission Internationale d'Eclairage
Mefp	Mytilus edulis foot protein
kDa	Kilodaolton
PEG	Poly(ethylene glycol)
LbL	Layer-by-layer
PTFE	Polytetrafluoroethylene
4HP	4-hydroxyproline
24DB	2,4-dihydroxybenzophenone

135SMP	1-(4-sulfophenyl)-3-methyl-5-pyrazolone
4ABC	*p*-aminobenzoic acid
H2BA	3,5-dihydroxybenzoic acid
H3BTC	Benzene-1,3,5-tricarboxylic acid
SPF	*p*-hydroxybenzoic acid *n*-butyl ester
XPS	X-ray photoelectron spectroscopy
Tris	Tris(hydroxymethyl)aminomethane
ISO	International organization for standization
AY	Acid yellow 11
D1	Dopamine moiety in dye
D2	Control dye
HRMS	High resolution mass spectrometry
TBDMS	*t*-butyldimethysiyl
THF	Tetrahydrofuran
TBAF	Tetra-n-butylammonium fluoride
DCE	1,2-Dichloroethane
EA	Ethyl acetate
TEA	Triethylamine
MF	Methylnaphthalene sulfonate formaldehyde condensate
DMSO-d_6	Dimethyl sulfoxide-d_6
$CDCl_3$	Chloroform
m/z	Mass-to-charge ratio
K_2Co_3	Potassium carbonate

$SOCl_2$	Thionyl chloride
TBAF	Tetra-n-butylammonium fluoride
CH_2	Methylene
DMF	Dimethylformaide

Chapter 1

Introduction

1.1 Background of research

Nature generates a great variety of materials with rather unique and optimized characteristics. With the gradual disclosure of their underlying mechanisms, those unique and fascinating properties are now adequately understood. The imitation of biologic process or life is termed as biomimicking. In recent years, barnacles and mussels, particularly the common blue mussels *Mytilus edulis* has attracted much attention because of its strong and versatile adhesion power. In a harsh tidal marine environment, the mussels have the ability to promptly build up adhesion to virtually any surface, including classically adhesion-resistant materials such as Telfon, and this adhesion is water-resistance and permanent. Intensive research discovered that once in contact with a substrate, the mussel secretes a liquid adhesive based on mussel adhesive proteins (MAPs) to form water-resistant bonds within a few seconds. One of the structural features of MAPs is the presence of 3,4-dihydroxy-L-phenylalanine (DOPA), an amino acid which is believed to be responsible for both adhesive and cross-linking characteristics of marine adhesives. DOPA is formed in these proteins through post-translational hydroxylation of tyrosine residues. It is generally believed that the versatile interfacial adhesion to substrates is due to physicochemical interactions between the unoxidized catechol form of DOPA and the surface of the solid substrate. These elusive interactions possibly involve metal coordination bonds, π electron interactions, hydrogen bonding, ionic bonds and covalent bonds.

Similar to DOPA, dopamine also possesses a catechol and an ethylamino functional group, and it easily polymerizes in the presence of oxidants or alkali at room temperature. According to these understandings, this study was to utilize dopamine as a biomimetic molecule of DOPA for textile colouration by mimicking the versatility of mussel adhesion to all substrates. Through the polymerization of dopamine at room temperature, textiles could be dyed with various colour appearances, which reduced colouration auxiliaries and energy consumption. The method works well on various textile fabrics, showing the substrate independence to some extent. It is an innovative direction of colouration on textile materials and is completely different from traditional process.

1.2 Project significance and value

Inspired by MAPs, the versatile adhesion induced by catecholic compounds has attracted great interest in developing bio-based innovative polymer materials in recent years. The MAPs mimetic materials are mainly synthesized by two approaches: one is polymerization or copolymerization using catechol-containing monomers and the other is conjugation of catechol moiety to synthetic polymers. These reported studies have succeeded to some extend in reproducing the main features of mussel adhesion, namely versatility and water resistance. However, none of these studies focus on dyes targeting colouration of textile materials so far.

This study aims to utilize dopamine as a biomimetic precursor molecule to develop a novel colouration method for textile materials. This dopamine-induced colouration can be easily applied to different kinds of textile materials at room temperature in a simple way.

In traditional colouration process, dyes selection strictly depends on the nature of textile fibres due to the specific interaction between dye molecules and fibres. In order to improve their colouration properties, high colouration temperature is often needed and hence high energy consumption. At the same time, different kinds of auxiliaries including dispersing agent, levelling agent, penetrating agent and accelerating agent are also used to improve colouration performance. At the end of colouration, these auxiliaries remain in the dye bath and are discharged as wastewater, which makes great adverse impacts on the environment. Even with high temperature and many auxiliaries, it still lacks the efficacy to dye different kinds of textile fibres with the same dye types.

Using the dopamine-induced adhesive colouration, various textile materials could be easily dyed at room temperature. The amount of colouration auxiliaries and energy consumption are greatly reduced in the whole colouration process, which meets the requirements of environmental-friendly process. The colour appearance of the dyed materials could be controllably tuned through the incorporation of a different nucleophilic species into the colouration bath. In order to enrich the colour gamut of the dyed materials, commercially available dyes could also be utilized in the method.

Furthermore, in the synthesis of catechol-containing dye, the chromophore employed in this study is not limited to types of dyes. Various commercial dyestuffs or components could be used to produce wide range of dyes with a variety of colour hues for different textile materials.

The dopamine-induced colouration shows the versatility to some extent via its various physicochemical interactions with fibres. In addition to commonly used fibres, it is promising as a good alternative for some special fibres which are difficult to be dyed with traditional process, such as polypropylene (PP), polylactic acid (PLA) and polybenzimidazoles (PBI).

The developed biomimetic method and its successful application in this study represent a step forward for textile material colouration. It breaks through the substrate-dependence in a traditional process and reduces the need of auxiliaries and much reduces the energy consumption. It should contribute to the effort of developing new generation of greener colouration processes for textile materials.

The following objectives were set up under the scope of this work:

1. To study dopamine polymerization-induced colouration of various materials
2. To tune the colour appearance of dyed materials obtained from dopamine
3. To enrich the colour gamut by introducing a chromophore to dopamine
4. To study the dyeability and colouration properties of the coloured materials

1.3 Methodology

In this study, the following methodologies will be employed:

1.3.1 Dopamine-induced colouration

After oxidation of dopamine, the formed dopamine quinone has the ability to react with various nucleophilic species, such as heterocyclic components, amino acids and aromatic amines. Thus its subsequent polymerization chemistry can be changed. Through this way, the colour appearance of the dyed materials could be tuned in a controllable way.

1.3.2 Dopamine-induced colouration with commercially available dyes

In order to enrich the colour gamut and verify the colouration feasibility with commercially available dyes, several dyes was used for the dopamine-induced substrate-independent colouration on different textile materials. In the process, the dye molecules are firstly adsorbed onto textile materials via a simple dip-coating process and then fixed through various physicochemical interactions between polydopamine and fibres. The dip-coating process can be repeated for several cycles based on the end use. Different dyes, such as natural dyes and synthetic dyes, can be used in this method.

1.3.3 Colouration with catechol dye

In order to enhance the fixation of dyes on fibres, a novel kind of catechol dye was designed and synthesized. In this dye, dopamine was introduced into a commercially available dye as a ‘molecule anchor’ through a covalent reaction. Thus, the obtained

catechol dye would display improved dyeability on textile materials through the multiple physicochemical interactions of dopamine. Herein, a commercial available dye of Acid Yellow was used as a model of chromophore. The chemical structure of the synthesized dye was confirmed from the analyses of high resolution mass spectrometry, proton and carbon nuclear magnetic resonance spectroscopy.

1.3.4 Characterization of the coloured textile materials

The colour appearance of the dyed textile materials were characterized through colorimetric analysis using a Macbeth colour-eye 7000A spectrophotometer. The CIE (International Commission on Illumination) system was used to define the colours of the textile materials. The colour yield was calculated using Kubelka-Munk equation based on the reflectance measured by the spectrophotometer. The colour fastness was evaluated according to AATCC Standard Test Methods. The surface morphology, compositions and wettability of coloured textile materials were studied by scanning electron microscopy, X-ray photoelectron spectroscopy and water contact angle measurement, respectively. The cross-sectional images of the coloured fibres were investigated using an optical microscope.

1.4 Framework of this thesis

This thesis stated that various textile materials were coloured using a novel substrate-independent method bio-inspired by the adhesive properties of marine mussels. It comprises six chapters.

Chapter 1 introduces the background of research, methodology, significance and value of the project.

In chapter 2, the traditional colouration of various textile materials is summarized. In addition, the characteristic and mechanism of marine mussels' adhesive are introduced. Some reported biomimetic studies related to dopamine were also presented.

In chapter 3, textile materials were dyed with various colour appearances through the oxidation-induced polymerization of dopamine at room temperature via a simple dip-coating procedure. The obtained colour appearances of the textile materials were tuned in a controlled way through adding second component to the polymerization bath or using oxidants with different oxidation ability.

In chapter 4, this bio-inspired method was advanced to achieve a wider range of colour appearances on textile materials through the incorporation of commercially available natural dyes into the dopamine polymerization bath. The dyed textile materials were characterized using colorimetric analysis and the related measurements.

In chapter 5, a novel kind of catechol dye was designed and synthesized through covalent introducing dopamine into a commercially available dye as a ‘molecule anchor’. The chemical structure of the synthesized catechol dye was confirmed using spectral analyses. The absorption property was also discussed. The dyeability of the obtained catechol dye was also investigated on various textile materials, especially those difficult to be coloured by traditional methods, such as polylactic acid and polypropylene.

Chapter 6 concludes the whole work of the thesis, and some suggestions are recommended for future research.

Chapter 2

Literature Review

2.1 Introduction

Colour is an important element for a quality textile product. The value of textile materials in the market can be greatly increased by colouration. To date, synthetic dyes have been widely used for textiles colouration due to their wide ranges of colour gamut and good colouration properties. However, the consumption of large amounts of synthetic dyes produces detrimental effects on our environment and human health. For this reason, there has been growing interest in colouring textiles with natural dyes, on account of their low toxicity and allergy as well as their better environmental-friendly property. In general, natural dyes are non-substantive and require the use of mordant to fix them on fibres for improvement of colouration properties including exhaustion and colour fastness. After colouration, certain portion of these metallic mordant remain in the dyebath, which may cause serious effluent problem.

To solve the above problems, it is a good choice to resort to nature. In nature, there are a large number of organisms with unique and optimised characteristics through long evolution process. Among these, marine mussels have attracted much attention due to their remarkable features including the permanent adhesive ability in underwater environment and the versatility to virtually all types of inorganic and organic surfaces[1-6]. Inspired by this, this study was to utilize dopamine as a biomimetic precursor for textile colouration by mimicking the versatility of mussel adhesion to various substrates.

In this chapter, the structure and colouration properties of textile fibres will be introduced. Moreover, the colouration mechanism and some recent development of the most popular dyestuffs in textile colouration including reactive dye, acid dye, disperse dye as well as natural dyes will be discussed. In the meantime, the features and the adhesive mechanism of marine mussels will be discussed. Some recent works related to mimicking mussel adhesive will also be presented.

2.2 Textile fibres

Textile fibres are generally divided into three types including cellulosic fibres, protein fibres and synthetic fibers[7-9]. Their structure and colouration behaviour will be discussed in following sections, respectively.

2.2.1 Cellulosic fibres

The common natural cellulosic fibres include cotton, linen, hemp, jute and flax. Cotton is the mostly used natural cellulose fibre worldwide to produce apparel, home furnishings and industry products. In the molecular structure of cotton fibre, there are regions of molecular order and disorder at different degrees resulting in crystalline and amorphous regions, respectively. The crystalline regions impart strength and rigidity to the fibre, while the amorphous regions are associated with sorption, reactivity and flexibility[8,9]. During the colouration process, the dye molecules and auxiliaries are first adsorbed on the fibre surface, and then diffuse only within the accessible amorphous regions of the fibre. The colouration behaviour of cotton depends on the relative

distribution and proportion of the amorphous and crystalline regions[9-12]. Meanwhile, the colouration properties of the fibres vary with their specific surface area, which is inversely related to the fibre fineness. The fibre is finer, the colouration rate is greater[9].

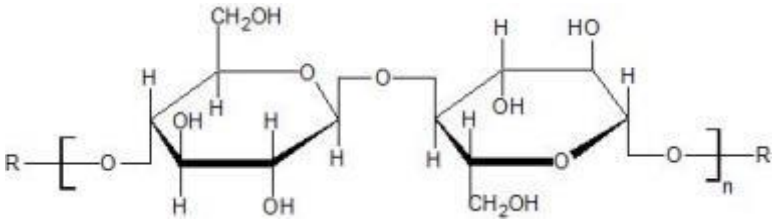

Figure 2.1 Chemical Structure of Cotton fibre

Cotton is a fibre made of almost entirely pure cellulose (up to 95%). From its chemical structure (Figure 2.1), cellulose is a polysaccharide, which is a high molecular weight polymer comprising of long chains of repeated glucose units. For each glucose unit, it contains three hydroxyl groups. These hydroxyl groups offer the cellulose molecules a polar character, which is favourable to the dye adsorption on the fibres. Moreover, these hydroxyl groups also provide a kind of dyeing site for the colouration of cotton fibers[7-9]. In addition, cellulose has considerable amount of open structure allowing dye molecules to penetrate into the fibre. Therefore, there are a large number of dyes including reactive dyes and direct dyes, which can be used for cellulose fibre colouration based on the end use and requirements.

2.2.2 Protein fibres

Wool and silk are the most important protein fibres, which are derived from animal sources. The protein molecules are composed of polypeptide chains containing many amino acid residuals. Each amino acid contains a basic amino group ($-NH_2$) and a carboxylic acid group (-COOH). Wool fibre is composed of extremely complex protein called as keratin (Figure 2.2), which is highly cross-linked by disulphide bonds (-S-S-) from a sulphur-containing amino acid of cystine. In addition, ionic bonds also form between the protonated amino ($-NH^{3+}$) and carboxylate ($-CO_2^-$) groups, which are presented in the side chains and the end of polypeptide chains. The proteins in the core of fibres can bind with dyes and allow the fibre to hold the dyes[7-9,11]. Wool fibres are stable to acid, but unstable to alkali, even to a weak alkali at low concentration[11-12].

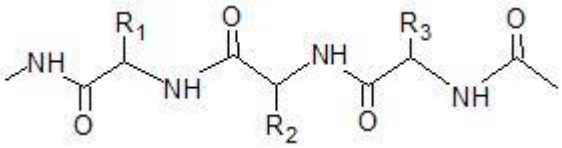

Figure 2.2 Chemical structure of protein keratin

Silk is secreted proteins, which are secreted as continuous filaments from the glands of the larve. Silk is composed of simple protein chains, which arranged in linear structure links through hydrogen bonds between amide groups of adjacent protein chains. Its molecules are arranged as crystalline and amorphous regions, which are similar to those of cellulose. Differently from wool, silk is not resistant to acids, but is more resistant to

alkali due to the absence of cysteine[9-12]. Protein fibres may be dyed using a wide variety of dyes. Most commonly used dyes are acid dye and mordant dyes.

2.2.3 Synthetic fibres

Compared with natural fibres, synthetic fibres have high crystallinity and are hydrophobic in nature because their moisture regain values are low. Synthetic fibres are usually dyed in the presence of dispersing agents which help dye molecules diffusing into the fibres. Even in the presence of dispersing or carrying agent, the colouration is usually carried out under a high temperature of over 100°C [7,9,10,12].

2.2.3.1 Polyester fibres (PET)

Polyester is the leading synthetic fibre in the worldwide textile market due to its several important properties, such as extremely strong, excellent resiliency and recovery from bending deformation. The major polyester in the market is polyethylene terephthalate. As shown in Figure 2.3, polyester is aromatic polyester, and a relatively hydrophobic fibre in nature compared to most natural fibres, mainly due to the presence of the benzene rings and $–CH_2CH_2–$ groups. The lack of basic or strong acidic groups in polyester results in little affinity for dyes that are ionic in character. Also, the polyester is a highly crystalline fibre that consists of tightly packed and highly ordered polymer molecules. Therefore, it is relatively inaccessible to even small molecules and it is difficult to be dyed[8,9,12]. Disperse dyes are an application class of dyes with low molecular weight and low water solubility. They can be applied as a fine dispersion to

these hydrophobic fibres at temperature of around 130°C under pressure. Instead of the use of high temperature, carriers may also be used to induce polyester fibres to take up disperse dyes, which can facilitate dye molecules easier penetrating into the fibre and obtain a deeper colour shade on fibers[9,11].

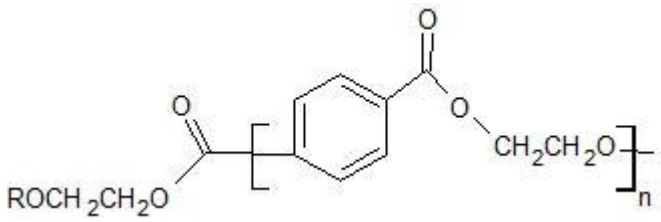

Figure 2.3 Chemical structure of polyester fibre

2.2.3.2 Poly(lactic acid) fibres (PLA)

Poly(lactic acid) is an aliphatic polyester derived from 100% renewable and non-polluting crops such as corn, cassava, which are used as raw materials to produce the monomer of lactic acid for PLA preparation (Figure 2.4). PLA is usually formed by two major synthesis routes, direct condensation of lactic acid and ring-opening polymerization of lactide. The processability of PLA is equivalent to that of petroleum-based synthetic fibres. Namely, PLA fibre can be produced by both conventional melt and solution spinning process. PLA has low affinity to many conventional disperse dyes, and it can only be dyed with good properties by few disperse dyes using a similar colouration procedure of PET. Because PLA's refractive index is lower than that of PET, thus it can be dyed to deeper and brighter shades[9,13,14]. The selection of colouration pH and temperature is important to PLA colouration without affecting its fibre physical properties. Compared to PET colouration, the

temperature is usually reduced to 90-115°C, since a high temperature often leads to severe loss of strength and elongation of PLA fibre. Due to the poor alkali resistance of PLA, alkaline, even neutral dyebath can cause substantial strength loss via hydrolysis. PLA fibre has better hydrophilicity than most of the thermoplastic polymers like PET, polypropylene and nylon, since water molecules have access to the polar oxygen linkages in the PLA molecule. This results in better wettability of fibres as well as the moisture vapour transmission of fabrics made with PLA fibers[8,9,13,14].

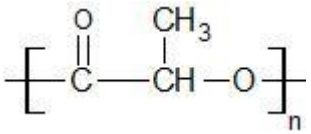

Figure 2.4 Chemical structure of PLA fiber

2.2.3.3 Polypropylene fibres (PP)

Polypropylene is a versatile thermoplastic polymer widely used in the industrial and home furnishing sectors due to its low cost, high toughness, high strength and resistance to chemicals. But poor moisture adsorption and its poor dyeability hinder its usage in the apparel sector of textile industry. Compared to other synthetic fibres, PP fibre is almost impossible to be dyed by conventional colouration techniques because of its high crystallinity, and lack of functional group in its chemical structure (Figure 2.5). This non-polar nature makes dye molecules difficultly fix on PP fibres. In order to improve its dyeability, many attempts have been made to modify the structure of PP fibres including the incorporation of dye-receptive additives in the polymer prior to fibre spinning[9], attaching functional groups or dye-repetitive monomers to the polymer via

grafting or copolymerization. Although these approaches can improve the dyeability of PP fibres to some extent, some excellent properties of PP fibre are lost. So far, very few colourations for unmodified PP fibres are reported[7-9].

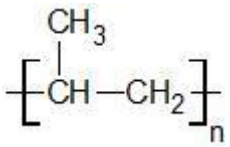

Figure 2.5 Chemical structure of PP fibre

2.2.3.4 Polybenzimidazole fibres (PBI)

Polybenzimidazole fibre is a synthetic fibre which is composed of a long chain aromatic polymer (Figure 2.6). The fibres are usually light gold shade to dark brown shade. It exhibits a non-inflammable because of it special chemical and thermal stability. Due to this superior stability, PBI fibres are suitable for the fabrication of high-performance protective clothing such as astronaut space units, fire fighter's gear, or other potential uses in furnishings. Successful application of any dye class on these fibres using standard colouration technologies is difficult since dye penetration into PBI fibres are generally poor, thus dye molecules easily fall off from fibre surface. In addition, PBI fibre has a relatively high glass transition temperature of around 350°C to 370°C, which perhaps also increase the colouration difficulty[7-10,12].

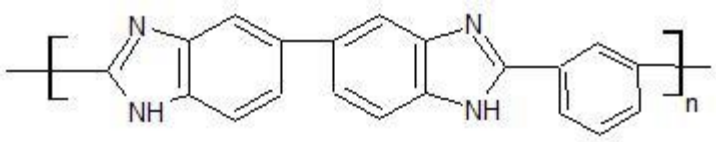

Figure 2.6 Chemical structure of PBI fibre

2.3 Commonly used dyes and pigments for textile fibres

For the colouration of above-mentioned textile fibres, there are several kinds of dyes used including reactive dyes, acid dyes, disperse dyes and natural dyes, and pigments are now commonly used to produce printed textile products.

2.3.1 Reactive dyes

Reactive dyes are the most important dye-class for cellulose materials such as cotton. It also can be used for the colouration of protein and polyamide fibres under weakly acidic condition. Unlike other kinds of dyes, reactive dyes can form covalent bonds with cellulose fibres through the chemical reaction between their reactive groups and the hydroxyl groups of cellulose fibre. Once the covalent bond is formed, the dye molecule has become a part of the fibre and is less readily to be removed by washing, which is different from other dyes just adhering onto fibres by physical adsorption. A typical reactive dye has four molecular structure features: (1) the chromophore, responsible for colour and much of the substantivity for cellulose, (2) the reactive group for the reaction with the hydroxyl group on cellulose, (3) a bridging group linking the reactive group to the chromophore, (4) one or more solubilizing groups, usually sulphonic acid substituents attached to the chromophore group[8-10,12] (Figure 2.7).

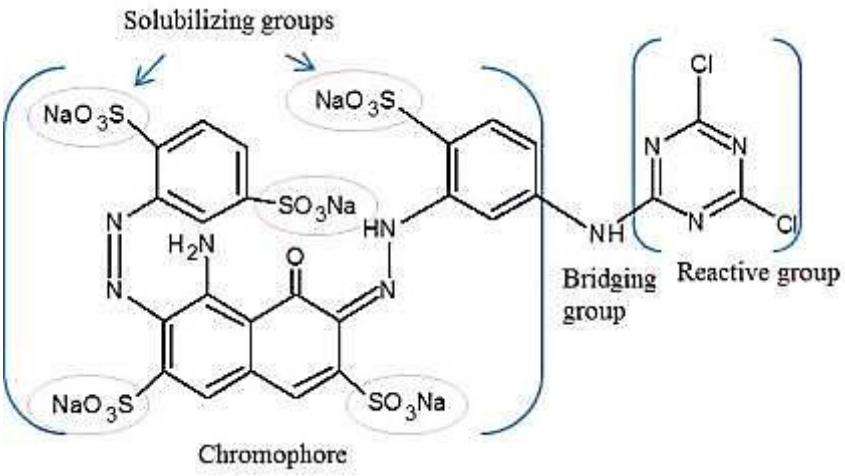

Figure 2.7 The chemical structure of reactive dye (C.I. reactive blue 109)

A typical colouration process with reactive dyes includes three stages: exhaustion, fixation and removal of hydrolysed dyes. During the exhaustion stage, dye molecules can uniform distribution in the cellulose fibres as they diffuse freely, and only little dye-fibre covalent bond forms. Upon the addition of alkali to colouration bath, the chemical reaction of the adsorbed dye with the fibre rapidly takes place then the dyes are fixed with the fibres by covalent bonds. After colouration, the dyed materials are rinsed and soaped to remove salt, alkali and unfixed dye which forms through the hydrolysis of reactive groups. Hydrolysed dye normally has low substantivity for cellulose and their removal are important to improve the fastness properties of the dye material[7-9,12].

In the reactive colouration of cellulose, the dyes commonly react with the cellulose fibres under alkali conditions, where deprotonation of the hydroxyl groups occurs. This

produces more active nucleophiles and performs either nucleophilic addition or nucleophilic substitution to form covalent bonds. In the case of nucleophilic addition reaction, an alkaline changes the reactive dye to an active species via converting the sulfateoethylsulfone to the vinyl sulfone, which reacts with cellulose fibre to form an ether bond. These dyes contain the reactive groups of vinyl sulphone, acrylaminde and α-chloro acrylaminde. On the other hand, dyes containing reactive groups of mono-fluoro-triazynylamino, di-chloro-triaynilamino, bis-triazinyl, mono-choloro-triazynylamino and di or tri-chloro-pyrimidylamino, are usually via nucleophilic substitution reactions. These reactions can be described in terms of the attraction of an electron-deficient carbon atom for the free lone pair electrons on the nucleophile[7-9,12,15].

Reactive dyes can be classified according to their types of reactive groups. Bis-reactive dye, which possess two reactive groups, which contain two monochlorotriazine or a combination of triazines and vinyl sulfone reactive groups. These dyes have the capacity to react with fibres in a multiple way. Vinylsulphone dye (VS), which are moderately reactive and show excellent fixation properties under proper alkaline condition. Its colouration temperature is usually at 60 °C and the pH value is adjusted to 11.5 with the addition of soda ash and caustic soda. Remazol Black B is one of the examples of these dyes. Compared to vinylsulphone dye, monochlorotriazine dyes (MCT), are less reactive. The colouration is generally carried out at 80°C and pH value of 10 for a proper fixation on cellulosic fibers[9-10,15].

2.3.1.1 Recent development of reactive dyes

In recent years, new ranges of reactive dyes designed to offer a considerable impact in term of better fixation properties, deeper shades, and hence eco-friendly property have been launched to market[15-29]. Huntsman introduced an Eriofast range of reactive dyes as a completely new metal-free dye molecule for polyamide fibres. Also, Avitera SE, a new range of multifunctional reactive dyes with three reactive groups per dye molecule, were launched in 2011. These dyes were designed for fibres with the advantages of time, energy saving and reduced water consumption. DyStar launched Remazol Ultra RGB for deep-shade colouration with 50% less dyes may be used to achieve the same depth as commodity dyes did. And Levafix CA dyes were developed for high fixation and excellent light fastness. Also, the first fluorescent reactive dye, Remazol Luminous Yellow FL, giving very brilliant greens and yellows, was introduced by DyStar[15].

In addition, much research interest related to reactive dyes for natural and synthetic fibres have been reported in literature. Ciba (now Huntsman) introduced tetrafunctional reactive dyes containing two vinylsulphone/monohalo-*s*-trazine residues, and a Proctor & Gamble patent[15] reported tetrafunctional reactive dyes prepared by dichloro-*s*-triazine dye with two mole of cysteamine. When being applied to cotton, these tetrafunctional dyes achieved total fixation efficiencies >95% in medium shade depths at 50°C with the addition of sodium sulphate and sodium carbonate. Lewis *et al.*[16] investigated the disulphide-ethylsulphone dyes containing two identical chromophores. These dyes showed good substantivity to cotton and could covalently fix to the fibre through the two formed vinylsuphone moieties.

Neutral-fixing reactive dyes for cellulose fibres have received much attention as it simplifies the colouration process by eliminating the fixation stage and thus shortens the colouration cycle. This concept was further studied by Croft *et al.*[15], who derived various quaternised dyes from the respective reactions of the bis-monochlorotriazine, Procion Red HE-3B, with DABCO, isonicotinic acid, nicotinic acid, nitcotinamide, trimethylamine, and pyridine. These dyes showed good exhaustion and fixation properties after colouration at boiling at pH 7 for 1 hour.

Besides, cationic reactive dyes were introduced for cellulose fibres with negative charges. The colouration was conducted at 85 °C for 100 min without the addition of electrolyte and only sodium carbonate was added to the bath after first 10 min colouration. A similar approach was further investigated by Zheng et al. [17]. They prepared green, red and blue anthraquinone glycidyl cationic dyes. Acid-fixing reactive dyes were also developed for the purpose of improving the colouration efficiency of cotton/polyester blends using mixture of reactive dyes and disperse dyes, mildly acidic fixation conditions would be favourable[18-22].

With the increasing awareness of the environmental concerns associated with heavy metals, reactive dyes are usually used as an alternative on wool for deep shades of black and navy blue to chrome dyes. Müller[23] investigated AOX residue from wool colouration using reactive dyes and recommended that it was more environmentally friendly to select reactive dyes containing only sulphatoethylsulphone residues as reactive group. Lewis and Shao demonstrated that good colouration performance on silk

in terms of colour yield, levelness and fixation, could be obtained via first preactivation of the SES dye to its vinylsulphone form by treating it on boiling at pH 8 for 5 min and the subsequent colouration for further 40 min at pH4.0 - 4.5 in the absence of salt.

Lewis and Sun[24] reported the synthesis of blocked vinylsulphone dyes using 2-thiol-choline for nylon fibre's colouration. The solubilising group of these dye was the trimethylammonium cation, which showed excellent substantivity when it was applied to nylon at pH 10. And then the thiol-choline residue was eliminated on boiling to form the vinylsulphone group which could readily react with the deprotonated amines in nylon. The results showed that these cationic reactive dyes gave better exhaustion and fixation properties when compared to anionic vinylsulpone dyes.

Much effort to enhance dye-fibre covalent bonding has concentrated on cellulose modification, and hence efficient reactive colouration in the absence of electrolyte or salt could be possible. Lewis and Lei[25] introduced water-soluble cationic agents through the reaction of dimethylamine and epichlorohydrin. These agents would fix to cotton by an alkali-catalysed pad-dry-bake method and that the obtained cotton was readily neutral dyeable with reactive dyes at the boil in the absence of electrolyte. It was found that such colouration displayed good light and wet fastness properties, which was similar to those of untreated cotton dyed with selected reactive dyes under the normal salt/alkali process. Lewis and Mcllroy[26] reported that cotton was reacted with nicotinoylthioglycollate (NTG) in high yields through the reaction of sodium thioglycollate with nicotinoyl chloride. NTG was applied to cotton fabric using a

pad-dry-cure method to prepare the modified cotton, which gave an overall fixation efficiency of 65% in the absence of electrolyte for reactive colouration. Another bioengineering approach was investigated by workers from the University of Ghent and Bayer Crop Science NV (Belgium)[27]. They demonstrated the growth of transgenic cotton to produce the *N*-acetyl-glucosamine oligosaccharide form of cellulose. The results showed that amino groups had been incorporated, which caused efficient reactive colouration in the absence of salt.

2.3.2 Acid Dyes

Acid dye is a kind of dye containing sodium salt or ammonium salts of sulphonic acid or carboxylic acid. Acid dye possesses direct affinity for protein fibres and shows effective colouration for wool, silk as well as nylon fibre. Acid dyes denote a large group of anionic dyes carrying one or more sulphonic ($-SO_3^-$) or carboxylic ($-COO^-$) acid groups. These groups provide solubility in water, the medium for the colouration. The colouration is usually carried out under acid conditions (pH 2-7) and the dyes adsorb on fibres through multiple interactions including electrostatic attraction, hydrogen bonding, dipolar forces and van der Waal's forces. In the colouration, sodium sulfate is commonly used for the promotion of exhaustion[7-10,12].

According to their chemical structures, acid dyes can be classified into three main classes of anthraquinone, azo and triphenylmethane dyes. In addition, acid dyes also include some other classes such as xanthene and azine dyes. However, the chemical class of dyes does not define their colouration properties. Numerous acid dyes consist of

one or more azo groups like monozo C.I. Acid Red 1 and disazo C.I. Acid Red 142. With the increase of azo groups in dye molecules, the colour shades of the dyes tend to be duller and darker. Anthraquinone acid dyes contain sulfonic acid group that enable them soluble in water and substantive for wool and silk fibers. C.I. Acid Blue 78 is one of the examples of anthraquinone acid dye. Pyrazolone azo dyes contain a heterocyclic structure, which comparatively good light fastness. Examples of pyrazolone azo dye are C.I. Acid Yellow 13, 17, 27 and 41. Triphenylmethane derivatives is the oldest dye class providing brilliant blues, violets and greens, such as C.I. Acid Blues 69, C.I. Acid Green 16 and Acid Violet 15. But, the dyes of this class provide poor wash fastness. Xanthene dervivatives are closely related to the triphrnylmathane dyes. Although anthene dyes have only moderate light fastness, they are widely used for brilliant pinks. Examples are, such as C.I. Acid Reds 50 and 52. . They Azine derivatives have high tinctorial power and provide navy blue shades with good fastness, such as C.I. Acid Blue 59 and 102. In general, the affinity of acid dyes increase with the increase of their molecular weight. Hence, a weak acid dyebath is required for adequate exhaustion[11-12].

Acid dyes can be divided into three types based on their application condition and colour fastness properties[9-12,30-35]. Firstly, levelling acid dyes are mostly azo and anthraquinone derivatives of low molecular weight. This allows the dyes easy to penetrate into the fibres and also permits a degree of migration within the fibre, thus producing a level uniform colour. In the colouration of levelling acid dyes, it shows rapid adsorption at pH 2-3 even at low temperature of 40°C. The addition of sulphuric acid and formic acid to the dyebath are required to promote exhaustion, and sodium

sulphate is also used to aid levelling by giving sulphate ions to compete for the dye sites. Examples of this dye types are C.I. Acid Yellow 17 and 23. However, the dyes do not strongly bind to the fibres, resulting in the poor wet and light fastness. These dyes are utilised on tightly traditional soft yarns as well as hard twist carpet yarns, whose good levelness is required and wet fastness is less critical. In general, there are two subdivisions of the acid dyes including monosulphonated and disulphonated dyes. Compared to disulphated dyes, the monsulphonated dyes have better fastness properties. The choice of these two kinds of dyes depends on the requirements of final products[9-12].

Secondly, milling acid dyes have remarkably larger molecules than levelling acid dyes. Their exhaustions are promoted under moderate acid condition with addition of acetic acid. The exhaustion increases rapidly at 70°C or above. The migration and coverage properties of these dyes are poor due to stronger nonpolar Van der Walls' forces and hydrophobic interactions between fibre and big dye molecule. In order to achieve a slower and more uniform rate of adsorption, the addition of a levelling agent is needed. These dyes exhibit a higher level of wet fastness than levelling dyes due to longer alkyl side chains. Some common milling acid dyes are C.I. Acid Yellow 79, Reds 111 and 134[7-10].

Thirdly, supermilling acid dyes are mostly complex anthraquinone compounds with high molecular weight and contain higher alkyl substituents to impart more hydrophobic character to the dye molecules. Examples are C.I. Acid Red 1 and 138. These dyes require neutral or weakly acidic condition for exhaustion. Their poor migration and

levelling performance are due to the big molecule size. In addition, they can achieve good wet and light fastness properties[10-11].

2.3.2.1 Premetallised acid dyes (Metal complex acid dyes)

In premetallised acid dyes, the dyes molecules are combined with metal, usually chromium or cobalt. Their wet and light fastness properties are excellent due to the presence of metal complex, but the levelling property is poor.

There are two types of metal complex acid dyes. One is 1:1 metal complex acid dye, which means one metal ion is complexed with one dye molecule. For good exhaustion and good levelling performance on wool fibres, strong acidic dyebath is required for the colouration of this kind of dyes. But, strong acidic condition inevitably causes fibre damage. Another type is 1:2 metal complex acid dyes in which each metal ion is complexed with two dye molecules. In order to obtain better colour fastness and reduce fibre damage, this kind of dye may be applied in neutral or weakly acid bath (pH~ 6.5 to 7) with addition of latent acid. But, the levelling performance of this kind of dyes is poor[9-11].

2.3.2.2 Recent development of acid dye

Some commercially available dyes derived from a carcinogenic amine could release the parent amine as a contaminant, which is genotoxic. In this regard, Gang and co-workers[31] reported the dye synthesis using eco-friendly aromatic amines. Novel

monazo dyes based on 5,10-dihdrophenophosphazine were synthesized and applied on wool and silk fibres as acid dyes containing only one sulfonic acid group. The dyes showed four shades similar to that obtained using C.I. Acid Black I with good colour fastness. Besides, Huang et al.[31] developed a dual functional acid dye, which was synthesized by the condensation reaction between acid and 2-amino-6-nitrobenzothiazole. From the results, this dye showed good ultraviolet radiation protection capability and excellent colouration performance on silk fabric. Recently, Mohamed et al.[32] presented some new mono- and diazo acid dyes of 3-[2-(cyanomethyl)-thiazol-4-yl]coumarin and 3-(2-amino-thiazol-4-yl)coumarin derivatives for the colouration of wool and silk fabrics. Results showed that blue to violet shades were obtained on dyed fabrics with good colouration performance in term of colour depth, levelness and fastness including light and rubbing, perspiration, washing and sublimation fastness.

2.3.3. Disperse dyes

Disperse dyes are non-ionic nature and insoluble in water, may contain some weak solubilising groups only like $-NH_2$, -NHR and -OH. Thus, they possess comparatively good affinity for hydrophobic fibres such as polyester, nylon and acetate fibres. Disperse dye are low molecular weight substances and mostly are anthraquinone and azobenzene derivatives. These dyes have high melting point >150°C and are usually used after milling with dispersing agent, e.g. a naphthalene sulphonic acid-formaldehyde condensate. The presence of dispersing agent in dyebath is important in the application of disperse dyes. The dispersing agent molecules exhibit dual characters in the

formation of micelles. Their hydrophobic tails are inside the micelles to solubilize the dyes molecules. This can provide a higher apparent solubility to the dye and transfer the dye from the micelles to the fibre, as shown in Figure 2.8. Synthetic fabric is usually dyed with disperse dyes via boiling with the carrier or heating the dye liquor to around 130 °C under elevated pressure. To maintain the dispersion stable during colouration, some auxiliaries including carriers and levelling agents are required. Some dye precipitations may formed on the fibre surface in the presence of surface active agents when the temperature is higher than 100°C, which could be removed after colouration by reduction clearing. Colour of the dyed fabric may fade readily when ironing due to the absence of ionisable groups. Therefore, it is important to evaluate sublimation fastness or fastness to dry heat of the dye. Disperse dyes show thermal migration which means that dye molecules migrate from core to surface when drying temperature of dyed goods rise to 170°C or above. For disperse dyes with low molecular weight, migration takes place more easily[7-10,12,36].

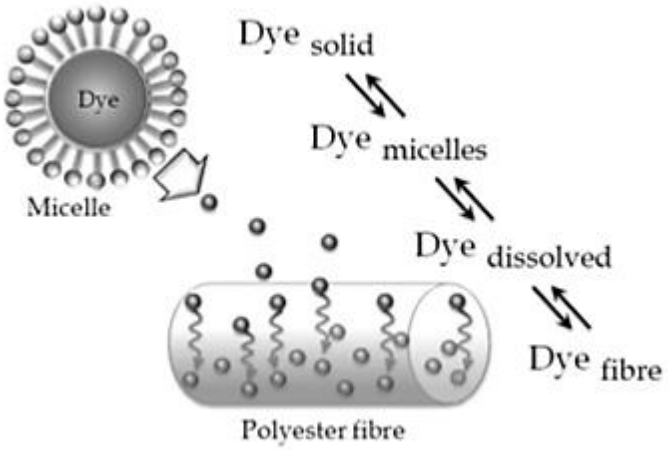

Figure 2.8 colouration mechanism of disperse dyes[36]

The Disperse dye committee of the Society of Dyers and Colourists (SDC) formulated several tests for disperse dyes according to their performances on range of hydrophobic fibres. These tests assess some characteristics such as colour build up, migration ability, the rate of colouration and sensitivity to changes in temperature. Low energy disperse dyes have low molecular weight and low polarity, inducing good levelling, rapid colouration dyes and poor heat resistance. On the contrary, high energy disperse dyes have higher molecular weight and higher polarity, leading to low colouration rates, poor migration and good sublimation and heat fastness[8-9,12].

Disperse dyes includes three main dye types of monoazo, disazo and anthraquinone dyes. In addition, disperse dyes also contain some other dye types including coumarin disperse dyes, nitroarylamino disperse dyes, methane disperse dyes. Azo dyes represent the largest and most important group in the market, as azo group is an intense chromophore in terms of tinctorial strength compared with anthraquinone chromophore, which is usually two or three times weaker in tinctorial strength[36-49].

2.3.3.1 Colouration in supercritical carbon dioxide fluid

Conventional textile colouration usually causes serious environmental problems due to the discharge of large amounts of wastewater to the environment. In recent years, the colouration of textile in supercritical carbon dioxide fluid has been extensively studied by many researchers as a clean and water free alternative to the conventional method[50-55]. The colouration of synthetic fibres such as polyester and polyamide 6 and 66 with disperse dye in supercritical carbon dioxide is easy to achieve due to their hydrophobic

in nature. However, it is difficult to be applied on natural fibres like cotton fibre as conventional water-soluble dyes for cotton colouration are difficult to be dissolved in hydrophobic supercritical carbon dioxide fluid. For this reason, much effort has been made on pre-treatment or modification of cotton fibre with various auxiliaries in order to increase the hydrophobicity or dyeability of cotton fibres with disperses dyes. Seili et al.[50] reported that the dye uptake on cotton fibre in supercritical carbon dioxide fluid was significantly increased after the pre-treatment with polyethylene glycol (PEG), and the adsorbed dye could be entrapped in the pores of the fibre. Ozcan et al.[51] employed benzoyl chloride to modify cotton fibre via a covalent attachment of hydrophobic aromatic group to the fibre. This modification improved the dyeability of cotton fibres with disperse dyes. N.N. Hoeschst studied the modicfication of cotton fibre by alkyl amino-group reagents before colouration. It was found that the nucleophilicity and hydrophobicity of the modified fibre were greatly increased, resulting in improved dyeability of the modified fibres with disperse dyes.

Although a satisfactory dyeability of cotton fibre was improved by pre-treatment, only limited improvement was achieved in dye fixation, and also those chemical treatments caused longer processing time, poor handle and large energy consumption, which are not suitable for industrial application of the supercritical carbon dioxide colouration. On the contrary, reactive diperse dyes can offer sufficient solubility in supercritical carbon dioxide. Therefore, different kinds of these dyes have been employed to dye cotton fibre in the absence of other co-solvents. Schmidt et al.[52] presented the modification of C.I. Disperse Yellow 23 using 1,3,5-trichloro-2,4,6-triazine and 2-bromoacrylic as reactive

groups. It was reported that the cotton fibres were successfully dyed with good washing, rubbing and light colourfastness by the modified reactive disperse dyes, although its obtained colour strength were lower than silk and wool fibres. Also, a polyester/cotton fibre can be dyed via a one step process. Recently, Fernandez Cid et al.[53] presented an acid-catalysed methanolysis reaction for the colouration of cotton fibre with triazine reactive disperse dye in supercrticial carbon dioxide. The electrophilicity of reactive groups in the triazine dyes were improved via the protonation of the triazine ring. In addition, Long et al.[54] investigated the colouration of cotton fabric with a vinylsulfone reactive red dye in supercritical carbon dioxide. Results showed that the dye fixation and colour strength of cotton fabrics were significantly increased using TEDA as the catalyst and their rubbing and staining fastness ratings were achieved 4-5 ratings.

2.3.3.2 Synthesis of novel disperse dyes

Amer et al.[56] reported that a series of novel 4-arylazo-3-hydroxythiophene disperse dyes were synthesized using ethyl 2-arylhydrazono-2-phenylthiocarbamoylacetates. The synthesized dyes were applied to polyester by conventional high temperature exhaust colouration. It was found that the dyed fabrics showed high colour depth, good washing and perspiration fastness. Etaibi et al[57] reported the synthesis of several novel pyrazolo [1,5-a] pyrimidine derivatives for the application as disperse dyes on polyester fibres using a new high temperature microwave heating method. The dyed fabrics displayed excellent wash fastness, but low light fastness. Patel presented some novel mordent and disperse heterocyclic dyes synthesized by coupling of various dizao solution of aromatic amines with 1-(2-butyl-2,3-dihydrobenzofuran-3-yl)-1-(4-hydroxyphenyl)methanone.

Results showed good penetration and affinity of the heterocyclic dyes with fibres and also gave excellent fastness to light, washing, perspiration and sublimation.

2.3.4 Natural dyes

Natural dyes, derived from natural resources, are non-toxic, renewable and sustainable resource with minimal environmental detrimental effects for colouration of various textile materials. Natural dyes are generally classified as plant, animal, mineral and microbial dyes. Plants are the major sources, and various shades can be obtained from various parts of the plants such as roots, leaves, barks, fruit and flowers. Natural dyes have a strong affinity to animal fibres like wool and silk, but less affinity to cellulosic fibres and synthetic fibres. Due to the increasing awareness of health and environment issues associated with synthetic dyes, there is a growing interest for the application of natural dyes on textiles[58-67].

2.3.4.1 Mordanting

Natural dyes are generally non-substantive to textile fibres, so their application often leads to some problems including low take-up and low colourfastness on the dyed textiles. In order to increase the affinity between dye and fibre, the use of mordant can improve the fixation of dye molecules with fibres, leading to a broad range of colour on various natural and synthetic fibres with better fastness properties[68]. Most commonly-used mordants for colouration with natural dyes are aluminium potassium sulphate, potassium dichromate, ferrous sulphate, stannous chloride and copper

sulphate[59]. While in these colourations, a certain proportion of metal salt mordant remains unexhausted in the residual dyebath and then is discharged as effluents. These lead to adverse impact on the public health and environment[61,66] .

Therefore, the selection of alternative mordants and improvement of conventional mordanting processes have attracted much attention in the development of natural colouration of textiles. Zheng et al.[58] presented rare earth chlorides as mordant for natural colouration of ramie fabrics. The results showed that the use of rare earth chlorides markedly reduced the ionic concentration in colouration. Thus, it could be a promising environmental friendly mordant in natural colouration, compared with those commonly-used metallic salts. Concerning the negative impact on environment, natural mordants are suggested instead of metallic salt mordants by some researchers. However, well-documented research record on their application in natural colouration is rarely reported. In general, bio-mordant source are metal hyperaccumulating plants and plants with high tannin content. Guesmi et al.[69] presented chlorophyll, extracted from various plants such as bark wood, leaves, roots, fruits and plant galls, has been successfully utilized as bio-mordant. Vegetable tannins are water soluble polyphenolic compounds from plant parts. These phenolic hydroxyl groups provide those crosslinks with dyes and various types of fibres, resulting in better colour fixation. Recently, Cunningham et al.[70] reported a review related to various Al-hyperaccumulating plants as natural metallic mordants as well as their applications in naural colouration of traditional Indonesian textiles. Vanka et al.[71] reported *Euriya acuminate* used as mordant for colouration with

Rubia cordifoloa dye. The dyeability of silk fabric was found to be improved through chelation due to the presence of high Al content.

2.3.4.2 Enzyme assisted colouration

The use of enzyme in textile processing is a kind of industrial biotechnology for the development of environmental friendly technologies in textile industry. Much effort has been contributed to the preparation, colouration and finishing of various textile fibers[72-74] with natural dyes using different types of enzymes. Kumbasar et al.[75] studied colouration properties of different proteinous materials with hydrolysable tannin based natural dyes derived from myrobalan, sumac, gallnut and oak bark in the presence of alkali proteases. After enzymatic treatment, the dye-uptake was markedly increased. Vankar and Shanker co-authors[76] investigated colouration characteristics of *Termonalia arjuna, Rheum emodi, Punica granatum, Tectona granis, Acacia catechu* and *Delonix regia* on a wide variety of textile fabrics using three enzymes of lipase, diasterase, protease. From the obtained results, the CIE Lab values of the dyed fabrics were improved by enzymatic treatment, and the total dye adsorptions were higher than untreated samples in all cases. However, no significant changes were found in fastness properties. They also indicated that the compatibility between dye and enzyme is important to improve colouration properties.

2.3.4.3 Sonicator-assisted colouration

Ultrasound can improve the efficiency of a wide variety of physical and chemical processes by generating cavitation in liquid medium and other mechanical effects including degassing, dispersion, diffusion as well as intense agitation of liquid[58,77-78]. Ultrasonic energy induces the oscillation and implosion of the cavitated bubbles, which enhance molecular motion and stirring in the dyebath. In order to make the process highly efficient, less pollution, low fibre damage, economical and energy saving, many different approaches have been developed to ultrasound-assisted natural colouration and finishing of textile fibres. Vanka et al. studied the effect of ultrasound for colouration various textile fibres with commercially available natural dyes like madder, tectona and catedhu[79]. The extraction identification and application of the naturals dyes from new vegetables sources was also reported[71-74,76,79]. It was found that sonicator-assisted colouration had a better performance than conventional colouration in terms of wastes reduction, electrolytes and dye concentration of in dyebath and effluent. Guesmi et al.[80] studied sonicator-assisted colouration modified acrylic fibres with indicaxanthin natural dye. In comparison with the results of conventional method, dye uptake, washing, light and water fastness significant improved.

2.3.4.4 Chemical and radiation pre-treatment and finishing

In recent years, a number of investigations have been carried out to natural textile colouration related to modern surface modification techniques for improvement in colour strength, fastness and functional properties of dyed fabrics in an environmental friendly way. Many researchers reported the usage of a biopolymer of chitosan as a

surface modification agent to enhance colouration performance on cotton[81] and wool fabrics[82]. The fabric pre-treated with chitosan increased the binding sites for the dye molecules to obtain better dye adsorption.

Low-temperature plasma (LPT) and sputtering are dry modification process generating no waste and have been recommended as an environmental-friendly alternative to wet chemicals method for the pre- and post-treatment of textile materials[83,84]. Park et al.[85] reported colouration PET with natural dye of *Caesalpinia sappan* using chitosan and/or O_2 low-temperature plasma as a pre-mordant. After the fabric was processed by padding, plasma-etching and immersion procedure, the colouration of the pre-treatment PET fabric with chitosan and/or plasma showed shorter colouration time and higher dye uptake, compared to the colouration with metal mordant. Kerkeni et al.[86] studied the pre-activation of PET fibrous surface with air atmospheric plasma and ultraviolet excimer to produce hydrophilic species, resulting in better colouration affinity with curcumin dye.

In order to modify hydrophobic acrylic fibre, amino groups was introduced to acrylic fabric by the treatment with hydroxylamine hydrochloride to enhance substantively of the fibre for some anionic natural dyes[69,80]. Some researchers[87,88] indicated the improved colouration performance of dye uptake and colour characteristics using high energy radiations such as UV radiation and gamma radiation.

2.3.5 Pigments

Pigments are widely used in textile industry to produce printed products for a variety of end uses such as home furnishings, apparel and nonwoven articles. Pigment prints offer a wide colour range at a reasonable cost on a variety of fabrics, particularly on blended fabrics. In a pigment dyeing system, there are three components required including pigments, thickener and binder, which are all dispersed in water. Generally, organic pigments are used for colouration of textiles; it includes azoic, carbazole, diarylide, pyrazolone, phthalocyanine, quinacridone and vat. Pigments are small insoluble particles which do not contain any groups capable of reacting with a textile fibre. A binder is required to bond the pigment particles on the fibre to achieve colour fastness. Most commonly used binders are acrylic copolymer emulsions or acrylic emulsions. The selection of binder has a significant effect on all performance properties of the printed fabric in term of crocking fastness, wash fastness and handle. The addition of the thickener in pigment printing is to offer a printable viscosity for colour formation, but they may cause an adverse effect on the handle of the printed fabric.[89-91] After the application of pigment and drying, the printed fabrics are usually heat cured to promote binder action. Moreover, various auxiliaries are usually used to correct or control the problems arise during printing process. However, the addition of an auxiliary may cause several negative effects on print properties at one time. For example, the presence of anti-wicking agent may lead to a negative effect on washing fastness and crocking fastness.[92-93]

2.3.5.1 Recent development of pigments

In recent years, some novel binders and dyeing method have been developed in order to achieve the pigment dyeing in a more environmental friendly way. Molla et al.[89] reported some eco-friendly binders of polyurethane acrylate based on either glycerol ethoxylate-co-propoxylate or polyethylene glycol having no volatile organic compounds can be used for printing of various types of textile fabrics. Fang et al.[90] studied the dyeing of cationised cotton by an exhaustion method using nanoscale pigment dispersions. It was found that the nanoscale pigment dispersion cause higher colour yield than those of conventional pigment dispersion and offer several advantages including improved handle and appearance. Also, Wang et al.[91] developed the surface modification of silk by N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride, then the modified silk dyed with superfine pigment using exhaust process. The results showed that the treated fabrics retain a soft handle, good crocking and washing fastness properties. Subsequently, Molla et al.[92] synthesized polyurethane acrylate oligomers as aqueous UV-curable binder. The obtained results indicated that the prepared binders can be used safely for pigment dyeing or inks of ink jet printing and imparted the coloured fabrics with soft handling and good colour fastness properties. Rafique et al.[93] developed a eco-friendly compatible pigment colouration system for dyeing of cotton/polyester. It was found that the combined treatment of modified dihydroxyethylene urea coupled with an appropriate softener resulted in good washing and crocking fastness, however, the tear strength of coloured materials slightly decreased.

2.4 Marine mussel

Marine mussel has attracted much attention due to their remarkable adhesion to a wide range of substrates. The blue mussel, *Mytilus Edulis*, is the most widely studied marine mussel[89-94]. Research efforts have concentrated on identifying the genes responsible for the adhesive proteins and the adhesion mechanisms in mussels[99-105]. In recent years, numerous studies focused on the development of innovative polymer materials by reproducing the main features of mussel adhesion [106-129].

2.4.1 Mussel adhesive proteins

Marine mussels such as *Mytilus Edulis*, attach to a variety of surfaces rapidly in an underwater environment by secreting liquid proteins based on mussel adhesive proteins (MAPs). These proteins are able to form moisture-resistance and permanent bonds in a few seconds to various surfaces. A range of various MAPs have been identified from the *Mytilus Edulis* and the type of mussel protein is expected to contribute fundamentally to the adhesion mechanism. The byssus structures were given in Figures 2.9 and 2.10, Mefp-1 to Mefp-6 contain 3,4-dihydroxy-L-phenylalanine (DOPA), an unusual amino acid which is believed to be responsible for both adhesive and crosslinking characteristics of MAPs[94-105,130,131].

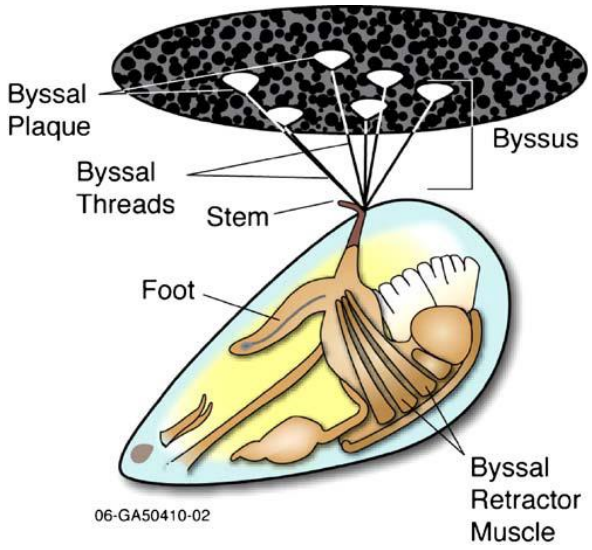

Figure 2.9 Anatomy of M. edulis mussel and byssus structures[91]

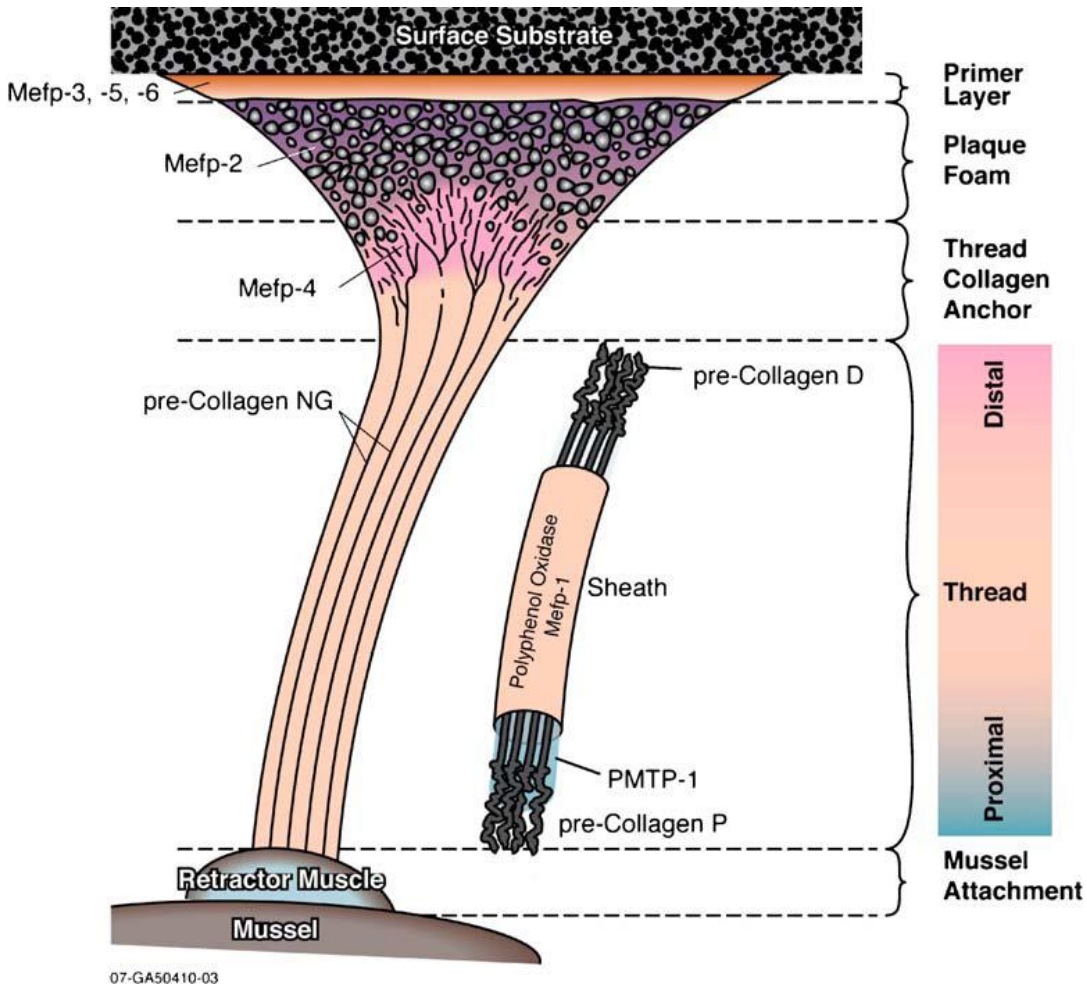

Figure 2.10 Location of adhesive-related proteins identified in the byssus of M. edulis[91]

Mefp-1 is the most studied mussel adhesive protein. It is large polyphenolic protein (molecular weight ~ 115kDa) located in the byssal threads and byssal plaques. It has 75-80 repeats of a decapeptide. Mefp-1 requires specialized catechol oxidase enzyme to oxidize tyrosine residues for its conversion to the reactive DOPA residues necessary for strong adhesion. The enzyme acts as an oxidative agent to catalyze oxidation. Molecular oxygen is required to further oxidize DOPA to a quinone. Polyvalent metal ions such as Fe^{3+} and Al^{3+}, oxygen and bi/polyfunctional cross-linker can be used as cross-linking

agents. To date, there are no commercial products of pure Mefp-1 in the market due to inconsistencies in the quality of protein and the expensive cost for extraction process[101-103,130,131]. Compared with Mefp-1, Mefp-2 is a smaller byssal adhesive protein (molecular weight ~ 42 to 47 kDa), with ~ 2 to 3 mol % DOPA only and contains 11 repeats of a 35 to 40 amino acid sequence. It can be found in byssal plaques only, and works as a major structural component[96,101-103]. Mefp-2 plays a stabilization role because of the high cysteine content (6-7 mol %) in the byssus[96,101-103,130,131].

Mefp-3 has the molecular weight of ~ 5 to 7 kDa, which is the smallest adhesive protein among the MAP family. It is located at the interface between the adhesive plaque and substrate surface. Mefp-3 contains no repeats and has 20 to 25 mol % DOPA and 4-hydroxyagrginine and tryptophan residues[96,130,131].

Mefp-4 contains arginine, glycine, histidine and 4 mol % DOPA and has a molecular weight of 79 kDa. As Mefp-2, it can be also found in byssal plaques. Mefp-4 also has a Tyrosine-rich octapeptide, which is a unique and very large protein likely acting as a coupling agent in the thread-plaque junction[96,130,131].

Mefp-5 is a the byssal adhesive protein which is recently found from *Mytilus Edulis*[96,130]. Mefp-5 is a relatively small adhesive protein with a molecular weight of 9.5 kDa. It has high level of DOPA content (27- 30 mol %) and also contains phosphoserine as well as lysine. The presence of phosphoserine may assist in adhesion of one animal to another mussel's shell and contribute interfacial adhesion on calcium-based mineralized

substrate. The lysine may also aid in adhesion by enhancing the solubility of protein and increasing interfacial adhesion through electrostatic force[130,131].

Mcfp-6 is a new protein identified along with the study of a different marine mussel species of Mytilus californianus by Zhao and Waite [97-99]. Mcfp-6 is a small protein which contains small amount of DOPA content and large amount of tyrosine. It may contribute to adhesion for providing a link between the DOPA-rich proteins and the plaque protein.

2.4.2 Adhesion mechanism in mussels

Marine mussels naturally attach themselves to diverse materials for various purposes such as protection, movement, and self-defence, as shown in Figure 2.11. Strong adhesion is essential to overcome tidal wave as well as wet saline environment[94,97]. Although extensive research has been made, the exact adhesion mechanism including the chemistry behind this is not fully understood. The mechanism seems to be dependent on several factors, including catechol content, oxidation rate, metal interactions, and a synergistic effect of several parameters [94,96,98-101,103,105,132-136].

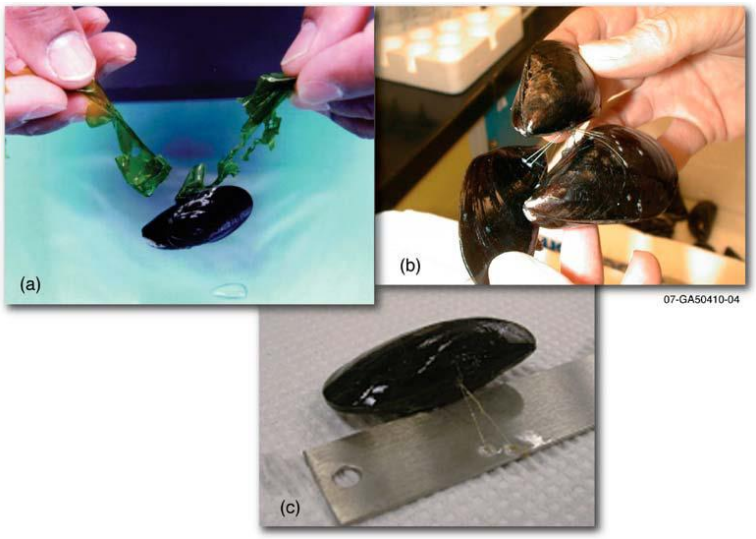

Figure 2.11 M edulis attachment to (a) seaweed, (b) other mussels, and (c) a stainless steel surfaces[91]

2.4.2.1 Mussel protein type

The type of mussel protein contributes to the adhesion mechanism in mussels respectively. Mefp-3 and Mefp-5 preferentially distribute at the adhesive surface between the substrate surface and the mussel adhesive plaque. These proteins contain high DOPA contents of 20-25% for Mefp-3 and 27-30% for Mefp-5, respectively and low molecular weight compared to other adhesive proteins. Lower molecular weight allows easy conformational changes that enable 4-hydroxy-L-arginine to build hydrogen bonds and DOPA to cross-link, resulting in improved adhesion to substrate[96,97].

High DOPA content and oxidative enzymes are important in processes of curing or forming cross-link on adhesive surface by individual adhesive proteins. The open conformation of proteins on the adhesive interface enhance the availability of functional

groups for hydrogen bonding and cross-linking, thus improve the adhesion strength[105,130,131].

The presence of chemical bonds is critical in mussel adhesion to substrates, especially attaching to biological materials. DOPA, 3,4-dihydroxyproline, 4-hydroxyproline, *o*-phosphoserine and 4-hydroxyarginine are the main post- or co-translationally modified amino acid groups found among MAPs. Mepf-3 and Mefp-5 are highly hydroxylated MAPs, which can form hydrogen bonds with many surfaces. DOPA form strong non-covalent bonds with metal oxides, metal ions, silicon dioxide on mineral surfaces, and also non-covalent π-π interactions between DOPA and other aromatic groups. Strong electrostatic forces are formed in mussel adhesion between positively charged mussel proteins and negatively charged marine surfaces. Mefp-2 plays vital roles in adhesion as it offers the bulk protein matrix[96,104,105,130-134].

2.4.2.2 DOPA in adhesion

One of the unique structure features of mussel adhesive proteins (MAPs) is the presence of 3,4-dihydroxy-L-phenylalanine (DOPA)[104,105,137]. Although the role of DOPA in mussel adhesion is not well understood, the high DOPA content in proteins such as Mefp-3 and Mefp-5 at the adhesion interface is believed to contribute to adhesion[96]. As indicated in Figure 2.12, DOPA will be oxidized to quinone or semiquinone in the presence of oxidizing agents, and followed by cross-linking reaction via aryl-aryl coupling or Michael additions in the presence of amine-containing protein residue. This is believed to provide the water-resistance characteristic of mussel adhesion in an underwater environment[104,105,133,136,137]. In a study on interfacial reactions of a single

molecule of DOPA with an inorganic surface (Ti), it suggested that unoxidized DOPA formed reversible and strong coordination bonds to inorganic surfaces, but the oxidized form of DOPA, quinones, created covalent bonds that promoted the adhesion to organic surfaces[102].

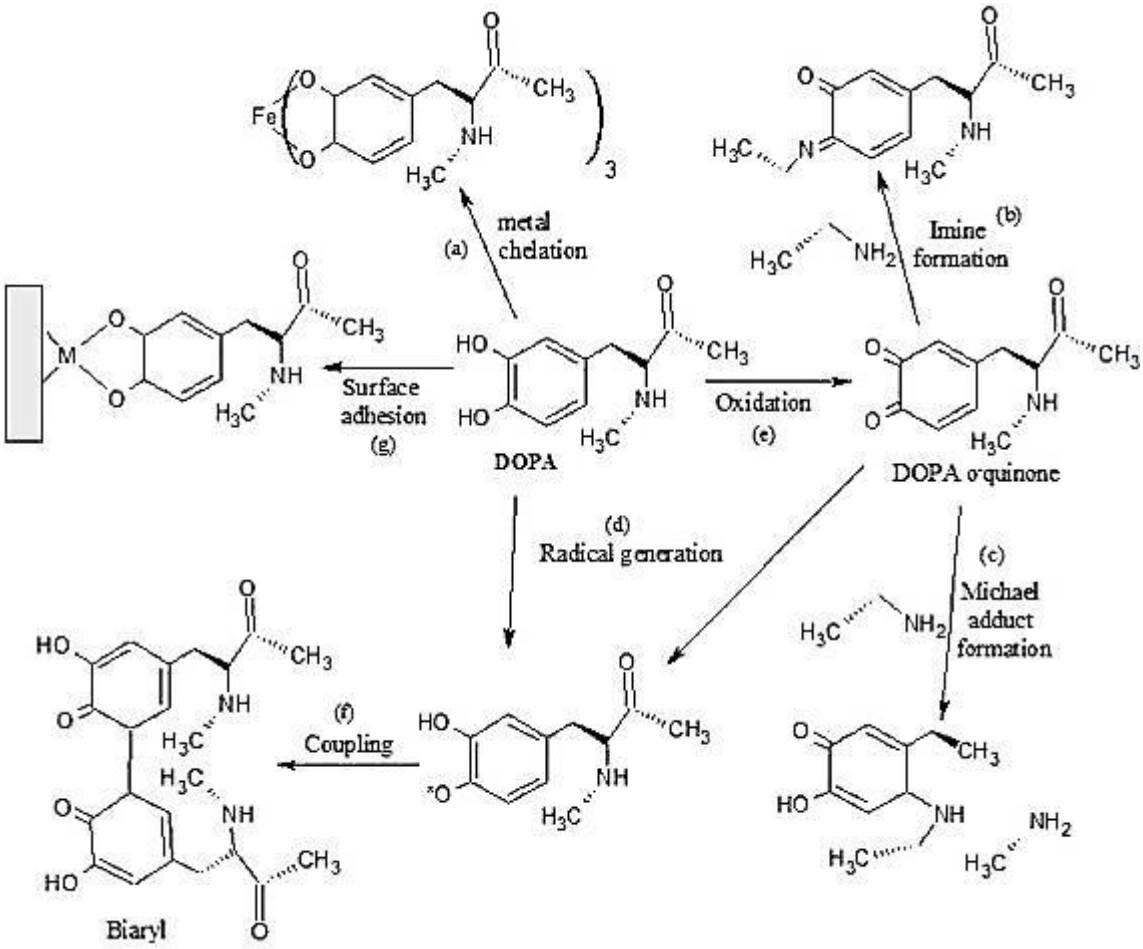

Figure 2.12 Schemes showing DOPA oxidation to o-quinone followed by crosslinking [91,125-127]

DOPA is formed in these proteins by post-translational hydroxylation of tyrosine residues. Other constituents of MAPs include lysine and glycine. Lysine may provide

adhesion by ionic bonding to surface with negative charge[96]. The open structure of glycine contributes to bonding of proteins to the surface groups of substrate. The repetitive nature of many individual proteins contributes to the exceptional strength of mussel adhesive proteins[101-103,130-132].

2.4.2.3 Metal ions on adhesion

Metal ions are cross-linking agents for DOPA-containing proteins in mussel adhesion[138,139]. Mussel adhesive proteins display specificity to certain metal ions like Mn^{3+} and Fe^{3+}, which can be found in adhesive plaque. They can oxidize catechol to quinone and initiate MAP curing, while Fe^{2+}, Al^{3+} and Cr^{3+} do not show this role. Mefp-2 shows self-interactions and interactions with Mefp-5 in the presence of Fe^{3+} and/or Ca^{2+}. However, Mefp-2 does not have interactions with Mefp-1 or Mefp-3[134].

2.4.2.4 Oxidation rate

In the formation of adhesive plaque, multilayer adsorption and aggregation play important roles in forming the aggregated structure of adhesive plaque. The multilayer formation and clustering depends on the rate of cross-linking [139-142]. Cross-linking can occur via autoxidation of quinone or aromatic nucleophiles[135,143]. pH and redox potential have direct effects on the oxidation rate, which finally determines the rate of cross-linking. When DOPA shifts to DOPA-quinone, the rate of oxidation plays an essential factor in the regard of autoxidation and cross linking. The presence of metal

ions induces cross-linking, which is enhanced by the addition of oxidants to achieve a synergistic effect.

2.4.3 Mussel protein biomimetic

Mussel adhesive proteins exhibit remarkable adhesive performance. However, the difficulty in extracting these proteins from natural mussels hinders their applications. Therefore, alternative approaches have been developed based on biomimetic. It is believed that catechol is the only functional element required for both adhesion and cross-linking[144,145]. Catechol and its derivatives provide a new approach to the preparation of functional composite materials and the modification of various substrates by simple chemistry. The synthesis and assembly of novel types of catecholic derivatives will be discussed in the following sections.

2.4.3.1 Synthesis of catecholic derivatives

Different novel catecholic derivatives including catecholic small molecules and catecholic polymers have been synthesized by various methods. Deming et al[146] synthesized MAP mimetic polypeptides by the polymerization of *N*-carboxyanhydride monomers of lysine and DOPA. After testing their adhesion to steel, aluminium, glass and several synthetic polymer surfaces, copolypeptides containing 10 mol% DOPA were cross-linked via oxidation and adhered approximately ten times stronger to aluminium than a polylysine control polymer.

Lee et al[108] chemically coupled DOPA residues to poly(ethylene glycol) (PEG) polymers for synthesis of MAP mimetic hydrogels. It demonstrated that the tissue adhesive potential of PEG-DOPA hydrogels exceeds that of fibrin glue. Besides, catechol-containing polymers for surface independent layer-by-layer (LbL) assembly were synthesized by bio-mimicking mussel adhesive protein adsorbs to virtually all surfaces[106]. To demonstrate the substrate versatility of LbL using catechol functionalized polymers, the LbL assembly was applied on PTFE, a particularly challenging substrate due to its anti-adhesive property. Also, LbL was demonstrated on several other polymeric surfaces including polyethylene, poly(ethylene terephthalate) and polycarbonate.

Westwood et al[123] prepared a simplified polymer mimicking of bio-adhesives. A polystyrene backbone was used to take the place of the protein polyamide chain. Cross-linkable catechol groups are appended to the polystyrene in order to mimic DOPA. Results showed that poly[(3,4-dimethoxystyrene)-co-styrene] polymers exhibited curing analogous to that of the proteins after which they were modeled. The styrene-catechol copolymers also possessed enhanced adhesion upon cross-linking.

2.4.3.2 Biomimetic natural biological process

Brown et al[147] reported a novel natural-based hair colouring process by imitating some of the basic steps from the natural biosynthetic pathway to melanin. In the hair colouring process, dopa was oxidized under controlled conditions to undergo a sequence of reactions that finally formed eumelanin-like pigments. It was found that addition of

cysteine into the melanogenic process resulted in red and yellow pheomelanins produced on hair, as shown in Figure 2.13. Also, obvious colour changes could be produced by incorporating a variety of nucleophiles to the system. The resulting dyed hair achieved good performance similar to that from conventional permanent hair dyestuff.

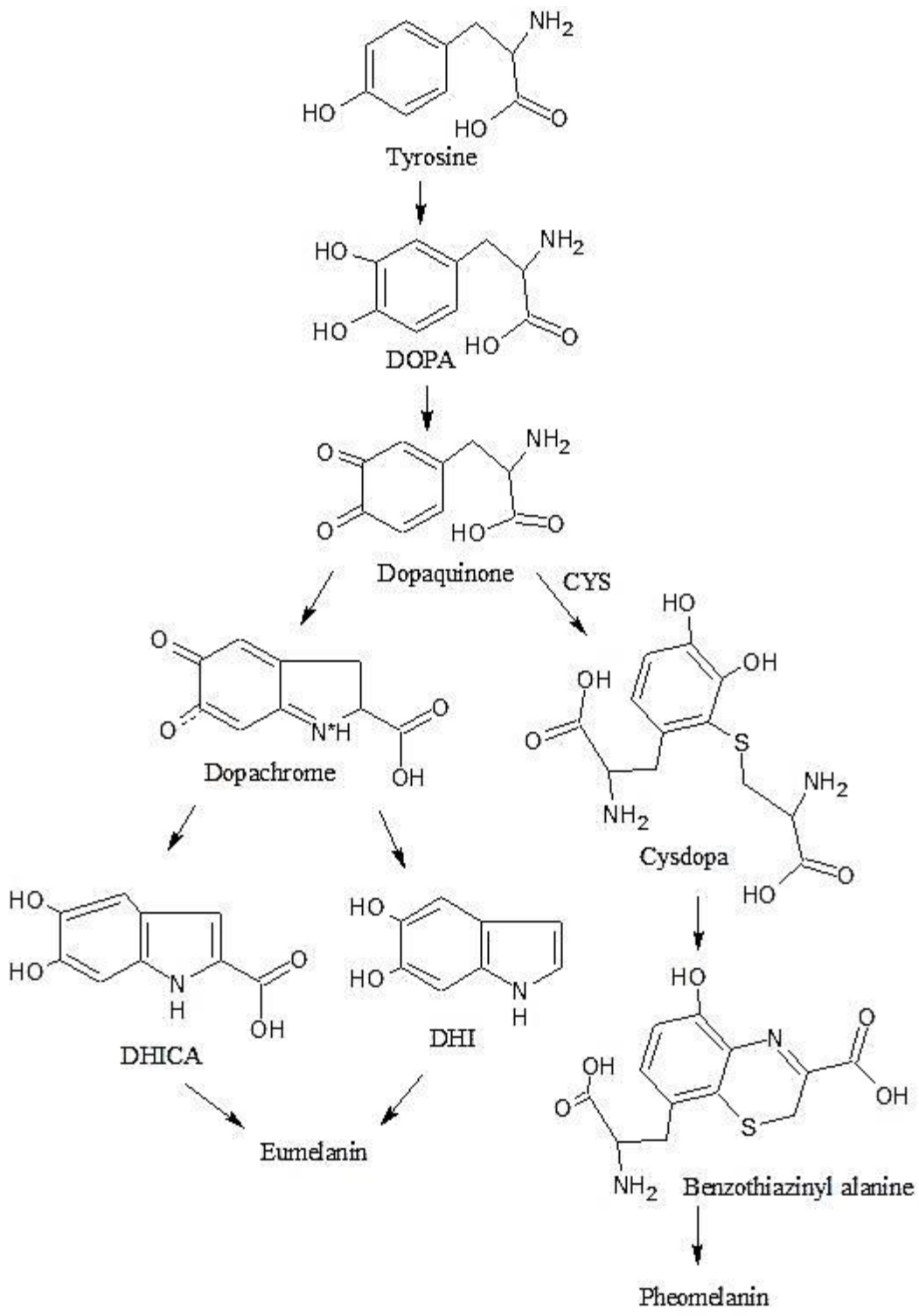

Figure 2.13 Simplified scheme for melanogenesis[142]

2.4.3.3 Surface modification by catecholic compounds

The adhesive biomimetic strategy based on catecholic chemistry has attracted significant research interest since Messersmith *et al* reported that multifunctional thin film of polydopamine, produced by dopamine oxidative polymerization in alkaline solution, readily adhered to any exposed surface during polymerization, including noble metals, metals with native oxide surfaces, oxides, semiconductors, ceramics, and synthetic polymers[106,110-112,116].

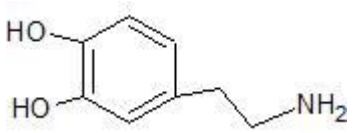

Figure 2.14 Chemical structure of dopamine comprising both alkylamine and catechol functionalities

Dopamine is a catecholic (1,2-dihydroxybenzene) compound with a primary amine functional group (Figure 2.14). This small molecule functions as a neurotransmitter whose deficiency causes Parkinson's disease[96,130-132]. As shown in Figures 2.15 and 2.16, Lee et al[106,112]reported that in an alkaline aqueous solution, dopamine undergoes self-polymerization to form an adherent polydopamine (Pdop) coating on the substrates and catechol groups are oxidized to the quinone form, which is responsible for cross-linking in adhesion. The material surfaces can be functionalized by the strong surface anchoring moieties produced by the oligo- or multimerization of catechols. The coated surfaces can be served as a versatile platform for several secondary

surface-mediated reactions including metal films by electroless metallization, bioactive functionalities and self-assembled monolayers etc., to produce a variety of functional materials (Figure 2.17). The advantages of two-step Polydopamine modification method is distinctive in its ease of application, substrate-independence, use of simple ingredients, mild reaction conditions, and capacity for multiple end-uses[96,130,106,112].

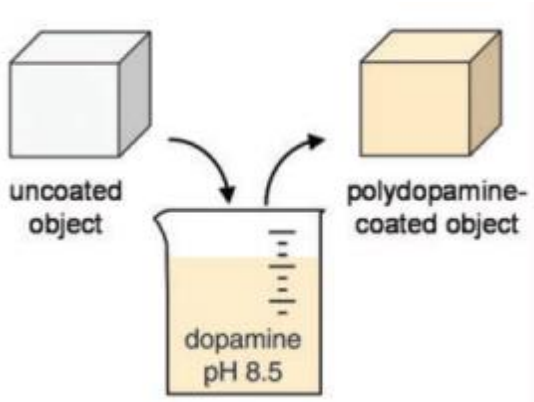

Figure 2.15 A schematic illustration of thin film deposition of polydopamine by dip-coating an object in an alkaline dopamine solution[101]

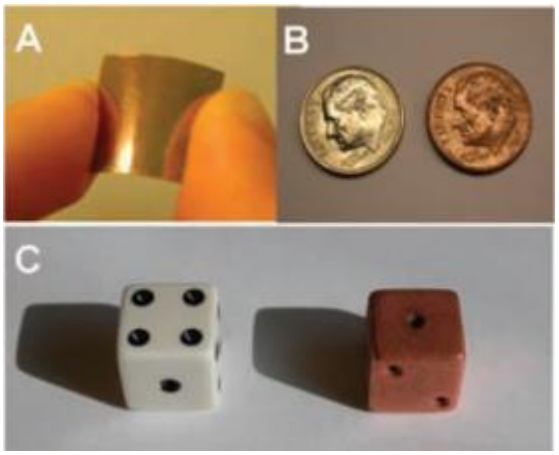

Figure 2.16 Polydopamine-assisted electroless metallization of substrates. (A to C). Electroless copper deposition on polydopamine-coated nitrocellulose film (A), coin (B), and three-dimensional plastic object (C)[101]

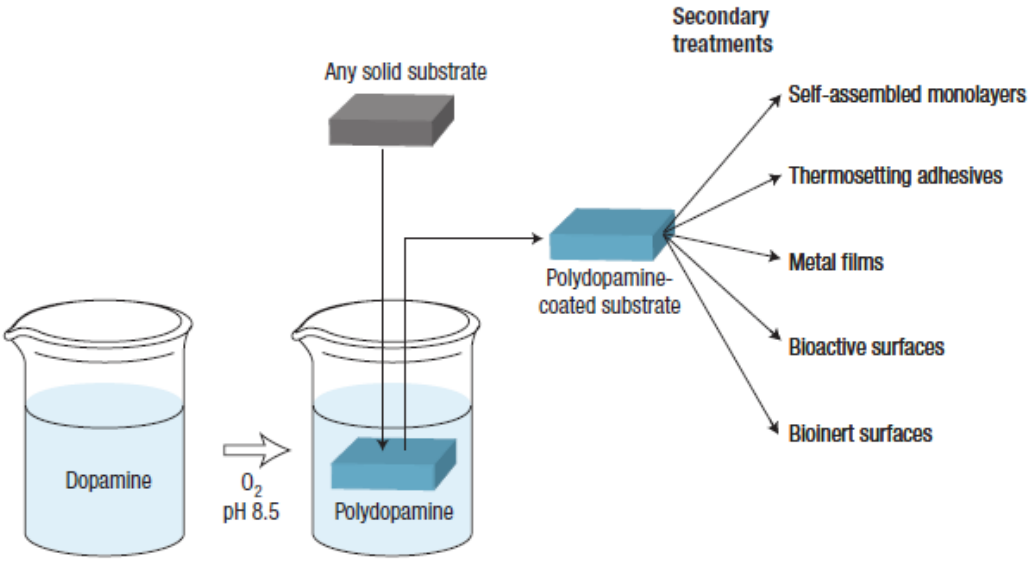

Figure 2.17 The polymer-coating and secondary treatment process[93]

Subsequently, Lee et al[112] developed one-step surfaces functionalization by immobilizing a wide variety of molecules. This strategy of surface medication can be applied to a wide variety of surfaces including oxides, noble metals, ceramics, and synthetic polymers. In addition, various functional compounds with a wide range in sizes and various chemistries containing amine, carboxyl, quaternary ammonium, thoil, and/ or catechol groups can be immobilized onto various surfaces by a one-step method without further chemical syntheses, as presented in Figure 2.18. The surface modification solution consists of three components: a substrate to be functionalized, dopamine, and a molecule to be immobilized. After the initiators were immobilized onto the surfaces, secondary modifications such as surface-initiated polymerization could be carried out. The above studies indicated a strong interest for MAP mimetic materials, and catechol and its derivatives can effectively modify a wide variety of substrates to obtain functional surfaces and materials via reproducing the main features of mussel adhesion.

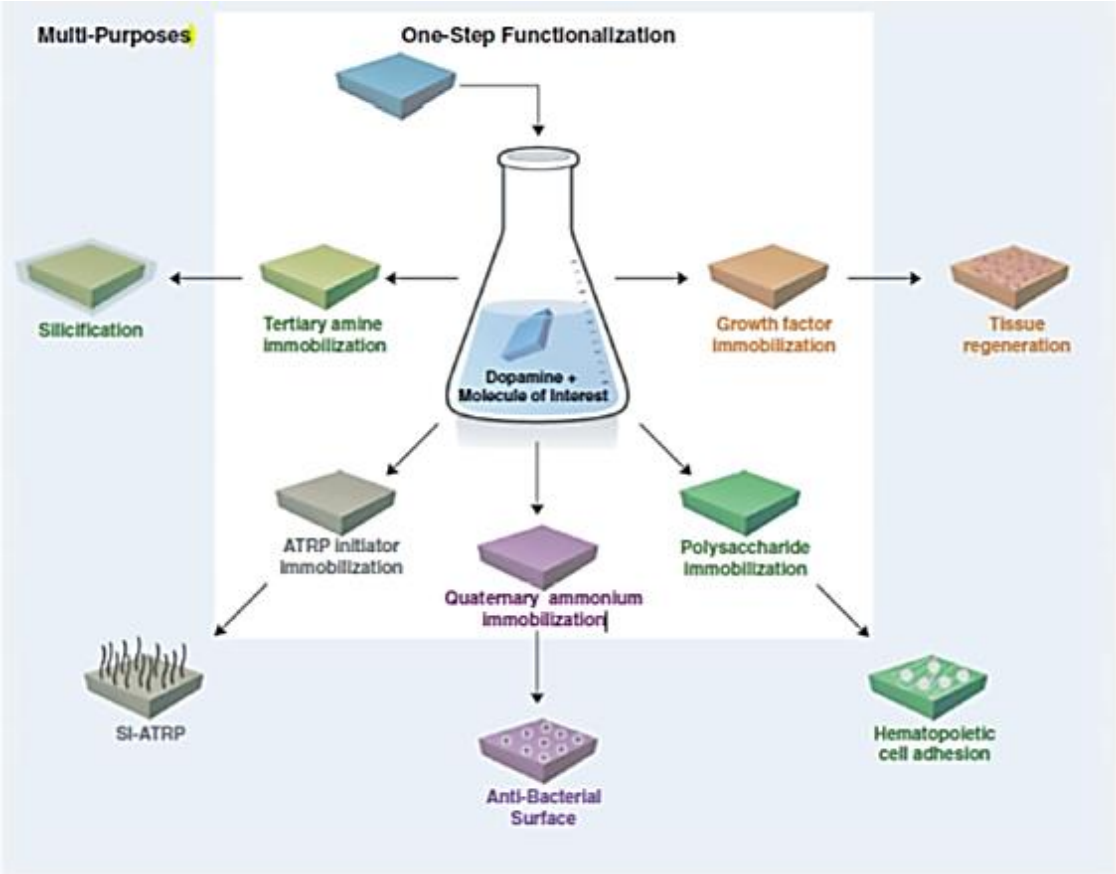

Figure 2.18 Schematics of the one-step modification of solid substrates[107]

2.5 Conclusion

The conventional colouration processes are complicated and the application of dyes highly depends on the nature of the fibres to be dyed due to the specific interactions between the dye molecules and the fibres. In order to improve the colouration performance, pre-treatment of textile materials is required prior to colouration or high temperature and various colouration auxiliaries are often needed in colouration process, resulting in complicated colouration process and high energy consumption. Inspired by MAPs, the versatile adhesion brought about by catecholic compounds has attracted

much interest in developing bio-based polymer materials in recent years. However, no studies focus on textile dyes targeting coloration of textile materials. This strategy is a promising environmental friendly alternative to the conventional colouration techniques.

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Chapter 3

Biomimetic dyestuffs for textile *in situ* colouration

3.1 Introduction

Various colours can be imparted to textile materials by two main types of dyes, natural and synthesized dyes. But the application of dyes depends on the nature of fibres to be dyed due to the specific interactions between dye molecules and the fibres. It lacks efficacy to dye various types of fibres with one dye. Although some researchers had developed a kind of universal dyes[1-2], its application in textile colouration industry is rarely reported. Moreover, high levels of energy and water consumption are involved in the dyestuff production and textile colouration process. After colouration, high levels of effluent contamination including dyes and auxiliaries like salts are released into the environment, resulting in adverse impacts to the environment. Therefore, a colouration method, which can be applied as a universal dye for a variety of textile fibres in a simple way, will be favourable to textile colouration industries.

In the natural environment, the long evolution process produces a large number of materials, objects and process with unique and optimized characteristics. The biomimetic and discovery in these fields has attracted increasing attention for many years. At the moment, although the complicated bioprocess hinder the full understanding of their exact mechanism leading to the difficulties in complete biomimetic, the interests in developing efficient biomimetic application never weaken but are growing fast[3-15]. In recent years, marine adhesive proteins (MAPs) have been

attracted much attention in biomimetic research due to their versatile adhesion[10]. These proteins are able to form moisture-resistant and permanent bonds in a few seconds to virtually all types of inorganic and organic surfaces. One of the unique structure features of MAPs is due to the presence of 3,4-dihydroxy-L-phenylalanine (DOPA)[6,7,10], which contains catechol and ethylamino functional groups.

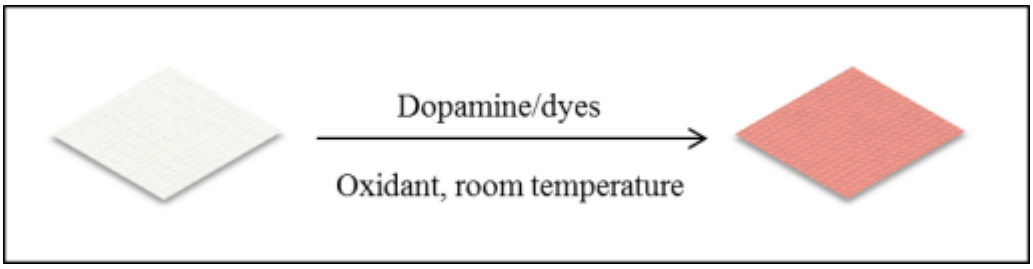
Dopamine also has these two groups, and can polymerize under alkali condition or in the presence of oxidants under room temperature[9,10]. Based on these understandings, in this study, dopamine was utilized as a biomimetic precursor for the adhesive coloration since it eventually changed to polymeric colour coating on textile substrates after polymerization. This method avoids the addition of auxiliaries in the colouration process, as indicated on Scheme 3.1. Various textile fabrics could be dyed with various colour appearances at room temperature via the oxidation-induced polymerization of dopamine. The colour produced on the fabrics could be tuned in a controllable way, such as adding a second component to the dye bath, or using oxidants with different oxidation ability. Commercially available dyes could also be utilized in this method to enrich the colour gamut. The surface chemical compositions, morphology and wettability of the dyed surfaces were evaluated by X-ray photoelectron spectroscopy, scanning electron microscopy and water contact angle measurement, respectively. It is expected to obtain a novel method for coloration of various textile fabrics with substrate independence. It is an effective alternative to traditional textile colouration.

3.2 Experimental

3.2.1 Materials

Four textile materials were used in this study including woven fabrics of wool (255 g/m^2), silk (101 g/m^2), cotton (116 g/m^2), polylactic acid (PLA, 118 g/m^2) and polybenzimidazole (PBI, 145 g/m^2). They were purchased from China Dyeing Holdings, Ltd. Before use, these fabrics were washed with 5gL^{-1} sodium dodecylsulfonate solution at 60 °C for 20 minutes to remove possible surface impurities. The fabrics were then rinsed thoroughly in deionized water and dried in air.

Glass and aluminium slides were selected as the representatives of ceramic and metal materials. They were commercially available and ultrasonically cleaned in ethanol for 5 minutes before use. Apart from dopamine, several commercially available second components (Figure 3.1) were also incorporated as representatives of phenols, amines, amino acids and heterocycles. Rhodamine B was selected as a model of a commercially available dye in this process. All chemicals were purchased from Sigma-Aldrich and used as received.



Scheme 3.1 A description of dopamine polymerization-induced coloration for textile materials

3.2.2 Colouration of fabrics

Washed fabrics were dipped in an aqueous solution containing 10% of dopamine at room temperature for 24 hours. Subsequently, it was taken out from the solution and sprayed with an aqueous solution containing 1% potassium periodate and then dried in air. In this process, several commercial available components were also incorporated as the second component with the mass ratio to dopamine of 5:1 to tune the colour hue of the fabrics. The fabric was dipped in an aqueous solution containing 1.7% of dopamine in the presence or absence of 8.3% of a second component at room temperature for 24 hours. Subsequently, the fabric was taken out of the bath and treated with 1% oxidant solution, and then dried in the air.

Other materials were dipped in an aqueous solution containing 5 mg mL^{-1} rhodamine B and 5 mg mL^{-1} dopamine hydrochloride at room temperature for 24 hours. The solution was buffered to pH8.5 with Tris. Afterward the resulting samples were taken out and then washed in deionized water for 10 minutes; the obtained samples were air dried.

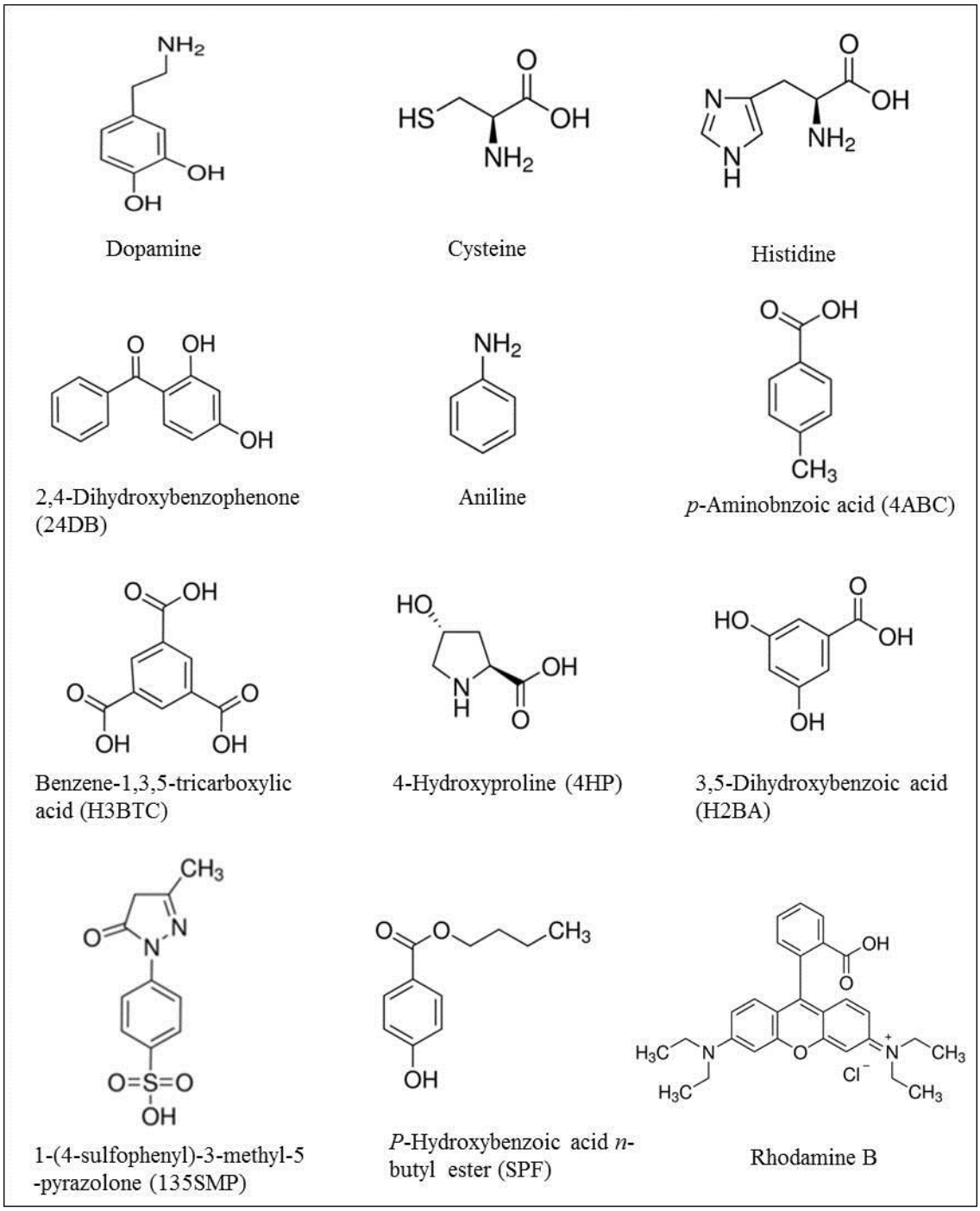


Figure 3.1 Chemical structures of dopamine and second components used in this study

3.2.3 Spray colouration for pattern design

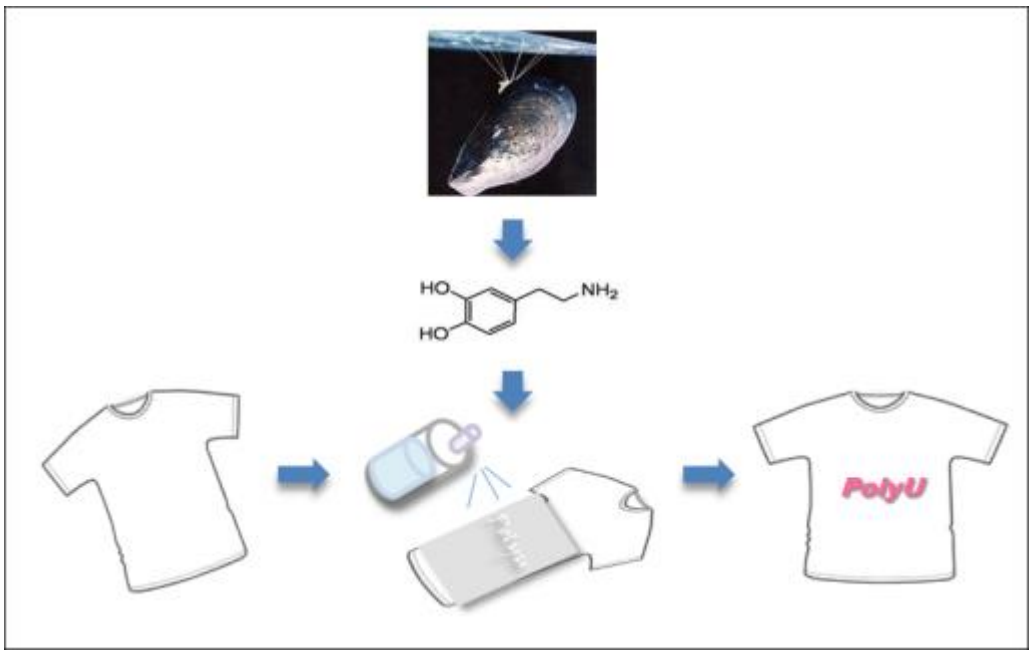


Figure 3.2 Simplified scheme for spray colouration process on textile materials

Washed fabric was dipped in a solution containing 1.7% of dopamine in the presence of absence of 8.3% of a second component at room temperature overnight. The fabric was then taken out from the solution, followed by spraying 1% oxidant solution on fabric directly or with a template for pattern design, as shown in Figure 3.2.

3.2.4 Colorimetric analysis

The UV-vis absorption of the dyed fabrics was measured using a Perkin Elmer Lambda 18 UV-vis spectrometer with a scanning speed of 240 nm min^{-1}.

The colorimetric analyses of dyed fabrics were evaluated using a Macbeth Color-Eye 7000A spectrophotometer with specular component excluded and UV component included. Average values of 4 times measurements were recorded.

The CIE system was (CIE L*a*b*, D65/10°) was used to assess the chromatic condition of the coloured fabrics. L^* is a measure of colour lightness and its value range from 0 to 100, 0 indicate perfect black while 100 indicate perfect white. a^* give a scale of red-green character of colour, in which positive value representing the redness and negative representing greenness. The value of b^* measure a yellow-blue character with positive value indicate yellowness and negative value indicate blueness. The total colour difference was calculated according to ΔL^*, Δa^* and Δb^* as following equations[16]:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

The colour strength in term of K/S values at the maximum absorption wavelength (400nm) of the dyed fabrics was calculated using Kubelka-Munk equation. The equation is shown below[11]:

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

Where K is the coefficient of absorption, S is the coefficient of scatter and R is the reflectance of the sample at a given wavelength.

The chemical composition of the material surfaces were studied by X-ray photoelectron spectroscopy (XPS). XPS measurements were conducted on a SKL-12 X-ray photoelectron spectrometer (Shenyang, China) equipped with a VG CLAM 4MCD electron energy analyser. XPS is configured with a dual anode source from VG (type XR3E2) and non-monochromatic Mg Kα radiation (1253.6 eV) at a current of 15mA with an ultrahigh vacuum (<8 X 10^{-10} Torr). To compensate for surface charging effects, all binding energies were referenced to the C1s hydrocarbon peak at 284.6 eV.

The wettability of the samples was evaluated by water contact angle measurement by a Model CAM- Micro Contact Angle Meter (Tantec, USA).

3.2.5 Microscopic analysis

The surface morphology of the fibres was studied using a scanning electron microscope (Hitachi Tabletop Microscope, TM-3000).

The cross-section images of dyed fibres were examined by an optical microscope (Nikon Optiphot-POL manufactured in Germany, high-performance Leica LAS software). The blue colour nylon yarns were used as a substrate to support fibre sample during sample preparation and testing.

3.2.6 Colourfastness testing

Samples were subjected to the standard methods of colourfastness to laundering: accelerated (AATCC Test method 61-2010, test no. 2A)[17] and colourfastness to crocking: crockmeter method (AATCC Test method 8-2007)[18]. The ratings were assessed using a grey scales, which ranges from 5 for no shade change (or no stain on the adjacent fibres) down to 1 for a severe shade change (or staining), with half points in between. Light fastness was evaluated according to the standard method: ISO 105 B02-2013 (xenon-arc lamp)[19].

3.3 Results and discussion

3.3.1 Colorimetric analysis

Dopamine has a catecholamine group, which would be capable of self-polymerization via spontaneous oxidation in the presence of oxidants at room temperature and displayed the adhesion to various substrates[15,18-22]. Dopamine was utilized as biomimetic molecule of DOPA for textile colouration by mimicking the versatility of mussel adhesion to all substrates. The catechol groups in dopamine are liable to be oxidized, turning dopamine into dopaquinone. This molecule undergoes rearrangement via intramolecular cyclization to leukodopaminechrome, and followed by cross-linking. It was reported that dopaquinone, formed during oxidation of DOPA, has the ability to react with various nucleophilic species[20]. According to this understanding, during the oxidation process, we attempted to tune the obtained colour appearances via adding various nucleophiles to the

polymerization bath, such as amino acids, UV absorbers, aromatic amines and heterocyclic components. The simply proposed scheme is shown in the Figure 3.3.

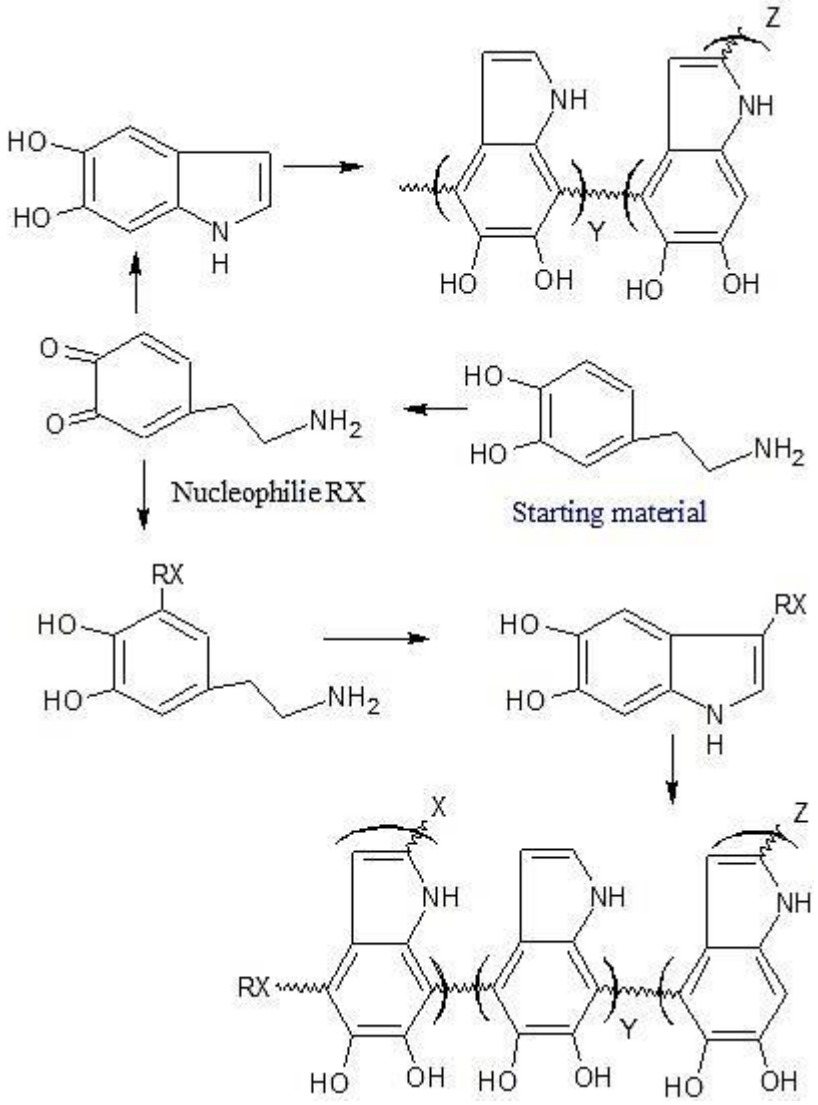


Figure 3.3 Simplified schemes for biomimetic coloration for textile

3.3.1.1 Colouration on wool fabrics

The dopamine solution was colourless at room temperature, and also no absorption was found in the visible region, as shown in Figure 3.4. In the presence of oxidant, it was observed that the dopamine solution gradually changed to yellowish brown. Due to dopamine polymerization induced by oxidation, there was absorption in the visible region and an absorption peak centred about 350 nm. Polydopamine has an adhesive ability, which was used to prepare adhesive polymers and coatings. This unique characteristic could be utilized to enhance its fixation on the fibres.

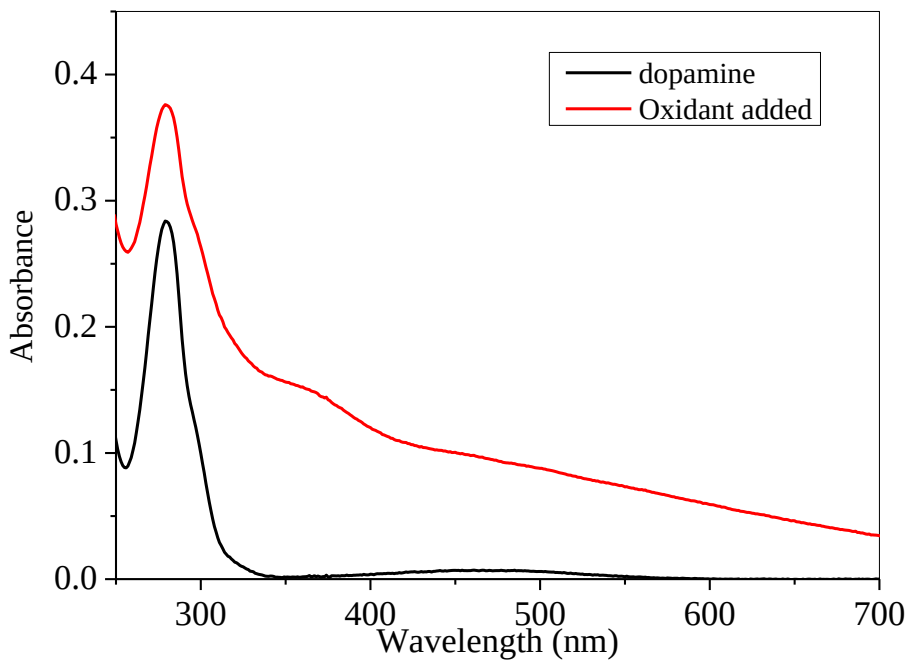


Figure 3.4 UV-vis absorption spectra of dopamine before and after oxidation

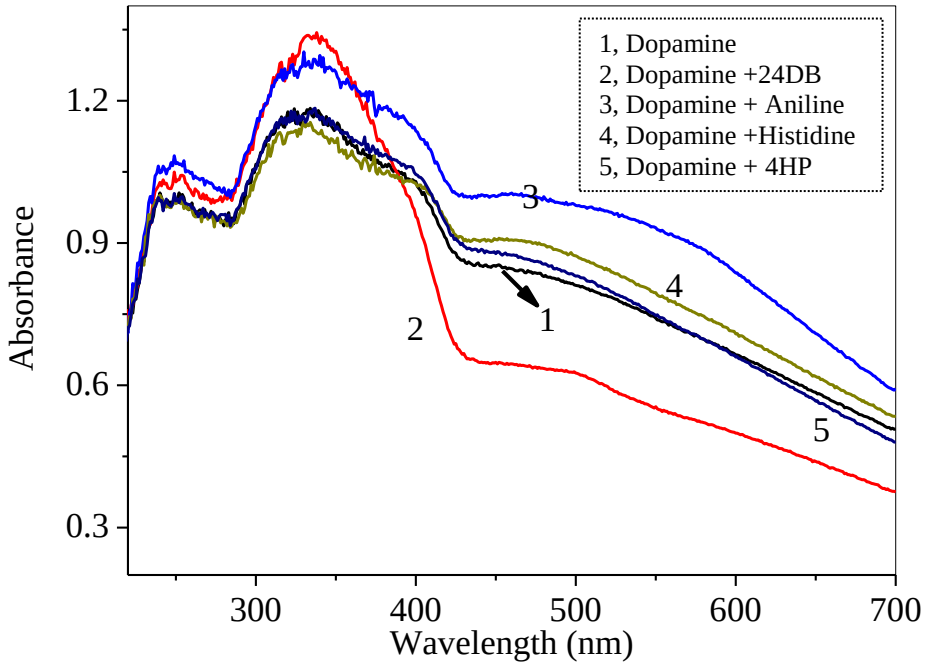


Figure 3.5 UV-vis absorption spectra of the coloured wool fabrics using dopamine and various components

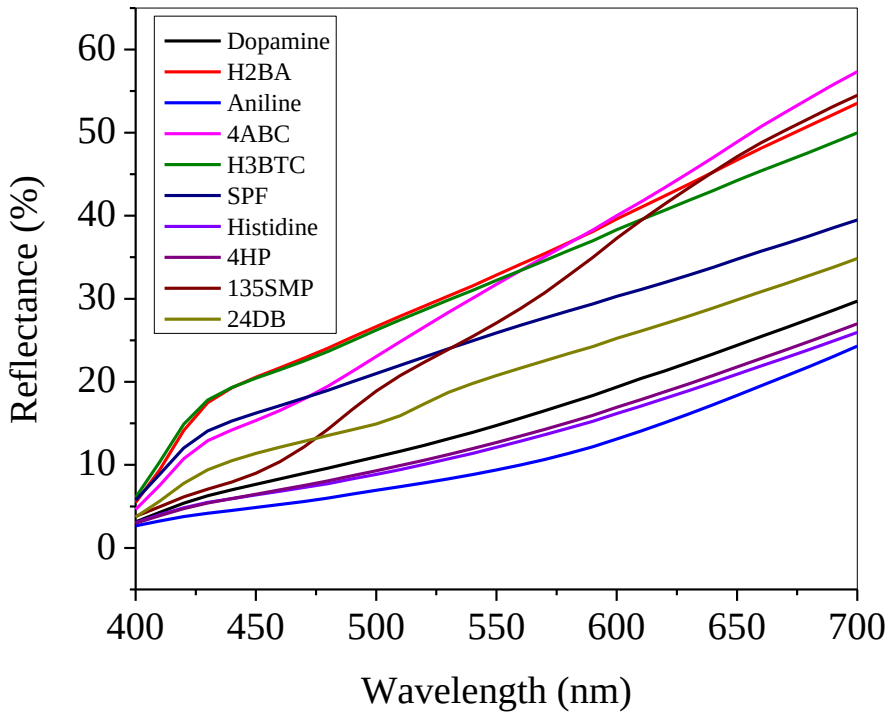


Figure 3.6 Reflectance curve of the coloured wool fabrics using dopamine and various components

After biomimetic colouration, the maximum UV absorptions of the coloured wool fabrics centred about 350 nm. However, there were variations in their visible absorption (Figure 3.5). The reflectance percentage of the coloured wool fabrics increased as the wavelength increased. At wavelength of 700 nm, the reflectance of the coloured fabrics ranged from 25% to 55%, as shown in Figure 3.6. There were noticeable differences in their colour appearance of the dyed wool fabric, as shown in Figure 3.7. This tuning of the obtained colour appearance in term of colorimetric parameters was listed in Table 3.1. Dopamine only was used for biomimetic colouration on wool fabric first, which

showed a natural yellow colour. In order to enrich the colour hues and therefore increase the consumer appeal, various nucleophilic species were added to the colouration bath of dopamine, such as amino acids (histidine, 4-hydroxyproline), UV absorbers (2,4-Dihydroxybenzophenone), aromatic amines (aniline, 3,5-dihydroxybenzoic acid, *p*-aminobenzoic acid, benzene-1,3,5-tricarboxylic acid, *p*-hydroxybenzoic acid *n*-butyl ester) and heterocyclic components (1-(4-sulfophenyl)-3-methyl-5-pyrazolone). Afterward they will incorporate into the self-polymerization process of dopamine and modify the formed colours on the fabrics. Due to the reaction ability of dopamine quinone with some nucleophiles, polymerization chemistry was usually altered by the added components, the L^*, a^* and b^* values of the obtained colours were obviously changed as shown in Table 3.1 and Figure 3.7. The presence of H2BA, H3BTC and SPF resulted in the obtained coloured on wool fabric toward less red and less yellow, which indicated that the carboxylic group in the components without amino group was favourable to form a bluer colour hue. The presence of aniline, histidine and 4HP tuned the obtained colour towards redder and less yellow hue, whiles the addition of 4ABC and 24DB caused the wool fabric towards slightly redder and yellower hue. The wool fabric could be coloured with yellower and redder hue in presence of 135SMP. Compared to the wool fabric coloured by dopamine only, the presence of aniline, histidine and 4HP gave the wool sample a deeper brightness, while the other four components of H2BA, 4ABC, H3BTC, SPF, 135SMP and 24DB caused the wool samples a lighter brightness.

The brightness and hue of the wool sample could be further tuned via different weight ratio of the second component to dopamine, as shown in Table 3.2 and Figure 3.8. As an example, when *p*-amino-benzoic acid was added to the colouration bath in different ratio from 10% to 50%, the wool samples showed significant changes in brightness and hue, which resulted in redder and yellower hue.

Table 3.1 Colorimetric analysis of the wool fabrics coloured with dopamine and various components

Components	L*	a*	b*	ΔL*	Δa*	Δb*
Dopamine only	45.82	7.41	21.27	-	-	-
Dopamine +H2BA	64.28	5.59	20.83	18.46	-1.82	-0.44
Dopamine +Aniline	37.72	8.97	19.06	-8.10	1.56	-2.21
Dopamine +4ABC	63.21	7.62	28.78	17.39	0.21	7.51
Dopamine +H3BTC	63.63	4.99	10.77	17.81	-2.42	-10.50
Dopamine +SPF	57.86	4.06	18.32	12.04	-3.35	-2.95
Dopamine +Histidine	42.00	7.97	19.71	-3.82	0.56	-1.56
Dopamine +4HP	42.89	7.78	20.77	-2.93	0.37	-0.50
Dopamine +135SMP	50.58	16.75	7.60	4.76	9.34	-13.67
Dopamine +24DB	59.00	9.50	37.80	13.18	2.09	16.53

Figure 3.7 The images of the wool fabrics coloured with dopamine and various components

Table 3.2 Influence of usage ratio on colour hues

Components	Weight ratio to dopamine	L*	a*	b*	ΔL*	Δa*	Δb*
	10%	63.21	7.62	28.78	17.39	0.21	7.51
Dopamine	30%	64.15	8.92	33.36	18.33	1.51	12.09
+4ABC	50%	55.01	10.91	32.67	9.19	3.50	11.40

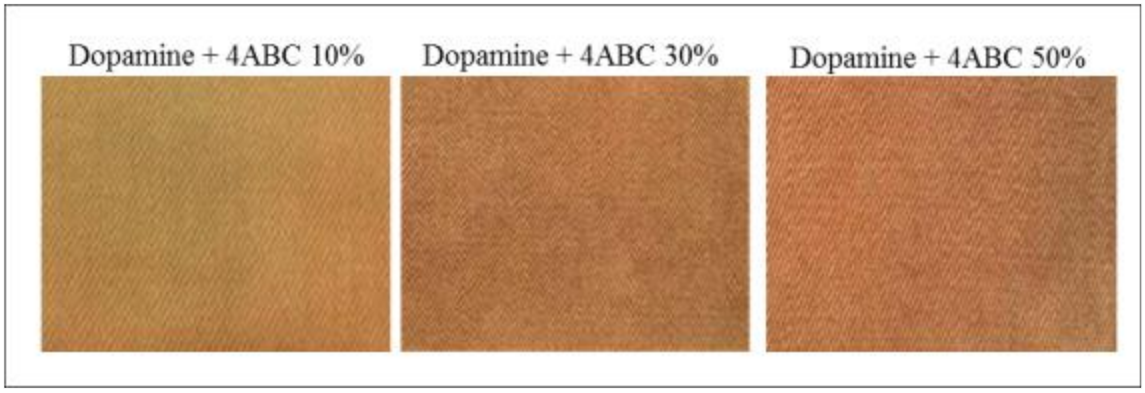


Figure 3.8 The images of coloured wool fabrics for influence of usage ratio

Moreover, the obtained colour appearances could be controlled easily using the oxidants with different oxidization ability. As presented in Figures 3.9, 3.10 and 3.11, colorimetric parameters listed in Table 3.3, under the same colouration conditions in the presence of 135SMP, wool fabric could be dyed with yellow colour if potassium periodate used as oxidants. Also, appearance of a pink colour could be obtained using hydrogen peroxide, while light yellow could be obtained if potassium persulfate used as oxidants.

Table 3.3 Influence of oxidization ability on colour hues

Components	Oxidant	L*	a*	b*	ΔL*	Δa*	Δb*
	Potassium Periodate	59.01	9.50	37.84	13.19	2.09	16.57
Dopamine	Hydrogen Peroxide	50.58	16.75	7.60	4.76	9.34	-13.67
+135SMP	Potassium persulfate	57.36	11.36	26.32	11.54	3.95	5.05

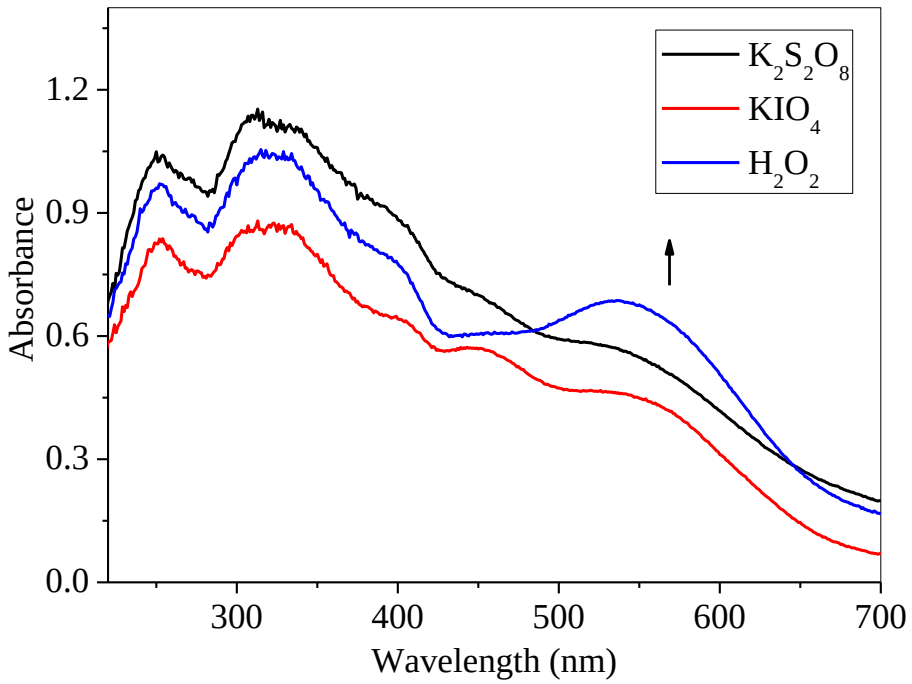


Figure 3.9 UV-vis absorption spectra of the coloured wool fabrics using dopamine and 135SMP in the presence of different oxidants

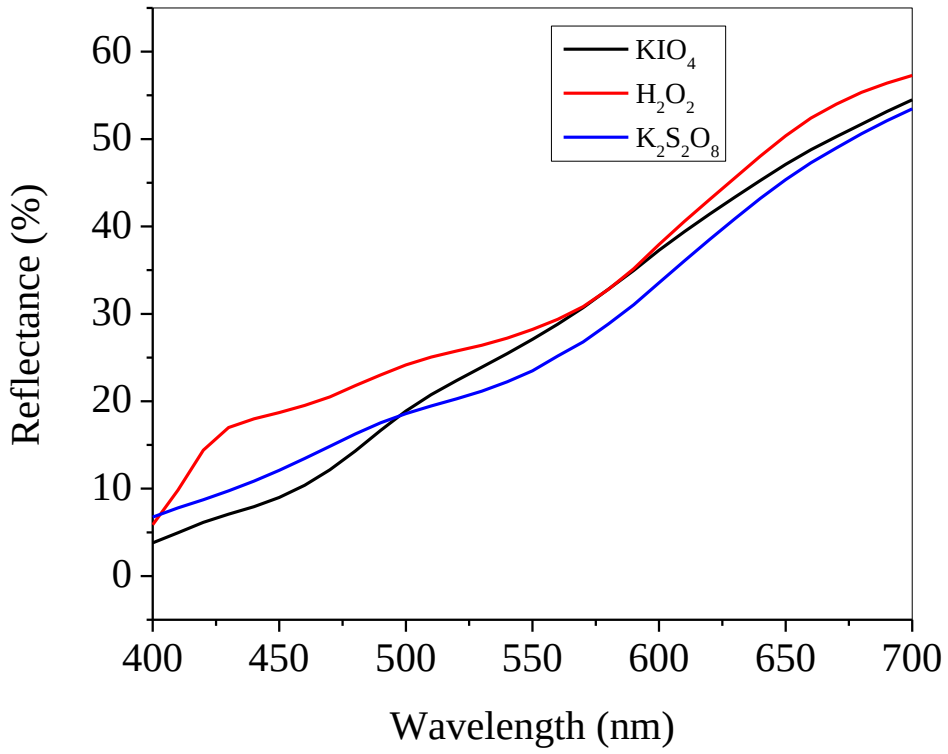


Figure 3.10 Reflectance curve of the coloured wool fabrics using dopamine and 135SMP in the presence of different oxidants

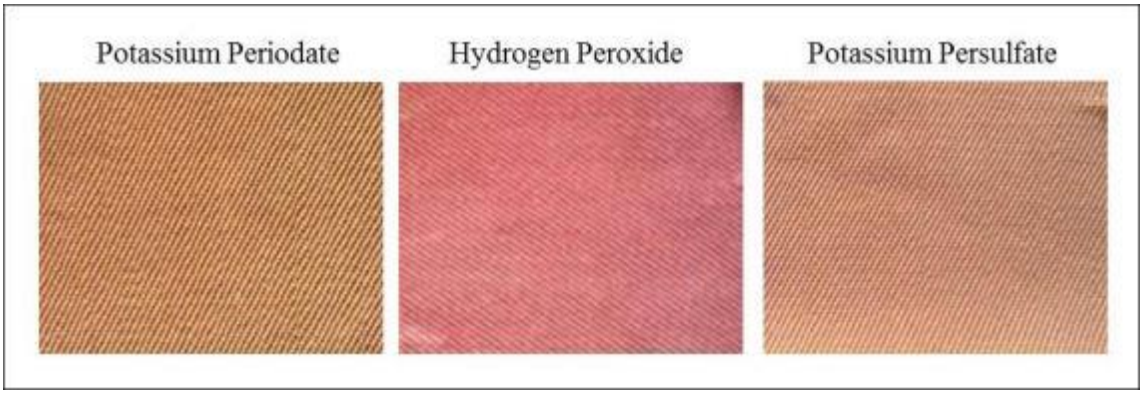


Figure 3.11 The images of coloured wool fabrics for influence of oxidization ability

Figure 3.12 The images of colour patterns formed on fabrics

Apart from single colour produced on fabrics, patterns with various colours could be obtained on the fabric in a simple way via this biomimetic method. Figure 3.12 showed the images of colour patterns designed on wool fabrics with the aid of design tools like templates or drawing pens. The clean fabric was firstly immersed in an aqueous solution of dopamine and second component, the colour patterns were then formed after the oxidant solution was applied or sprayed on the fabric. A wide variety of patterns with multiple colours could be produced on fabrics through the incorporation of a second component or using oxidants with different oxidation ability.

3.3.1.2 Colouration on silk fabrics

The method also works well on silk fabrics as shown in Table 3.4 since wool and silk are protein fibres, belonging to the same natural melanin type that found in human hair and skin. Silk fabric was dyed in dopamine solution and displayed a yellowish colour hue with L*, a*, b* value of 47.44, 7.13 and 20.13, respectively. After the incorporation

of a second component, the L*, a*, b* values of the dyed silk fabrics had significant change, showing the effective adjustment for the obtained colour hues. The addition of H2BA, 4ABC, H3BTC, cysteine, histidine, 4HP and 24DB caused the colour obtained on silk fabrics towards redder and yellower hues. This trend was due to the carboxylic group in the second components. Compared to wool samples, the presence of aniline led to an opposite influence on the colour hue of silk, while the addition of SPF caused a similar influence on colour hue. In regard to the brightness of the silk fabrics was coloured with a deeper brightness in presence of aniline, histidine and 4HP compared to the silk coloured with dopamine only, while the other six were coloured with a lighter brightness.

Table 3.4 Colorimetric analysis of the silk samples

Components	L*	a*	b*	ΔL*	Δa*	Δb*
Dopamine only	47.44	7.13	20.13	-	-	-
Dopamine +H2BA	63.87	7.17	22.58	16.42	0.04	2.45
Dopamine +Aniline	40.76	10.44	22.36	-6.68	3.30	2.27
Dopamine +4ABC	57.04	8.32	25.65	9.60	1.18	5.52
Dopamine +H3BTC	65.09	7.27	21.57	17.65	0.14	1.44
Dopamine +SPF	65.84	4.65	16.86	18.40	-2.49	-3.26
Dopamine +Cysteine	52.30	7.50	22.00	4.86	0.37	1.87
Dopamine +Histidine	46.50	7.90	22.00	-0.94	0.77	1.87
Dopamine +4HP	46.80	7.30	20.60	-0.64	0.17	0.47
Dopamine +24DB	61.30	7.20	23.00	13.97	0.07	2.87

3.3.1.3 Colouration on cotton fabrics

It was observed that the results were not so satisfactory on other textile fabrics, such as cotton and PLA, since these textile fibres cannot offer a similar medium of human skin and hair. Hence, they only depended on the adhesive ability of polydopamine derivatives to fibres for colouration. As mentioned in Table 3.5, the brightness of all the dyed cotton fabrics was slightly lighter than those of wool and silk fabrics. Compared to the cotton fabric coloured with dopamine only, all other added components resulted in a lighter brightness of the dyed cotton fabrics, and the influence of aniline was much smaller than other four components including H2BA, 4ABC, H3BTC and SPF, which were close to the result of fabric coloured with dopamine only. The addition of 4ABC, H3BTC and SPF tuned the cotton fabric toward less red and less yellow hue, while the presence of H2BA gave the cotton fabric a little bit greener and less yellow hue. The colour hue of dyed cotton fabric had no significant change in the presence of aniline.

Table 3.5 Colorimetric analysis of coloured cotton samples

Components	L*	a*	b*	ΔL*	Δa*	Δb*
Dopamine only	50.27	7.28	18.38	-	-	-
Dopamine +H2BA	72.34	4.61	20.19	22.07	-2.67	1.82
Dopamine +Aniline	55.72	7.31	20.16	5.45	0.04	1.79
Dopamine +4ABC	78.62	3.46	15.08	28.35	-3.81	-3.30
Dopamine +H3BTC	78.71	3.14	9.58	28.44	-4.14	-8.80
Dopamine +SPF	87.84	1.65	11.46	37.57	-5.63	-6.92

3.3.1.4 Colouration on PLA fabrics

PLA fabrics are difficult to be dyed on account of their low affinity to traditional dyestuffs[21-23]. By the biomimetic colouration method, various colour appearances could be produced on PLA fabric even colouration at room temperature. As presented in Table 3.6, the colour of the PLA fabric coloured with dopamine only displayed a yellowish colour hue with L*, a* and b* values of 45.38, 6.73 and 16.63, respectively. The addition of all second components gave the PLA fabrics a lighter brightness. The PLA fabric was coloured with a yellower and greener colour in presence of H2BA, the addition of aniline tuned the colour of PLA fabric towards greener and redder hue, while 4ABC and SPF caused an opposite changes on fabric.

Table 3. 6 Colorimetric analysis of coloured PLA samples

Components	L*	a*	b*	ΔL*	Δa*	Δb*
Dopamine only	45.38	6.73	16.63	-	-	-
Dopamine +H2BA	80.31	4.64	22.09	34.93	-2.09	5.46
Dopamine +Aniline	52.91	8.50	23.01	7.53	1.77	6.38
Dopamine +4ABC	75.99	4.70	16.52	30.60	-2.03	-0.11
Dopamine +SPF	70.41	4.77	15.86	25.03	-1.96	-0.77

3.3.1.5 K/S values of dyed fabrics

The colour strength in term of K/S values at the maximum absorption wavelength (400nm) of wool, silk, cotton and PLA fabrics calculated. The coloured fabrics had good colour yields with K/S values as summarized in Table 3.7 and 3.8. The colour

yields of the fabrics dyed with dopamine were only over 6.66 and up to 14.94. In most cases, the addition of second components to the colouration bath led to the decrease of K/S values of dyed fabrics. The K/S value of wool fabrics were in the range of 7.23 to 17.86, while silk fabrics were within the range of 2.62 to 13.77. On cotton and PLA fabrics, their K/S values were in the range of 1.32 to 4.74 and 0.89 to 4.87 respectively. As expected the protein fibres, wool and silk samples had higher K/S values than cotton and PLA samples since the chemical structure of protein fibres are similar to dopamine.

Table 3.7 The K/S values of the coloured wool and silk fabrics after washing

Components	Wool	Silk
Dopamine only	14.94	8.07
Dopamine +H2BA	8.17	3.99
Dopamine +Aniline	17.86	13.77
Dopamine +4ABC	9.81	5.61
Dopamine +H3BTC	7.23	3.36
Dopamine +SPF	7.73	2.62
Dopamine + Cysteine	-	6.67
Dopamine +Histidine	15.41	9.02
Dopamine +4HP	15.82	8.3
Dopamine + 24DB	12.45	5.18
Dopamine +135SMP	7.96	-

Table 3.8 The K/S values of the coloured cotton and PLA fabrics after washing

Components	Cotton	PLA
Dopamine only	6.66	6.54
Dopamine +H2BA	2.53	1.01
Dopamine +Aniline	4.74	4.87
Dopamine +4ABC	1.53	0.89
Dopamine +H3BTC	1.47	-
Dopamine +SPF	1.32	1.25

3.3.1.6 Colouration on natural and synthetic fabrics using rhodamine B

As shown in Figure 3.4, polydopamine has absorption peak centred about 350 nm. In order to investigate its influence on the obtained colour appearance, rhodamine B was preliminarily chosen as an example to be used in the colouration method. Dopamine polymerization was induced by a typical seawater pH value of 8.5 buffered with Tris so as to prevent the influence of oxidants on the chromophore.

First, the effect of dopamine polymerization on the colour appearance of rhodamine B was investigated by spectroscopy at room temperature. Figure 3.13 shows the UV –vis absorption spectra of rhodamine B in pH 8.5 buffer solution in the presence and absence of dopamine. The results showed that the presence of dopamine did not cause significant changes in the λ_{max}, under the experimental conditions, although the absorption intensity of other wavelengths had increase due to dopamine polymerization. Also, there was no significant naked-eye-visible change in the solution colour. In addition, there was no

precipitation observed from the solution, even after centrifugation at a speed of 14 000 rpm for 10 minutes.

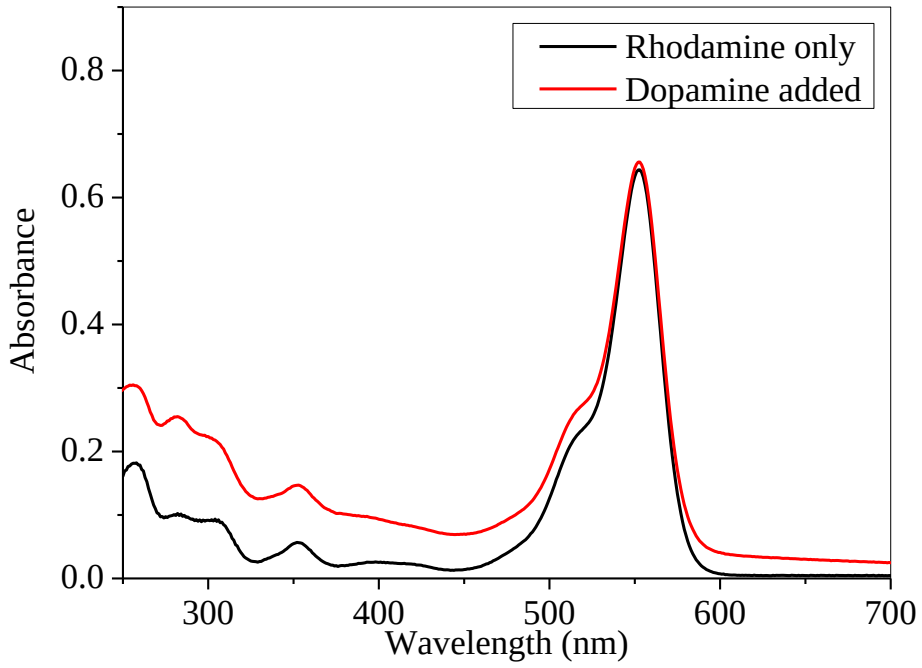


Figure 3.13 UV-vis absorption spectra of rhodamine B with and without dopamine

With the addition of dopamine to the colouration, cotton and PBI fabrics could be also dyed with red colour using rhodamine B. Figure 3.14 shows their visible absorption spectra at about 550 nm similar to that of rhodamine B solution. Table 3.9 also listed their colour measurement results. The presence of dopamine caused small colour changes in wool fabrics, but larger colour changes in cotton and PBI fabrics, in comparison with the case in the absence of dopamine. Nevertheless, the K/S values of

the cotton and PBI fabrics were significantly better than the case in the absence of dopamine showing the improved dyeability of the fabrics.

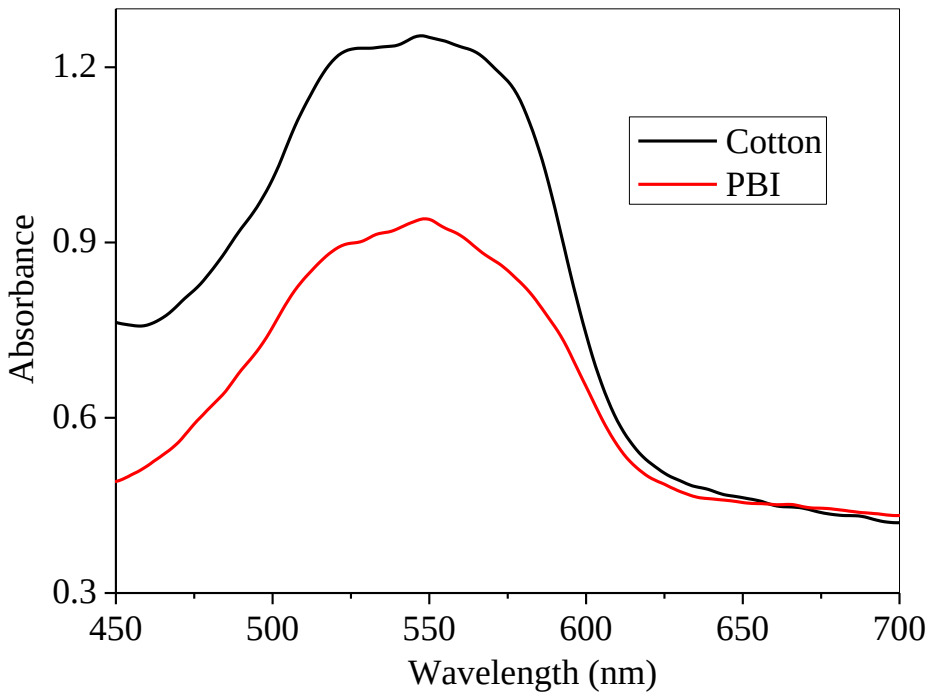


Figure 3.14 UV-vis absorption spectra of fabric coloured with rhodamine B in the presence of dopamine

Table 3.9 The colorimetric analysis of fabrics coloured by rhodamine B

	Presence of dopamine				Absence of dopamine			
Fabric	K/S	L*	a*	b*	K/S	L*	a*	b*
Cotton	14.2	32.6	33.5	-3.1	4.2	58.0	47.3	-28.3
Wool	20.1	33.9	49.4	-16.9	20.0	38.8	57.9	-20.5
PBI	14.3	28.2	22.6	-0.9	5.2	50.2	33.6	-2.0

Furthermore, the surface wettability of PBI fabrics was investigated. Its surface wettability was changed significantly after colouration. The water contact angle decreased from about 130° to 83° as presented in Figure 3.15. Also, the slope test further confirmed these changes as shown in Figure 3.16. It can be seen that the water droplets on the un-dyed PBI fabric surface rolled rapidly down at a 45° slope under gravity due to no adsorption on this superhydrophobic surface, while the water droplets stayed still on the dyed PBI fabric surface and did not roll down the slope. These results clearly indicated the different interfacial interactions of the PBI fabric surfaces before and after colouration, demonstrating the successful colouration on the hydrophobic surface in the presence of dopamine.

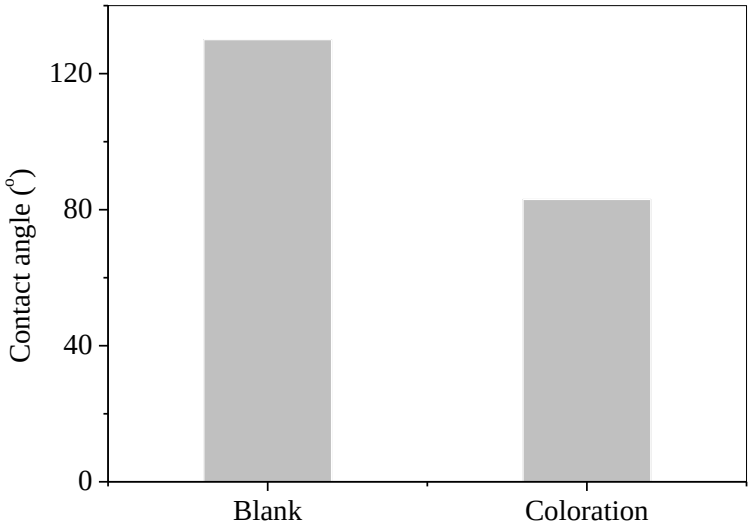


Figure 3.15 Water contact angles of PBI fabric before and after colouration with rhodamine B in the presence of dopamine

Figure 3.16 The images of the wetting properties of water droplets on a 45° slope before and after colouration with rhodamine B in the presence of dopamine

3.3.2 Microscopic analysis

3.3.2.1 Scanning electron microscope

The SEM images of various dyed fibres before and after colouration were given in Figure 3.17. It was found that the blank wool fibres have clear scales covering their surface, which serve as a barrier to hinder the dyes molecules to penetrate into the fibres in a conventional colouration process. By this bio-inspired colouration method, the surface morphology of the dyed fibres changed to smoother after colouration and the fibre surfaces were effectively covered by small particles of dye, namely polydopamine derivatives, formed due to the polymerization of catecholamine dye through spontaneous oxidation. The SEM images also showed that dyes were deposited on the surfaces of silk, cotton and PLA fibres, which formed with the fast oxidization of dopamine derivatives in the presence of oxidant solution. Moreover, it was observed from the images that the dyed fibres had no damage after colouration, which further confirmed the feasibility of this novel method applied on textile materials.

3.3.2.2 Optical microscope

The cross section views of the fibres were further investigated with optical microscope. The cross section images of wool, silk, cotton and PLA fibres before and after colouration were shown in Figure 3.18. It can be observed from the images that all the fibres were beige before colouration, showing their original colour. After using the biomimetic colouration method, the cross section views of the fibres were clearly changed. The fibres were obviously dyed with dark red colour for wool, dark brown for

silk, cotton and PLA. It showed that the dye molecules penetrated into the interior part of the fibres and the dyes were hold inside the fibres after the oxidative polymerization of catecholamine in the presence of oxidant. This change also confirmed the successful colouration on various fabrics using the biomimetic colouration method.

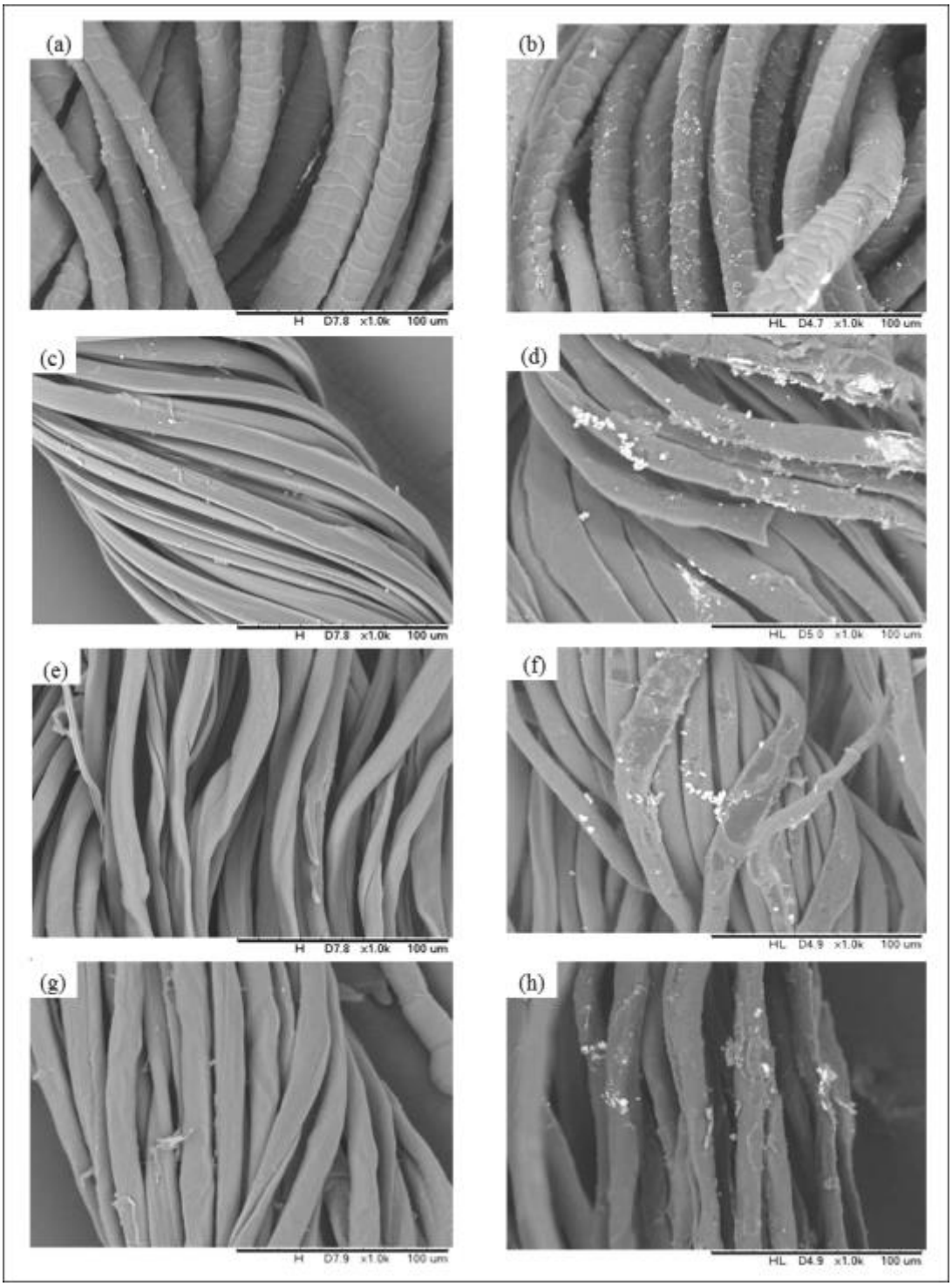


Figure 3.17 The images of fibers before (left) and after (right) colouration. (a), (b) wool, (c), (d) silk, (e), (f) cotton and (g), (h) PLA.

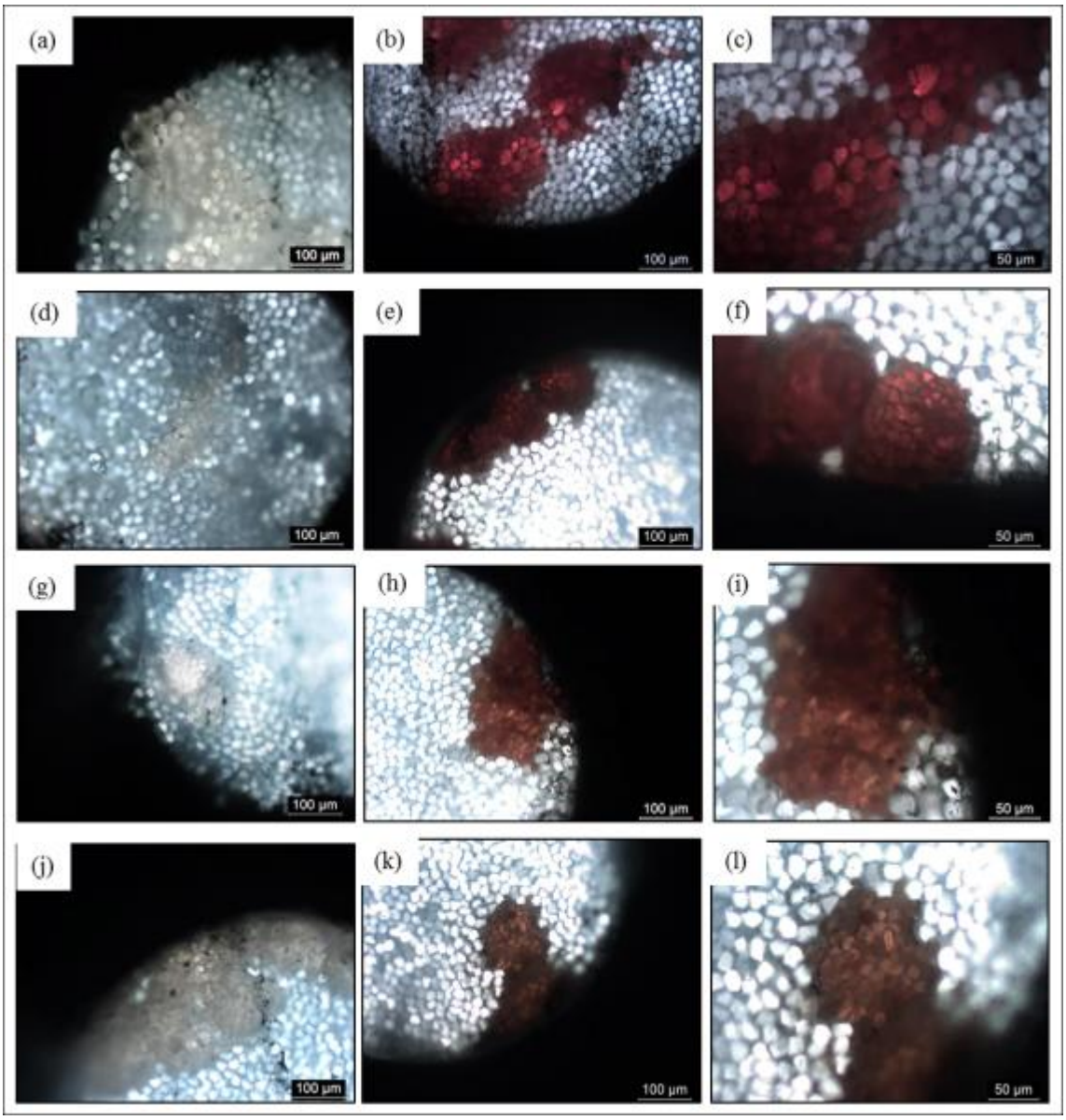


Figure 3.18 The cross section images of fibers before (left) and after (middle & right) colouration. (a), (b), (c) wool, (d), (e), (f) silk, (g), (h), (i) cotton and (j), (k), (l) PLA. (c), (f), (j) and (l) are magnified images of (b), (e), (h) and (k) fibers after

3.3.3 Colour fastness test

3.3.3.1 Laundering fastness test

The laundering fastness results of the dyed fabrics are listed in Tables 3.10 and 3.11. The results showed that the dyed protein fabrics exhibited good laundering fastness properties. The ratings of shade change were in the range of 4 to 5 in most cases of wool and silk fabrics, demonstrating the good fixation of the dyes molecules on fibres. The ratings of shade change of protein fabrics were slightly better than cotton and PLA fabrics. In addition, most of the dyed fabrics had good fastness of shade staining; the ratings were in the range of 4 to 5, except some cases on nylon fibres.

For the results of crocking fastness test in Table 3.12, most of the results of dry crocking test were within the range of 4 to 5, which was slightly better than their wet crocking fastness. For the wet crocking fastness test of cotton and PLA fabrics, the result of fabric dyed in presence of aniline was better than fabrics with dopamine only. Their ratings were 4 and 3/4 respectively, while the results of dopamine only were 2/3 and 1/2.

It was found that the laundering fastness and crocking fastness properties of the dyed fabric were better than light fastness as presented in Table 3.13. Due to the fact that underwater mussels' protein expose to less direct light radiation, so their photo-stability is probably not superior to their adhesion, perhaps resulting in the poor photo-stability of the dyes bio-mimicked from the underwater mussel's adhesive. However, the photo-stability of the dyed fabrics could be improved by the incorporation of photo-stable heterocyclic compounds to the colouration process.

Table 3.10 Laundering fastness of the coloured wool fabrics

Fabrics	Components	Laundering test						
		Shade change	Shade staining					
			Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
Wool	Dopamine only	4-5	5	5	5	5	5	5
	Dopamine +H2BA	4-5	5	5	5	5	5	5
	Dopamine +Aniline	4	5	5	5	5	5	5
	Dopamine +4ABC	4	5	5	5	5	5	5
	Dopamine +H3BTC	4-5	5	5	5	5	5	5
	Dopamine +SPF	4-5	5	5	5	5	5	5
	Dopamine +Histidine	4	5	5	5	5	5	5
	Dopamine +4HP	4	5	5	5	5	5	5
	Dopamine +135SMP	3/4	5	5	5	5	5	5
	Dopamine +24DB	4/5	5	5	5	5	5	5

Table 3.11 Laundering fastness of the coloured silk, cotton and PLA fabrics

Fabrics	Components	Laundering test						
		Shade change	Shade staining					
			Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
Silk	Dopamine only	4/5	4/5	5	4	3	5	5
	Dopamine +H2BA	3/4	5	5	4/5	3/4	5	5
	Dopamine +Aniline	4	4/5	5	4	3/4	5	4
	Dopamine +4ABC	3/4	5	5	4/5	4/5	4/5	4/5
	Dopamine +Cysteine	4	5	5	5	2/3	5	5
	Dopamine +Histidine	3/4	3/4	4/5	4/5	2/3	5	5
	Dopamine +4HP	4/5	5	5	4/5	3	5	4/5
	Dopamine +24DB	4/5	5	4/5	4/5	3/4	5	5
Cotton	Dopamine only	2	5	5	5	4	5	5
	Dopamine +Aniline	4	4	4/5	3	4	5	5
PLA	Dopamine only	3	5	4/5	4/5	4	4/5	4/5
	Dopamine +Aniline	3	4	4/5	3	3	4	3/4

Table 3.12 Crocking fastness of the coloured textile fabrics

Fabrics	Components	Crocking test	
		Dry	Wet
Wool	Dopamine only	4/5	4/5
	Dopamine +Histidine	4/5	3
	Dopamine +4HP	4/5	3/4
	Dopamine +24DB	4/5	3/4
	Dopamine +135SMP	4/5	4
	Dopamine +24DB	4/5	3/4
Silk	Dopamine only	5	5
	Dopamine +Cysteine	5	5
	Dopamine +Histidine	4/5	4/5
	Dopamine +4HP	5	4/5
	Dopamine +24DB	4/5	4/5
Cotton	Dopamine only	3/4	2/3
	Dopamine +Aniline	4/5	4
PLA	Dopamine only	3/4	1/2
	Dopamine +Aniline	4	3/4

Table 3.13 Light fastness of the coloured wool fabrics

Fabrics	Components	Light fastness
Wool	Dopamine only	3
	Dopamine +Histidine	3
	Dopamine +4HP	2/3
	Dopamine +24DB	2/3
	Dopamine +135SMP	3/4
	Dopamine +Anline	2/3

3.3.4 Colouration on inorganic materials

By using this approach, other kinds of materials such as metal (Al slide) and ceramic (glass) could be also successfully coloured with red colour using rhodamine B in the presence of dopamine. The coloured surfaces of the materials were characterized with XPS, SEM, and water contact angle measurement.

The chemical composition of the material surface was determined qualitatively using XPS analysis. For the bank materials, as shown in Figures 3.19 and 3.20 (left), the material signals of Si2s, Si2p, A12s and A12p were found, while no nitrogen (N1s) was found in the XPS spectra. However, there was no obvious substrate signal found in the XPS spectra of the coloured materials. On the contrary, as presented in Figures 3.19 and 3.20 (right), peaks from the atomic composition of colouration components were found, especially the nitrogen signal (N1s).

In addition, the C1s and O1s XPS spectra signals were evidently altered after colouration in comparison with the initial surface (Figure 3.21 and 3.22). In the case of glass, two peaks species at the binding energy of about 284.6 eV and 287.7 eV, attributable to C-C and C=O species, respectively, were found in the C1s core-level spectrum of pristine glass. After colouration, the C1s core-level spectrum can be curved-fitted into four peak species at binding energies of about 284.6 eV, 285.5 eV, 286.5 eV and 287.7eV, attributable to the carbon in C-C/C=C, C-O, C-N and C=O species, respectively. The glass surface coloured with the rhodamine B/polydopamine system caused two additional peak species for C-N and C-O. Both the C-O and C=O signals existed, which confirmed the carboxyl group in rhodamine B and the catechol and quinone groups in polydopamine. The colouration of glass was further investigated by the O1s core-level spectrum of pristine glass and the dyed glass. In the O1s spectrum of pristine glass, a species at binding energy of about 532 eV was found. The O1s spectra of the dyed glass can be curve-fitted into two species at binding energies of about 532 eV and 533 eV , attributable to C=O and C-O, respectively. The C1s and O1s XPS spectra of the coloured Al surface gave similar results.

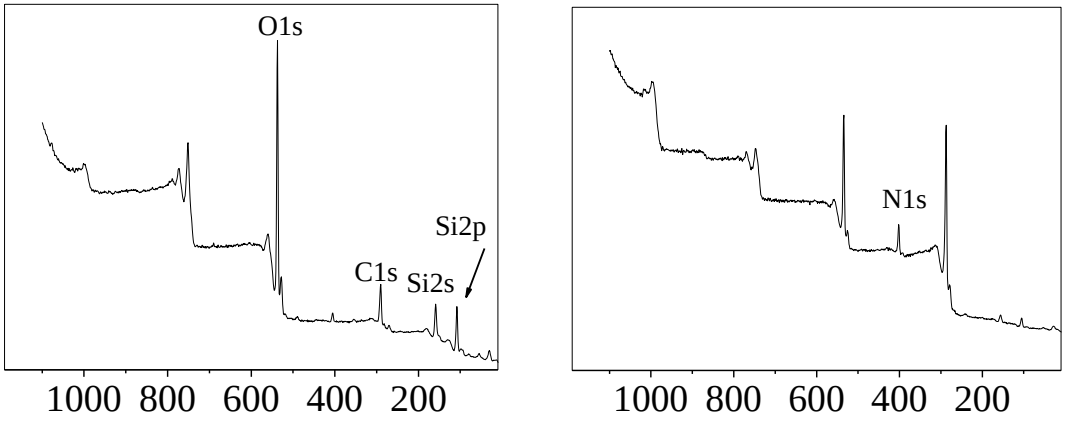


Figure 3.19 XPS spectra of glass slides before (left) and after (right) colouration

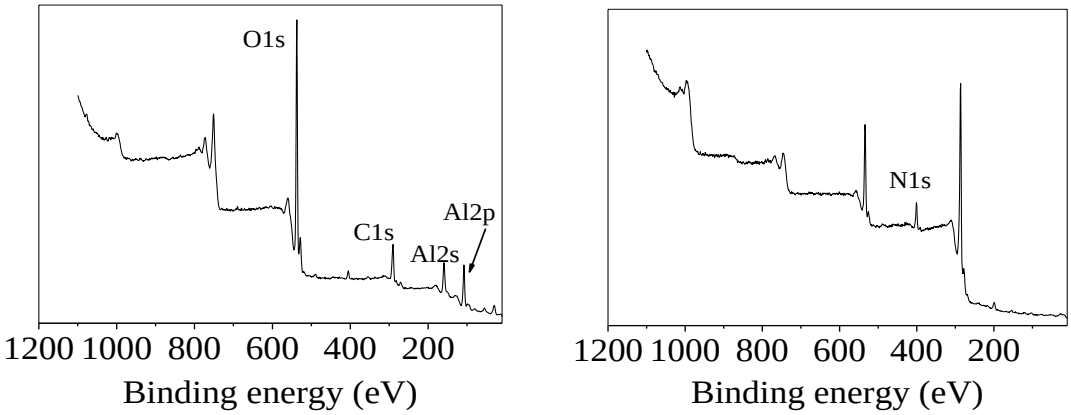


Figure 3.20 XPS spectra of Al slides before (left) and after (right) colouration

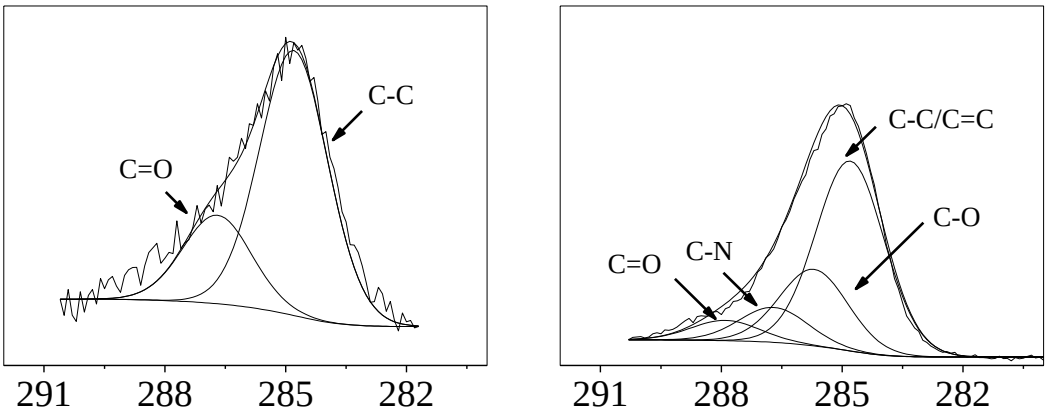


Figure 3.21 XPS spectra of Cls core-level spectra for glass before (left) and after (right) colouration

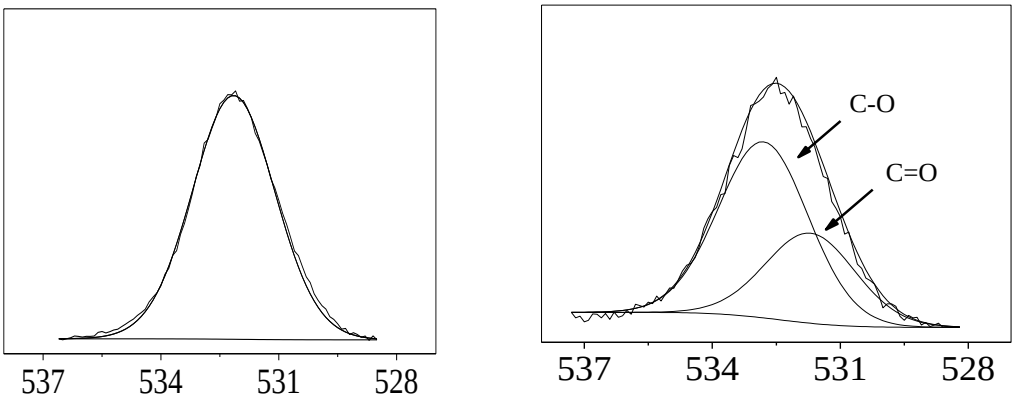


Figure 3.22 XPS Ols core-level spectra for glass before (left) and after (right) colouration

The surface morphologies before and after colouration were further investigated using microscopic analysis. As shown in Figure 3.23, in the case of the pristine surfaces, it can

be observed that their surfaces are much smoother. After colouration, the blank surfaces were completely covered by the lamellar ad-layers and aggregated nano-particles, indicating the rhodamine B was attached on the smooth surface in the presence of dopamine. Therefore, the coloured surfaces gave a higher roughness, showing noticeable contrasting results to the blank surfaces. This change in their surface morphology before and after colouration further confirmed the successful colouration on inorganic materials.

The wettability of the coloured glass and Al slides was investigated using water contact angle measurements. For the pristine surfaces, the results indicated that the water contact angles were about 100°. After colouration, the contact angles decreased to 80°, as indicated in Figure 3.24. All these results showed that the material surfaces were successfully coloured with rhodamine B in the presence of dopamine.

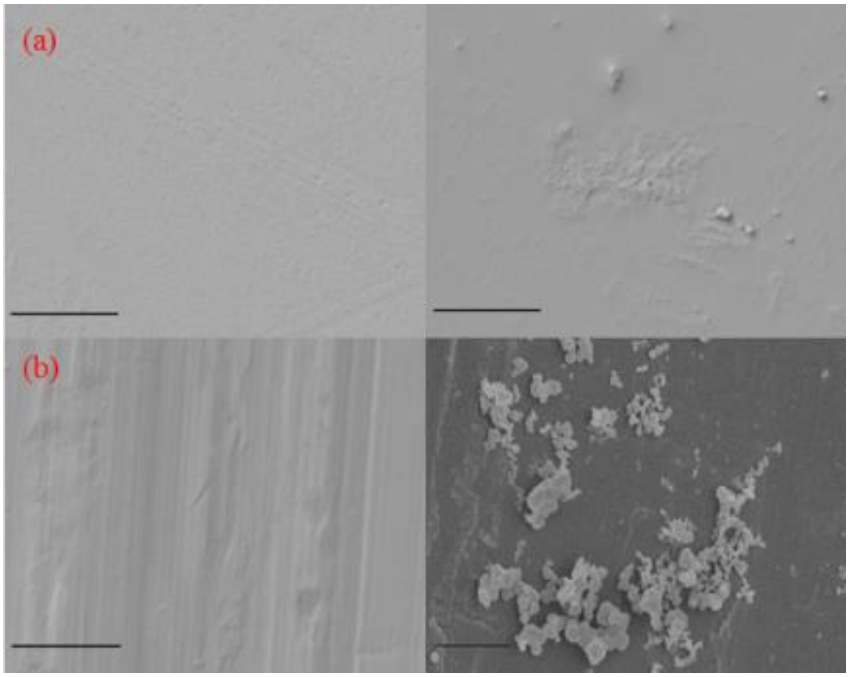


Figure 3.23 SEM images of the surface morphology of glass (a) and Al (b) slides before (left) and after (right) colouration. Bar = 5 μm

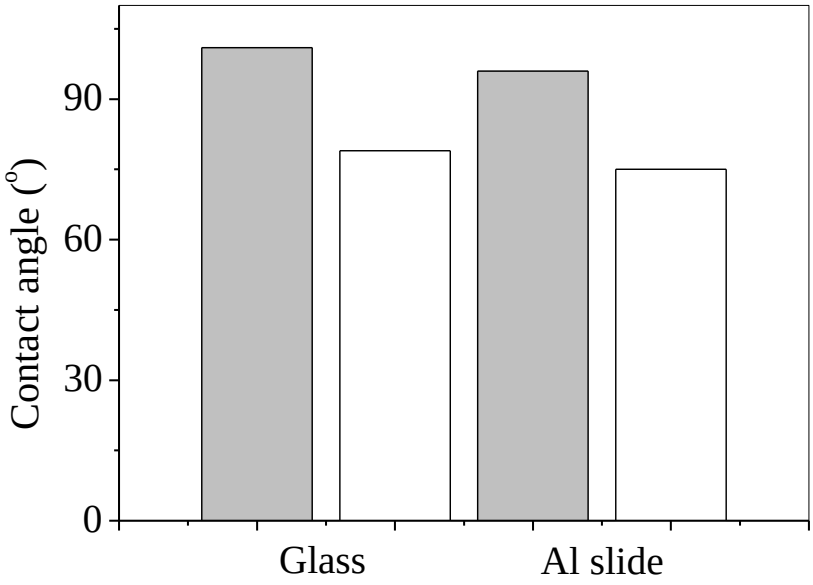


Figure 3.24 Water contact angles of glass (a) and Al (b) slides before (left) and after (right) colouration.

3.4 Conclusion

In this chapter, it has been demonstrated a simple method for colouration of various materials via dopamine polymerization in aqueous media. In this method, dopamine was oxidized under the controlled conditions to form polymeric colour coatings on various textile fabrics. The incorporation of a different nucleophilic species was an effective way to tune the colour brightness and hue on textile materials. This method could be successfully applied to different kinds of materials, including textile materials, organic and inorganic materials and even the materials resistant to colouration. This method showed a substrate-independence to some extent, ease of application and could be achieved at room temperature. It was a promising alternative to the traditional colouration process due to its few operation steps and less energy consumption. It is very interesting and worthy to be further investigated in the future.

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Chapter 4

Dopamine-induced colouration with commercially available dyes

4.1 Introduction

Inspired by the adhesive properties of marine mussels[1-5], a novel method had been demonstrated for colouration on various textile materials in chapter 3; however, the colour spectrum produced on the textile was still not rich. In order to enrich the colour gamut, in this chapter, commercially available dyes were used for the dopamine-induced colouration on different textile materials.

In recent years, there has been an increasing interest towards the application of natural dyes on textiles due to increasing awareness of the environmental consciousness and health hazards from synthetic dyes[6-9,13,15-18]. In textile industry, synthetic dyes have been widely used for colouration due to good colouration properties and wide ranges of colour gamut. However, the consumption of large amounts of synthetic dyes on textiles has adverse effects on environment and human health associated with toxic, carcinogenic and allergic properties. Most of the synthesized dyes were synthesized from hazardous chemical processes threatening the eco-friendliness[8]. Also, the colouration process usually consume large amount of dispersing agent, levelling agent and surfactant to improve the dyeability of textiles. Those colouration auxiliaries are normally hard to be destroyed by conventional biological treatment[6-7].

Natural dyes are derived from natural sources such as plants, animals and minerals, which are usually renewable and biodegradable with minimum detrimental impact on environment[8,10-11]. And they can provide diversity of tints and shades for colouration. But the characteristic of substrate-dependence and complicated colouration procedure are common defect for natural dye and synthetic dye. Natural dyes have a strong affinity to fibres of animal origin such as wool and silk, but less affinity to plant fibres and synthetic fibres[6,8]. Also, natural dyes are generally non-substantive and hence they must be used in conjunction with mordant to fix them on the textile substrates for improvement of exhaustion and colour fastness properties. The commonly used mordants for natural dyes are aluminium sulfate, ferrous chloride, copper sulphate, tannic acid and bichromte of potash, etc[7,13-14]. After colouration, certain portion of these metallic mordants remains unexhausted in the dye bath and this may cause serious effluent problems.

By using this novel colouration method, various textile fabrics were dyed at room temperature via a one-step immersion of materials in a one-pot mixture of a commercial available natural dye and dopamine. The colour gamut produced on the textile fabrics could be largely enriched through the incorporation of a natural dye as a chromophore. The dyed fabrics were evaluated by colorimetric analysis, scanning electron microscopy, optical microscopic analysis and colour fastness tests. This colouration method was suitable for those textile materials difficult to be dyed with traditional method like polylactic acid, polypropylene and polyethylene terephthalate. Compared to the

conventional methods, this strategy was more eco- friendly since natural dyes are renewable, low toxicity and allergic response.

4.2 Experimental

4.2.1 Materials and instruments

Three textile materials were used including woven fabrics of polyethylene terephthalate (PET, 123 g/m^2), polylactic acid (PLA, 118 g/m^2) and knitted polypropylene (PP, 79 g/m^2). They were purchased from China Dyeing Holding, Ltd. Before colouration, these fabrics were washed with 5 g/L sodium dodecyl sulfate solution at 60 ^{o}C for 20 min to remove possible surface impurities. Afterward the fabrics were rinsed thoroughly in deionized water and dried in air. Commercial natural dye powders were supplied by Brenntag Co Ltd (Thailand), a distribution company for Silva Chimica (Italy). The dyes originate from the wood of Schinopsis lorentzii, Natural orange (O) and Chlorophora tinctoria, and Natural yellow (Y). Gardenia blue (G) and Curcumin (C) were purchased from Shaanxi King Stone Enterprise Co Ltd and Sigma-Aldrich respectively. The chemical structures of the dyes are shown in Figure 4.1.

All chemical reagents were obtained from Sigma-Aldrich and used as received.

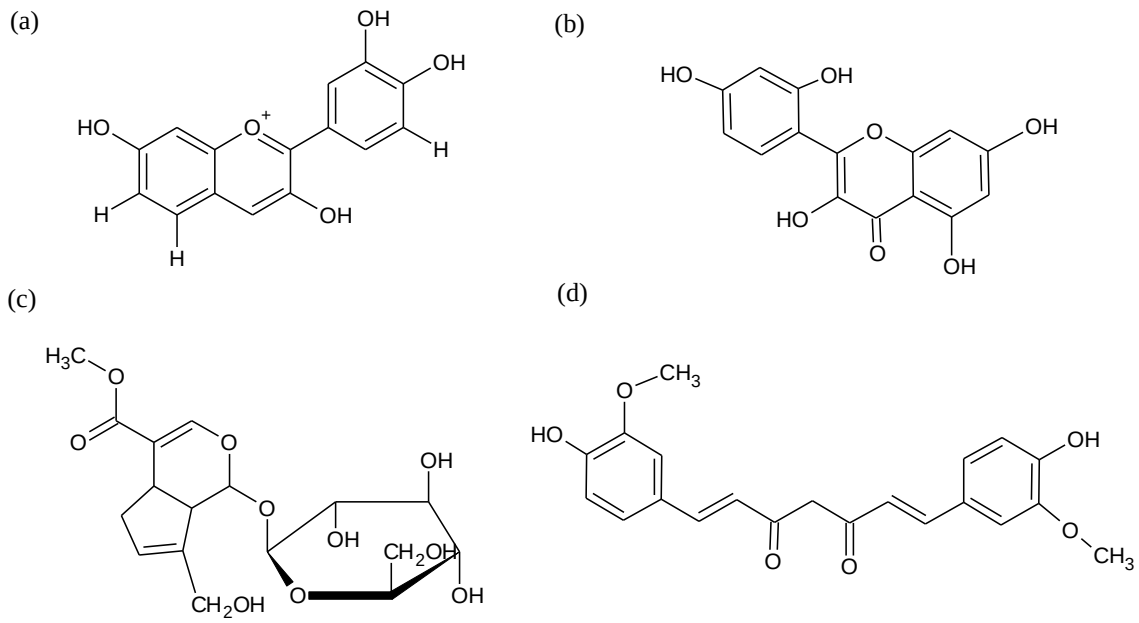

Figure 4.1 Chemical structure of natural dyes used: the main component of (a) natural orange (schinopsis lorentzii), (b) natural yellow (chlorophora tinctoria), (c) gardenia blue (geniposide) and (d) curcumin

4.2.2 Colouration procedure

All fabrics were immersed in an aqueous solution containing 0.05% w/v of natural dye and 0.002% w/v of dopamine at room temperature for 24 hours. Subsequently, they were taken out of the bath and sprayed with 1 wt% oxidant solution (potassium periodate) and air dried. After washing with deionized water, the above mentioned processes were repeated for 6 cycles. The colouration process was shown in Figure 4.2.

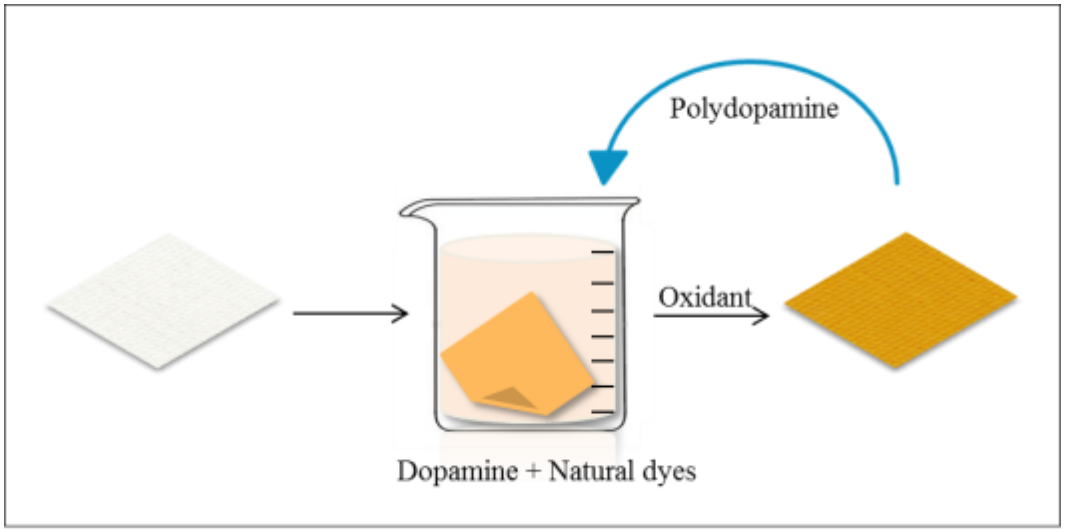

Figure 4.2 Schematic of colouration process via immersion of textile fabric in a one-pot mixture of a natural dye and dopamine with repeat cycles

4.2.3 Colouration measurements

Colorimetric analyses of the dyed fabrics were conducted according to Section 3.2.4.

Wash fastness of dyed fabrics were tested according to AATCC Test Method 61-2010, test no. 3A at 71°C for 45 min in the presence of 0.15% powder detergent and 100 pieces of steel ball[21]. Crocking fastness was assessed using Crockometer method according to AATCC Test method 8-2007[22]. The ratings were assessed using a grey scales, which ranges from 5 for no shade change (or no stain on the adjacent fibres) down to 1 for a severe shade change (or staining), with half points in between.

The surface morphology of the fibres was investigated using a scanning electron microscope (Hitachi Tabletop Microscope, TM-3000).

The cross-section images of dyed fibres were studied by an optical microscope (Nikon Optiphot-POL manufactured in Germany, high-performance Leica LAS software). The blue colour nylon yarns were used as a substrate to support fibre sample during sample preparation.

4.3 Results and discussion

4.3.1 Colorimetric analysis

Due to the hydrophobicity and high crystallinity in the fibres nature, PET and PP are very difficult to be dyed with conventional disperse dyes. Similarly, PLA fibres could be dyed with only a few dyes at certain colouration conditions because of its relatively hydrophobic nature like PET. In this study, using dopamine polymerization to form adhesive coating, various textile materials could be easily coloured with extensive colour at room temperature by natural dyes. Polydopamine has an adhesive ability; therefore, it was utilized to prepare adhesive coatings to fix the dye molecules on the fibres. The natural dyes are co-dissolved with dopamine in the dye bath in which the fabric is immersed. After a period of time, the natural dyes are immobilized onto the fabric with a polydopamine layer via self-polymerization of dopamine in presence of oxidant at pH 8.5, regardless of the types of nature dye.

In the presence of dopamine, the obtained colour depth on the PLA, PET and PP fabrics were obviously better than those control fabrics under the same conditions, as shown in Figure 4.3. Their colour difference could be further indicated by their K/S values, as summarized in Table 4.1. The results showed that the PLA samples had higher K/S

values than PET and PP samples after one colouration cycle in the presence of dopamine. As showed in Figures 4.4, 4.5 and 4.6, on the various fabrics of PLA, PET and PP, when the number of colouration cycles increased, the obtained colour depth with dopamine only slightly increased, while the presence of dopamine resulted in the obtained colour depth with natural dyes increased markedly. These results indicated more dye molecules were immobilized onto the fabrics with the number of the polydopamine layers increased. The increases of colour yield for most of the cases were stable after five cycles. The addition of natural yellow and curcumin resulted in the colour depth of all fabrics higher than those with natural orange and gardenia blue.

The colour coordinates CIE L^*, a^*, b^* of the dyed fabrics were listed in Tables 4.2, 4.3 and 4.4. The L^* values of all fabrics coloured with all natural dyes decreased when the number of cycle increased, which indicated higher colour depth obtained on the fabrics. When the number of colouration cycle increased, the addition of gardenia blue caused the obtained colour on the PP fabric to less red and less yellow than those on PLA and the PET fabrics. The presence of natural orange and natural yellow resulted in the obtained coloured on the PET and the PP fabrics a little bit redder and yellower than those on PLA. The addition of curcumin gave the PLA fabric redder and less yellow than those on PET and PP fabrics.

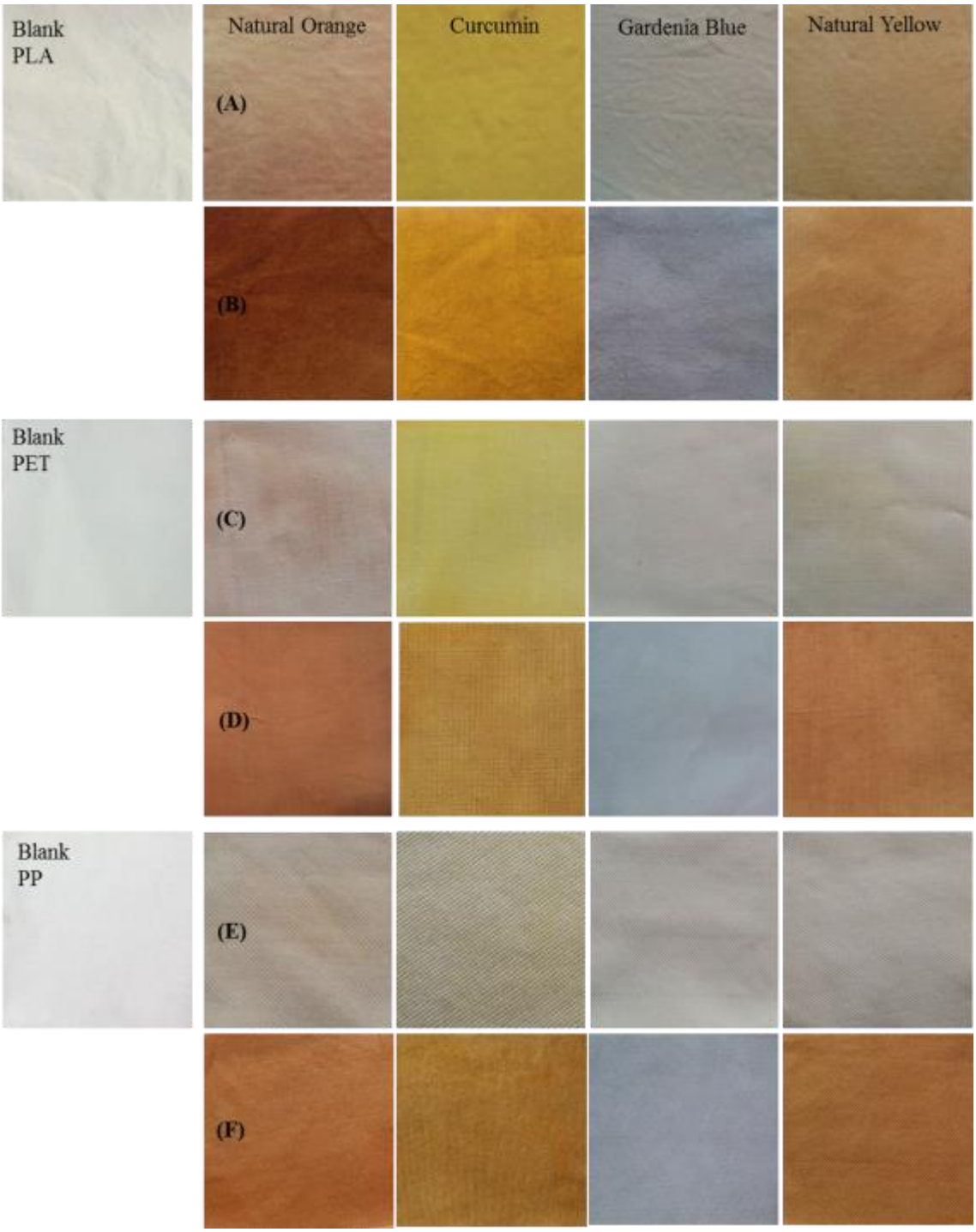

Figure 4.3 The photographic images of the dyed fabrics. (A), (C), (E) PLA, PET, PP control fabric dyed with natural dye only, (B), (D), (F) PLA , PET, PP fabrics dyed with natural dye in presence of dopamine

Table 4.1 The K/S values of the fabrics coloured with one cycle

Fabrics	Dyes	Natural dye only	Natural dye + dopamine
PLA	Gardenia blue	0.20	0.83
	Natural orange	0.43	1.76
	Natural yellow	1.57	2.43
	Curcumin	1.76	3.30
PET	Gardenia blue	0.10	0.45
	Natural orange	0.26	0.41
	Natural yellow	0.23	0.83
	Curcumin	1.02	1.17
PP	Gardenia blue	0.05	0.35
	Natural orange	0.21	0.53
	Natural yellow	0.11	0.80
	Curcumin	0.32	1.93

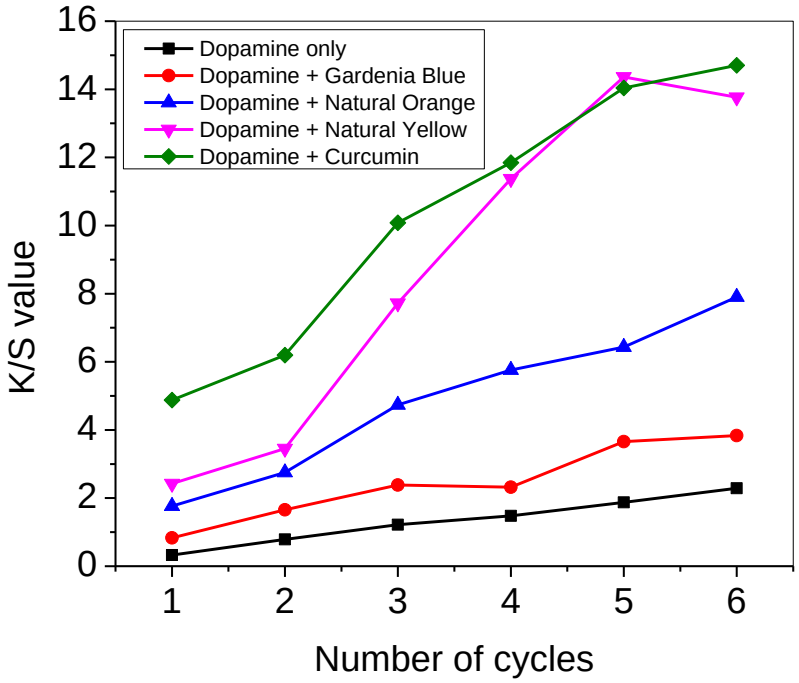

Figure 4.4 The K/S values of the PLA fabrics with repeated colouration cycles

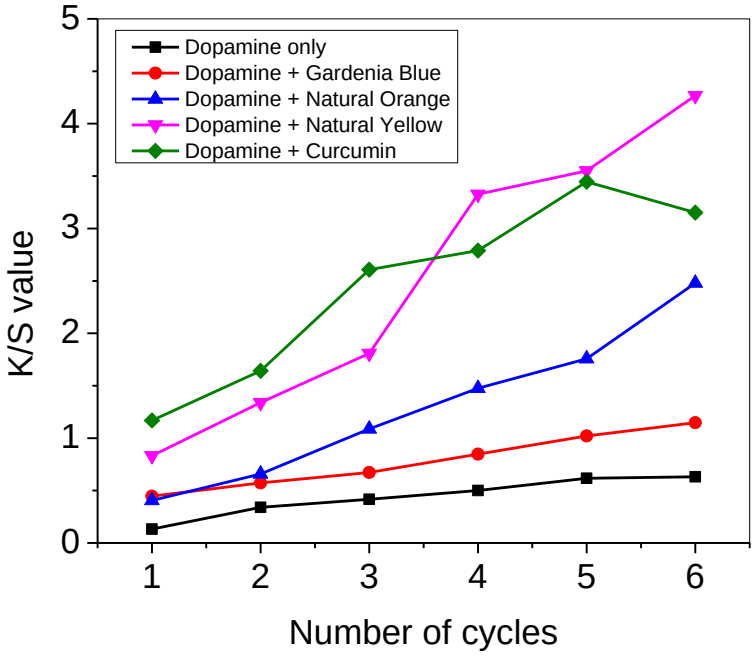

Figure 4.5 The K/S value of the PET fabrics with repeated colouration cycles

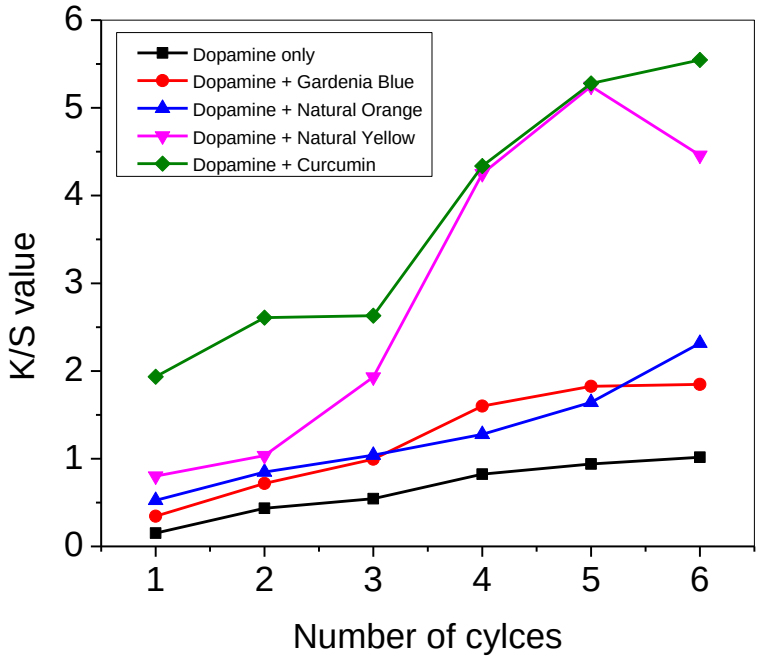

Figure 4.6 The K/S values of the PP fabrics with repeated colouration cycles

Table 4.2 Colorimetric analysis of the coloured PLA fabrics

	Number of cycles	L*	a*	b*
	Blank	90.02	0.68	8.81
Gardenia blue	Control	59.80	1.54	11.05
	1	66.40	-0.67	3.70
	2	58.78	0.55	6.74
	3	54.47	1.15	8.15
	4	54.01	1.04	9.78
	5	49.84	0.95	10.04
	6	49.08	1.63	10.32
Natural orange	Control	79.76	7.70	13.90
	1	61.27	12.60	17.89
	2	54.14	12.18	16.80
	3	47.00	12.02	16.98
	4	44.85	12.42	17.76
	5	44.86	12.22	18.81
	6	40.60	14.79	18.71
Natural yellow	Control	79.38	2.34	25.45
	1	68.78	5.30	23.24
	2	61.00	6.45	21.68
	3	48.57	8.52	21.39
	4	43.57	12.16	23.94
	5	40.35	13.25	23.92
	6	39.06	12.70	22.85
Curcumin	Control	70.86	9.67	30.16
	1	65.14	9.37	38.67
	2	61.00	6.45	21.68
	3	48.57	8.52	21.39
	4	43.57	12.16	23.94
	5	40.35	13.25	23.92
	6	39.06	12.70	22.85

Table 4.3 Colorimetric analysis of the coloured PET fabrics

	Number of cycles	L*	a*	b*
	Blank	90.02	0.68	8.81
Gardenia blue	Control	59.80	1.54	11.05
	1	66.40	-0.67	3.70
	2	58.78	0.55	6.74
	3	54.47	1.15	8.15
	4	54.01	1.04	9.78
	5	49.84	0.95	10.04
	6	49.08	1.63	10.32
Natural orange	Control	83.30	6.28	10.19
	1	79.73	8.61	13.41
	2	74.89	10.40	15.39
	3	71.06	11.80	19.15
	4	65.88	11.54	18.54
	5	64.09	12.58	18.87
	6	58.00	16.88	20.33
Natural yellow	Control	88.93	-1.46	9.85
	1	78.15	3.29	16.53
	2	72.23	5.15	18.79
	3	68.55	6.39	20.26
	4	61.48	10.52	23.66
	5	59.31	10.18	22.18
	6	57.10	10.12	23.12
Curcumin	Control	88.93	-1.46	9.85
	1	78.15	3.29	16.53
	2	72.23	5.15	18.79
	3	68.55	6.94	20.26
	4	61.48	10.52	23.66
	5	59.31	10.18	22.18
	6	57.10	10.12	23.12

Table 4.4 Colorimetric analysis of the coloured PP fabrics

	Number of cycles	L*	a*	b*
	Blank	92.28	-0.13	0.81
Gardenia blue	Control	64.48	-0.46	5.72
	1	76.17	-2.42	0.95
	2	67.79	-2.82	1.50
	3	63.99	-2.93	2.10
	4	57.86	-1.10	5.11
	5	56.98	-1.01	5.63
	6	56.09	-0.88	5.41
Natural orange	Control	87.24	3.89	14.60
	1	76.93	8.25	15.80
	2	71.83	10.10	17.38
	3	70.34	10.11	19.03
	4	67.11	10.92	19.28
	5	65.21	11.42	19.56
	6	59.91	16.59	22.61
Natural yellow	Control	90.71	-1.03	5.851
	1	79.56	2.21	16.61
	2	76.31	3.47	17.87
	3	69.02	6.26	20.88
	4	59.89	10.66	25.46
	5	58.48	11.84	27.49
	6	57.87	9.68	23.96
Curcumin	Control	90.71	-1.03	5.85
	1	79.56	2.21	16.61
	2	76.31	3.47	17.87
	3	69.02	6.26	20.88
	4	59.89	10.66	25.46
	5	58.48	11.84	27.49
	6	57.87	9.68	23.96

4.3.2 Microscopic analysis

The surface morphologies of the coloured fibres were examined using microscopic analysis. The SEM images of PLA, PET and PP fibres before and after colouration were shown in Figure 4.7. It was observed that the blank fibres have smooth and clear surfaces. After the colouration, the changes in their surfaces roughness were noticeable. Their surfaces were wrapped by numerous micro-scaled particles, especially on PLA fibres surfaces. These results were consistent with their photographic images in Figure 4.3 and K/S values in Table 4.1 since they were coloured with higher colour depth than PET and PP. This change in their surface morphology confirmed the successful application of natural dyes on various fibres with the aid of dopamine.

The cross-sections of the PLA, PET and PP fibres before and after colouration were also examined with optical microscope, as shown in Figure 4.8. The microscopic images show that the cross-sections of blank fibres were pale brownish, indicating their original fibre colours. After colouration, their cross-sections were changed to dark orange and dark blue accordingly. Compared to PET and PP fibres, the cross-sections of PLA fibres gave much darker colour, showing more dye molecules penetrating into the interior part of the PLA fibres, as higher colour depth was obtained on PLA fabric.

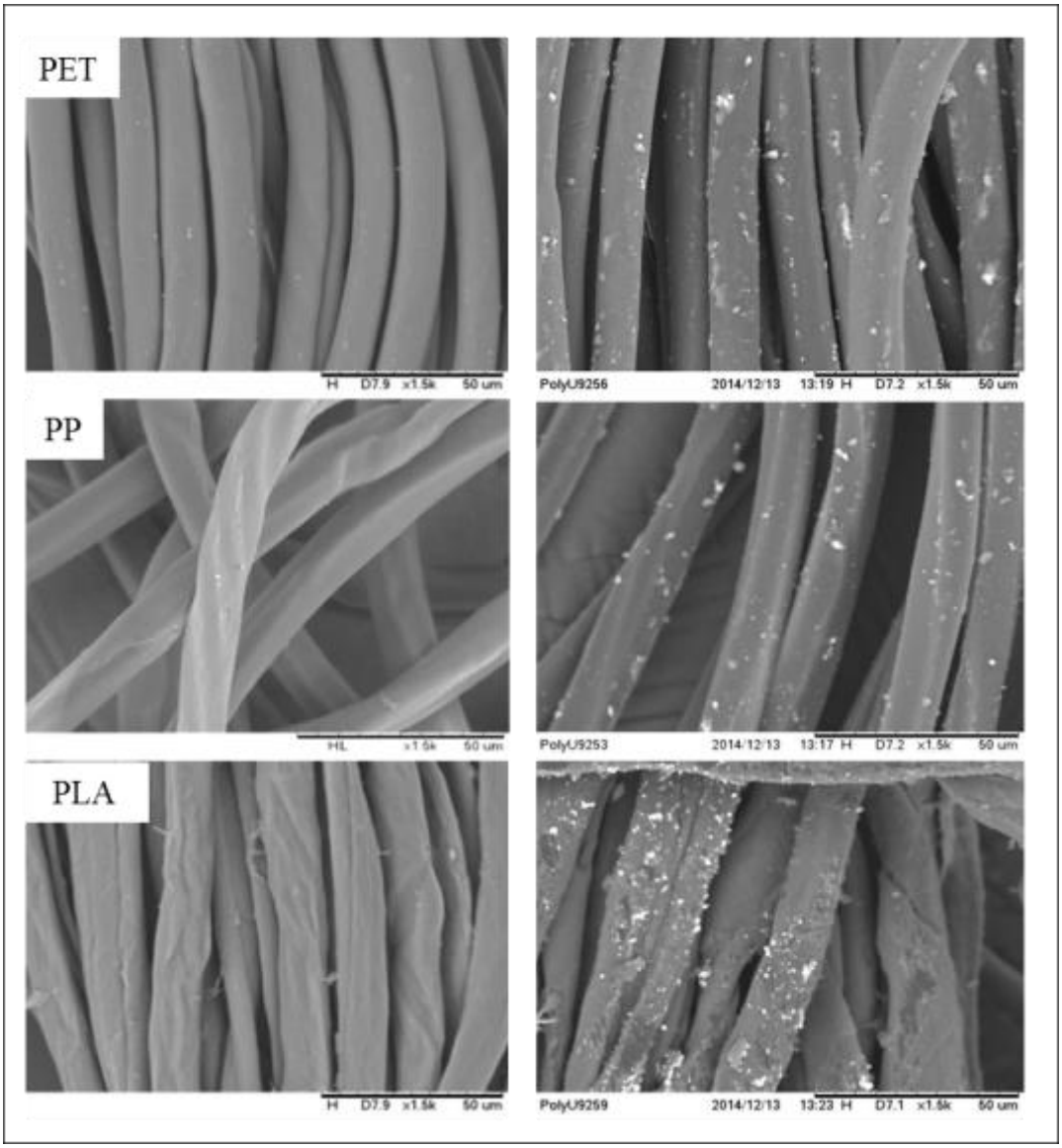

Figure 4.7 The SEM images of fibres before (left) and after (right) colouration

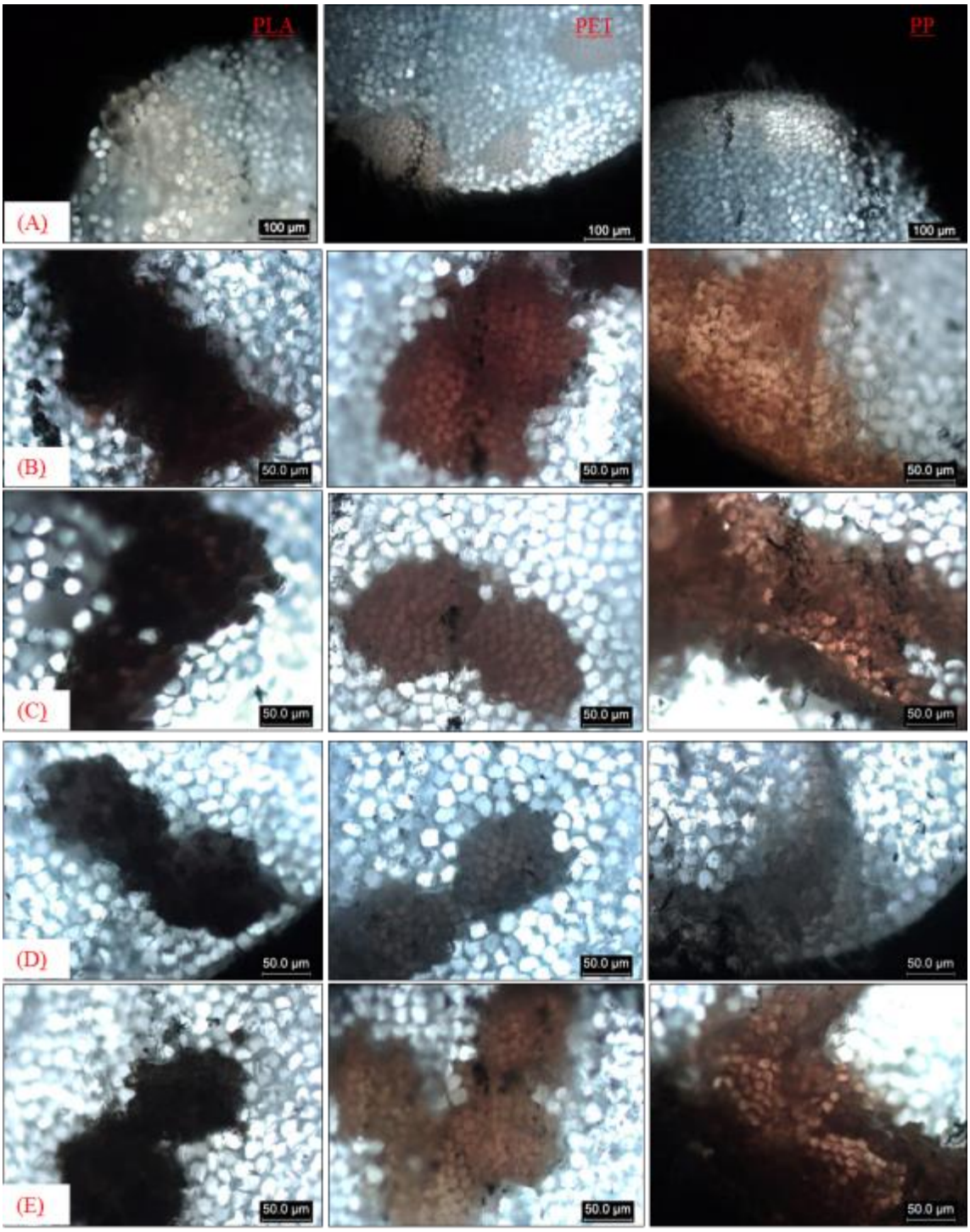

Figure 4. 8 The microscopic images of the cross-section view of fibres before and after coloration. (A) Blank fibre, (B) dyed with natural orange, (C) dyed with natural yellow, (D) dyed with gardenia blue, (E) dyed with curcumin

4.3.3 Colour fastness test

Table 4.5 Colour fastness to washing of the fabrics coloured with natural dyes in the presence of dopamine

Fabric	Dye[a]	Colour change	Fastness to washing					
			Staining					
			Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
PLA	G	4	5	5	5	2/3	5	5
	O	2	4	5	4/5	2/3	4	3/4
	Y	2	4/5	5	5	2/3	3	4/5
	C	3	4/5	5	4/5	1/2	3	2
PET	G	3/4	4/5	5	5	5	5	5
	O	3	4/5	5	4/5	3/4	4/5	4
	Y	3/4	4/5	5	5	3	4	4/5
	C	3	4/5	5	5	2/3	3/4	4
PP	G	2/3	4/5	5	5	2/3	4/5	4/5
	O	1/2	4/5	5	3/4	2	5	2/3
	Y	3	4/5	5	5	2	4/5	5
	C	2/3	4/5	5	5	1/2	3/4	3/4

[a]G, Gardenia blue; O, Natural orange; Y, Natural yellow; C, Curcumin

Table 4.6 Colour fastness to crocking of the fabrics coloured with natural dyes in the presence of dopamine

Fabric	Dye	Crocking fastness	
		Dry	Wet
PLA	Gardenia blue	5	4
	Natural Orange	5	4
	Natural Yellow	5	4
	Curcumin	4/5	3/4
PET	Gardenia blue	5	4/5
	Natural Orange	4/5	4/5
	Natural Yellow	5	4
	Curcumin	5	4
PP	Gardenia blue	5	4
	Natural Orange	4/5	3/4
	Natural Yellow	5	3/4
	Curcumin	3/4	2/3

The colour fastness of the fabrics coloured with natural dyes in presence of dopamine were also evaluated, including wash fastness and crocking fastness, as listed in Table 4.5 and 4.6. The results showed that PLA and PET fabrics had better washing fastness than PP fabrics; the ratings of colour change were within the range of 3 to 4 in most cases of PLA and PET, while the ratings of PP were within 1/2 to 3. For the colour staining results, most of their ratings achieved the range of 4/5 to 5, except some serious stains on nylon and acetate fabric.

Concerning the crocking fastness, their dry crocking fastness results were in the range from 3/4 to 5, which were slightly better than their wet fastness results, most of their ratings were within the range of 3/4 to 4/5.

4.4 Conclusion

The dopamine-induced colouration method was also developed to achieve a wider range of colour hues on textile materials through the incorporation of commercially available natural dyes. Using this method, textile materials were successfully dyed at room temperature in a simple way. The results showed that high colour depth was obtained on various textile materials, even the fibres difficult to be dyed with traditional dyes, and also the dyed fabrics achieved better crocking and washing fastness properties. This strategy is much more eco-friendly in comparison with the conventional colouration method since the substances used in the colouration process are biocompatible and biodegradable.

4.5 Reference

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Chapter 5

Synthesis and application of a novel catecholamine dye for textile materials

5.1 Introduction

In the previous chapters, dopamine was successfully applied to adhesive surface colouration in a simple way. These methods worked well on different kinds of materials, including textile materials and even the materials resistant to colouration. It is a promising alternative to the traditional colouration method. However, the colour gamut was still not so rich, although several methods were employed, including changes in the nucleophilic species, oxidant types, ratio of dopamine to nucleophilic species and natural dyes. In this chapter, a novel kind of catecholamine dye was designed and synthesized for textile material colouration as an approach to enhance the versatility of the dyes and further enrich the colour gamut produced on textile materials.

It is believed that catechol-containing DOPA is responsible for the versatile adhesive of MAPs through cross-linking and different physicochemical interactions between DOPA and solid surface, including π electron interactions, coordination bonds, hydrogen bonds, ionic bonds and covalent bonds[1-6]. Inspired by this, extensive efforts have been made to develop bio-based functional surface coatings using catechol-containing molecules[5-9]. However, no study targets the biomimetic adhesive on textile colouration using catechol-containing dye.

Well-known, the existed commercially available dyestuff demonstrate rich colour gamut. If dopamine is covalently bound to those commercially available dyes acting as a 'molecule anchor' to attach to the fibres, not only the colour range would greatly enrich, but also the obtained catechol dyes would exhibit good dyeability on textile materials via the multiple physiochemical interactions of dopamine.

To continue our interest on adhesive surface colouration, in this chapter, a versatile colouration method on various textile materials using a novel catechol dye was developed, as shown in Figure 5.1. In this method, a commercially available dye of Acid Yellow 11 (AY) was used as a model of chromophore. After the modification, dopamine moiety in dye (D1) would act as a colouration 'anchor' to fasten on the fibres. In addition, a control dye (D2) with similar structure but without catechol group was also synthesized for colouration evaluation. The chemical structure of the synthesized dye was confirmed from the analyses of high resolution mass spectrometry, proton and carbon nuclear magnetic resonance spectroscopy. Its dyeing properties on various fabrics were investigated. The results revealed that at room temperature the synthesized catechol dye had good colour yield on various fibres, especially for those textile materials difficult to be coloured by traditional dyestuff, such as polylactic acid and polypropylene. It was found that the dyed fabrics had good fastness properties.

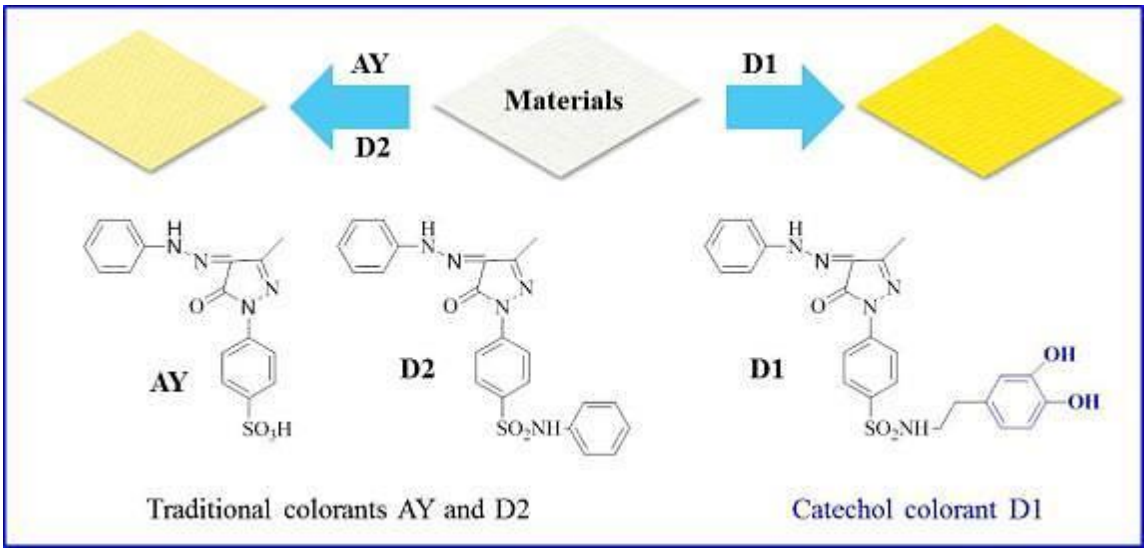

Figure 5. 1 Colouration with catechol dye and traditional dyes

5.2 Experimental

5.2.1 Materials and instrument

Six different types of fabrics were used including wool (255 g/m^2), polyethylene terephthalate (PET, 123 g/m^2), polylactic acid (PLA, 118 g/m^2), polypropylene (PP, 79 g/m^2), polybenzimidazole (PBI, 145 g/m^2) and silk (101 g/m^2). They were purchased from China Dyeing Holding, Limited. Prior to colouration process, these fabrics were washed with 5 g/L sodium dodecyl sulfate at 60 ^{o}C for 20 min to remove possible surface impurities. The fabrics were then rinsed thoroughly in deionized water and air dried. All chemicals were purchased from Sigma-Aldrich and used as received.

High resolution mass spectrometry (HRMS) was recorded using a Micromass Q-TOF 2 mass spectrometer. Proton and carbon nuclear magnetic resonance spectroscopy (^{1}H

NMR and ^{13}C NMR) were recorded on a Varian 400 spectrometer using TMS as an internal standard. The absorption spectra were recorded on a Pekin Elmer Lambda 18 UV-vis spectrophotometer.

5.2.2 Synthesis of control dye D2

For comparison purpose, a control dye without catecholic group (D2) was also synthesized for the colouration study. As shown in Figure 5.2, compound 4 was synthesized using AY as starting material by the reaction with thionyl chloride according to a method reported previously[10]. Then, the compound 4 (0.377 g, 1 mmol) was added to a solution of aniline (0.186 g, 2 mmol) in 20 mL acetone and the mixture was stirred for 2 h at room temperature. The solvent was then removed under reduced pressure. The residual was re-dispersed in acidic water and washed for several times. After filtration, dye D2 was obtained as a yellow powder and purified by crystallization from chloroform. Yield: 93.1%. ^{1}H NMR ($CDCl_3$): δ 13.51 (br, 1H), 8.14 (d, 2H) 7.83 (d, 2H), 7.48 (m, 4H), 7.29 (m, 3H), 7.17 (d, 1H), 7.10 (d, 2H), 6.57 (br, 1H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 174.29, 158.30, 149.81, 141.83, 140.87, 136.30, 134.37, 129.82, 129.43, 128.50, 126.39, 125.73, 122.10, 117.73, 116.06, 11.88; HRMS (TOF, ES^+) m/z = 434.1302 $(M+H)^+$, Calcd for $C_{22}H_{20}N_5O_3S$ = 434.1287.

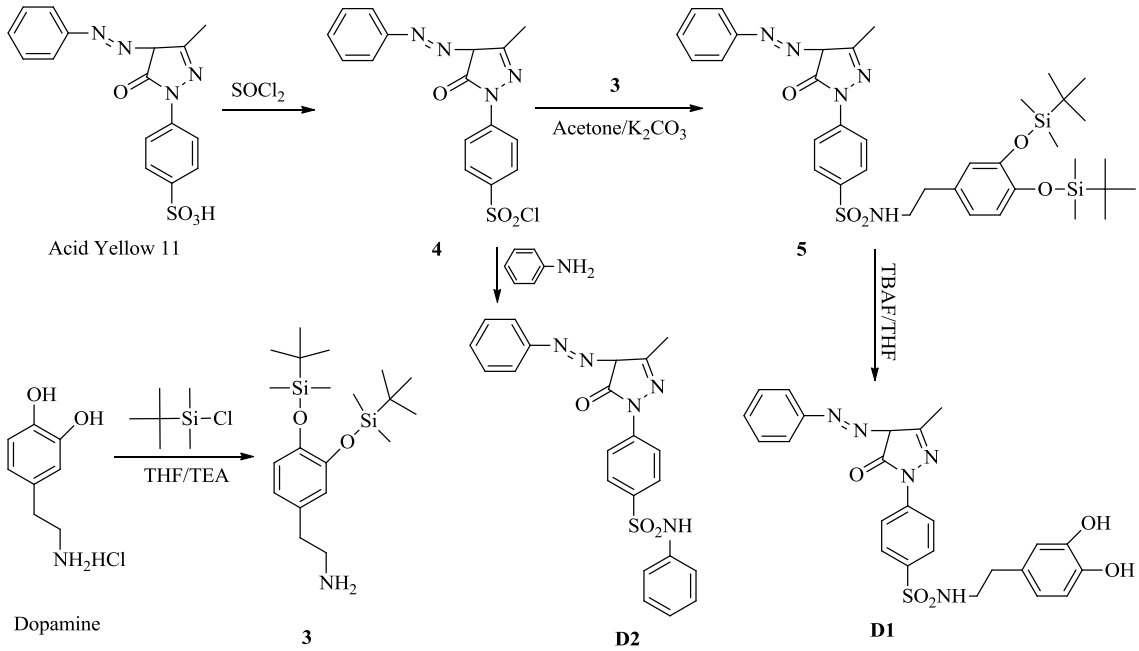

Figure 5. 2 Synthesis routes for the dyes

5.2.3 Synthesis of catecholamine dye D1

Using a reported method of hydroxyl group protection[10], the protection of the catecholic oxygens in dopamine was achieved by the reaction of dopamine hydrochloride with *t*-butyldimethylsilyl (TBDMS) chloride, as shown in Figure 5.2. Intermediate compound 5 was synthesized through the reaction of protected dopamine (compound 3) and AY chloride (compound 4) using a similar method to synthesize compound 2. The crude compound 5 (0.144 g, 0.2 mmol) was added into 2 mL tetrahydrofuran (THF). Under stirring, tetra-n-butylammonium fluoride (TBAF) (0.41 mmol) solution in THF was added, the mixture was then stirred for another 30 minutes at room temperature. Next, THF was removed under reduced pressure and the residual was purified with column chromatography using DCE/EA (v/v, 3:1) as eluent to obtain 0.060 g of dye D1 as a

yellow powder. Yield: 60.8%. ^{1}H NMR (DMSO-d_6): δ 13.24 (br, 1H), 8.76 (s, 1H), 8.68 (s, 1H), 8.17(d, J=8, 2H), 7.88 (d, J=8, 2H), 7.66 (d, 3H), 7.48 (t, 2H), 7.26 (t, 1H), 6.61 (d, J=8, 1H), 6.53 (s, 1H), 6.39 (d, J=8, 1H), 2.89 (q, 2H), 2.48 (t, 2H), 2.35 (s, 3H); ^{13}C NMR (DMSO-d_6): δ 187.16, 145.00, 143.64, 129.55, 129.33, 127.86, 127.80, 125.90, 125.85, 119.18, 117.15, 117.06, 116.48, 116.42, 116.38, 115.92, 115.45, 44.59, 34.77, 11.75; HRMS (TOF, ES$^+$) m/z = 494.1514 $(M+H)^+$, Calcd for $C_{24}H_{24}N_5O_5S$ = 494.1498.

5.2.4 Colouration of fabrics

All fabrics were immersed in 0.05% w/v dye solution in methanol (liquor ratio 20:1) overnight at room temperature. Then, the fabrics were taken out of the solution, and post-treated with 1% potassium periodate solution for one minute. After drying, the fabrics were washed in 0.5% detergent at 60°C for 10 minutes to remove the unfasten dyes, and then air dried.

5.2.5 Dispersion of dyes

AY and D1 were mixed with dispersant (Methylnaphthalene sulfonate formaldehyde condensate, MF) with the mass ratio of 1:3, respectively. The mixture was milled for 5 hours at room temperature. Then, the colourations of fabrics were conducted in deionized water under the same condition as 4.2.4.

5.2.6 Colorimetric measurement

Colorimetric analyses of dyed fabrics were conducted according to Section 3.2.4.

5.2.7 Microscopic analysis

The cross-section images of the specimens were investigated using an optical microscope (microscope: Nikon Optiphot-POL from Germany, software: high-performance Leica LAS software). During specimen preparation, the blank or dyed yarns were closely packed with light blue nylon yarns in the sample holder, which were easy to cut into a flat cross section. The light blue nylon yarns were used to support the specimen during the measurement of fibre cross-section. The surface morphology of the specimen was analyzed by a scanning electron microscope (SEM) (Hitachi Tabletop Microscope, TM-3000).

5.2.8 Colourfastness testing

The colourfastness of the dyed fabrics was tested according to the standard methods of colourfastness to crocking: crockmeter method (AATCC Test Method 8-2007)[12], colourfastness to laundering: accelerated (AATCC Test Method 61-2010, test no. 2A)[13] and colourfastness to light: ISO 105 B02-2013 (xenon-arc lamp)[14]. The rating was assessed using AATCC grey scale for staining and grey scale for colour change.

5.3 Results and discussion

5.3.1 Synthesis and characterization

Concerning the synthesis of AY chloride (compound 4), several reagents can be used to obtain a chlorosulphonyl group from the sulphonic acid group. These reagents contain chlorosulphonic acid, phosphorus trichloride, phosphorous oxychloride and thionyl

chloride. Among these, thionyl chloride is commonly used because its reactivity is moderate and the final by-products are gases, which are easy to be after-treated.

Before the reaction of compound 4 with dopamine, there is a need to protect the catecholic group in dopamine due to its competing reactivity with the amino group. The *tert*-butyldimethylsilyl chloride is often used for the catecholic group protection because *tert*-butyldimethylsilyl group has moderate stability with regard to hydrolysis, which is an important factor for the deprotection. The deprotection of silylated dopamine dye (compound 5) was successfully carried out in THF by the reaction with TBAF under mild conditions. The final target dye D1 was then obtained and purified via thin layer chromatography.

The mass spectra of the dyes revealed the expected molecular ion peaks. It was found that the base peaks of dyes D1 and D2 correspond to the protonated species $[M+H]^+$ generated using positive ion electrospray ionisation.

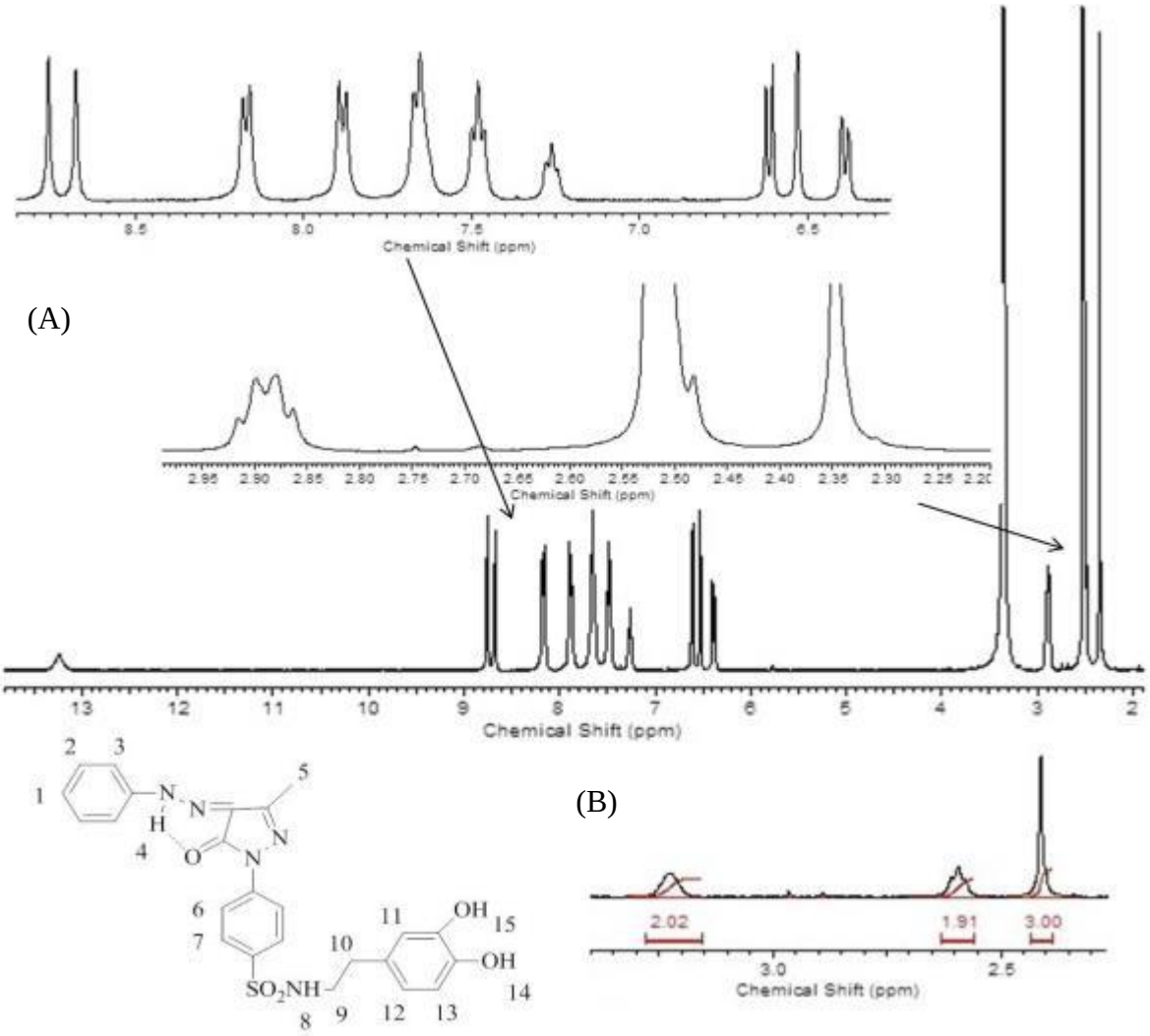

Figure 5.3 1H NMR spectrum for the catecholamine dye D1: (A) in DMSO-d6 and (B) the aliphatic proton signals in CDCl3

The chemical structure of dyes D1 and D2 were further confirmed by their proton and carbon nuclear magnetic resonance spectral analyses, as listed in the experimental section. As an example, a representative ^{1}H-NMR spectrum of target dye D1 is given in Figure 5.3. As shown in Figure 5.3(A), the spectrum contains two 1H singlet peaks at δ 8.76 and 8.68 ppm for the two hydroxyl protons H_{15} and H_{14} in the dopamine part. The

two 2H doublets at δ 8.17 and 7.88 ppm are attributable to aromatic protons H_7 and H_6, respectively. Peaks at δ 7.66 and 7.48 are attributed to aromatic protons $H_{3,8}$ and H_2, while the 1H triplets at δ 7.26 are attributed to aromatic H_1. The two doublets at δ 6.61 and 6.39 ppm arise from the neighbouring aromatic protons H_{13} and H_{12} in dopamine, while the 1H singlet at δ 6.53 arises from the proton H_{11}. The 2H quartet at δ 2.89 is assigned to CH_2 group (H_9), and the 3H singlet at δ 2.35 is assigned to CH_3 group (H_5). The signal peak from another CH_2 group (H_{10}) arises at δ 2.48 under this condition. Although partially covered by the solvent peaks, this proton signal still can be clearly read. In order to avoid the influence of the solvent and make sure the assignment for H_{10}, ^{1}H NMR spectrum was also measured in $CDCl_3$. The partial spectrum for the aliphatic protons is shown in Figure 5.3(B). A 2H triplet peak is clearly found between the 3H singlet for H_5 and the 2H signal for H_9, which further confirmed the structure of dye D1. It is interesting to note, a 1H brand singlet at upfield of δ 13.24 was also found in the ^{1}H-NMR spectrum of the catecholamine dye D1, which is attributed to the proton in NH group (H_4). The same case was also found in the ^{1}H-NMR spectrum of control dye D2. This indicated that the azo bond in the molecules existed in the hydrazone tautomer in solution, as shown in Figure 5.4. These results are consistent with the literatures[15].

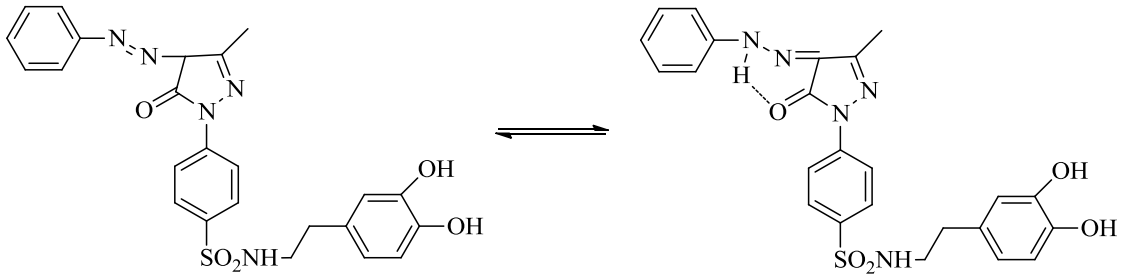

Figure 5.4 Isomerization forms of the catecholamine dye D1

5.3.2 UV-visible analysis

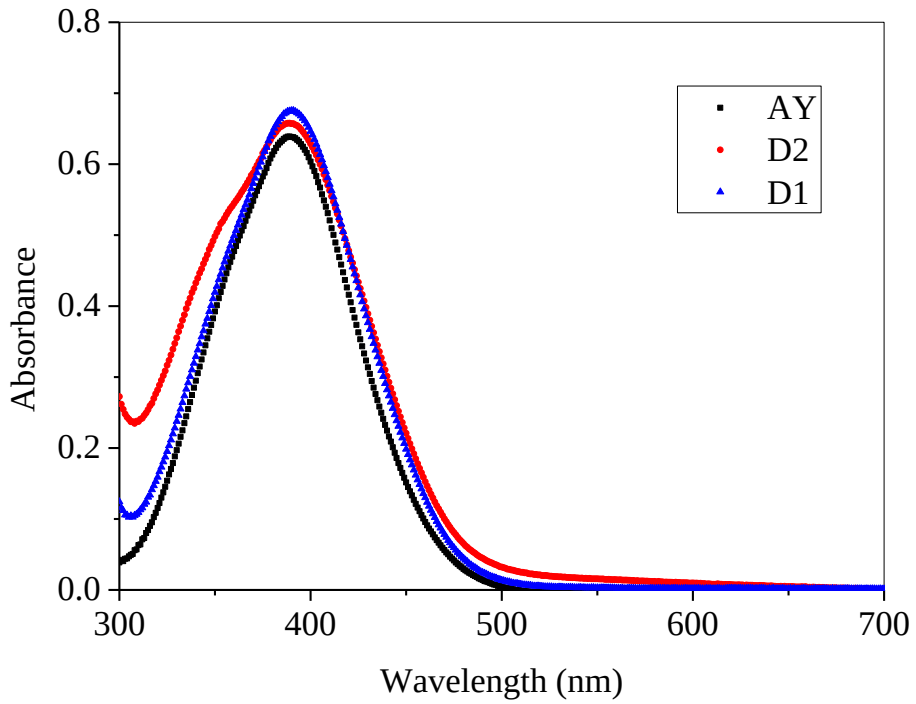

Figure 5.5 The absorption spectra of the dyes in methanol

The absorption behaviours of the three dyes were investigated in various solvents. Figure 5.5 gives an example of their absorption spectra in methanol. It can be seen that their maximum absorption wavelengths (λ_{max}) were similar and located at *ca*. 390 nm. Similarly, the λ_{max} of D1 in the other solvents were also more or less the same compared to its parent dye AY and control dye D2, as listed in Table 5.1. This was the expected result since their chromophores were not changed after the chemical reaction. In more polar solvents, such as ethanol, methanol and acetic acid, three dyes had absorptions at *ca.* 387-391 nm, which was slightly lower than those in less polar solvent like toluene and DMF. Their absorption indicated a slight dependence on solvent polarity.

Table 5.1 The maximum absorption wavelength of the dyes in different solvents[α]

Dye	Toluene	DMF	Acetone	EA	Methanol	Ethanol	Acetic Acid
AY	395	392	388	387	389	386	387
D1	391	402	388	385	391	387	386
D2	390	397	390	386	388	387	386

[α] DMF, *N*,*N*-dimethylformamide; EA, ethyl acetate

5.3.3 Colorimetric analysis

Fabrics dyed with D1, D2 and AY were evaluated using colorimetric analysis. PLA fabrics are difficult to be dyed as they have low affinity to traditional dyestuffs. As yet, only a limited number of dyes have been found to have good adsorption on PLA fabric at the appropriate colouration conditions[16,17]. Similarly, PBI and PP are also very difficult to be dyed with the traditional dyes owing to their high crystallinity and hydrophobicity.

In this study, the catechol dye D1 contained a catecholamine group, which would be capable of self-polymerization via spontaneous oxidation. It is expected that the D1 would demonstrate the ability of adhesive adsorption to various textile materials[5-9]. Once dye molecules contacted with fibres, the existence of catechol functional group could enhance the exhaustion of dye molecules on fibre surfaces. Therefore, the dyes were not easily to be removed away from the textile materials, even in the washing process.

Compared to the colour yields of AY and D2 under the same conditions, the colour yield of catechol dye D1 is much higher with a darker colour appearance, as shown in Figures 5.6 and 5.7. It can be seen that dye AY gave the better colour depth on wool fabrics. It was expected as AY is a typical acid dye for wool fabrics[18]. It was still found that D1 gave better result than traditional disperse dye D2. Their colouration difference was shown in term of the *K/S* values, listed in Table 5.1. The control dyes AY and D2 were smaller in molecular volumes than that of catechol D1, showing their stronger colour strength. However, the results indicated that AY and D2 gave the coloured fabrics lower *K/S* values than D1 under the same conditions. It indicated that catechol dye D1 remained more on the fabrics after soaping and displayed better dyeability on various fabric due to the presence of a 'catechol anchor'.

Table 5.2 also showed the colour coordinates CIE L^*, a^*, b^*, the total colour difference ΔE and *K/S* value of the dyed fabrics. All fabrics coloured with D1 have lower values of lightness L^*, which indicated higher colour depth comparing to those coloured with AY and D2. This correlated to the results shown by the photographic images in Figures 5.6 and 5.7. The total colour difference values ΔE of the PLA, PP and PET fabrics dyed with the catechol D1 were obviously higher, especially compared to the results of the fabrics dyed by AY. This was mainly attributable to big difference in b^* values, indicating that these fabrics showed a yellower colour compared to those fabrics coloured with AY and D2. This further confirmed that D1 gave better colour depth on various fabrics since the dyes used in this study are yellow colour. These results were

consistent with their photographic images shown in Figure 5.6 and 5.7, and *K/S* values listed in Table 5.2.

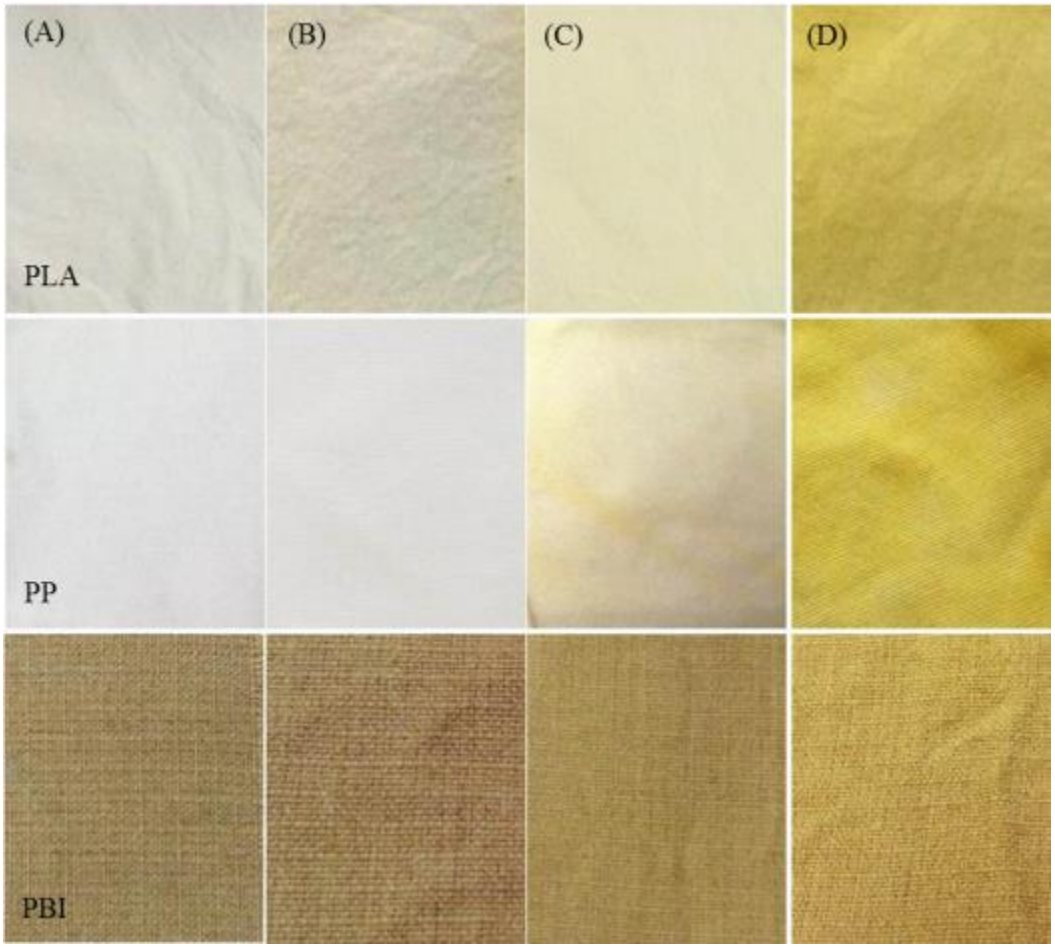

Figure 5.6 The photographic images of the colouration results of PLA fabrics, PP fabrics and PBI fabrics. (a) Blank fabric, (b) coloured with AY, (c) coloured with control D2, (d) dyed with catechol D1

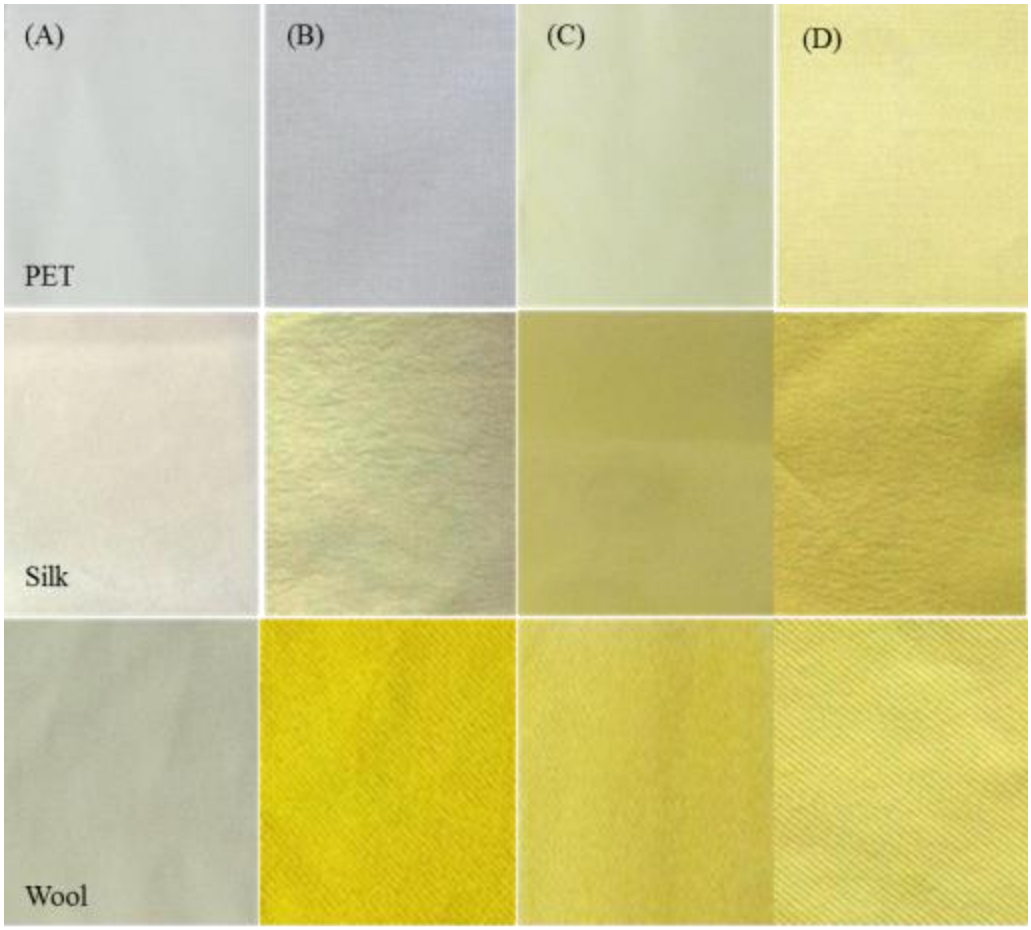

Figure 5. 7 The photographic images of the colouration results of PET fabrics, silk fabrics and wool fabrics. (a) Blank fabric, (b) coloured with AY, (c) coloured with control D2, (d) dyed with catechol D1

Table 5.2 Colorimetric analysis of the coloured fabrics

Dyed fabrics	Dyes	L*	a*	b*	ΔE[a]	*K/S*
PLA	Blank	90.02	0.68	8.81	-	-
	AY	90.03	-1.48	62.31	7.46	0.32
	D2	88.40	-3.07	27.14	18.78	0.73
	D1	86.74	-0.91	36.20	27.63	1.36
PP	Blank	92.28	-0.13	0.81	-	-
	AY	92.23	-0.64	3.02	2.27	0.05
	D2	89.20	-4.19	25.86	25.57	0.52
	D1	87.06	2.18	49.28	48.81	1.57
PET	Blank	92.32	-0.67	1.46	-	-
	AY	91.79	-2.42	6.60	5.45	0.14
	D2	90.11	-5.69	26.36	25.50	0.59
	D1	88.94	-4.35	35.23	34.23	0.99
PBI	Blank	68.54	3.44	20.25	-	-
	AY	68.00	2.50	33.01	12.51	4.95
	D2	68.20	2.20	31.60	10.70	3.90
	D1	66.10	2.82	32.92	12.90	4.84
Wool	Blank	89.98	0.56	2.23	-	-
	AY	83.39	0.07	68.26	66.36	13.02
	D2	85.47	-3.47	42.45	40.68	5.27
	D1	84.72	-0.68	50.83	48.89	7.07
Silk	Blank	90.06	3.72	-1.50	-	-
	AY	87.29	-2.12	24.92	27.20	1.46
	D2	85.43	-4.74	47.38	49.82	3.28
	D1	85.50	-3.61	43.28	46.21	3.61

[a] The coloured samples compared to the corresponding blank fabrics.

In dye development, enhancing the performance of poor water soluble dye remains most challenging aspects. In this study, dopamine with hydrophilic group can gain the improvement in the dye solubility and wettability due to surrounding with dispersing agent.

In order to achieve the colouration in a more environmental way, the colouration procedure was performed in water. AY and catechol dye D1 were mixed with dispersing agent to produce stable dye suspension for colouration. In the dispersion process, the dye was broken down into smaller particles by mechanical shear and then dispersed. The dye dispersion is stabilized by dispersing agents in order to prevent the formation of uncontrolled flocculates.

On the various fabrics of PLA, PP, PET and silk, the obtained colour depth with catechol dye D1 were better than those with control dye AY except wool fabric, as shown in Figure 5.8. In addition, catechol D1 gave the coloured fabrics higher *K/S* values than AY, listed in Table 5.3. These results indicated that catechol D1 also gave better dyeability on various fabrics than control dye when the colouration process performed in water.

Table 5.3 also listed the colour coordinates CIE L^*, a^*, b^* and the total colour difference ΔE of the coloured fabrics. All fabric coloured with catechol D1 had lower L^* values of lightness, indicating higher colour depth than those coloured by control AY. Due to their close a^* values, the values of total colour difference ΔE of the coloured

fabrics were mainly attributed to their *b** values. Apart from individual cases, fabrics coloured with catechol D1 showed higher *b** values, showing that the coloured fabrics gave a yellower hue compared to those fabrics coloured with AY. These results were consistent with their photographic images displayed in Figure 5.8.

Most of the fabrics coloured with catechol D1 had higher colour depth those fabrics coloured with D1 in presence of dispersing agent, except silk and wool had similar results. D1 had good solubility in methanol due to their structural similarity, and the dye molecules were easily adsorbed to the fabric. The presence of dispersing agent resulted in stable dye suspension in water for colouration. However, the dyes particles were not easily adsorbed to the fabric during the colouration process.

Figure 5. 8 The photographic images of the colouration results of fabrics. (a) Blank fabric, (b) coloured with disperse AY, (c) coloured with disperse catechol D1

Table 5.3 Colorimetric analysis of the fabrics coloured by disperse dyes

Dyed fabrics	Dyes	L*	a*	b*	ΔE_1[a]	*K/S*
PLA	Blank	90.02	0.68	8.81	-	-
	AY	87.35	-1.12	21.63	18.58	0.54
	D1	85.26	-2.24	26.84	25.53	0.91
PP	Blank	92.28	-0.13	0.81	-	-
	AY	91.63	-2.85	12.45	11.98	0.19
	D1	89.77	-4.32	19.75	19.57	0.45
PET	Blank	92.32	-0.67	1.46	-	-
	AY	89.50	-3.57	26.62	25.49	0.54
	D1	88.72	-4.86	23.16	22.39	0.59
Wool	Blank	89.98	0.56	2.23	-	-
	AY	85.08	-1.98	40.89	39.06	6.04
	D1	84.02	-2.67	40.18	38.55	6.55
Silk	Blank	90.06	3.72	-1.50	-	-
	AY	84.14	-7.93	33.64	37.50	1.75
	D1	81.32	-7.16	44.04	47.64	3.67

[a] The coloured samples compared to the corresponding blank fabrics.

5.3.4 Microscopic analysis

The coloured fibres were further investigated using microscopic analysis. Their surface morphology before and after colouration with catechol dye D1 were studied with the aid of SEM, as shown in Figure 5.9 and 5.10. It can be observed that the blank fibres (left, Fig 5.9 & 5.10) have clear and smooth surfaces. After colouration with D1, the fibre surfaces roughness was obviously changed. On the fibre surfaces, some micro-scaled particles were found on the fibre surfaces, which were obviously from the adsorbed dyes. It was observed that those micro-scales particles were deposited on various fibres including PLA, PET, PP, PBI, silk and wool. The clear changes in the surface morphology of the coloured fibres confirmed the successful colouration on the various fabrics using the catechol dye.

The cross-sections of various fibres were also evaluated with optical microscope. Figure 5.11 and 5.12 showed the cross-section views of various fibres before and after colouration with catechol D1. It can be observed that the cross-sections of blank fibres (left, Figure 5.11 & 5.12) were pale brownish, indicating their original colours. After coloration, the cross-section views of all fibres were obviously changed since the D1 dye molecules penetrated into the interior part of the fibres, which gave a yellower colour.

The SEM images of various fibres before and after coloration with disperse catechol D1 were presented in Figure 5.13. It can be also observed that some micro-scaled particles were deposited on various fibre surfaces after colouration including PLA, PET, PP, PBI,

silk and wool. These result also confirmed that the successful colouration on various fibres with D1, and also the application feasibility of this method on various textile materials including those difficult to be dyed via conventional colouration process.

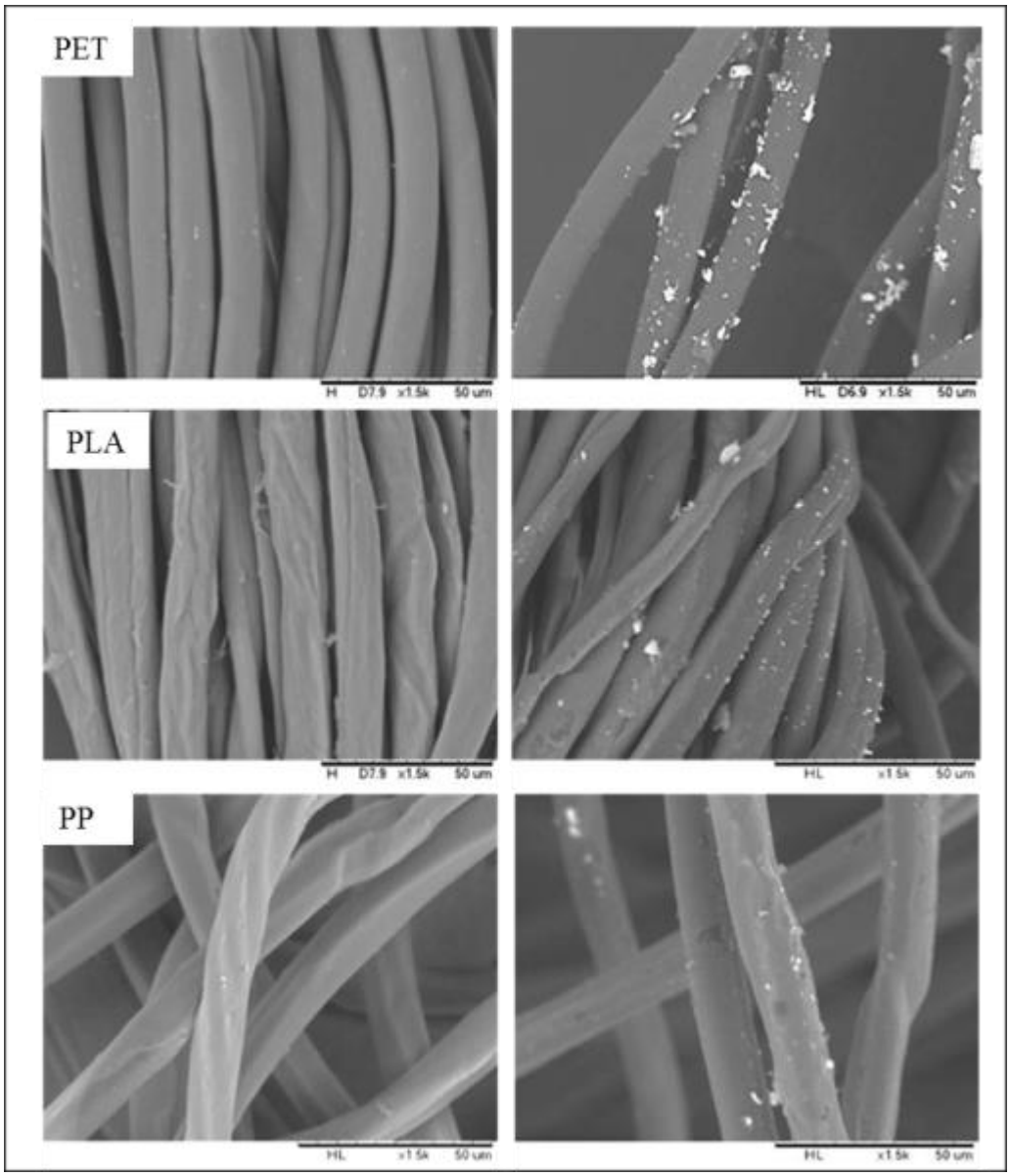

Figure 5.9 The photographic images of the colouration results of fabrics. (a) Blank fabric, (b) coloured with disperse AY, (c) coloured with disperse catechol D1

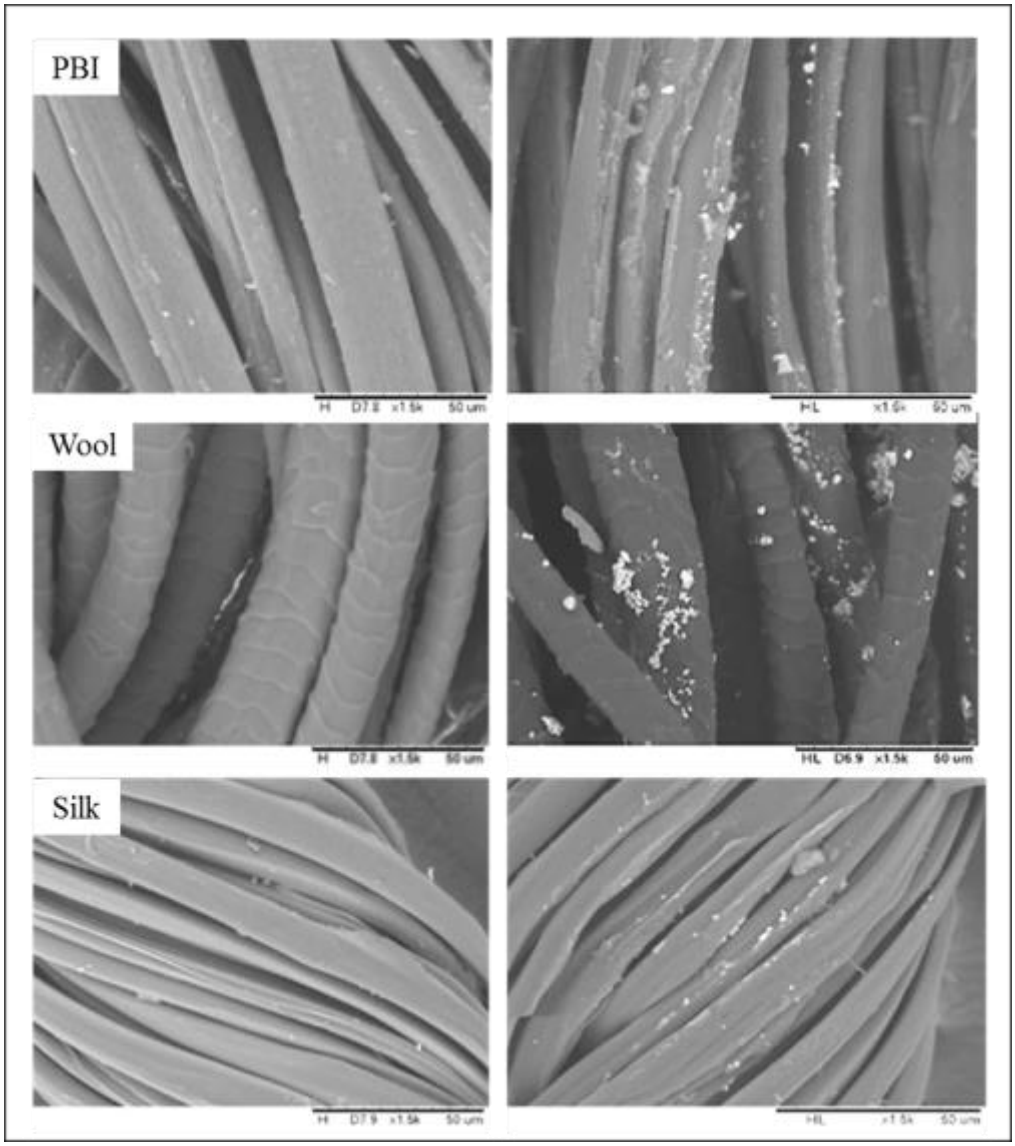

Figure 5.10 The surface morphology of PBI, wool and silk fibers before (left) and after (right) colouration with catechol dye D1

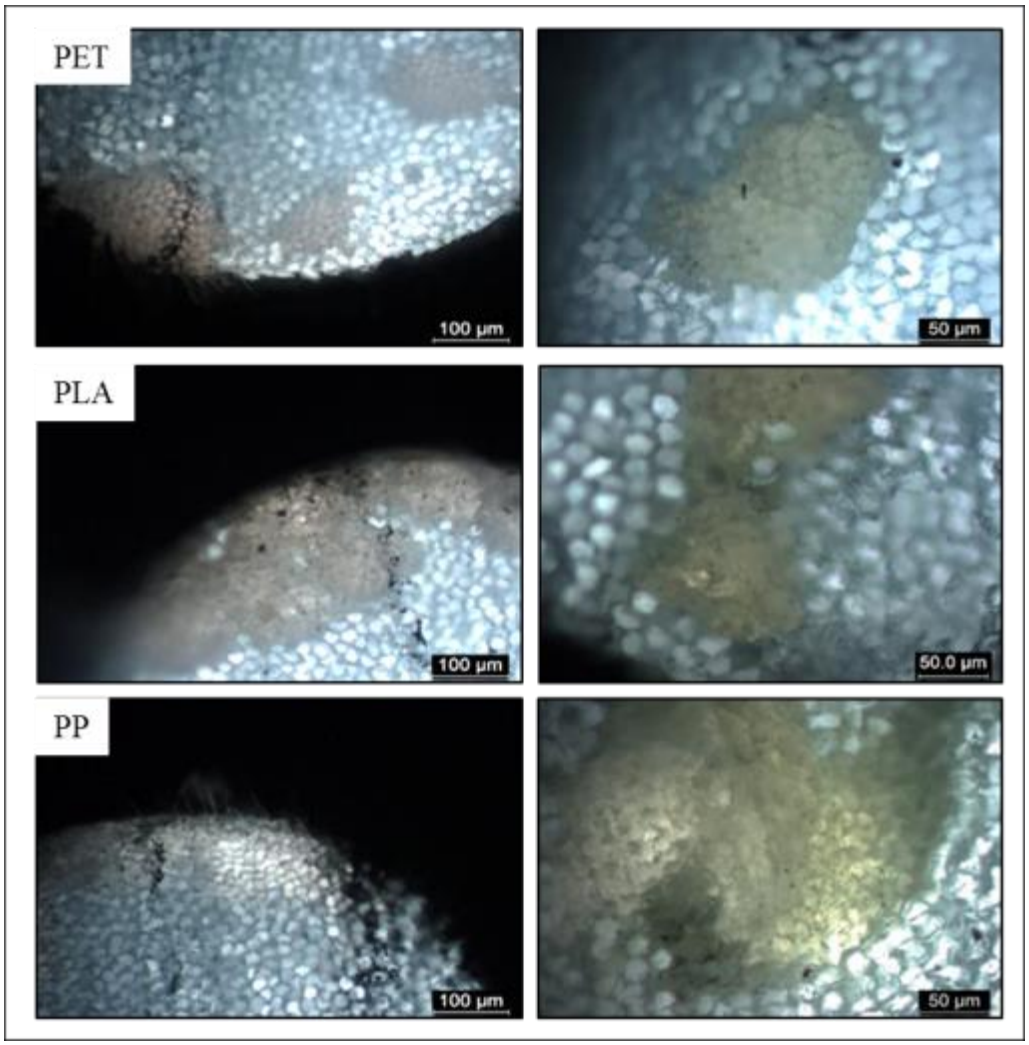

Figure 5.11 The microscopic images of the cross-section view of PET, PLA and PP fibers before (left) and after (right) colouration

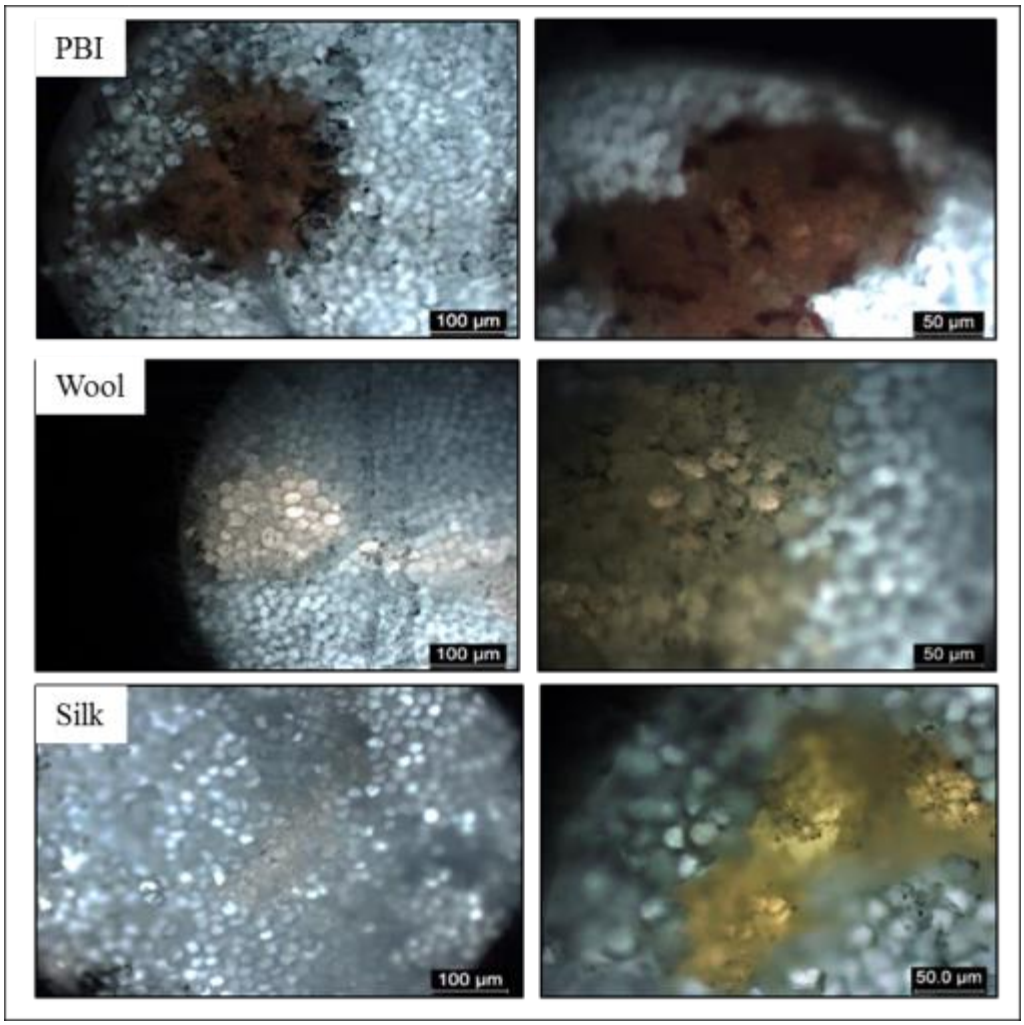

Figure 5.12 The microscopic images of the cross-section view of PBI, wool and silk fibers before (left) and after (right) colouration

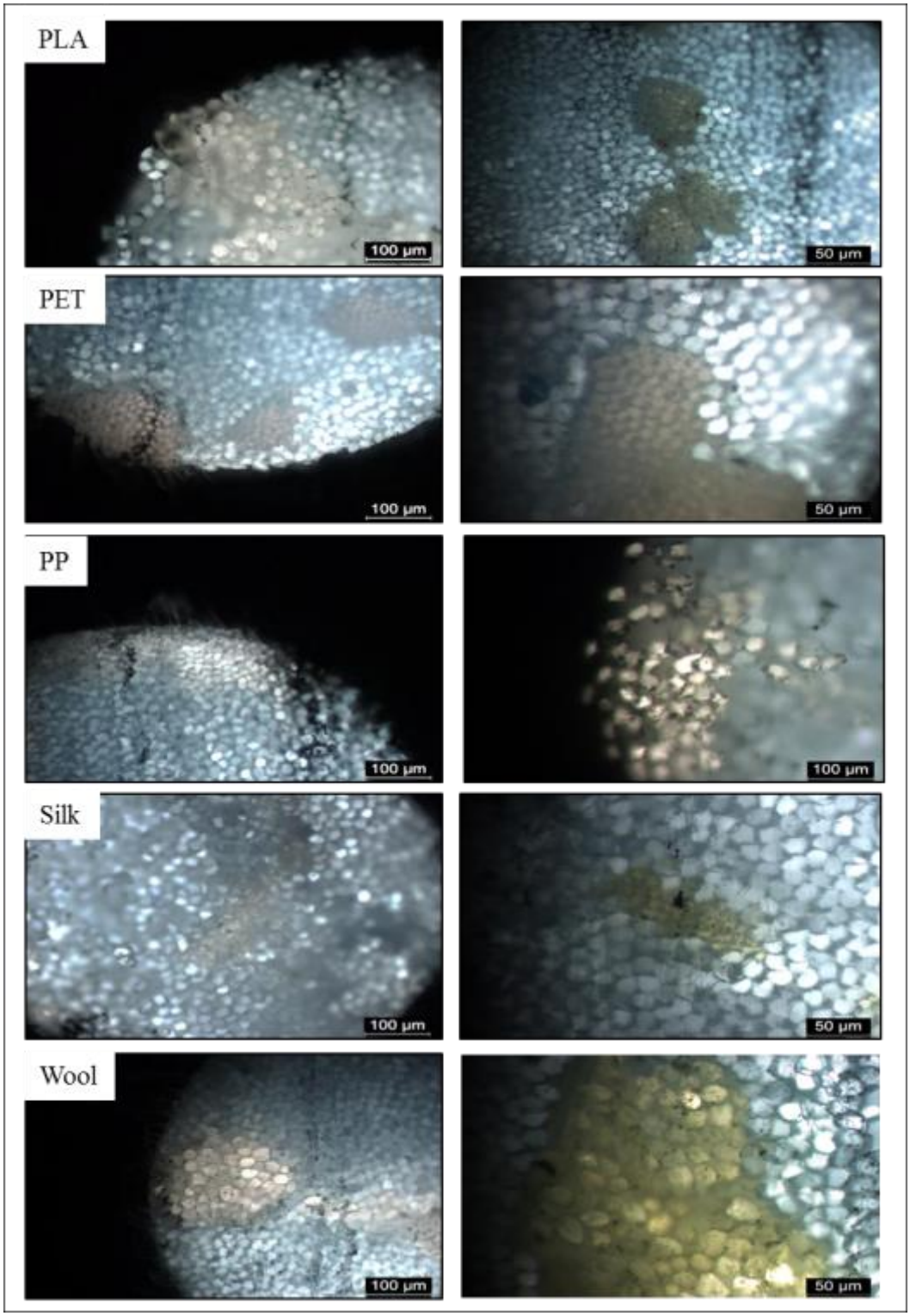

Figure 5.13 The microscopic images of the cross-section view of the fibers before (left) and after (right) colouration of disperse catechol D1

5.3.5 Colour fastness test

5.3.5.1 Laundering fastness test

The laundering fastness of coloured with the catechol dye D1 was investigated, as listed in Table 5.4. The results indicated that D1 gave good laundering fastness on all fabrics. The ratings of colour changes were in the range of 4 – 4/5. This results indicated that only small amount of dyes were washed away during the test, showing the good fasten of the catechol dye D1 molecules on the fibres. For the colour staining results, all the samples achieved a highest rating of 5, except for the silk fabric which have a slightly lower rating of 4/5. These results showed that there are nearly no staining on the neighbouring multi-fibre fabrics.

Table 5.4 Laundering fastness of the fabrics coloured with D1

Fabric	Laundering fastness						
	Colour change	Staining					
		Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
PLA	4	5	5	5	5	5	5
PET	4/5	4	5	5	5	5	5
PP	4/5	5	5	5	5	5	5
Wool	4/5	5	5	5	5	5	5
Silk	4/5	4/5	5	5	5	5	5

The crocking and light fastness of the fabrics coloured with D1 was listed in Table 5.5. Concerning the crocking fastness, D1 achieved 4/5 ratings of dry crocking fastness on PLA , PET and silk fabrics while 3 and 4 on PP and wool fabrics, respectively. Their

ratings of wet crocking fastness were in the range of 4 – 4/5. For the light fastness evaluations, the wool and silk samples achieved better ratings of 4, while other fabrics had lower ratings, which would be perhaps improved by the increase of their obtained colour depth.

Table 5.5 Crocking and light fastness of the fabrics coloured with D1

Fabric	Crocking fastness		
	Dry	Wet	Light fastness
PLA	4/5	4	2/3
PET	4/5	4	1/2
PP	3	4	1/2
Wool	4	4/5	4
Silk	4/5	4/5	4

5.4 Conclusion

A novel yellow dye with catechol functional group was synthesized using dopamine and Acid Yellow 11 as raw materials. Its chemical structure was confirmed with the aid of spectral analyses and its ^{1}H NMR analysis indicated that it mainly exists in the hydrazine form. Compared to the control dyes, the introduction of a catecholic group imparts the versatility to the dye, as verified by the successful colouration of various kinds of fabrics. The results of this study point out a promising alternative to the traditional dyes, especially for those fibres which are difficult to be dyed with traditional dyes. With the colouration at room temperature, the new colouration method indicated the convenience to application and low energy consumption.

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Chapter 6

Conclusions and suggestions for future research

6.1 Conclusion

In this study, bio-inspired by the adhesive properties of marine mussels, a novel method was developed for colouration of various textile materials in a simple way, including various textile materials, organic and inorganic materials, and even materials resistant to colouration.

6.1.1 Dopamine-induced colouration

Dopamine-induced colouration was successfully developed through its *in situ* polymerization for various materials, including natural and synthetic textile materials, even the materials resistant to colouration. The colour brightness and hue of the coloured materials can be tuned in a controllable way through the incorporation of a different nucleophilic species into the colouration bath. The colouration performance of dyed fabrics was studied by colorimetric analysis and colourfastness test. The surface compositions, morphology and wettability of the dyed surfaces were evaluated by X-ray photoelectron spectroscopy, scanning electron microscopy and water contact angle measurement, respectively.

The obtained results indicated that the materials surfaces were successfully coloured, which was verified by the significant changes in surface properties in comparison with

the blank samples. This method showed advantages of substrate-independence, ease of application and could be achieved at room temperature, which was totally different from the conventional colouration approach.

6.1.2 Dopamine-induced colouration with commercially available dyes

In chapter 3, various textile fabrics could be easily dyed using this bio-inspired colouration method. However, the colour spectrum was not rich enough although several methods were employed such as changes in nucleophilic species, types of oxidant and ratio of dopamine to nucleophilic species. For this reason, the incorporation of commercially available natural dyes instead of nucleophilic species was used to enrich the colour gamut for the dopamine–induced substrate-independent colouration on different textile materials. This strategy is much more environmental friendly in comparison with the conventional colouration industry since natural dyes are renewable, low toxicity and allergic response. The dyed fabrics were evaluated by colorimetric analysis, scanning electron microscopy, optical microscopic analysis and colour fastness tests. The obtained results indicated that the fabrics were successfully dyed, which were verified by the obviously deeper colour appearance and higher K/S value when compared to the control samples. This colouration method was suitable for those textile materials difficult to be dyed with traditional method like polylactic acid and polypropylene.

6.1.3 Colouration with novel catechol dye

The colouration feasibility with commercially available dyes was verified in chapter 4. In order to enhance the fixation of dyes on fibres, a novel catechol dye was synthesized using a commercially available dye of Acid Yellow 11 as a model of chromophore. Dopamine was covalently bound to these available dyes as an adhesive 'anchor' to fasten on the fibres through the multiple physiochemical interactions of dopamine, not only the colour gamut could greatly enrich, but also the obtained catechol dyes could exhibit good dyeability on various textile materials. The UV-visible results showed that the introduction of the catechol group did not significantly change the absorption of the parent dyes. Compared to the control colouration, the results revealed that this novel method gave textile materials a better colouration, which was verified in term of obviously deeper colour appearance and higher K/S values. This method could successfully colour various textile materials, including natural fibres and synthetic fibres and even the fibres difficult to be dyed with traditional dyes.

6.2 Suggestion for future research

In recent years, there has been growing concern about the health and environmental impact caused by conventional textile colouration. Thus, an environmental friendly colouration process is always desire and promising in textile industry. Some research efforts have been made to study a kind of universal dye, which is expected to be applied to all different fibres. But its application in textile colouration industry is seldom reported so far. Therefore, if there is a simple method which can be applied at room temperature for all different fibres, the colouration process could be simplified and the

amount of energy and wastewater could be reduced markedly, leading to a greener environment. It is interesting and worthy to be further studied in the future.

As it has been demonstrated in chapter 5, through the adhesive adsorption of a catechol group, colouration of various textile materials could be easily achieved using a catechol dye. But only one of the commercially available dyes was used as a model of chromophore. Apart from yellow colour, it is suggested to introduce commercially available dye of other primary colour like red and blue dyes as chromophore, thus the obtained dyes can mix together to make any of the other colours on textiles, the colour gamut could be further extended.

On the other hand, it was found that this colouration approach works well on wool and silk fabrics. Note that they are protein fibres, thus, they belong to the same type as human hair, in which natural melanin forms. Therefore, we believe that this versatile colouration method can be applied to human hair through the incorporation of commercially available natural dyes as chromophore, showing the advantages of easy to application and room temperature colouration. It is promising to be an environmental friendly choice compared to the conventional method for colouration of human hair since those synthetic dyes may easily cause carcinogenic or allergic to human body.