
Preparation, Characterization and Application of Ultra-Fine Modified Pigment in Textile Dyeing

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1. Introduction

Pigments are kinds of insoluble colorants used for fibers, plastics and other polymeric materials, which can retain stable chemical structure throughout the coloration process in its dispersed solution [1]. The pigments were obtained from mineral materials, vegetable materials, animal waste materials since 1200 BC. The significant development of pigment in textile field from 18th century attributed to a huge expansion in the range of synthetic pigments [2,3]. Currently, pigment perhaps is one of the most commonly and extensively colorations in fiber dyeing, due to its easy application to a variety of fibers and environmental friendly aspects [4].

As a result of the different physical and chemical characteristics between pigments and dyes, dyes are able to dissolve in water and penetrate into the substrate in the soluble form, while pigments are insoluble and difficult to be dispersed in water without the aid of dispersants [1]. The major drawback of pigments is the poor dispersing stability, which is affected by the particle size and surface charge on account of the imperfection of the dispersants [5]. Pigment dispersing system includes two main types according to the medium: solvent-based pigment and water-based pigment.

Solvent-based pigment systems, in which the organic solvent is used as dispersion medium, are more suitable for certain applications [6]. However, it is difficult to obtain pigment particles that are smaller than 100 nm in organic solvents. When the particle size of pigment is large, the interactions between pigments and organic solvents (e.g., hydrogen bonding) can disrupt the interactions with stabilizing dispersants. As a result, distinct particle aggregation that influences optical properties and viscosity occurs. To obtain a stable solvent-based pigment system, appropriate pigment amount, dispersants and solvents are the key factors [7].

Water-based pigment systems are environment-friendly pathways. Pigments are dispersed into water with the aid of auxiliaries, such as dispersants, emulsifiers, anti-setting agents, etc. Water-based pigment has been widely applied in coloration for textiles, paints, architecture, wood and so on [8,9]. But the unmodified pigment dispersion that contains pigments with large particle size is unstable and also suffers from the problems as precipitation and floating color. And then the color, fastness, handle and uniformity of the fabrics dyed with the unmodified pigment dispersion are influenced.

Ultra-fine modified pigment (UMP) is referred to nanometer or micrometer pigment particle by physical and/or chemical modifications in a composite disperse system with attaching functional groups for pigment dispersion. These functional groups often have contribution to appear the vivid color for the chromophoric groups in the pigment particle by selectively reflecting and absorbing certain wavelengths of visible light [6]. The UMP dispersion usually shows relative stability and higher color strength (K/S value) which closely approaches to that of dyes [10]. When UMP is used to color, the finely divided, insoluble particle remains throughout the coloration process [1]. Without the binder or less the amount of binder added in printing paste, the good handle will be achieved. And the better fastness is attained with the stronger attraction between the UMP and the fiber [10,11]. The UMP systems are divided into nonionic pigment dispersion, anionic pigment dispersion and cationic pigment dispersion according to the charged particles. Compared to the nonionic pigment dispersion, the pigment dispersion with ionic dispersant may produce the stronger combining power to the fabric [12,13].

The cationic disperser has been widely used in many fields. It had been reported in Japanese patents that cationic disperser was applied in electrodeposits coat. Being prepared with cationic disperser, the cationic pigment dispersion is able to decrease the migration of the pigment, and favorable dyeing deepness and color fastness are also obtained when such pigment is applied to pretreated cotton fabric and terylene-cotton fabric in pad dyeing [14]. The cationic surfactant is grafted onto the acrylic acid copolymer to attain disperser which is then applied to the anthraquinone pigment to prepare ink for ink-jet printing on paper [15]. In addition, there are many applications of cationic disperser in other fields, such as paper-making, image thermomigration, ink-jet printing paper, inorganic nano-scale powder and preparing hydrophilic ethylene copolymer dispersion. Moreover, pigment dyeing by exhaust process is possible by imparting substantivity with cationic reagents to induce the necessary affinity between pigments and fibers. The chemical modification of fiber with cationic reagents has been carried out to improve the dyeing properties [1,16].

In this chapter, the preparation of UMP, such as dispersing process, grinding process, ultrasonic wave process, microencapsulated process and microfluidics process are all summarized. And the particle size, disperse stability, Zeta potential and color properties, which are used to characterize the UMP are also analyzed. Moreover, the dyeing properties of UMP on cotton, silk, wool and acrylic yarns are mainly reviewed.

2. Preparation of UMP

Different from dyes, UMPs are totally insoluble in organic mediums due to its strong intermolecular aggregation, and they are required to be finely ground and dispersed in an

organic medium to warrant their gloss appearance, lighting efficiency and maximizing material utilization. In order to prepare stable UMP, the particle size of UMP needs diminishing sharply to smaller than 1 μm and the process can be achieved via dispersant, microencapsulation, grinding, ultrasonic wave, microfluidizer processes and their combined process [17-19].

The stability of UMP is determined by forces among the UMP particles, when the repulsive force is higher than attractive force, the UMP particles will stably disperse into the media, otherwise, the UMP particles will aggregate together. In UMP with polymer dispersant, the repulsion forces among particles including static-electronic and steric repulsion are produced by the adsorbed polymer. The former can be measured by the Zeta potentials. The latter is closely connected with the thickness of adsorbed polymer layer [14]. The dispersant and microencapsulation processes are usually utilized together with other methods in the preparation process.

2.1. Dispersing process

2.1.1. Low molecular weight dispersant

The UMP dispersion is a surface modification technique, typical of which is a chemical bonding of low molecular weight hydrophilic moieties on UMP surfaces. Hydrophilic moieties work by electrostatic interaction between UMP particles and vehicle solvents. Usually there are no polymeric substances, surfactants or dispersion to aid in surface-modified UMP dispersions, it is necessary to add binder resins before it is applied to textiles [20].

Low molecular weight dispersants are commonly used for wetting and dispersing the UMP particles. The effect of Triton X-100 on the colloidal dispersion stability of CuPc pigment nanoparticles was investigated by Dong et al [18]. The influence of the hydrophobic chain of quaternary dispersers on the properties of pigment dispersion was discussed by Fang et al and good dispersion effects were obtained when the hydrophobic chain were 14 or 16 [21]. The aqueous suspensions of organic pigment particles using cetyltrimethylammonium bromide (CTAB) and sodium dodecylbenzene sulfonate (SDBS) as additives were prepared by Wu et al and a uniform hydrous alumina film could be formed on the organic pigment particle surface with anion surfactant SDBS [22].

But the dispersion system only using low molecular weight dispersants is still suffered from the lack of stability for long-term storage or at high temperature [8], so additional process or dispersant are necessary.

2.1.2. Polymeric dispersant

Polymeric dispersants are a class of specially designed, structured materials and show good properties in the stabilization of organic UMP. In aqueous media, polymeric dispersants are adsorbed onto UMP surface via anchor groups to build voluminous shells or intensify the charges around UMP surface, thereby preventing flocculation and coagulation of the UMP, which can greatly improve the stability of the UMP dispersion [23-25].

The UMP particles are usually quite hydrophobic. In order to achieve a good stabilization in aqueous UMP dispersions, many formulations have been proposed. The application of polymer surfactants in combination with ultrasonic action can significantly improve the quality of dispersed systems. Some aspects concerning UMP-polymer interaction and formation of adsorption layers under mechanical action need additional elucidation. The colloid stabilization of aqueous dispersions with polymer surfactants is believed to be a consequence of adsorption of the amphiphilic macromolecules on the particle surface resulting in mono- or multi-layers of certain structure and thickness which provide certain sterical and/or electrostatic stabilization effects.

Polymer adsorption from aqueous solution on a particle surface is a result of specific interactions of various active sites on the particle surface with corresponding sites (groups) of the macromolecule. Therefore the chemical structures of the stabilizers are believed to be adjusted to the nature of each type of the particles [26]. Fu and his coworkers reported that pigment particles with the diameter of 20-120 nm were uniformly distributing in aqueous media. -COOH of PSMA which encapsulated onto the surface of pigment would build a voluminous shell and also intensify the charges of particles, which could effectively hinder the attraction among particles [27].

2.1.3. Copolymer dispersant

Copolymer dispersants are advantageous for providing multiple anchoring sites toward UMP surface as well as structurally more designable for solvating with the selected solvents. Polymeric structures of random, A-B block, comb-like copolymers prepared by various synthetic techniques have been employed as stabilizers against particle flocculation. However, the methods of anionic and group transfer polymerization are less appropriate since the synthesis of dispersants often involves the monomers with polar functionalities.

Copolymer dispersants are suitable for stabilizing the UMP particles against flocculation during the grinding disruption and storage. The principle for achieving a fine dispersion is a thermodynamically driven interaction among dispersant molecules, UMP particles, and solvents in a collective manner of mutual non-covalent bonding such as electrostatic charge attraction, hydrogen bonding, p-p stacking, dipole-dipole interaction, and van der Waals forces [28].

Copolymer dispersants of high molecular weight have been employed as dispersants to resolve some problems through the molecular designs with multiple anchoring functionalities for interacting with the UMP surface and simultaneously with the involved solvents. The inhomogeneity in geometric shapes of any two nanoparticles may also play an important role for excluding each other from [8]. Recent developments in living/controlled polymerization including nitroxide mediated polymerization (NMP), reversible addition-fragmentation chain transfer (RAFT), and atom transfer radical polymerization (ATRP) have been reported. The copolymers with specific functionalities can be prepared from the monomers with diversified functionalities such as C_1 - C_{12} alkyl(meth)acrylate, amine-functionalized (meth)acrylate, and acid-functionalized (meth)acrylate. In addition, copolymer structures

can be controlled for their molecular weight distribution and are tailored for specific UMP applications [28].

2.1.4. Siloxane dispersant

Siloxane dispersant can make UMP well dispersed in organic binders due to their hydrophilic/ hydrophobic nature. They convert the hydrophilic surface of UMPs into hydrophobic components which make UMPs compatible with hydrophobic organic resins. Siloxane dispersants can be incorporated very easily into liquids and showed an increase of storage stability, as they tend to deposit more slowly. The dispersing extent and flowability of UMP treated with different siloxane dispersants in water medium are excellent. And siloxane also shows better affinity to UMP than ammonium and nonionic polyether [30]. Siloxane with long alkane chain shows great potential to be a new type of high performance dispersant [29].

Moreover, when the pigment powder modified by siloxane dispersant (10%) is added into the water, the treated sample (b) is able to easily be wetted and enter into the water while the untreated one (a) still floats on the water surface. It is obvious that the siloxane dispersant brings good wettability to Pigment Red CI 170.

2.2. Grinding process

It is necessary to de-aggregate and de-agglomerate the UMP particles. This is usually accomplished by mechanical action provided by high impact mill equipment, such as the sand mill and ball mill. As the UMP powder is broken down to individual particles by mechanical shear, higher surface areas are exposed to the vehicle and larger amounts of additives are required to wet out newly formed surfaces.

The grinding process can be regarded as a de-flocculation process. In the absence of stabilizing agents, some changes such as reducing K/S value, decreasing gloss and altering rheology probably occur. Grinding process offers UMP in liquids and is suitable for discrete pass as well as for circulation operation. The product passes through a high energy grinding zone inside a grinding chamber and is reduced to the targeted particle size, down to the nanometer range if required. Using a higher specific weight grinding media is likely to reduce the bead size without losing milling energy by use of equal bead filling volumes. The milling process is improved and an optimum grinding result from both a quality and cost perspective can also be achieved by selecting the best bead material, bead size and mill speed from their dependence on the milling product properties [31].

The mechanical grinding of UMPs with the aid of a dispersant is the most convenient method used to produce UMP particles [1]. But mechanical grinding process inevitably has such defects as the relatively large particle size and broad size distribution. The typical size range for particles and/or aggregates produced by traditional mechanical grinding was from 200 nm to 1000 nm. This process often combines with the utilization of ceramic grinding media for particle size reduction. K. Hayashi et al investigated the dry grinding of UMPs with sili-

ca particles generates core-shell structures with an average size comparable to the parent silica particles (20 nm) [5].

2.3. Ultrasonic wave process

As an environmental and efficient approach, ultrasonic energy was firstly reported to assist various textile processes by Sokolov and Tumansky in 1941 [32]. Sound is transmitted through a medium by inducing vibrational motion of the molecules through which it is travelling. Power ultrasound induces cavitations in liquids, which is the origin of the sound effect in cleaning and in chemical processes [33]. Ultrasound has been widely applied in textiles, for example, preparing nano-scale pigments, fabric pretreatment, dyeing and finishing processes.

Power ultrasound can enhance a wide variety of chemical and physical processes, mainly due to the phenomenon known as cavitation in a liquid medium, which is the growth and explosive collapse of microscopic bubbles. Sudden and explosive collapse of these bubbles can generate hot spots, i.e. local high temperature, high pressure, shock waves, and severe shear force capable of breaking chemical bonds. Dispersion of UMPs involves the application of shear forces to the agglomerates so that they break down into primary particles [34]. If a proper amount of Ultramarine is added to water and stirred briskly, the agglomerates will simply be carried within the flow and hardly change their nature. Ultrafine modified pigment blue FFG was mixed with dispersant and dispersed with an ultrasonic homogenizer for 30 min, and the particle size was reduced to 91 nm from the original size 220 nm [35].

2.4. Microencapsulated process

Encapsulating UMP with various polymers is a promising approach for improving the quality of the UMP dispersion. In the last decade, many techniques have been developed for encapsulating UMP [36]. It must be noted that a successful encapsulation technique should not impair the original color appearance of UMP but enhance their dispersion stabilities. Polymeric resins in encapsulation work basically as an adsorbed surface layer around UMP particles and also a fixing agent upon being colored on a substrate. The microencapsulated UMP supplies dispersion stability, and the surface-modified UMP gives fixing on a hydrophilic body, such as the fiber in textiles [20].

The whole encapsulation process probably divides into four steps below [37]. Organic UMP are dispersed into solution of polymeric dispersant leading to the polymeric dispersant absorbing onto the UMP. The absorption auxiliary is added slowly and the copolymers precipitate and encapsulate onto the UMP surface by van der Waals forces. After the precipitate is filtered and dried, the copolymer is tightly encapsulated onto the UMP surface. The copolymer onto the encapsulated UMP is hydrolyzed, and then the UMP is dispersed uniformly in aqueous media.

Dispersion is controlled by attractive force between the UMP and the hydrophobic part of the polymer, and the stability of the particles is made both by electrostatic repulsive force

between the particles in water and the polymer-polymer entropic effect. The UMP are dispersed in the solid phase, and then the encapsulation and flocculation are presented. Re-dispersion is necessary to separated microcapsules and finally the complete encapsulation in the medium occurs [20]. The main differences between the surface-modified and the microencapsulated UMP are that the hydrophilic moiety on the surface of particles, i.e. the carboxylic groups in the microencapsulated UMP and the sulfonated groups on the surface of the modified UMP, and additionally the existence of a polymer shell only in the microencapsulated UMP [20,36].

2.5. Microfluidics process

Microfluidics with excellent dispersing and smashing effects is in favor of leading particles in liquid to reducing particle size to a submicron level to create pure and stable nano-emulsions and suspensions [38]. With this process, the effectiveness of high-performance materials increases, because particles are more uniformly and stably dispersed. Through microfluidizer high shear fluid processors, the fabrics with UMP easily achieve high K/S value and gloss, and the amount of volatile organic compounds by increasing water content is declined. Microfluidizer high shear fluid processors are frequently used to reduce particle size to less than 150 nm.

For example, Pigment Red CI 22 was stirred with an aqueous solution of an anionic polymeric dispersant for 30 min at 10,000 rpm, and the average particle diameter of the obtained UMP dispersion was 1,500 nm. Whereas, the average particle diameter of 128 nm was available as the dispersion was converted to modified dispersion in a microfluidizer at pressure 22,000 Pa for 2.5 h [13]. Also, a UMP suspension system was prepared by adding the Gemini dispersant and water. Then it was mixed and dissolved and the deformer was added in the mixing process. The Pigment Red CI 22 was added into the above dispersant solution stirring at 600 rpm for 10 min and 9000 rpm for 30 min. The UMP system was treated using a microfluidizer at 172, 368 kPa for 50 min to prepare UMP suspension system. And particle size of the UMPs was the 211.9 nm, the Zeta potential was 32.4 mV and the viscosity was 1.33 Pa•s [16].

2.6. Combined process

It is exceedingly difficult to handle a dry powder comprising of UMP particles as the UMP is in the form of larger soft agglomerates. These agglomerates must be broken down into the medium in a process called dispersion. The UMP dispersion can be stabilized by dispersing agents in order to prevent the formation of uncontrolled flocculates. Combining two or more dispersing methods, for example, grinding/ultrasonic wave, microencapsulation/grinding and dispersant/microfluidizer, the homogeneity of making UMP dispersion along with the use of organic dispersants for viscosity control and the prevention of particle from further agglomeration can be realized [8].

Dispersions are usually prepared by ball grinding a mixture of the pigment, dispersant and solvent. This is a simple combined process in which grinding process is used together with

dispersant. The ultrasonic process can also disperse the UMP and this method can endow a high-throughput approach. The methacrylic copolymer was used to disperse carbon black in water using both ball mill and ultrasonic approaches. The particle size distribution was determined by laser diffraction. After 16 min both ultrasonification and ball grinding achieve the same particle size distribution (Figure 1). The ultrasonic approach could be used to obtain much smaller sample volumes than the ball mill approach [39].

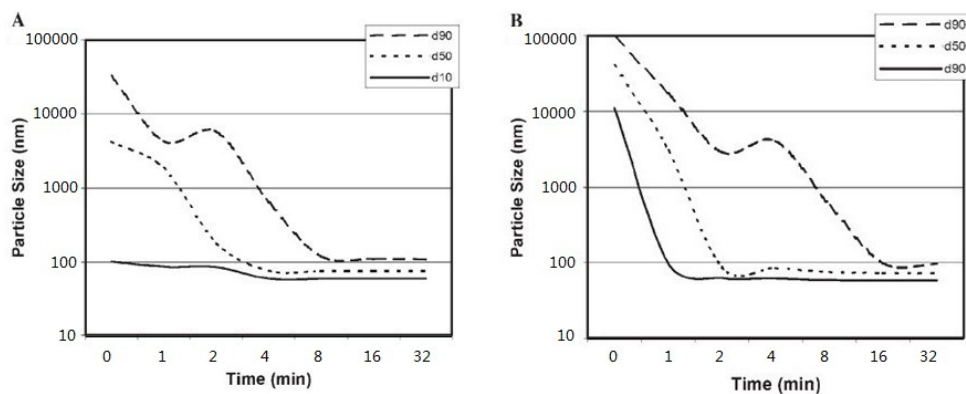


Figure 1. (A) Particle size distribution data from ball grinding; (B) Particle size distribution data from ultrasonication

3. Characterization of UMP

The properties of UMP dispersion can be described by the stability, the adsorbed layer thickness and the Zeta potentials, which are greatly affected by ionic strength, dispersants and dispersing methods. The adsorbed layer thickness and the Zeta potentials can reflect the forces among polymeric dispersants, media, and UMP particles. The characteristics of UMP dispersion affect the applications of the dyed fabric on K/S value, gloss, brightness, and transparency. Some key dispersion characteristics, such as particle size, disperse stability, color properties and Zeta potential properties are investigated as follows.

3.1. Particle size

UMPs are composed of fine particles which are normally in the submicrometer size range. The UMPs particle size has influence on the color, hide and settling characteristics. Large particles usually settle faster than smaller ones. UMP size and its distribution also influence the light scattering, colloidal stability, appearance and the color properties of the dyed fabric. Therefore, an assessment on the degree of dispersion is necessary to be considered in terms of these critical measurements. In general, color properties, such as strength, transparency, gloss and light fastness of all UMP systems, are affected to a greater or lesser extent by the size and distribution of the UMP particles in the dispersion [1].

UMP particle size and its distribution are greatly influenced by the dosage of dispersants. The particle size decreases at first and then increases with the enhancement of the dispersant, and the particle size reaches its minimum when the ratio is about 10% for phase separation method. The smaller the particle size is, the larger the UMP surface is, thus the more amount of dispersant is needed. However, excessive dispersants, higher than 10%, will dissolve in media instead of attaching onto UMP surface, resulting in increasing viscosity of dispersing media and poor wetting performance in that excess dispersants (Figure 2) [30].

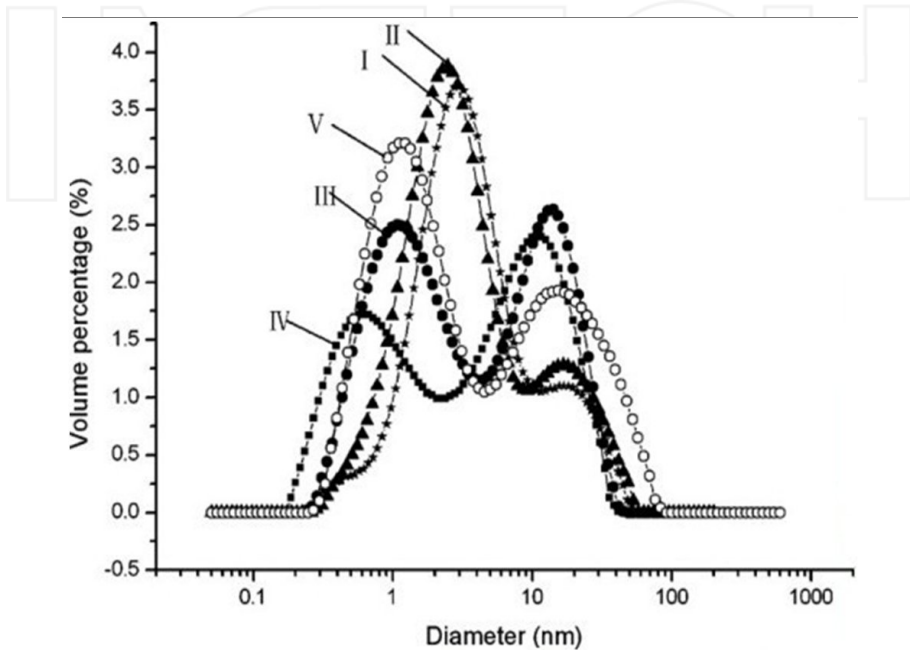


Figure 2. Particle size distribution of treated and untreated pigment red 170. (I) 1wt% pigment, 0 wt% dispersant; (II) 1wt% pigment, 0.01wt% dispersant; (III) 1wt% pigment, 0.02wt% dispersant; (IV) 1wt% pigment, 0.1wt% dispersant; (V) 1wt% pigment, 10wt% dispersant.

The -COOH group of copolymers encapsulated onto the surface of UMPs would form a polymeric shell around the particles and also increase the surface charges of UMP particles. The interaction between UMP particles is weakened due to the existence of these charges and polymeric layer on the UMP particle surface, so that the UMP particles can be finely dispersed in aqueous media [37]. With the dosage of siloxane dispersant descending, the percentage of big particle ascends at first. However, while the dispersant is greatly excessive (10 wt%), the particle size increases.

Initial experiments, using dilute aqueous dispersions of carbon black of known average-particle size distribution, were performed using both a standard UV/Vis spectrometer and a digital camera to estimate light-transmission/attenuance. The results, summarized in Figure 3(A) and

(B), showed a strong relationship between average particle size and light-transmission/attenuance over the size range examined by both these approaches, as demonstrated by the high R^2 values of the polynomial trend-line. Because the limited nature of the particle size distributions obtained during these initial experiments, we were only able to demonstrate a correlation over a small size. The digital image method was developed further on account of its potential to allow parallel analysis of multiple samples from the same image [39].

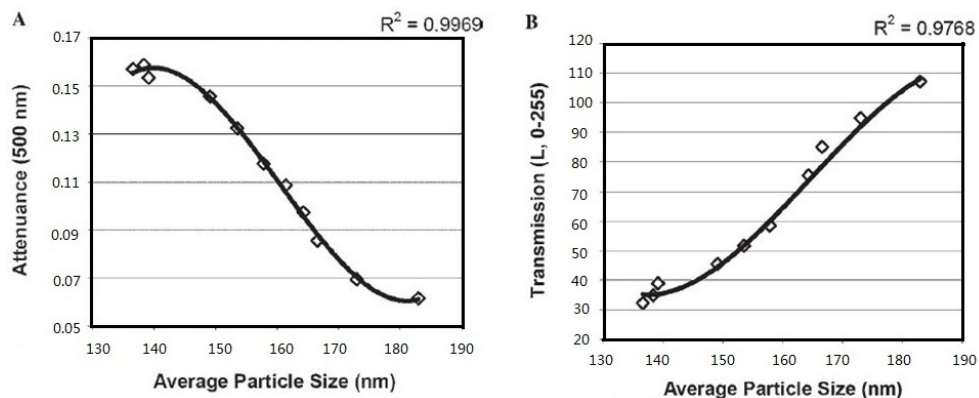


Figure 3. (A) Pigment average particle size versus attenuance (D) using UV/Vis analysis. (B) Pigment average particle size versus light-transmission using image analysis

There was a very interesting phenomenon of the particle size distribution of Pigment Red CI 170 with the increase of the cationic siloxane dispersant. In order to clearly describe the distribution process of UMP in water, an experiment was proposed according to the principle of physical chemistry. UMP could not be well dispersed in water with the absence of dispersant. Then, a small amount of dispersant was added into the system. Since the siloxane group of dispersant showed great affinity to the UMP, it tended to anchor on the surface of UMP particle.

3.2. Disperse stability

Stability of aqueous UMP dispersion is referred to that colloidal properties such as Zeta potentials, viscosity, and storage stability will not change in certain period. It's an important performance of UMP dispersion. Disperse stability can be supported by two generally mechanisms: steric stabilization and charge stabilization. Steric stabilization is due to steric hindrance resulting from the adsorbed dispersing agent, the chains of which become solvated in the liquid medium, thus creating an effective steric barrier that prevents the other particles from approaching too close. Charge stabilization is due to electrical repulsion forces, which are the result of a charged electrical double layer surrounding the particles. The charged electrical double layer developed around the particles extends well into the liquid medium, and since all the particles are surrounded by the same charge (positive or nega-

tive), they repel each other when they come into close proximity. The disperse stability usually includes deposited stability, heat stability, pH stability, electrolyte stability and centrifugal stability [35].

Repulsive and attractive forces among UMP particles determine the stability of the UMP dispersion. When the van der Waals forces between UMP particles are higher than steric and static repulsive forces, the UMP particles will combine each other and generate large particles. Instead, the dispersion will stably exist in aqueous media. In aqueous UMP dispersion, polymeric dispersants encapsulated onto the surface of UMPs are ionized in acid solution, and produce some negative charges onto the surface of UMPs to create the static forces between UMP particles. Further, the PSMA encapsulated onto the surface of UMPs can also generate steric repulsion [27]. The whole steric and static forces are larger than van der Waals force between UMP particles, the dispersion will exist in long time, even under centrifugal force or treated at high temperature. It was reported the effect of Triton X-100 on the colloidal dispersion stability of CuPc-U (unsulfonated and hydrophobic copper phthalocyanine) particles and was concluded that the stabilization mechanism for the CuPc-U is inferred to be primarily steric and adding NaNO_3 had no obvious effect on the dispersion stability [18].

Stabilization of UMP with polymeric dispersants has been proven to be a good way for the preparation of UMP dispersion with high stability, small particles size, low viscosities, and low moisture sensitivity. In aqueous media, the polymeric dispersant can build polymeric shell around the UMP particles and increase the surface charge on the UMP particles, so that the UMP particles are able to finely dispersed in the aqueous media.

3.3. Zeta potential

The Zeta potentials of UMP dispersion are analyzed to estimate their disperse stability. The stability of UMP dispersion determined by forces among the UMP particles. When the repulsive force is higher than attractive force, the UMP particles will stably disperse into the media. Otherwise, the UMP particles will aggregate together. In the UMP dispersion with polymer dispersant, the repulsion forces among particles produced by the adsorbed polymer include static-electronic and steric repulsion [40]. The former can be measured by the Zeta potentials, and the latter is closely connected with the thickness of adsorbed polymer layer. The studies on the change of Zeta potentials and thickness of adsorbed polymer layer after the addition of solvent are important in understanding the effects of solvent on the stability of UMP dispersion [35,41].

The dispersion mechanism may be interpreted with a pair of electricity layers principle. Although many cationic dispersants gathered on the UMP surface neighbourhood, the quiet balance of positive negative charge didn't change. The cation on the UMP surface adsorbed a great many anions. With cation gathering gradually on the UMP surface, a pair of electricity layers formed. The particles stably existed in dispersion system for the electric charge rejected function mutually. An optimum dispersant dosage would exist, which promoted the formation of double electricity layers [16,42].

3.4. Color properties

UMP particles which are dispersed finely in dispersions enhance the color depth of UMP dispersions (e.g. transmittance, chroma, and lightness) and improve color display performance. The transmittances were enhanced with decreasing the mean size of dispersion (Figure 4). A color analysis program estimated the lightness (L^*) and chroma (C^*) from a spectrum of dispersion samples at a wavelength of 380 to 780 nm based on the $L^*a^*b^*$ Color System and D65 light source. The finer sizes of UMP particles in dispersion resulted in the higher lightness (L^*) and chroma (C^*). Serious aggregation of UMP particles without a dispersant in the dispersion would be performed. Holding the supercritical fluid-assisted dispersion process at the supercritical region conduced to better dispersion [43].

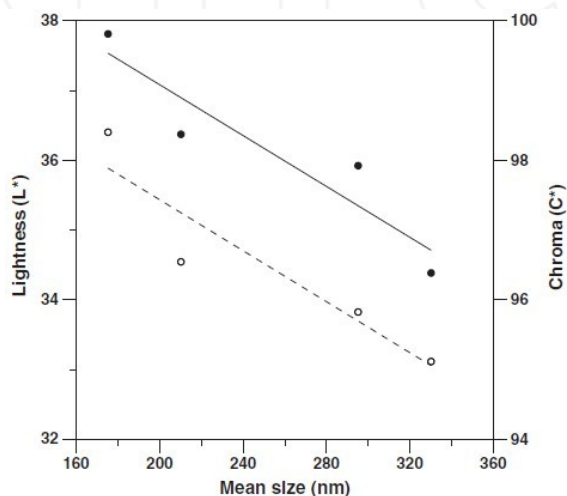


Figure 4. The color analyses from the four representative samples of dispersions. (o), Lightness; (•), chroma

Color properties are presented the color of the UMP dispersion. The absorbance of UMP hydrous dispersion is slightly larger than that of containing organic solvents. The change is mainly attributed to the disparate polarities of the solutions. In these two solutions, while the polarity of solvent UMP dispersion, which contains more ethanol, is weaker. The color of UMP is aroused by the $\pi \rightarrow \pi^*$ energy transition when the chromophore groups are irradiated. The weak ionization of the UMP increases in a solution with high polarity (such as H_2O), and the electric charge in the conjugated system can transport more easily, which leads to an increases in the absorbance. However, the maximum absorption wavelengths for both systems with or without solvent nearly remain the same. This indicates that the chromophore groups of the UMP are not damaged in the UMP dispersion containing organic solvent and the conjugated systems are essentially not altered, therefore, the color hue of the solvent UMP dispersion remains identical to that of the UMP hydrous dispersion [35].

4. Dyeing properties

4.1. Dyeing cotton fabric with UMP

In order to improve the dyeability with UMP, the cationic pretreatment of fabric is used. It can introduce positively charged sites on cotton fabric. Without pigment modification, there are two inhibiting factors. Firstly, pigments are insoluble and have no affinity for cotton and, secondly, the surfaces of pigment particles are usually negatively charged. UMP dyeing has several noticeable advantages compared to dyes. This method is a short process, simple operation, saving energy consumption and low costs, and matching intuitive easy color imitation, steady color hue, hiding power. Because UMP particles have no affinity for fibers, the UMP dyeing fibers does not exist the selective problem and is appropriate for all spices.

There are many reports on cationic modification of cotton. Karrer researched the cationic pretreatment to the cellulose fiber [44]. Guthrie studied the cationic pretreatment of cellulose fiber and dyed it with acidic dye [45]. The chemical modification of cotton to promote dyeability, light fastness and washing fastness has been researched by Cai [12]. Wang investigated chemical modification of cotton to promote fiber dyeability [46]. Burkinshaw analyzed cationic pretreatment of cellulose fiber to improve the dye reactivity [47]. Hauser examined the dyeing behavior of cotton that had been rendered cationic by reaction with 2,3-epoxy propyltrimethylammonium chloride and the result showed that excellent dye yields and color fastness properties were obtained without the use of electrolytes, multiple rinsings or fixation agents [48].

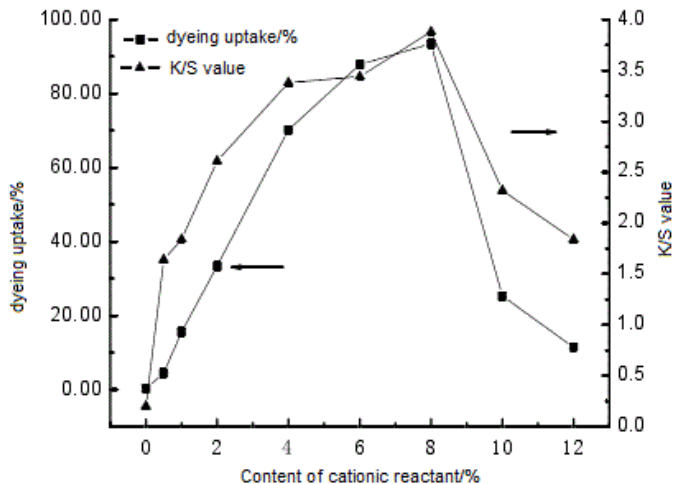


Figure 5. Effect of cationic reactant concentration on pigment exhaustion and the K/S value

During exhaustion dyeing process, the dyeing uptake of cotton fabric without modification was very low. Via cationic reagent modification, the uptake of the cationic fabric was increased significantly. Cationic reagent with higher proportions increased the number of positive charges on the cotton fiber, in turn increased pigment uptake.

For example, the cationic polymerization modifier was used to modify the charge of cotton fiber, and this could enhance the uptake of UMP and K/S value with different cationic reagent concentration (Figure 5). The application of cationic polymerization modifier on fibers for cationic modification could reduce the production cost, reduce dyeing temperature, shorten the dyeing process and improve production efficiency [49].

4.2. Dyeing silk fabric with UMP

Silk is a natural protein fiber, and the shimmering appearance of silk is due to the triangular prism-like structure of the silk fiber, which allows silk cloth to refract incoming light at different. But the silk fiber also has some defects, such as the problem of bleaching, the loss of pupa protein and the yellowing [50,51].

In order to improve the performance of the silk fiber, silk was modified with cationic dispersant [52]. This improved substantivity of UMP due to the introduction of cationic groups into the silk fabric, and the balance might be due to the adsorption of cationic reagent on surface of silk fabric reaching saturation values. In this situation, more cationic reagent molecules combined with UMP. The bounds between UMP and silk fabric led to a higher K/S values. The different amount of the cationic reagent in pretreatment could impart different amount of positive charge to silk surface, which could affect the K/S values. The UMP was not substantive to silk, the K/S values were low on silk without cationization pretreatment. The K/S values greatly increased and then kept in a balance with the increase of the cationization concentration [53].

Furthermore, penetration property and content of ammonium of silk would also restrict to produce the stronger ionic attraction between the cationic fiber and the anionic UMP. As a result, the adsorption of UMP on silk fabric did not change any more accordingly [54]. Wei reported that after modifying with glycidyltrimethylammonium chloride (EPTAC), the reactions of some amino acids were more rapid than the reaction of glucose. The dyeing ability of modified silk fiber had been improved remarkably. A theory which was called "fixed points" was given to this phenomenon [51]. Wang found that pH in pretreatment affected significantly on the dyeing properties of silk fabric with UMP, because in alkali condition, the chlorohydroxypropyl group of 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHTAC) converted to an epoxy group and then formed 2,3-epoxypropyltrimethylammonium chloride which reacted with the nucleophilic amine group in the silk. And The highest K/S values could achieve at pH 8 [53].

With the increase of cationic reagent concentration, the rubbing fastness values appeared increasing trend (Table 1). The washing stain fastness of treated fabric was similarly comparable to the results without fastness improving reagent treatment because the UMP had no affinity with silk without treatment. Compared with untreated silk, the washing change fast-

nesses of cationic silk increased greatly. This was probably due to the fastness improving reagent acting as the binder between UMP and silk fabric [53].

Fastness improving reagent conc. (g/L)	Rubbing fastness (Grade)		Washing fastness (Grade)		
	Dry	Wet	Color change	Stain cotton	Stain silk
0	2	1-2	2	4	4
10	2-3	2	3-4	4-5	4
20	3	3	4	4-5	4
40	3-4	3	4	4-5	4-5
80	4	3-4	4	4-5	4-5

Table 1. Color fastness at different cationic reagent concentration

Cationic pretreatment depended on the extents of reaction between cationic reagent and silk. This might affect the physical properties of the treated fabrics. The tensile strength and elongation at break of fabrics changed with the increase of pH. It was clear that the reaction between cationic reagent and silk took place significantly when pH of the pretreatment solution increased. The tensile strength decreased with the peptide chain hydrolyzation when the pH increased. Also the elongation at break kept slightly decreasing. This revealed that the cationic pretreatment has little effect on the physical properties. The bending rigidity and hysteresis of cationization silk had no change compared with untreated silk. It revealed that the cationization treatment had no impact on the soft properties of fabrics. The handle of fabric decreased a little after dyeing, it might be due to the action of fastness improving reagent.

4.3. Dyeing wool fabric with UMP

The wool fabric was modified by cationic reagent and dyed with UMP which was prepared with anionic polymer disperser via exhaust method [55]. The influence of pretreatment conditions such as concentration of cationic reagent, pH value of the bath, temperature and duration of treatment on the dyeing property of the fabric was of importance to the drying properties. With the increase of the cationic content, the K/S value enhanced sharply and then kept a constant value when the content on cationic reagent was higher than 10% (Figure 6). The dry and wet rubbing fastness of the wool fabric dyed with UMP via exhaustion was gray scale ratings of 3-4 and 4, respectively. The tensile strength and elongation at break decreased slightly with the increase of bath pH value. The test results of bending rigidity and hysteresis of bending revealed that the wool fabric had soft handle and good elasticity.

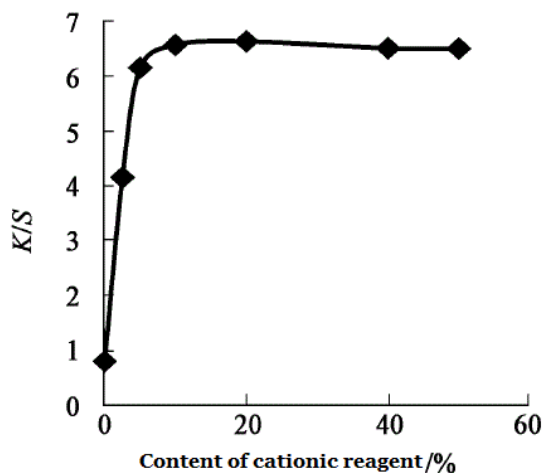


Figure 6. The contents of cationic reagent on the K/S value of dyed fabric

4.4. Dyeing cotton fabric with carbon black UMP

The excellent color and fastness properties make carbon black (CB) particles possible application in textile dyeing. Compared with common sulfur dye, the dyeing process of carbon black UMP can save water and energy due to the shorter dyeing time. However, the dispersion of carbon black UMP in aqueous solutions and adsorption of the particles to cotton fibers are critical in exhaustion dyeing process, because carbon black UMP is hydrophobic and easily aggregate in aqueous solutions.

On the basis of cotton fabrics modified with cationic reagent, the dyeing process and properties of CB dispersions were reviewed (Figure 7). The mechanism of cationic cotton dyed by an exhaustion process using aqueous carbon black UMP dispersions was investigated. Cotton modified with a cationic reagent enhanced the dyeing properties of aqueous carbon black UMP dispersions. There were higher affinity between carbon black UMP and cationic cotton. CB particles could quickly adsorb on the surface of cationic cotton fibers within 5 min and diffuse into the inner pores and cracks on the surface layer of cationic cotton step by step [56]. The cross sections of cationic-modified cotton fibers dyed with different sizes of CB particles were colorless region, and CB particles were only in the cotton fiber grooves, just as “ring-dyeing”. After cationic modification, the cotton fiber could have a dark color for the adsorbability of the anionic CB [13].

The color assessment of CB dyed cellulose is correlative to the amount carbon black UMPs on the cotton via electrostatic force. It made possible to compare the charge density difference between nanoparticle ionic materials (NIMs) deposition process and chemical modified process.

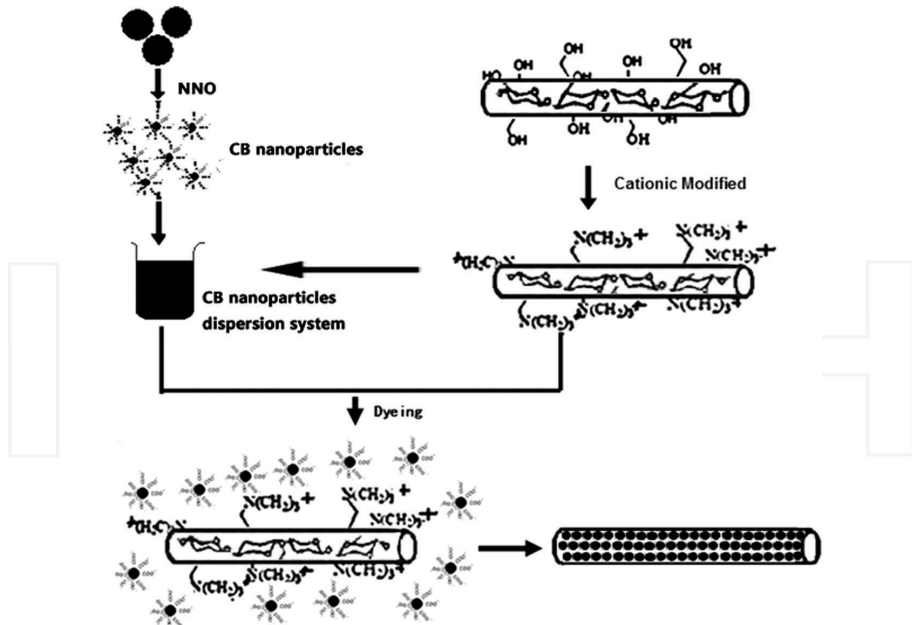


Figure 7. The dyeing process of carbon black UMP on modified cotton fabric

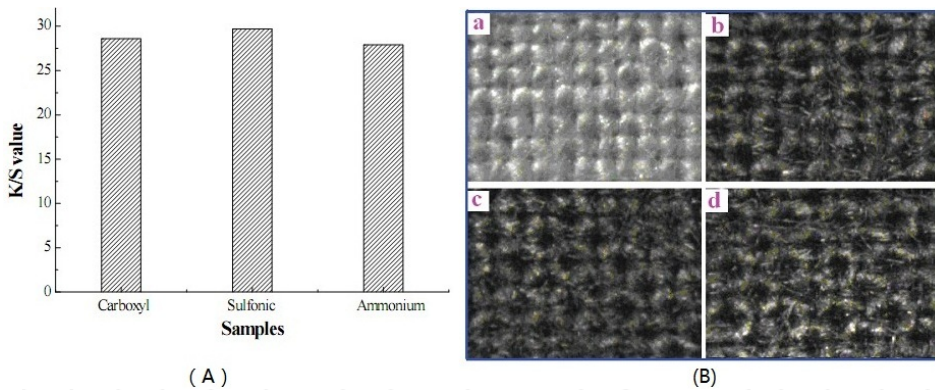


Figure 8. Color assessment of CB dyed cellulose matrices: (A)K/S values; (B) Video microscope microscope:(a) Cotton fabrics without modification, (b) Carboxyl modified cotton fabric deposited with positive NIMs and carbon black UMPs, (c) Sulfonated modified cotton fabric deposited with positive NIMs and carbon black UMPs, (d) Ammonium modified cotton fabric deposited with carbon black UMPs

The results of the K/S presented that the sulfonated cellulose had the higher K/S value of 29.7 than the carboxyl of 28.6 and aminocellulose of 27.9 (Figure 8(A)). The results proved the conclusion about the color depth of the decorated samples. The images (Figure 8(B)) of

the samples before and after the dyeing showed that the color depths of the dyed carboxyl and ammonium fabrics were not as deep as the sulfonated cellulose fabric, which further confirmed the color depth conclusion. Especially for the image of the ammonium sample, the fabric surface was uncoated with carbon black UMP, and there were some star-shaped white flakes on the fabric.

4.5. Dyeing cotton fabric with cationic UMP

Surface treatments are effective for UMP because its surface contains polar or polarized functional groups, which can serve as adsorption sites for the hydrophilic or lipophilic groups of the surfactants [1]. The cationic UMP dispersion has great prospects in cellulose dyeing, ink-jet printing, and so on. Compared with the anionic and non-ionic UMP, the cationic UMP has a stronger combining force with the cellulose substrate, a better K/S value, and vividness, thus it can increase the uptake of the UMP, reduce the environmental pollution, and improve the quality of final products.

For the specific structure, there are a lot of characteristics on Gemini cationic dispersant. The Zeta potential of the Gemini cationic UMP is higher than that of the ordinary cationic UMP. Therefore, it is easier to color. The dry and wet rubbing fastness is good with both Gemini cationic UMPs after film fixation (Table 2). With the dispersant dodecyltrimethylammonium, the dyeing of Gemini cationic UMPs exhibits deeper K/S values and the fabric is easier to be colored. The adsorption capacity of the Gemini cationic UMPs to cotton fabric is stronger, and can cover more fiber surface. Cotton fabric shows negative in a water solution, which has a weak charge bonding force with cationic UMPs. The more cationic UMPs containing electropositive, the easier the cotton fabric adsorbs the UMPs [16].

Sample	K/S value	Dye rubbing fastness	Wet rubbing fastness
Traditional pigment	42.64	3-4	2
UMP	51.99	4	2

Table 2. K/S value and fastness of Gemini cationic UMP dispersion on cotton

4.6. Dyeing acrylic yarns with cationic UMP

Acrylic fibers can be dyed by cationic UMPs, and the electrostatic attraction between UMPs and acrylic fibers is beneficial to the dyeing properties, especially its light fastness property. Compared with anionic and nonionic UMP systems, the cationic UMPs could bond with the acrylic fibers by electrostatic attraction. Therefore, the UMP presented a better dyeing result and a higher utilization ratio [57].

The dye bath pH presented great influences on cationic UMP dispersion stability during dyeing acrylic fiber with cationic UMP. The increase of UMP dosage resulted in lower dye uptake and more brilliant colors, and dyeing acrylic yarns with UMP (40%, o.w.f) could reach the maximum K/S value. The K/S value of acrylic yarns reduced after adding adhesives, compared to the cationic dyes, the light fastness was improved significantly [58].

From Figure 9, when the temperature was lower than 65 °C, the dyeing rate was quite low, and the adsorption of pigments was unstable, while the temperature was higher than 65 °C, the dyeing rate increased significantly with the dyeing time prolonging. A higher dyeing temperature would shorten the dyeing time. As the temperature was higher than 95 °C, the dyeing time was only 15 min. The reason was that in a low temperature condition, the acrylic molecular chains were not moving and the adsorption only took place in the surface of fiber. The pigments adsorbed to the yarns were easily re-dissolved into the dye bath.

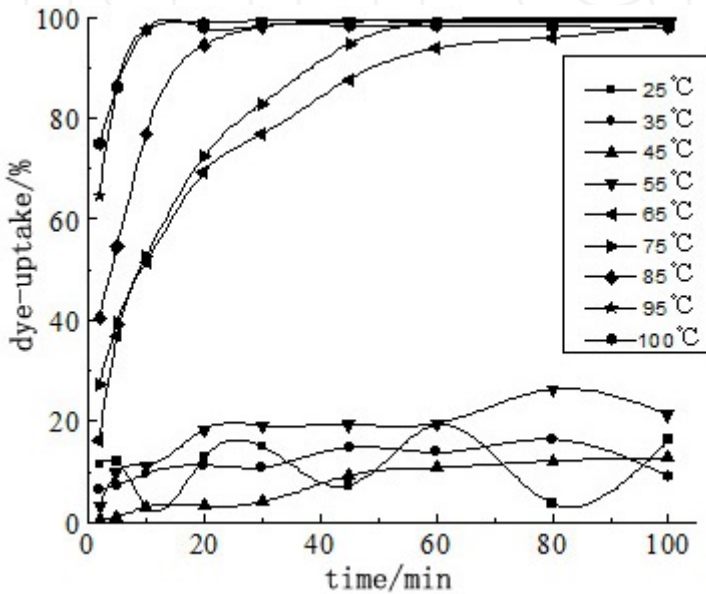


Figure 9. Effects of dyeing temperature on dye-uptake of acrylic yarns

In order to evaluate the light fastness of acrylic yarns dyed by cationic dye, the light fastness of cationic dye is attempted and assessed (Figure 10).

Cationic UMP presented better light fastness than that of the cationic dye. Acrylic yarns dyed by cationic UMP presented higher stability to light than that dyed by cationic dye. The main reason was that the chromophoric group of pigment was more difficult to destroy for its stable chemical structure.

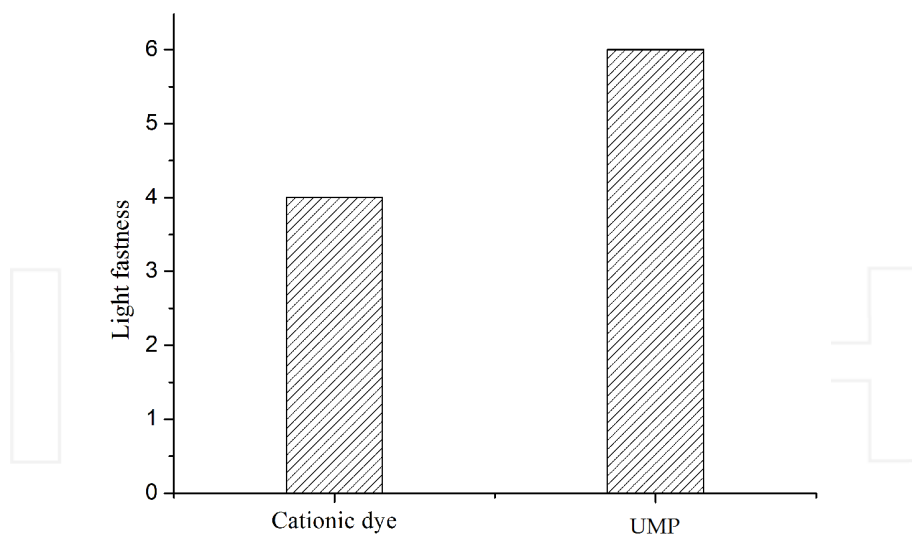


Figure 11. Light fastness of acrylic yarns dyed by cationic dye and ultra-fine pigment

5. Conclusion

A stable UMP dispersion is able to be prepared via grinding, ultrasonic wave, microencapsulation and microfluidics processes with different dispersants like low molecular weight dispersant, polymeric dispersant, copolymer dispersant and siloxane dispersant. It's more efficient to prepare the uniform and stable UMP dispersion via comprehensive utilization of these dispersing processes.

The key dispersion characteristics of UMP dispersion be evaluated by particle size, disperse stability, Zeta potential, color properties and dyeing properties, which are greatly affected by ionic strength, dispersants and dispersing methods. The disperse stability and color performance are promoted with the smaller particle size and higher charged UMP.

The dyeing properties of UMP on many fabrics such as cotton, silk and wool pretreated with cationic reagent is enhanced. The K/S value and rubbing fastness are able to be distinctly improved. Cationic cotton can also enhance the dyeing properties of aqueous carbon black UMP dispersions due to the higher affinity between carbon black UMP and cationic cotton. The cotton fabric dyed with cationic UMP can also promote the K/S value and color fastness. For acrylic yarns, the increase of UMP dosage results in lower dye-uptakes and more brilliant colors, and dyeing with UMP (40%, o.w.f) can reach the maximum K/S value on acrylic yarns.

As an advanced pigment dyeing method, the UMP takes many advantages of pigment. The specific characteristics of the UMP, including stability and high K/S value, reveal its signifi-

cant potential on fabric dyeing, and especially for its environment-friendly characteristics, the development of UMP will present a more sharply speed than that of the dyes. Base on the textile application, the further research interests about UMP are focus on the novel dispersing process to obtain stable UMP system, modification with functional organic or inorganic materials, developing the multifunction and multipurpose of UMP.

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