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Original Research Paper

Utilizing cellulase as dispersant to prepare stable nano-pigment suspension and investigating its coloring performance on cotton fabrics

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ABSTRACT

In this research, a novel nano-pigment suspension was successfully prepared in an ultrasonic disruptor using crude cellulase as dispersant. The colloidal and rheological properties of this cellulase-based suspension such as zeta potentials, particle distribution and apparent viscosity were analyzed. The measurement of zeta potentials showed that the surface charges of pigment were adjustable along with the acid–base properties of external environment due to the amphoteric character of cellulase proteins. Subsequently, its stability to high-speed centrifuge, freeze–thaw treatment and ion intensity was carefully investigated. Thermo-gravimetric analysis (TGA) was conducted to demonstrate the coverage of pigment particles by cellulase proteins. Furthermore, X-ray diffraction (XRD) characterization was utilized to disclose the combined impacts of cellulase and ultrasonic power on the crystal structures of pigment. At last, the coloring performance of this charge-adjustable nano-pigment suspension on cotton substrates was evaluated by measuring their *K*/*S* values and color fastness. Scanning Electron Microscope (SEM) was carried out to give a direct observation of the nano-pigment distributed on cotton surfaces.

1. Introduction

Organic pigments have been widely used as colorants in the coatings, inks, plastics and textile industry since they possess many favorable advantages such as high light stability, color strength, weather fastness and brilliance [1,2]. During manufacturing, primary pigment particles would easily form aggregates of a few hundred nanometers through collisions in the reaction apparatus and further produce 2–5 μm size of agglomerates by weak bonding among aggregates [3]. Presence of these aggregates or agglomerates will undoubtedly go against the pigment utilization in many cases. For industrial applications, a pigment-vehicle system in which pigment particles are finely and stably separated is considered a good dispersion because particle size and stability are key factors in determining their physicochemical properties [4]. Recently, nano-pigment suspension, especially the waterborne nano-pigment, has drawn a lot of attentions in textile industry due to its excellent ecological and coloring performance [5–10].

Generally, nano-pigment suspension is classified as a colloidal system because its particle size lies in the submicron region [11]. To fabricate a nano-pigment suspension, three stages including wetting, mechanical disintegration and stabilization are usually involved. In wetting, clusters of pigment particles are wetted by propriety liquid to replace the adsorbed air on the hydrophobic pigment surface. Subsequently, the wetted pigments are dispersed into smaller clusters by the mechanical forces from ball grinder, high-pressure homogenizer or ultrasonic disruptor [12,13]. The main purpose of this procedure is to utilize external forces to smash pigment aggregates, reducing the particle size as much as possible [14]. It is important to note that smaller pigment particles will readily reagglomerate due to their larger specific surface area, higher superficial free energy and hydrophobic interaction. Therefore, single pigment particle must strongly interact with appropriate surfactant or dispersant in the dispersion medium to stabilize the suspension system [11].

Once adsorbed onto the pigment surfaces, these surfactant or dispersant molecules will provide enough electrostatic or steric hindrances to overcome attractive forces acting among the pigment particles [15–19]. Surfactant-based pigment suspensions are usually suffered from the low stability for long-term storage. By contrast, polymeric dispersants are more widely employed in

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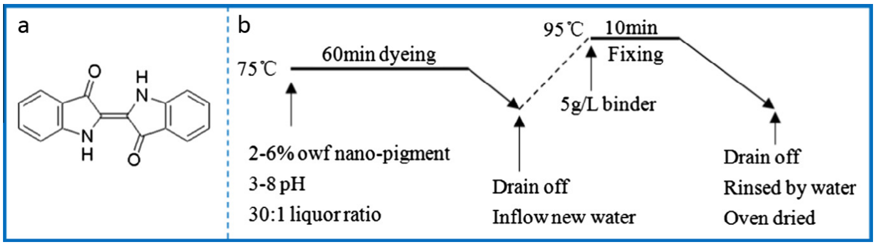

Fig. 1. (a) Molecular structure of indigo pigment and (b) coloring procedure for nano-pigment suspensions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

aqueous pigment system because they usually assume a flat conformation and are easily adsorbed onto the pigment surface to fabricate a protective polymeric shell for the bare particles. A lot of homopolymerized or copolymerized dispersants with various chemical natures and architectures have been synthesized and employed for acquiring good nano-pigment dispersions [20,21]. Some intricately structured polymeric dispersants such as diblock, triblock, graft and star-like polymers have also been successfully designed and applied in aqueous pigment suspensions [22].

Besides, some proteins such as collagen, polypeptide, casein and albumin have previously been employed as dispersants for inorganic or organic pigment materials [23–28]. Sano and Shiba have found that the hexapetide motif, RKLPDA, can disperse the titanium dioxide well and bring active biological functions to its surface [27]. Garris and Sikes have designed a triblock protein and well explored its potential as a high-quality dispersant for organic pigment [24]. However, in the textile coloring industry, few works involving the protein-based dispersants have been carried out.

Cellulase is the most widely used protein in the textile industry because cellulase treatment is an eco-friendly way to improve the properties of cellulosic fabrics without excessive damages [29–36]. In enzymatic process, delicate and proper three-dimensional structures are required for cellulase to promote its hydrolysis capability. It is reported that cellulase protein demonstrates a unique and inherent colloidal property similar with dispersants because the hydrophobic and hydrophilic sections in cellulase molecules are totally separately [37]. Therefore, the cellulase protein can bind the organic pigment by virtue of its hydrophobicity and, at the same time, stabilize the pigment particles via its hydrophilicity [37,38]. However, the delicate dispersion performance and coloring characteristics of this pigment–cellulase complex have not been investigated further in the previous literatures.

In this paper, cellulase proteins from *Trichoderma reesei* were utilized as a potential dispersant to prepare aqueous nano-pigment suspensions using an ultrasonic grinding device. During the process, cellulase proteins will gradually be bound onto the pigment surface and function as a biological dispersant to create a perfect solid suspension. As a result, the bound cellulase proteins can provide sufficient repulsive forces to conquer the attractive forces among pigment particles. The colloidal characteristics of this cellulase-based suspension such as the particle size, zeta potential, apparent viscosity and stability will be carefully investigated. Moreover, the coloring performance of as-prepared pigment suspension on cotton substrate in terms of pigment uptake, color depth and fastness will be detailedly evaluated. To the best of our knowledge, no similar research has been reported before.

2. Experimental

2.1. Materials

A total cellulase (100 mg ml^{-1} protein content) from *T. reesei* without chemical additives was provided by Haiyi Chemicals Company of China. Indigo pigment (C.I. 73000, structure shown in Fig. 1a) was purchased from Zhicheng Chemicals Company of China and used without further purification. Scoured and bleached pure cotton knit fabrics (150 g/m^2) were generously offered by Sunvim Textile Groups of China. Binder PSA (copolymer of styrene and butyl acrylate, Mn: 85,000) was kindly provided by Haiyi Chemicals Company of China. All other chemical agents in this research were A.R. grade. Deionized water was used throughout the experiment.

2.2. Preparation of nano-pigment suspensions using an ultrasonic grinding device

For 50 ml suspensions, indigo pigment (5 g) was separately weighed into different 100 ml glass beakers containing 45 ml of cellulase solutions (protein content ranging from 0.5 to 4 mg ml^{-1}). The mixtures were immediately homogenized for 15 min using an ultrasonic cleaner at a frequency of 59 kHz and output power of 60 W. Subsequently, the resultants were further treated by a more powerful ultrasonic grinding device for 60 min at a frequency of 25 kHz and output power of 600 W to prepare nano-pigment suspensions.

2.3. The coloring procedure of nano-pigment suspensions on cotton substrates

The coloring procedure of nano-pigment was described in Fig. 1 (b). Cotton samples (10 g) were colored in nano-pigment baths (2–6% o.w.f nano-pigment) with a liquor ratio 1:30 at different pH values (3–8) for 60 min under 75 °C. After coloring, the fabrics were taken out and fixed in the solutions containing 5 g/L binder at 95 °C for 10 min with a liquor ratio 1:30. Finally, the samples were dried in a 100 °C oven.

2.4. Characterizations of nano-pigment suspensions

2.4.1. Particle size and zeta potentials

The nano-pigment dispersions were diluted by 2000 times using distilled water and poured into different vials. Subsequently, different amounts of 0.1 mol/l HCl or NaOH solutions were added into the samples to set the pH values from 3 to 8. The prepared samples were respectively put into a Malvern Nano-ZS Zetasizer at 25 °C for the measurement of their particle sizes by dynamic light scattering (DLS) and zeta potentials by electrophoretic mobility. The measurements were conducted with a fixed angle of 90°. Particle size was calculated by the translational diffusion coefficient (D) in terms of the Stokes–Einstein equation. The measured electrophoretic mobility (U) was converted into Zeta potentials according to Smoluchowski's equation. All the samples were measured 5 times to ensure the reproducibility and the average results were quoted.