Industrial Crops and Products xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

The modification of cotton substrate using chitosan for improving its dyeability towards anionic microencapsulated nano-pigment particles

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ARTICLE INFO

Article history:
Received 25 August 2016
Received in revised form 7 October 2016
Accepted 23 October 2016
Available online xxx

Keywords:
Cotton
Chitosan
Dyeability
Anionic microencapsulated nano-pigment

ABSTRACT

The cotton samples were treated by chitosan solution at acidic condition to modify their dyeing properties to anionic coloring materials. By fluorescence spectrum together with FTIR, XRD and TGA analysis, it was concluded that the chitosan molecules could spontaneous transfer from solution onto cotton surface yet would not influence its internal structure. In order to color the chitosan-treated cotton, an anionic polystyrene-encapsulated copper phthalocyanine (CuPc) pigment was prepared in a miniemulsion process. The full encapsulation of nano-pigment could be directly observed by TEM. The encapsulation would not alter the crystal structure and color properties of CuPc while could make the nano-pigment more stable against centrifuge and temperature variation. Finally, the dyeing properties of this encapsulated nano-pigment on chitosan-treated cotton samples were studied. It was indicated the chitosan molecules on cotton had great capability to improve the uptake of encapsulated nano-pigment mainly due to the accessible amino groups introduced.

1. Introduction

Cotton is an abundant natural vegetable fiber consisting of about 88–96% cellulose in its secondary cell wall (Rattanaphani et al., 2007). Industrially, cotton can be colored by various soluble dyes (Adeel et al., 2015; Khan et al., 2014; Pisitsak et al., 2016; Ticha et al., 2013) or insoluble organic pigments (Hao et al., 2016a, 2012a, 2012c; Hao et al., 2016b). Currently, the waterborne nano-pigment system has been widely used in textile industry due to its easy application, high dyeing efficiency, excellent light fastness and environmentally friendly aspects (Fang et al., 2005; Fu et al., 2010, 2013; Fu and Fang, 2008; Hao et al., 2011).

Anionic nano-pigment system is commonly used because it can provide greater electrostatic repulsion to overcome attractive forces acting among pigment particles. The encapsulation of nano-pigment by some polymers can further protect it from unwished environmental influences such as UV radiation or pH alteration. Miniemulsion method can be utilized for encapsulating the water-insoluble pigment in aqueous phase because this strategy presents some advantages such as better control of droplet size and higher encapsulation efficiencies (Landfester, 2009). Steiert and Landfester (2007) successfully encapsulated anionic pigment particles with different monomers including styrene, various acrylate or their mixtures and produced hybrid structures using a miniemulsion method. They confirmed this hybrid structure had lower densities compared to pure pigment resulting in better sedimentation and storage stability. Employing a polymerizable anionic surfactant, also fabricated a polystyrene-encapsulated pigment dispersion via the miniemulsion technique. They found the polymer-encapsulated pigment exhibited good stabilities because the attractive forces between the polymer and pigment surface were strong enough to resist the damages from temperature variation and centrifugal forces.

Cotton is naturally electronegative in the aqueous medium due to the presence of hydrophilic carboxylic groups from marginally oxidation and hydroxyl in its molecular chains (Ripoll et al., 2012). Cotton fibers have a constant negative zeta potential with an IEP = 2.8 and around −15 mV plateau at pH 9 (Bellmann et al., 2005). Therefore, when employing the anionic dyes or pigments for coloring, the negative charges on cotton surface would lead to inefficient exhaustion. Physical method such as gamma irradiation can be selected for tuning the surface of cotton to get high color strength (Adeel et al., 2015, 2017; Bhatti et al., 2016; Gulzar et al., 2015). Chemical approaches can also be used to modify the cotton surface for increasing its affinity to anionic colorants. Among various

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http://dx.doi.org/10.1016/j.indcrop.2016.10.043
0926-6690/

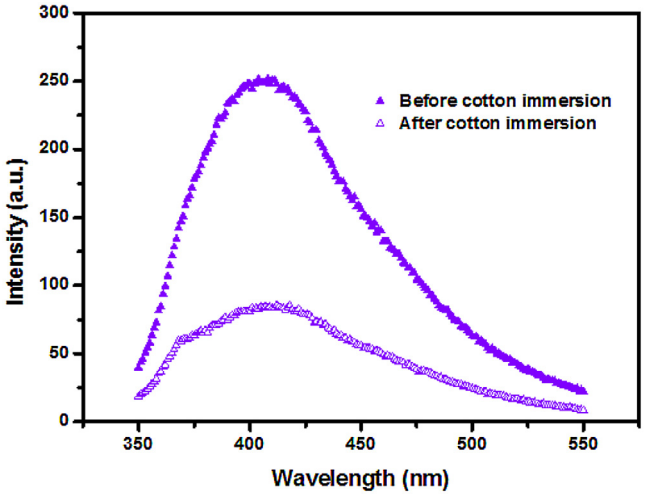

Fig. 1. The emission spectra of chitosan solution (2 g/l, pH = 4) before and after cotton immersion.

available chemicals, the polysaccharide chitosan is highly recommendable since it shows unique chemical and biological properties and is easily available for industrial purposes.

Chitosan is commercially produced by deacetylation of chitin in the shells of crustaceans such as shrimp, crab and lobster. Structurally, chitosan is a linear polysaccharide composed of randomly distributed β-(1–4)-linked D-glucosamine and N-acetyl-D-glucosamine (Bashar and Khan, 2013; Beyki et al., 2014; Lin et al., 2015). This biodegradable polysaccharide contains hydroxyl, amino groups as well as ether linkages in its chemical structure and has unique physiological properties (Aranaz et al., 2016; Croce et al., 2016; Gupta and Haile, 2007; Li et al., 2016; Wijesena et al., 2015). The polycationic nature makes chitosan very attractive as a surface modifier for cellulosic substrate to improve its dyeability to anionic dyes (Naebe et al., 2016). Bandyopadhyay et al. (1998) applied chitosan to cationize cotton fabrics by padding method. They found the chitosan-treated fabric showed improvement in both exhaustion and fixation of reactive dyes. Kitkulnumchai et al. (2008) modified the surface of cellulose fabrics with chitosan before dyeing with mono-chloro-triazine and vinyl sulfone reactive dyes. They confirmed this method brought about an improved dyeing process in which the dye and salt consumed could be reduced by half and 14%, respectively. Therefore, it is reasonable to hypothesize that chitosan on cotton surface could also have the ability to enhance its attractive forces to anionic encapsulated nano-pigment and thus improve its uptake and final coloring depth. However, there is very few, if any, relevant research has been reported.

In this research, a stable anionic polystyrene-encapsulated nano-pigment dispersion was prepared using sodium dodecyl sulfate (SDS) as dispersant based on a miniemulsion technique. The colloidal properties and stability of this encapsulated particle system would be carefully analyzed. For investigating its coloring performance, cellulosic cotton would be modified by chitosan solutions with different concentrations for altering its surface properties. Finally, the coloring properties of anionic encapsulated nano-pigment on it would be detected and analyzed in detail under various dyeing conditions.

2. Experimental

2.1. Materials

Pure cotton knit fabrics (plain single jersey, 24tex yarn, 150 g/m^2, white) were offered by Furi Textile Factory, China. To thoroughly remove non-cellulosic impurities, the cotton fabrics were subjected to conventional alkaline scouring and bleaching procedures using sodium carbonate and hydrogen peroxide, respectively. Then, these fabrics were treated with 0.1M HCl at room temperature for 10 min and further rinsed within 98 °Cdeionized water for 10 min. Finally, they were washed with deionized water until the rinsed water neutral to eliminate any residual chemicals and dried in air for further use. Chitosan powder with the molecular weight of 100,000 and the deacetylation degree of 85% was purchased from Zhejiang Golden-Shell Biochemical Co. Ltd. Phthalocyanine blue Pigment (CuPc, C.I. 74160, CAS 147-14-8) and sodium dodecyl sulfonate (SDS, CAS 151-21-3) was also purchased from Aladdin Chemical Company and directly used without further purification.

2.2. Cotton modification by chitosan

A 2% (w/v) stock solution of chitosan was prepared by dissolving the required amount of chitosan powder in a 1% (v/v) aqueous acetic acid solution. Cotton samples (3 g per piece) were submerged in 90 ml solutions (pH = 4) containing different amounts of chitosan for 30 min at 50 °C. And then, the samples were separately padded in a laboratory padder between two squeezing roller at a speed of 2m/min to reach an average 80% wet pick-up. The padded ones were dried at 80 °C for 5 min and then cured at 150 °C for 5 min to fix the chitosan. Finally, the cured samples were rinsed in 50 °C deionized water for 10 min to leave irreversibly deposited chitosan on cotton surface, dried in open air and placed in a dessicator till further use.

2.3. The preparation of encapsulated nano-pigment dispersion

The anionic nano-pigment dispersion was fabricated by adding 5 g CuPc pigment to a solution of 0.5 g SDS in 44.5 g deionized water and immediately stirring the mixture at 2000 rpm for 2 h. Afterwards, it was homogenized by a mechanical disperser at 20,000 rpm for 15 min and finally sonicated by an ultrasonic disintegrator for 90 min at 20KHz and 600 w amplitude. The entire sonication process was done with 2 s pulse on and 2 s pulse off cycles under ice-cooling using a 6 mm amplitude transformer.

For preparing the miniemulsion, an oil phase consisting of 1.5 g styrene, 60 mg hexadecane and 30 mg oil-soluble initiator 2, 2-azobisisobutyronitrile (AIBN) was mixed into a solution of 120 mg SDS in 10 g water. A powerful agitation at 1000 rpm for 1 h was conducted as pre-emulsification and the ultimate miniemulsion was got after 3 min sonication at 400w. The resultant miniemulsion was added into the above fabricated nano-pigment suspension, stirred at 1500 rpm for 30 min, and sonicated for 10 min at 400 w to get a full blending. Heating process was started to improve the mixture temperature to 76 °C for initiating the polymerization process and finished after a 12 h isothermal duration at this temperature. For obtaining a complete polymerization the reaction process was protected at nitrogen atmosphere and the gas room of the reaction flask was minimized. The blank nano-pigment dispersion was also prepared as the above methods but not any monomer, initiator, hexadecane were added.

2.4. The coloring procedure of cotton substrates

Using a laboratory dyeing machine with temperature control unit, the original and chitosan-modified cotton samples were separately dyed in different shaking baths containing encapsulated nano-pigment (4%, owf) at the water/fabric weight ratio of 30:1. All samples were immersed into the dye baths at room temperature and the temperature was then raised to 60 °Cand held for 60 min. The amount of nano-pigment in baths was monitored by a UV–vis

Please cite this article in press as: Hao, L., et al., The modification of cotton substrate using chitosan for improving its dyeability towards anionic microencapsulated nano-pigment particles. Ind. Crops Prod. (2016), http://dx.doi.org/10.1016/j.indcrop.2016.10.043