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Utilization of biopolymer in resist printing of linen fabrics using reactive dyes

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ABSTRACT

A novel utilization of chitosan as a cationic biopolymer in the chemical resist printing of linen fabrics and its polyester blend using reactive dyes. The effects of ratio and concentration of various resist-printing agents and processing conditions are observed and discussed. The concentration of chitosan, type of resist agent, and the ratio of chitosan to resist agent were varied to determine their effects on the efficiency of resist-printing. Regardless of the type of fabric, the resist effect on printed fabrics expressed as % decrease in *K*/*S* was obtained at optimal chitosan concentration of 1% with a mixture of chitosan/maleic acid as a resist salt at a ratio of 25:75. Thus, chitosan can be used pure or in admixture with different resist salts successfully in chemical resist printing.

1. Introduction

Chitosan is a cationic natural carbohydrate biopolymer prepared by partial N-deacetylation of chitin (Kurita, 1998). It comprises copolymers of glucosamine and N-acetyl glucosamine (Ilium, 1998). The primary unit in chitin polymeric chain is 2-deoxy-2-(acetylamino) glucose. These units are combined through (l, 4) glycosidic linkages, forming a long linear polymer chain. Chitosan dissolves in most weakly acidic solutions, including formic, acetic, tartaric, and citric acid, at pH < 6.5. The D-glucosamine unit has a pK_a value of 7.5 (Hoppe Seiler, 1994; Roberts, 1992).

At low pH, chitosan is present as a cationic polymer, with a high charge density, and therefore may function as a good flocculent for negatively charged polymers. The oppositely charged polyelectrolyte interacts rapidly with chitosan in solution to form an insoluble precipitate (Bayomi, 2003).

Thus, chitosan has been studied as partner of several intermolecular complexes (IMC) with natural or synthetic anionic polyelectrolytes, such as: chondroitin sulphate (Denuziere, Ferrier, Damour, & Domard, 1998; Mi et al., 2006), poly(acrylic) acid (Davidenko, Peniche, Díaz, San Roman, & Sastre, 2007; Peniche & Argüelles-Monal, 2001; Peniche et al., 1999; Pérez-Gramatges, Argüelles-Monal, & Peniche-Covas, 1996; Wang, Li, Lu, Wang, & Zhong, 1996), poly (galacturonic) acid (Argüelles-Monal, Cabrera, Peniche, & Rinaudo, 2000; Peniche & Argüelles-Monal, 2001), sodium alginate (Mitrevej, Sinchaipanid, Rungvejhavuttivittaya, & Kositchaiyong, 2001; Peniche & Argüelles-Monal, 2001), K-carageenan (Peniche & Argüelles-Monal, 2001). Chitosan complexation with carboxymethylated polysaccharides, such as carboxymethyl cellulose or carboxymethyldextrin has been also studied (Argüelles-Monal, Gárciga, & Peniche-Covas, 1990; Argüelles-Monal & Peniche-Covas, 1988; Kaihara, Suzuki, & Fujimoto, 2011; Peniche & Argüelles-Monal, 2001; Rosca, Popa, Lisa, & Chitanu, 2005), and this principle has been used for the production of chitosan beads and microspheres.

Carboxymethylcellulose (CMC) is another anionic polysaccharide, a cellulose derivative obtained by its reaction with alkali and chloroacetic acid as follows (Cheng & Biswas, 2011; Ragheb, Nassar, Abd El-Thalouth, Ibrahim, & Shahin, 2012; Toğrul & Arslan, 2003; Varshney et al., 2006):

$$\text{Cell·OH} + \text{NaOH} \rightarrow \text{Cell·ONa(alkalicellulose)}$$

$$\text{Cell·ONa} + \text{ClCH}_2\text{COOH} \rightarrow \text{Cell·O·CH}_2\text{COONa} + \text{NaCl}$$

The CMC structure is composed of β-(1 → 4)-D-glucopyranose units similar to those of cellulose. Different esterification methods may conduct to different substitution degrees; this parameter is generally in the range of 0.6–0.95 derivatives per monomer unit. This anionic polymer forms polyelectrolyte complexes with chitosan. The self-assembly conditions for CMC–chitosan complexes (Aelenei, Popa, Novac, Lisa, & Balaita, 2009; Ichikawa, Iwamoto, & Watanabe, 2005; Yoshioka, Hirano, Shioya, & Kako,

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1990), used as hydrogels for controlled release, membrane formulations (Ichikawa et al., 2005), and for nanoparticle formation (Yoshioka et al., 1990), were earlier analysed.

Due to the characteristic properties of chitosan such as nontoxicity, biodegradability, antifungal activity, water-binding capacity, bioactivity, biocompatibility, and its IMC ability, chitosan and its modified have found many applications in pharmaceutical, medical applications, fibre formation, waste water treatment, paper production, cosmetics, textile dyeing and finishing (Hudson, 1998; Ilium, 1998; Jocic et al., 2005; Kitkulnumchai, Ajavakom, & Sukwattanasinitt, 2008; Lim & Hudson, 2003; Morimoto et al., 2001; Najafi, Assefipour, Hajilari, & Movahed, 2009; Shantha, Bala, & Rao, 1995; Trung, Ng, & Stevens, 2003). It is used in textile dyeing and finishing as a substituent for various other chemicals traditionally used in textile processing.

Printing on fabrics is a centuries-long traditional method of textile colouration. It is done by using a thickening agent along with the dye and the required chemicals. Printing can be classified into three types according to the method used: (1) direct printing, (2) resist printing, and (3) discharge printing. The mechanism employed in resist printing includes physical and chemical resist printing. Physical resist printing is used primarily to prevent penetration of dyes (to make them water repellent), whereas chemical resist printing is conductive for: (1) dye dissolution (oxidative or reductive), (2) dye insolubility (by adding anti-solution agent), and (3) the blocking of dye sites on fibres. To reinforce the resist-printing effect, both physical and chemical methods may be used in combination. The use of chitosan in acetic acid as a printing paste dates back to the 1940s. Once dried, chitosan acts as an insoluble membrane with good coverage capability and makes an excellent chemical resist-printing agent (Provost, 1988; Vigo, 1997).

The current study explores the effect of chitosan on the resist printing of linen and linen/polyester fabrics with reactive dye pastes thickened with CMC.

2. Experimental

2.1. Materials and reagents

2.1.1. Fabrics

Linen fabric, semi-finished for dyeing and printing, used in this work were supplied by Textile Industries, Egyptian Co., Ointex Egypt. Fabric specifications were: weight 120 g/m^2, warp 28 threads/cm, 20 tex, weft 26 threads/cm, 20 tex.

The fabric was scoured at 100 °C for 60 min with a solution containing 1 g/L non-ionic detergent and 2 g/L sodium carbonate, then washed thoroughly and finally air dried at room temperature.

Linen/polyester 50/50 fabric was also supplied by Textile Industries, Egyptian Co., Ointex Egypt.

2.1.2. Materials

- Reactive dye used was Sunzol blue RS (C.I. Reactive blue 19), based on vinyl sulphone.
- High molecular weight chitosan of M.W. 10104, with a viscosity of 800,000 cps (Aldrich).
- Urea, sodium alginate, sodium bicarbonate, formic acid, tartaric acid, oxalic acid, fumaric acid and maleic acid were of reagent grade.

The carboxymethylcellulose sodium salt used was laboratory prepared from rice straw cellulose according to a previously published author's work (Ragheb et al., 2012), with different D.S. values (0.66, 0.81, and 1.03).

2.2. Methods

2.2.1. Preparation of printing pastes

Each dye (0.3 g) was first mixed with 10 g urea and a small amount of water. The solution was stirred to ensure homogenization and poured into a thickener suspension (3 g sodium alginate mixed with a small amount of water). The whole mixture was thoroughly stirred with 3 g sodium bicarbonate. The total weight of the whole paste was adjusted to 100 g by the addition of water.

2.2.2. Preparation of resist-printing pastes

Resist-printing pastes were prepared by mixing solutions with various concentrations of chitosan (0.5, 1, 1.5, and 2.0%) in 1% acetic acid at a concentration of 1 g/L. Each solution was then poured into a thickener suspension (1.25 g CMC mixed with a small amount of water). The whole mixture was thoroughly stirred and brought to 25 g by the addition of water.

2.2.3. Printing procedure

The resist printing paste was applied to samples of cotton fabric using a flat-screen printing technique. The printed samples were then pre-dried at 80 °C for 3 min to avoid printing paste migration. Samples were then screen printed with the printing paste by squeegee using the same processing conditions described earlier.

An additional resist-printing paste, with a constant chitosan concentration of 1% and individually mixed with citric, acid (1%) at various ratios (100:0, 75:25, 50:50 25:75, and 0:100), was prepared for comparison. The resist printed fabrics were fixed via thermo fixation at 150 °C for 3 min.

2.2.4. Washing

The fixed discharge and discharge–resist printed fabrics were subjected to washing through five stages as follows:

- Rinsing thoroughly with cold water.
- Treatment with hot water.
- Treatment near the boiling temperature (90–95 °C) with a solution containing 2 g/L Aspkon 1030 (neutral detergent).
- Washing with hot water.
- Rinsing with cold water.

2.3. Analysis and measurements

2.3.1. Colour measurements

The colour strength (K/S) was measured by reflection spectroscopy with a Hunter Lab UltraScan PRO spectrophotometer according to a standard method (Judd & Wyszecki, 1975).

2.3.2. Fourier transform infrared (FT-IR) spectral analysis

Fourier transform infrared spectroscopy (FT-IR) was performed by using a Pye-Unicam Spectra 1000 spectrophotometer (England) to determine the functional groups on the surface of the linen samples. A potassium bromide (KBr) disc was used.

3. Results and discussion

As previously indicated, the main aim of the present work was to investigate the suitability of using chitosan CMC complexes in resist printing of linen and linen/polyester fabrics with reactive dye pastes. To achieve this goal, series of resist printing pastes thickened with CMC derivatives of different D.S. values (0.66, 0.81 and 1.03) were prepared. For the sake of comparison, another paste thickened with sodium alginate was also prepared. After printing and drying of the printed goods, fixation was carried out via steaming.