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Full Length Research Paper

Effect of chitosan on resist printing of cotton fabrics with reactive dyes

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The concentration of chitosan, types of resist agent, curing temperature and curing time were varied to determine their effects on resist-printed cotton fabrics. An optimal chitosan concentration of 1.6% resulted in the greatest resist effect on printed cotton fabrics. For mixtures, a 6:4 ratio of citric acid : chitosan and an 8:2 mixture of tartaric acid : chitosan yielded the greatest resist effects. A curing temperature of 150°C for 180 s was optimal.

Key words: Chitosan, resist printing, reactive dyes, cotton fabrics.

INTRODUCTION

Chitosan is a cationic natural biopolymer obtained by alkaline N-deacetylation of chitin (Kurita, 1998), the most abundant natural polymer after cellulose. It comprises copolymers of glucosamine and N-acetyl glucosamine (Illum, 1998) and exhibits many unique properties such as non-toxicity, biocompatibility and biodegradability (Illum, 1998; Singla and Chawla, 2001). It ideally consists of 2-amino-2-deoxy-(1-4)-β-D-glucopyranose residues (D-glucosamine units) and may include a small number of N-acetyl-D-glucosamine units. Chitosan is a remarkable biomaterial because of its numerous biological and immunological activities (Lim and Hudson, 2003; Jia et al., 2001). In particular, its non-toxic and biodegradable properties have attracted considerable attention for biomedical, textile and chemical industrial applications (Jocic et al., 2005; Julià et al., 2000). In addition, chitosan may be used in textile dyeing and finishing as a substitute for various other chemicals traditionally used in textile processing (Najafi et al., 2009).

Printing on fabrics is a centuries-long tradition. Rotary printing, popular in Europe, was originally done by hand. Machine printing emerged around 1776. Today, thanks to the presence of high-performance printers, through which continuous mass production of exquisite patterns in as many as 30 different colors is possible. Printing can be classified into three types according to the methods used: (1) direct printing, (2) resist printing and (3) discharge printing. The mechanisms employed in resist printing include physical resist printing and chemical resist printing. Physical resist printing is used primarily to prevent penetration of dyes (to make them water-repellant), whereas chemical resist printing is conducive for: (1) dye dissolution (oxidative or reductive), (2) dye insolubility (by adding anti-solution agent), and (3) the blocking of dye sites on fibers. To reinforce the resist-printing effect, both physical and chemical methods may be used in combination (Datye et al., 1984; Vigo, 1997; Provost, 1988). In the current study, chitosan was used as the resist-printing agent. 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 (Doong et al., 1999).

The current study explores the effect of chitosan on the resist printing of cotton fabrics with reactive dyes, as well as the physical properties of the printed cloths. The effects of ratio and concentration of various resist-printing agents and processing conditions are also discussed.

EXPERIMENTALS

Materials and reagents

Milled, desized, scoured, bleached and mercerized plain-weave cotton fabric ends (130)*picks (80)/50^s*50^s were supplied by the Yi Hwa Textile Company. The chitosan had a molecular weight of 180,000 with 85% acetylation (Sigma). Reactive dyes were Cibacron Yellow F-4G (C.I. Reactive Yellow 143), Cibacron Red F-B

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(C.I. Reactive Red 184) and Cibacron Blue F-GFN (C.I. Reactive Blue 204). NP-9 (Taiwan Surfactant Co.) was used as the detergent. Urea, sodium bicarbonate, formic acid, tartaric acid, citric acid and Turkey red oil were of reagent grade.

Methods

Preparation of printing pastes

Each dye (0.4 g) was first mixed with 5 g urea and a small amount of water. The solution was stirred to ensure homogenization and poured into a thickener suspension (3 g CMC mixed with a small amount of water). The whole mixture was thoroughly stirred with 2 g sodium bicarbonate and 0.5 g Turkey red oil. The total weight of the whole paste was adjusted to 50 g by the addition of water.

Preparation of resist-printing pastes

Resist-printing pastes were prepared by mixing solutions with various concentrations of chitosan (0.4, 0.8, 1.2, 1.6 and 2.0%) in formic acid at a ratio of 1:6. Each solution was then poured into a thickener suspension (1.5 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.

Printing procedure

Screen printing was performed with a 200-mesh screen. The resist-printing paste was applied to samples of cotton fabric by squeegee using a flat-screen printing technique. The printed samples were then pre-dried at 80°C for 3 min to avoid printing paste migration. The printed samples were then fixed by thermosol at different temperatures (130, 140, 150, 160 and 170°C) for different durations of time (120, 150, 180, 210 and 240 s). Samples were then screen printed with the printing paste by squeegee using the same processing conditions described earlier. The printed fabrics were subsequently washed with cold water for 15 min, then with warm water at 90°C and a solution containing NP-9 detergent (2 g/l) at 80°C for 10 min. After soaping, the samples were washed with water and dried.

An additional resist-printing paste, with a constant chitosan concentration of 1.6% and individually mixed with citric acid and tartaric acid at various ratios (10:0, 8:2, 6:4, 4:6, 2:8 and 0:10), was prepared for comparison.

Analysis

Reflectance measurements on the printed fabrics were performed on an automatic filter spectrophotometer (HunterLab Miniscan 45/0 LAV). The relative color strength (expressed as K/S values) between the resist printed fabric and gray fabric was determined by applying the Kubelka–Munk equation (Fred, 1981):

$$K/S = \frac{(1-R)^2}{2R} - \frac{(1-R_0)^2}{2R_0}$$

where R and R_0 are the decimal fractions of the reflectance of the printed and unprinted fabrics, respectively. A smaller K/S value represents a higher resist-printing effect.

Analysis of the evenness (ΔE) of the printed fabrics was measured by evaluating the color difference between the largest and the smallest K/S values obtained on the same fabrics.

RESULTS AND DISCUSSION

Chitosan concentration

Resist-printing pastes containing different concentrations of chitosan were prepared in order to observe the effect of chitosan on processed cotton fabrics. Three different colors were evaluated. Figure 1 shows that the resist-printing effect is generally higher with the addition of chitosan to the resist-printing paste. The resist-printing effect increases with increasing chitosan concentration from 0.4 to 1.6%. These results indicate that chitosan induces a physical resist-printing effect. Furthermore, the chitosan may also distinguish a chemical resist-printing effect resulting from the structure of chitosan which is same as cellulose except for hydroxyl group which is substituted with amino group in case of chitosan (Gupta and Haile, 2007). As the concentration was increased to 2.0%, however, the resist-printing effect declined. The optimal chitosan concentration was 1.6%. High chitosan levels may cause the dyes to form a partial covalent bond with chitosan, thereby diminishing the resist-printing effect. In such a case, the resist printing would not be linear as a function of chitosan concentration. Red 184 exhibited the highest resist-printing effect, followed by Blue 204 and Yellow 143. Red 184, however, showed the poorest relative effect with 0.4% chitosan. In this case, the chitosan membrane formed by the resist-printing paste on the processed cotton fabrics may have been too thin, thereby impairing the physical resist-printing effect. The evenness of dyeing, shown in Table 1, was in most cases acceptable. Cotton fabrics that were processed with chitosan appeared to have poorer evenness than those that were not. This may be attributed to the reaction of chitosan with the dyes themselves, which could have resulted in partial coloring and inferior evenness. Evenness was relatively poor at chitosan concentration less than 0.8%, presumably due to gelation of the resist-printing paste, leading to uneven dying.

Resist-printing agent ratios

Figures 2 and 3 illustrate the effects of processing performed with different ratios of resist-printing agents. The results show that, when each component was used alone, citric acid exhibited the best resist-printing effect on processed cotton fabrics, followed by tartaric acid and chitosan. This is because citric acid is composed of three carboxyl radicals that are only active in alkali solution. Therefore, the bond strength between the dyes and the processed cotton fabrics is decreased, resulting in a chemical resist-printing effect. Tartaric acid, on the other hand, is a bicarboxylic acid, which occupies a smaller footprint than citric acid and allows more bonding opportunities on the processed fabrics. Figure 2 shows that the resist-printing effect of the combination of tartaric

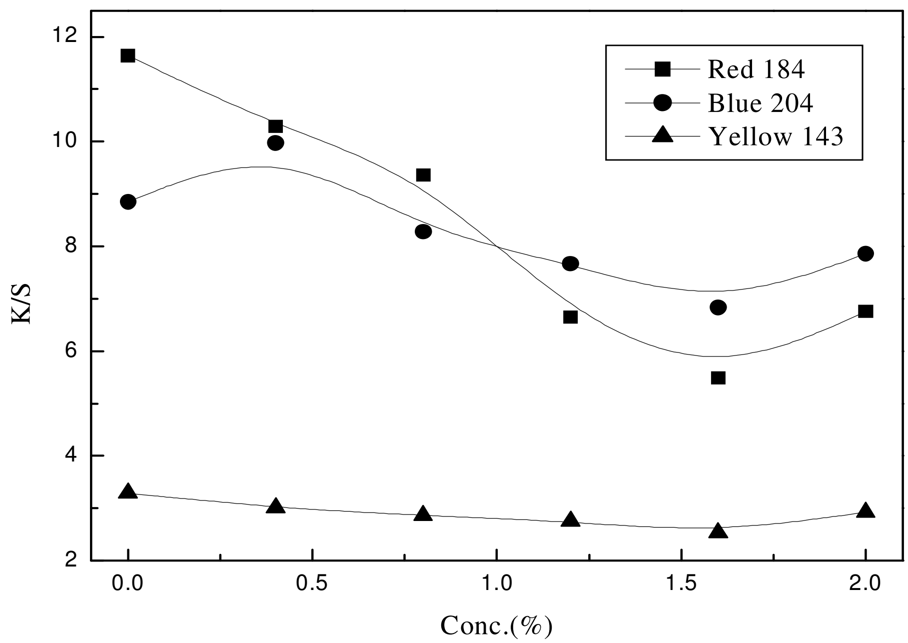

Figure 1. Variation of K/S for resist processed fabrics by different chitosan concentration.

Table 1. Variation of △E for resist processed fabrics by different chitosan concentration.

Concentration (%) / Dye	0	0.4	0.8	1.2	1.6	2.0
Red 184	0.24	0.98	1.49	1.15	0.77	1.36
Blue 204	0.19	0.87	1.14	1.35	0.91	0.75
Yellow 143	0.45	0.65	1.08	0.95	0.56	0.68

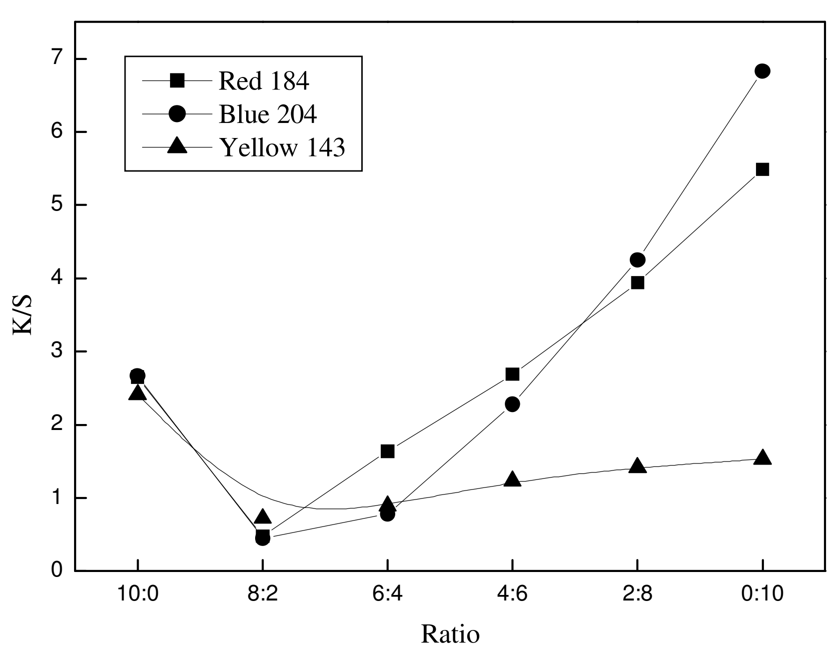

Figure 2. Variation of K/S for resist processed fabrics by different ratio of tartaric acid/chitosan.

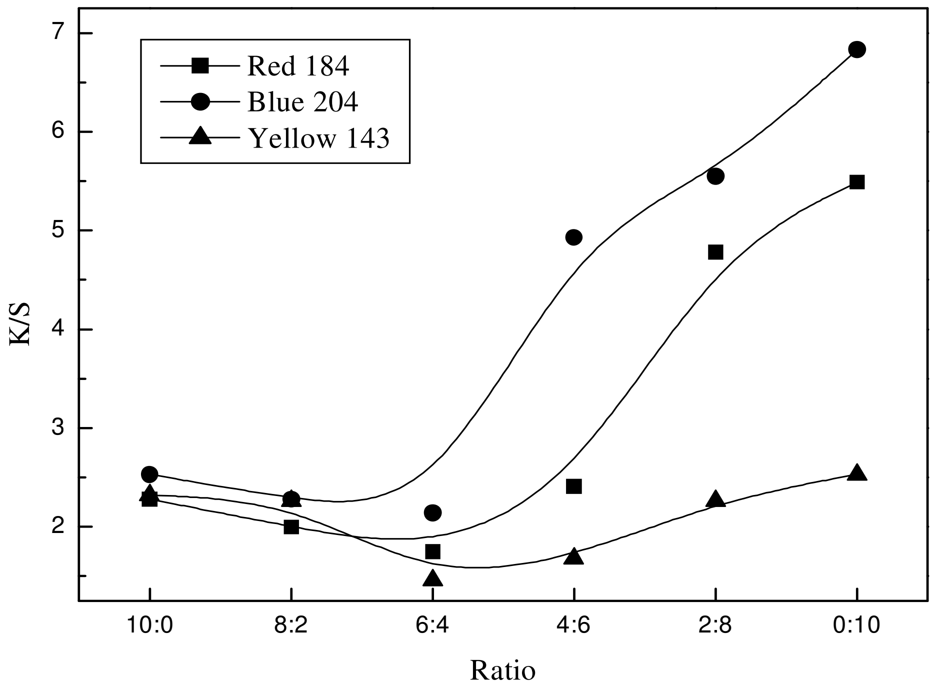

Figure 3. Variation of K/S for resist processed fabrics by different ratio of citric acid/ chitosan.

Table 2. Variation of △E for resist processed fabrics by different ratio of tartaric acid/chitosan.

Ratio / Dye	10:0	8:2	6:4	4:6	2:8	0:10
Red 184	0.76	0.82	1.06	1.34	0.78	0.69
Blue 204	1.21	0.64	1.12	1.28	0.48	0.52
Yellow 143	0.64	0.35	0.45	1.36	0.67	0.57

Table 3. Variation of △E for resist processed fabrics by different ratio of citric acid/chitosan.

Ratio / Dye	10:0	8:2	6:4	4:6	2:8	0:10
Red 184	0.75	1.12	0.97	1.74	0.94	0.85
Blue 204	0.72	1.13	0.48	1.25	1.45	0.89
Yellow 143	0.45	1.03	0.59	0.89	0.34	0.45

acid and chitosan was greatest when the two were used at a proportion of 8:2. Conversely, a ratio of 6:4 was the best for combination of citric acid and chitosan, as shown in Figure 3.

The above data shows that different resist-printing agents, used at different ratios, can result in synergic effects through the combination of chemical and physical resist printing. Note that, as shown in Tables 2 and 3, the combined use of tartaric or citric acids and chitosan at a proportion of 4:6, respectively, exhibited relatively poor evenness; this was caused by inconsistencies in the strength or angle of application during the squeegee process.

Curing temperature

Figure 4 shows higher printing effects at higher curing temperatures. However, at temperatures above 150℃, the resist-printing effect subsided, with an increased probability of yellowing or carbonization of the processed cotton fabrics. It is therefore advisable to cure at 150℃. Table 4 shows that the evenness of the three dyes was generally acceptable.

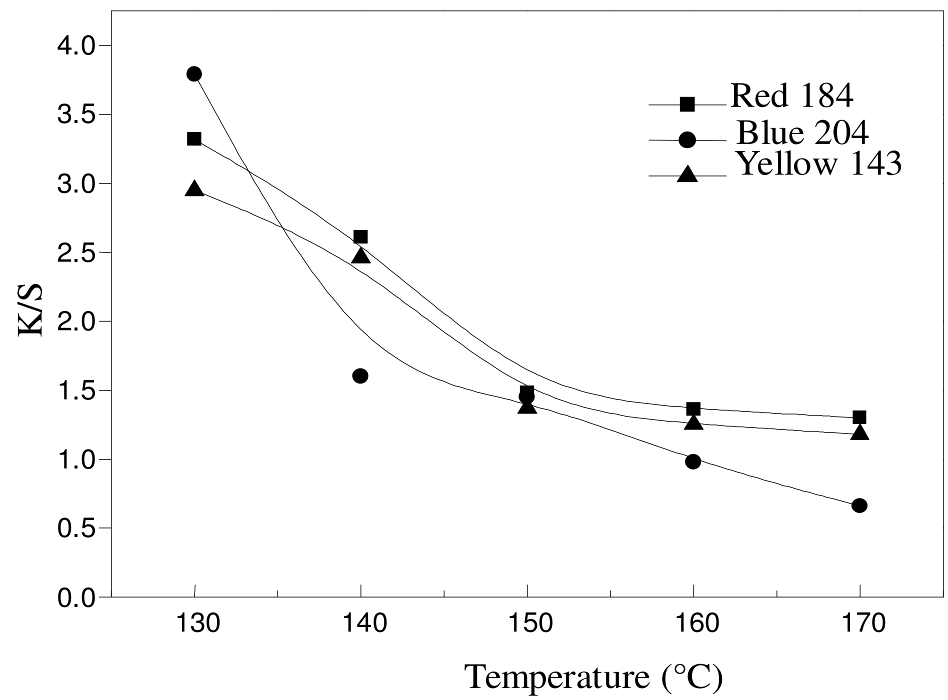

Figure 4. Variation of K/S for resist processed fabrics by different curing temperature.

Table 4. Variation of △E for resist processed fabrics by different curing temperature.

Temperature (℃) / Dye	130	140	150	160	170
Red 184	1.24	0.74	0.91	0.85	1.68
Blue 204	1.08	0.75	0.74	0.45	0.84
Yellow 143	0.76	0.87	0.35	0.97	0.49

Curing time

The data in Figure 5 show an increasing resist-printing effect with curing time. However, curing times greater than 180 s were unnecessarily long and would not be cost-effective if implemented on an industrial scale. Therefore, it is suggested that the curing time be set at 180 s. Table 5 shows that the evenness of the three dyes was generally acceptable.

Washing fastness

Washing fastness tests were conducted on each processed cotton fabrics by different ratios of tartaric acid : chitosan as shown in Table 6. The results showed that washing fastness was almost constant as most of them reached up to grade 4. The washing fastness of processed cotton fabrics were almost unchanged when a combination of different ratio of tartaric acid/chitosan and color schemes of dyes were used.

Rubbing fastness

Table 7 shows the results of tests of rubbing fastness under the same printing condition for different color schemes which show similar results. Therefore, the processed cotton fabrics printed with different color scheme was chosen for a complete test of its rubbing fastness. The results depicted that dry rubbing fastness can be as high as grade 4, while wet rubbing fastness was in the range of grade 3 to 4. This implies that chrome dyes have a positive effect on the rubbing fastness of processed cotton fabrics.

Conclusion

Resist printing of processed cotton fabrics was enhanced by the inclusion of chitosan in the resist-printing paste. The resist-printing effect exhibited a nonlinear relationship with chitosan concentration and was optimal at 1.6% chitosan. The process was optimized with a tartaric acid :

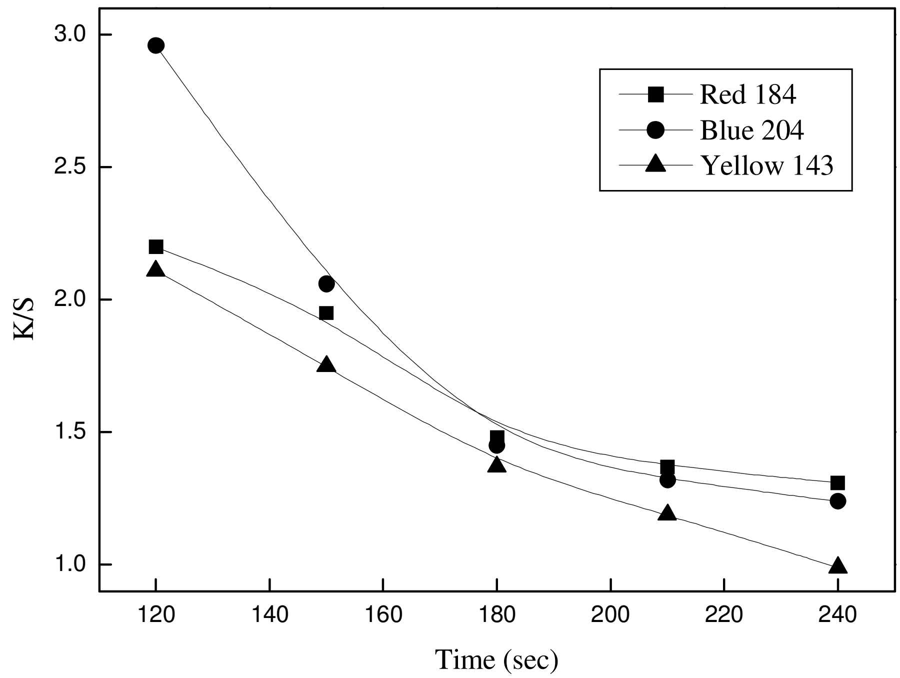

Figure 5. Variation of K/S for resist processed fabrics by different curing time

Table 5. Variation of ΔE for resist processed fabrics by different curing time.

Time (s) / Dye	120	150	180	210	240
Red 184	1.4	1.32	0.91	0.76	0.69
Blue 204	1.3	1.48	0.84	0.72	0.52
Yellow 143	0.53	0.64	0.35	0.15	0.86

Table 6. Washing fastness results of resist processed fabrics by different ratio of tartaric acid : chitosan.

Ratio Dye	10:0		8:2		6:4		4:6		2:8		0:10	
	S.C.	C.C.	S.C.	C.C.	S.C.	C.C.	S.C.	C.C.	S.C.	C.C.	S.C.	C.C.
Red 184	5	4 - 5	5	5	5	4 - 5	4 - 5	5	4 - 5	4 - 5	4 - 5	4 - 5
Blue 204	4	4	4 - 5	4 - 5	4	4	4	4 - 5	4	4 - 5	4 - 5	4
Yellow 143	4	4	4 - 5	4	4 - 5	4	4 - 5	4	4-5	4	4	4

S.C.: Staining of color; C.: change in color.

Table 7. Rubbing fastness results of resist processed fabrics by different ratio of tartaric acid : chitosan.

Ratio Dye	10:0		8:2		6:4		4:6		2:8		0:10	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Red 184	4	4	4	4	4	3 - 4	4	3 - 4	3 - 4	3 - 4	4	3 - 4
Blue 204	3 - 4	3 - 4	3 - 4	3 - 4	4	3 - 4	4	4	4	3 - 4	4	3
Yellow 143	4	4	4	3 - 4	3 - 4	3 - 4	3 - 4	3	4	3	3 - 4	3

chitosan ratio of 8:2 and a citric acid : chitosan ratio of 6:4. The combined use of chemical and physical resist-printing agents yielded an effect superior to that obtained with each agent separately. The evenness of resist printing on processed cotton fabrics was generally acceptable. Additionally, the washing fastness of processed cotton fabrics by different ratio of tartaric acid : chitosan can reach up to grade 4. The dry rubbing fastness of processed cotton fabrics can reach up to grade 4 and wet rubbing fastness can reach up to grade 3 to 4.

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