

Dyeing Chitin/Cellulose Composite Fibers with Reactive Dyes

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ABSTRACT

The dyeing properties of chitin/cellulose composite fibers—Crabyon® (CR)—for four reactive dyes are examined and compared with those of viscose rayon and partially deacetylated chitin. The CR fibers show high fixation for dyeing with CI Reactive Blue 5 with a monochlorotriazinyl group in a weakly acidic solution and with CI Reactive Blue 19 with a sulfatoethylsulfonyl group from weakly acidic to weakly alkaline solutions. The CR fibers can be dyed with CI Reactive Blue 19 in wide pH ranges, compared with viscose rayon, which cannot be dyed at these same pH ranges.

Chitin, a polysaccharide made up of poly[(1 → 4)-2-acetoamido-2-deoxy-D-glucopyranose], is widely distributed in nature as a component of bacterial cell walls and exoskeletons of crustaceans and insects. Recently, chitin and deacetylated chitin (chitosan) have been used more often in various fields [1], for example, in the fiber industry, especially in fiber processes such as deodorant finishing. Also, fibers have been prepared from chitin or chitosan alone or blended with other components. In Japan, the representative fibers derived from chitin or chitosan are Chitopoly® (Fuji Spinning Co.) and Crabyon® (Ohmikenshi Co.). The former is prepared by wet spinning from cellulose viscose containing a fine chitosan powder [9], and the latter is prepared by wet spinning from a mixed solution of chitin viscose and cellulose viscose [14]. Chitopoly fibers have antimicrobial activities and deodorant properties [9]. Crabyon fibers have both those properties plus high water regain [14] and high adsorption ability for metal ions [4]. These properties are attributable to the presence of amino groups in the fibers.

In this work, we elucidate the chemical properties of Crabyon, designated as CR. In earlier work, we examined the dyeing properties of an acid dye [13] and a direct dye [6] and proved that CR had a high affinity for an acid dye

with which cellulose fibers could not be dyed. CR could also be dyed more quickly with a direct dye than silk, because the chitin of CR fibers was partially deacetylated during their manufacture, and the amino groups derived from the acetoamido groups produced sites for acid dyes and additional sites for direct dyes. Also, we revealed that the maximum dye uptake of the acid dye by three kinds of CR fibers with different chitin contents at equilibrium agreed roughly with the calculated values of amino groups. This suggests that the chitin part of the substrate will be present in the amorphous region.

In this report, we investigate the dyeing properties of CR fibers for a few reactive dyes compared with those for viscose rayon and partially deacetylated chitin as reference samples.

Experimental

MATERIALS

When chitin/cellulose composite fibers contain 3, 10, and 20% chitin, we designate them as CR3, CR10, and CR20, respectively. These samples and viscose rayon (Ohmikenshi Co., Ltd., 14.6 tex) used as a reference sample were in the yarn state and were used after washing in a nonionic detergent, Noygen HC (5×10^{-3} kg dm⁻³), for

1 hour at 80°C. The fiber properties of CR20 were described in our preceding paper [13].

We used four reactive dye types: monochlorotriazinyl, dichlorotriazinyl, and sulfatoethylsulfonyl types, and the type containing two reactive groups (monochlorotriazinyl and sulfatoethylsulfonyl). The representative dyes were CI Reactive Blue 5, CI Reactive Red 1, CI Reactive Blue 19, and CI Reactive Red 194. These were used as marketed without further purification, except for CI Reactive Blue 19, which was purified by dimethylsulfoxide-acetone [10]. Table I shows the chemical formulas, molecular weights, and symbols of these dyes.

TABLE I. Reactive dyes used.

Chemical structure	Molecular weight	Symbol
	627	Blue 19
	717	Red 1
	828	Blue 5
	985	Red 194

Chitin powder (degree of deacetylation, 10.3%) was purchased from Nacalai Tesque Co. Ltd. A partially deacetylated chitin was prepared as follows: 10 g of chitin was heated for 1 hour at the boil in a 30% aqueous solution of sodium hydroxide under reflux, neutralized with 6 mol dm⁻³ hydrochloric acid, filtered, and washed with distilled water. After drying in a vacuum, the resulting solid was ground into a powder with a typical diameter of about 100–300 μm. The degree of deacetylation of the partially deacetylated chitin was 29.0%.

DYEING AND DYE UPTAKE BY SUBSTRATES

A dye of 50% on weight of fibers in a yarn was dissolved in 0.10 dm³ of 0.1 mol dm⁻³ buffer solution at

pH values of 3.0 to 13.5. Mixed solutions of two electrolytes were used as buffer solutions as follows: hydrochloric acid and sodium acetate for pH 3, acetic acid and sodium acetate for the range from pH 4 to 6, potassium dihydrogenphosphate and sodium tetraborate for the range from pH 7 to 8, sodium hydrogencarbonate and sodium carbonate for the range from pH 9 to 11, and disodium hydrogenphosphate and sodium hydroxide for the range from pH 12 to 13. The mixtures were poured in test tubes, and 0.01 g of fibers hung on a stainless steel wire were put inside the tubes and dyed for 1 hour at 80°C with Blue 5, Blue 19, and Red 194, or for 1 hour at 25°C with Red 1 (liquor ratio, 10,000:1). At the end of the dyeing, the fiber samples were removed and rinsed lightly with distilled water. The dye concentrations in the residual baths were determined spectrophotometrically with a UV-VIS spectrophotometer (Hitachi U3210) at a wavelength of maximum absorbance. Dye uptake, the amount of exhausted dye (m_1) was determined on the basis of the calibration curve. The amount of exhausted but unreacted dye (m_2) was estimated by colorimetry of the extract from the dyed fiber with formamide at 60°C. The amount of fixed dye (reacted dye) was determined by subtracting m_2 from m_1 .

When dyeing in an alkaline aqueous solution in which the hydrolyzed dye and the ether-type dye are formed, as described later, the errors are large with the method above. So we used color depth (K/S) as a measure of dye concentration on the dyed sample. That is, the relationship between the reflectance (R) and the dye concentration (C) for a thick opaque pattern is given by the Kubelka-Munk Equation 1 [3]. Thus, we determined the K/S value from the reflectances of the dyed samples after formamide extraction and the undyed sample at a selected wavelength.

$$K/S = (1 - R_A^1)^2/2R_A^1 - (1 - R_A^0)^2/2R_A^0 = k \times C, \quad (1)$$

where K = the extinction coefficient, S = the scattering coefficient, R_A^1 = the reflectance of the dyed sample, R_A^0 = reflectance of the undyed sample, and k = the constant for a particular dye.

Partially deacetylated chitin powder was dyed as follows: 0.05 g partially deacetylated chitin was weighed exactly and placed in a bottle. To this 5.00 × 10⁻³ g dye and 0.10 dm³ of each buffered solution at the various pH values were added, and permitted to react under stirring for 1 hour at 80°C. After the reaction, the content was filtered through a G3 glass filter, the water was removed in a vacuum, and any unreacted dye was extracted with formamide. The extract was made up to 0.05 dm³ and its absorbance was measured at λ_{max} . The amount of fixed dye was determined as mentioned earlier.

Amino group contents in partially deacetylated chitin before and after dyeing with the reactive dye were determined by the ninhydrin method [5].

Results and Discussion

DYEING WITH CI REACTIVE BLUE 5

We dyed CR10, CR20, and viscose rayon with Blue 5, which has a monochlorotriazinyl group, in the buffer solution at the various pH values for 1 hour at 80°C. Figure 1 shows the exhaustion and fixation curves for CR20.

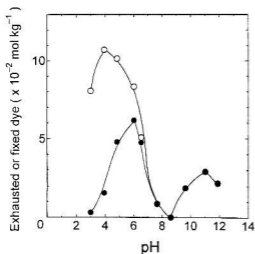


FIGURE 1. Effect of dyebath pH on exhaustion and fixation of CI Reactive Blue 5 for CR20: ○ exhaustion, ● fixation.

The exhaustion was higher at low pH regions, with a maximum at around pH 4. Then it abruptly declined with rising pH to almost zero in the vicinity of pH 8, and increased somewhat again at pH levels above 9. Fixation increased abruptly from pH 4 to pH 6, at which point it reached a maximum amount of fixed dye. Exhaustion and fixation were the same values at around pH 7. The reaction of this dye with CR fibers is a nucleophilic substitution. Therefore, free basic groups in the fiber seem to react more easily with the dye than protonated basic groups. This dye can also react with hydroxylate anion in both cellulose and chitin components above pH 8. These situations explain the fixation behaviors above.

The trends were also similar for CR10 (data not shown). The exhausted and fixed dye amounts with CR20 were higher than those with CR10 because the former contained more amino groups than the latter.

DYEING WITH CI REACTIVE BLUE 19

We dyed CR3, CR10, and CR20, and viscose rayon with Blue 19, which has a sulfatoethylsulfonyl group, in the buffer solution at various pH values for 1 hour at 80°C.

Figure 2 shows the exhaustion and fixation curves for CR20. Exhaustion and fixation increase with rising pH, achieving a maximum at around pH 7 and then decreasing with further increases of pH. That is, exhaustion and fixation are highest in the neutral pH region. This is characteristic of the dyeing properties of CR fibers with Blue 19. The sulfatoethylsulfonyl group in the dye structure converts to a vinylsulfonyl group during dyeing, which can react with functional groups in the fiber [2, 7]. The conversion of a sulfatoethylsulfonyl group to a vinylsulfonyl group occurs more easily at a pH range of 6–7. This conversion occurs slightly at a pH below 4, and the vinylsulfonyl group is easily hydrolyzed to the hydroxyl group (the hydroxyl type cannot react with the fibers) in the pH region above 9 [11]. The nucleophilic character of amino group is much greater in the free state than the protonated state. The amounts of the former increase with rising pH. If the pKa value of the amino group is 6.3 (this value is the pKa of chitosan [8]), the free amino group will be only 4.8% at pH 5, whereas it will be 83.3% at pH 7. From these two points, it is likely that the fixation of Blue 19 for CR20 is very high in this pH region.

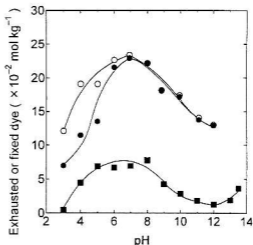


FIGURE 2. Effect of dyebath pH on exhaustion and fixation of CI Reactive Blue 19 for CR20 and a partially deacetylated chitin: ○ exhaustion for CR20, ● fixation for CR20, ■ fixation for a partially deacetylated chitin.

For comparison, the fixation curve of Blue 19 by a partially deacetylated chitin in the solutions at the vari-

ous pH values is also shown in Figure 2. High fixation was obtained from weakly acidic to weakly alkaline solutions. This trend is similar to that for CR20 fibers. With the ninhydrin method, we determined the amino group contents of the partially deacetylated chitin before and after dyeing with Blue 19, followed by extraction with formamide. The results are listed in Table II. The amino group content of the reactive dyed samples decreased compared to that of the undyed sample. This decreased amount corresponds to the amount of reacted amino groups with Blue 19. Therefore, we confirmed that the amino groups in the substrate react most highly at around pH 6.

TABLE II. Amounts of amino groups reacted with a ninhydrin reagent.

Sample	Amounts of amino groups reacted with ninhydrin. $\times 10^{-2}$ mol kg^{-1}
Undyed, partially deacetylated chitin	38.1
Dyed partially deacetylated chitin	
at pH 3	36.4
at pH 6	32.0
at pH 9	34.5

When we looked at the dyed samples in this experiment with the naked eye and compared the fixation value with the practical shade at each pH, it seemed to us that the fixation values were too high in high pH regions. As we mentioned previously, exhaustion is determined by the colorimetry of the solution after dyeing in this experiment. Because a hydrolyzed dye and an ether-type dye would be formed during dyeing [12], the exhaustion values would contain considerable errors. So we also measured color depth, the K/S of CR fibers dyed with Blue 19 followed by extraction with formamide.

Figure 3 shows the K/S values of dyed CR fibers after formamide extraction compared with that of viscose rayon dyed under the same conditions. The fixation curve for CR20 shown in Figure 2 corresponds approximately to its K/S curve. The K/S value at pH 12 was considerably lower and compatible with the actual appearance of the dyed sample. Viscose rayon was not dyed in solutions at pH values below 8 and showed small K/S values in the pH region above 9. This is due to the reaction of Blue 19 with the dissociated hydroxyl group in viscose rayon. The CR10 and CR20 fibers exhibited high fixation even in the alkaline region (\sim pH 11) where Blue 19 would be hydrolyzed rapidly.

The fixed dye amount (9.53×10^{-2} mol kg^{-1}) of Blue 19 for CR3 at pH 7 was nearly equal to that for silk dyed six times repeatedly with the same dye (10% owf) at the same pH [11]. This is because the amino group contents

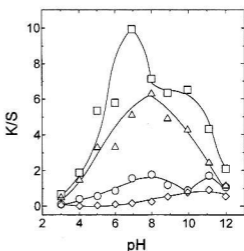


FIGURE 3. Relation between K/S of dyed substrates with CI Reactive Blue 19 and dye bath pH: \square CR20, \triangle CR10, \circ CR3, \diamond viscose rayon.

of these fibers are similar each other [13]. Also, the fixed dye amount (2.26×10^{-1} mol kg^{-1}) of Blue 19 for CR20 at pH 6 substantially exceeded that (1.4×10^{-1} mol kg^{-1}) for wool [7].

DYEING WITH CI REACTIVE REDS 1 AND 194

We dyed CR fibers with Red 1, which has a dichlorotriazinyl group, in the buffer solution at various pH values for 1 hour at 25°C. As we see in Figure 4, the fixation was lower in the reactive dyeing of CR10 with Red 1 compared to those with Blue 5 and Blue 19. This seems to be responsible for the lower substantivity of Red 1 for the CR fibers.

We also dyed the CR fibers with Red 194, which has two reactive groups (monochlorotriazinyl and sulfatoethylsulfonyl), in the buffer solution at various pH values for 1 hour at 80°C. Figure 5 shows the relation between the K/S value of the dyed substrate and dye bath pH. This relation very closely resembles that of Blue 19 (Figure 2). It seems that the K/S value mainly reflects the reaction of the sulfatoethylsulfonyl group in the chemical structure of this dye with CR20. Owing to the high reactivity of sulfatoethylsulfonyl groups for CR20, the contribution of the monochlorotriazinyl group to fixation does not seem to be evident. However, fixation of Red 194 on the CR fibers was lower than we expected. For example, the maximum value of a fixed amount of Red 194 by CR20 was 3.79×10^{-2} mol kg^{-1} at pH 7. This may be due to the large molecular weight of this dye.

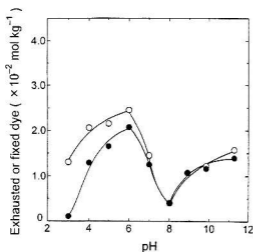


FIGURE 4. Effect of dyebath pH on exhaustion and fixation of CI Reactive Red 1 for CR10: ○ exhaustion, ● fixation.

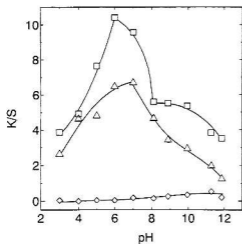


FIGURE 5. Relation between K/S of dyed substrates with CI Reactive Red 194 and dyebath pH: □ CR20, △ CR10, ○ viscose rayon.

Conclusions

Chitin/cellulose composite fibers [Cabyon (CR fibers)] have been dyed with a few reactive dyes. Among these dyes, high fixation is obtained with CI Reactive Blue 5, which has a monochlorotriazinyl group as a reactive group, in a weakly acidic solution, and also with CI Reactive Blue 19, which has a sulfatoethylsulfonfyl group, in weakly acidic to weakly alkaline solutions. The amount of Blue 19 fixed on CR3 containing only 3% chitin resembles that for silk. Also, the amount of Blue

19 fixed on CR20 containing 20% chitin substantially exceeds that for wool. On the other hand, viscose rayon cannot react entirely with Blue 19 at the same pH region (~pH 8) where CR fibers could react sufficiently. Therefore, the advantage of CR fibers in dyeing with these reactive dyes is pronounced compared with viscose rayon. We expect that the demand for chitin or chitosan fibers and their blends with other fibers will continue to grow in the near future.

ACKNOWLEDGMENTS

We wish to thank Mr. H. Tokuda (Ohmikenshi Co.) and Mrs. H. Aoki for their assistance.

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