

Evaluation of the Dyeability of the New Eco-friendly Regenerated Cellulose

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(Received September 3, 2007; Revised November 7, 2007; Accepted January 12, 2008)

Abstract: Three commercial dyes-direct, reactive, and vat dye-were applied to the new regenerated cellulose fiber which was prepared from cellulose acetate fiber through the hydrolysis of acetyl groups with an environmentally friendly manufacturing process. The effect of salt, alkali, liquor ratio, temperature, and leveling agent on the dyeing behavior and fastness were evaluated and compared with regular viscose rayon. From the results, we found that new regenerated cellulose fiber exhibited better dyeability and fastness than regular viscose rayon.

Keywords: Regenerated cellulose fiber, Dye, Dyeability, Fastness, Viscose rayon

Introduction

Cellulose as a raw material has been used in fiber form as a component of paper, textiles, film, and flexible packing material. The excellent fiber-forming properties of the cellulose polymer are used for textile fibers in natural and man-made cellulose materials. Highly purified cellulose comes from wood pulp [1,2]. Rayon, the man-made cellulose fiber, has been made either by using the viscose process or the cuprammonia process. In both methods, the starting raw material is a high degree of polymerization of cellulose and the solvents used in both methods are difficult to recycle [3,4]. In the case of the viscose process, cellulose is converted to cellulose xanthate with carbon disulphide (CS₂), which causes environmental problems due to the difficulty of recovering CS₂ from the process. The cuprammonia method involves the use of heavy metal (copper), which is also detrimental to the environment [5].

More recently, SK Chemicals introduced novel regenerated cellulose, which was prepared from a cellulose acetate fiber with a degree of substitution of 2.0 or higher by saponifying 75 % or greater of the total acetyl groups of the cellulose acetate fiber into hydroxyl groups [6]. Figure 1 and Figure 2 show the flow diagram of new regenerated cellulose preparation and products. Besides birefringence data determined by a polarized microscope; birefringence of viscose rayon (3.63) was higher than that of the new regenerated cellulose (1.93). These results point out that the chain packing of viscose rayon fiber is better than that of the new regenerated cellulose, which indicates the poor dyeability of viscose rayon. The estimated values of crystallinity also were 39±2 % and 27±2 % for viscose rayon and new regenerated cellulose, respectively. The lower value of crystallinity of the new regenerated cellulose has a chance to exhibit better solvent

absorption processing [7].

We claim this regenerated cellulose fiber offers environmental advantages over other conventional regenerated fibers because it does not emit toxic materials such as carbon disulfide and heavy metal ions [8]. Three different dyes were applied to regular viscose rayon and the new regenerated

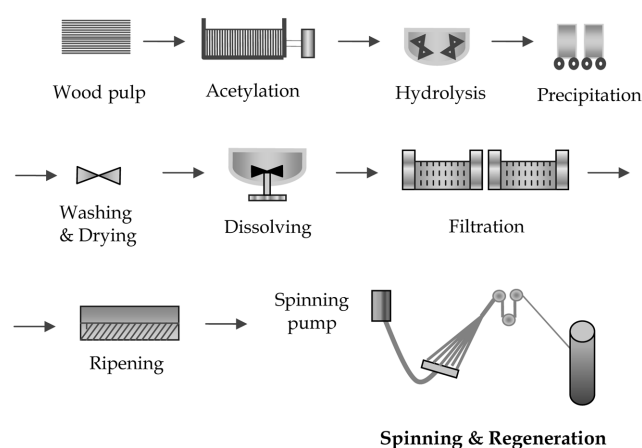


Figure 1. Flow diagram of new regenerated cellulose preparation.

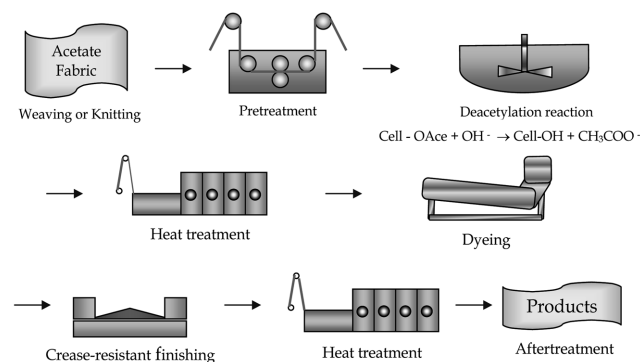


Figure 2. Flow diagram of new regenerated cellulose products.

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cellulose which was prepared from cellulose acetate fiber; their dyeing properties and fastness properties were compared and these results were also explained by the structural differences between the two materials.

Experimental

Fabrics

Viscose rayon fabric (plain weave, warp 82 filament/inch, weft 62 filament/inch), and the new regenerated cellulose fabric (plain weave, warp 96 filaments/inch, weft 56 filaments/inch) obtained from cellulose acetate fibers by alkali-hydrolysis were supplied, by courtesy of SK Chemicals (South Korea).

Dyes and Auxiliaries

Direct Dyeing

A 50 ml dyebath, suitable for a 2.0 g sample of rayon and

the new regenerated cellulose (liquor ratio 1:25), containing Direct Benzo Purpine 4B (C.I. Direct Red 2) and Glauber’s salt was prepared. Dyeing was performed for 30 min. at 100 °C in an Ahiba Nuance laboratory dyeing machine (Ahiba, Datacolor International, and Switzerland). The dye structure and dyeing method used are shown in Figure 3(a) and Figure 4(a), respectively. The fabric which had been dyed with direct dye was rinsed and after-treated with fixing agent (Neofix RP-70C, a polyethylene-polyamine-based cationic resin, 2.5 % on the weight of fabric) for 15 min at 60 °C. Samples were dyed at various salt concentrations (Na₂SO₄, 0-40 g/l) in order to investigate their effects on the dyeing properties of the regenerated cellulose. Exhaustion behavior of direct dye on the fabric was also investigated by monitoring the exhaustion (%) values of dyed fabrics as dyeing proceeds.

Reactive Dyeing

A 50 ml dyebath, suitable for a 2.0 g sample of rayon and

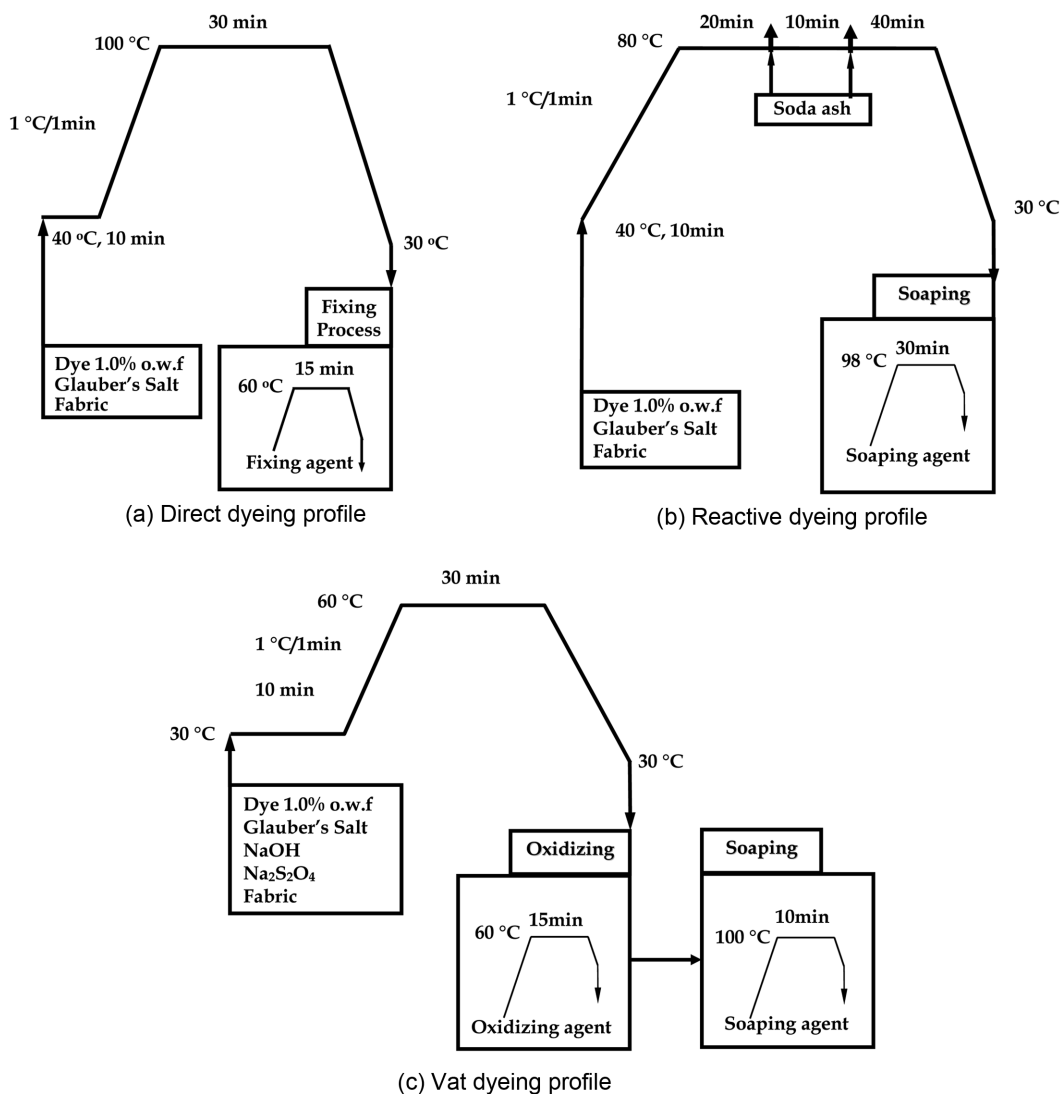


Figure 3. Dyeing profiles for (a) direct dye, (b) reactive dye, and (c) vat dye.

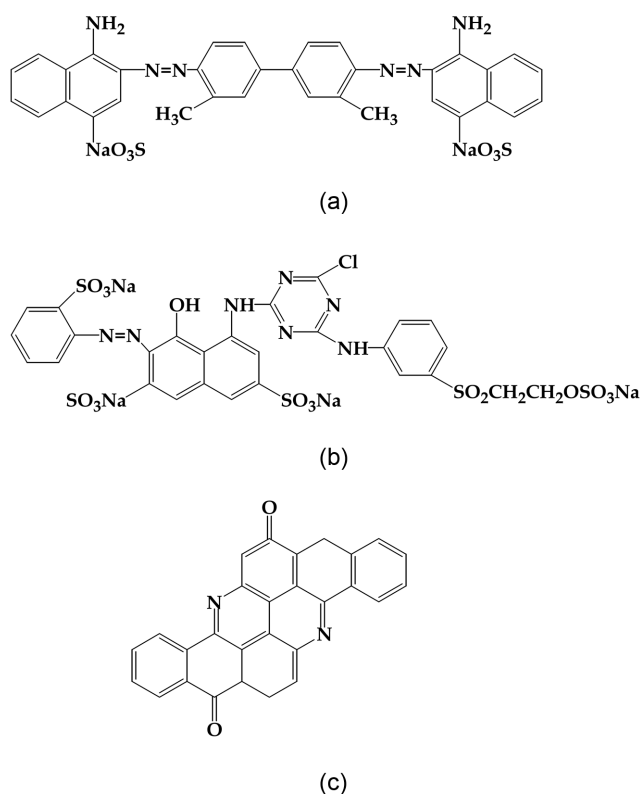


Figure 4. Structures of dyes used in this study; (a) Direct Benzo Purpine 4B (C.I. Direct Red 2, MW=462.58), (b) Sumifix Supra Brilliant Red 2BF (C.I. Reactive Red 194, MW=853.14), and (c) Indanthren Yellow G (C.I. Vat Yellow 1, MW=411.43).

the new regenerated cellulose (liquor ratio 1:25), containing a Sumifix Supra Brilliant Red 2BF (C.I. Reactive Red 194) and Glauber's salt was prepared. Dyeing was started at 40 °C, and the temperature was then raised to 80 °C and maintained there for 70 min. in an Ahiba nuance laboratory dyeing machine. The dye structure and dyeing method used are shown in Figure 3(b) and Figure 4(b), respectively. After cooling, the samples were removed and then after-treated with a soaping agent (SNOGEN CS-940N, non-ionic, 0.5 g/l) for 30 min. at 98 °C.

Samples were dyed at various liquor ratio (1:5-1:40) and alkali (Na₂CO₃, 0-10 g/l) in order to investigate their effects on the dyeing properties of the regenerated cellulose. Exhaustion behavior of reactive dyes on the fabric was also investigated by monitoring the exhaustion (%) values of dyed fabrics.

Vat Dyeing

Samples were dyed in Ahiba Nuance laboratory dyeing machine. The dye structure and dyeing method used are shown in Figure 3(c) and Figure 4(c), respectively. Dyeing began at 30 °C. Samples were dyed at various dye bath conditions of temperature (40-90 °C) and leveling agent (0.0-2.0 ml/l) in order to investigate their effects on the dyeing properties of the regenerated cellulose. Pregel P and

Setamol SN were used as a leveling agent and a dispersing agent, respectively. Dekol SN and sodium hydrosulfite (Na₂S₂O₄) also were used as a soaping agent and a reducing agent, respectively. At the end of dyeing, the dyed fabrics were removed and rinsed thoroughly in cold water. Oxidation was carried out with 2 ml/l hydrogen peroxide solution (30 % w/v) for 15 min. at 60 °C. Finally, the dyeings were soaped in an aqueous solution of Dekol SN (2.5 g/l) for 15 min at the boiling point.

Measurements of Exhaustion and Color Strength

The extent of dye exhaustion (%) achieved for an appropriate dye concentration on each of the two types of fiber was determined using equation (1) [9] by the absorbance spectroscopic analysis of the dyebath before and after dyeing.

$$\text{Exhaustion (\%)} = \frac{A_b - A_a}{A_b} \quad (1)$$

where A_a : absorbance of the dyebath after dyeing and
 A_b : absorbance of the dyebath before dyeing.

Color strength (K/S) of the dyed samples was measured using a Datacolor Spectroflash SF 600 Plus-CT spectrophotometer with the following: illuminant D65, large area view, including specular component and the CIE 1964 Supplemental Standard Observer (10 degree observer) by using Kubelka-Munk equation (see equation (2)). Each sample was folded twice and reflectance was measured four times at different surfaces and averaged [9].

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

where, R : the reflectance of an infinitely thick layer of the material illuminated with light of a known wavelength

K : the absorption coefficient

S : the scattering coefficient

Leveling Properties

The leveling of the dyed new regenerated cellulose was assessed using a Datacolor Spectroflash SF 600 Plus-CT spectrophotometer, which measured the color differences within each sample at five separate points in order to determine the average color difference (ΔE) between these points [10].

Color Fastness Tests

The regenerated cellulose was dyed (1/1 standard depth), after-treated with a fixing agent and heat-set (170 °C, 60 sec) in order to test the color fastness. The color fastness was determined according to International Standards; the specific tests used were ISO 105 C06/C2S (color fastness to washing), ISO 105 E04 (color fastness to perspiration), ISO 105 X12 (color fastness to rubbing), and ISO105 B02 (color fastness to light) [11]. Staining and change in color were assessed

using gray scales.

Results and Discussion

Direct Dyeing Property

In Figure 5, the dyeing properties of two materials were compared with direct dye. The purpose of this work was to compare the dyeability of the new regenerated cellulose to that of viscose rayon. The affinity of direct dye for cellulose is due to the linear and planar structure of dye molecule, which enables close alignment with chains of cellulose molecules resulting in significant hydrogen bonding. The generally accepted model for diffusion of direct dyes into cellulose is based on a heterogeneous system in which dye anions diffuse through the liquid in the pores of the substrate and are simultaneously absorbed on pore walls [12]. The extent to which direct dye is affected by the addition of electrolytes to the dyebath is known as salt sensitivity. Direct dyes vary appreciably with regard to the effect of electrolytes.

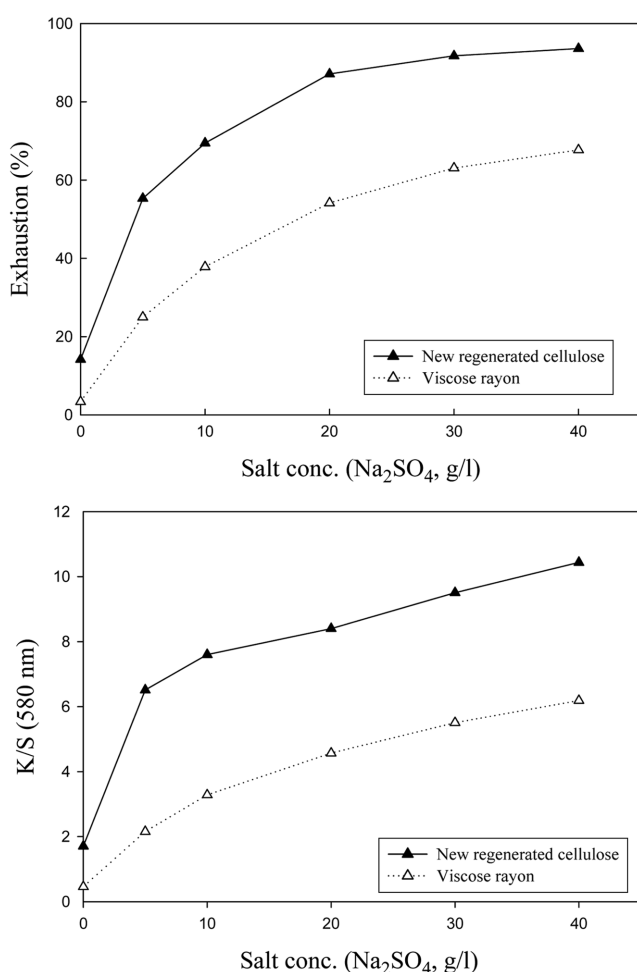


Figure 5. Effect of salt addition to dye bath on exhaustion (%) and color strength (K/S) of dyeings (dye 2.0 % o.w.f., liquor ratio 1:25) of C.I. Direct Red 2.

The addition of electrolytes increases the rate of the dye.

Commonly used electrolytes are Glauber's salt (sodium sulfate, Na₂SO₄). When cellulose is immersed in a solution of a direct dye it absorbs dye from the solution until equilibrium is attained, and at this stage most of the dye is taken up by the fiber. Cellulose carries a negative charge in pure water. As the dye is also an anion, hence negatively charged, there is electrostatic anion-anion repulsion between the dye and cellulose. Therefore, the substantivity or the probability of the dye absorbing onto the fiber is reduced. The substantivity of the dye for cellulose is the proportion of the dye absorbed by the fiber compared with that of the dye remaining in the dyebath. By adding inert electrolyte such as common salt or Glauber's salt to the dyebath, this electrostatic barrier, known as the Donnan potential, can be largely suppressed, thus facilitating dye-fiber contact and allowing better interaction of the Van der Waals forces to enhance substantivity. The diffusion coefficient of the dye is therefore a function of both the dye and electrolyte concentration [13].

The results in Figure 5 corroborate this statement, so that the exhaustion (%) of the dyeings increased with increasing the concentration of salt. The dye exhaustion (%) value of direct dye is a linear function of salt concentration particularly at lower dye concentrations within the cellulose. In the presence of a fixed amount of added dyes, the slope decreases with an increase in salt concentration. We consider that this initial rapid rise is due to the response of the dye to the lowering of electrical potential barriers of diffusion as the concentration of electrolyte increases. The differences that do exist between the fiber types are in the total micellar surface available for dye absorption and in the electrical charge on the fibers. In the manufacture of the new regenerated cellulose, dissolution of the natural cellulose produces intense swelling and leads to a much greater micellar surface in the finished new regenerated cellulose than in viscose rayon.

Reactive Dyeing Property

Figure 6 shows the exhaustion (%) of the dyeings on the new regenerated cellulose are higher than that on the viscose rayon for each of reactive dye, and this result is also consistent when investigating the dyeing properties of direct dye. The exhaustion values of reactive dye applied reached the saturation levels at a low alkaline concentration presumably because of the excellent dyeing properties of regenerated cellulose. Generally, salt and alkali requirements are lower for reactive dyes on regenerated cellulose than for the corresponding dyeings on cotton.

The substantivity of Sumifix Supra Brilliant for cellulose is enhanced as the precursor groups lose their ionic charge by 1,2-elimination. They showed the higher substantivity contributed by the triazine bridging residue linked a sulphatoethylsulphone grouping to a wide range of chromogens. In addition, their hydrogen bonding capability enhanced their flat molecular structure which enabled them to lie along a cellulose chain

and register with hydroxyl groups.

Figure 7 shows the liquor ratio effects on the dyeability of

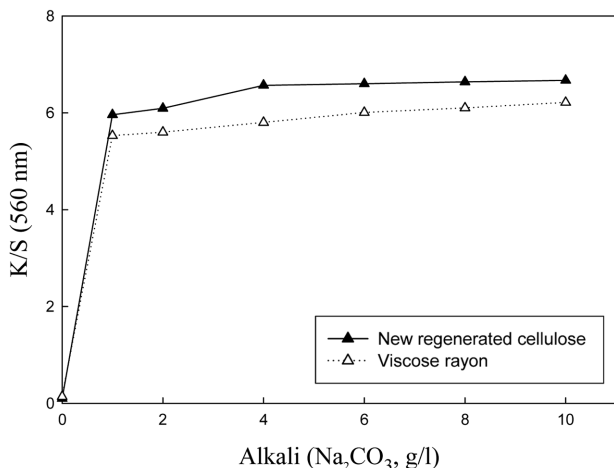
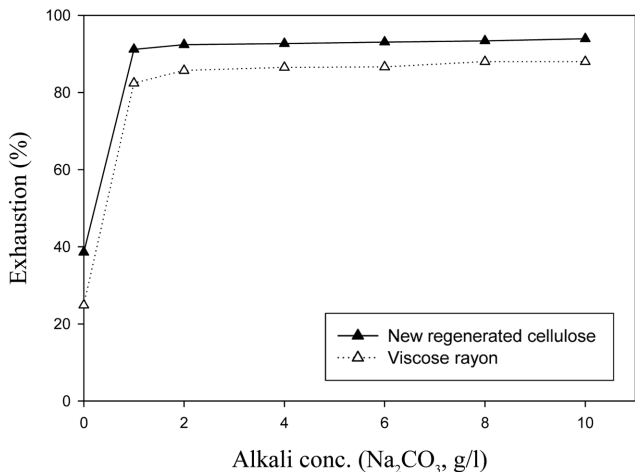


Figure 6. Effect of alkali addition to dye bath on exhaustion (%) and color strength (K/S) of dyeings (dye 2.0 % o.w.f., liquor ratio 1:20) of C.I. Reactive Red 194.

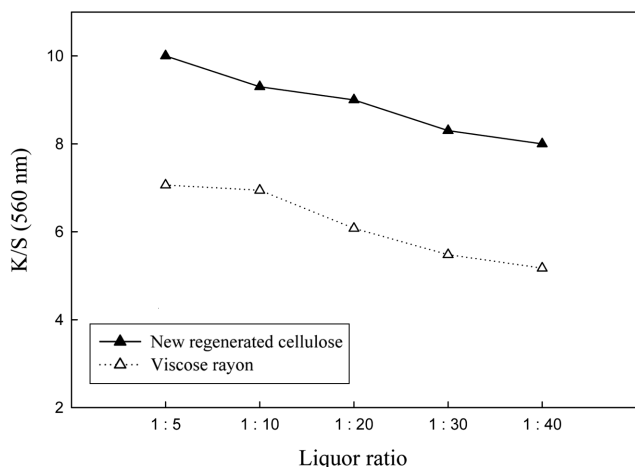


Figure 7. Effect of liquor ratio on color strength (K/S) of dyeings (dye 2.0 % o.w.f., salt 20 g/l) of C.I. Reactive Red 194.

the regenerated cellulose. It is well known that higher liquor ratios lead to reduced dye uptake by fibers. Expectedly, the reactive dye decreases in substantivity to a greater or lesser extent when the liquor ratio is increased. It follows logically that as the liquor ratio increases the probability of contact between the dye molecules and the fiber surface decreases. Equilibrium between absorption and desorption is thus displaced, so desorption becoming stronger. We also note better reproducibility on the new regenerated cellulose compared with that of viscose rayon, since it is particularly resilient to changes in the liquor ratio. We can also see that the new regenerated cellulose is relatively insensitive to process variables.

Vat Dyeing Property

Figure 8 shows the effect of dyeing temperature on exhaustion (%) and on the color strength of C.I. Vat Yellow 1 on viscose rayon and the new regenerated cellulose. This can be explained by the molecular structure of the fiber. According to the results of the X-ray analysis in the previous

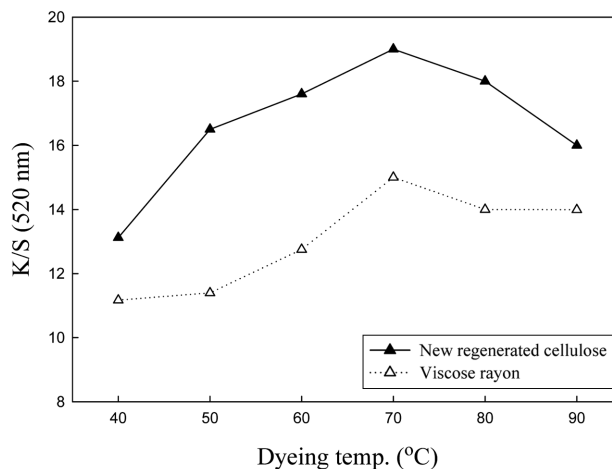
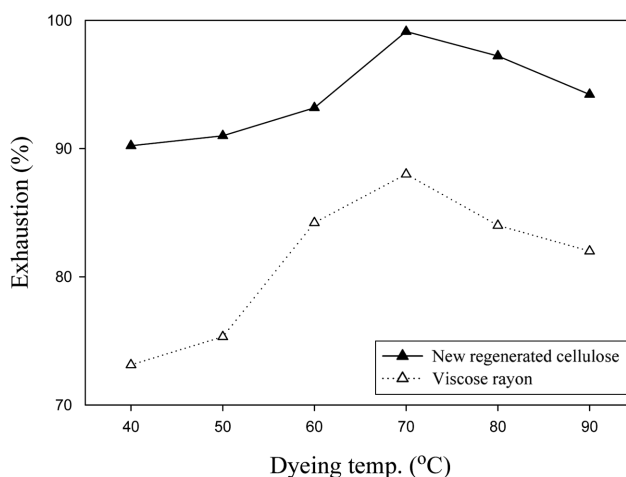


Figure 8. Effect of temperature on exhaustion (%) and color strength (K/S) of dyeings on C.I. Vat Yellow 1 (dye 1 % o.w.f., liquor ratio 30:1).

work, the crystalline structures of both fibers were similar each other, but the value of crystallinity of the new regenerated cellulose was lower than that of viscose rayon. The new regenerated cellulose exhibited higher exhaustion and color yield than viscose rayon. It is clear that the exhaustion of the dyeings increased markedly with increasing the application temperature: reaching maximum exhaustion at 70 °C and decreasing slightly above 80 °C. At the low dyeing temperature, the reduction of vat dye and formation of leuco form, which has substantivity to cellulose, would not be enough for a satisfactory dye uptake. A similar trend was obtained for color yield. The dyeing rate of vat dye on cellulose increases considerably with a rise in temperature, but at the same time the substantivity diminishes, resulting in an increase of the dye concentration in the liquor and thus a decrease of exhaustion. In general, the increase in dye-uptake can be explained by fiber swelling, which can be enhanced by diffusion. A study also reported that chemical changes such as dehalogenation, hydrolysis of carbonamide groups, or

over-reduction might take place at high dyeing temperatures with some vat dyes [14]. It is well known that it is more difficult to produce level dyeing in practice with vat dyes than with other dyes. Without the careful control of the dyeing condition, the initial dyeing rate of leuco vat dye to cellulose would be too fast, which might cause ring dyeing with an uncolored center core of the fiber. The leveling agent decreases the initial dyeing rate in the vat dyeing process to ensure level dyeing. The effect of the amount of leveling agent on the color yield of C.I. Vat Yellow 1 on viscose rayon and the new regenerated cellulose was given with an increased amount of leveling agent in Figure 9, which was attributed to the interaction between the vat dye and the leveling agent. Pregelal P, the leveling agent used in this study is a cationic surfactant and shows high affinity to vat dyes. It can interact with anionic leuco vat dye and can make a temporary complex with the dye during the dyeing process, thus lowering the dyeing rate on cellulose fiber. The color strength was very low when the large amount of leveling agent was added. It seems that the attraction force of the leveling agent with vat dye was so strong that it was difficult for the dye molecule to be separated from the leveling agent and migrate into the fiber when there is a high concentration of leveling agent. Therefore, the minimum amount of leveling agent should be used for good color strength as long as level dyeing can be obtained. The color strength of the dye on the new regenerated cellulose was higher than that on viscose rayon in all cases, indicating that it was easier for the vat dye to migrate into the less compact new regenerated cellulose fiber than viscose rayon.

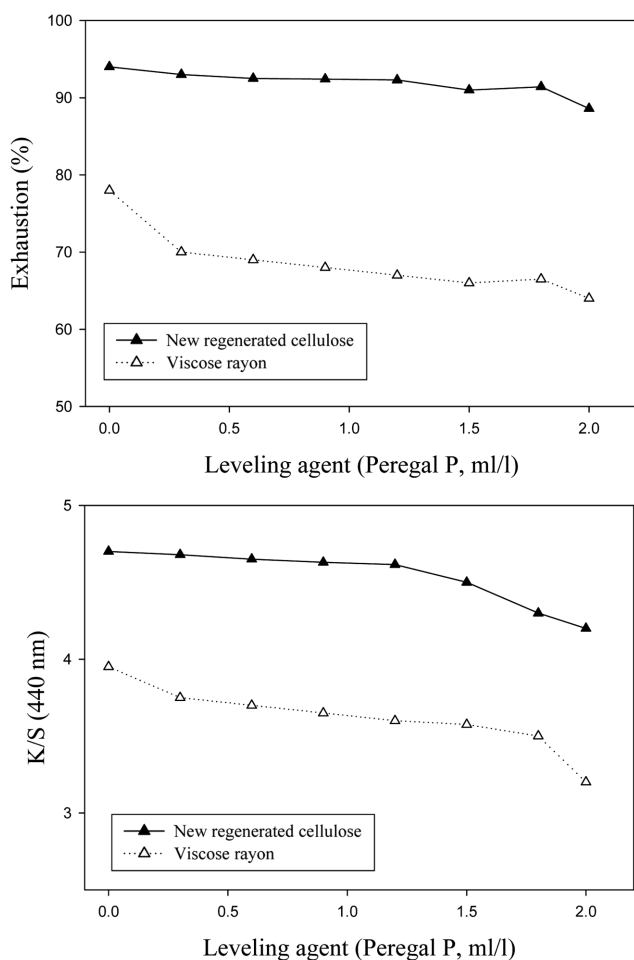


Figure 9. Effect of leveling agent addition to dye bath on exhaustion (%) and color strength (K/S) of dyeings on C.I. Vat Yellow 1 (dye 1 % o.w.f., liquor ratio 30:1).

Leveling Property

The leveling properties of the dyed new regenerated cellulose at different concentrations (0.5 %, 1.0 %, 1.5 %, 2.0 %, 3.0 %, and 4.0 %) of direct, reactive, and vat dye are illustrated in Figure 10, from which it is clear that the

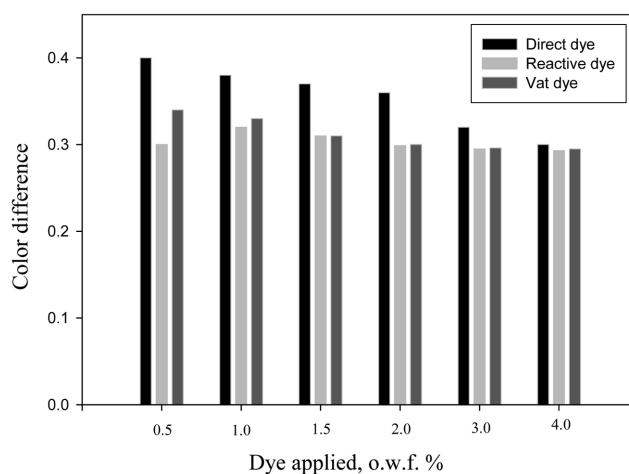


Figure 10. Average color difference (ΔE) of dyed new regenerated cellulose at different dye concentration.

average color difference (ΔE , calculated from the CIE L^*a^*b coordinates) indicated very good leveling properties. However, the results show that the leveling of the dyed new regenerated cellulose using reactive dye is slightly better than that of direct and vat dye. This can be attributed to the fact that the β -elimination reaction of reactive dye allows good dispersion because of the consequent reduction in the dye molecular size.

Color Fastness

Table 1 shows that the fastness to washing of 1/1 standard depth dyeings of C.I. Direct Red 2 on the new regenerated cellulose was slightly higher than that of comparable depth dyeings on viscose rayon. Table 1 also reveals that the rubbing fastness of the 1/1 standard depth dyeing of C.I. Direct Red 2 on the new regenerated cellulose was identical to that of the dye on viscose rayon. The fastness to light of the two dyeings was excellent (a rating of over 5), irrespective of dye applied. The results could be attributed to the new regenerated cellulose's excellent affinity to dyes presumably due to its the lower crystallinity (%) value and degree of orientation. In all types of cellulose fiber there are crystalline regions and non-crystalline regions. The crystallites lie preferentially parallel to the fiber axis and are separated by regions of lower order and intermicellar spaces. The average size of the crystallites and the quantitative ratio of crystallites to lower order fiber regions are strongly fiber-specific. Only water-swollen intermicellar spaces and lower order regions of the fiber are accessible to large dyes molecules. It is impossible for a dye to diffuse into the more highly oriented

Table 1. Wash fastness/rubbing of the direct dye (C.I. Direct Red 2)

Material ^b	Wash fastness				Rubbing fastness			
	Staining ^a		Change		Dry		Wet	
	R	V	R	V	R	V	R	V
A	5	5						
C	3	2						
N	5	5						
P	5	5	4	3/4	5	5	5	5
Ac	5	5						
W	5	5						

^aA: acetate, C: cotton, N: nylon, P: polyester, Ac: acrylic, W: wool,

^bR: new regenerated cellulose, V: viscose rayon.

Table 2. Perspiration/rubbing fastness of the reactive dye (C.I. Reactive Red 194)

Material ^a	Perspiration fastness				Rubbing fastness			
	Alkali		Acid		Dry		Wet	
	R	V	R	V	R	V	R	V
	5	5	4/5	4	5	5	4/5	4/5

^aFor key, see Table 1.

Table 3. Light/rubbing fastness of the vat dye (C.I. Vat Yellow 1)

Material ^a	Light fastness		Rubbing fastness			
	R	V	Dry		Wet	
			R	V	R	V
	7	7	5	4/5	4	3/4

^aFor key, see Table 1.

crystallites. Dyeing thus just initiates at the outer walls of the crystallites and in the less oriented cellulose [15].

In the case of rubbing fastness (Table 2), C.I. Reactive Red 194 showed slightly better rubbing fastness on new regenerated cellulose than on viscose rayon. Table 2 also reveals that the perspiration fastness of the 1/1 standard depth dyeing of the reactive dye on new regenerated cellulose was almost identical to that of the dye on viscose rayon. The fastness to light of the two dyed materials were excellent (a rating of over 5), irrespective of dye applied. Table 3 gives the light and rubbing fastness tests. The light fastness of vat dye was very good for both fibers. However, the rubbing fastness result was moderate possibly due to the physical properties of rayon such as low tenacity and poor abrasion resistance.

Conclusion

The dyeing properties of the new regenerated cellulose, which was prepared from cellulose acetate fiber by the hydrolysis of acetyl groups have been evaluated and compared with viscose rayon. The color strength of new regenerated cellulose for three dyes was higher than that of viscose rayon. Owing to the lower crystallinity (%) and degree of orientation, the molecules of the dye presumably diffuse into new regenerated cellulose more easily than viscose rayon. In addition, the new regenerated cellulose showed stable final color strength, irrespective of liquor ratio changes in dyeing process; hence the reproducibility of dyeing of new regenerated cellulose is expected to be excellent. Fastness properties of dyes on new regenerated cellulose were also better than on viscose rayon. The new regenerated cellulose has a lot of advantages over viscose rayon such as good dyeing and fastness properties and is part of an environmentally friendly manufacturing process. Based on these results, this new regenerated cellulose can be used as a momentous alternative to conventional viscose rayon in the near future.

Acknowledgement

We were gratefully supported by the American Association of Textile Chemists and Colorists (AATCC) Foundation Support Program, USA and the Graduate Student Support Plan (GSSP) in the college of Textiles, NC State University, USA and Industrial Technology Development Program in the Ministry of Commerce, Industry and Energy, South Korea.

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