

Printing Properties of Novel Regenerated Cellulosic Fibers

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Abstract: The reactive printing properties of regular viscose rayon and a new regenerated cellulosic fiber (*enVix*[®]) which was prepared from cellulose acetate fiber was investigated in a comparative manner. From the results, it was found that *enVix* exhibited better printing properties than regular viscose rayon. It showed stable final color yields, irrespective of the amount of thickener, hence reproducibility of printing of *enVix* is expected to be excellent. In addition, urea requirements were less for the printings on *enVix* than for the corresponding printing on viscose rayon. Therefore, *enVix* is also expected to reduce the amount of the urea which causes environmental problems in dyehouse effluent.

Keywords: Reactive dye, Regenerated cellulosic fiber, Printing properties, Supramolecular structure

Introduction

Rayon was the first man-made fiber. In 1924, the name "rayon" was adopted officially by the National Retail Dry Goods Association; before that time, it had been termed artificial silk, fiber silk, wood silk or viscose silk. Rayon fibers are a diverse group, all consisting of regenerated cellulose derived from wood pulp. Rayon fiber is defined by the U.S. Federal Trade Commission as "a manufactured fiber composed of regenerated cellulose, as well as manufactured fibers composed of regenerated cellulose in which substituents have replaced not more than 15 % of the hydrogens of the hydroxyl groups" (Rules and Regulations Under the Textile Fiber Products Identification Act, U.S. Federal Trade Commission). Substituents consist of manufacturing impurities, pigments, fire retardants or other additives [1].

Most rayon is made by the viscose process; rayon fibers are made from chemical cellulose (dissolved wood pulp), sodium hydroxide, carbon disulfide and sometimes modifiers, which are usually based on ethoxylated natural fatty acid amines. Some of the raw materials used in production of rayon are recoverable. By-product sodium sulfate is recovered and sold by rayon producers. Carbon disulfide is recovered in varying degrees by larger plants; on the average, 30-35 % is recovered, the balance being lost through volatilization or decomposition. Also, some zinc is collected as precipitates (zinc sulfide) in the spinning process and reworked by some producers [2]. However, although efforts by the major producers are expected to reduce carbon disulfide and zinc emissions, increasing environmental concern has centered on the conventional preparation of conventional regenerated cellulosic fibers since still more amount of the remaining zinc and carbon disulfide need to be recovered in waste treatment facilities at the plant site to meet established water pollution regulations.

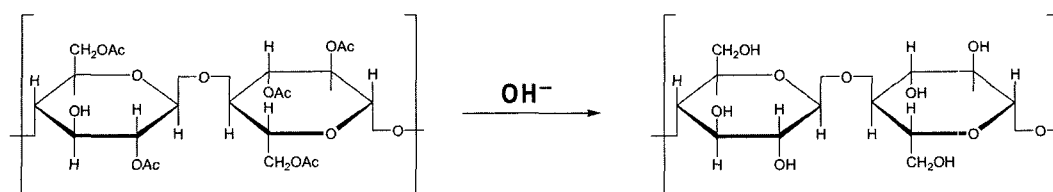
Recently, Acordis Cellulosic Fibers (Netherlands) and Lenzing (Austria) introduced a lyocell fiber, the newest member of the cellulosic fibers, using a more efficient and economical process than the universally used viscose process. Lyocell fiber is manufactured directly from high-purity cellulosic wood pulp, whereas rayon is manufactured from a cellulose derivative that is chemically "regenerated" back to cellulose during the spinning process. The cellulose is dissolved into a solvent, an amine oxide and then wet-spun; the solvent is recycled, eliminating the chemistry of the viscose process, which uses caustic soda, carbon disulfide and sulfuric acid to dissolve the pulp. Although environmentally safer, solvent-spun cellulose fibers are unlikely to replace viscose rayon to a significant extent in the near future because of the high cost of converting or building facilities.

More recently, SK Chemicals introduced a novel regenerated cellulosic fiber, *enVix*[®] 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 and has a composite crystalline structure of cellulose II and IV (Scheme 1) [3-5]. This regenerated fiber is claimed to offer environmental advantages over other conventional regenerated fibers because it does not emit toxic materials such as carbon disulfide and heavy metal ions.

In previous work, supramolecular structures of *enVix* and viscose rayon were investigated in a comparative manner [5-7]. The crystallinity of *enVix* was found to be lower than that of viscose rayon and the orientation of crystallites along the fiber axis in the former somewhat lower according to measurements of birefringence. Also, careful comparison of the dyeing properties of two rayons confirms that there is a correlation between supramolecular structures and the dyeing properties [8,9].

In the textile industry more than 70 % of all printed substrates are cellulosic fabrics and *enVix* is also a cellulosic fiber and therefore can be printed with any class of dyestuff suitable

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Scheme 1. Alkali-hydrolysis of cellulose acetate fibers.

for other cellulose. The most important printing method after pigment printing is that with reactive dyes. The consumption of reactive dyes continues to increase, since these dyes produce brilliant shades of very good fastness and leveling properties on cellulosic fibers [10].

The reactive printing properties of regular viscose rayon and a new regenerated cellulosic fiber which was prepared from cellulose acetate fiber was investigated in a comparative manner; the effect of thickeners, urea, alkali, and steaming time on the printing properties was compared between two regenerated cellulosic fibers.

Experimental

Materials

Viscose rayon fabric (interlock, 58 inch, 360 g/yd) and new regenerated cellulosic fabrics (interlock, 58 inch, 360 g/yd) obtained from cellulose acetate fibers by alkali-hydrolysis [3-5] were generously supplied by SK Chemicals (South Korea).

The reactive dye used was commercial samples that were not purified prior to use; Sunicion Blue P-3R (C.I. Reactive Blue 49, Figure 1) was kindly supplied by Ohyoung Corp. A commercial sample of synthetic thickener (XTN, polyacrylic acid) (Table 1) and soaping agent (SNOGEN CS-940N, non-ionic) were supplied by Libert Chemicals and Daeyoung Chemicals, respectively. All other reagents were of general purpose grade.

Table 1. Thickener used in present study

Thickeners	Ingredients
A	Sodium alginate
B	XTN (Synthetic thickener)
C	Sodium alginate + XTN

Table 2. Print paste recipes (unless otherwise stated)

Ingredients	Amount (g)
Stock thickener (8 %)	500
Urea	100
Alkali	15
<i>m</i> -Nitrobenzenesulfonate ^{a)}	15
Water	370
Total	1000

^{a)} Anti-reducing agent.

Printing

The printing paste was prepared by first dissolving 8 % of the thickener in water at a liquor ratio of 8:100. The dissolved reactive dye (2.0 wt% based on the print paste) either in the masked or free form was then added to the thickener solution with continuous stirring. Finally the other additives used were added to the printing paste according to the conditions presented in Table 2.

The flat screen printing technique was applied. The silk screen frame used in the printing process was made of natural silk strings (42 cm × 42 cm) fixed on a rectangular wood frame. The fabric to be printed is put under the silk screen and the printing paste is then applied on the fabric by using a wooden applicator with a rubber edge. All prints were carried out with one squeegee wipe with high reproducibility.

The printed fabric was left to air dry and steaming was carried out at 102 °C for 15 min in an autoclave using superheated steam. The steamed fabrics were then washed with cold water, hot water for 5 min and finally at 80 °C for 2 min with a solution containing 1 g/l non-ionic detergent (SNOGEN CS-940N). The printed fabrics were rinsed in cold water and air dried (Table 3).

Color Measurement

The color strength (K/S) of the dyed samples was measured using a spectrophotometer (Color-Eye 3000, Macbeth, Standard light D65, 10° standard observer, specular component included) interfaced with a personal computer.

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

where, R is the reflectance of an infinitely thick layer of material illuminated with light of a known wavelength, K is absorption coefficient and S is the scattering coefficient. The

Table 3. Printing conditions

Stage of work	Conditions for work
Printing	Flat screen printing, squeezing pressure 1.5 kg/cm ²
Drying	5 min in drying machine at 80 °C
Steaming	Pressure 0.4 kg/cm ² , saturated steam, 15 min at 102 °C
Soaping	Liquor ratio 10:1, non-ionic surfactant, 2 min at 80 °C
Drying	5 min in drying machine at 80 °C

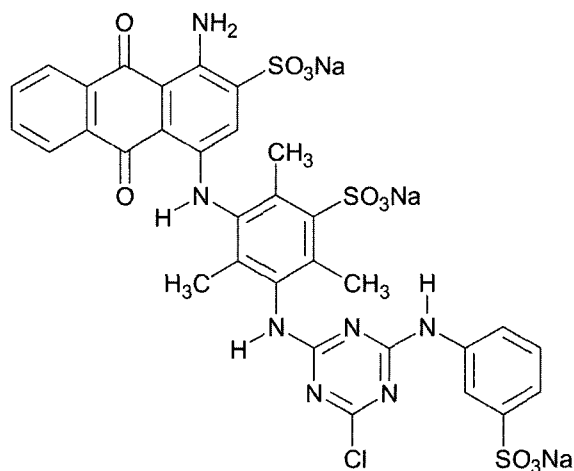


Figure 1. Chemical structure of C.I. Reactive Blue 49.

function K/S is directly proportional to the concentration of colorant in the substrate [11].

Results and Discussion

Textile printing is an important method of decorating textile fabric. The coloration is achieved either with dyes or pigments in a printing paste. Printing pastes are viscous liquids and thickeners provide the viscosity. A successful print involves correct color, sharpness of mark, levelness, good hand and efficient use of dye ("color yield"): all of these factors depend heavily on the type of thickener used and the resulting print paste rheology. When using dyes the paste also has to include all necessary wetting, dispersing and fixing agents. The thickener must be stable and compatible with all these components. In addition, the solids content of the thickener must provide sufficient adhesion of the dye on the fabric between printing and fixation [12].

In Figures 2-7, the reactive printing properties of two rayons were compared. The authors investigated the variation in dye yield with variation in thickener concentration, urea concentration, steaming time and viscosity of print paste, comparing the effect on the shade of *enVix* with that on viscose rayon.

Figure 2 shows the effect of various thickeners on the color strength of printed fabrics. Thickening agents form an essential part of any printing process. Thickeners used in textile printing are generally high molecular weight polymers. These act as vehicles for carrying dyestuffs, chemicals and other printing assistants to the textile material during the process of printing. Thickeners impart adhesivity and plasticity to the printing paste which can be applied on to the fabric without spreading and holding the dye molecule at the desired place until the transfer of dye into the fabric and its fixation are complete [13]. It is evident from Figure 2, the K/S values of the dyeings on *enVix* are higher than that on viscose rayon, irrespective of each of three thickeners, and these results are consistent with the previous work investigating their supramolecular structures

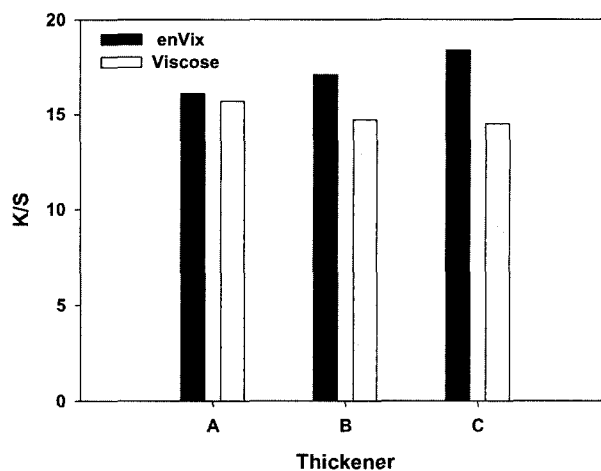


Figure 2. Effect of various thickeners on the color strength of printed fabrics (2.0 % of C.I. Reactive Blue 49).

and dyeing properties in a comparative manner [5,8,9]. The excellent color yields on *enVix* can be ascribed to the lower crystallinity (%) values (*enVix* 27 %, viscose rayon 39 %) and degree of orientation (*enVix* 1.93, viscose rayon 3.63); as a useful generalization, fibers may be regarded as structures in which there is a spread of molecular order, ranging from highly ordered crystalline domains to disordered amorphous regions [14]. The strength originates in the crystalline material while the amorphous material provides the flexibility, porosity and the regions generally accessible to liquids, dyes and other reagents such as thickeners. Therefore, the fiber properties, including dyeing properties, vary depending upon the relative degrees of order and disorder in the structure (often described loosely as the crystalline/amorphous ratio) and also molecular alignment (degree of orientation), i.e., lower orientation and crystallinity mean a higher rate of dye diffusion within these fibers.

Also, taking a closer look reveals that, *enVix* showed higher color yield when the mixed thickener rather than other thickeners (sodium alginate or synthetic thickener only) was used. The quality of print depends largely on the chemical and physical properties of the thickeners used. To a certain extent the depth, brightness of color and especially sharpness and smoothness of the print depend on nature of the thickeners. The essential requirements of thickeners are desirable physical and chemical properties such as viscosity, flow property, ability to wet and adhere to the surface of printing machine. It should give a good color yield, must be economical and abundantly available. The thickener paste must not have any affinity for or reactivity with the dye and should not withhold the diffusion of the dye into the fabric. It should also be easily washable once the printing is over [13].

At present, sodium alginates are the most widely used thickeners in reactive dye printing. Alginates are chain-forming heteropolysaccharides made up of blocks of mannuronic acid and guluronic acid; their use in printing with reactive dyes

represents the largest application for these polymers. Alginates offer the printer several advantages: they wash out easily and cause no fabric stiffness. However, the fluctuation in the price and quality of the products is a major deficiency of these polymers which affects the development and use of alternative thickeners [10]. Especially, the relatively high cost and limited supply of alginates has spurred efforts to find alternatives such as synthetic thickeners. Synthetic thickeners of polyacrylic acid can be produced in many forms. They predominate in the printing of pigments where their low solids content and low VOC (Volatile organic compounds) content are important. They additionally offer advantages over natural thickeners in quick and easy paste preparation and viscosity adjustment, and consistency of quality and supply. As used, polyacrylic acid is anionic (the carboxylic acid groups are neutralized, typically with ammonia) and does not react with typical reactive dyes, and many efforts have been made to adopt them for reactive dye printing. However, alginates, polyacrylic acids, or carboxymethyl starches each have not only advantages but also disadvantages for the printing of reactive dyes: none is ideal. The situation is that the use of mixed thickener is not new [15].

Figure 3 shows the effect of various thickeners on the chromaticity (C^*) of printed fabrics. Evidently, chromaticity values (C^*) of *enVix* were higher than those of viscose rayon, irrespective of thickeners used. Although it is not easy to guess the clear reason for the brighter color properties on *enVix* compared with the viscose rayon, it seems to have a relation to the difference in their supramolecular structure.

Figure 4 shows the effect of urea concentration on the color strength of printed fabrics. In the absence of urea color yields are low, unless fixation can take place during drying. For many dyes, color yield increases up to a maximum when 150-200 g/kg of urea is used. Urea promotes water absorption during steaming in varying ways depending on polymer

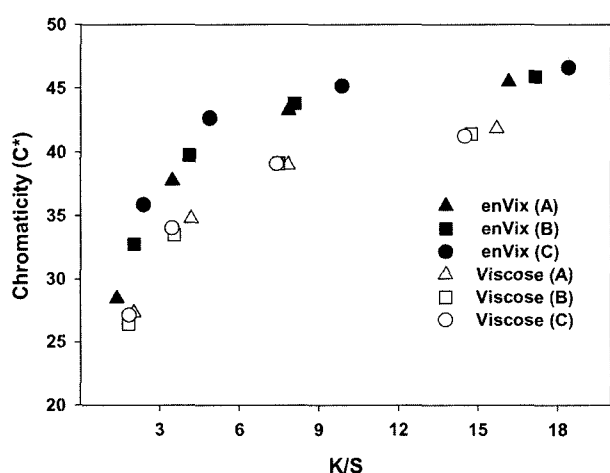


Figure 3. Effect of various thickeners on the chromaticity (C^*) of printed fabrics (0.25, 0.5, 1.0 and 2.0 % of C.I. Reactive Blue 49, thickeners A, B and C).

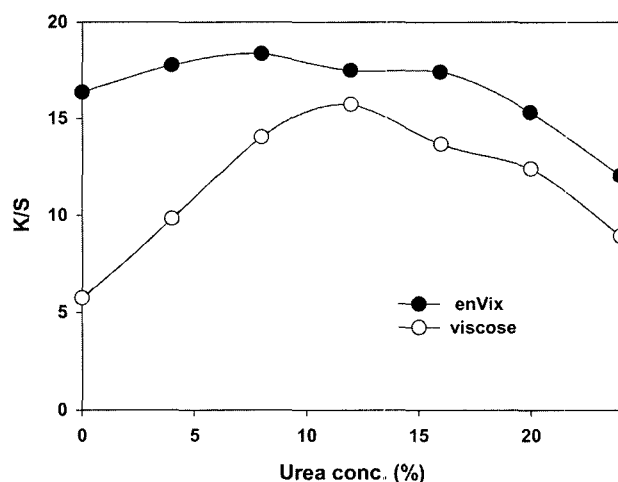


Figure 4. Effect of urea concentration on the color strength of printed fabrics (2.0 % of C.I. Reactive Blue 49, thickener C).

thickener [16]. The hydration spheres of the urea molecules taken up onto the polymers are the amino groups directed outwards. The hydrophilicity of polymers is therefore increased by the amino groups; but the take up can also promote the swellability of the polymers without increasing hydration if the cohesion of the macromolecules is reduced. In addition, urea functions in the dried on print paste (also in the preparation of the print paste) as a hydrotropic agent. As a water-soluble compound itself, urea increases the water solubility of the dyes broken down in the dried print paste, depending on the quantity used. However, urea causes environmental problems. There are official measures to discharge nitrates from drinking water. These are produced in excess due to the ground water being overloaded with nitrogen compounds via the natural nitrogen circulation and their equilibrium transfer. That is why the elimination of urea from printing recipes or at least the reduction of its concentration in the wastewater from after-print washings is striven for. But for reasons of print technology and colloidal chemicals, the elimination of urea from the recipes is not easy.

Figure 4 shows that the less amount of urea is required for *enVix* than viscose rayon to get the highest color strength; the optimum concentration urea for *enVix* was 8.0 % and that for viscose rayon was 12 %, respectively. Therefore, it can be stated that lower concentration of urea is required for the printing of *enVix* and consequently, the amount of urea in the wastewater can be reduced. Once again, the color yield (K/S) of the printings on *enVix* is higher than that on viscose rayon and this result is also consistent with the previous work investigating exhaust dyeing properties [5,8,9]. Furthermore, taking a closer look reveals that *enVix* is relatively insensitive to the urea concentration, compared with viscose rayon in the range of 0-24 %.

Further evidence that the printing properties of *enVix* is better than that of viscose rayon was provided by the results

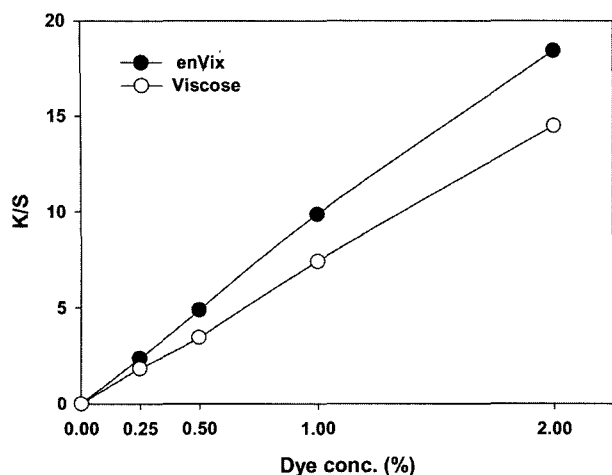


Figure 5. Build-up properties of C.I. Reactive Blue 49 on regenerated cellulosic fibers (thickeners C).

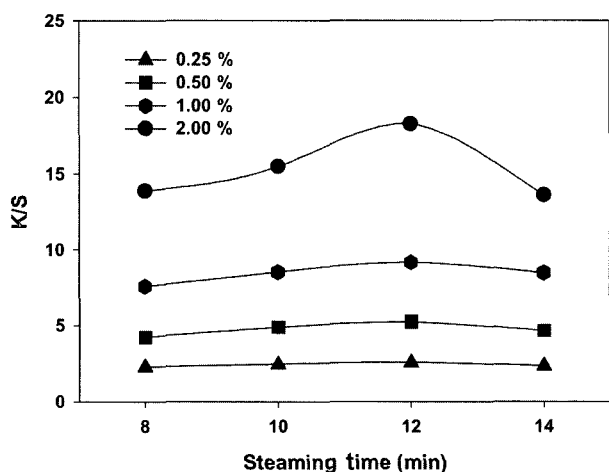


Figure 6. Effect of steaming time on the color strength of printed *enVix* fabrics (C.I. Reactive Blue 49, thickener C, steaming at 102 °C).

of build-up properties obtained for Reactive Blue 49 (Figure 5); *enVix* exhibited a deeper shade than viscose rayon (higher K/S values by 27.1 % in 2.0 % printing).

Figure 6 shows the effect of steaming time on the color strength of printed *enVix* fabrics. It is clear that steaming time plays an important role in the printing process. The operation of steaming printed fabrics may be likened to a dyeing operation. Before steaming, the bulk of the dyestuff is held in a dried film of thickening agent; a small proportion may have penetrated into the fiber during drying but this is insufficient to be of much consequence. During the steaming operation the printed areas absorb moisture and form a very concentrated dyebath from which dyeing of the fibre takes place. The function of the thickening agent during this period is to prevent the dyestuff from spreading outside the area originally printed, that is, to prevent 'bleeding'. The

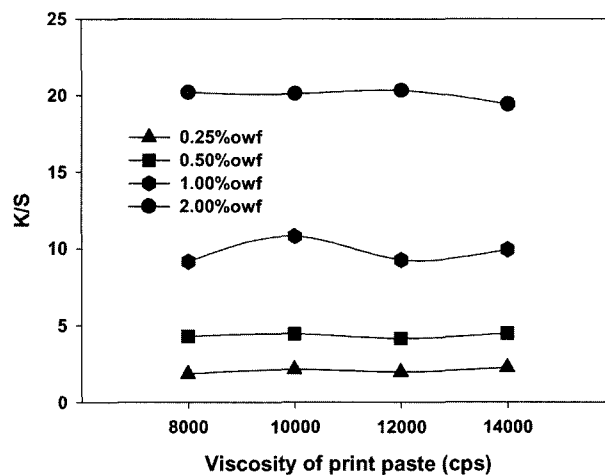


Figure 7. Effect of viscosity of print paste on the color strength of printed *enVix* fabrics (C.I. Reactive Blue 49, thickener C).

concentrated 'dyebath' formed on the fiber exists more in the form of a gel than a solution and any tendency to bleed is restricted. In addition to promoting the formation of a localized dyebath the steam may have other functions demanding more exact control on the steamer. Relatively short steaming treatments are required to fix the reactive dyestuffs where reaction with the fiber as opposed to a simple dyeing operation is involved. Dichlorotriazine type reactive dyes will fix by steaming for as short a time as 15 seconds while the less reactive monochlorotriazine type reactive dyes require a minimum time of 10 min [17]. Figure 5 shows the printed *enVix* fabrics exhibited similar levels of K/S values except high dye concentration printing, irrespective of steaming time; in the case of 2.0 % reactive dye printing, relatively longer steaming time (12 min) was required to obtain the highest K/S values probably because it takes more steaming time to develop full color shade depth in higher dye concentration.

Figure 7 shows the effect of viscosity of printing paste on the color strength of printed *enVix* fabrics. Typical print pastes are described as non-Newtonian, because their viscosity changes as the rate of shear is changed. Measurement of their viscosity, therefore, is not so straightforward. Information is required, nevertheless, because the viscosity of a print paste during the shearing that occurs in the printing process will determine the quality of the print. It can be seen from Figure 7, the viscosity of print paste did not affect the color yield of printed *enVix* fabrics in the range of 800-1400 cps.

Conclusions

A new regenerated cellulosic fiber was prepared by saponifying at least 75 % of the total acetyl groups of a cellulose acetate fiber with a degree of substitution of 2.0 or higher into hydroxyl groups. As is to be expected, the printing properties of two regenerated cellulosic fibers were not the same because of their supramolecular structures [5]. The printing properties

on new regenerated cellulosic fiber, *enVix* was compared with those on regular viscose rayon, and shown to be excellent. Careful comparison of reactive printing properties on two regenerated cellulosic fibers confirms that there is a correlation between supramolecular structures and the printing properties; *enVix* exhibited higher K/S values and better build-up properties than viscose rayon, presumably due to the lower crystallinity (%) and degree of orientation. It also showed stable final color yields, irrespective of the amount of thickener, hence reproducibility of printing of *enVix* is expected to be excellent. In addition, urea requirements were less for the printings on *enVix* than for the corresponding printing on viscose rayon. Therefore, *enVix* is expected to reduce the amount of the urea which causes environmental problems in the wastewater. The overall results obtained suggest that this novel regenerated cellulosic fiber could be used as an important alternative to conventional viscose rayon although more detailed studies on the new regenerated cellulosic fiber is necessary before any definite conclusions can be drawn.

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References

1. S. Marash, F. Dubois, and Y. Sakuma, *CEH Marketing Research Report, Rayon and Lyocell Fibers*, 2001.
2. W. Hickman, *J. Soc. Dyers Color.*, **109**, 32 (1993).
3. I. S. Kim, J. S. An, and B. H. Kim, *Korea Patent*, 2000-0015443.
4. I. S. Kim, J. S. An, and B. H. Kim, *U. S. Patent*, **6**, 361, 862 (2002).
5. J. Koh, I. S. Kim, S. S. Kim, W. S. Shim, J. P. Kim, S. Y. Kwak, S. W. Chun, and Y. K. Kwon, *J. Appl. Polym. Sci.*, **91**, 3481 (2004).
6. J. Koh and D. H. Cho, *Fiber Polymer.*, **5**, 134 (2004).
7. J. Koh, S. H. Park, G. H. Shim, D. H. Cho, and J. P. Kim, *Fiber Polymer.*, **5**, 110 (2004).
8. J. Koh, I. S. Kim, S. S. Kim, W. S. Shim, and J. P. Kim, *Fiber Polymer.*, **1**, 44 (2004).
9. W. S. Shim, J. J. Lee, J. P. Kim, S. W. Chun, S. Y. Kwak, I. S. Kim, J. S. An, J. Koh, and Y. K. Kwon, *Text. Res. J.*, in press.
10. S. Š. Turk and R. Schneider, *Dyes and Pigments*, **47**, 269 (2000).
11. W. Ingamells, "Colour for Textiles: A Users Handbook", p.154, Society of Dyers and Colorists, Bradford, 1993.
12. L. W. C. Miles, "Textile Printing", 2nd ed., p.240, Society of Dyers and Colorists, 1994.
13. M. D. Teli, V. Shanbag, P. R. Kulkarni, and R. S. Singhal, *Dyes and Pigments*, **31**, 119 (1996).
14. A. Johnson, "The Theory of Coloration of Textiles", 2nd ed., p.184, Society of Dyers and Colorists, Bradford, 1989.
15. E. P. A. Kumbasar and M. Bide, *Dyes and Pigments*, **47**, 189 (2000).
16. H. K. Rouette, "Encyclopedia in Textile Finishing", p.2464, Springer, Berlin, 2000.
17. W. Clarke, "An Introduction to Textile Printing", 4th ed., p.61, Newness-Butterworths, London, 1974.