Fibers and Polymers 2004, Vol.5, No.1, 44-51

Dyeing Properties of Bi-functional Reactive Dyes on a Novel Regenerated Cellulosic Fiber

Joonseok Koh*, Ik Soo Kim[1], Sung Soo Kim[2], Woo Sub Shim[2], and Jae Pil Kim[2]

Fiber and Textile R&D Center, Hyosung Coporation, Anyang, Kyonggi-Do 431-080, Korea
[1]enVix R&D Team, SK Chemicals, Suwon, Kyonggi-Do 440-745, Korea
[2]School of Materials Science & Engineering, College of Engineering, Seoul National University, Seoul 151-742, Korea
(Received September 30, 2003; Revised December 12, 2003; Accepted December 19, 2003)

Abstract: Three bi-functional reactive dyes such as Bis(vinylsulphone) type, Bis(monochlorotriazine) type and Bis(mononicotinotriazine) type were applied to regular viscose rayon and new regenerated cellulosic fiber (*enVix*®) which was prepared from cellulose acetate fiber by the hydrolysis of acetyl groups, and their dyeing properties and fastness properties were compared. *enVix* exhibited better dyeability and fastness than regular viscose rayon and these results were also explained by the differences in the supramolecular structure of these two fibers.

Keywords: Bi-functional reactive dyes, Regenerated cellulosic fiber, Dyeing properties, Fastness

Introduction

The name "Rayon" was adopted officially by the National retail Dry Goods Association in 1924; 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].

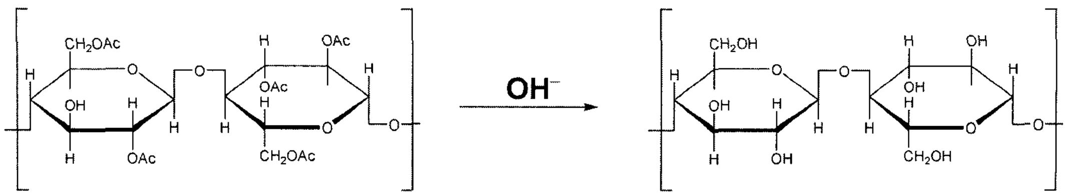
Most rayon is made by the viscose process ; rayon fibers are made from chemical cellulose (dissolved wood pulp), sodium hydroxide, carbon disulfide and sometimes modifiers which are usually based on ethoxylated natural fatty acid amines. Some of the raw materials used in production of rayon are recoverable. 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]. Although efforts by the major producers are expected to reduce carbon disulfide and zinc emissions, 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.

In 1980's, Acordis Cellulosic Fibers (Netherlands) 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, replacing the viscose process, which uses caustic soda, carbon disulfide and sulfuric acid to dissolve the pulp. Although environmentally safer, solvent-spun cellulosics are unlikely to replace viscose rayon to a significant extent in the near future because of the high cost of converting or building facilities.

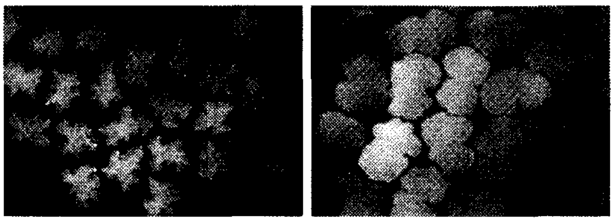
Recently, SK Chemicals introduced a novel regenerated cellulosic fiber, *enVix*® which was prepared from a cellulose acetate fiber with a degree of substitution of 2.0 or higher by saponifying 75 % or greater of the total acetyl groups of the cellulose acetate fiber into hydroxyl groups and has a composite 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 dose not emit toxic materials such as carbon disulfide and heavy metal ions.

enVix is a cellulosic fiber and therefore can be dyed with any class of dyestuff suitable for other cellulosics. Information in this article is confined to reactive dyes as they are seen as the major dye class used on cellulosic fibers in the world. Three types of bi-functional reactive dye was applied to regular viscose rayon and a new regenerated cellulosic fiber which was prepared from cellulose acetate fiber; their dyeing properties and fastness properties were compared and the results were also explained by the differences in the supramolecular structure of these two fibers.

*Corresponding author: ccdjko@hyosung.com



Scheme 1. Alkali-hydrolysis of cellulose acetate fibers.



(a) Viscose rayon (b) en Vix

Figure 1. Cross-section of the regenerated faibers.

Experimental

Materials

Viscose rayon fabrics (Plain weave, Warp 82 threads/inch, Weft 62 threads/inch, filament fineness 2.5 denier/filament) and new regenerated cellulosic fabrics (Plain weave, Warp 96 threads/inch, Weft 56 threads/inch, filament fineness 2.5 denier/filament) obtained from cellulose acetate fibers by alkali-hydrolysis [3-5] were generously supplied by SK Chemicals (South Korea) (Figure 1).

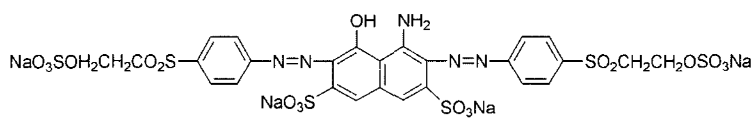
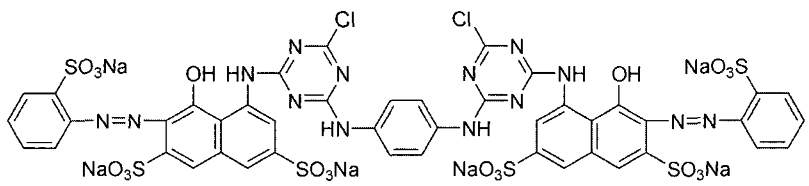
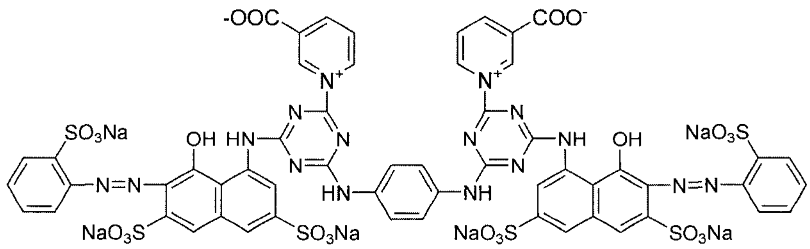
The three bi-functional reactive dyes used were commercial samples that were not purified prior to use; Remazol Black B (C.I. Reactive Black 5, Bis(vinylsulphone) type), Procion H-E3B (C.I. Reactive Red 120, Bis(monochlorotriazine) type), and Kayacelon React CN-3B (C.I. Reactive Red 221, Bis (mononicotinotriazine) type) were kindly supplied by BASF and Nippon Kayaku (Table 1). A commercial sample of soaping agent (SNOGEN CS-940N, non-ionic) was supplied by Daeyoung Chemicals. All other reagents were of general purpose grade.

Dyeing

A 50 m*l* dyebath, suitable for a 2.0 g sample of rayon (liquor ratio 1:25), containing a reactive dye and Glauber's salt was prepared. Dyeing was performed under each appropriate condition (Figure 2) in an Ahiba Nuiance laboratory dyeing machine (Ahiba, Datacolor International, Switzerland). The fabric which had been dyed with reactive dyes were rinsed and after-treated with soaping agent (0.5 g/*l*) for 30 min at 98 °C.

The rayon was dyed at various dyebath conditions (salt concentration, alkali concentration, liquor ratio, and dye

Table 1. Structures of the reactive dyes used in this study

Dyes/Type	Chemical structures
C.I. Reactive Black 5 Bis(vinylsulphone) (Bis-VS)	
C.I. Reactive Red 120 Bis(monochlorotriazine) (Bis-MCT)	
C.I. Reactive Red 221 Bis(mononicotinotriazine) (Bis-MNT)	

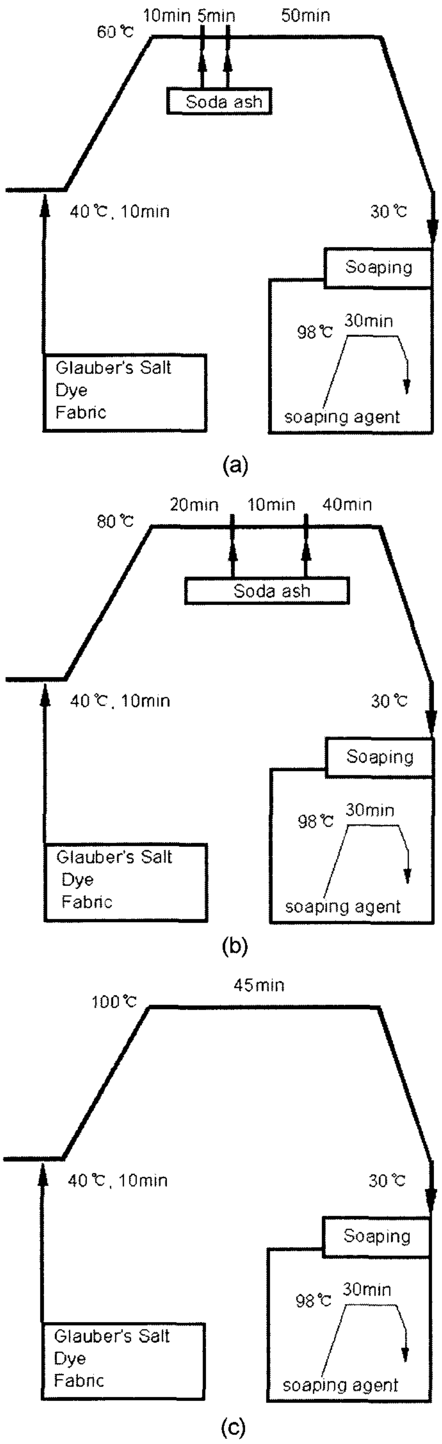


Figure 2. Reactive dyeing profiles (a) Bi-VS type, (b) Bi-MCT type, (c) Bi-MNT type.

concentration) in order to investigate their effects on the dyeing properties of the regenerated cellulosic fibers. Exhaustion behavior of reactive dyes on the fabric was also investigated by monitoring the exhaustion (%) values of dyed fabrics.

The extent of dye exhaustion (%) was determined using equation (1) 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
A_b : Absorbance of the dyebath before dyeing

Color Fastness

The regenerated cellulosic fibers were dyed (1/1 standard depth), after-treated with soaping agent and heatset (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 ISO 105 B02 (color fastness to light). Staining and change in color were assessed using gray scales.

Results and Discussion

In Figures 3-7, the dyeing properties of two rayons were compared. The authors investigated the variation in dye yield with variation in salt concentration, alkali concentration and liquor ratio, comparing the effect on the shade of *enVix* with that on viscose rayon.

The molecules of reactive dyes are smaller than those of direct dyes, and their smaller size is accompanied by a correspondingly lower substantivity. The molecules of direct dyes are made deliberately large so as to build up the physical attraction between fiber and dye, thus making them more substantive. Much smaller molecules may be suitable for reactive dyes because one covalent bond is about thirty times as strong as one van der Waals bond.

The generally accepted model for dyeing of reactive dyes into cellulosic fibers consists of two phases; adsorption and diffusion phase in which the reactive dye is adsorbed onto the cellulose surface and then diffuses into the fiber matrix, and fixation phase in which dye anions react with cellulose [6]. Reactive dyes are usually applied with the addition of electrolyte and the extent to which reactive dyes are affected by the addition of electrolytes to the dyebath is known as salt sensitivity. The addition of electrolyte increases the rate of strike of the dye. The commonly used electrolytes are Glauber's salt (sodium sulphate) and common salt (sodium chloride); when cellulose is immersed in a solution of a reactive 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. There is an electrostatic repulsion between the anionic reactive dye and cellulose. Therefore, the probability of the dye adsorbing onto the fiber, i.e. its level of substantivity, is reduced. The substantivity of the dye for cellulose is the proportion of the dye absorbed by the fiber compared with that remaining in the dyebath. By adding inert electrolyte such as common salt or Glaubler's salt to the dyebath, this electrostatic barrier, known as the Donnan Potential, can be largely suppressed, facilitating dye/fiber contact and allowing better interaction of the Yoshida and van der Waals forces and hence improving substantivity. The diffusion coefficient of the dye is therefore a function of both dye and electrolyte concentration [7]. The result in Figure 3 supports this statement, in that the exhaustion (%) of the dyeings increased with increasing concentration of salt applied. The dye exhaustion (%) value of reactive dye is linear function of salt concentration particularly at lower dye concentrations although the slope decreases with increasing salt concentration. It is considered that the initial rapid rise is due to the response of dye to the lowering of electrical potential barrier to diffusion as the concentration of electrolyte increases. Of the three bi-functional reactive dyes applied, the dyebath exhaustion (%) of C.I. Reactive Red 221 (Bis-MNT type) was the lowest, that of C.I. Reactive Black 5 (Bis-VS type) is of lower than that of C.I. Reactive Red 120 (Bis-MCT type). In the case of Bis-MNT reactive dyes (C.I. Reactive Red 221), the negative charge on the nicotino group increase an electrostatic repulsion between dye and cellulose and consequently, its level of substantivity is reduced. Also, C.I. Reactive Black 5 showed relatively low substantivity because of its high solubility due to four solubilizing groups in the structure. In the case of Bis-MCT reactive dyes, unlike the sulphatoethylsulphone group, substituted triazine reactive systems readily lend themselves to substantivity enhancement [8]. It is natural result the low affinity-dye (c. C.I. Reactive Red 221) shows the greater sensitivity than the high-affinity dye (b. C.I. Reactive Red 120) to salt concentration.

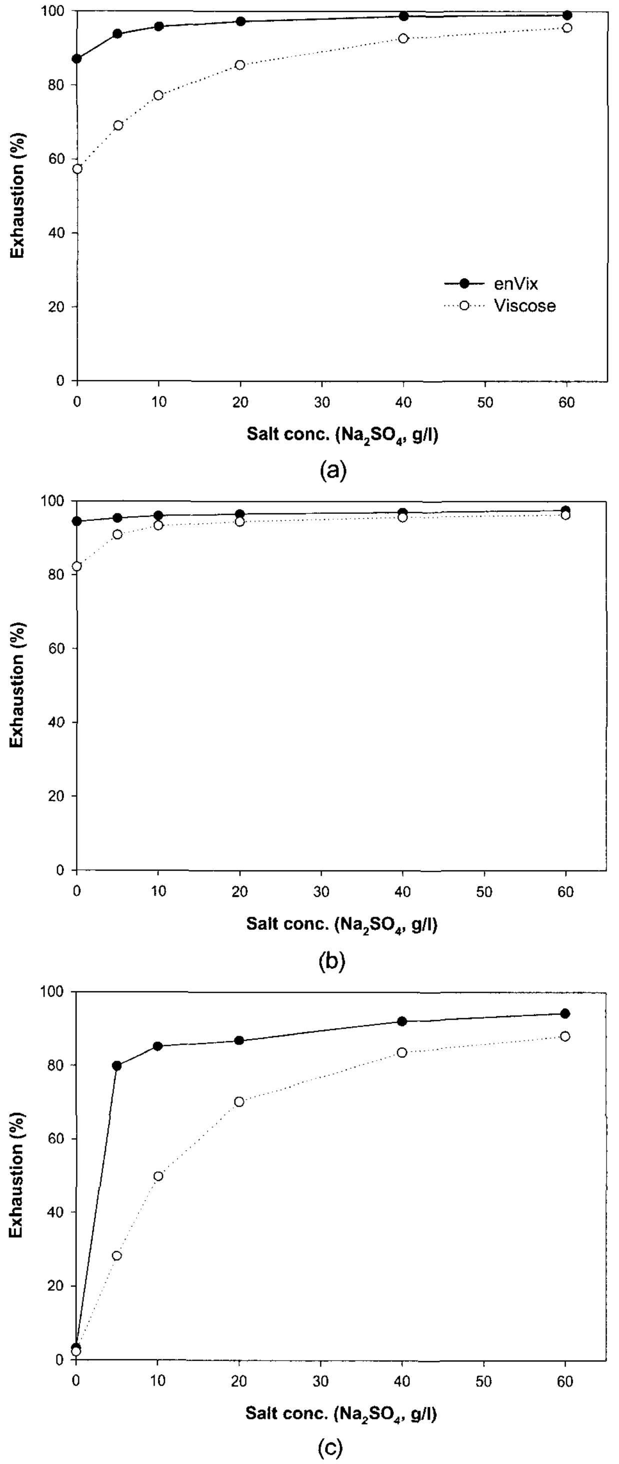


Figure 3. Salt effects on exhaustion (%) of dyeings (dye 2.0 %o.w.f., liquor ratio 1:20) (a) C.I. Reactive Black 5 (Bis-VS), (b) C.I. Reactive Red 120 (Bis-MCT), (c) C.I. Reactive Red 221 (Bis-MNT).

It is also evident from Figure 3, the exhaustion (%) of the dyeings on *enVix* are higher than that on viscose rayon for all dyes and these results are consistent with the previous work investigating dyeing properties of direct dye [5]. The excellent dyeing yields on *enVix* could be presumably ascribed to the lower crystallinity (%) values (*enVix* 27 %, viscose rayon 39 %) and degree of orientation (*enVix* 1.93, viscose rayon 3.63) which was previously investigated ; 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 [9]. 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. Therefore, the fiber properties, including dyeing properties, vary depending upon the relative degrees of order and disorder in the structure and also molecular alignment, i.e. lower orientation and crystallinity mean a higher rate of dye diffusion with these fibers.

Figure 4 shows the exhaustion (%) of the dyeings on *enVix* are higher than that on viscose rayon for each of two reactive dyes, and this result is also consistent with the previous work investigating dyeing properties of direct dye. The exhaustion values of two dyes applied were reached to the saturation levels at low alkaline concentration presumably because of the excellent dyeing properties of regenerated

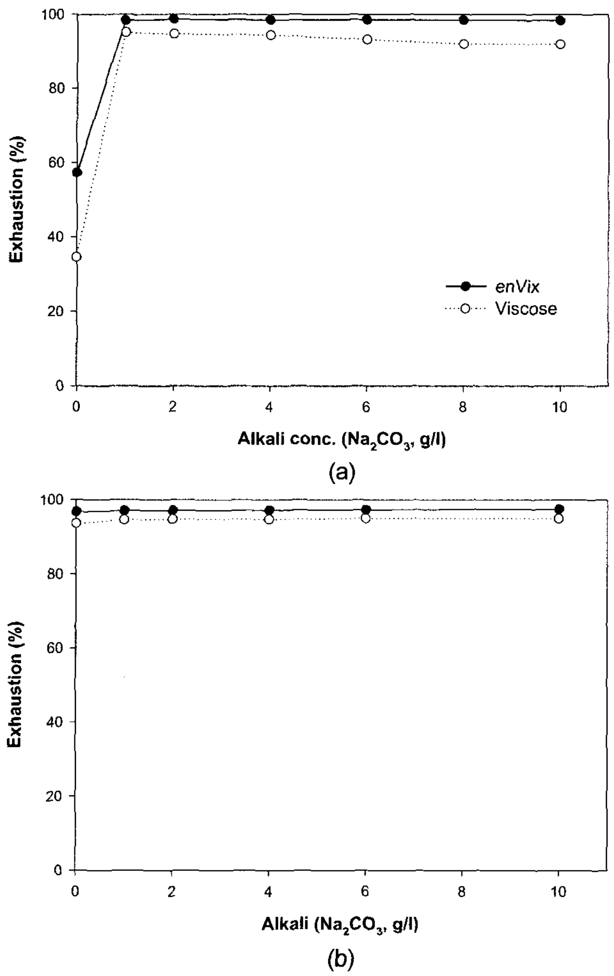


Figure 4. Alkali effects on exhaustion (%) of dyeings (dye 2.0 %o.w.f., liquor ratio 1:20) (a) C.I. Reactive Black 5 (Bis-VS), (b) C.I. Reactive Red 120 (Bis-MCT).

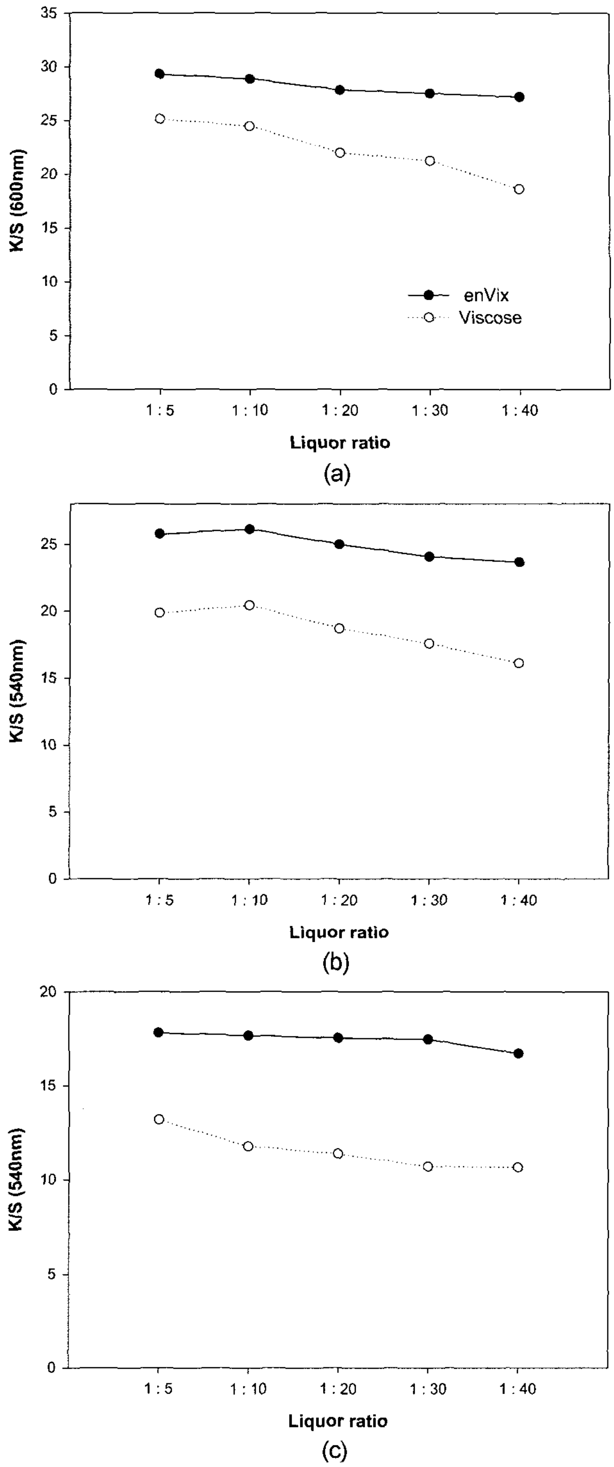


Figure 5. Liquor ratio effects on K/S of the dyed fabrics (dye 2.0 %o.w.f., salt 20 g/*l*) (a) C.I. Reactive Black 5 (Bis-VS), (b) C.I. Reactive Red 120 (Bis-MCT), (c) C.I. Reactive Red 221 (Bis-MNT).

cellulosic fibers ; generally, salt and alkali requirements are lower for reactive dyes on regenerated cellulosic fibers than for the corresponding dyeings on cotton. Especially the Bis-MCT dye showed excellent exhaustion (%) even without alkali addition while the Bis-VS dye showed low exhaustion (%) without alkali. In the case of the Bis-VS dye, the subtantivity for cellulose is enhanced as the precursor groups lose their ionic charge by 1,2-elimination.

Figure 5 shows the liquor ratio effects on the dyeability of the regenerated cellulosic fibers. As expected, the reactive dyes decrease 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 fiber surface decreases, i.e. fewer dye molecules (per unit of time) are adsorbed onto the fiber surface. Equilibrium between adsorption and desorption is thus displaced, desorption becoming stronger, i.e. substantivity is lower. This decrease in substantivity as the liquor ratio was relatively less marked with *enVix* than viscose rayon especially in the case of C.I. Reactive Black 5. It is interesting to note that reproducibility on *enVix* compared with that of viscose rayon is better, being particularly resilient to changes in liquor ratio. It can be seen that *enVix* is relatively insensitive to process variables.

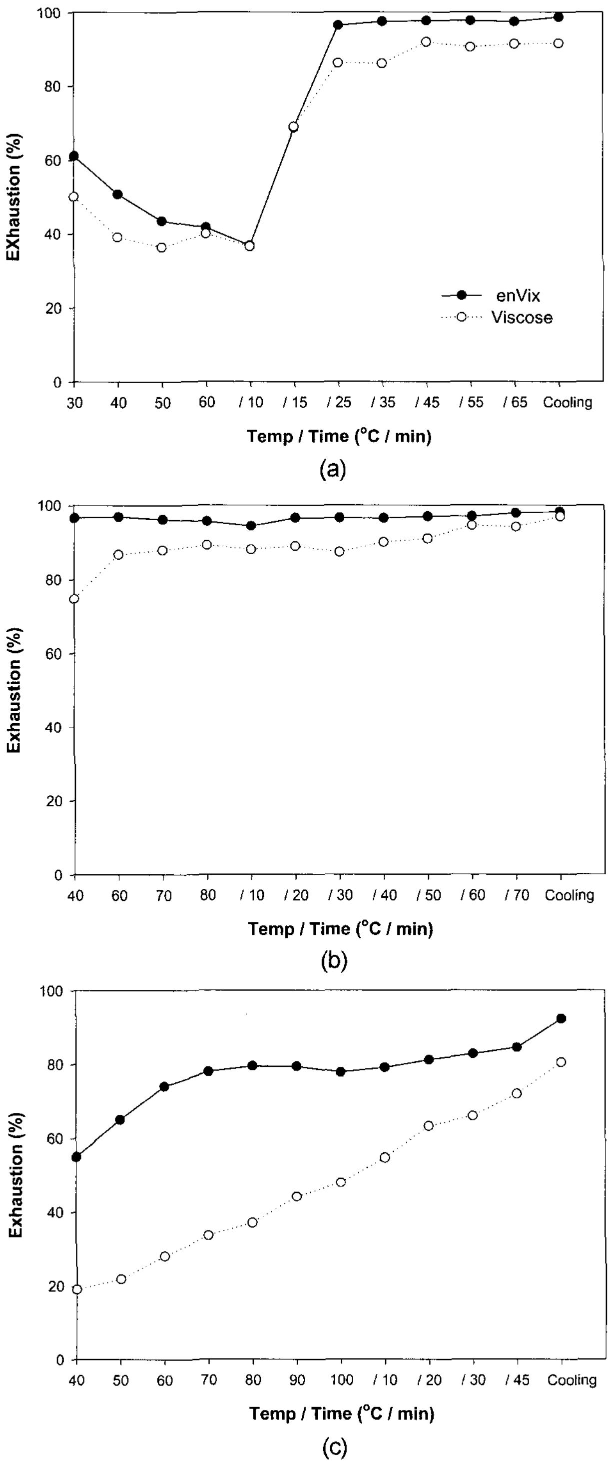


Figure 6. Exhaustion behaviors of reactive dyes on regenerated cellulosic fibers (dye 2.0 %o.w.f., salt 20 g/*l*, liquor ratio 1:20) (a) C.I. Reactive Black 5 (Bis-VS), (b) C.I. Reactive Red 120 (Bis-MCT), (c) C.I. Reactive Red 221 (Bis-MNT).

Figure 6 shows the exhaustion behaviors of reactive dyes on regenerated cellulose fibers during dyeing. As is to be

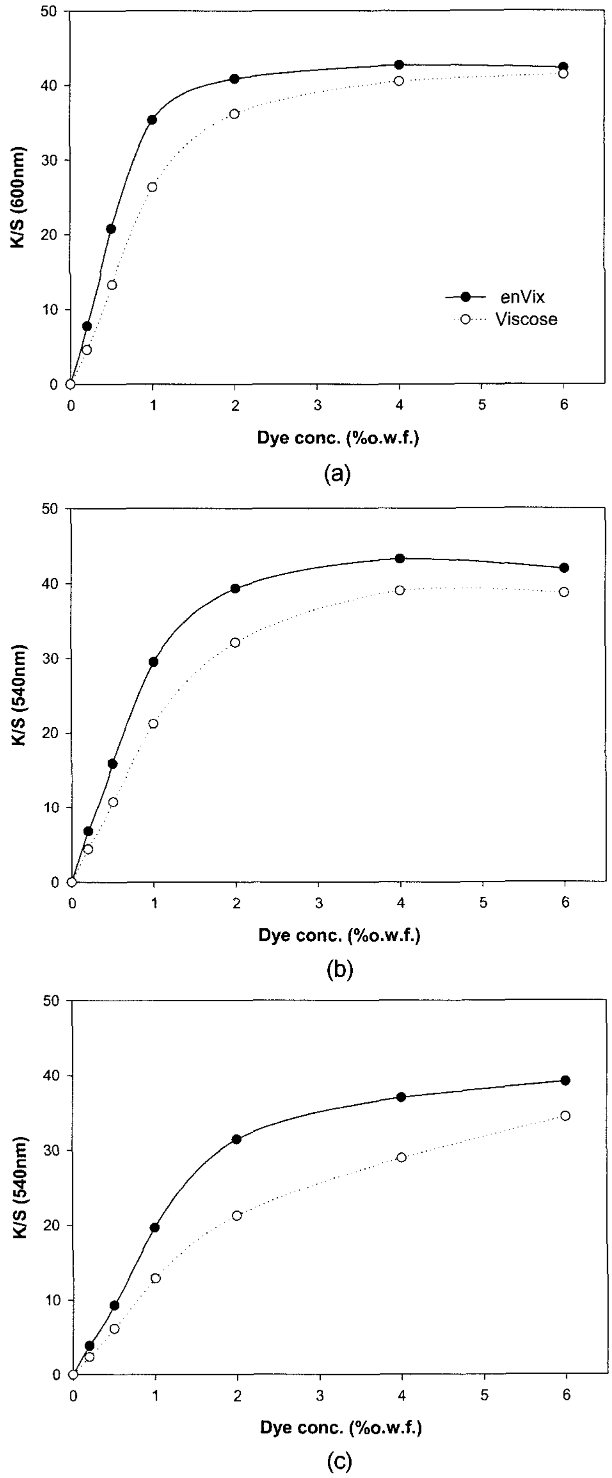


Figure 7. Build-up properties of reactive dyes on regenerated cellulosic fibers (salt 20 g/*l*, liquor ratio 1:20) (a) C.I. Reactive Black 5 (Bis-VS), (b) C.I. Reactive Red 120 (Bis-MCT), (c) C.I. Reactive Red 221 (Bis-MNT).

expected, the dyeing rate of two rayons is not the same because of their supramolecular structures [5]. Different dyeing rates brought about by the difference in physical structure are clearly of practical importance. Predictably, *enVix* showed faster exhaustion behavior than viscose rayon, presumably due to the lower crystallinity (%) values 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 regions of lower order are strongly fiber-specific. Only water-swollen intermicellar spaces and regions of lower order of the fiber are accessible to large reactive dyes molecules. It is completely impossible for a dye to diffuse into the highly oriented crystallites. Dyeing therefore only proceeds at the outer walls of the crystallites and in the non-oriented cellulose.

As seen in Figure 6, it is evident that the bis-MNT reactive dye shows slower dyeing rate than the Bis-VS reactive dye and the Bis-MCT reactive dye, presumably because of its lower substantivity, bigger molecular size and steric hindrance (Molecular weight: Bis-MNT=1511.39, Bis-MCT=1338, Bis-VS=991.82).

Further evidence that the dyeability of *enVix* is better than that of viscose rayon was provided by the results of build-up properties obtained for the three types of reactive dye; as Figure 7 shows *enVix* dyed to a much deeper shade than viscose rayon.

Table 2. Wash fastness of the reactive dyes on regenerated cellulose fibers

Dyes	Change		Staining	
	enVix	Viscose	*enVix*	Viscose
C.I. Reactive Black 5 (Bis-VS)	4-5	4	4[b]	3[b]
C.I. Reactive Red 120 (Bis-MCT)	4-5	4	4-5[a]	4[a]
C.I. Reactive Red 221 (Bis-MNT)	4	3	3[b]	2-3[b]

[a]Staining on Cotton, [b]Staining on Nylon.

Table 3. Rubbing fastness of the reactive dyes on regenerated cellulose fibers

Dyes	Dry		Wet	
	enVix	Viscose	*enVix*	Viscose
C.I. Reactive Black 5 (Bis-VS)	5	5	4-5	4-5
C.I. Reactive Red 120 (Bis-MCT)	5	3	4	3-4
C.I. Reactive Red 221 (Bis-MNT)	5	4-5	4	4-5

Table 4. Perspiration fastness of the reactive dyes on regenerated cellulose fibers (staining on nylon)

Dyes	Alkali		Acid	
	enVix	Viscose	*enVix*	Viscose
C.I. Reactive Black 5 (Bis-VS)	5	5	4-5	4-5
C.I. Reactive Red 120 (Bis-MCT)	4-5	4-5	4-5	4-5
C.I. Reactive Red 221 (Bis-MNT)	4-5	4-5	5	4-5

Table 2 shows that the fastness to washing (especially the change of the dyed fabric) of 1/1 standard depth dyeings of the reactive dyes on *enVix* was slightly higher than that of comparable depth dyeings on viscose rayon. The results could be attributed to *enVix*'s excellent affinity to dyes due to its supramolecular characteristics. In the case of rubbing fastness (Table 3), C.I. Reactive Red 120 showed slightly better rubbing fastness on *enVix* than on viscose rayon although the other reactive dyes showed similar rubbing fastness figures on both the regenerated fibers. Table 4 reveals that the perspiration fastness of the 1/1 standard depth dyeing of the three reactive dyes on *enVix* was almost identical to that of the dyes on viscose rayon. The fastness to light of the two dyed rayons was excellent (a rating of over 5), irrespective of dyes applied.

Conclusions

The dyeing properties on a new regenerated cellulosic fiber, *enVix* was compared with those on a regular viscose rayon, and shown to be excellent. Careful comparison of the dye yield on two rayons with reactive dyes confirms that there is a correlation between supramolecular structures and the dyeing properties; *enVix* exhibited higher exhaustion values and better build-up properties than viscose rayon, presumably due to the lower crystallinity (%) and degree of orientation. In addition, it showed stable final color yields, irrespective of liquor ratio, hence dyeing reproducibility of *enVix* is expected to be excellent. Fastness properties of reactive dyes on *enVix* were also slightly better than on viscose rayon. The 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.

Acknowledgement

The authors appreciate the financial support from the Ministry of Commerce, Industry and Energy, South Korea (Support for Industrial Technology Development program, No. D11-08-007).

References

1. S. Marash, F. Dubois, and Y. Sakuma, "CEH Marketing Research Report, Rayon and Lyocell Fibers", p.7, 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 (2000).
4. I. S. Kim, J. S. An, and B. H. Kim, *U. S. Patent*, 6361862 (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, *Journal of Applied Polymer Science*, **91**, 3481 (2004).
6. Ciba Specialties, "Technical Information, Reactive Dyes, Basic Principles", p.7, 1987.
7. F. Jones in "The Theory of Coloration of Textiles", 2nd ed. (A. Johnson Ed.), p.405, SDC, Bradford, 1989.
8. A. H. Renfrew and J. A. Taylor, *Rev. Prog. Coloration*, **20**, 1 (1990).
9. W. C. Ingamel in "The Theory of Coloration of Textiles", 2nd ed. (A. Johnson Ed.), p.184, SDC, Bradford, 1989.