Experimental Study on Dyeing Technical PET Yarns Having Different TiO$_2$ Contents

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Abstract: TiO$_2$ contents in yarns can influence color yield so that dyeing quality of industrial poly ethylene terephthalate (PET) yarns can be improved through the adjustment of TiO$_2$ contents. To evaluate the dyeing performance of color yield, the chips which included the different TiO$_2$ contents of 330, 550, and 1,100 ppm respectively were used to produce the yarns of different TiO$_2$ content by a spin-draft machine. The physical and structural properties of the yarns were measured to investigate effect of the TiO$_2$ contents on them. Dye uptake and dyeing rate were also evaluated using a colorimeter to compare the yarns having different TiO$_2$ contents. The experimental results showed that there were no appreciable variation in physical and structural properties among the yarn samples and no difference were observed among the dyed fabric samples with regard to dyeing uptake and dyeing rate. However, the color yield of dyed fabrics increased as TiO$_2$ contents decreased in the yarns especially when the fabric samples were dyed to pale shade. The physical reasoning could be proposed on why the yarns having low TiO$_2$ contents appeared to have higher color yield after dyeing.

Keywords: Additives, Disperse dyes, Technical yarns, Light scattering, Titanium dioxide (TiO$_2$), Polyethylene terephthalate

Introduction

Titanium dioxide is one of the most basic additives for many industrial products [1]. It has been widely used in a variety of paints, cosmetics and foodstuffs. Recently, many studies on TiO$_2$ have been achieved in order to use a photocatalyst that lets the TiO$_2$ containing materials decompose dirt, malodorous chemicals, irritants, smoke residue, bacteria, etc. [2,3]. Also, a great deal of work was made on the dispersion of titanium dioxide agglomerates during PET polymerization or spinning process to modify its final properties [4,5]. The effectiveness of catalysts and additives has been studied in terms of their contents and sizes during PET polymerization [6]. Particularly, some researchers have studied the spinning process of PET in relation with the addition effect of some kinds of various additives [7,8]. Some can accelerate the crystallization of PET polymer and give good processability during spinning [9]. Yarn properties can be protected from several guides on yarn path when the protrudent additives on yarn surface would touch the guides instead of yarn itself.

Melt spun fibers usually show high gloss that may interfere aesthetic quality in many textile applications. It is often needed to eliminate the undesirable shine of synthetic fibers to decrease the specular lights. The gloss of yarn is largely determined by its optical characteristics. A yarn shape, deniers of yarn and constituent monofilament, and additives can influence the visual perception. Masrani *et al.* [10] studied the several factors on apparent shade depth differences. Especially, they reported that fibers in which TiO$_2$ contents contain above 5,000 ppm appeared white in shade. Therefore, TiO$_2$ is added to the yarn in amount of 0.03 % (3,000 ppm)

to 0.2 % (20,000 ppm) for modifying the glossy appearance of garment fabrics.

In the manufacture of high denier yarns, the contents of additives are cautiously adapted for the optimal spinning process because of the possibility of blocking the nozzle. As the higher the contents of additives are, the shorter the changing period of the nozzle is, which results in rise of the production cost and labor works. The yarn makers in the industrial parts use the chips which contain the TiO$_2$ ranging from the super bright chips (0 ppm) up to the bright one (1,500 ppm) according to its application area. The technical yarns will be sometimes dyed to a light color in some applications. In these cases, the dyeing performance and depth of shade shall be considered to obtain high quality products. As it is common to dye the seat belt fabrics of light color using thermo sol dyeing in which the fabrics are shortly dipped in dye bath and heated in hot chamber, the yarns need to improve for enhancing dyeing performance such as color yield [11].

It has been known to the manufactures that the small difference of TiO$_2$ content within yarn will significantly influence the color yield of yarn appearance. In this study, the dyeing effect of yarns containing lower than 1,100 ppm TiO$_2$ on the apparent depth of shade was investigated. Three kinds of chips having different TiO$_2$ contents 330, 550, 1,100 ppm respectively were prepared and spun to make yarn samples using the same spinning machine. The physical and structural properties of yarn samples were measured to evaluate the effect of TiO$_2$ addition on the dyeing results of fabrics. Finally, the dyeing performance of three types of yarn samples was discussed with actual dyeing results.

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Experimental

Preparation of Chip Samples

Three kinds of chips with different TiO_2 contents were prepared for experimental tests. Each chip did not directly obtain from the process of PET polymerization, which was a useful method to get each type of chip, but it was too troublesome to make them by adding the TiO_2 during the polymerization. It could be easier to prepare each type of chip by mixing 3,000 ppm and 330 ppm TiO_2 chips together, which have been used to produce the industrial yarns at present in our factory. I obtained two kinds of chips as the following. Two chips of 550 ppm and 1,100 ppm TiO_2 were prepared by blending of two chips through a mixing ratio and the third chip contained 300 ppm TiO_2. Each chip was dried the moisture regain below 30 ppm with a tumble dryer at 135 °C for 12 hours. The inherent viscosity of each chip was about 1.00 so that the spun yarns could have enough tenacity to cope with industrial applications. The TiO_2 size was normally in the range of 0.2 to 1.5 μm, which was measured by the additive producer.

Preparation of Yarn Samples

Industrial spinning machine was used to produce the yarn samples using the three kinds of chips. The machine system with five pairs of godet rollers (GR) could change the temperature of each GR, spin draft, and relax ratio. From the spin draft method, three kinds of yarn samples had 1,300 denier. In the spinning, the normal spin draft (SD) and the relax ratio (RR) were 5.5 and 1.8 % respectively, where the SD was $GR4/GR1$ and the RR (%) was $(GR4 - GR5)/GR4 \times 100$.

The SD and the RR are closely related to the physical properties of yarn so that both conditions during the spinning process have to be carefully adjusted to achieve the required yarn properties. Normally, technical yarns have been produced by the SD roughly 5.0~6.5 and the RR under 12 %. The condition of spinning in this experiment test was shown in Table 1.

Dyeing the Fabric Samples

The fabric samples were knitted with each yarn sample by a circular knitting machine. The fabric samples were dyed by two dyeing methods. The one used a infra-red (IR) method in which the fabric samples were dipped in covered tubes and heated according to the dyeing profile as shown in Figure 1. To measure the dye uptake on each fabric samples after dyeing, the dyed fabrics were completely extracted with 15 ml
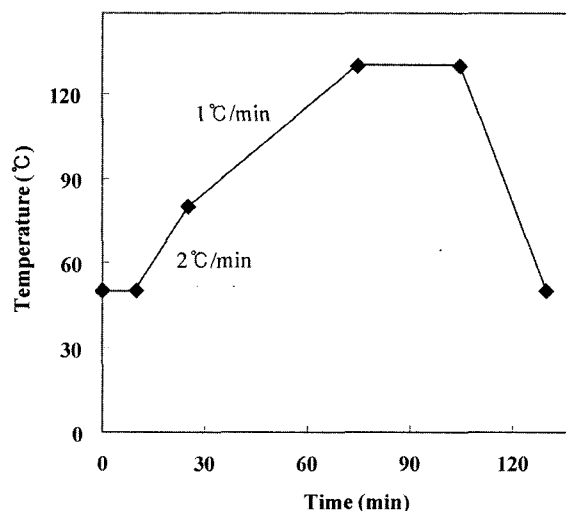

Figure 1. Dyeing profile for industrial PET yarns.

N,N-dimethyl formamide (DMF) at 110 °C for 30 minutes. After cooling to room temperature, a UV/VIS spectrometer was used to measure the amount of dyes which was not adsorbed by the fiber. Therefore the UV absorbance profile could infer the relative weight rate of dye uptake in the dyed fabric samples. The dye bath as follows;

- Black disperse dye (Ciba) = 1.0 % owf
- Liquor ratio   = 1:20 (fiber 10 g, Liquor 200 ml)
- Dispersing agent = 1.0 g/l
- Acid   = 1.0 g/l

The other method used a dye-o-meter that could measure the dye uptake and dyeing rate in real time during dyeing. In this method, similar dye bath and dyeing profile to above mentioned IR method were applied. The absorbance of each dye bath was measured repeatedly after a certain time interval with the dye-o-meter instrument. The low UV absorbance value implied that the black solution of dye bath became clearer because the black dyes penetrated the amorphous region within a fiber structure. The specific absorbance at the wavelength of 580 μm was set to read the variation of exhaustion. The selected wavelength was sensitive to subtle exhaustion changes relating with the black disperse dye.

Finally, K/S value and the lightness of the dyed fabric samples were measured by an automatic colorimeter. The Kubilka-Munk equation, $K/S = (1 - R)^2/2R$, is known to be proportional to the concentration of colorant in the substrate, where R is reflectance.

Table 1. Conditions of temperature and speed of GR during spinning process

Items	GR 1	GR 2	GR 3	GR 4	GR 5	Winder	Units
Speed	500	515	2,054	2,750	2,709	2,700	m/min
Temperature	off	105	125	226	off	-	°C

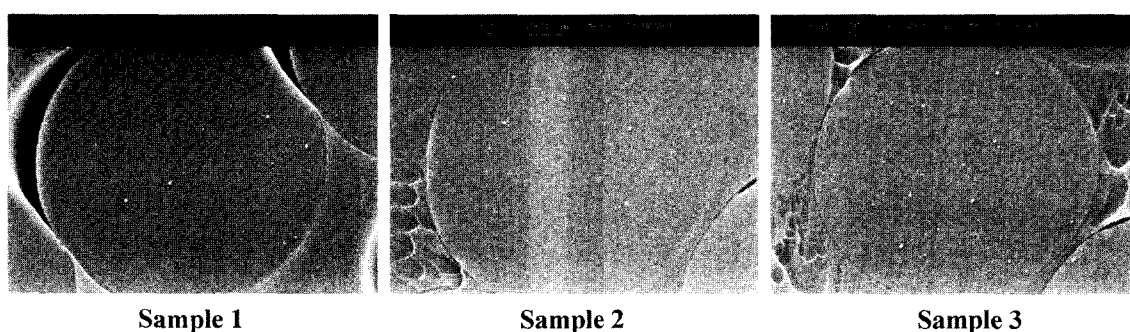**Sample 1**   **Sample 2**   **Sample 3**

Figure 2. Cross section images of each fiber sample including TiO₂ by SEM.

Results and Discussion

Analysis on Properties of Yarn Samples

The physical and micro-structural properties of yarns were measured by several measuring instruments. TiO₂ distribution in a fiber was examined by observing fiber cross-section of yarns with SEM at 3,000 magnifications. As shown in Figure 2, TiO₂ was randomly distributed within each yarn sample. The physical properties of each yarn sample were shown in Table 2. Tensile testing was performed using an Instron machine with 500 N load cell. Thermal shrinkage was measured using an automatic instrument with a hot chamber box when a yarn was exposed to hot air at 190 °C for 15 minutes.

As shown in Table 2, three samples had almost the same physical properties because each yarn was produced under equal spinning condition using the same raw material except TiO₂ contents. Therefore, the small difference of TiO₂ contents did not make the significant difference in the basic properties of the yarn samples. The crystal and amorphous regions were investigated using differential scanning calorimeter (DSC) and x-ray diffractometry to analyze whether the crystal structure of the spun yarns were different or not. The melting behavior of the samples was examined on the DSC using about 10 mg of each sample and at scanning rates of 20 °C/min.

The results of fine structural analysis were shown in Table 3. The crystallite dimensions of the samples such as crystal orientation factors (f_c) and crystal sizes (C.S.) were also

Table 2. Physical properties of the yarn samples

Parameters	Sample 1	Sample 2	Sample 3	Units
TiO₂ contents in yarn	327	542	1,070	ppm
Linear density	1,320	1,318	1,325	denier
Tenacity	8.1	8.0	8.1	g/d
Elongation at 5.9 kgf	5.4	5.4	5.4	%
Breaking elongation	14.4	14.1	14.4	%
Shrinkage	9.0	8.9	9.0	%
Birefringence	0.225	0.227	0.227	Δn
Density	1.392	1.391	1.392	g/cm³

Table 3. Results measured by X-ray and DSC analysis

	Items	Sample 1	Sample 2	Sample 3
WAXS	f_c	0.991	0.991	0.990
	C.S. (Å) 010	35.78	35.69	35.64
	C.S. (Å) 110	29.75	29.17	29.55
	C.S. (Å) 100	30.88	30.93	30.89
SAXS	L.P. (Å)	154.4	153.2	152.9
	I.Sax	237	235	238
DSC (1st heat)	T_m (°C)	252.8	253.0	252.4
	Onset (°C)	240.2	240.3	239.3
	ΔH_f (J/g)	48.7	49.0	48.5

measured. It showed that there was the subtle variation in the orientation of the crystallites, the crystal size to the each axis, the long period values (L.P.) of crystal-amorphous region, and the intensity difference ones (I.Sax) between crystallite and non-crystallite from wide angle X-ray scattering (WAXS) and small angle X-ray scattering (SAXS). Also DSC results of melting points and heat of fusion values to melt did not give significant difference. Based on these results, the yarn's physical and structural difference was too small to be meaningful.

Normally, when more TiO₂ is added, the crystallization speed can be the faster [9]. And the temperature of polymer is a very sensitive to crystallization. The experiment using DSC was installed to investigate that the difference between small amount of TiO₂ in yarn contents would accelerate the crystallization rate. As the yarn samples were treated to form the crystal at 220 °C with DSC instrument, the isothermal plots for crystallization of the samples were obtained. Based on the isothermal plots, the reduced crystallization plot was calculated by measuring the volume of crystal according to the treated time as shown in Figure 3. As the slope of reduced graphs was the same at the range of linear line, the small quantity of TiO₂ contents within fibers did not influence the crystal rate. Therefore the crystal rate in fiber had not been differentiated among the yarn samples. It could be said that the internal crystal and amorphous structures between the prepared samples were very similar.
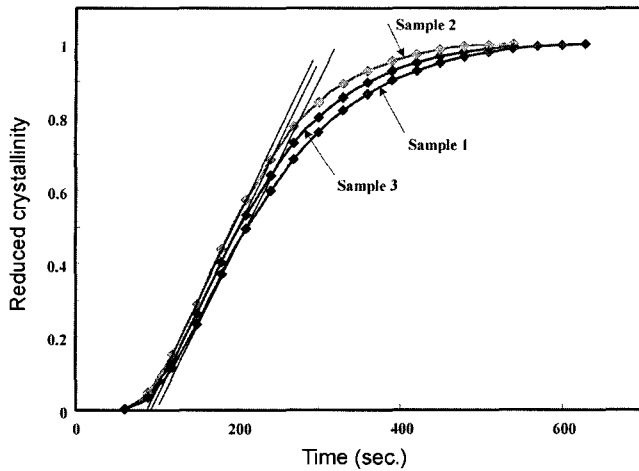
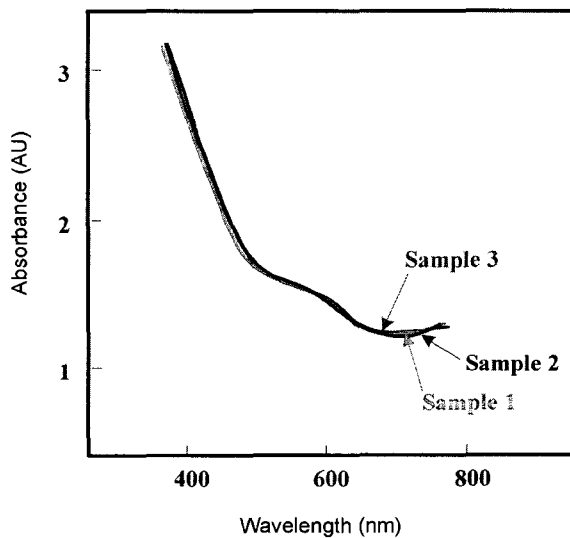**Figure 3.** Plots of reduced crystallization as a function of time for the yarn samples.

Figure 4. Absorbance results of dye solution extracted from dyed fabric samples using a colorimeter.

Dyeing Results

After IR dyeing, the dyed fabrics were extracted with DMF. The dye concentration in the extracts was measured colourimetrically using a spectrophotometer so that the dye uptake could be estimated from the UV absorbance results. As shown in Figure 4, the absorbance curves of three samples were a very similar shape. It meant that the dye uptakes of the dyed fabric samples were regarded as the same.

In Figure 5, there was a captured absorbance plot of each fabric sample in real time during dyeing. The dye uptakes of the fabric samples were sharply increased as bath temperature was roughly 80 °C. The disperse dyes easily entered internal chains in fibers after the rigid chain became soft above the glass transition temperature (T_g). Although the results of the sample 3 had more dye uptakes than other samples, there
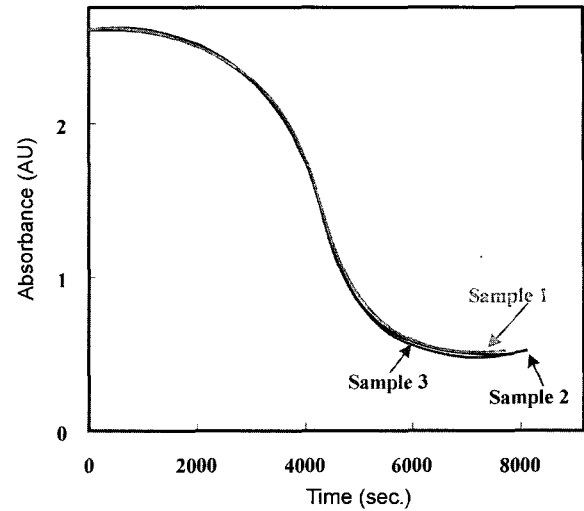

Figure 5. Plot of UV absorbance in real time during dyeing with Dye-o-meter.

Table 4. L* and K/S values of the yarn samples and the dyed fabrics using a colorimeter

Items		Sample 1	Sample 2	Sample 3
Yarns	L^*	77.98	82.40	87.96
Dyed fabric samples	L^*	19.23	19.92	20.49
	K/S	19.3	17.9	15.8

was no significant difference of dye uptakes and dyeing rate among the fabric samples because of only the small differences of the curves.

Analysis on Color

Color yield of dyed fabrics was measured using a UV-VIS spectrophotometer. The sample 1 had the highest color yield. And the color yield of the sample 2 was higher than that of the sample 3 as shown in Table 4. As long as the results of dye uptake and dyeing rate were considered, the K/S values were inconsistent to the upper mentioned dye uptake because the dye uptake and dyeing rate were similar in all the samples. Normally, the color yield values depended on not only dye uptake but also scattering effect of yarn surface.

The lightness (L^*) values of the raw yarns (non-dyed) and dyed fabrics were measured using a colorimeter. The physical meaning of L^* is that $L^* = 100$ means light and $L^* = 0$ dark. As shown in Table 4, the L^* values showed a large difference among the yarn samples. The difference of L^* values explained that TiO_2 contents did influence lightness. When a yarn had higher TiO_2 contents, its color became whiter. Although the L^* values gave much less differences among the dyed fabric samples than those of K/S, there was a trend that the L^* value of sample 1 was lower than other samples like the yarns. The fabric sample 1 obtained the highest color yield than other

samples, which coincided with ones of K/S values.

Conclusively, TiO_2 contents in yarn contributed the color yield of dyed fabrics, which was resulted from not being affected the increase of dye-uptake but changing the reflectance and the scatter of lighting path on sample surface.

In Figure 6, the light path was well described according to fiber condition. The color of a material can be understood on optical properties of surface and bulky region. Like (a) in Figure 6, the full reflection of light on the surface gives shinning phenomena. In case of (b), the light goes through the material of whose color is transparent. Otherwise, the light path like (c) is scattering on surface so that the glossy lights diminish. And the color of a material itself is expressed due to the light path of (d). When TiO_2 particles in fiber have enough contents, the occurrence frequency of (c) and (d) can accordingly increase so that the color of raw yarn becomes whiter.

The TiO_2 contents in fibers must be directly related to color yield instead of dye uptake and dyeing rate in the experiment. The K/S value of dyed fabrics could be similarly explained. In case of dyed fabrics shown in Figure 7, the occasion of the (a') in dyed fabrics made light reflection and looked like glossy effects on material surface. After light dyeing, the TiO_2 particles in yarn largely influenced the color because the absorbance coefficient 'K' value of K/S was linear to quantity of dye uptake in yarn. Upon the experiment, the 'K' was almost the same regardless of TiO_2 contents in yarns. And the scattering coefficient 'S' values
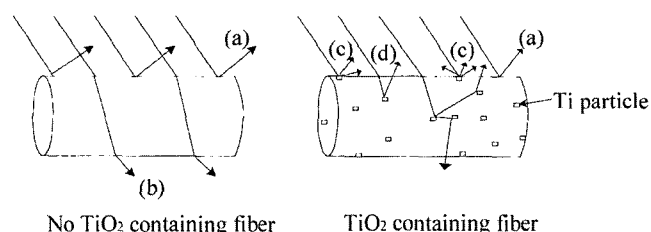

No TiO₂ containing fiber   TiO₂ containing fiber

Figure 6. Schematic paths of lights on TiO_2 particles in yarn; (a) full surface reflection (gloss), (b) no absorption (transparent), (c) diffuse surface reflection, (d) light scattering (mattering).
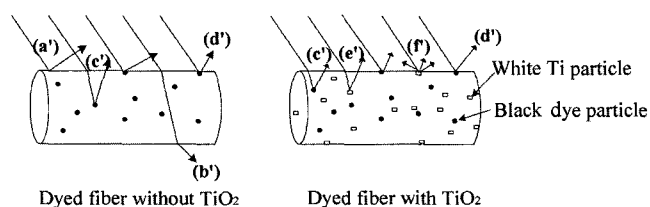

Dyed fiber without TiO₂   Dyed fiber with TiO₂

Figure 7. Schematic patterns of light paths on dyed yarns; (a') full surface reflection, (b') no absorption, (c') light scattering of dye particle, (d') diffuse surface reflection on dye particle, (e') light scattering of whiteness additive (TiO₂), (f') diffuse surface reflection on TiO_2.

were larger in high TiO_2 contents than ones in low ones. Therefore, the dyed fabrics with higher TiO_2 contents had lower K/S value. In the case of deep dark dyeing, the effects of dye particles on diffuse reflection and matting like (c') and (d') had much larger contribution to K/S values than those of TiO_2 particles like (e') and (f'). Here, the cases of (c') and (d') gave deep color and those of (e') and (f') made lighter color. Anyway, these phenomena will need to be explained by further studies in the future.

As mentioned above, small addition of TiO_2 in fiber did not affect the physical and structural properties of the yarn sample. There were the difference results of color yield resulting from not dyeing uptake and dyeing rate but different TiO_2 contents. Small TiO_2 addiction ranging from 300 ppm and 1,100 ppm did not change crystallization and orientation in fiber structure. The dye uptake and dyeing rate was very similar with the yarns having a little containing TiO_2. Therefore, the color of raw yarns and their dyed fabrics was differently seen due to TiO_2 contents in yarns.

The scattering situation on yarns makes the end-use goods more expensive enough to seemingly reduce the glossy lights considered as cheap. However, the products that contain too high TiO_2 are presented as a milky color so that the products have a difficulty in deep dyeing.

Conclusion

Through experimental evaluations, there were no differences of crystallization and orientation in the yarn samples containing the TiO_2 additives as 330, 550, and 1,100 ppm respectively. Dyeing results showed that the dye uptake and dyeing rate were not influenced largely by the TiO_2 contents in fibers. There was an apparent trend on color yield of the dyed fabric samples from the evaluation results of K/S and L^* values. The less TiO_2 contents in the fabric samples resulted in higher color yield on the sample appearance. Schematic paths of lights on the samples were explained with relation to each situation of color yield in yarns having different TiO_2.

References

1. F. Fourne, "Synthetic Fibers", Chap. 6, Hanser Publisher, Munich, 1964.
2. R. B. Towne, "Tappi Polymer Coating and Laminations Conference", 2000.
3. A. Fujishima, K. Hashimoto, and T. Watanabe, "TiO₂ Photocatalysis Fundamentals and Applications", BKC, Inc., Tokyo, 1999.
4. A. Joshi, *Chemical Weekly*, **December 6**, 129 (1994).
5. J. Batra, A. Khettry, and M. G. Hansen, *Polym. Eng. Sci.*, **34**(23), 1767 (1994).
6. R. Grebe and M. Rabe, *Acordis Reports*, 2000.
7. L. Meng and M. P. Santos, *Mat. Res. Soc. Symp. Proc.*, **436**, 523 (1997).

8. Y. J. Lee, I. Manas-Zloczower, and D. L. Feke, *Polym. Eng. Sci.*, **35**(12), 1037 (1995).

9. S. Cheng and R. A. Shanks, *J. Appl. Polym. Sci.*, **47**, 2149 (1993).

10. K. V. Masrani and J. L. Handu, *Colourage*, **May 3**, 15 (1984).

11. K. W. Lee, Y. S. Chung, and J. P. Kim, *Text. Res. J.*, **73**(9), 751 (2003).