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Weight Reduction of Sea-island-type PTT/PET Conjugate Fiber and Dyeing of Polytrimethylene Terephthalate Flock Microfibers

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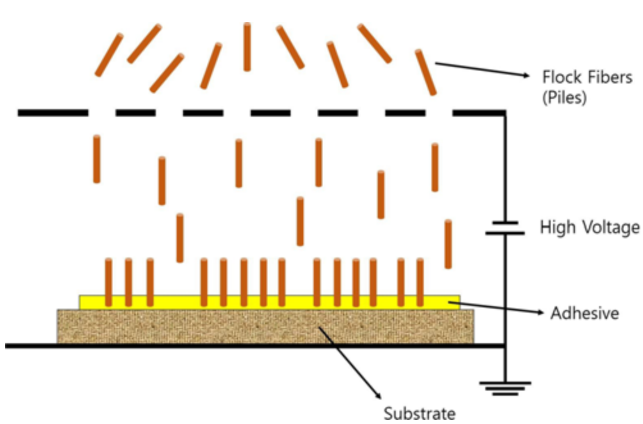
Abstract: The weight reduction behavior of short sea-island polytrimethylene terephthalate/polyethylene terephthalate (PTT/PET) conjugate fibers, the dyeing properties of the resulting PTT flock microfibers with five disperse dyes, and the fastness of the flocked fabric were investigated for a new flocking process application, which mitigates the drawbacks of the existing process. The weight reduction ratio of the PTT/PET conjugate fiber depends on the temperature, time, and concentration of the sodium hydroxide solution used in the alkali treatment. The optimum treatment condition to obtain the theoretical weight reduction ratio and PTT microfiber separation was determined using scanning electron microscopy (SEM). When the PTT flock microfibers were dyed with five disperse dyes, the adsorption or dyeing rates of the low- and medium-energy disperse dyes were higher than those of the high-energy disperse dyes. The high-energy disperse dyes exhibited good color yield, suggesting good build-up properties. The wash fastness was poor to good, the rubbing fastness was poor to moderate, and the light fastness was fair to moderate.

Keywords: Flocking, Microfiber, Sea-island type, Weight-reduction, Disperse dye

Introduction

The flocking process, which involves fixing short flock fibers of fixed lengths on a fabric surface, results in an imitation leather finish. Flocking is carried out by mechanical or electrostatic processes. The electrostatic process is preferred as it produces better-quality products with improved adhesive strength and density. In a typical electrostatic flocking process, the adhesive-coated substrate fabric is placed between two planar electrodes, and the charged flock fibers are subjected to an electric field, resulting in nearly perpendicular flock fiber embedding (Scheme 1). Electrostatic flocking, also referred to as electric flocking, can provide unique aesthetic and functional properties. Therefore, it is used in carpets, car seats, mats, wall coverings, hats, and slippers. The demand for better aesthetic and functional properties has resulted in complications in the flocking process. The process now uses finer microfibers as the flock fibers [1-4].



Scheme 1. Schematic diagram of flocking machine.

Microfibers can be produced by direct or conjugate spinning processes. Microfibers produced by conjugate spinning can be classified as split, multilayer, or dissolved depending on the polymer composition and cross-sectional shape of the conjugate fiber [5]. The dissolved or sea-island-type process involves the conjugate spinning of sea and island components to produce the finest microfibers. These components exhibit varying solvent extraction properties with subsequent sea component dissolution.

The island component in the production of polytrimethylene terephthalate (PTT) sea-island-type microfibers is regular PTT, while the sea component is alkali-soluble polyethylene terephthalate (PET). The microfiber is produced by extracting the alkali-soluble PET sea component from the conjugate fiber by an alkaline weight reduction process. In this process, in order to obtain the microfibers, sufficient extraction of the sea component is required. However, excess extraction can lead to the extraction of the island component along with the sea component, causing strength loss. Thus, to produce good quality microfibers, it is imperative to find the optimum weight reduction condition [6-15].

A typical process used in flocking microfibers is to prepare the microfibers by the alkaline weight reduction of conjugate filament fibers (Figure 1(a)). Following this, dyeing and cutting are conducted to produce flock fibers of the required lengths before flocking. This method is inefficient as microfibers of inappropriate length are discarded, although they underwent weight reduction and

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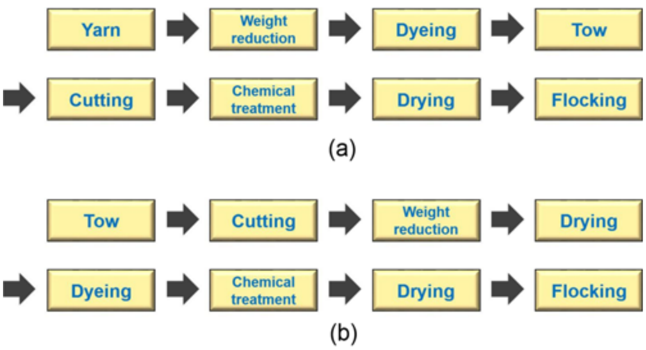

Figure 1. Manufacturing process of flocked fabric with microfiber piles; (a) conventional process and (b) modified processes.

dyeing. As shown in Figure 1(b), a modified process, which consists of cutting the conjugate filament fiber to obtain flock fibers of required lengths, weight reduction, and dyeing, results in better dyeing quality and productivity through a simple change in the production sequence. In summary, this modified process can reduce costs, time and effort in manufacturing the aesthetic flocking fabrics with flock microfibers. To apply this improved process, weight reduction of the flock fibers and dyeing are required. However, research on weight reduction and dyeing has been carried out only on filament fibers, woven, or knit fabrics [6-16]. Research on the weight reduction of short conjugate fibers, dyeing, and the fastness properties of disperse dyes on flock microfibers has not been reported.

In this study, the weight reduction behavior of short sea-island-type PTT/PET conjugate fibers and the dyeing properties of five disperse dyes on short PTT flock microfibers were investigated. The wash, light, and rubbing fastnesses of the flocked fabric were also studied.

Experimental

Materials

Sea-island-type PTT/PET fibers composed of 65 % and 35 % island (37 islands, regular PTT) and sea (alkali-soluble PET) components, respectively were provided by Ryuhan Inter-tech Co. Ltd. Figure 2 shows the SEM image of the sea-island-type PTT/PET conjugate fibers before alkaline weight reduction. Reagent-grade CH_3COOH, NaOH, and $Na_2S_2O_4$ were used in the weight reduction and dyeing processes. The dispersing agents used in weight reduction. i.e., (KF Neocrystal K-2500) and dyeing (Lyocol RDN) were provided by NICCAKOREA Co. and Clariant International Ltd., respectively. To study the dyeing behavior of the disperse dyes of different energy types, three disperse dyes provided by Kyung-In Synthetic Co. and two disperse dyes provided by Dystar were used (Table 1).

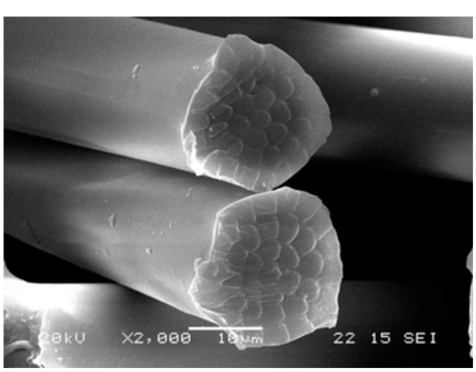

Figure 2. Cross-section of sea-island-type PTT/PET conjugate fiber.

Table 1. Disperse dyes used in this study

Dyes	Dye manufacturer	Energy type
Synolon Red EN-F	Kyung-In Synthetic Co.	E
Synolon Red KRD-SE	Kyung-In Synthetic Co.	SE
Synolon Red HWF-3BF	Kyung-In Synthetic Co.	S
Dianix Yellow 4GSL	Dystar	S
Dianix Red BS	Dystar	S

Weight Reduction

The weight reduction of the sea-island PTT/PET conjugate fibers was carried out with 2-5 % NaOH aqueous solution at 80-100 ^oC for 60 min (Figure 3). The samples were heated in the NaOH solution to the designated temperatures at a heating rate of 2 ^oC/min, and then removed every 10 min, filtered, and dried. The dried sample weight was measured three times and average value was used. The weight reduction ratio was obtained using equation (1). The average value of three-times measurements

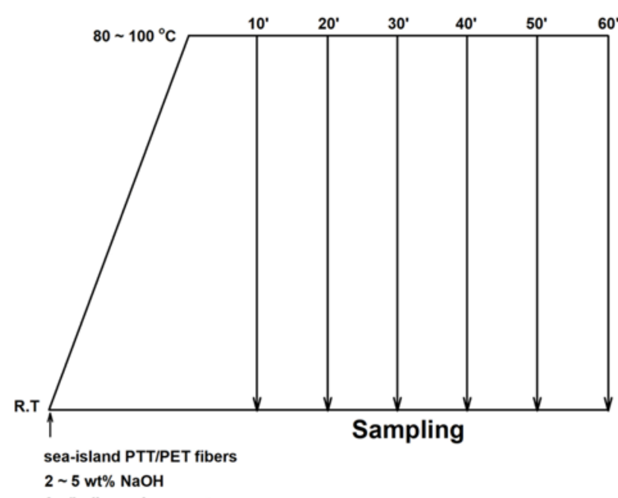

Figure 3. Weight reduction profile of sea-island-type PTT/PET conjugate fibers.

$$\text{Weight reduction ratio (\%)} = (a - b)/a \times 100 \quad (1)$$

where a is the sample weight before the alkali treatment (g) and b is the weight after the alkali treatment (g).

Dyeing

Dyeing of 2 g of the weight-reduced PTT flock fiber samples, under optimum conditions (2 % NaOH, 90 °C, 30 min), was conducted for the five dyes using the method shown in Figure 4.

An infrared dyeing machine (DaeLim Starlet Co., Ltd.), which operated with a liquor ratio of 20:1 was used, and CH_3COOH was used to adjust the pH of the dyeing liquor in the range 4.5-5.0. Dyeing was conducted using different dyes and various concentrations at 110 °C for 30 min. Reduction clearing was carried out with NaOH (1 g/*l*) and $Na_2S_2O_4$ (2 g/*l*) at 80 °C for 20 min.

To compare the dyeing behavior of the different dyes on short PTT flock microfibers, a Dye-O-meter (HanBat Automatic Control Co. Ltd., Software: Dyemax-L) with 50:1 liquor ratio and a heating rate of 1 °C/min was used to dye 20 g samples with 2.0 % owf dyes at 110 °C for 40 min. The dye exhaustion was calculated from the absorbance at the maximum absorption wavelength in the isothermal experiments in 5 min intervals. Using the equilibrium exhaustion value (%E), the half dyeing time ($t_{1/2}$, the time to achieve 50 % of equilibrium dye exhaustion), adsorption initiation temperature (T_1, temperature required to obtain 20 % equilibrium dye exhaustion), and adsorption termination temperature (T_2, temperature required to obtain 90 % equilibrium dye exhaustion) of the respective dyes were obtained.

The dyed PTT flock microfibers were filtered to remove the residual dye liquor, collected in a cake form, and dried.

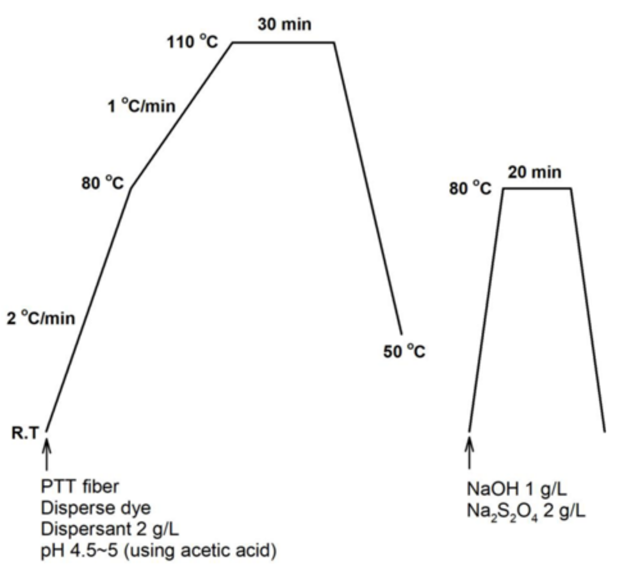

Figure 4. Disperse dyeing profile of PTT flock microfibers.

The *K/S* values of the dyed sample were measured using a spectrometer (Coloreye 3100, Gretag-Macbeth, USA) with a D65 standard illuminant and a 10 ° standard observer. Color measurement was carried out four times for each dyed sample and average value was used. According to the Kubelka-Munk theory, the *K/S* value is calculated from the surface reflectance at the maximum absorption wavelength as follows:

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

where K is the absorption coefficient, S is the scattering coefficient, and R is the reflectance ($0<R\leq1$).

Flocking and Fastness Evaluation

Flocking with the dyed PTT flock microfibers was conducted at 35 kV-DC (Down method) with a 100 mm electrode distance, nonaqueous polyurethane binder (100 part), methylene diphenyl diisocyanate curing agent (15 part), and curing at 100 °C for 15 min. The sample fastness of the flocked fabric was evaluated based on color fastness to washing (ISO 105-C06:1994), color fastness to rubbing (ISO 105-X12:2001), and color fastness to light (ISO 105-B01:1994) standards.

Results and Discussion

Weight Reduction Behavior

The sea-island-type PTT conjugate fibers used in this study were composed of regular PTT island and alkali-soluble PET sea components (Figure 5). The alkali-soluble PET is a copolyester containing sulfonated isophthalate monomers, where the sulfonate groups have increased solubility in aqueous alkaline solutions and contribute to the bulky polymer structure and nonlinearity, resulting in easier alkaline extraction [11,17-19]. As the PTT/PET conjugate fiber contains 35 wt.% alkali-soluble PET, the theoretical weight reduction ratio should be 35 %. Microfibers can be obtained by alkali-soluble PET extraction during weight reduction. If the weight reduction is insufficient and only a few alkali-soluble PET parts are extracted, then some PTT microfibers will be attached. In the flocking process, each flock fiber must be evenly deposited on the adhesive-coated substrate fabric. However, if unseparated PTT microfibers are present, the flocking efficiency will decrease, and the deposited flock fibers may have an irregular height distribution, causing poor contact and durability. Therefore,

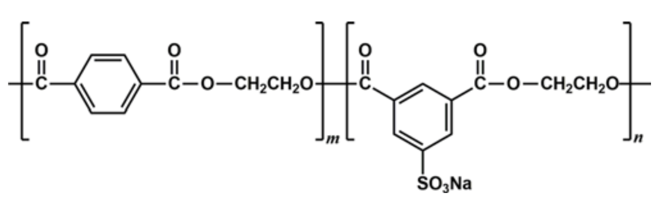

Figure 5. Structure of alkali-soluble PET.

choosing a weight-reducing condition to obtain a weight reduction ratio that is 35 % of the theoretical weight reduction ratio is critical for obtaining final products of the best quality.

Figure 6 shows the effect of temperature (80-100 °C), aq. NaOH concentration (2-5 %), and weight reduction time on the weight reduction ratio. The weight reduction ratio generally increases with an increase in temperature, aq. NaOH concentration, and time. This is because an increase in the hydrolysis rate, temperature, and alkali concentration causes a higher degree of extraction. A 35.8 % weight reduction ratio, which is close to the theoretical value, is obtained when weight reduction is carried out with 2 % NaOH at 80 °C for 60 min. The approximate theoretical value, i.e., 34.2 % or 37.3 %, can be obtained in 30 min with 3 or 4 % NaOH, respectively, and in 20 min with 5 % NaOH. Under the same NaOH concentration and time conditions, the weight reduction at 90 °C was higher than that at 80 °C. On the other hand, the weight reduction at 100 °C was greater than that at 80 or 90 °C. The theoretical weight reduction ratio, which is 35.3 %, can be obtained in 10 min with 2 % NaOH.

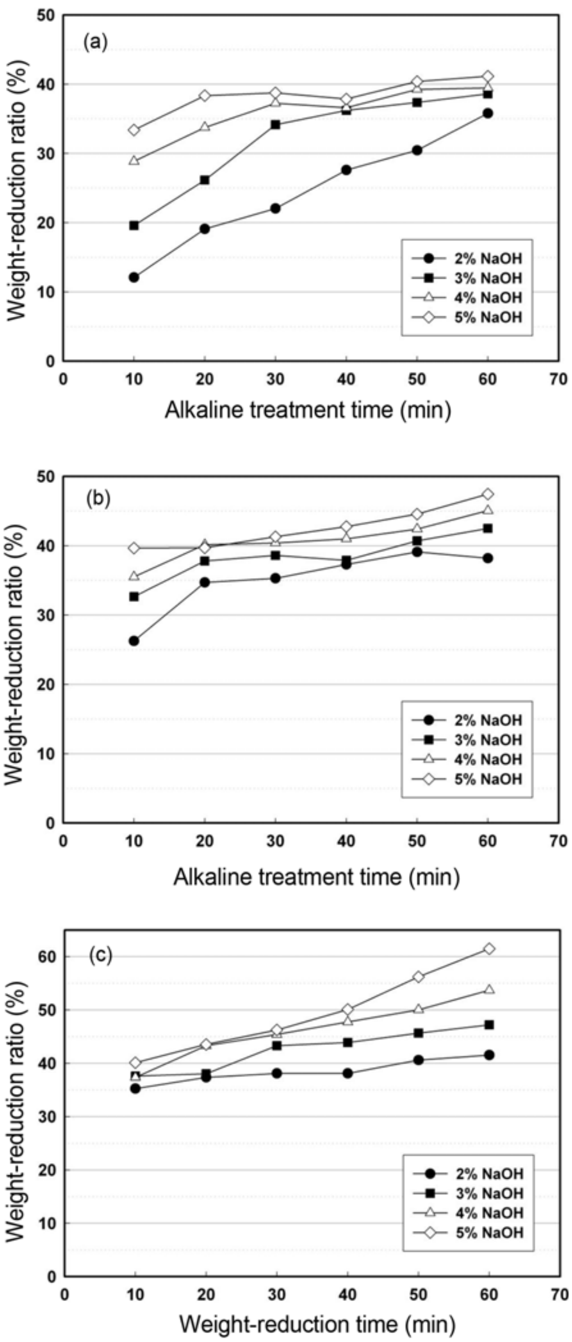

Figure 6. Weight reduction behavior of sea-island-type PTT/PET conjugate fibers during alkaline treatment at (a) 80 °C, (b) 90 °C, and (c) 100 °C.

Under severe conditions (high NaOH concentration, long duration), 50-60 % weight reduction is obtained as a result of significant PTT extraction along with alkali-soluble PET. As the PTT flock microfibers are completely separated in this case, the flocking process shows no problems. However, due to flock fiber degradation, its physical property, touch, and durability can reduce.

Figure 7 shows the SEM images which depict the appearance changes in the sea-island-type PTT flock microfibers due to variations in the weight reduction ratio. As seen in Figure 7(a) and (b), all the microfibers are not formed, as the theoretical weight reduction ratio is not achieved due to the remaining alkali-soluble PET being held together. When the weight reduction ratio is greater than the theoretical value, all microfibers are separated, as seen in Figure 7(c)-(e). However, at a 61.5 % weight reduction ratio, microfiber degradation is apparent in the ×10,000 SEM image (f).

The optimum weight reduction condition that is required to obtain a weight reduction ratio similar to the theoretical value was determined from the weight reduction ratio data and the SEM images. The weight-reduced samples with 2 % NaOH at 90 °C for 30 min were used for the dyeing experiments.

Dyeing Properties

The dyeing properties of PTT flock microfibers were studied with three types of low-energy disperse dyes with molecular weight below 300 g/mol, medium-energy dyes with molecular weight in the range of 300-400 g/mol, and high-energy dyes with molecular weight above 400 g/mol.

Table 2 shows the T_1, T_2, $t_{1/2}$, and %E of the PTT flock microfibers. These values were obtained by weight-reducing PTT/PET conjugate fibers under the optimum condition (2 % NaOH, 90 °C, 30 min) and then dyeing them with five disperse dyes on the Dye-O-meter. For the low- and medium-energy dyes (Synolon Red EN-F and Synolon Red KRD-SE) T_1 is 78 °C and T_2 is 95-101 °C; these are relatively low values, suggesting that adsorption of dyes on the PTT

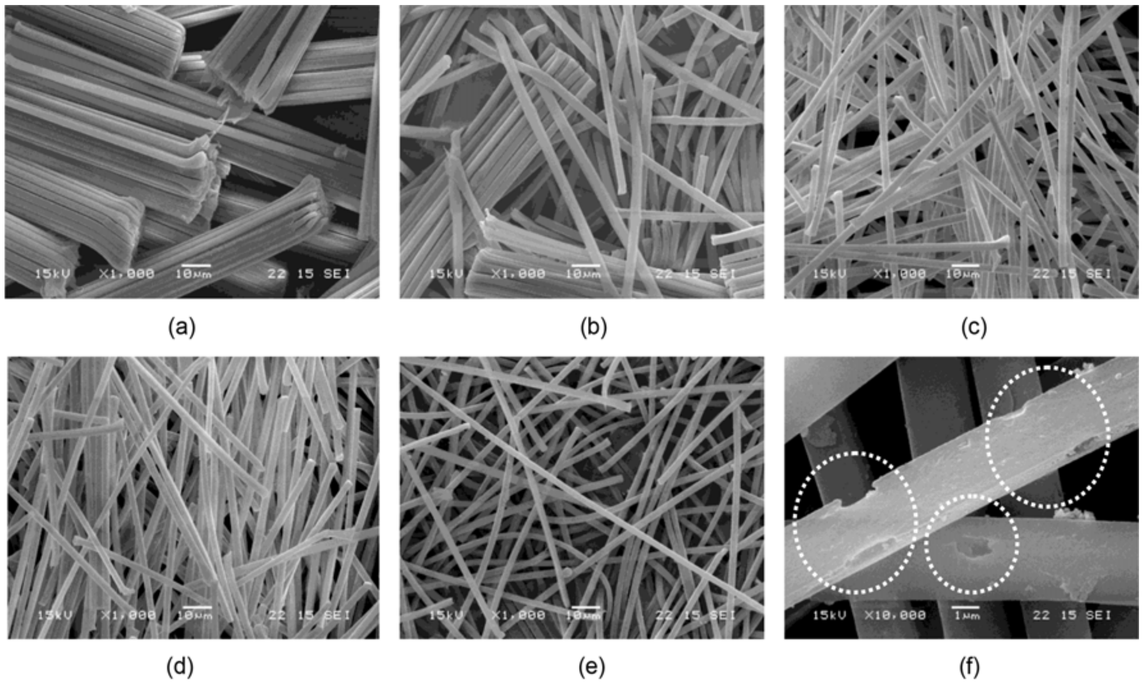

Figure 7. SEM images of sea-island-type PTT/PET conjugate fibers after alkali treatment. Weight reduction ratio/magnification; (a) 19.6 %/×1000, (b) 30.4 %/×1000, (c) 40.2 %/×1000, (d) 50.1 %/×1000, (e) 61.5 %/×1000, and (f) 61.5 %/×10,000.

Table 2. Adsorption initiation temperature (T_1), adsorption termination temperature (T_2), time of half-dyeing ($t_{1/2}$), and equilibrium dye exhaustion (%E) of the disperse dyes on PTT flock microfibers

Dyes	T_1 (°C)	T_2 (°C)	$t_{1/2}$ (min)	%E
Synolon Red EN-F	78	95	25	76.5±0.65
Synolon Red KRD-SE	78	101	24	81.3±0.91
Synolon Red HWF-3BF	87	107	35	69.7±0.85
Dianix Yellow 4GSL	87	110+4 min.	38	66.9±1.15
Dianix Red BS	88	110+1 min.	38	83.6±1.05

fibers occurs at low temperatures. However, for the high-energy dyes (Synolon Red HWF-3BF, Dianix Yellow 4GSL, Dianix Red BS), significant adsorption started at higher temperatures of 87-95 °C. The adsorption termination occurred at 107 °C or for 1-4 min after reaching T_2 (110 °C), which suggests that their adsorption rates are comparatively low. These results are due to a smaller low- and medium-energy dye size. Thus, the adsorption and diffusion rates at the PTT fiber non-crystalline region are higher, compared to those of the large-sized high-energy dyes [20,21]. Similarly, $t_{1/2}$ values of the low- and medium-energy dyes are 24-25 min, while those of high-energy dyes are 35-38 min. %E is 66.9-83.6 % and no significant correlation exists between the energy type and equilibrium exhaustion. Levelling properties of all the dyed samples were good.

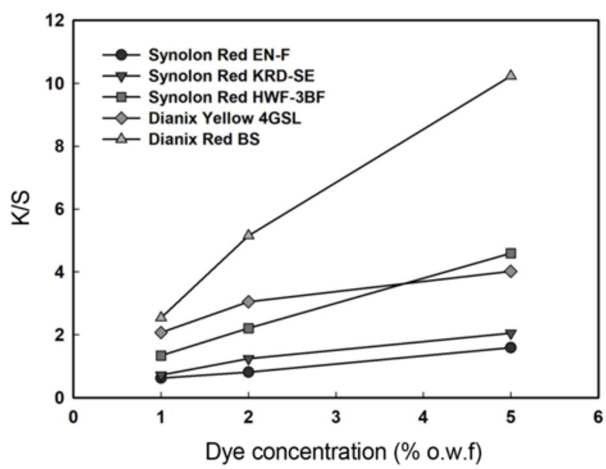

Figure 8. Build-up properties of disperse dyes on PTT flock microfibers.

Figure 8 shows the dyeing properties of the PTT flock microfiber, which includes their build-up properties. Generally, the *K/S* values increase with an increase in the dye concentration, suggesting that they have good build-up properties. For low- and medium-energy dyes, although the *K/S* values increased with dye concentration, the *K/S* value was lower than 2 for a 5 % dye concentration, suggesting limitations for dark color dyeing. This is because low- and medium-energy disperse dyes are used for light to medium colors, and the flock microfibers have very low linear density and large surface area, resulting in a lower color yield as compared to regular fibers with the same amount of dye in the fiber [10,13]. In contrast, the high-energy dyes exhibited high *K/S* values of 4-10 obtained at 5 % owf dye concentration.

Fastness Properties

The wash, rubbing, and light fastnesses of the samples flocked with dyed flock microfibers are shown in Table 3. Wash fastness was determined in terms of multi-fiber fabric staining. The disperse dye released from the sample can easily stain hydrophobic fibers, such as nylon, acetate, and PET, due to its hydrophobic nature. It would stain nylon and acetate more at the washing temperature. It can also stain cotton, which is a hydrophilic fiber but has a natural pore structure [10]. The wash fastness was above level 3-4, which falls under the category of fair to good fastness. However, that of the flocked sample dyed with Synolon Red HWF-3BF was level 2 for nylon staining. The wash fastness of microfiber is generally very low, as finer fibers cause disperse dyes to thermomigrate easily toward the surface during heat setting after dyeing, which then easily desorb [13]. Regular PTT fabrics undergo heat setting at a temperature of approximately 150 ^{o}C for 1 min after dyeing, but as the PTT microfiber flocked samples in this study were heat-treated (cured) at a relatively low temperature of 100 ^{o}C for 15 min, lesser thermomigration occurred, resulting in a medium wash fastness level. For rubbing fastness, dry and wet rubbing generally show low levels of 2 or 3. The high-energy dyes (Synolon Red HWF-3BF, Dianix Yellow 4GSL, Dianix Red BS), which generally exhibit good rubbing fastness, also show very low levels. This is due to the higher probability of dye distribution near the microfiber surface based on the microfiber fineness and flocked sample structure, such that the flock fibers are directly exposed to rubbing and the rubbing force can detach the dyes more easily. Rubbing fastness improvement by post-treatments is required for the commercialization of microfiber flocked fabric. The light fastness is average (level 3 or 4). Due to the small microfiber diameter, light can easily penetrate the microfiber, while the large surface area allows more dyes to be exposed. This causes a lower light fastness as compared to that of normal fibers [12,13]. Therefore, the light fastness must be improved using post-treatments.

Conclusion

For the application of the new flocking process, which mitigates the drawbacks of the existing process, the weight reduction of sea-island-type PTT/PET fibers and the dyeing characteristics of the weight-reduced PTT flock microfibers with disperse dyes were studied to obtain the following results.

The weight reduction ratio increased with an increase in temperature, NaOH concentration, and weight reduction duration. The optimum conditions causing a 35 % weight reduction ratio, which is equivalent to the theoretical value, could be determined. At severe conditions (high temperature, NaOH concentration, and duration), the weight reduction ratio was higher than the theoretical value, showing that PTT was extracted along with the alkali-soluble PET. The effect of the processing conditions on the weight reduction behavior, which was observed using SEM, is close to that observed in the weight reduction ratio data.

When the weight-reduced PTT flock microfibers are dyed with five different disperse dyes, the low-energy and medium-energy disperse dyes adsorb faster at low temperatures, but the high-energy-type disperse dyes start to adsorb at a higher temperature and the adsorption rate is also lower. Although the *K/S* values of the samples dyed with low- and medium-energy disperse dyes increase with dye concentration, the *K/S* values are generally low and hence limiting the dyeing to deep colors. The high-energy dyes exhibit relatively high *K/S* values and have good build-up properties.

The wash fastness levels of the flocked microfiber samples ranged from normal to good, generally 3-4 (excluding the staining level of Synolon Red HWF-3BF on nylon). The dry and wet rubbing fastnesses were poor to fair, generally level 2 or 2-3. The light fastness was average, level 3 or 4. The somewhat low fastness levels occur due to fineness of the flock microfiber. Further research on the post-treatment processes of the microfiber flocked fabric that enhance the

Table 3. Wash, rubbing, and light fastness of disperse dyes in PTT microfiber flocked fabric

Dyes	Wash fastness						Rubbing		Light
	Staining								
	Acetate	Cotton	Nylon	PET	Acrylic	Wool	Dry	Wet	
Synolon Red EN-F	4-5	4	4	4	4	4	3	3	4
Synolon Red KRD-SE	4	3-4	4	4	4	4	2-3	2	3
Synolon Red HWF-3BF	4-5	4-5	2	4	4	4	2-3	2	3
Dianix Yellow 4GSL	4	4-5	4-5	4-5	4-5	4	2-3	2	4
Dianix Red BS	3-4	3-4	3-4	3-4	3-4	4	2-3	2	3

fastness properties is recommended.

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