

## Alkaline Weight Reduction Monitoring of Sea-island Type Polyamide Microfiber Fabrics

Yoon-Jung Kwon, Joonseok Koh\*, Myung Joon Oh<sup>1</sup>, and Sung Dong Kim

*Department of Textile Engineering, NITRI, Konkuk University, Seoul 143-701, Korea*

<sup>1</sup>*Korea Institute of Industrial Technology Evaluation & Planning, Seoul 135-080, Korea*

(Received January 2, 2006; Revised January 22, 2006; Accepted February 22, 2006)

**Abstract:** The alkaline dissolution behavior of sea-island type polyamide microfibers were successfully monitored using a cationic dye staining method. Weight reduction behavior of the alkali-treated microfiber fabrics and the treated fabrics stained with cationic dye were investigated in a comparative manner. The termination of dissolution monitored by both methods was also confirmed by scanning electron microscopy.

**Keywords:** Alkaline dissolution, Polyamide, Sea-island type microfiber, Weight reduction, Cationic dye

### Introduction

Fabric constructions based on microfilament synthetic yarns are commonly referred to as "microfibers". Microfibers are now well established in many apparel markets, as well as in other outlets, being used either as single-fiber fabrics or in conjunction with coarser synthetic or natural fibers, providing fabrics of enhanced drapeability, luster, softness, smoothness and, in many cases, novel tactile and visual aesthetics [1-6]. Microfibers are used in various applications, for example in high-grade woven and knitted fabrics with a soft hand and water- and oil-absorbent fabrics, such as towels and typewriter ribbon. Wiping cloths, filter cloths and clean-room garments utilize the large fiber surface. Moisture-permeable, waterproof and water-repellent high-density woven fabric is another use. In these end-uses, a suitable combination of the fiber assembly structure and the fiber material is important in realizing excellent performance [7].

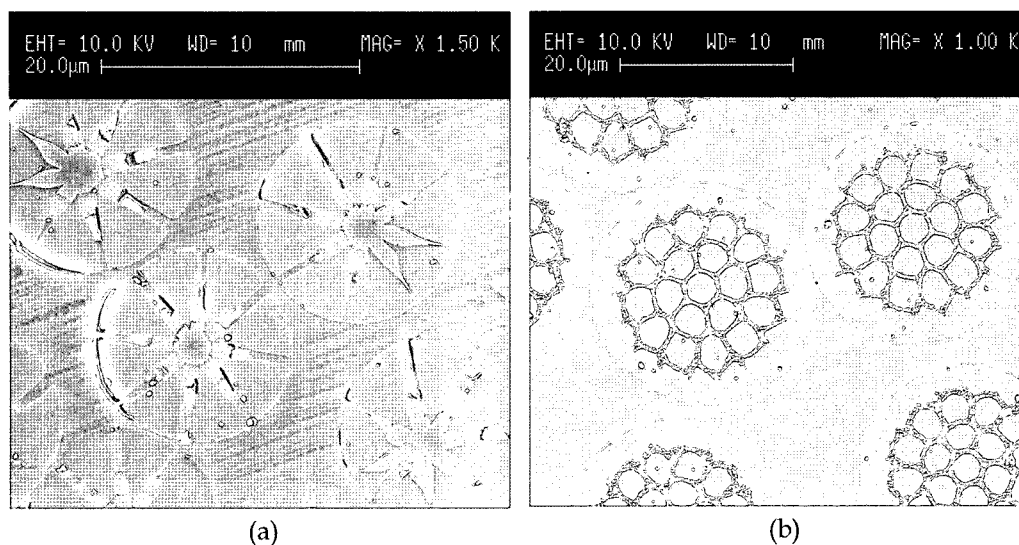
Conventional direct spinning method and conjugate spinning method are employed to produce microfibers. In the case of direct spinning, single component filaments are extruded through spinnerets to give highly uniform microfibers. Although all three conventional spinning methods (melt, wet and dry) can be employed and polyester, polyamide and acrylic microfibers can be obtained [8], the direct spinning of microfibers is a complex process and involves the modification of the spinning methods that are used to produce conventional denier fibers. Generally, there is a limit to the fineness of fibers produced using direct spinning, as exemplified by polyester which cannot be extruded at less than *ca.* 0.15 g/min owing to the breakage of the filament. Typically, microfibers in the range 0.2-0.9 denier are secured using conventional spinning methods although filaments of 0.1 denier have been reported [1]. In the case of conjugate spinning, two different methods have been devised, namely separation and dissolution. The separation technique involves the spinning of a bicomponent filament,

typically one comprising polyamide and polyester although polyolefin/polyester and polyolefin/polyamide bicomponents have also been developed (Figure 1a) [1]. After weaving, the ensuing fabric is exposed to solvent/alkali swelling or thermal/mechanical treatment such that the two immiscible components separate resulting in individual polyamide/polyester microfilaments. In the dissolution technique, two polymers are extruded through a suitable spinneret to produce a bicomponent filament that comprises either several individual 'islands' of one component embedded within a 'sea' of the other component or a sheath of one component that surrounds the core of the other component (Figure 1b). After weaving or knitting, one of the components is removed by dissolution in a solvent thereby producing microfilaments.

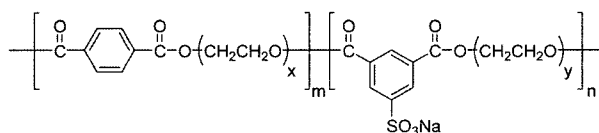
In the case of polyamide microfilament production, the polyester island is commonly used in conjunction with a polystyrene or alkali-soluble polyester sea component. When the 'sea' is dissolved with a certain solvent, the 'island' polymer remains and forms the finest fibers. The number of islands, the ratio of island to sea components and the cross-sectional shape of the ensuing microfilaments can be varied. With copolymerization technology, it is possible to control alkali weight reduction speed (polymers which are susceptible to alkali weight reduction) [9]. When polyester, i.e., poly(ethyleneterephthalate) (PET) (formed through an esterification of terephthalic acid and ethylene glycol), is copolymerized with another monomer, the physical and chemical characteristics of the polymer decline. Heat and chemical resistance drop, but this means that the polymer has a faster alkali weight reduction speed than homogeneous PET. This characteristic is used in making sea-island type microfibers, especially in South Korea. In order to obtain a polymer which is susceptible to alkali weight reduction, copolymerization is carried out with sodium 5-sodiosulphoisophthalate (Figure 2).

Although scanning electron microscopy is a useful tool for the verification of the dissolution process, the method is expensive and time-consuming. Therefore, in this study, a much simpler dissolution-monitoring method has been investigated

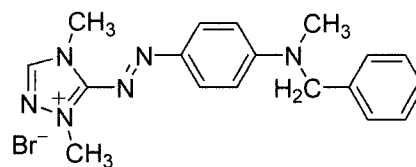
\*Corresponding author: ccdjko@konkuk.ac.kr



**Figure 1.** Microfibres produced by conjugate spinning (a) separation type, (b) sea-island type.



**Figure 2.** Poly(ethyleneterephthalate-co-5-sodiosulphoisophthalate).



**Figure 3.** C.I. Basic Red 46 (Astrazon Red FBL).

using cationic dye staining. Weight reduction behavior of the alkali-treated microfiber fabrics and the treated fabrics stained with cationic dye were investigated in a comparative manner. The termination of dissolution monitored by both methods was also confirmed by scanning electron microscopy. The alkaline dissolution behavior of sea-island type polyamide microfibers were successfully monitored using this cationic dye staining method.

## Experimental

### Materials

The sea-island type polyamide(nylon 6) microfiber (75 d/36 f, sea-to-island ratio 30:70) was obtained from Hyosung Corporation (South Korea). Circular-knitted microfiber fabrics and woven microfiber fabrics (Table 1) were then used to

investigate the weight reduction behavior of the sea-island type polyamide microfibers. The cationic dye used, Astrazon Red FBL (CI Basic Red 46; Figure 3), was a commercial sample and was not purified prior to use. All chemical reagents were of general purpose grade.

### <sup>1</sup>H NMR Spectroscopy

Polyamide (nylon 6) chips (island component) and alkali-soluble PET chips (sea component) were analyzed by <sup>1</sup>H NMR spectroscopy. The samples were prepared by dissolving 1.0 mg of polymer chips in an appropriate solvent (deuterated trifluoroacetic acid for alkali-soluble PET and formic acid for polyamide). The <sup>1</sup>H NMR spectra were recorded on a 500 MHz Bruker Avance machine equipped with a temperature control unit.

**Table 1.** Fabric compositions and theoretical dissolution values of sea-island type polyamide microfibers fabrics

	Structure	Composition	Theoretical dissolution <sup>a</sup> (%)
Circular knit	Single jersey	SIPAM <sup>b</sup> 75d/36f (28 Guague)	30.0 %
Woven-1	Satin	Warp : PET 75d/72f (120 threads/inch)	14.1 %
		Weft : SIPAM 75d/36f (106 threads/inch)	
Woven-2	Plain	Warp : PA6 <sup>c</sup> 70d/24d (124 threads/inch)	10.4 %
		Weft : SIPAM 75d/36f (66 threads/inch)	

<sup>a</sup>Theoretical weight reduction for the complete dissolution of sea component out of sea-island type polyamide microfibers, <sup>b</sup>sea-island type polyamide microfiber, <sup>c</sup>nylon 6.

### Differential Scanning Calorimetry

The general thermal properties of polyamide chips (island component) and alkali-soluble PET chips (sea component) were examined using differential scanning calorimetry (DSC) (Perkin Elmer DSC7). Samples (*ca.* 10 mg) were preheated to 250 °C for 5 min in order to eliminate all crystalline nuclei and then rapidly cooled down to 20 °C. Subsequently, samples were heated up to 250 °C with a heating rate of 20 °C/min, and the melting temperature ( $T_m$ ) was determined.

### Scanning Electron Microscopy

Scanning electron microscopy (SEM) of the fibers before and after alkali-treatment was carried out using a scanning electron microscope (JSM-840A). Epoxy resin was chosen as an embedding medium and the epoxy resin sections of the fibers were prepared for the SEM by removal of the epoxy using a concentrated solution of sodium methoxide.

### Alkaline Weight Reduction

A 50 ml/ alkaline bath, suitable for a 2.0 g sample of microfiber fabric (liquor ratio 1:25), containing sodium hydroxide (1.2 %) was prepared. Alkaline weight reduction was performed for 30 min at 100 °C in a laboratory dyeing machine (Ahiba, Datacolor International). Each pot was removed from the dyeing machine at intervals of 10 min and the fabrics were rinsed and dried at 60 °C. Fabrics were weighed before and after treatment and the change in mass calculated as a percentage of the initial value (weight reduction).

### Cationic Dyeing

A 50 ml/ dyebath, suitable for the alkali-treated microfiber fabrics (liquor ratio 1:25), containing cationic dye (Figure 3)

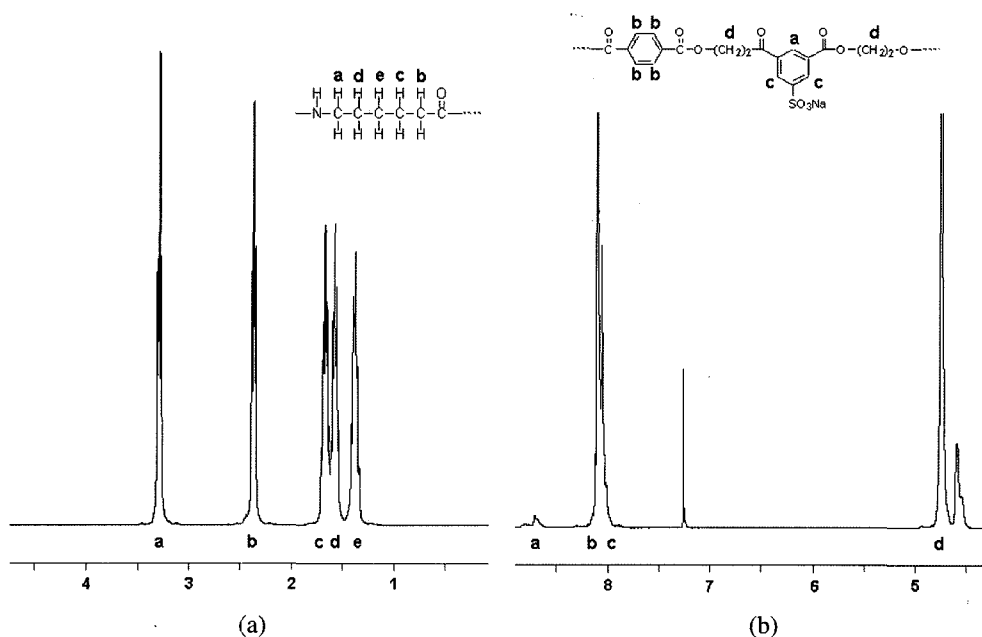
(0.5 % owf) was prepared. Dyeing was performed for 20 min at 80 °C in a laboratory dyeing machine. After dyeing, all the samples were rinsed and dried at 60 °C. The color strength ( $K/S$ ) values of the dyed fabrics which had been alkali-treated at 10 min intervals were measured using a spectrophotometer (Color-Eye 7000, Macbeth, standard light D65, 10° standard observer, specular component included,  $\lambda = 540$  nm) interfaced with a personal computer. The weight reduction behavior of the microfiber fabrics containing sea-island type polyamide under alkaline conditions, expressed in the form of weight reduction and color strength were investigated in a comparative manner.

## Results and Discussion

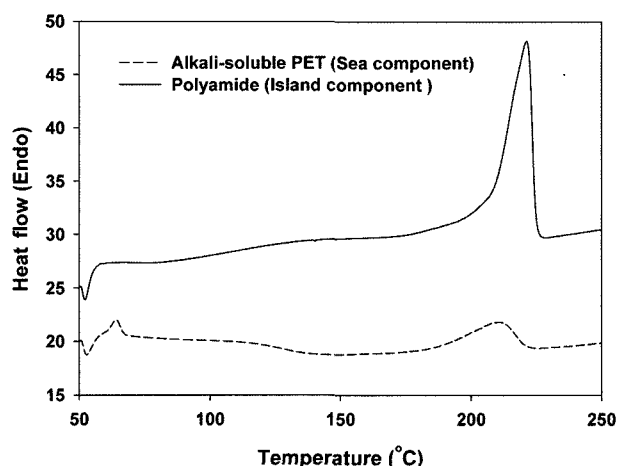
### Characterization of Microfibers

Figure 4 shows the  $^1\text{H}$  NMR spectra of polyamide (island component) and alkali-soluble PET (sea component). For the island component (Figure 4a), signals for the aliphatic groups are found at 3.27-3.31 (peak a), 2.35-2.39 (peak b) and 1.36-1.70 (peak c) ppm, respectively. For the sea component (Figure 4b), signals for the aromatic ring and aliphatic groups are found at 8.71 (peak a), 8.06-8.11 (peaks b and c), and 4.61-4.77 (peak d) ppm, respectively.

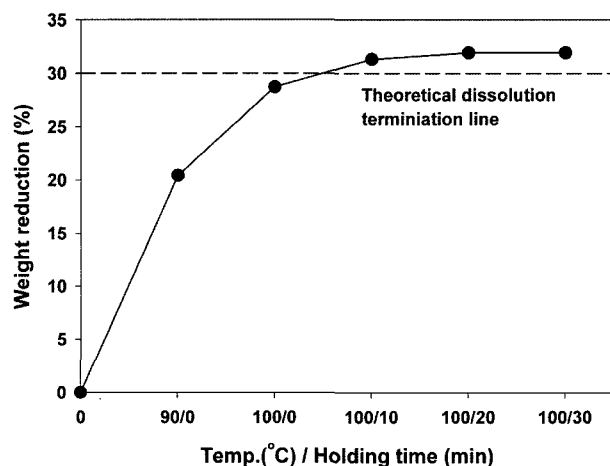
The DSC thermogram (Figure 5) of the alkali-soluble PET shows that the sea component (alkali-soluble PET, 210-211 °C) has a lower melting point than regular PET (255-260 °C). It is considered that the meta linkage and the presence of the sulphonyl group of 5-sulphoisophthalate can prevent the close packing of the polymer chain and also reduce the  $T_m$  of the copolymer. In the case of island component, it shows typical melting point of nylon 6 (220-221 °C).



**Figure 4.** NMR spectra of (a) polyamide (island component) and (b) alkali-soluble PET (sea component).



**Figure 5.** DSC heating thermograms of polyamide (island component) and alkali-soluble PET (sea component).



**Figure 6.** Alkaline weight reduction behavior of circular-knitted microfiber fabrics during alkali-treatment at 100 °C (theoretical dissolution termination value = 30 %).

### Circular-knitted Microfiber Fabrics

Figure 6 shows the alkaline weight reduction behavior of the circular knitted microfiber fabrics during alkali-treatment. The weight reduction of the microfiber fabrics increases rapidly, particularly in the early stages of the alkali-treatment, and

appears to reach a maximum before 30 min of alkali-treatment at 100 °C. It is considered that the initial rapid rise is due to the relatively easy hydrolysis of the sea component which is located around the polyamide components. The copolymer containing 5-isophthalate has a 60° bending of polymer chains due to the modification with isophthalic acid. This disturbs the straight zig-zag structure of the chains, and steric hindrance of an optimum chain arrangement is generated [10]. A sodium salt of 5-sulphoisophthalic acid affects the steric arrangement still more adversely. Therefore, modified fibers (owing to the higher accessibility of the amorphous regions) are subject to a much more rapid hydrolysis than regular PET. The modified PET fibers are sensitive to temperatures of *ca.* 100 °C, at which nonmodified PET fibers are practically stable. The differences in the rate of hydrolysis in PET and a copolymer containing 5-sulphoisophthalic acid are due to the ‘loosening’ of the structure. The loosening of the amorphous phase is initiated by the effect of heterogeneities of the PET chains caused by the modification component.

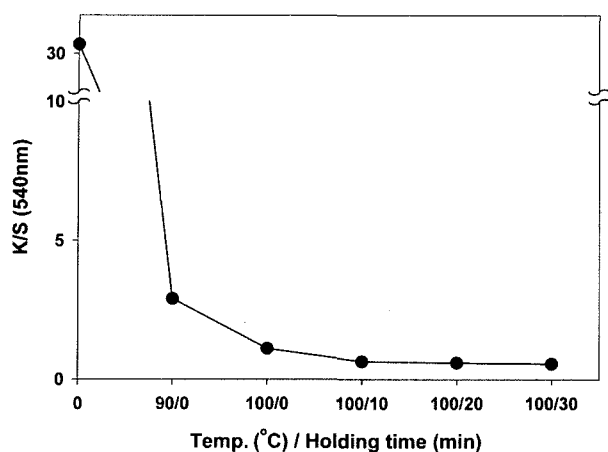
In the reaction with alkali, the highly nucleophilic  $\text{OH}^-$  ion attacks the electron-deficient carbonyl carbon atom in the polyester. The nucleophilic substitution reaction results in chain scission and the generation of terminal carboxyl and hydroxyl groups [1]. Hydrolytic degradation provoked by the effect of aggressive liquid media proceeds in three phases: adsorption of the aggressive substance on to the fiber surface, diffusion into subsurface layers, and chemical reaction with the least stable polymer groups. Rather prone to hydrolysis (especially in alkaline environments) in PET fibers are the ester bonds.

The theoretical weight reduction values required for the completion of dissolution of the sea component out of the sea-island type polyamide microfibers is 30.0 % (Table 1) and these can be verified by SEM as shown in Table 2. It is clear from the micrographs that the alkali-treated sea-island polyamide microfibers dissolve and separate into each island component gradually as the alkali-treatment proceeds.

The SEM micrographs reveal that dissolution of the sea component is complete after 10 min, and the results are also consistent with the alkaline weight reduction behavior (Figure 6). The dissolution speed is determined by the content of 5-sulphoisophthalate in the polymer chain and the sea-island

**Table 2.** Cross-sections of circular-knitted microfiber fabrics during alkali-treatment

Temp./Time	Before alkali-treatment	90 °C/0 min	100 °C/0 min	100 °C/10 min
Circular knit				



**Figure 7.** Staining of cationic dyes on circular-knitted microfiber fabrics during alkali-treatment at 100 °C.

ratio. SEM is a useful tool for the verification of dissolution of sea-island type microfibers. However, it is an expensive and time-consuming process. An alternative method to monitor the dissolution is by measuring the extent of cationic staining. Owing to the presence of the sulpho-group in the sea component, it can be dyed with cationic dyes. During dyeing, cationic dyes diffuse into the fiber and are immobilized on accessible sulpho-groups. The immobilization itself occurs by an ion exchange mechanism as shown in equation (1) [10].

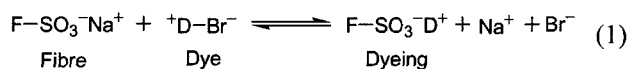
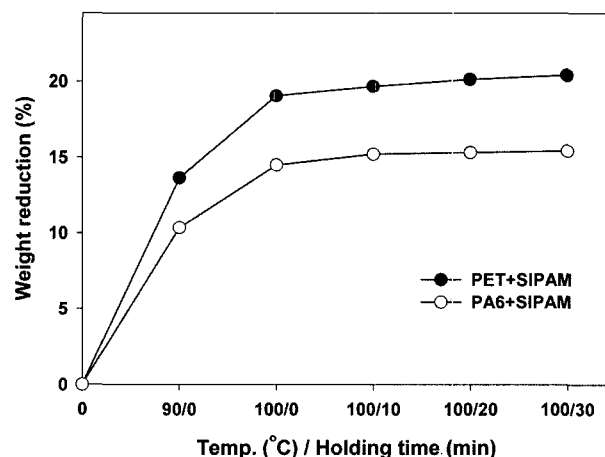


Figure 7 shows the staining of cationic dyes on alkali-treated circular-knitted microfiber fabrics during alkali-treatment. It is clear that the color strength of the staining decreases as alkali-treatment time increases and finally reaches a leveling-off point after 10 min, after which no further changes are observed. The leveling-off points demonstrate that the alkali-soluble sea component has been dissolved out and only island components (polyamide), which are hardly stained by cationic dyes, remained.

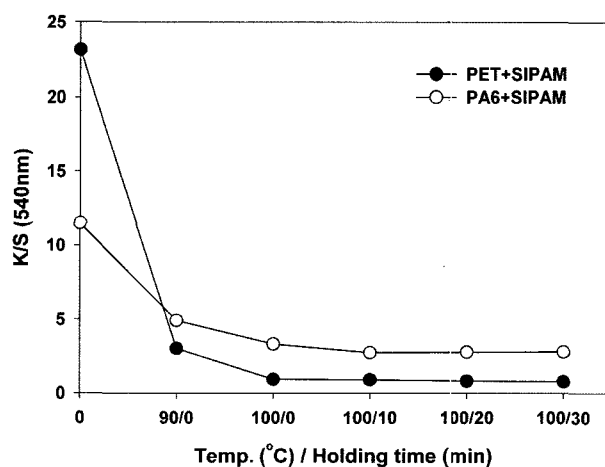
### Woven Microfiber Fabrics

Microfibers are applied to a very wide range of fabrics including circular-knitted or woven fabrics through fabrication with other fibers. For example, in the case of woven fibers, polyester or polyamide can be used as warp yarns and microfibers as weft yarns, respectively, and vice versa. In this case, the termination point of dissolution is more difficult to predict since the calculation of theoretical weight reduction required for the completion of dissolution is complicated due to the weight reduction of other fibers used together. Figure 8 shows the alkaline weight reduction behavior of woven microfiber fabrics during alkali-treatment. The weight reduction values of the two microfiber fabrics increase rapidly particularly in the early stages of alkali-treatment and the slope decreases



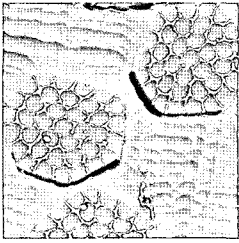
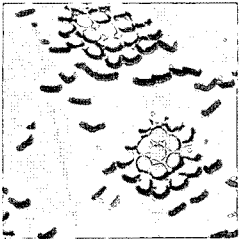
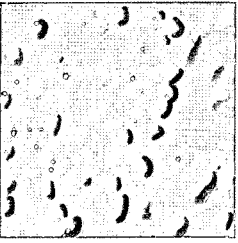
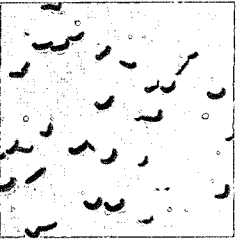
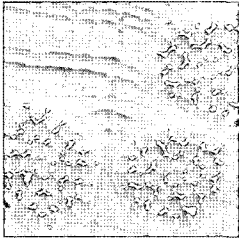
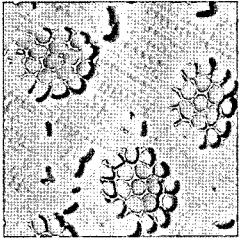
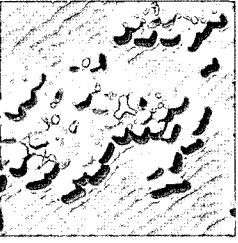

**Figure 8.** Alkaline weight reduction behavior of woven microfiber fabrics during alkali-treatment at 100 °C.

with increasing alkali-treatment time. It is considered that the initial rapid rise is ascribed to the relatively easy hydrolysis of the sea-island type microfiber which was used as the weft yarn. However, it is difficult to predict the exact termination point of dissolution from this figure since the theoretical weight reduction values for the completion of dissolution of the sea component out of sea-island type microfibers are not known and sometimes the curves does not level off. Also, the predicted dissolution termination value calculated from the yarn denier and fabric density is not accurate enough due to the unconsidered factors such as fabric shrinkage and hydrolysis of sea component and other fabric compositions used together; (theoretical dissolution termination value)/(measured dissolution value after weight reduction) is (14.1 %)/(20.4 %) for Woven-1 and (10.4 %)/(15.4 %) for Woven-2 (Table 1 and Figure 8). It is considered that the higher hydrolysis (%) of Woven-1 compared with Woven-2 is ascribed to the lower content (lower weft yarn density) of sea-island



**Figure 9.** Staining of cationic dyes on woven microfiber fabrics during alkali-treatment at 100 °C.

**Table 3.** Cross-sections of woven microfiber fabrics during alkali-treatment

Temp./time	Before alkali-treatment	90 °C/0 min	100 °C/0 min	100 °C/10 min
Woven-1 PET + SIPAM				
Woven-2 PA6 + SIPAM				

type microfiber in the fabric. Also, in the case of Woven-1, the additional alkaline hydrolysis of PET which was used as a warp yarn seems to make the difference between the theoretical value and the measured value bigger compared with Woven-2 (Woven-1 6.3 %, Woven-2 5.0 %).

The dissolution of the woven fabrics containing the sea-island type microfibers was monitored using the cationic dye staining method (Figure 9). The color strength (K/S value) of the staining on alkali-treated samples decreases as alkali-treatment time increases and finally reaches a leveling-off point just after reaching to the 100 °C for Woven-1 and 10 min at 100 °C for Woven-2, after which no further changes were observed. Especially, in the case of Woven-1, while the weight reduction curve (Figure 8) did not reach an equilibrium state, the cationic dye staining curve does exhibit leveling off (Figure 9), and therefore, it is easier to determine the termination point of dissolution. SEM observations confirmed the predicted termination points obtained by the cationic dye staining method (Table 3).

### Conclusions

It is not easy to predict the termination point of the dissolution process from the weight reduction curves of the fabrics containing sea-island type microfiber. Although scanning electron microscopy is a useful tool for the verification of the dissolution process, the method is expensive and time-consuming. Therefore, in this study, a much simpler dissolution-monitoring method has been investigated using cationic dye staining. The alkaline dissolution behavior of sea-island type polyamide microfibers were successfully monitored using

this cationic dye staining method.

### Acknowledgement

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (KRF-2005-003-D00480).

### References

1. S. M. Burkinshaw, "Chemical Principles of Synthetic Fiber Dyeing", Blackie Academic & Professional, Glasgow, 1995.
2. S. D. Kim, M. J. Kim, B. S. Lee, and K. S. Lee, *Fibers and Polymers*, **5**, 39 (2004).
3. J. Koh, I. S. Kim, S. S. Kim, W. S. Shim, and J. P. Kim, *Fibers and Polymers*, **5**, 44 (2004).
4. I. S. Kim, J. Koh, N. K. Han, and J. P. Kim, *Fibers and Polymers*, **5**, 219 (2004).
5. B. Becerir and M. A. Iskender, *Fibers and Polymers*, **5**, 309 (2004).
6. K. S. Lee, B. S. Lee, Y. H. Park, Y. C. Park, Y. M. Kim, S. H. Jeong, and S. D. Kim, *Fibers and Polymers*, **6**, 35 (2005).
7. O. Wada, *J. Text. Inst.*, **83**, 322 (1992).
8. Anonymous, *Jpn Text. News*, **83**, 81 (1992).
9. Y. Washino, "Functional Fibers, Trends in Technology and Product Development in Japan", Toray Research Center Inc., Shiga, 1993.
10. J. Militky, J. Vanicek, J. Krystufek, and V. Hartych, "Modified Polyester Fibers", Elsevier, Prague, 1991.