

# Alkaline Dissolution Monitoring of Radial-Type Polyester Microfiber Fabrics by a Cationic Dye-Staining Method

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**ABSTRACT:** The alkaline dissolution behavior of radial-type polyester microfibers during high-temperature alkali treatment and cold-pad batch alkali treatment was successfully monitored using a cationic dye-staining method. The weight reduction behavior of the alkali-treated microfiber fabrics and their staining behavior with a cationic dye were compared. In addition, the termination of dissolution mon-

itored by both methods was confirmed by scanning electron microscopy. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 279–285, 2006

**Key words:** dyes/pigments; polyesters; copolymerization; fibers; electron microscopy

## INTRODUCTION

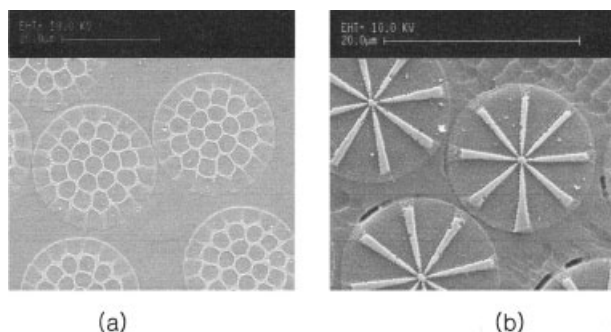
The use of microfibers is now well established in many apparel markets, as well as in other outlets. Microfibers are used either as single-fiber fabrics or in conjunction with coarser synthetic or natural fibers, providing fabrics that have enhanced drapability, luster, softness, smoothness, and, in many cases, novel tactile and visual aesthetics.<sup>1,2</sup> Microfibers are used in various applications, for example, in high-grade woven and knitted fabrics with a soft hand and in water- and oil-absorbent fabrics, such as towels and typewriter ribbons. Wiping cloths, filter cloths, and clean-room garments utilize the large fiber surface. They are also used as moisture-permeable, waterproof, and water-repellent high-density woven fabrics. In these end uses, a suitable combination of the fiber assembly structure and the fiber material is important in realizing excellent performance.<sup>3</sup>

In a broad sense, especially in Europe, the term *microfiber* means fine fibers of less than 1.0 denier. However, in South Korea and Japan, where fine-fiber technology is more advanced, fine fibers of 0.04–0.4 denier class are generally used in this filament area. Two methods can be employed to produce microfibers: conventional direct spinning and conjugate spinning. With 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 em-

ployed and polyester, polyamide, and acrylic microfibers can be obtained, the direct spinning of microfibers is a complex process and involves the modification of the spinning methods used to produce conventional denier fibers.<sup>4</sup> Generally, there is a limit to the fineness of fibers produced using direct spinning, as exemplified by polyester that cannot be extruded at less than about 0.15 g/min because of breakage of the filaments. Typically, microfibers in the range of 0.2–0.9 denier are secured using conventional spinning methods, although filaments of 0.1 denier have been reported.<sup>1</sup> For conjugate spinning, two methods have been devised, separation and dissolution. The separation technique involves the spinning of a bicomponent filament, typically one comprising nylon 6 and polyester, although polyolefin/polyester and polyolefin/polyamide bicomponents also have been developed.<sup>1</sup> After being woven, the 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 in a “sea” of the other component [the sea-island type, Fig. 1(a)] or several sectors of one component embedded in a radial type of the other component [the radial type, Fig. 1(b)]. After weaving or knitting, one of the components is removed by dissolution in a solvent, thereby producing microfilaments.

With the sea-island type of polyester microfilament production, a polyester island is commonly used in

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**Figure 1** Cross sections of dissolution-type microfibers produced by conjugate spinning techniques: (a) sea-island type; (b) radial type.

conjunction with a polystyrene or alkali-soluble polyester as the sea component. When the sea is dissolved with a certain solvent, the polymer that is the island remains and forms the finest fibers. The number of islands, the ratio of island components to sea components, and the cross-sectional shape of the resulting microfilaments can be varied, as this method is capable of producing supermicropolyester filaments of  $1.0 \times 10^{-4}$  denier as well as hollow microfibers. The finest polyester supermicrofibers are produced using sea-island technology (also known as islands-in-the-sea technology).

Also, with radial-type polyester microfilament production, a polyester sector is commonly used in conjunction with a polystyrene or alkali-soluble polyester matrix component. When the matrix is dissolved with a certain solvent, the polymer sector remains and forms the microfibers. With copolymerization technology, it is possible to control the speed of alkali weight reduction (polymers that are susceptible to alkali weight reduction).<sup>5</sup> When polyester, that is, poly(ethylene terephthalate) (PET), which is 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 speed of alkali weight reduction than does homogeneous PET. This characteristic is used in making dissolution-type (sea-island- or radial-type) microfibers, especially in South Korea. To obtain a polymer that is susceptible to alkali weight reduction, copolymerization is carried out with sodium 5-sodiosulfoisophthalate (Fig. 2).

In this study, the dissolution of radial-type polyester microfibers was monitored by a cationic dye-staining method. The weight reduction behavior of alkali-treated microfiber fabrics and of treated fabrics stained with cationic dye was compared. Termination of monitoring of dissolution by both methods also was confirmed by scanning electron microscopy.

## EXPERIMENTAL

### Materials

Interlaced textured yarns (ITY) were obtained from Hyosung Corporation (Anyang, South Korea). ITY are combined yarns of widely differing properties (i.e., shrinkage, cross-section, and denier) by air-entangling treatment or composite false twisting. The ITY used in this study were composed of radial-type microfibers (90d/36f/2-ply) and high-shrinkage PET (30d/12f). The sector-matrix ratio was 75 : 25, and the theoretical dissolution (%) was 21.4%, which was calculated from the theoretical weight reduction for the perfect dissolution of the border component out of radial-type polyester microfibers.

Circular-knit microfiber fabrics (single jersey 28 gauge, consisting of ITY) and woven microfiber fabrics ( $\frac{1}{4}$  satin weave; width: 54 in; warp yarn: PET 75 denier, 126 threads/inch; weft yarn: ITY, 92 threads/inch, 134 g/m<sup>2</sup>) were then used to investigate the weight reduction behavior of the radial-type PET microfibers. Circular-knit fabrics are those fabrics whose courses are composed of a single strand of yarn. The single jersey is the simplest circular-knit fabric, in which all the stitches are brought toward the face of the fabric.

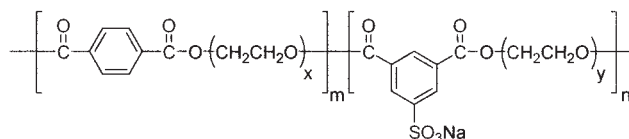
The cationic dye used, Astrazon Red FBL (CI Basic Red 46; Fig. 2), was a commercial sample that was obtained from BASF (Seoul, South Korea). All chemical reagents were of general-purpose grade.

### <sup>1</sup>H-NMR spectroscopy

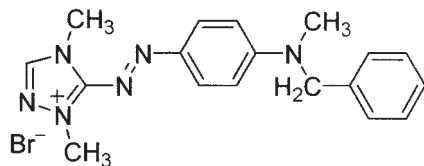
Regular PET chips (sector component) and alkali-soluble PET chips (matrix component) were analyzed by <sup>1</sup>H-NMR spectroscopy. The samples were prepared by dissolving 1.0 mg of polymer chips in deuterated trifluoroacetic acid. The <sup>1</sup>H-NMR spectra were recorded on a 500 MHz Bruker Avance machine equipped with a temperature control unit.

### Differential scanning calorimetry

The general thermal properties of regular PET chips (sector component) and alkali-soluble PET chips (matrix component) were examined using a differential scanning calorimetry (DSC; Perkin Elmer DSC7). Samples (ca. 10 mg) were preheated to 280°C for 5 min in



**Figure 2** Poly(ethylene terephthalate-co-5-sodiosulfoisophthalate).



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

order to eliminate all crystalline nuclei and then rapidly cooled to 20°C. Subsequently, samples were heated to 280°C at a rate of 20°C/min, and the melting temperature ( $T_m$ ) was determined.

### Dissolution

Two dissolution methods were used, high-temperature method and cold-pad batch method.

For the high-temperature method, 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. Dissolution was performed for 50 min at 98°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. The fabrics were weighed before and after treatment, and the change in mass was calculated as a percentage of the initial value (weight reduction).

For the cold-pad batch method, a 2.0-g sample of microfiber fabric was impregnated with an alkaline solution containing sodium hydroxide (75, 100 g/L), a penetrating agent (1.0 g/L; Neorate CM-32; Korean Fine Chemicals), and a scouring agent (8.0 g/L; Scourwet 105B; Daedong Oil Chemicals) and padded at ambient temperature by passing through the mangle nip to squeeze the surplus liquor (60% pickup). The batched roll of wet fabric was wrapped in polyethylene film and stored at 25°C for a selected time (4, 8, 12, or 20 h), followed by washing and drying.

### 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 sections of the fibers were prepared for the SEM.

### Cationic dyeing

A 50-mL dye bath, suitable for the alkali-treated microfiber fabrics (liquor ratio 1:25), containing cationic dye (Fig. 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 that 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,  $\lambda = 530$  nm) interfaced with a personal computer. The dissolution behavior of the microfiber fabrics containing sea-island-type polyester under alkaline conditions, expressed in the form of weight reduction and color strength, were compared. The color strength of stained fabric from the cationic dye was estimated by measuring  $K/S$  values [eq. (1)], defined as

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

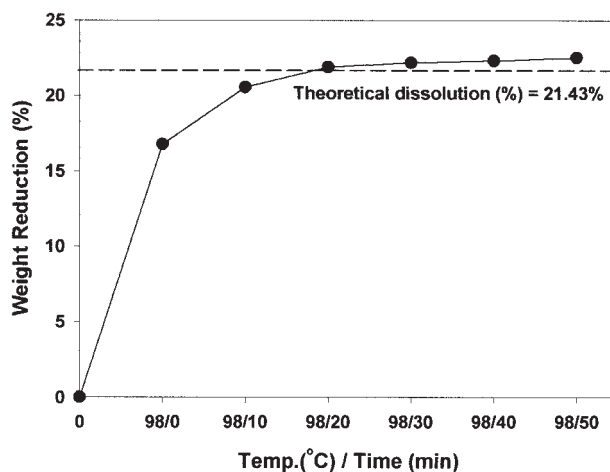
where  $R$  is the reflectance of an infinitely thick layer of material illuminated with light of known wavelength,  $K$  is the absorption coefficient, and  $S$  is the scattering coefficient. The function  $K/S$  is directly proportional to the concentration of colorant in the substrate.<sup>6</sup>

## RESULTS AND DISCUSSION

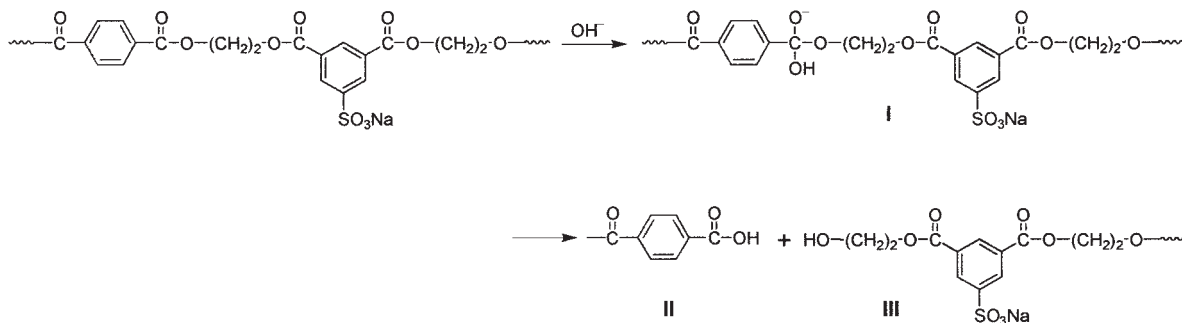
### Characterization of microfibers

The <sup>1</sup>H-NMR spectra of regular PET (the sector component) and alkali-soluble PET (the matrix component) revealed some differences. For the sector component, signals for the aromatic ring and aliphatic groups were found at 8.11 and 4.61–4.77 ppm, respectively. For the matrix component, a new peak appeared at 8.71 ppm that was a result of the proton of sodium 5-sulfoisophthalate in the polymer chain. The proton peak, attributed to the other protons of sodium 5-sulfoisophthalate, appeared at 8.06 ppm, although it overlapped with the peak of protons in terephthalate.

The DSC thermogram of the regular and alkali-soluble PET showed that the matrix component (alka-



**Figure 4** Dissolution behavior of circular-knit microfiber fabrics during high-temperature alkali treatment (98°C).



li-soluble PET, 210°C–211°C) had a lower melting point than the sector component (regular PET, 255°C–256°C). The meta linkage and the presence of the sulfonyl group of 5-sulfoisophthalate were considered as preventing the close packing of the polymer chain and also reducing the  $T_m$  of the copolymer.

#### Alkaline dissolution monitoring of circular-knit microfabrics

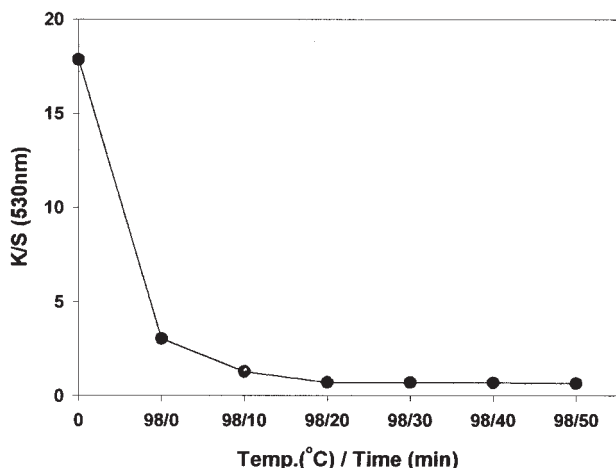
Figure 4 shows the dissolution behavior of the circular-knit microfiber fabrics during high-temperature alkali treatment. The weight reduction of the microfiber fabrics increased rapidly, particularly in the early stages of the alkali treatment, and appeared to reach a maximum after 50 min of treatment. The initial rapid rise was considered a result of the relatively easy hydrolysis of the matrix component, which was located around the sector (regular PET) components. The copolymer containing 5-isophthalate had a 60° bending of the polymer chains because of modifica-

tion with isophthalic acid (Fig. 2). This disturbed the straight zigzag structure of the chains, and steric hindrance of an optimum chain arrangement was generated.<sup>7</sup> A sodium salt of 5-sulfoisophthalic acid had an even greater adverse effect on the steric arrangement. Therefore, modified fibers (because of the higher accessibility of the amorphous regions) were subject to much more rapid hydrolysis. The modified PET fibers were sensitive to temperatures of about 100°C, at which nonmodified PET fibers were practically stable. The differences in the rate of hydrolysis in PET and a copolymer containing 5-sulfoisophthalic acid are the result of the “loosening” of the structure. The loosening of the amorphous phase was initiated by the effect of the heterogeneity of the PET chains, which was caused by the modification component.

In the reaction with alkali, the highly nucleophilic  $\text{OH}^-$  ion attacked the electron-deficient carbonyl carbon atom in the polyester (Scheme 1). The nucleophilic substitution reaction, which occurred via the forma-

TABLE I  
Cross Sections of Microfiber Fabrics after High-Temperature Alkali Treatment

Hydrolysis time (min)	Before hydrolysis	98°C, 0 min	98°C, 10 min	98°C, 20 min
Circular knitted fabrics				
Woven fabrics				



**Figure 5** Staining of cationic dyes on circular-knit microfiber fabrics during high-temperature alkali treatment (98°C).

tion of an intermediate anionic species (I), resulted in chain scission and the generation of terminal carboxy (II) and hydroxy (III) groups.<sup>1</sup> Hydrolytic degradation provoked by the effect of aggressive liquid media proceeded in three phases: adsorption of the aggressive substance onto 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 were the ester bonds, as shown in Scheme 1. The theoretical weight reduction value required for the completion of dissolution of the matrix component out of the radial-type PET microfibers was 21.43%, which could be verified by SEM, as shown in Table I. It is clear from the micrographs that the alkali-treated radial-type PET microfibers dissolved and separated into each sector component gradually as the alkali-treatment proceeded. The SEM micrographs reveal that dissolution of the sector component was complete after 20 min, and the results also were consistent with the dissolution behavior (Fig. 4). SEM is a useful tool for the verification of dissolution of radial-type microfibers. However, it is an expensive and time-consuming process. An alternative method for monitoring the dissolution is to measure the extent of cationic staining. Because of the presence of the sulfo 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 sulfo groups. The immobilization itself occurs by an ion exchange mechanism [eq. (2)].<sup>7</sup>

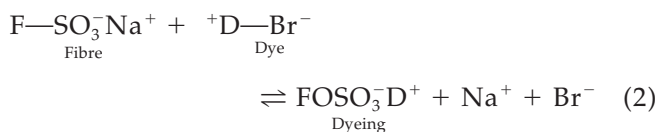
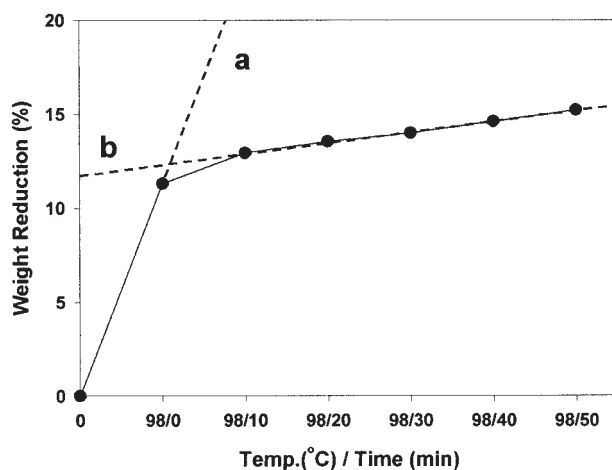


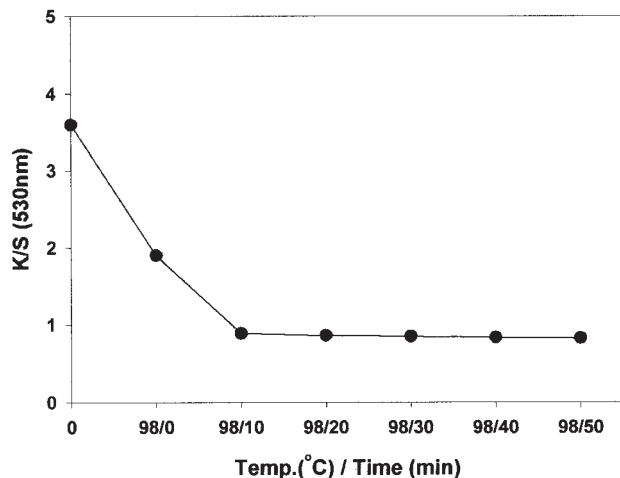
Figure 5 shows the staining of cationic dyes on alkali-treated circular-knit microfiber fabrics during high-temperature alkali treatment. It is clear that the color strength of the staining decreased as alkali-treatment time increased, finally reaching a leveling-off point after 20 min, after which no further changes were observed. The leveling-off points demonstrated that the alkali-soluble matrix component had been dissolved out, and only sector components (regular PET), which were hardly stained by cationic dyes, remained.

**Alkaline dissolution monitoring of woven microfabrics**

Microfibers are applied to a very wide range of fabrics including circular-knit and woven fabrics through fabrication with other fibers. For example, with woven fibers, regular PET can be used as warp yarns and microfibers as weft yarns, and vice versa. In this case, the termination of dissolution is more difficult to predict because the calculation of theoretical weight reduction required for the completion of dissolution is complicated by the weight reduction of other polyester fibers used together. Therefore, it was not easy to predict the termination of dissolution from the weight reduction curves of the fabrics. Figure 6 shows the dissolution behavior of woven microfiber fabrics during high-temperature alkali treatment. The weight reduction of the microfiber fabrics increased particularly rapidly in the early stages of alkali treatment, and the slope decreased with increasing alkali treatment time. The initial rapid rise (Fig. 6, regression line a) was considered ascribable to the relatively easy hydrolysis of the matrix component that surrounded the sector component. However, it was difficult to predict the exact termination point of dissolution from this weight reduction curve because the theoretical

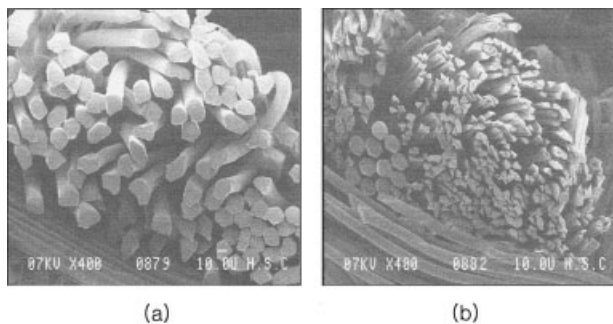


**Figure 6** Dissolution behavior of woven microfiber fabrics during high-temperature alkali treatment (98°C).

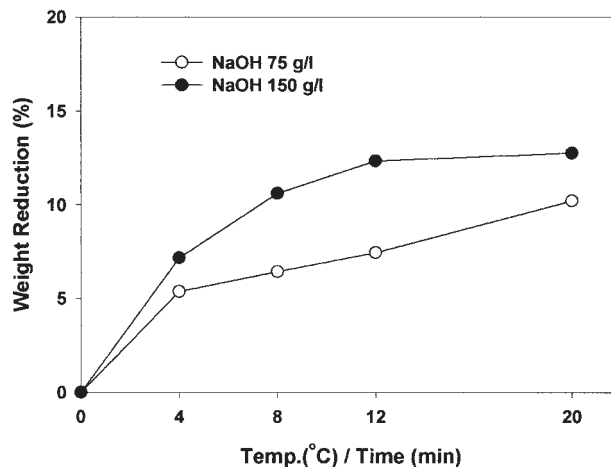


**Figure 7** Staining of cationic dyes on woven microfiber fabrics during high-temperature alkali treatment (98°C).

weight reduction values for the completion of dissolution of the matrix component out of radial-type polyester microfibrils were not known, and also the curves did not level off because of the slow and steady weight reduction of the regular polyester fibers (line b). Instead, the dissolution of the woven fabrics containing the radial-type microfibrils could be monitored and the termination points determined using the cationic dye-staining method (Fig. 7). The color strength of the staining decreased as alkali treatment time increased, finally reaching an equilibrium state after 10 min, after which no further changes were observed. Although the weight reduction curve (Fig. 6) did not reach an equilibrium state, the cationic dye-staining curve did not exhibit leveling off (Fig. 7), and therefore, it was easier to determine the termination point of dissolution. SEM observations confirmed the predicted termination points obtained by the cationic dye-staining method, as illustrated in Table I. The cross sections of the radial-type microfibrils of the gray



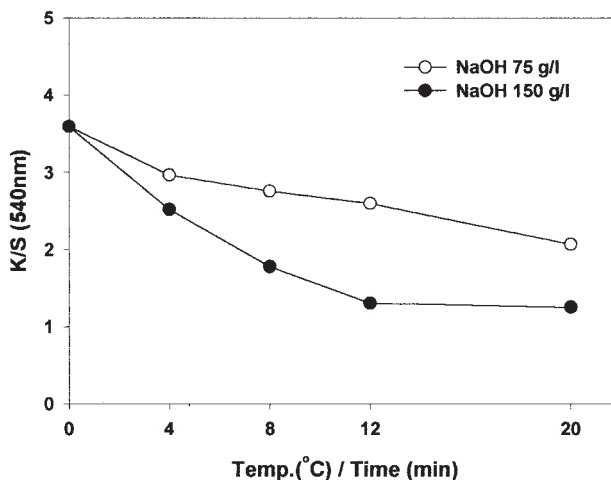
**Figure 8** Cross sections of radiation-type microfiber fabrics (98°C, 20 min): (a) gray fabric, (b) alkali-treated fabric.



**Figure 9** Dissolution behavior of woven microfiber fabrics during cold-pad batch alkali treatment (25°C).

fabric and the alkali-treated fabric are shown in Figure 8.

Figure 9 shows the dissolution of the woven microfibrils during cold-pad batch alkali treatment, which was successfully monitored by the cationic dye-staining method (Fig. 10). The color strength of the microfibrils stained by the cationic dye decreased slowly, and a leveling-off point was reached after about 12 h of aging at a concentration of 150 g/L. However, at a concentration of 75 g/L the saturation level was not reached, even after 20 h of aging, indicating that the concentration was not high enough to complete the dissolution of microfibrils within 20 h of aging time. Evidence of the completion of dissolution observed by the cationic dye-staining method was obtained by SEM observation (results not shown).



**Figure 10** Staining of cationic dyes on woven microfibrils during cold-pad batch alkali treatment (25°C).

### CONCLUSIONS

In the dissolution of the matrix component out of radial-type microfibers, it is not easy to predict the termination point of the dissolution process from the weight reduction curves of the fabrics. Although scanning electron microscopy is a useful tool for verification of the dissolution process, this method is expensive and time consuming. Therefore, in this study, a much simpler dissolution-monitoring method was investigated, using cationic dye staining. The alkaline dissolution behavior of radial-type poly(ethylene terephthalate) microfibers was successfully monitored using this cationic dye-staining method.

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