Surface Hydrolysis of Filaments Based on Poly(trimethylene terephthalate) Spun at High Spinning Speeds

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ABSTRACT: The surface alkaline hydrolysis of fibers made from poly(trimethylene terephthalate) (PTT) was studied after extruding the polymer at high spinning speeds from 2000 to 6000 m/min and heat setting in the range of temperatures from 100 to 180°C. Fiber weight loss increased with an increasing heat-setting temperature but it was also dependent on the spinning speed. Some of the partially hydrolyzed fibers had a well-developed, hydrophilic surface, and pore size in the range of 0.69 to 1.20 μm. The optimum reaction and morphological conditions for increasing porosity in PTT fibers depends on spinning speed and heat-setting temperature. A temperature of 180°C is the upper limit for heat-setting PTT filaments but seems to be the most effective for making porous fibers. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1724–1730, 2004

Key words: poly(trimethylene terephthalate); polyesters; alkaline hydrolysis; porous fibers; high speed spinning; extrusion; polyesters; surfaces

INTRODUCTION

Melt spinning of polyester fibers is thought to cause differences in morphology from the skin to the core of a fiber, because the outer regions cool more quickly than the fiber interior.[1–2] This results in a greater degree of molecular orientation and lateral order in the outer skin than in the core of the fiber. This differing morphology across the fiber cross section would be expected to affect the dyeing characteristics of polyester but it also may affect the alkaline hydrolysis of polyester fibers.

The effect of alkali on polyester was first disclosed by ICI in a 1952 patent.[3] The treatment, then applied to the fabric of flat (untextured) yarn, provided softer tactility with less synthetic hand. Although poly(ethylene terephthalate) (PET) fiber is generally resistant to chemical attacks, the ester linkage in the PET molecular chain can be attacked by some reagents such as aqueous NaOH solution to give soft and hydrophilic finishes to the fabric. Hydrolysis with aqueous sodium hydroxide removes successive layers of polymer from the fiber surface through chain scission and renders the surface more hydrophilic.[3–5]

Aminolysis has also been studied in relation to the changes in fine structure and morphology of PET fiber and film.[6–9] Several investigations were reported on the alkaline hydrolysis of polyester. They demonstrated that weight loss was a function of several variables such as temperature, treatment time, and alkali concentration.[10] Several reports were published on the rate of hydrolysis and showed either a linear or an exponential relationship to these variables.[11] Furthermore, some researchers studied the effect of heat-setting temperature on the hydrazine treatment of PET.[12]

Although the alkaline hydrolysis of PET fibers usually leads to a slightly pitted surface, we thought that varying the fiber structure could affect the rate of hydrolysis and perhaps would result in the development of a more porous and hydrophilic fiber surface. Poly(trimethylene terephthalate) (PTT) was then chosen for the investigation. In this article, we have carefully studied the partial alkaline hydrolysis (etching) of fibers spun from PTT polymer at high spinning speeds from 2000 to 6000 m/min and heat set at various temperatures. Porosity of these fibers was also characterized.

EXPERIMENTAL

Materials

We thank Shell Chemical Co. (USA) for supplying PTT chips, which we used in this study. The intrinsic vis-

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cosity (IV) of the polymer chip was 0.97 dL/g. The corresponding molecular weight of PTT was 75,500 g/mol. Sodium hydroxide was supplied by Fisher Scientific (Hampton, NH).

Spinning process

PTT polymer chips were dried at 140°C under vacuum for 12 h. A Fourne single screw with a diameter of 27 mm was used. The motor speed of the extruder was kept at 24.9 rpm. A spin pack was designed for mono-filament spinning. The round orifice of the spinneret plate was 0.6 mm in diameter and 1.38 mm in length. The threadline was cooled at room temperature through a 4-m cooling path. Take-up speeds varied from 2000 to 6000 m/min and pumping speed was adjusted from 14.378 to 48.938 rpm to prepare 13 denier fibers at the various take-up speeds.

Intrinsic viscosity and molecular weight

Intrinsic viscosity of PTT was determined by using Huggins' equation:

$$\eta_{red} = [\eta] + K_H[\eta]^2 C \tag{1}$$

where η_{red} is the reduced viscosity; $[\eta]$ is the intrinsic viscosity; C is the polymer concentration; and K_H is the constant.

A mixture of phenol and 1,1,2,2,-tetrachloroethane $1:1$ (w/w) was used as a solvent for PTT polymer. Viscosity measurements were performed at 25°C by using a Ubbelohde-type viscometer.

The molecular weight of a PTT polymer was determined from the Mark–Houwink equation

$$[\eta] = KM^\alpha \tag{2}$$

where $K = 8.2 \times 10^{-2}$ ml/g[13]; $\alpha = 0.63$[13]; and M is the molecular weight.

Heat-setting

PTT as-spun fibers were heat treated at a fixed length of 2 in. The heat-set temperature was 100, 120, 140, 160, and 180°C. A Fisher isothermal oven was used for 10 min.

Hydrolysis

One-half a gram of PTT as-spun fibers wound from 2000 to 7000 m/min take-up speed was treated with 50 mL of 25% aqueous sodium hydroxide solution at 86°C for 30, 60, 90, and 120 min in a shaking bath. The partially hydrolyzed fibers were washed with distilled water. A similar treatment was also given to heat-set fibers. Weight loss from hydrolysis was determined by

TABLE I
Birefringence of PTT Filaments as a Function of Spinning Speed

Spinning speed (m/min)	Birefringence
2000	0.038
3000	0.047
4000	0.054
5000	0.055
6000	0.052
7000	0.052

weighing a sample before and after hydrolysis. Duplicate runs for weight loss varied within a 2% range.

SEM photographs

SEM photographs were taken on a Hitachi S-3200N scanning electron microscope. The magnification was ×2000.

Crystal size

A Siemens Type-F X-ray diffractometer operated at 30 kV and 20 mA with nickel-filtered CuKα radiation was used for equatorial wide-angle scans. Fiber samples were mounted as a bundle of parallel fibers on specially designed brass holders. Crystal size L was calculated by using Scherrer's equation[14]

$$L = \frac{0.9\lambda}{\beta\cos\theta} \tag{3}$$

where λ is the radiation wavelength of 1.54 Å; β is the half-width of the reflection peak in radians; and θ is the Bragg angle in degrees.

Measurements of pore size

Pore size was measured with Adobe Photoshop software. SEM micrographs of hydrolyzed samples were opened on a computer screen and the screen ruler was used to measure the pore size. An average of 20 individual measurements was taken for each sample.

Birefringence

Birefringence was determined by using a Zeiss interference microscope.

RESULTS AND DISCUSSION

Surface hydrolysis of PTT fibers

As can be seen in Table I, the birefringence of PTT filaments increases to 0.055 with an increasing spinning speed up to 5000 m/min and then slightly de-
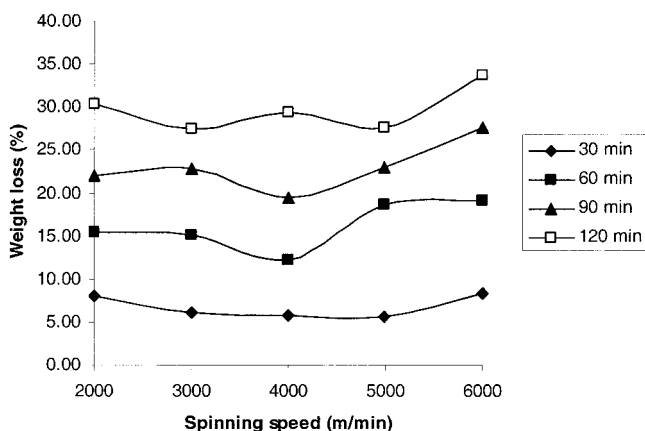
Figure 1 Effect of spinning speed on the weight loss of non-heat-set PTT as-spun fibers at various reaction times.

Figure 2 Effect of hydrolysis time on the weight loss of non-heat-set PTT as-spun fibers at various spinning speeds.

creases as a result of the stress-induced crystallization. This is typical behavior for the high spinning of PTT[15–16] and some other types of thermoplastic polymers such as nylon 6, nylon 66, and PET. It may also indicate that molecular orientation increases only when the spinning speed is increased to 5000 m/min; however, the degree of crystallinity tends always to increase.[15–16] As shown in Table I, the birefringence of PTT filaments is relatively low but agrees with results reported by Grebowicz et al.[16] These low birefringence values are because the intrinsic birefringence n_c^0 of PTT crystal is only 0.029.[17]

The effect of alkali on polyester was first disclosed by ICI[3] and is now primarily used to reduce fiber fineness and to improve esthetics. Change in esthetics is a direct function of fabric weight loss. In this study, PTT as-spun fibers are tested by alkali hydrolysis to determine weight loss and perhaps to develop porosity. The weight loss of PTT as-spun fibers after alkali hydrolysis at 30, 60, 90, and 120 min is shown in Figure 1. At low hydrolysis times up to 90 min, weight loss slightly decreased with an increase in take-up speed, passed through a minimum at around 4000 m/min take-up speed, and then slightly increased above 4000 m/min take-up speed. This effect can be linked to some changes in the fine structure, namely to an increase in the degree of crystallinity and changes in molecular orientation for the PTT as-spun fiber at each take-up speed.

Figure 2 shows the effect of hydrolysis time on the weight loss of hydrolyzed PTT as-spun fibers at 30, 60, 90, and 120 min. As the hydrolysis time increases, weight loss also increases, although this relationship is not linear. However, Zeronian[18] reported a linear relationship between the reaction time and the weight loss for the hydrolysis PET filaments when the experiments were carried out at 21°C.

The weight loss of the fiber in the alkaline hydrolysis can be described by the following kinetic equation
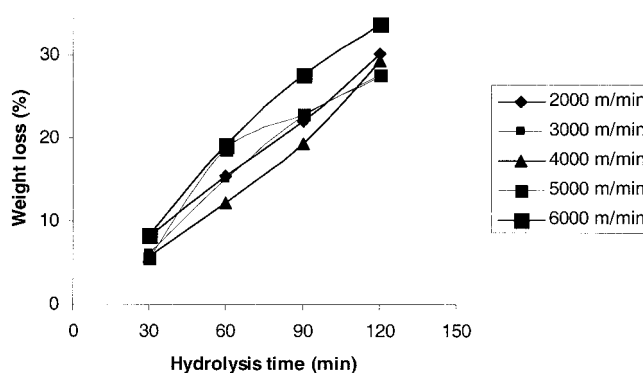
$$\frac{dm}{dt} = -kAc_{\text{NaOH}} \qquad (4)$$

where t is the time; m is the weight of fiber; k is the rate constant; A is the fiber surface area; and c_{NaOH} is the concentration of sodium hydroxide.

A similar equation is also given by Grancaric and Kallay.[19] Interestingly, Haghighat Kish[20] demonstrated that calcium hydroxide can be equally as effective as sodium hydroxide in the hydrolysis of PET fibers. Apparently, as can be seen in eq. (4), weight loss can be affected by the fiber surface area too. Denier of our filaments was 13; therefore, the surface area for these filaments was relatively large. As expected, the measured weight losses are relatively small for our samples and do not exceed 35%.

Figure 3 shows the effect of take-up speed on the weight loss of hydrolyzed PTT as-spun fibers with different heat-setting temperatures. As can be seen in
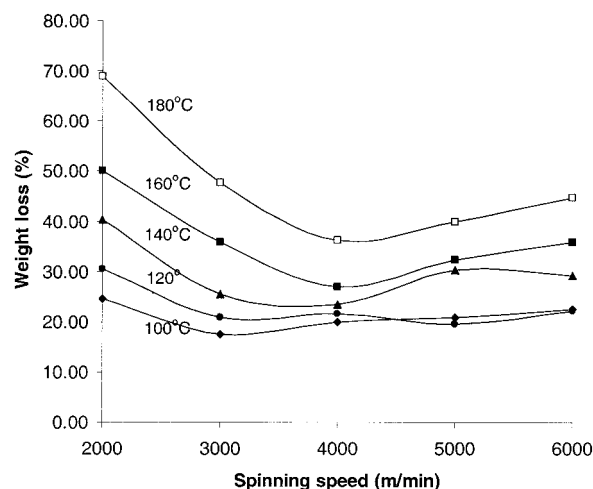

Figure 3 Effect of spinning speed on the weight loss of heat-set PTT as-spun fibers at various heat-setting temperatures. Hydrolysis temperature was 86°C and reaction time was 90 min.

this figure, heat-setting temperature has a very pronounced effect on weight loss in the alkaline hydrolysis of PTT filaments. The trend of weight loss at each take-up speed is similar to that of the non-heat-set filaments. Again a minimum is found around 4000 m/min take-up speed and is most distinct for filaments spun and heat set at 180°C. The latter filaments may have the lowest molecular orientation. We may postulate that this factor contributed to the larger weight loss.

Niu and Wakida[12] studied PET fibers that were heat set in the range from 100 to 200°C and then hydrolyzed with 10% aqueous sodium hydroxide. They first reported that, as the result of the surface hydrolysis, the weight loss for PET fibers decreased with an increasing heat-setting temperature up to 140°C and then increased at temperatures above 140°C. The authors attributed this phenomenon to changes in the fine structure, especially in the amorphous regions of the fiber. This resulted in an increase of the crystallinity and perhaps the formation of larger crystals because of the heat-induced crystallization. We believe that a similar phenomenon may have occurred for our heat-set PTT filaments[21]; however, the measurement of crystal dimension (see Fig. 4) also revealed that the crystal size depends on the spinning speed.

Figure 5 shows the effect of heat-setting temperature on the weight loss of hydrolyzed PTT as-spun fibers after 90 min. Indeed, as a result of the more open structure of heat-set PTT fibers, the weight loss for as-spun PTT fibers increases with an increasing heat-setting temperature.

Surface characteristics of PTT fibers

Untreated melt-spun PTT or PET filaments often have a round cross section and a smooth surface. As the outer layer of non-heat-set PET fiber is hydrolyzed, the fiber surface becomes rougher and relatively small
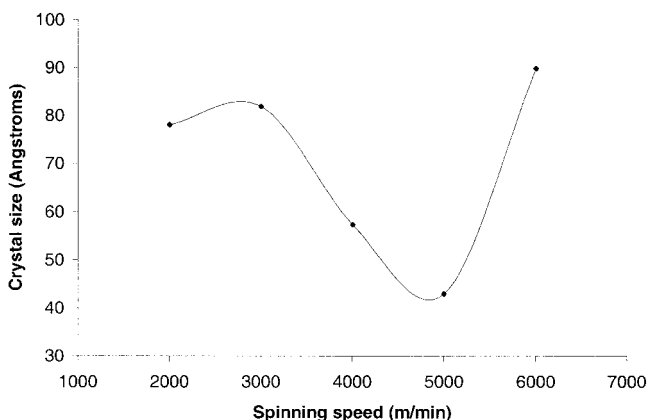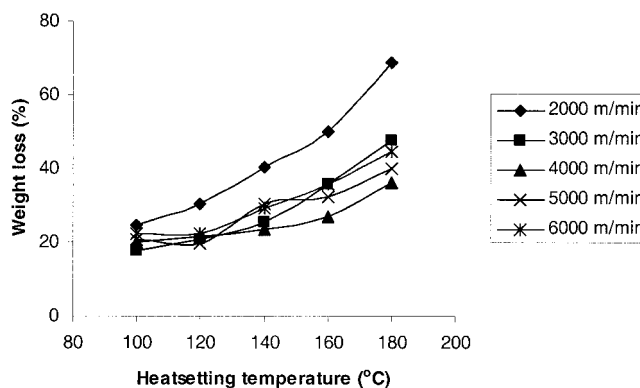
Figure 5 Effect of heat-setting temperature on the weight loss of heat-set PTT as-spun fibers. Hydrolysis time was 90 min and temperature was 86°C.

irregular pits are observed.[12,18] Because heat setting increases the crystallinity, it may also produce more open fiber structure[12,21]; consequently, one could expect that the surface of our heat-set and hydrolyzed PTT filaments should be more porous.

Typical SEM photographs of PTT as-spun fibers hydrolyzed for 90 min at 86°C are shown in Figure 6(a, b, c). As can be seen in these figures, the surface of the filament spun at a take-up speed of 4000 m/min is less rough than other filaments. A similar trend was seen for all the heat-setting temperatures; however, only a small amount of porosity can be developed when the relatively low heat-setting temperatures of 120 or 140°C are used. Definitely, it can be observed that increasing the heat-setting temperature tends to increase the pore size. It can be noted that, as the heat-setting temperature increased, the pore size was also increased for the same spinning speed. Fascinatingly, some of the etched fibers [see Fig. 6(c)] even have unique honeycomb structures. Figure 7 shows pore size as a function of spinning speed for the highest heat-setting temperature of 180°C. Interestingly, pore size initially increased with an increasing take-up speed passed through a minimum at around 5000 m/min take-up speed and then increased at above 5000 m/min.

In his elegant and detailed article, Dave et al.[22] documented that the hydrolysis of PET fabric leads to a highly hydrophilic fiber surface due to the formation of hydroxyl polymer end groups. He also observed that as a result of the reaction, the fiber surface became slightly rougher and only relatively small irregular pits were observed. It is, therefore, plausible to point out that the partially hydrolyzed PTT fibers having pore size in the range of 0.69 to 1.20 μm should have more developed surface area and enhanced hydrophilic surface.

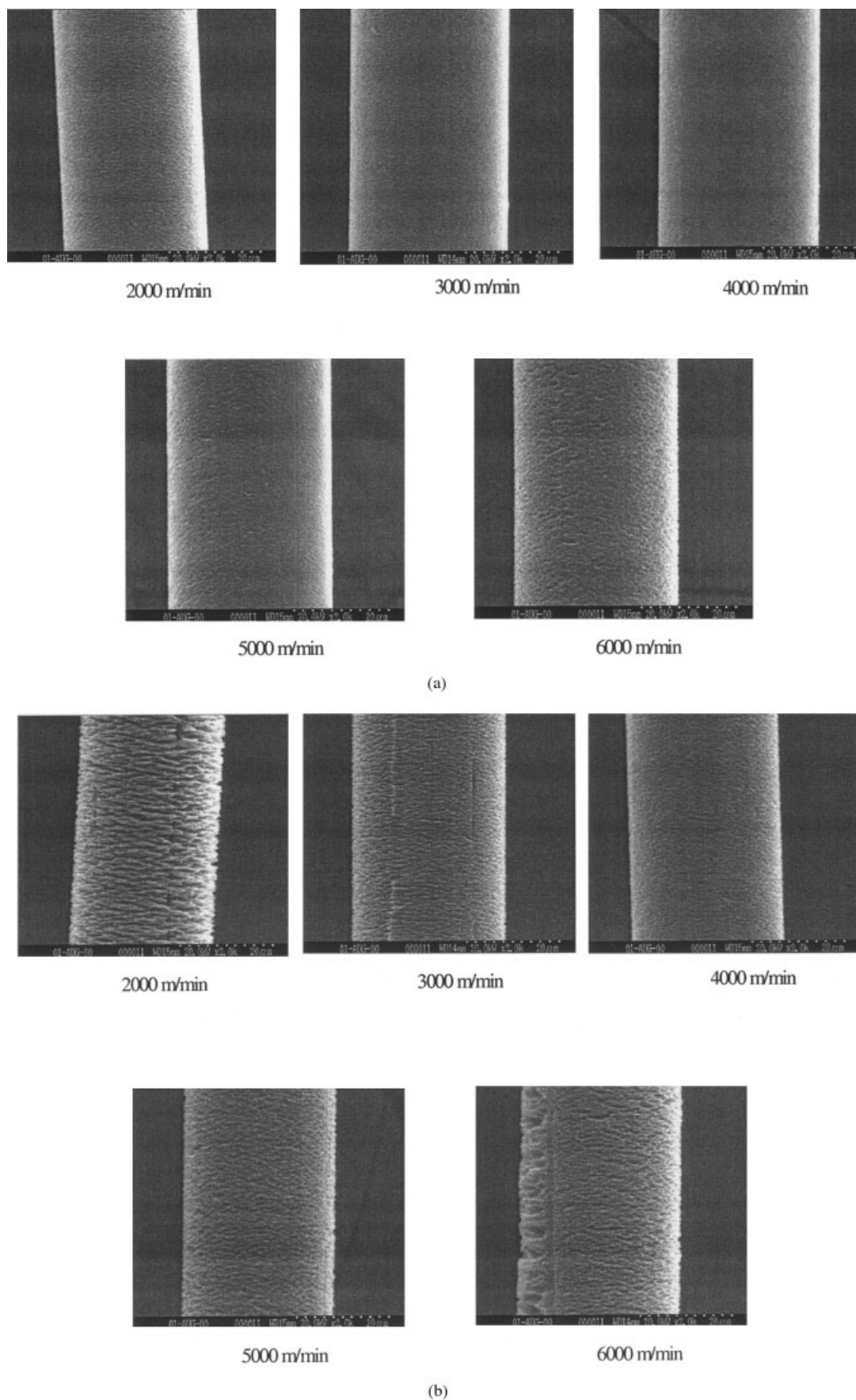The development of highly porous synthetic fibers could be a technological breakthrough. Cooman et

Figure 4 Apparent crystal sizes for heat-set PTT as-spun fibers. Heat-setting temperature was at 180°C for 10 min.

2000 m/min

3000 m/min

4000 m/min

5000 m/min

6000 m/min

(a)

2000 m/min

3000 m/min

4000 m/min

5000 m/min

6000 m/min

(b)

Figure 6 SEM micrographs of PTT fibers hydrolyzed at 86°C for 90 min at various spinning speeds after heat setting at (a) 120°C, (b) 160°C, and (c) 180°C.
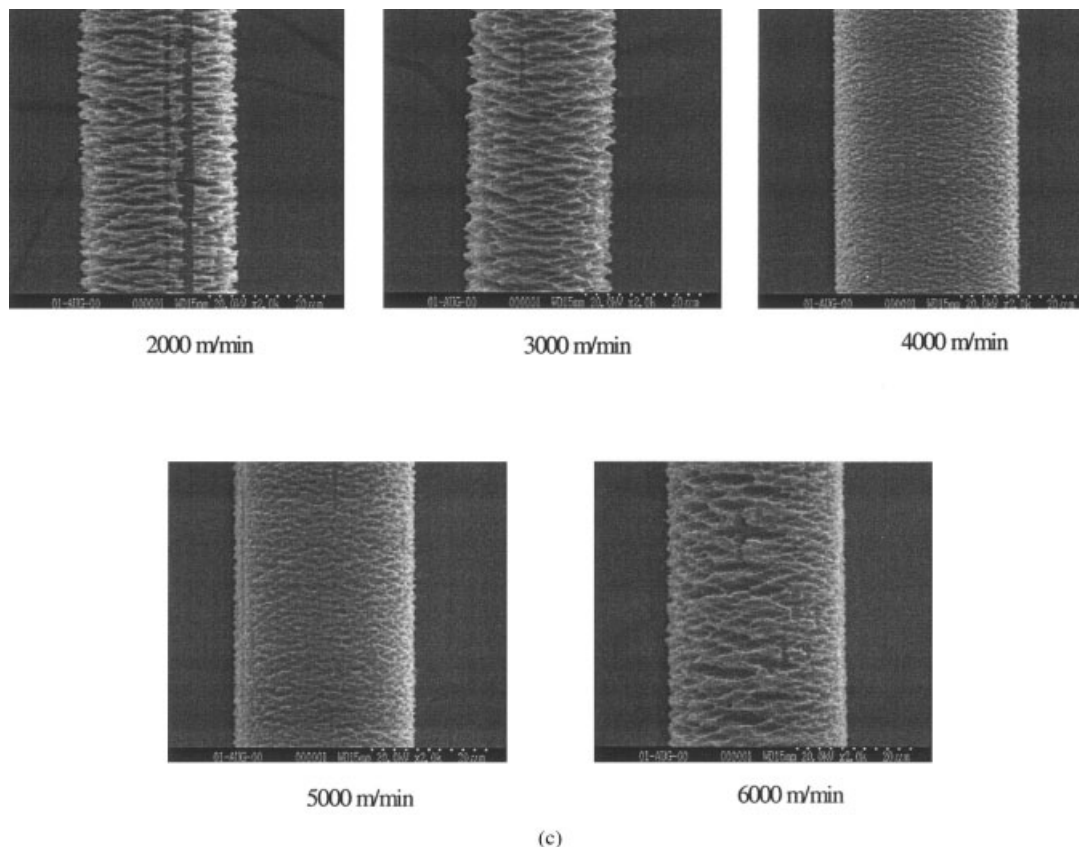
2000 m/min   3000 m/min   4000 m/min

5000 m/min   6000 m/min

(c)

Figure 6 (*Continued from previous page*)

al.[23] proposed the preparation of porous fibers from a quasi-ternary system poly(methyl methacrylate)/poly(ethyl methacrylate-1-butanol) based on the combination of different liquid–liquid demixing process that interferes with the vitrification process. The results presented in this article seem to show that a simple process also can be developed based on selective heat-setting and surface hydrolysis of high-denier PTT fibers spun at high spinning speeds.
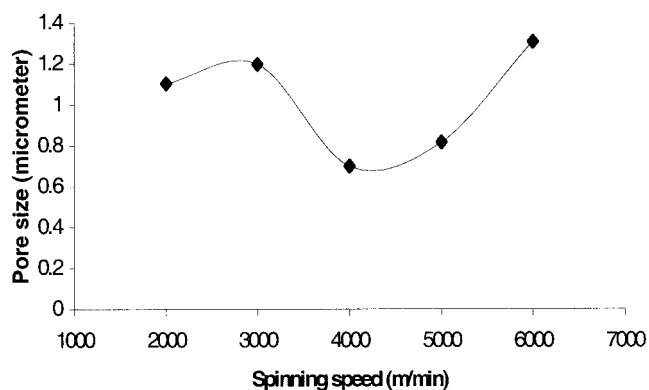

Figure 7 Apparent pore sizes for heat-set PTT as-spun fibers. Heat-setting temperature was at 180°C for 10 min.

CONCLUSION

The surface alkaline hydrolysis of high-denier PTT fibers spun at high spinning speeds from 2000 to 6000 m/min and heat set in the range of temperatures from 100 to 180°C is a relatively complex phenomenon. Although the fiber weight loss clearly increased with an increasing heat-setting temperature, the effect of spinning speed or molecular orientation was only dominant at speeds lower than 4000 m/min.

Because increasing spinning speed and heat-setting temperature lead to some changes in the fine structure of PTT fibers, we can postulate that the rate constant in the kinetic equation

$$\frac{dm}{dt} = -kAc_{\text{NaOH}} \qquad (5)$$

for weight loss in the alkaline hydrolysis can be affected by fiber morphology.

Some of the partially hydrolyzed PTT fibers had a well-developed, hydrophilic surface, and pore size in the range of 0.69 to 1.20 μm. The optimum reaction and morphological conditions for increasing porosity in PTT fibers depend on spinning speed and heat-setting temperature. A temperature of 180°C is the

upper limit for heat-setting PTT filaments but seems to be the most effective for making porous fibers.

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