Kinetics of Alkaline Hydrolysis and Morphologies of Novel Poly(ethylene terephthalate) Micro-Porous Hollow Fibers and Functional Characteristics of Fabrics

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ABSTRACT: This investigation explores the kinetics of the alkaline hydrolysis of regular poly(ethylene terephthalate) (PET) solid fibers and PET micro-porous hollow fibers, using statistical regression analysis. Statistical regression analysis results concerning the kinetics of the alkaline hydrolysis of regular PET solid fibers and PET micro-porous hollow fibers yielded a β value of 1. The R^2 of the kinetic equation for α values from 1.07 to 1.16 exceeded that for $\alpha = 1$. The rate constants of alkaline hydrolysis followed the order PET micro-porous hollow fibers $\gg$ regular PET solid fibers. A morphology of large pores of diameter 0.1–3.5 μm was observed following alkali treatment of the PET micro-porous hollow fibers. The weight loss percentage of the hollow fibers was around 20%. The hollowness of the PET micro-porous hollow fibers after alkali treatment was between 30 and 32%. The PET micro-porous hollow fibers exhibited simultaneous water-absorption/release and keep-warm functions. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1822–1827, 2009

Key words: PET; micro-porous; hollow; water-absorption; water-release; keep-warm

INTRODUCTION

Poly(ethylene terephthalate) (PET) has a regular linear structure, which is characterized by repeated units that form the backbone of the molecular chain.[1] PET is a useful fiber because it is strong, inert, and thermally stable. These properties also favor its use in microelectronics and solid-state devices. Hall and Whinfield was the first to treat PET successfully with aqueous sodium hydroxide (NaOH) solution to improve the handling of the fiber and fabric.[2] Nishida and Latta also discovered that treatment with alkali promoted the absorption of moisture, as well as the antistatic and soil release properties of the fiber.[3,4] Some works have addressed the kinetics of alkaline hydrolysis, as follows. Namboori found that when PET is treated with various concentrations of aqueous NaOH, the initial concentration of NaOH markedly affects the weight loss of the fiber. At a fixed temperature, the weight loss was proportional to the period of hydrolysis.[5] Although this observation corresponded to that of Waters, Pficer posited that the weight lost by PET during alkaline hydrolysis varied exponentially with the treatment time.[6,7]

In a study of the alkaline hydrolysis of PET fiber, Kallay et al. stated that at a constant concentration of aqueous NaOH solution, the weight loss was proportional to the specific area of the fiber.[8] Heidemann found that the radius of the fiber decreased as the concentration of aqueous NaOH solution increased.[9] Hsiao et al. noted that the kinetics of the alkaline hydrolysis of the PET/CDPET polyblended hollow fiber were similar those of PET hollow fiber.[10,11] In light of the above findings, this work extensively examines the kinetics of alkaline hydrolysis and the morphology of novel PET micro-porous hollow fibers following alkali treatment. Moreover, the functional characteristics of various fabrics were also discussed.

EXPERMENTAL

Materials

Regular (PET) solid fibers were kindly donated by the Shinkong Synthetic Fiber Corporation (Taoyuan, Taiwan). PET micro-porous hollow fibers (trade mark HydroPore®) without alkali treatment were obtained from the Material and Chemical Research Laboratories/Industrial Technology Research Institute (Hsinchu, Taiwan). The cross-sections of PET

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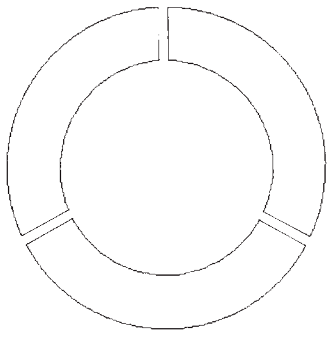


Figure 1 Hollow spinneret with "3C" shape.

micro-porous hollow fibers were triangular and hollow, obtained from the hollow spinneret with the "3C" shape (as shown in Fig. 1). The plain weave fabrics (120–240 g/m^2) were produced using the PET micro-porous hollow fibers and then treated with aqueous NaOH.

Measurements

Stress–strain data for all samples were obtained with an extension rate of 200 mm/min using a Zwick 1511 Instron instrument. The increase in the tenacity and elongation of the specimen was recorded on a moving chart. To measure shrinkage in boiling water, a loop of fibers whose initial length (l_0) was 50 cm under slight tension that did not cause deformation, was immersed in boiling water for 30 min. The length after shrinkage (l_s) was measured under the same tension. Shrinkage in boiling water was determined using the follow equation, shrinkage (%) $= [(l_0 - l_s)/l_0] \times 100$ (%).[12–15] The measured weight loss of the samples after treatment with alkali was calculated as follows; weight loss (%) $= (W_1 - W_2)/W_1 \times 100$ (%), where W_1 and W_2 were the weight of the samples before and after alkaline hydrolysis, respectively.[16] A scanning electron microscope (SEM), Cambridge Steroscan-600, was adopted to examine the morphological structure of each sample, which was sputter-coated with Au to prevent oxidation. The specific area of the samples was measured using a Micrometrics Flowsorb II 2300 specific area meter. Hollowness (%) was measured using the area method following SEM observation. The height of water absorbed by the fabric was measured. The samples were 200 mm long × 25 mm wide. Both ends of the samples were fixed to an acrylic strip. One was immersed in water to a depth of approximately 5 mm. The height of water absorbed by the fabric was measured after 10 min. The water-release rate of fabric was measured. The strip samples were 50 mm long by 50 mm wide. The water was captured using a suction tube, of which one end was put into the fabric. The weight was recorded as W_3. The fabric weight (W_4) was measured after 12 min at 23°C and R.H. 65%. The water release rate (%) was taken to be 100 $(W_3 - W_4) \div W_3$ (%). The heat retention ratio of the fabric was estimated using a heat retention machine. The fabric specimens were 50 mm long by 50 mm wide. The heat retention ratio was taken to be 100 $(H_1 - H_2) \div H_1$ (%), where H_1 was the exothermic heat (J/cm^2 s) of the reference holder and H_2 was the exothermic heat of the fabric that was placed in the same holder after 2 h.

RESULTS AND DISCUSSION

Physical properties of fibers

Table I provides the physical properties of regular PET solid fibers and PET micro-porous hollow fibers before alkali treatment. The specification of the two fibers was 75 denier/36 filaments. The fineness of the fiber was around 2.1 denier/filament (den/f; dpf). Since the fibers were hollow, the tenacity of the PET micro-porous hollow fibers was less than that of regular PET solid fibers. The elongation of PET micro-porous hollow fibers was similar to that of regular PET solid fibers. The tenacity, elongation, and boiling water shrinkage (BWS) of two fibers were suitable for weaving and knitting. The wall thickness/hollowness of PET micro-porous hollow fibers before alkali treatment was about 5.4 μm/24.3%. The well-known advantage of hollow fibers is their low-thermal conductivity. Hence, regular hollow fibers are applied only in keep-warm fabrics. Micro-porous fabrics are produced from PET micro-porous hollow fibers following alkali treatment. Therefore, alkali-treated PET micro-porous hollow fibers have a wider range of applications than regular PET solid fibers. They include, for example, ladies' blouses, dresses, blousons, casual coats, skirts, sports casual wear, and other clothes. The next section will discuss the kinetics of alkaline

TABLE I
Physical Properties of Regular PET Solid Fibers and PET Micro-Porous Hollow Fibers before Alkali Treatment

Type	Specification (den/f)	Tenacity (g/den)	Elongation (%)	BWS[a] (%)	Wall thickness (μm)	Hollowness (%)
Regular PET solid fibers	75/36	4.46	34.2	8.2	–	–
PET micro-porous hollow fibers	75/36	3.93	32.9	8.1	5.4	24.3

[a] Boiling water shrinkage.

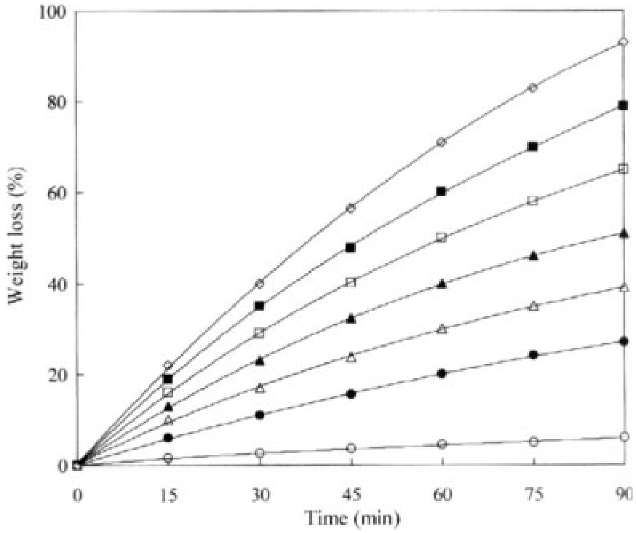


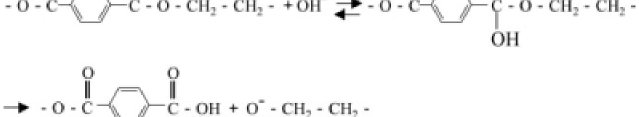
Figure 2 Percentage weight loss as function of time for regular PET solid fibers and PET micro-porous hollow fibers at 120°C for 15–90 min. (○): Regular PET solid fibers, 1.0% NaOH alkali treatment; (●): PET micro-porous hollow fibers, 0.5% [NaOH] alkali treatment; (Δ): PET micro-porous hollow fibers, 0.6% [NaOH] alkali treatment; (▲): PET micro-porous hollow fibers, 0.7% [NaOH] alkali treatment; (□): PET micro-porous hollow fibers, 0.8% [NaOH] alkali treatment; (■): PET micro-porous hollow fibers, 0.9% [NaOH] alkali treatment; (◆): PET micro-porous hollow fibers, 1.0% [NaOH] alkali treatment.

hydrolysis and the morphologies of regular PET solid fibers and PET micro-porous hollow fibers before and after alkali treatment.

Kinetic behavior associated with alkaline hydrolysis of fibers

Figure 2 summarizes the percentage weight losses by all fibers on treatment with 0.5–1.0% sodium hydroxide solution at 120°C for various intervals. Clearly, the percentage weight loss of PET micro-porous hollow fibers exceed that of regular PET solid fibers.

This work examined the kinetics of the alkaline hydrolysis of regular PET solid fibers and PET micro-porous hollow fibers, using statistical regression analysis. eq. (1) describes the dissolution of PET.[17]



(1)

In the first step, OH^- in aqueous sodium hydroxide (NaOH) solution attacks $\overset{-C-}{\underset{O}{\|}}$ with a lower electron cloud density, yielding an intermediate. In the second step, a further reaction between OH^- and —C— breaks the macromolecular chain and generates —COOH and O^-—CH_2—CH_2—; the final product is —COONa in alkaline solution. Quantitative results reveal that the reaction rate is related to the concentration of OH^- and $\overset{-C-}{\underset{O}{\|}}$ in the reaction system. Hence, the reaction rate can be expressed as eq. (2).[8]

$$-\frac{dW}{dt} = KC^{\alpha}A^{\beta} \tag{2}$$

where W is the weight of the sample (gram); t is the reaction time (minute); C is the concentration of NaOH (%, g/L); A is the reactive surface area (m^2); K is the rate constant of alkaline hydrolysis, and α and β represent the reaction progression.

The kinetic equation of the alkaline hydrolysis of regular PET solid fibers and PET micro-porous hollow fibers is $-dW/dt = K\cdot C^{\alpha}\cdot A^{\beta}$. If α is one, then the $|R^2 - 1|$ increases with an increase of the β value because the percentage weight lost is proportional to the reactive surface area of the sample.[8] The β value was at least one. When β is one, $|R^2 - 1|$ is at its minimum, indicating that β value is equal to 1. Figure 3 summarizes the kinetic measurements.

When β is one, the kinetic equation for alkaline hydrolysis has a minimum $|R^2 - 1|$ between 1.07 and 1.16 for α values. Because the percentage weight loss was proportional to the concentration of NaOH

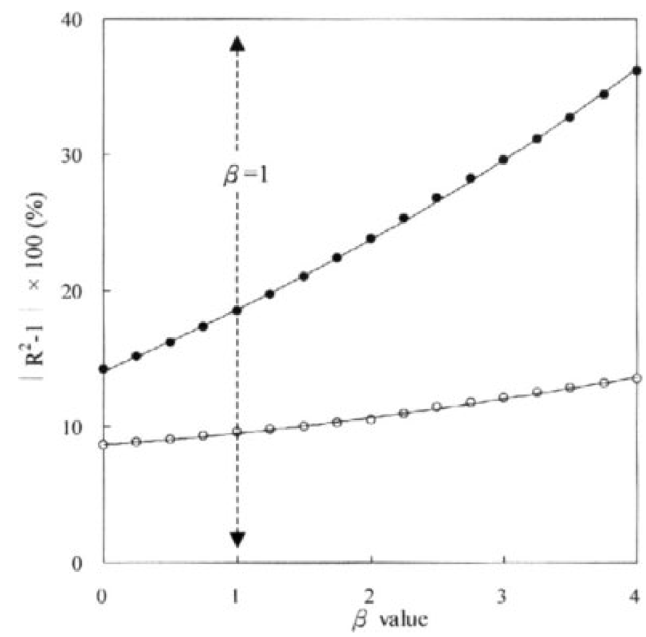


Figure 3 $|R^2 - 1|$ as function of β for regular PET solid fibers and PET micro-porous hollow fibers, given $\alpha = 1$. (○): Regular PET solid fibers, (●): PET micro-porous hollow fibers.

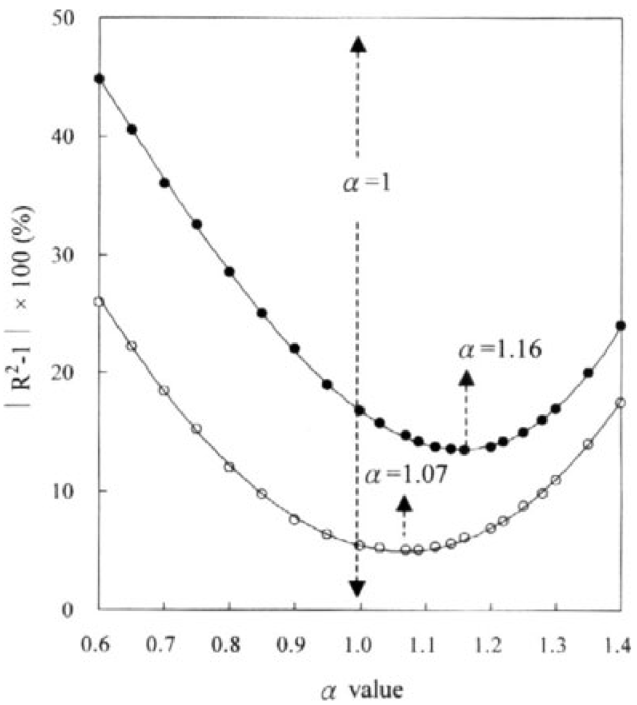


Figure 4 $|R^2 - 1|$ as function of α for regular PET solid fibers and PET micro-porous hollow fibers, given $\beta = 1$. (○): Regular PET solid fibers, (●): PET micro-porous hollow fibers.

in aqueous solution,[5] α is at least one. When α is between 1.07 and 1.16, $|R^2 - 1|$ is at its minimum. Figure 4 summarizes the kinetic measurements.

The statistical regression analysis of the kinetics of the alkaline hydrolysis of regular PET solid fibers and PET micro-porous hollow fibers demonstrated that β equaled one and that the R^2 of the kinetic equation for an α value from 1.07 to 1.16 exceeded that for $\alpha = 1$. Table II summarizes the kinetic measurements. Experimental results revealed that the rate constants of alkaline hydrolysis followed the order PET micro-porous hollow fibers ≫ regular PET solid fibers.

Morphologies of PET micro-porous hollow fibers following alkali treatment

A SEM was utilized to visualize the microstructure of the PET micro-porous hollow fibers following alkali treatment with various concentrations of aqueous NaOH (Fig. 5). As presented in Figure 5(a), both the inside and outside of the walls of the PET micro-porous hollow fibers were smooth before alkali treatment. Under constant treatment conditions (120°C/45 min), the surface voids of PET micro-porous hollow fibers after alkali treatment increased with increase in aqueous NaOH content. Figure 5(b–g) displays the morphologies of PET micro-porous hollow fibers after alkali treatment. Both the external surface and the internal surface of the hollow wall were etched, indicating that the wall of PET micro-porous hollow fibers between the exterior and interior surfaces was penetrated. Clearly, the wall thickness/hollowness of the PET micro-porous hollow fibers decreased/increased as the aqueous NaOH content increased.

Figure 5(c) presents the PET micro-porous hollow fibers following alkali treatment with 0.6% sodium hydroxide solution at 120°C for 45 min. The percentage weight loss of the hollow fibers was around 20%. PET micro-porous hollow fibers had large micro-pores with diameter of 0.1–3.5 μm after alkali treatment, and the hollowness of the fibers was between 30 and 32%.

Functions of fabrics

The plain weave fabrics (120–240 g/m²) were produced using the PET micro-porous hollow fibers and were then treated with aqueous NaOH. The water-absorption and water-release rate of fabrics of the regular PET solid fibers were compared with those of PET micro-porous hollow fibers, as shown in Figures 6 and 7. The breath-ability of the fabrics was enhanced by the porous morphology of the fiber surface. Absorbed water was quickly transported through the porous morphology of the fabric. After sweat or moisture has rapidly spread across the fabric, body heat can promote the evaporation of the sweat, leading to quick water-release/or drying. Moreover, the keep-warm ratio of the fabrics of regular PET solid fibers was compared with that of PET micro-porous hollow fibers, as shown in Figure 8. The hollowness of the PET micro-porous hollow fibers made their keep-warm ratio better than that of the regular PET solid fibers, suggesting that the air in the hollow channel was not a good transmitter of heat and therefore was insulating. The experimental results demonstrate that the fabrics made of PET micro-porous hollow fibers simultaneously exhibited water-absorption/release and keep-warm.

TABLE II
Kinetics of Regular PET Solid Fibers and PET Micro-Porous Hollow Fibers

Type	$K \times 10^{-3}$ (g/min m² %)	α	β	R^2
Regular PET	0.043	1	1	0.9942
Solid fibers	0.039	1.07	1	0.9992
PET micro-porous	9.125	1	1	0.9876
Hollow fibers	8.736	1.16	1	0.9987

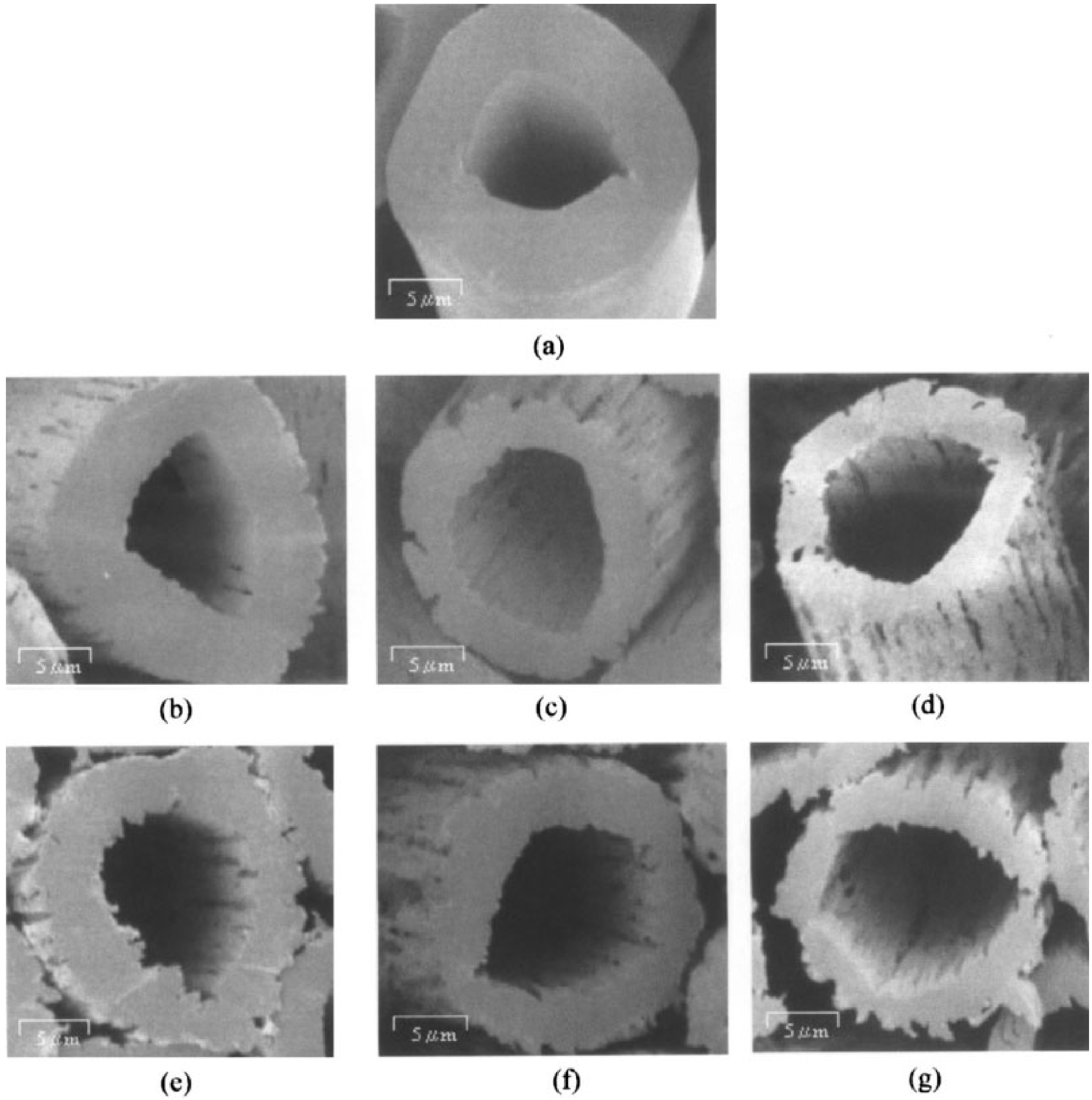


Figure 5 SEM observations of PET micro-porous hollow fibers: alkali treatment condition, 0.5–1.0% [NaOH]/120°C /45 min. (a): Before alkali treatment, (b): 0.5% [NaOH], (c): 0.6% [NaOH], (d): 0.7% [NaOH], (e): 0.8% [NaOH], (f): 0.9% [NaOH], (g): 1.0% [NaOH].

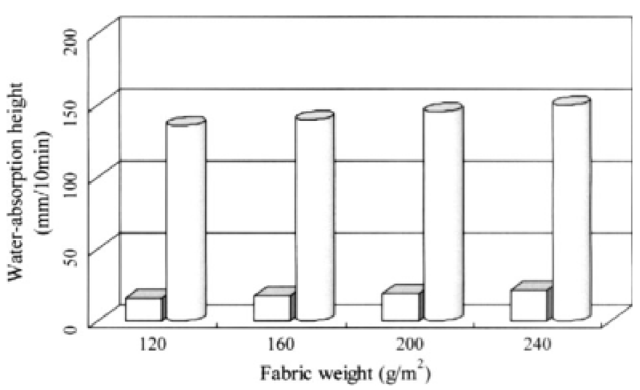


Figure 6 Comparison of water-absorption height for various fabrics. (□): Regular PET solid fabrics, (○): PET micro- porous hollow fabrics after alkali treatment.

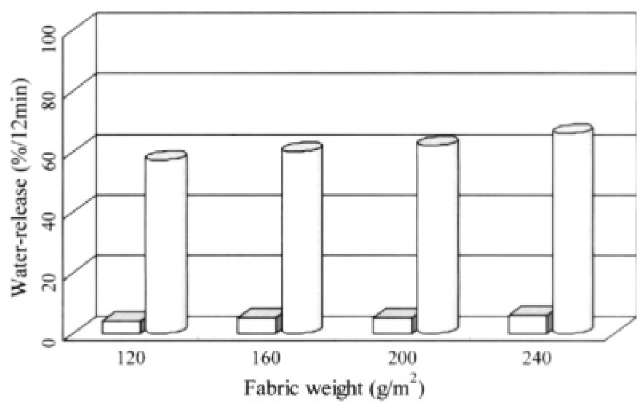


Figure 7 Comparison of water-release ability for various fabrics. (□): Regular PET solid fabrics, (○): PET micro-porous hollow fabrics after alkali treatment.

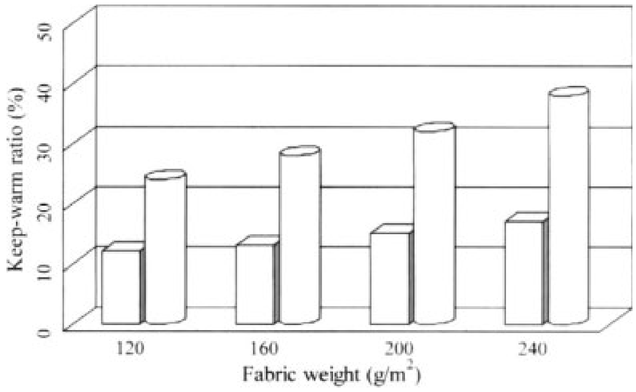


Figure 8 Comparison of keep-warm ratio for various fabrics. (□): Regular PET solid fabrics, (○): PET micro- porous hollow fabrics after alkali treatment.

CONCLUSION

This study investigated the kinetics of the alkaline hydrolysis of regular PET solid fibers and PET micro-porous hollow fibers, using statistical regression analysis. The β value was determined to be equal to one, based on a statistical regression analysis of the kinetics of the alkaline hydrolysis of regular PET solid fibers and PET micro-porous hollow fibers. The R^2 of the kinetic equation for an α value from 1.07 to 1.16 exceeded that for $\alpha = 1$. Experimental results further reveal that the rate constants of alkaline hydrolysis followed the order PET micro-porous hollow fibers ≫ regular PET solid fibers. Large pores of 0.1–3.5 μm in diameter were observed in the PET micro-porous hollow fibers after alkali treatment (0.6% aqueous NaOH/120°C/45 min). The hollowness of the PET micro-porous hollow fibers was between 30 and 32%. The percentage weight loss of the hollow fibers was around 20%. The PET micro-porous hollow fibers simultaneously exhibited water-absorption/release and keep-warm functions.

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