Analysis of Physical Properties of PET/CD-PET Polyblend Hollow Fiber and Its Kinetics of Alkaline Hydrolysis

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ABSTRACT: Cationic dyeable poly(ethylene terephthalate) (CD-PET) was formed by copolymerizing dimethylterephthalate (DMT),5-sodium sulfonate dimethyl isophthalate (SIPM) with a molar ratio of 2% and ethylene glycol (EG). Blends of regular poly(ethylene terephthalate) (PET) and CD-PET were spun into hollow fibers. The fibers were then treated with aqueous NaOH. This study investigated the physical properties of PET/CD-PET polyblend hollow fibers and their kinetic behavior of alkaline hydrolysis using differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), the density gradient method, a gel permeation chromatograph (GPC), a rheometer, and regression analysis of the statistical method. For the alkaline hydrolysis kinetics equation of PET, CD-PET, and PET/CD-PET polyblend materials: $-\ dW/dt = KC^{\alpha}A^{\beta}$, β values of chip and POY/ FOY hollow fibers are equal to 1. Moreover, R^2 of the kinetics equation of chip/POY/FOY for a from 1.09–1.35/1.08–1.32/1.06–1.29 were better than those of a = 1. Experimental results indicate that the rate constant of alkaline hydrolysis was CD-PET hollow fiber > PET/CD-PET polyblend hollow fibers > PET hollow fiber and FOY > POY > > Chip. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3601–3610, 2002

INTRODUCTION

Hall et al. successfully treated regular polyester (PET) with aqueous NaOH solution to improve the handling of the fiber and fabric for the first time.[1] Pensa et al. also found that alkali treatment could improve the moisture absorption, antistatic, and soil release properties of the fiber.[2,3] There were some reports on the kinetics of alkaline hydrolysis as follows. Namboori found that treating polyester with different concentrations of aqueous NaOH solution would cause NaOH initial concentration to significantly affect the weight loss of the fiber. Meanwhile, at a constant temperature, the weight loss percent was also proportional to hydrolysis time.[4] Although this observation was consistent with Waters,[5] Pficer suggested that the weight loss of polyester after alkaline hydrolysis was exponential to treatment time.[6] While investigating the alkaline hydrolysis of polyester fiber material, Kallay et al. indicated that at a constant concentration of aqueous NaOH solution, the weight loss percent was proportional to a specific area of the fiber.[7] Heidemann noted that the radius of the fiber decreased when increasing the concentration of aqueous NaOH solution.[8] In light of the above developments, this study thoroughly investigated the structural, mechanical, and rheological properties as well as the kinetic behavior of alkaline hydrolysis for PET/CD-PET polyblend materials.

EXPERIMENTAL

Materials

Regular poly(ethylene terephthalate) (PET) was generously donated by Far Eastern Textile Ltd. Ethylene glycol (EG), dimethylterephthalate (DMT), manganese acetate tetrahydrate [$Mn(OAc)_2 \cdot 4H_2O$], sodium acetate trihydrate [$Na(OAc) \cdot 3H_2O$], phosphoric acid (H_3PO_4), and antimony trioxide (Sb_2O_3) were purchased from Merck Taiwan Ltd. 5-Sodium sulfonate dimethyl isophthalate (SIPM) was obtained by Tokyo Chemical Industry Co., Ltd.

Synthesis of cationic dyeable poly(ethylene terephthalate)

A glass flask having a rectification column was charged with a copolymerization mixture consisting of 297 g of DMT, 195 g of EG, 9.1 g of SIPM, 0.084 g of $Mn(OAc)_2 \cdot 4H_2O$, and 1.22g of $Na(OAc) \cdot 3H_2O$. The copolymerization mixture was subjected to an ester interchange process. After a theoretical amount of methyl alcohol was distilled from the copolymerization mixture, the reaction product was placed in a condensation polymerization flask having a rectification column. The product was then mixed with 0.09 g of a stabilizer consisting of a 56% normal H_3PO_4 aqueous solution and 0.135 g of Sb_2O_3 as a polymerization

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TABLE I
Synthetic Characteristics of PET and CD-PET Chips

Chip	SIPM (mol %)	$[\eta]^a$ (dL/g)	M_w (g/mole)	M_w/M_n	DEG (%)	R-COOH (mEq/kg)	T_m (°C)	T_d^b (°C)
PET	0	0.64	38,696	3.56	1.04	32.4	253.8	396
CD-PET	1.99[c]	0.50	32,571	2.39	2.10	55.3	248.2	383

[a] Intrinsic viscosity.
[b] Degradation temperature.
[c] SIPM content was measured by NMR analysis.

catalyst. The mixture was subjected to a copolymerization process at a temperature of 275°C, under an ambient pressure for 20 min, under a reduced pressure of 30 mmHg for 15 min, and then, under a high vacuum for 100 min. The final pressure was 0.38 mmHg. The resultant copolyester was pelletized by an ordinary pelletizing process.[9,10] Table I lists the synthetic characteristics of PET and CD-PET chips.

Preparation of PET/CD-PET polyblend hollow fibers

PET chips with CD-PET chips of 2 mol % SIPM content were blended mechanically in the proportions of 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100 in a melt twin-screw extruder. These blended chips were extruded in the pilot spinning machine under identical conditions, with a spinning temperature of 285°C and spinning speed of 3200 m/min to produce partially oriented yarns (POY yarns). The POY yarn had a yarn count of 220 denier/48 filament and hollowness of 25%. Next, the six POY yarns were drawn at a draw ratio of 1.41 times by using a draw-winder machine to obtain fully oriented yarns (FOY yarns). The draw temperature and draw speed of these POY yarns were 160°C and 800 m/min, respectively. The FOY yarn had a yarn count of 156 denier/48 filament and a hollowness of 24%. Table II lists the compositions of PET/CD-PET polyblend materials.

Measurements

Differential scanning calorimetry (DSC) scans of filaments were made using a Perkin-Elmer Pyrix-1. Both heating rate and cooling rate were 10°C/min from 30 to 300°C, and the temperature was held for 3 min at 300°C. The crystallinity of DSC method was calculated from the following equation: crystallinity (%) = $\Delta H_f / \Delta H_f^\circ \times 100$ (%), where ΔH_f and ΔH_f° are the heat of fusion in J/g of repeating unit for the sample and 100% crystallinity, respectively. ΔH_f° of PET is equal to 140.1 J/g.[11] Next, wide-angle X-ray diffraction (WAXD) studies of samples were conducted using a MAC Science X-ray unit operated at 35 kV and 20 mA. X-ray diffracttion was then used with Cu Kα radiation and scan from 5 to 50° (2θ) with a scan speed of 4°/min. The crystallinity of WAXD method is given by the following expression: crystallinity (%) = $C/(C+A) \times 100$ (%), where C is the area under the crystalline curve and A is the area under the amorphous curve.[12] The density of samples was determined using the density gradient method. A mixture of *n*-heptane and carbontetrachloride was used for the purpose. Densities of *n*-heptane and carbontetrachloride solvents were 0.68 g/cm^3 and 1.59 g/cm^3, respectively. The scale of density gradient method was prepared from 1.30 g/cm^3 to 1.50 g/cm^3. The crystallinity was calculated from the following equation: crystallinity (%) = $d_c(d - d_a)/d(d_c - d_a) \times 100$ (%), where d_c is the crystalline density and d_a is the amorphous density, 1.445 and 1.335 g/cm^3 were used as their values, respectively.[13,14] The apparent viscosity was measured by a capillary rheometer, and the length-to-diameter ratio of the capillary is 5. Fineness of the samples was calculated by the equation as follows, Denier = W_1 (g) × 9000 (m) , where W_1 is the weight of fiber.[15] Extension stress–strain measurements were taken on a Zwick 1511. Samples were extended at a constant

TABLE II
Compositions of PET/CD-PET Polyblend Materials

Type	Code	PET/CD-PET Blend Ratio	SIPM content (mol %)
Chip	Sample 1	100/0	0
	Sample 2	80/20	0.4
	Sample 3	60/40	0.8
	Sample 4	40/60	1.2
	Sample 5	20/80	1.6
	Sample 6	0/100	2.0
POY[a]	Sample 7	100/0	0
	Sample 8	80/20	0.4
	Sample 9	60/40	0.8
	Sample 10	40/60	1.2
	Sample 11	20/80	1.6
	Sample 12	0/100	2.0
FOY[b]	Sample 13	100/0	0
	Sample 14	80/20	0.4
	Sample 15	60/40	0.8
	Sample 16	40/60	1.2
	Sample 17	20/80	1.6
	Sample 18	0/100	2.0

[a] POY hollow fiber:220 denier/48 filament.
[b] FOY hollow fiber:156 denier/48 filament.

TABLE III
Crystallinities of PET/CD-PET Polyblend Materials

	WAXD		DSC		Density	
Type	Code	*Xc* (%)	ΔH_f (J/g)	*Xc* (%)	*D* (g/cm^3)	*Xc* (%)
Chip	Sample 1	—	43.8	31.3	1.3756	35.8
	Sample 2	—	43.5	31.0	1.3743	34.6
	Sample 3	—	43.2	30.8	1.3730	33.5
	Sample 4	—	42.8	30.6	1.3717	32.4
	Sample 5	—	42.5	30.3	1.3704	31.3
	Sample 6	—	42.2	30.1	1.3690	30.2
POY	Sample 7	37.6	55.5	39.6	1.3672	28.6
	Sample 8	35.4	53.9	38.5	1.3659	27.4
	Sample 9	33.3	52.3	37.3	1.3646	26.3
	Sample 10	31.2	50.6	36.1	1.3633	25.2
	Sample 11	29.0	49.0	35.0	1.3620	24.1
	Sample 12	26.9	47.4	33.8	1.3607	22.9
FOY	Sample 13	41.4	61.1	43.6	1.3700	31.0
	Sample 14	39.4	60.0	42.8	1.3687	29.8
	Sample 15	37.5	58.8	42.0	1.3674	28.7
	Sample 16	35.5	57.7	41.1	1.3661	27.6
	Sample 17	33.6	56.8	40.5	1.3648	26.5
	Sample 18	31.6	55.8	39.8	1.3635	25.3

crosshead speed of 500 mm/min up to elongation at break and crosslength of 254 mm. The increasing value of the tenacity was recorded on a moving chart. Weight loss percent measurement of samples after alkali treatment was calculated as follows: weight loss percent (%) = $(W_2 - W_3)/\ W_2 \times 100$ (%), where W_2 and W_3 were the weight of samples before and after alkaline hydrolysis, respectively.[16] Specific area of samples were measured by a Micromeritics Flowsorb II 2300 specific area meter.

RESULTS AND DISCUSSION

Structural properties

The crystallinities of PET, CD-PET, and PET/CD-PET polyblend materials were determined using differential scanning calorimetry (DSC), density gradient method, and wide-angle X-ray diffraction (WAXD). The experimental results in Table III indicate that the crystallinity of PET/CD-PET polyblend materials decreased when increasing SIPM content in the polymer. This observation was corresponded to the studies of Teli[17] and Pal.[18] Obviously, the crystallinity of density method was lower than those of WAXD and DSC methods for POY and FOY hollow fibers except chip. The primary reason was that the measurement of density method was deeply affected by the hollowness of the hollow fiber. Both WAXD and DSC methods were also independent of the hollowness of the hollow fiber. This phenomenon is discussed later.

Figure 1 reveals that the crystalline peak of the PET FOY hollow fiber was sharper than that of the CD-PET hollow fiber. Meanwhile, the peak of diffracting angles (2θ) for (010), $(\bar{1}10)$, and (100) reflecting planes in equator direction, which are 17.8°, 23.0°, and 25.9°, did not obviously shift except for the diffraction intensities. Additionally, the peak of diffracting angles (2θ) for $(\bar{1}05)$ reflecting planes in meridian direction, which is 43.1°, did not obviously also shift except for the diffraction intensities. The WAXD of PET/CD-PET polyblend FOY hollow fibers closely resembled those

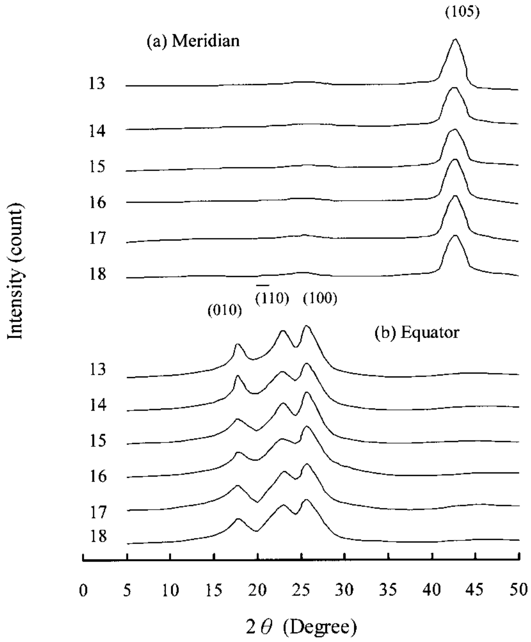


Figure 1 WAXD curves of FOY hollow fibers. (a) Meridian direction: sample 13–sample 18. (b) Equator direction: sample 13–sample 18.

TABLE IV
Thermal Properties of PET/CD-PET Polyblend Materials

		Heating process						Cooling process	
Type	Code	T_g (°C)	T_{ch} (°C)	ΔH_{ch} (J/g)	T_m (°C)	ΔH_f (J/g)	Xc (%)	T_{cc} (°C)	ΔH_{cc} (J/g)
Chip	Sample 1	71.2	131.9	22.9	253.8	43.8	31.3	193.3	39.8
	Sample 2	71.0	134.0	24.0	252.7	43.5	31.0	188.5	35.1
	Sample 3	70.8	136.1	25.2	251.6	43.2	30.8	183.7	30.5
	Sample 4	70.7	138.2	26.3	250.4	42.8	30.6	178.9	25.8
	Sample 5	70.5	140.3	27.5	249.3	42.5	30.3	174.1	21.2
	Sample 6	70.3	142.4	28.6	248.2	42.2	30.1	169.3	16.5
POY	Sample 7	71.6	97.9	11.8	259.6	55.5	39.6	213.2	41.5
	Sample 8	71.2	100.4	12.9	258.2	53.9	38.5	212.0	41.2
	Sample 9	71.0	102.9	14.1	256.8	52.3	37.3	210.8	40.9
	Sample 10	70.9	105.5	15.2	255.5	50.6	36.1	209.5	40.5
	Sample 11	70.7	108.0	16.4	254.1	49.0	35.0	208.3	40.2
	Sample 12	70.5	110.5	17.5	252.7	47.4	33.8	206.1	39.9
FOY	Sample 13	—	—	—	260.9	61.1	43.6	217.9	45.1
	Sample 14	—	—	—	259.8	60.0	42.8	215.7	44.8
	Sample 15	—	—	—	258.7	58.8	42.0	213.2	44.2
	Sample 16	—	—	—	257.2	57.7	41.1	211.5	43.9
	Sample 17	—	—	—	256.3	56.8	40.5	208.9	43.6
	Sample 18	—	—	—	254.9	55.8	39.8	206.6	43.3

of PET and CD-PET FOY hollow fibers. The reason was that the SIPM did not pack into the original polyester unit cell but concentrated at the polyester crystalline surface and the amorphous regions.

In the DSC method, the heat of fusion was used to indicate the crystalline fraction in the fiber. Higher crystallinity was expected from a higher value of heat of fusion. Notably, increasing SIPM content in the PET/CD-PET polyblend materials decreased the heat of fusion leading to a decrease in the crystallinity. Table IV displays the thermal properties of PET, CD-PET, and PET/CD-PET polyblend materials. The melting endothermal (T_m) of the DSC curve in the heating process was different from different samples. Figure 2 shows that a double melting endothermal peak was obtained from CD-PET FOY hollow fiber, and only a single melting peak was observed for PET FOY hollow fiber. The high melting temperature peak of CD-PET FOY hollow fiber was also lower than that of PET FOY hollow fiber. Interestingly, a large —SO_3Na side group in CD-PET polymer could prevent the chain molecules from crystallizing close to each other and obstructing the formation of bigger crystals.[19] No glass transition temperature (T_g) and melting exothermal peak (T_{ch}) appeared in the DSC heating process for all FOY hollow fibers, indicating these materials were originally crystalline. In the DSC cooling process, the crystallization exothermal peak (T_{cc}) of the PET FOY hollow fiber was higher than that of the CD-PET FOY hollow fiber, implying that the crystallization rate of PET polymer was faster than that of CD-PET polymer. Namely, a large —SO_3Na side group in CD-PET polymer could inhibit the formation of crystalline particles. Owing to the effect of a —SO_3Na side group on polymer, thermal behavior of the PET/CD-PET polyblend FOY hollow fibers resembled that of the CD-PET FOY hollow fiber.

The degree of crystallinity was compared from WAXD, DSC, and density methods for PET, CD-PET, and PET/CD-PET polyblend hollow fibers including POY and FOY. According to that comparison, quantifying the crystallinity by DSC and density methods was difficult. In DSC analysis, the heat of fusion of repeating unit was theoretically computed for 100%

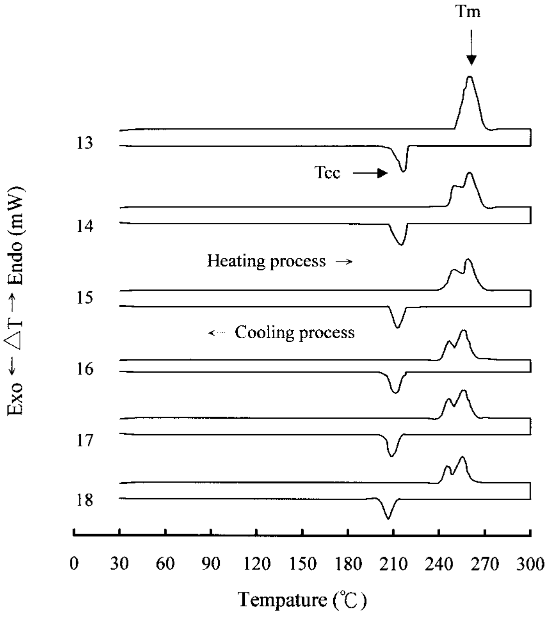


Figure 2 DSC curves of FOY hollow fibers, sample 13–sample 18.

TABLE V
Compare of the Crystallinities for PET/CD-PET Polyblend Hollow Fibers with Round Filbers

Type	Code	WAXD *Xc* (%)		DSC *Xc* (%)		Density *Xc* (%)	
		Round	Hollow	Round	Hollow	Round	Hollow
POY	Sample 7	39.2	37.6	40.3	39.6	42.9	28.6
	Sample 8	36.2	35.4	38.7	38.5	41.8	27.4
	Sample 9	32.5	33.3	37.0	37.3	40.6	26.3
	Sample 10	30.7	31.2	35.7	36.1	39.5	25.2
	Sample 11	28.7	29.0	35.2	35.0	38.4	24.1
	Sample 12	27.8	26.9	34.2	33.8	37.3	22.9
FOY	Sample 13	41.8	41.4	42.9	43.6	46.4	31.0
	Sample 14	39.7	39.4	42.5	42.8	45.3	29.8
	Sample 15	37.3	37.5	42.4	42.0	44.2	28.7
	Sample 16	35.8	35.5	41.6	41.1	43.1	27.6
	Sample 17	32.9	33.6	40.3	40.5	42.0	26.5
	Sample 18	32.1	31.6	39.4	39.8	40.8	25.3

crystallinity of polyester polymer.[20] Regarding the density method, the density of crystalline and amorphous polyester polymer could not be measured accurately, and literature values for crystalline and amorphous density were assumed theoretically as well.[21] Importantly, although density of hollow fiber could not be measured accurately by using the density gradient method, that of the round fiber could be obtained. Additionally, the hollow part of the hollow fiber significantly affected the density value of the hollow fiber. The hollowness of the hollow fiber played a role of buoyancy. Owing to the influence of floatation, the density of the hollow fiber was obviously lower than that of the round fiber. In the same FOY (156 denier/48 filament, hollowness is 24%) and POY (220 denier/48 filament, hollowness is 25%) specifications, the drops of FOY/POY in average crystallinities of the density gradient method from the round fiber to FOY/POY hollow fiber were 35.5 and 35.9%, respectively. Tables V and VI compare the results for two kinds of fibers. Notably, the WAXD method was adopted to quantitatively analyze the crystalline structure in polymeric fiber field.[22–26]

Mechanical properties

Table VII clearly reveals that with an increase of SIPM content in PET/CD-PET polyblend hollow fiber, the tenacity and breaking elongation of POY and FOY hollow fibers became inferior. Structural studies inidicated that the crystallinity decreased with an increasing SIPM content. Hong et al. also reported that the intrinsic viscosity gradually decreased with an increasing SIPM content, indicating a decrease in molecular weight.[27] Moreover, adding a compound containing the —SO_3Na side group disturbed the regularity of the polyester polymer chain molecules that make the structure of CD-PET hollow fiber less compact than that of the PET hollow fiber. This was reflected in the lower tenacity and breaking elongation of the CD-PET hollow fiber. The tenacity and breaking elongation of the PET/CD-PET polyblend hollow fibers also gradually decreased with an increasing SIPM content. Furthermore, experimental results of the mechanical properties were consistent with those of crystallinities for the PET/CD-PET polyblend hollow fibers. In the hot drawing process (from POY to FOY, drawn ratio

TABLE VI
Compare of the Crystallinities of Density Method for PET/CD-PET Polyblend Hollow Fibers

Type	Code	Round		Hollow	
		Density (g/cm^3)	*Xc* (%)	Density(g/cm^3)	*Xc* (%)
POY	Sample 7	1.3839	42.9	1.3672	28.6
	Sample 8	1.3826	41.8	1.3659	27.4
	Sample 9	1.3813	40.6	1.3646	26.3
	Sample 10	1.3800	39.5	1.3633	25.2
	Sample 11	1.3787	38.4	1.3620	24.1
	Sample 12	1.3774	37.3	1.3607	22.9
FOY	Sample 13	1.3881	46.4	1.3700	31.0
	Sample 14	1.3868	45.3	1.3687	29.8
	Sample 15	1.3855	44.2	1.3674	28.7
	Sample 16	1.3842	43.1	1.3661	27.6
	Sample 17	1.3829	42.0	1.3648	26.5
	Sample 18	1.3815	40.8	1.3635	25.3

TABLE VII
Mechanical Properties of PET/CD-PET Polyblend Hollow Fibers with Different Amount of SIPM

Type	Code	Tenacity (g/den)	Elongation at break (%)	ID[c] (μm)	OD[d] (μm)	Wall thickness[e] (μm)	Hollowness[f] (%)
POY[(a)]	Sample 7	2.60	118.7	13.0	25.8	6.4	25.4
	Sample 8	2.55	117.0	12.9	25.7	6.3	25.2
	Sample 9	2.46	115.3	13.0	25.8	6.4	24.4
	Sample 10	2.41	113.5	13.0	25.8	6.4	25.4
	Sample 11	2.34	111.8	13.0	25.7	6.3	25.6
	Sample 12	2.28	110.1	12.9	25.7	6.4	25.2
FOY[(b)]	Sample 13	4.42	35.5	10.6	21.6	5.5	24.1
	Sample 14	4.17	35.0	10.6	21.5	5.5	24.3
	Sample 15	3.93	34.5	10.6	21.6	5.5	24.1
	Sample 16	3.68	33.9	10.5	21.4	5.5	24.1
	Sample 17	3.44	33.4	10.5	21.4	5.5	24.1
	Sample 18	3.19	32.9	10.6	21.5	5.5	24.3

[a] 220 denier/48 filament.
[b] 156 denier/48 filament.
[c] Inside diameter of hollow fiber.
[d] Outside diameter of hollow fiber.
[e] Wall thickness (μm) = (OD-ID)/2.
[f] Hollowness (%) = $(ID/OD)^2 \times 100$ (%).

of 1.41 times), the average drop in inside and outside diameters of the PET/CD-PET polyblend hollow fibers were 18.3 and 16.5%, respectively, while the wall thickness and hollowness only decreased slightly. Figure 3 summarizes those results. This tendency resembled the observation of Beyreuther and Hofmann in the hot drawing process for polyester fiber.[28]

Rheological properties

Figure 4 shows the apparent viscosity of PET and CD-PET at 260°C with shear rate. From 1000 to 20,000 s^{-1}, all polymers exhibited pseudoplastic flow behavior. The apparent viscosity of PET exceeded that of CD-PET over the entire shear rate range. Figure 5 displays the apparent viscosities of PET/CD-PET polyblends at 260°C with shear rate. The apparent viscosities of PET/CD-PET polyblends also exhibited pseudoplastic flow behavior. This tendency was independent of the blend ratio. Figure 6 shows the apparent viscosities of PET/CD-PET polyblends exhibited positive deviations. The 40/60 blend of PET/CD-PET showed a maximum value of apparent viscosity than that predicted by the additivity rule.[29,30]

Kinetic behavior of alkaline hydrolysis

This study also investigated the kinetic behavior of alkaline hydrolysis of PET, CD-PET, and their blend

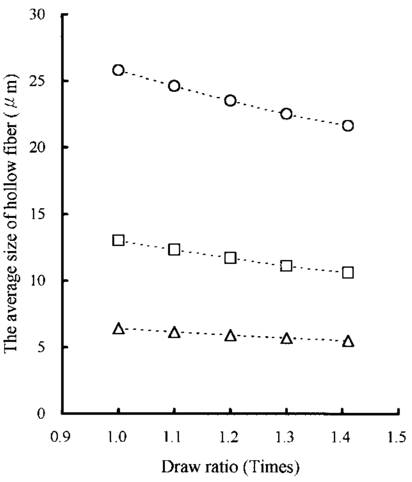


Figure 3 Relation between the average size and draw ratio of hollow fiber. (○): Outside diameter; (□): inside diameter; (△): wall thickness.

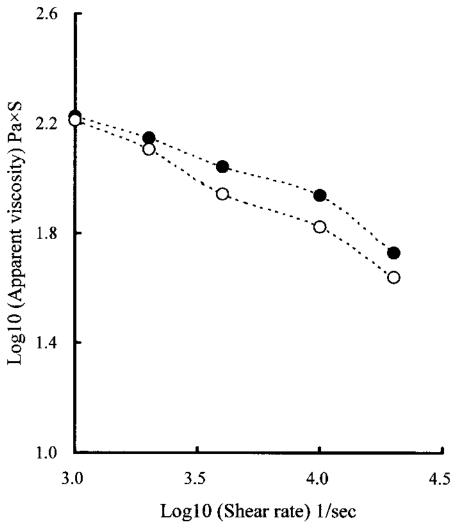


Figure 4 Apparent viscosity of PET and CD-PET with shear rate at 260°C. (●): PET; (○): CD-PET.

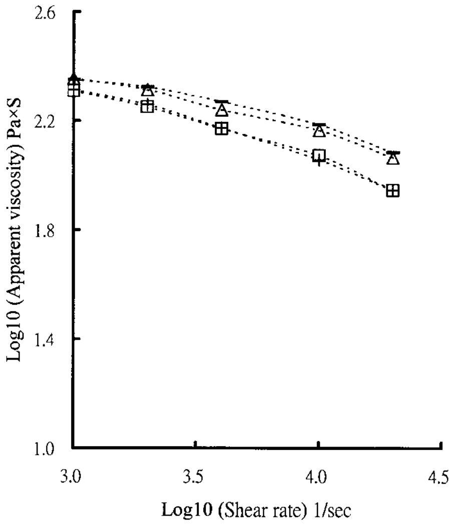
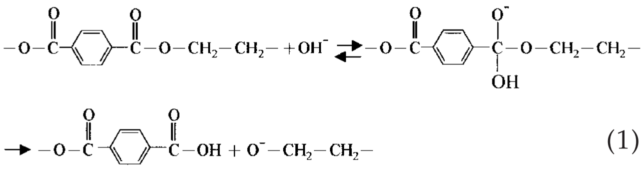


Figure 5 Apparent viscosity of R-PET /CD-PET polyblends with shear rate at 260°C. (□): PET/CD-PET(80/20); (—): PET/CD-PET(60/40); (△): PET/CD-PET(40/60); (+): PET/CD-PET(20/80).

PET/CD-PET materials by using regression analysis of the statistical method. The dissolution of PET can be represented in the following eq. (1):[31,32]



(1)

The first step, OH^- in aqueous sodium hydroxide (NaOH) solution attacks $\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\text{—C—}}$ with lower electron

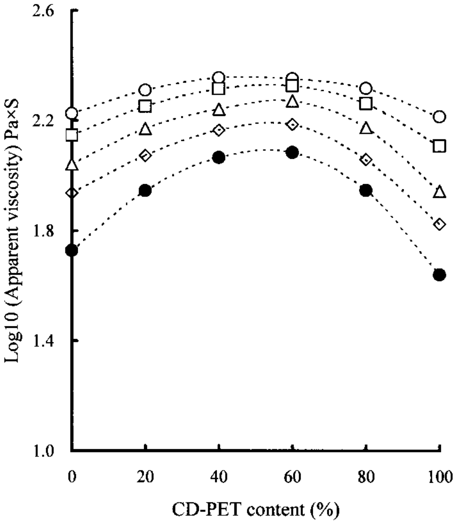


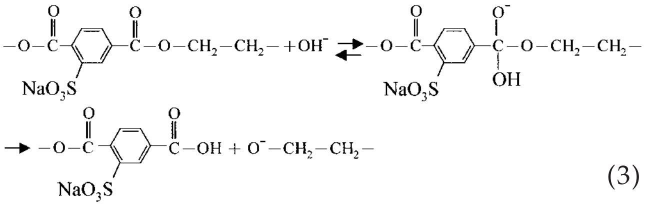
Figure 6 Relation between apparent viscosity and CD-PET content of PET/CD-PET polyblends at 260°C. (○): Shear rate:1000 s^{-1}; (□): shear rate:2000 s^{-1}; (△): shear rate:4000 s^{-1}; (◇): shear rate:10,000 s^{-1}; (●): shear rate:20,000 s^{-1}.

cloud density and an intermediate is produced. The second step, further reaction between OH^- and —C— breaks the macromolecular chain and produces —COOH and O^-—CH_2—CH_2—, the final product is —COONa in alkaline solution. Quantitative results indicate that the reaction rate is related to the concentration of OH^- and $\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\text{—C—}}$ in the reaction system. Therefore, the reaction rate can be expressed by eq. (2):

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

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

According to DSC and WAXD results, the SIPM did not pack into the original polyester unit cell but rather concentrated at the polyester crystalline surface and the amorphous domains. This tendency was owing to the introduction of —SO_3Na functional group and a preferred hydrolysis that the OH^- group had towards the CD-PET phase than to R-PET phase. The dissolution of CD-PET can be represented as the following eq. (3):[33]



(3)

Comparing eq. (1) and eq. (3) reveals that the dissolution of CD-PET resembled that of PET. Therefore, the reaction rate of the eq. (2) was also used in CD-PET system. The main difference of two polymers was the existence of SIPM. A larger decrease in crystallinity caused by SIPM content implies a larger percentage weight loss of the fiber. Figures 7 and 8 illustrates the percentage weight loss of PET (sample 13) and CD-PET (sample 18) FOY hollow fibers, respectively, on treatment with 0.5, 1.0, 1.5, 2.0, and 2.5% sodium hydroxide solution at 100°C for various time periods. According to this figures, the saponification of PET and CD-PET FOY hollow fibers was proportional to time of treatment and the initial concentration of hydroxide ions solution. The tendency was the same as Namboori and Haith observed for PET round fiber.[34] Figure 9 summarizes the percentage weight loss of PET/CD-PET polyblend FOY hollow fibers on treatment with 2.5% sodium hydroxide solution at 100°C for various time intervals. Obviously, the percentage weight loss of PET/CD-PET polyblend FOY hollow

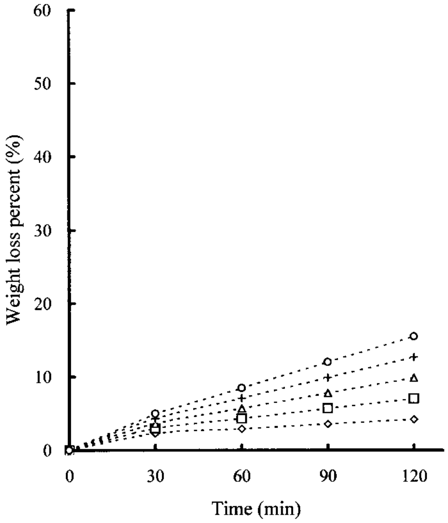


Figure 7 Weight loss percent of PET hollow fiber at 100°C. (◇): [NaOH]: 0.5%; (□): [NaOH]: 1.0%; (△): [NaOH]: 1.5%; (+): [NaOH]: 2.0%; (○): [NaOH]: 2.5%.

fibers raised with an increasing SIPM content. The percentage weight loss of CD-PET FOY hollow fiber was approximately 3.66 times that of PET FOY hollow fiber.

For the alkaline hydrolysis kinetics equation of PET, PET/CD-PET polyblend, and CD-PET FOY hollow fibers: $-\,dW/dt = \;\cdot C^{\alpha} \cdot A^{\beta}$. If α equals 1, the R^2 error percent with 1 of the alkaline hydrolysis kinetics equation increased with an increase of the β value. This is owing to that the percentage weight loss was proportional to the reactive surface area of the fiber.[7] The β value was ≥ 1. When β equals 1, the R^2 error percent with 1 of the alkaline hydrolysis kinetics equation was the minimum, indicating η is equal to 1. Figure 10 summarizes the results of the kinetics measurements.

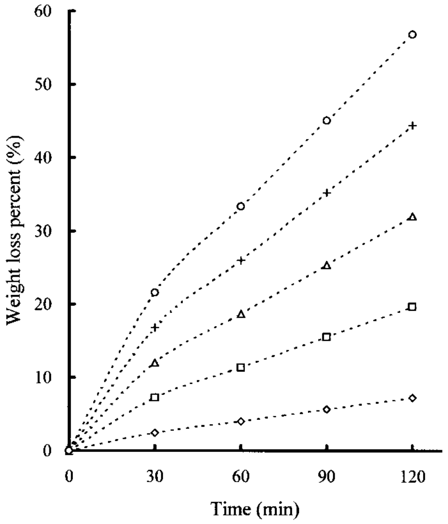


Figure 8 Weight loss percent of CD-PET hollow fiber at 100°C. (◇): [NaOH]: 0.5%; (□): [NaOH]: 1.0%; (△): [NaOH]: 1.5%; (+): [NaOH]: 2.0%; (○): [NaOH]: 2.5%.

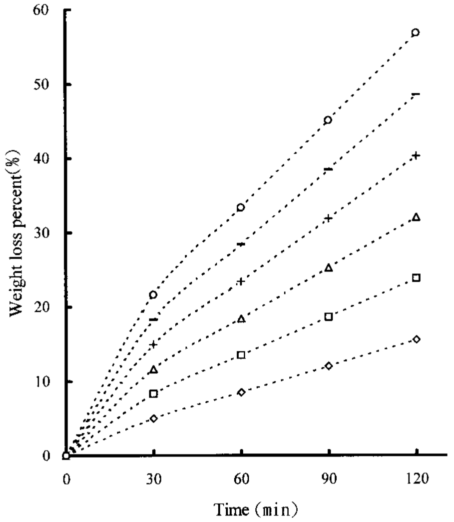


Figure 9 Relation between weight loss percent and time of PET/CD-PET polyblends hollow fiber at [NaOH]: 2.5% and100°C condition. (◇): PET/CD-PET(100/0); (□): PET/CD-PET(80/20); (△): PET/CD-PET(60/40); (+): PET/CD-PET(40/60); (—): PET/CD-PET(20/80); (○): PET/CD-PET(0/100).

If β equals 1, the alkaline hydrolysis kinetics equation had a minimum R^2 error percent with 1 between 1.06 and 1.29 for α value. This is owing to the fact that the percentage weight loss was also proportional to the concentration of aqueous NaOH solution.[4] The α value was also ≥ 1. When the α value was between 1.06 and 1.29, the R^2 error percent with 1 of the alkaline hydrolysis kinetics equation was the minimum. Figure 11 summarized the results of the kinetics measurements.

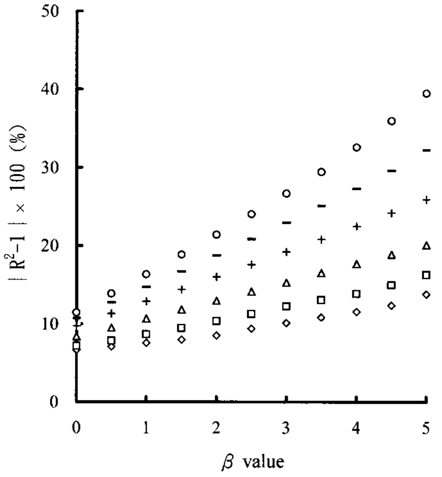


Figure 10 Relation between R^2 error percent with 1 and β value, when α equals 1. (◇): PET/CD-PET(100/0); (□): PET/CD-PET(80/20); (△): PET/CD-PET(60/40); (+): PET/CD-PET(40/60); (—): PET/CD-PET(20/80); (○): PET/CD-PET(0/100).

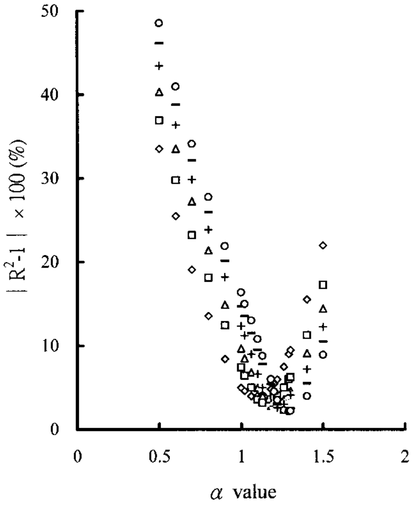


Figure 11 Relation between R^2 error percent with 1 and α value, when β equals 1. (◇): PET/CD-PET(100/0); (□): PET/CD-PET(80/20); (◇): PET/CD-PET(60/40); (+): PET/CD-PET(40/60); (—): PET/CD-PET(20/80); (○): PET/CD-PET(0/100).

From the regression analysis came results of the statistical method for kinetic behavior of alkaline hydrolysis of PET, CD-PET, and their blend PET/CD-PET FOY hollow fibers. The β value is equal to 1. Moreover, R^2 of the kinetics equation for α from 1.06–1.29 was better than that of $\alpha = 1$. The kinetic behavior of alkaline hydrolysis of the POY hollow fiber and chip closely resembled that of the FOY hollow fiber. Tables VII–X summarize the results of the kinetics measurements. The rate constant of the alkaline hydrolysis for the CD-PET FOY hollow fiber and the PET FOY hollow fibers were 7.58×10^{-3} [g/(min · m² · %)] and 2.44×10^{-3} [g/(min · m² · %)], respectively. The rate constant of alkaline hydrolysis of the CD-PET FOY hollow fiber was approximately 3.11 times that of the PET FOY hollow fiber. The measurement results of the rate constant of alkaline hydrolysis were close to 3.66 times that of the percentage weight loss.

Table XI summarizes the comparison of the rate constant of alkaline hydrolysis for the PET/CD-PET polyblend chip and POY/FOY hollow fibers. Obviously, the rate constant of the alkaline hydrolysis of the POY/FOY hollow fibers was higher than that of the chip. The reason was the surface area of the chip was lower than those of the POY/FOY hollow fibers before alkaline hydrolysis. In the same weight condition (5 g), the surface area of the FOY, POY, and chip were approximately 0.9 m², 0.7 m², and 0.007 m², respectively. Therefore, the rate constant of the alkaline hydrolysis of chip was obviously lower than those of the POY/FOY hollow fibers in the same alkaline hydrolysis condition treatment. Additionally, the rate constant of the alkaline hydrolysis of the FOY hollow fiber was slightly higher than that of the POY hollow fiber, owing to the higher surface area of the hollow

TABLE VIII
Kinetic Behavior of Alkaline Hydrolysis for PET/CD-PET Polyblend Chips[a]

Code	$K \times 10^{-3}$ (g/min · m² · %)	α	β	R^2
Sample 1	0.042	1	1	0.9954
Sample 1	0.037	1.09	1	0.9900
Sample 2	0.088	1	1	0.9857
Sample 2	0.078	1.17	1	0.9985
Sample 3	0.128	1	1	0.9687
Sample 3	0.119	1.27	1	0.9962
Sample 4	0.174	1	1	0.9606
Sample 4	0.156	1.31	1	0.9950
Sample 5	0.221	1	1	0.9560
Sample 5	0.196	1.34	1	0.9943
Sample 6	0.272	1	1	0.9529
Sample 6	0.234	1.35	1	0.9938

[a] Surface area of 5-g chips was approximately 0.007 m².

TABLE IX
Kinetic Behavior of Alkaline Hydrolysis for PET/CD-PET Polyblend POY Hollow Fibers[a]

Code	$K \times 10^{-3}$ (g/min · m² · %)	α	β	R^2
Sample 7	2.32	1	1	0.9975
Sample 7	2.12	1.08	1	0.9999
Sample 8	3.25	1	1	0.9937
Sample 8	2.97	1.15	1	0.9998
Sample 9	4.35	1	1	0.9863
Sample 9	3.99	1.23	1	0.9996
Sample 10	5.78	1	1	0.9791
Sample 10	5.01	1.27	1	0.9996
Sample 11	7.27	1	1	0.9736
Sample 11	6.05	1.30	1	0.9995
Sample 12	8.82	1	1	0.9671
Sample 12	7.09	1.32	1	0.9994

[a] Surface area of 5-g POY hollow fibers was approximately 0.7 m².

TABLE X
Kinetic Behavior of Alkaline Hydrolysis for PET/CD-PET Polyblend FOY Hollow Fibers[a]

Code	$K \times 10^{-3}$ (g/min · m² · %)	α	β	R^2
Sample 13	2.54	1	1	0.9978
Sample 13	2.44	1.06	1	0.9999
Sample 14	3.76	1	1	0.9909
Sample 14	3.44	1.13	1	0.9998
Sample 15	5.03	1	1	0.9840
Sample 15	4.46	1.18	1	0.9996
Sample 16	6.35	1	1	0.9772
Sample 16	5.49	1.22	1	0.9996
Sample 17	7.73	1	1	0.9700
Sample 17	6.53	1.26	1	0.9996
Sample 18	9.17	1	1	0.9620
Sample 18	7.58	1.29	1	0.9997

[a] Surface area of 5-g FOY hollow fiber was approximately 0.9 m².

TABLE XI
Compare of Rate Constant of Alkaline Hydrolysis for PET/CD-PET Polyblend Chip, POY, and FOY Hollow Fibers

Code	$K \times 10^{-3}$ $(g/min \cdot m^2 \cdot \%)$	α	β	R^2
Sample 1	0.037	1.09	1	0.9900
Sample 2	0.078	1.17	1	0.9985
Sample 3	0.119	1.27	1	0.9962
Sample 4	0.156	1.31	1	0.9950
Sample 5	0.196	1.34	1	0.9943
Sample 6	0.234	1.35	1	0.9938
Sample 7	2.12	1.08	1	0.9999
Sample 8	2.97	1.15	1	0.9998
Sample 9	3.99	1.23	1	0.9996
Sample 10	5.01	1.27	1	0.9996
Sample 11	6.05	1.30	1	0.9995
Sample 12	7.09	1.32	1	0.9994
Sample 13	2.44	1.06	1	0.9999
Sample 14	3.44	1.13	1	0.9998
Sample 15	4.46	1.18	1	0.9996
Sample 16	5.49	1.22	1	0.9996
Sample 17	6.53	1.26	1	0.9996
Sample 18	7.58	1.29	1	0.9997

fiber. For the alkaline hydrolysis kinetics equation of PET, the PET/CD-PET polyblend, and the CD-PET materials: $-\ dW/dt = KC^{\alpha}A^{\beta}$, β values of the chip and POY/ FOY hollow fibers are equal to 1. Moreover, R^2 of the kinetics equation of the chip/POY/FOY for the α from 1.09–1.35/1.08–1.32/1.06–1.29 were better than those of $\alpha = 1$. Experimental results indicate that the rate constant of alkaline hydrolysis were CD-PET hollow fiber > PET/CD-PET polyblend hollow fibers > PET hollow fiber, and FOY > POY >> chip.

CONCLUSIONS

The crystallinity of the PET/CD-PET polyblend hollow fibers decreased with an increasing SIPM content in the system at the same process condition. SIPM did not change the unmodified PET unit cell parameter. The —SO_3Na functional group only gathered on the crystal surface and amorphous regions. Additionally, the hollow part of hollow fiber significantly affected the density value of hollow fiber. The hollow rate of hollow fiber played a role of buoyancy. Owing to the influence of floatation, the density of the hollow fiber was obviously lower than that of the round fiber. It was found from the regression analysis results of the statistical method for the kinetic behavior of the alkaline hydrolysis of PET, CD-PET, and their blend PET/CD-PET materials. Our results further demonstrated that the rate constant of alkaline hydrolysis was CD-PET hollow fiber > PET/CD-PET polyblend hollow fibers > PET hollow fiber, and FOY > POY >> chip.

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