

The Thermal Shrinkage of the Drawing Poly(Ethylene Isophthalate Terephthalate) Copolyester Films

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Synopsis

The objective of this study is to use the copolymerization method to improve the thermal shrinkage property of poly(ethylene terephthalate) (PET), so that the resultant copolyester can be used for the application of thermal shrinkage packing materials. The poly(ethylene isophthalate terephthalate) (PEIT) copolyester films were prepared and studied. The thermal shrinkage rate of PET films and the thermal shrinkage rate of the copolyester films were measured by using a thermomechanical analyzer (TMA). The thermal shrinkage of copolyester was found to be dependent on such factors as composition, molecular weight, and draw temperature. The highest thermal shrinkage was obtained when the copolymer contained 40 mol % of ethylene isophthalate. Its shrinkage ratio and shrinkage rate were consistently 1.3 and 2.4 times those of PET. The increase of molecular weight and decrease of drawing temperature resulted in the increase of the thermal shrinkage. The best drawing temperature range was between glass transition temperature and soft temperature of the copolymer. The relationship of shrinkage rate and temperature indicates that the shrinkage mechanism of the copolyester belongs to two-step thermal shrinkage.

INTRODUCTION

Thermal shrinkage is an excellent method to detect the structural change of the partially oriented polyester yarns.¹ By using rubber elasticity theory, Bosley concluded that the shrinkage occurred in a free rotation phase.² Since rotational freedom prevails only in the amorphous phase, the shrinkage occurs only at the oriented amorphous region at $T > T_g$. The T_g is the temperature at which large enough numbers of polymer segments possess enough kinetic energy to overcome the rotational barriers. Shrinkage thermograms reveal the degree of orientation of the amorphous regions, which changes at a certain temperature for an oriented polymer.

The shrinkage properties of amorphous polymers at $T > T_g$ are determined by the network structure formed by molecular entanglements.³ In the same way, when an oriented polyester is heat-treated, the chains will return to random coils, and this results in the shrinkage of the sample if there is an entangled chain network for the polymer. However, there is a time limitation for a molecular entanglement to form a physical crosslink.

Several researchers⁴⁻⁶ had investigated PET using the statistical theory of rubber elasticity. The most complete study was done by Pinnock and Ward.⁶ They found that the mechanical properties of the spin-oriented amorphous

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PET filaments were similar to those of rubber. However, their work was done with samples having a maximum effective draw ratio = 2. If the draw ratio was higher than 2, a strain-induced crystallization occurred.

Samuels⁷ and Wilson⁸ have shown that the semicrystalline PET fiber can be treated as a two-phase system and that macroscopic shrinkage in PET comes from a disorientation of the oriented amorphous regions. The shrinkage coming from the recrystallization by chain folding near the melting point of the polymer was also significant.⁹

The objective of this study is to use the melt copolymerization of isophthalic acid (IPA), dimethyl terephthalate (DMT), and ethylene glycol (EG) to improve the thermal shrinkage properties of the PET so that the synthesized copolyesters can be used as heat-shrinkable packing materials. The thermal shrinkage ratio and rate of the obtained poly(ethylene isophthalate terephthalate) (PEIT) copolyesters were measured by the thermomechanical analyzer. The effects of copolyester composition, molecular weight, draw temperature, and draw ratio on the thermal shrinkage properties were studied. A simulated thermal shrinkage experiment was also conducted so as to understand the shrinkage of the polymers under actual process condition.

EXPERIMENTAL

Materials

Dimethyl terephthalate (fiber-grade) was obtained from China Petrochemical Develop Co. Ltd.; ethylene glycol (fiber-grade) was obtained from Tonlang Chemical Co. Ltd.; dimethyl isophthalate (reagent grade) was obtained from Fluka AG Co. (Swiss); isophthalic acid (fiber-grade) was obtained from Shinkung Synthetic Fiber Co. Ltd.; and Zn(OAc) and Sb₂O₃ (reagent grade) are from Wako.

Preparation of the Copolyester

The copolyesters were synthesized via the polycondensation reactions of isophthalic acid, dimethyl terephthalate, and ethylene glycol at different mole ratios and reaction times.

Sample Preparation¹⁰

Compression Molding

The synthesized copolyesters were ground into 20 mesh fine particles, dried under vacuum at 60°C for 10 h, and pressed on a hot press to form films with 5 mm in thickness. The temperature was controlled at 20°C above the melting temperature of the polymer. The pressure of the hot press was 20 kg/cm², and the pressing time was 3 min. The films were demolded by quenching in cold water.

Drawing of the Film

The films were drawn on an Instron (model 1122), the clip head distance was 5 cm, and the strain rate was 5 cm/min. The oven temperature was controlled at 70, 80, 100, and 120°C, respectively.

Tests of the Properties

Determination of Thermal Shrinkage Properties of the Copolyesters

The thermal shrinkage of the copolyesters was measured by a Perkin-Elmer TMA-2 thermomechanical analyzer. The samples were cut into the dimension of 1.5×2.5 mm. Some of the thermal shrinkage properties were defined as follows:

(a) Draw Ratio (λ).

$$\lambda = l_d/l_0$$

where l_0 = length before drawing (cm) and l_d = length after drawing (cm).

(b) Shrinkage Ratio S (%).

$$S\% = [(l_d - l_s)/l_d] \times 100\%$$

where l_s = length after shrinkage (cm).

(c) Maximum Shrinkage Ratio S_m (%). Maximum value of the shrinkage ratio.

(d) Shrinkage Rate, dS/dt (%/min).

$$dS/dt = S\%/t$$

where t = time elapsed for the sample to obtain $S\%$ shrinkage ratio (min).

(e) Maximum Shrinkage Rate (dS/dt) $_m$, (%/min). Maximum value of the shrinkage rate.

(f) Elastic Recovery Ratio R (%).

$$R\% = [(l_d - l_s)/(l_d - l_0)] \times 100\%$$

Determination of T_g and T_m

The T_g and T_m of the polymer were determined by a Perkin-Elmer DSC-2 differential scanning calorimeter. The heating rate was $20^\circ\text{C}/\text{min}$.

Determination of Molecular Weight

The average molecular weight of the polymer was measured by using Waters HPLC 201 instrument. The measurements were made using the UV detector, a mixture of m-cresol-chloroform (1 : 3) as solvent, and a calibration plot constructed with polystyrene standards.

Determination of Acid Number

Five grams of the sample was refluxed in mixture of phenol- CHCl_3 (2 : 3). After 40–60 min, the polymer was completely dissolved. The solution was titrated with 0.2N KOH/benzyl alcohol standard solution and the bromophenol blue was used as indicator. The color of the solution changed from yellow to green and finally from green to blue. The end point was determined at the moment of changing color from green to blue. The acid number (A.N.) is

calculated from the following equation:

$$\text{A.N. (meq KOH/kg)} = 0.2 \times V \times 1000 / \text{sample weight (g)}$$

where V = total titration volume of KOH standard solution (mL).

RESULTS AND DISCUSSION

Effects of Compositions of the Copolymers

Figure 1 shows the DSC traces of the synthesized copolymers. The thermal transitions, weight and number average molecular weights, and acid numbers of the copolymers were summarized in Table I. Figure 2 presents the relationship between the thermal transitions and the ethylene isophthalate (EI) contents of the copolymers. As can be seen from this figure, the glass transition temperature of the copolymers decreases gradually as the EI content increases. When the copolymer contained 40 and 60 mol % of the ethylene isophthalate, no melting temperature (T_m) was detected. When EI content is less than 40 mol %, the T_m decreases as the EI content increases. This property is advantageous from the point of view of processing.

As shown in Table I, the acid numbers of the copolymers are all very low (15–18 meq KOH/kg). This means that the thermal degradation of the copolymer was very small during the processing.

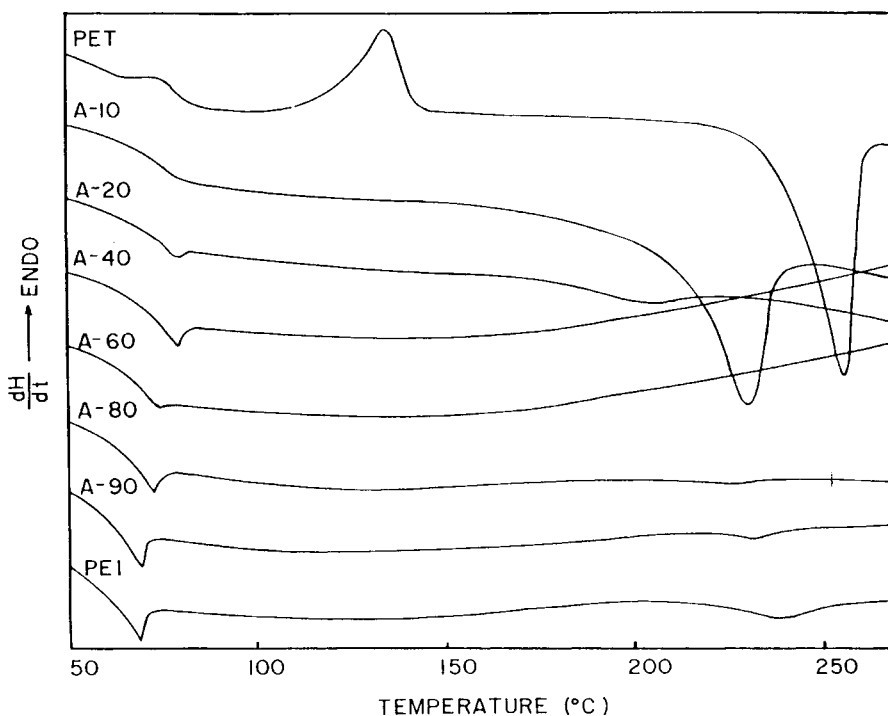


Fig. 1. DSC traces of the copolyesters.

TABLE I
Characterization of the Copolyesters

Polymer	EI ^a (mol %)	T_g (°C)	T_m (°C)	\overline{M}_w	\overline{M}_n	A.N. (meq/kg)
PET	0	79	257	34300	15200	15.2
A-10	10	77.5	231	41500	22300	16.0
A-20	20	75.5	206	39500	18500	16.5
A-40	40	72.5	—	42000	21300	17.6
A-60	60	68	—	45700	20700	16.5
A-80	80	64	226	47500	22300	18.1
A-90	90	61	232	45800	21300	16.8
PEI	100	59	240	51900	26900	17.5

^aEI = ethylene isophthalate.

Figure 3 shows the thermal shrinkage curves of the copolymers at the draw ratio $\lambda = 2$. Recrystallization occurred for the samples of PET, A-10, and A-20 during the thermal shrinkage process and the films became opaque. Their recrystallization temperatures are 124, 131, and 143°C, respectively. The maximum shrinkage ratios are plotted against the ethylene isophthalate content in Figure 4. As shown in Figure 4, the maximum values of the ratios occur at the 40 mol % EI content for both draw ratios $\lambda = 2$ and 4. These

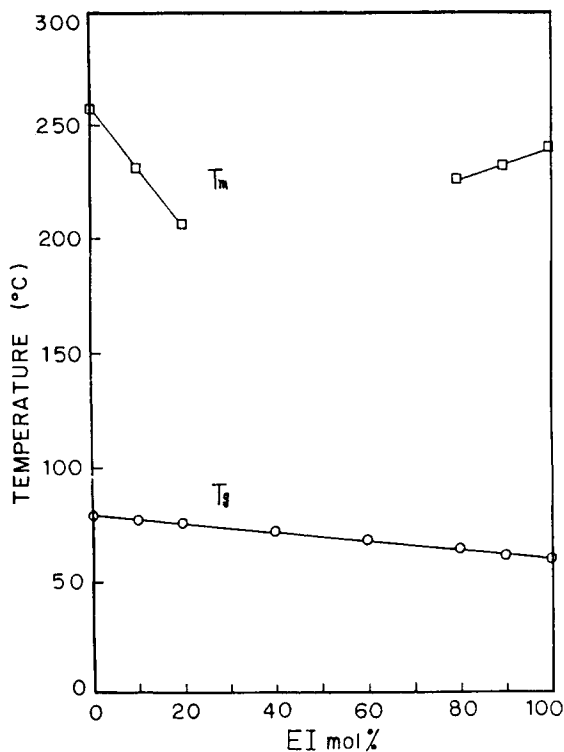


Fig. 2. The effect of EI content on the melting temperature and glass transition temperature of the copolyesters: (○) T_g ; (□) T_m .

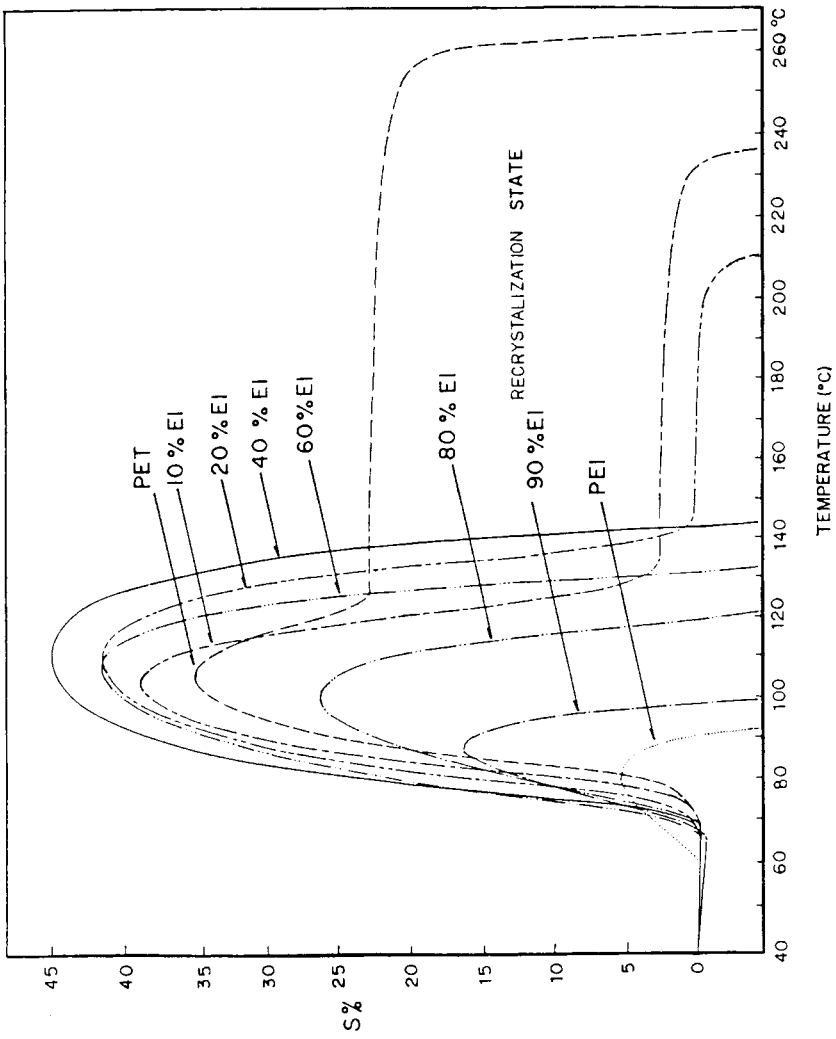


Fig. 3. The effect of EI content on the thermal shrinkage rate of the PEIT copolyester.

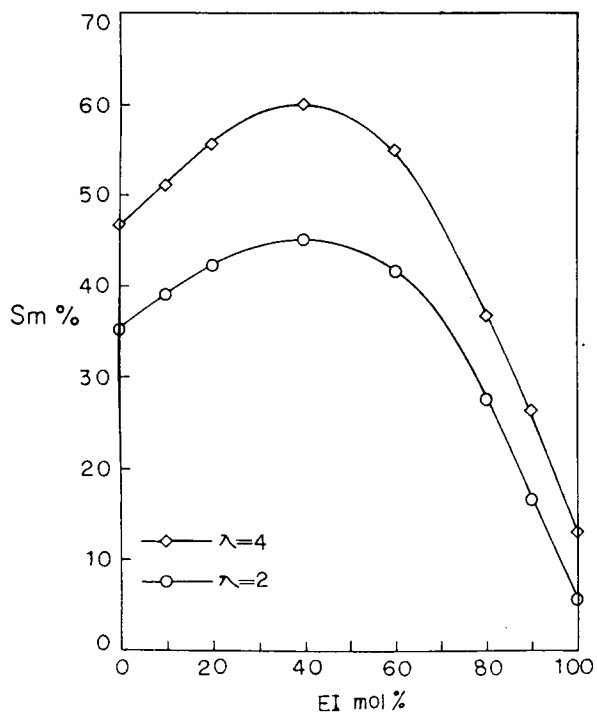


Fig. 4. The effect of EI content on the maximum thermal shrinkage ratio of the copolyesters. λ : (\diamond) 4; (\circ) 2.

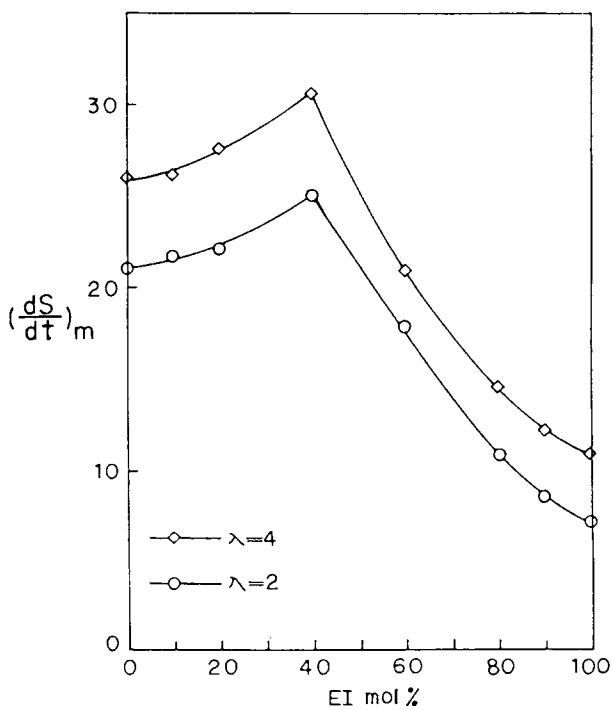


Fig. 5. The effect of EI content on the thermal shrinkage rate of the copolyesters. λ : (\diamond) 4; (\circ) 2.

TABLE II
Thermal Shrinkage Properties of the Copolyesters^a

Samples	$\lambda = 2$			$\lambda = 4$		
	S_m (%)	dS/dt (%/min)	R (%)	S_m (%)	dS/dt (%/min)	R (%)
PET	35.2	21.0	70.4	46.9	26.0	62.5
A-10	38.9	21.7	77.8	51.0	26.1	68.0
A-20	42.1	22.0	84.2	55.5	27.5	74.0
A-40	45.0	25.0	90.0	60.0	33.2	80.0
A-60	41.6	17.8	83.2	54.7	20.8	72.9
A-80	27.5	10.8	55.0	36.4	14.5	48.5
A-90	16.6	8.5	33.2	26.4	12.0	35.2
PEI	5.4	7.1	10.8	12.9	10.9	17.2

^a Drawn at 80°C.

values are about 1.3 times of those of PET. In Figure 5, the maximum shrinkage rates are plotted against the EI contents. As can be seen in this figure, the maximum values occur also at 40 mol % of EI content and the values are about 1.2–1.3 times of those of PET. The thermal shrinkage properties of copolyesters were summarized in Table II.

When the EI contents are in the range of 0–20 mol %, the thermal shrinkage ratio increases linearly with the EI content. On the other hand,

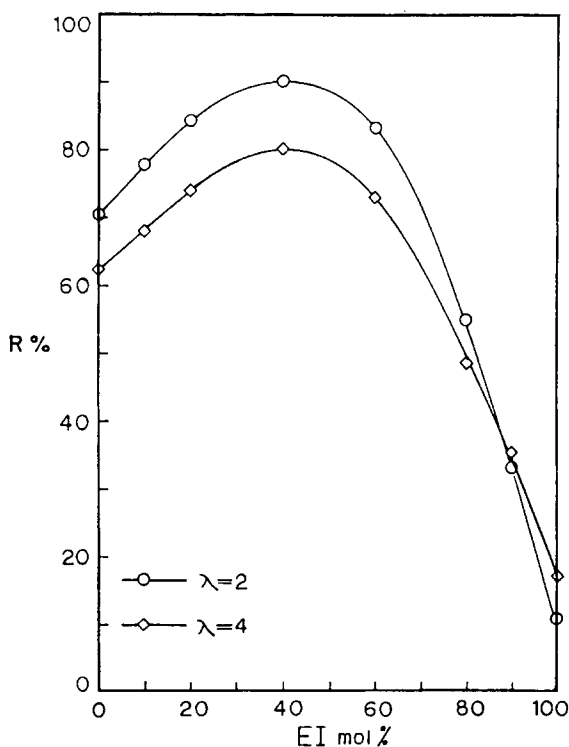


Fig. 6. The effect of EI content on the recovery ratio of the copolyester. λ : (\diamond) 4; (\circ) 2.

when the EI contents are in the range of 80–100%, the thermal shrinkage ratio decreases linearly as the EI content increases. As shown in the Figure 1, the melting enthalpy of the copolymers decreases when the EI content increases from 0 to 20 mol % and increases when the EI content increases from 80 to 100 mol %. The decrease in melting enthalpy means that the crystallinity of the polymer decreases. In conclusion, both the thermal shrinkage ratio and rate increase as the crystallinity of a polymer decreases for a semicrystalline copolyester. The results agree with Samuel's theory.⁷

Figure 6 presents the plot of the recovery ratios against EI contents. The maximum values are obtained when the EI content is 40%. The values are about 1.3 times of those of PET. However, the recovery ratio decreases as the draw ratio increases. For $\lambda = 2$, the recovery ratio is 90% when the EI content is 40%. For $\lambda = 4$, the recovery ratio is only 80% for the same EI content. This means that the chain slipping behavior is more obvious when the draw ratio increases.

The Effects of the Molecular Weight

In Table III, for the copolyesters containing 40 mol % of EI, both the thermal shrinkage ratio and rate increase as the molecular weight increases, because the increased molecular weight of a polymer cause the chain entanglement to increase. This results in a decrease of the chain slipping and an increase of the thermal shrinkage ratio and rate. Figure 7 represents the plot of both the maximum shrinkage ratio and rate against the weight average molecular weight; a linear relationship was obtained. This result implies that higher molecular weight is necessary for better thermal shrinkage properties. However, higher molecular weight polymers require longer polymerization time. This may result in easier thermal degradation of the polymers and difficulties in the processing. Therefore, the suitable molecular weight of a polymer should be optimized according to these considerations.

Effect of the Draw Temperature

The TMA thermograms of non-drawn films of sample C-40 and PET are presented in Figure 8. For the sample C-40, the T_g is 68°C, the soft beginning temperature (T_{sb}) is 80°C, and the soft temperature (T_s) is 108°C. For the

TABLE III
The Thermal Shrinkage Properties of the Copolyesters with Different Molecular Weights^a

Properties	B-40	C-40	D-40
M_n	20,100	17,700	14,300
M_w	37,000	32,300	26,100
S_n (%)	40	35.5	30.8
dS/dt (%/min)	23.5	20.3	15.6
R (%)	80	70.9	61.6

^a EI 40 mol %. $\lambda = 2$, drawn at 80°C.

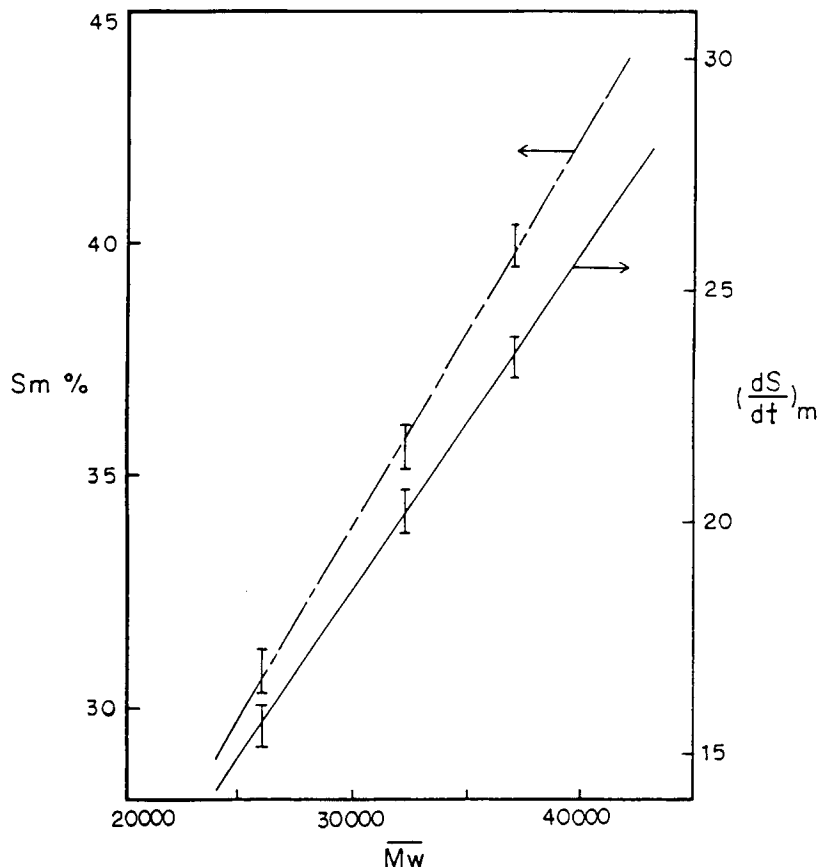


Fig. 7. The effect of the weight average molecular weight on the maximum shrinkage ratio and rate of the copolyester.

PET sample, because of the recrystallization, the polymer melts after melting point (T_m).

Figure 9 presents the thermal shrinkage traces for the sample C-40 at four different draw temperatures (70, 80, 100, and 120°C). The glass transition temperatures of drawn samples are a little bit lower than that of nondrawn samples. The T_{sb} decreases as the draw temperature decreases (see Table IV). When the draw temperature decreases, the thermal shrinkage of a polymer increases. The thermal shrinkage ratio of the film drawn at 70°C is similar to that of the film drawn at 80°C. However, the thermal shrinkage rate of the former is 1.7 times faster than that of the latter. The thermal shrinkage properties of the films drawn at 100 and 120°C are rather poor. The reason is that the draw temperatures are higher than the T_{sb} and hence the polymer chains slip. This results in the decrease in the efficiency of the extension of the film. This result agrees with that of PE studies by Watts et al.¹¹ In conclusion, a better thermal shrinkage property of a copolyester can be obtained at the draw temperature that is located between T_g and T_{sb} .

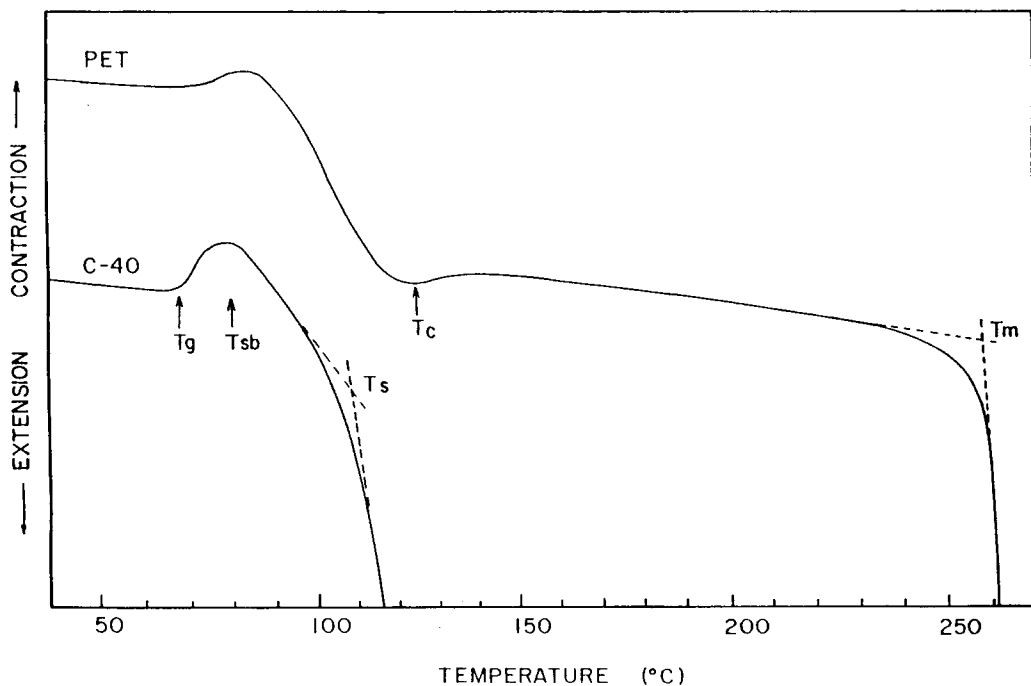


Fig. 8. The TMA thermograms of the undrawn PET and the C-40 samples.

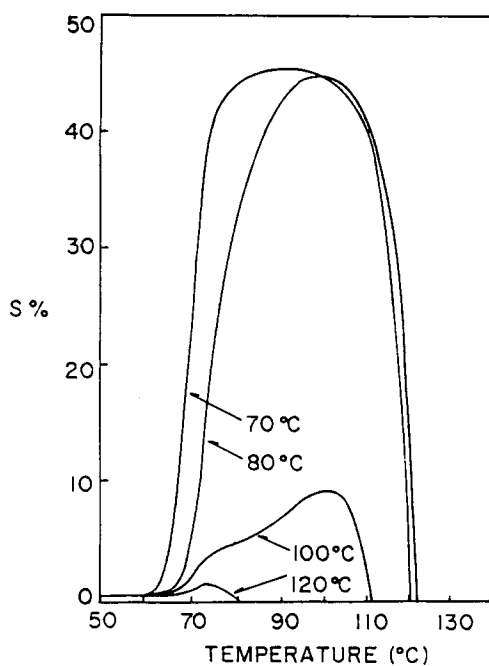


Fig. 9. The effect of draw temperature on the thermal shrinkage ratio of the C-40 sample.

TABLE IV
The Thermal Shrinkage Properties of the C-40 Sample ($\lambda = 2$)
at Four Different Draw Temperatures

Properties	C-40-70	C-40-80	C-40-100	C-40-120
T ($^{\circ}\text{C}$) ^a	70	80	100	120
S_m (%)	45.2	44.8	0.5	0.84
dS/dt (%/min)	50.4	28.5	1.7	1.7
R (%)	90.5	89.6	18.0	1.7
T_i ($^{\circ}\text{C}$) ^b	60	61.5	64	65

^a T = draw temperature ($^{\circ}\text{C}$).

^b T_i = initial temperature of shrinkage ($^{\circ}\text{C}$).

Thermal Shrinkage Model Experiment

Figure 10 shows the result of thermal shrinkage experiment of the C-40 sample drawn at 70°C . The experiment was performed by TMA at 80°C . After 1 min, the shrinkage ratio was 33.1%, which was about 73% of the value of the maximum shrinkage ratio and the surface temperature of the film was about 73°C . It took, respectively, 92 s and 125 s for the film to reach 90 and 95% of its maximum shrinkage ratio. When the surface temperature of the film was 80°C , the shrinkage ratio was 44.7%, about 98.6% of the value of the maximum shrinkage ratio. Thereafter, the shrinkage rate was increased very slowly. The maximum shrinkage ratio 45.3% was obtained at 1000 s.

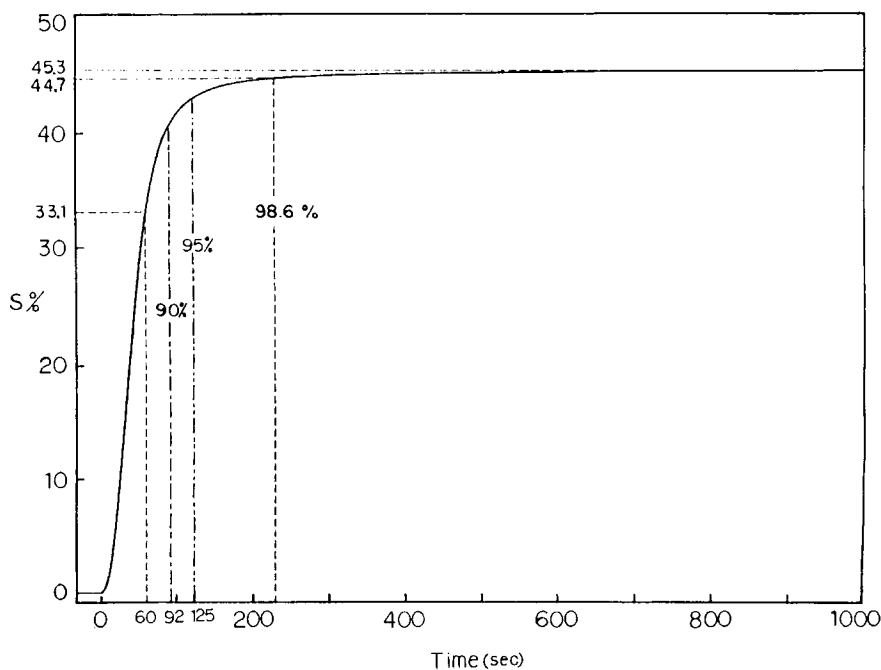


Fig. 10. The plot of thermal shrinkage ratio against time for the sample C-40-70 at 80°C .

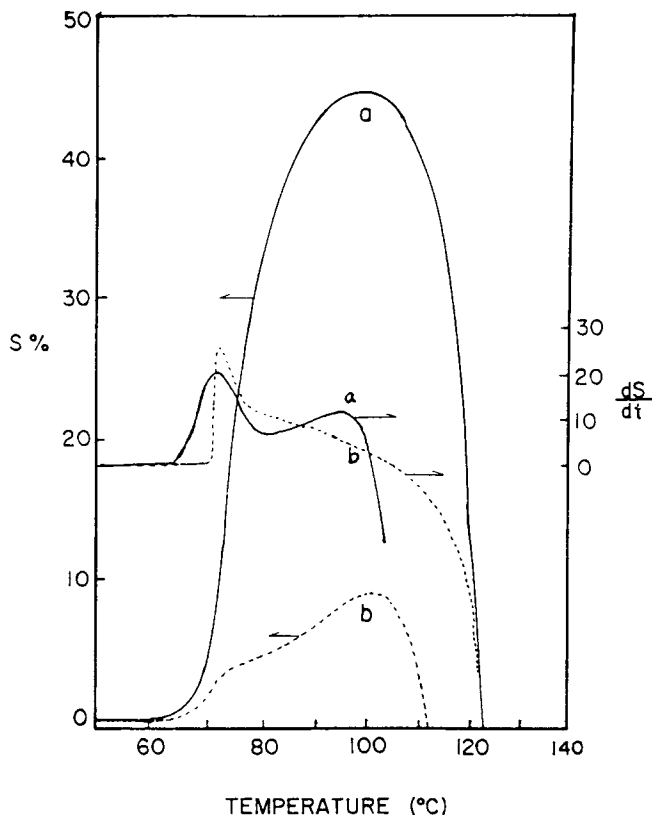


Fig. 11. The change of thermal shrinkage ratio and rate with temperature for the sample A-40-80 (a) drawn at 80°C and the sample C-40-100 (b) drawn at 100°C.

Mechanism of the Thermal Shrinkage of the Copolyester

In Figure 9, the curve for the film drawn at 100°C shows two damping peaks at 75 and 103°C. The values are very close to the maximum shrinkage temperatures (T_{ms}) of PEI and PET, i.e., T_{ms} of PEI = 80°C and T_{ms} of PET = 104°C. Therefore, the first damping peak may be due to the shrinkage of ethylene isophthalate chain segment, and the second one may be due to the shrinkage of ethylene terephthalate chain segment. The plot of the shrinkage rate against the temperature is shown in Figure 11. As can be seen in this figure, the curves show two damping peaks for sample C-40-100 and one damping peak and one shoulder for sample A-40-80. The other synthesized copolyesters show the same behavior. According to the Kato's studies on PMMA and polycarbonate systems,^{12,13} the thermal shrinkage mechanism of the copolyester is considered to be two-state thermal shrinkage.

CONCLUSIONS

The chains of the copoly(ethylene isophthalate terephthalate) are oriented more loosely than those of the poly(ethylene terephthalate). The copolyesters have more amorphous regions and the polymer chains move faster. All these

will result in the increase of the thermal shrinkage. The thermal shrinkage mechanism is two-state thermal shrinkage.

The best thermal shrinkage properties were obtained when the copolyester contained 40 mol % of ethylene isophthalate. Increase in the molecular weight and decrease in the draw temperature will result in the increase of thermal shrinkage of a polymer. The suitable draw temperature is located between T_g and T_{sb} .

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