Synthesis and Characterization of Poly[(butylene succinate)-*co*-(butylene terephthalate)]-*b*-poly(tetramethylene glycol) Segmented Block Copolymer

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ABSTRACT: Polyester-polyether segmented block copolymers of poly[(butylene succinate)-*co*-poly(butylene terephthalate)] (PBS–PBT) and poly(tetramethylene glycol) (PTMG) (M_n = 2000) with various compositions were synthesized. PBT content in the PBS was adjusted to ca. 5 mol %. Their thermal and mechanical properties were investigated. In the case of copolymer, the melting point of the PBS–PBT control was 107.8°C, and the melting point of the copolymer containing 70 wt % of PTMG was 70.1°C. Crystallinity of soft segment was 5 ~ 17%, and that of hard segment was 42 ~ 59%. The breaking stress of the PBS–PTMG control was 47 MPa but it decreased with increasing PTMG content. In the case of copolymer containing 70 wt % of PTMG, breaking stress was 36 MPa. Contrary to the decreasing breaking stress, breaking strain increased from 300% for PBS–PBT control to 900% for a copolymer containing 70 wt % of PTMG. The shape recovery ratios of the copolymer containing 70 wt % PTMG were almost twice of those of copolymers containing 40 wt % PTMG. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 2067–2075, 2001

Key words: poly(butylene succinate); terephthalate; poly(tetramethylene glycol); segmented block copolymer; biodegradable

INTRODUCTION

Many researchers have tried to adapt aliphatic polyesters as biodegradable materials. Polyglycolide and polylactide are well-known aliphatic polyesters, and are used as absorbable surgical sutures and drug carriers for controlled release.[1] Other aliphatic polyesters, such as polycaprolactone, poly(ethylene succinate) (PES), poly(butylene succinate) (PBS), etc., have low melting temperature, poor mechanical properties, and poor processability, so they are not widely used. Some researchers have tried to improve these drawbacks of biodegradable polymers. Kricheldorf[2] reported blending studies of polycaprolactone copolymers with polyamide and polyethylene to improve mechanical properties. Albertsson et al.[3] tried to apply the PES–poly(tetramethylene glycol) (PTMG) copolymers as absorbable surgical sutures or drug carriers, and Xiong et al.[4] studied the polylactide–PTMG copolymer to see if it could be used as a drug carrier for controlled release. Huang et al.,[5] however, tried to find new application as possible ion-conducting polymers through the study of the complexes formed by PBS and alkali-metal salts.

PBS has relatively high melting temperature and fast crystallization rate compared with simi-

lar aliphatic polyesters, but it has poor thermal stability and mechanical properties like other aliphatic polyesters. In order to be applied in industry, better mechanical properties or other interesting characteristics are necessary. It was also reported that the copolymerization or blending of an aliphatic polyester with nonbiodegradable polymer lowered the biodegradability, but the block copolymerization with polyether did not show any appreciable lowering of the biodegradability.[6] In this research, we synthesized polyester–polyether segmented block copolymers using PBS as the hard segment and PTMG as the soft segment, and tried to develop biodegradable thermoplastics with good elastic property. The properties of copolymer (elasticity, elongation, and hydrophilicity) can be controlled by the type and the weight percent of the soft segment. Until now, almost all research on polyester–polyether segmented block copolymers has been concerned with using aromatic polyesters like polyethylene terephthalate or poly(butylene terephthalate) (PBT) as the hard segment[7] to make copolymers with good mechanical properties. Some researchers tried to adapt these copolymers to the medical fields by using poly(ethylene glycol) (PEG) as the corresponding soft segment.[8–10]

By using PBS as the hard segment, biodegradability is expected in the copolymer. By using PTMG as the soft segment, better mechanical properties are expected because it is well known that the thermal and mechanical properties of PTMG are better than the other polyglycols such as PEG and poly(propylene glycol) when it is transformed to a segmented block copolymer.[11] In our previous research,[12] PBS–PTMG segmented block copolymers of PBS–PTMG were synthesized and their thermal and mechanical behaviors were investigated to find an industrially applicable polymeric material containing potentially biodegradable PBS moiety. In this research, a small amount of PBT was incorporated into PBS to prepare a segmented block copolymer with improved mechanical properties. It has been reported that the mechanical properties (breaking stress and strain) of PBS were improved by incorporation of a small amount of aromatic units to PBS.[13] Also, our previous research showed that around 6 mol % of PBT in PBS gave a copolymer with increased breaking stress of about 30% and increased breaking strain of about 200%.[14] Therefore, polyester–polyether segmented block copolymers of PBS–PBT and PTMG (M_n = 2000) with various compositions, were synthesized in this research.
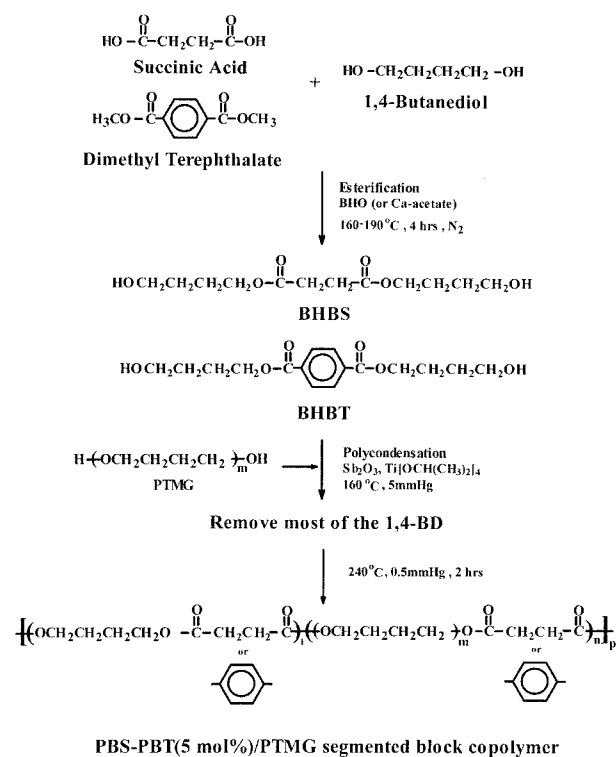
Scheme 1 Synthesis of PBS-PBT/PTMG segmented block copolymer.

The relationships between the compositions of copolymers and the thermal and mechanical properties of copolymers were investigated.

EXPERIMENTAL

Materials

Succinic acid (Shinyo Chemical, Japan), 1,4-butanediol (Junsei Chemical, Japan), and PTMG (TERATHANE 2000 from DuPont) were used as received. Dimethyl terephthalate (DMT) and calcium acetate were obtained from SK Chemicals (Korea) and used as received. Titanium isopropoxide, antimony trioxide, and butyltin hydroxide oxide were obtained from Aldrich Chemical and used as received.

Synthesis

The polyester–polyether segmented block copolymers were prepared as in Scheme 1 by a two-step melt polycondensation technique. Succinic acid (or DMT), 1,4-butanediol, and a small amount of butyltin hydroxide oxide (or Ca-acetate for DMT) as esterification catalyst were added to a carefully

dried three-necked kettle, and the temperature was raised to 190 ~ 200°C and maintained for 3 h with stirring in a stream of nitrogen throughout the esterification reaction. From this first step, bishydroxybutyl succinate or bishydroxybutyl terephthalate was obtained. At the second step, PBS–PBT (5 mol % of PBT)/PTMG copolymers were obtained from the reaction of bishydroxybutyl succinate, bishydroxybutyl terephthalate, and PTMG. Mixed antimony trioxide and titanium isopropoxide catalyst (each 5×10^{-6} mol/g of oligomer) was used, and reaction was performed at 240°C under a vacuum of 0.5 mmHg for 2 h.

Analysis

Contents of PBT and PTMG were determined by proton nuclear magnetic resonance (NMR) in $CDCl_3$ solvent by using a Varian Germini 200 MHz NMR spectrometer. The concentration of each sample was about 5 wt % in the solvent. Chemical shifts are presented in ppm. Intrinsic viscosity was measured in *o*-chlorophenol at 25 $\pm$ 0.1°C.

Thermal analysis was performed with a differential scanning calorimeter (DSC7; Perkin-Elmer) equipped with intracooler II under nitrogen atmosphere. The temperature scale was calibrated against high purity standards (zinc and indium) and the apparent heats of fusion (ΔH_f) were calculated by comparing the area of the melting endotherm of a weighed polymer sample with that of a weighed sample of indium. We weighed 10 $\pm$ 0.1 mg of each sample in an aluminum sample pan, and the temperature of the sample block was maintained at -70°C for 10 min. Then the sample was heated to 150°C with the heating rate of 20°C/min for the first heating scan and held for 10 min at 150°C. After quenched to -70°C, at a rate of -500°C/min, the sample was heated to 150°C with the heating rate of 20°C/min for the second heating scan, then cooled to -20°C/min for the cooling scan. T_g, T_m, and cold crystallization temperature on heating (T_{cc}) were obtained from the second heating scan. The peak melting temperature from the second heating scan was taken as the melting point.

Tensile tests were performed according to ASTM D638-91[ε1].[15] Each specimen (width, 6 mm; length, 115 mm; thickness, 0.35 ~ 0.40) was dried at room temperature overnight *in vacuo* and conditioned for 40 h (temperature, 23 $\pm$ 2°C; relative humidity, 50 $\pm$ 5%).[16] Uniaxial stress-strain data were obtained with an Instron model 4465 testing instrument (crosshead speed, 20 mm/min; gauge length, 64 mm; load cell capacity, 1 kN) equipped with a series IX automatic materials testing system for automatic data acquisition. At least five samples were examined for each averaged result.

Shape Recovery Ratio (S.R.R.) Test

Shape recovery tests were performed to examine the elasticity of the copolymers containing 45 wt % and 67 wt % PTMG in PBS-PBT (5 mol %)/PTMG copolymer. All experimental conditions were the same as those of the tensile test except crosshead speed (50 mm/min at this experiment).

1. The specimen was extended to the fixed extension ratio at the temperature (18°C) between T_g and T_m and held for 1 min. 1) ST5G64 copolymer (45 wt % PTMG): extended 100, 200, 300%; 2) ST5G46 copolymer (67 wt % PTMG): extended 100, 200, 300, 400, 500, 600, 700% (corresponding extension ratio, k = 2, 3, 4, 5, 6, 7, 8, respectively)

2. After loosening the fixation, the specimen was held for 10 min at the temperature (18°C) between T_g and T_m, the gauge length (L_1) was measured, and the S.R.R. was calculated from the following equation:

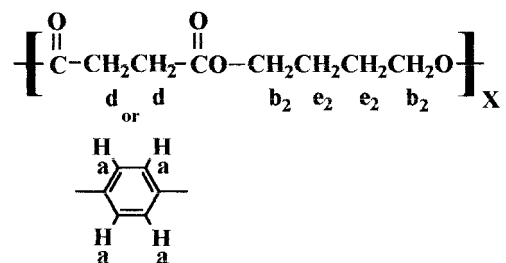$$\text{S.R.R.}(\%) = \frac{k \cdot L_0 - L_1}{(k - 1) \cdot L_0} \times 100$$

where k = extension ratio, L_0 = gauge length (64 mm), and L_1 = gauge length after being recovered.

RESULTS AND DISCUSSION

Compositions of Copolymers

Three series of polyester-polyether segmented block copolymers consisting of hard and soft segment were synthesized. Their structures are:
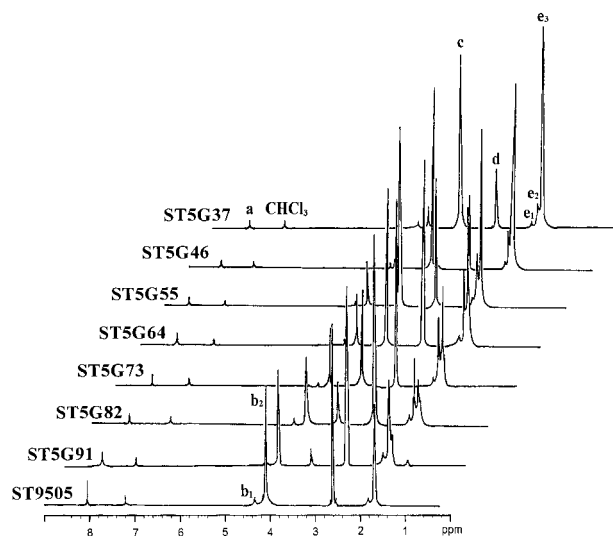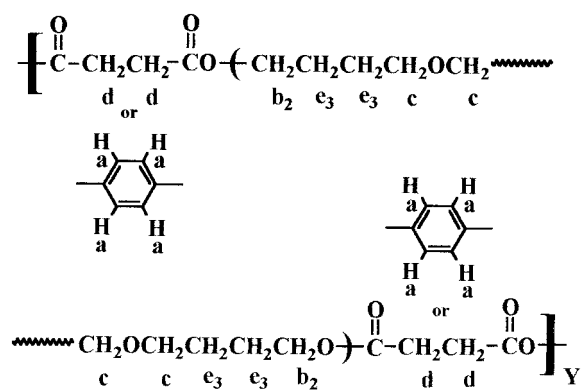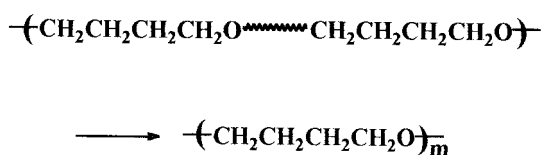
Hard segment:

Figure 1 A 200 MHz ^{1}H-NMR spectra of PBS-PBT/PTMG copolymers in CDCl$_3$.

Soft segment:

The PTMG repeating unit can be described as follows:

The compositions of the copolymers were determined by proton NMR as in Figure 1. The contents of each component in the copolymer can be calculated based on the chemical shifts of the various hydrogen atoms in the copolymer as listed in Table I, and the composition of the copolymer (in weight ratio) can be calculated from these equations.

$$4X + 4mY = e_1 + e_2 + e_3$$

(protons of —CH$_2$—CH$_2$— in butylene group)

$$4(m - 1)Y = c$$

(protons of —CH$_2$—O—CH$_2$ in PTMG group)

The number average molecular mass of PTMG is 2000, and m can be calculated from:

$$m = \frac{2000 - 18.02(\text{H}_2O)}{72.11(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2)} \approx 27.49$$

In Figure 1, ST9505 shows the proton peak (d: 2.61 ppm) originating from succinate and the peak (b_2, 4.08 $\sim$ 4.12 ppm; e_2, 1.61 $\sim$ 1.71 ppm) from the butylene group. Aromatic proton in PBT shows a new resonance peak at 8.07 $\sim$ 8.12 ppm(a). PTMG shows peaks at 3.37 $\sim$ 3.40 ppm(c) and the peak around 1.6 ppm splits into e_1, e_2, and e_3. The intensity of proton peaks assigned to e_3 increases with increasing PTMG content. Table II shows that the compositions of the copolymer calculated by proton NMR agree well with those expected from the feed composition.

Thermal Characterization

The crystallization and melting behavior of the segmented block copolymer were compared and contrasted with each other. For Figure 2, T_m and T_g values of ST9505 and segmented block copolymers were obtained from second heating scans. Reported T_m and T_g values of PBS are around 115.2°C and −32.5°C, respectively.[5,17–19] Incorporation of 5 mol % of terephthalate resulted in T_m at 107.8°C and T_g at −31.9°C.

There are two melting peaks in the second heating scan of segmented copolymer, the one at the upper temperature (70 $\sim$ 107°C) originates from the hard segment and the other at lower temperature (9 $\sim$23°C) is from the soft segment. This proves that the copolymers synthesized confirm to the targeted segmented block copolymers. Melting behavior like this was also observed from the research of PBT–PEG thermoplastic elastomers by Slonecki.[20] The melting temperature of hard segment of the segmented block copolymer was depressed from 107.8°C to 70.1°C with increasing PTMG content, but the trend of the melting temperature of soft segment was different from that of hard segment. The melting temperature of soft segment decreased with increasing

Table I ^{1}H-NMR Chemical Shifts of PBS-PBT/PTMG Copolymers

Segment	Proton	Symbol	Chemical Shift (δ/ppm)
PBS	$-O-\overset{O}{\overset{\|}{C}}-C\underline{H}_2-C\underline{H}_2-\overset{O}{\overset{\|}{C}}-O-$	d	2.6
	$-\overset{O}{\overset{\|}{C}}-O-C\underline{H}_2-$	b_2	4.1
	$-C\underline{H}_2-C\underline{H}_2-$	e_2	1.69
PBT	$-O\overset{O}{\overset{\|}{C}}-\underset{\underline{H}\quad\underline{H}}{\overset{\underline{H}\quad\underline{H}}{\bigcirc}}-\overset{O}{\overset{\|}{C}}O-$	a	8.1
	$-\overset{O}{\overset{\|}{C}}-O-C\underline{H}_2-$	b_1	4.4
	$-C\underline{H}_2-C\underline{H}_2-$	e_1	1.8
PTMG	$-C\underline{H}_2-O-C\underline{H}_2-$	c	3.4
	$-\overset{O}{\overset{\|}{C}}-O-C\underline{H}_2-$	b_2	4.1
	$-C\underline{H}_2-C\underline{H}_2-$	e_3	1.6

Table II Molecular Characteristics of PBS-PBT/PTMG Copolymer

Code	PTMG (wt %) Feed	PTMG (wt %) Copolymer (^{1}H-NMR)	PBT (mol %) in Hard Segment Feed	PBT (mol %) in Hard Segment Copolymer (^{1}H-NMR)	I.V.	$X_{c,s}$ (%)	$X_{c,h}$ (%)
PBS homo	0	0	0	0	1.62	—	56.1
ST9505	0	0	5	5.9	1.46	—	47.9
ST5G91	10	10.4	5	6.7	1.45	5.3	43.7
ST5G82	20	21.9	5	5.4	1.56	7.8	45.7
ST5G73	30	32.6	5	5.1	1.62	6.4	45.5
ST5G64	40	45.2	5	5.2	1.71	8.0	44.5
ST5G55	50	56.5	5	5.3	1.70	9.7	59.2
ST5G46	60	67.7	5	5.6	1.85	14.2	59.2
ST5G37	70	77.4	5	4.9	2.03	16.6	42.4

I.V., intrinsic viscosity; $X_{c,s}$, % crystallinity of soft segment; $X_{c,h}$, % crystallinity of hard segment.
The calculated percent crystallinity was based on the composition obtained from ^{1}H-NMR.

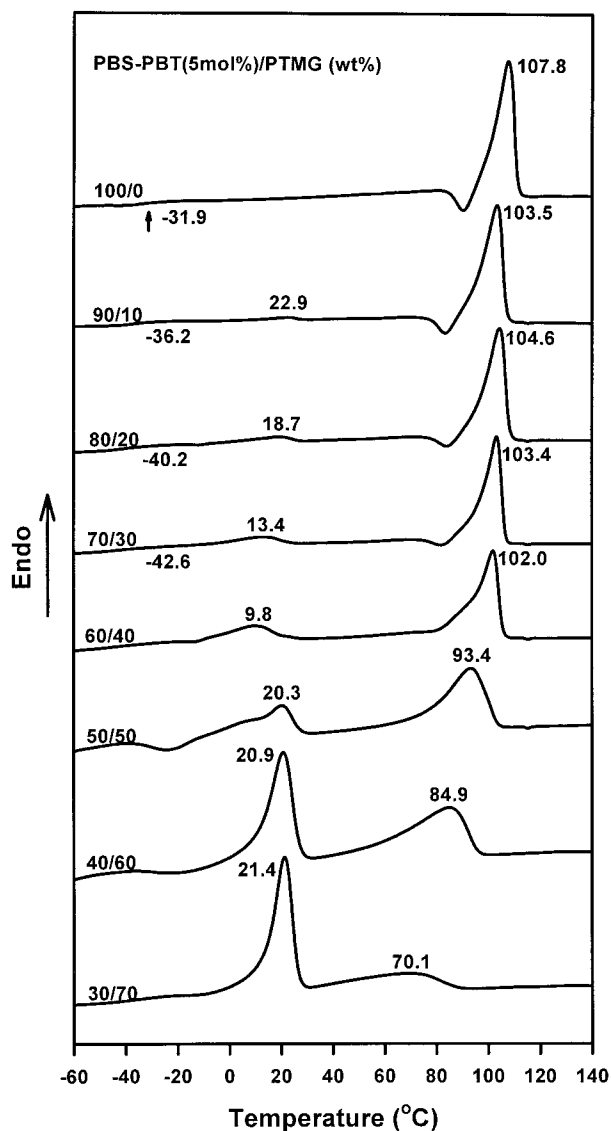**Figure 2** DSC thermograms (second heating scans) of PBS-PBT/PTMG copolymers.

exotherms. The peak at the upper temperature was broadened with increasing PTMG content, which could be explained by the incorporated PTMG chains disturbing the crystal growth of the PBS–PBT domain, so that the crystallization rate of the PBS–PBT domain was slowed down. The exothermic peak at lower temperature is attributed to the crystallization of the PTMG. As the PTMG content increased from 50 to 60%, only one exotherm appeared.

Measurement of Crystallinities of Copolymers

Crystallinity of copolymer was measured from the heat of fusion of hard and soft segments obtained
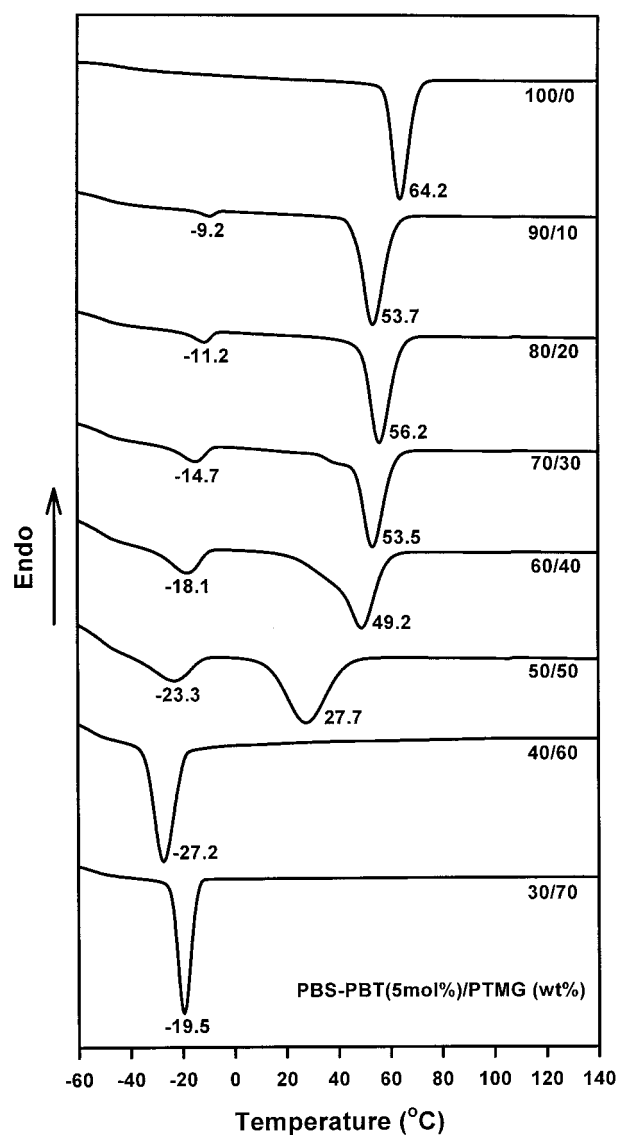

Figure 3 DSC thermograms (cooling scans) of PBS-PBT/PTMG copolymers.

PTMG content up to 40 wt %, then increased from 9.8°C (40 wt % PTMG) to 21.4°C (70 wt % PTMG). This can be explained by the melting behavior of soft segment to the 40 wt % PTMG copolymer being influenced by hard segment domain, but as the PTMG content becomes higher (>40 wt %), it is less affected by hard domains, so the shape of the soft segment melting endotherm is sharp and the peak of soft segment moves to the higher temperature range.

Figure 3 shows the cooling curves of the copolymers. ST9505 copolymer has a steep and narrowly shaped crystallization exotherm. Segmented block copolymers have two crystallization

from the DSC second heating scan. The heats of fusion of PBS, PBT, and PTMG perfect crystal were calculated and obtained from the references.[17,21,22] We calculated the heat of fusion (ΔH_f) of PBS, PBT, and PTMG perfect crystal from the group contribution theory[21] and the calculated ΔH_f of PBS, PBT, and PTMG was 110.4 J/g, 149.8 J/g, and 235.8 J/g, respectively. These values show some differences from the experimental values (200.0 J/g to PBS,[18] 140.8 ∼ 145.3 J/g to PBT,[22] and 171.9 J/g to PTMG[22]) of other researchers. We used the calculated values of ΔH_f of PBS, PBT, and PTMG to calculate the crystallinities of hard and soft segments using the following equations:

$X_{c,h}$ (% crystallinity of hard segment)

$$= \frac{\Delta H_{m,h}}{\Delta H_f \text{ of PBS} \times \text{wt. fraction of PBS} + \Delta H_f \text{ of wt. fraction of PBT}} \times 100$$

$X_{c,s}$ (% crystallinity of soft segment)

$$= \frac{\Delta H_{m,s}}{\Delta H_f \text{ of PTMG} \times \text{wt. fraction of PTMG}} \times 100$$

where $\Delta H_{m,h}$ = the heat of fusion of the hard segment obtained from the DSC second heating scan, and $\Delta H_{m,s}$ = the heat of fusion of the soft
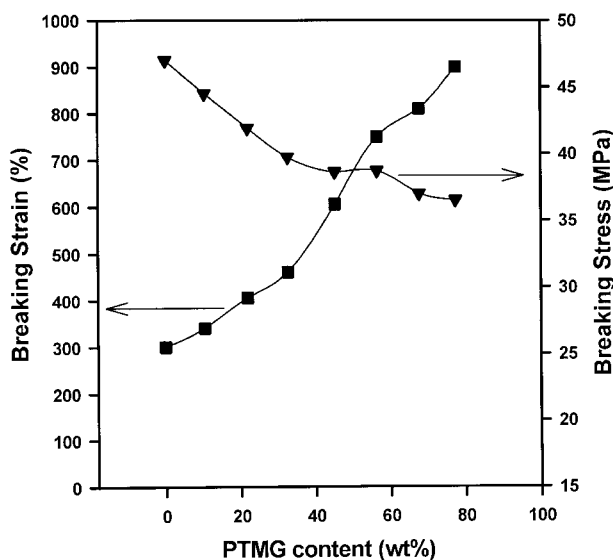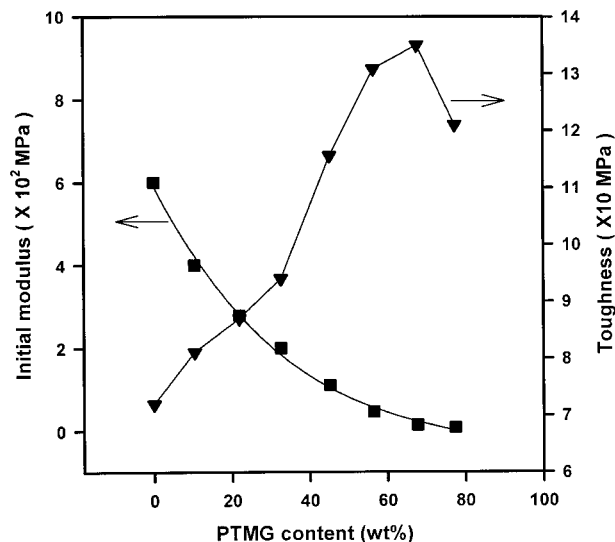

Figure 5 Toughness and initial modulus of PBS-PBT/PTMG copolymers versus PTMG wt %.

segment obtained from the DSC second heating scan.

As shown in Table II, the crystallinities of hard and soft segment of copolymers were 42 ∼ 59% and 6 ∼ 16%, respectively. In the copolymer, the crystallinity of the soft segment showed a low value at low PTMG content copolymer and a high value at the higher PTMG content copolymer. This can be explained by the volume of the soft block increasing with increasing PTMG content, so the regularity of the soft segment is increased. The crystallinity of the hard segments showed the highest values at PTMG contents from 50 to 60 wt % and these copolymers' crystallinities for soft segment were also high. This shows that relatively higher content of soft segment gives good crystallinity for both segments.

Tensile Properties

In Figure 4, the change of tensile stress and strain at break of copolymers are plotted against PTMG content. Tensile strain at break was increased with increasing PTMG, but tensile stress at break was decreased with increasing PTMG. Similar results were also reported by Albertsson et al.[23] by using PES/PTMG copolymers. Tensile stress at break of ST9505 was 47 Mpa, which is a higher value than that of PBS control (37.3 MPa), and decreased to 36 MPa as the PTMG content increased (ST5G37). Tensile strain at break of copolymers was gradually increased from 300%
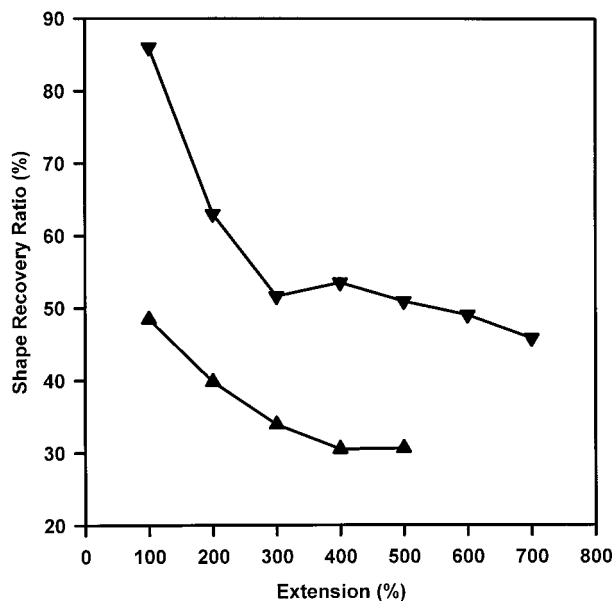

Figure 4 Breaking stress and breaking strain of PBS-PBT/PTMG copolymers versus PTMG wt %.

Figure 6 Change of shape recovery ratio of ST5G64 (▲) and ST5G46 (▼) copolymers versus % extension.

(ST9505) to 900% (ST5G37) with increasing PTMG content.

In Figure 5, initial modulus of the copolymer decreases monotonically as the PTMG content increases. Reduction of the hard segmental volume is directly related to the decrease of the initial modulus. These phenomena (increased strain, decreased stress, and initial modulus) show that the toughness of PBS was improved by adding PTMG. The toughness (the work of rupture) of copolymers was obtained from the area of stress-strain curves.[24,25] The obtained toughness was increased from 70 Mpa (PBS control) to 135 Mpa (SG46), and showed a maximum at 67% of PTMG.

Shape Recovery Ratio

To examine whether the copolymer can be applied as an elastic rubbery material, a shape recovery test was performed, and the results are shown in Figure 6. ST5G64 and ST5G46 copolymers were chosen for testing S.R.R. After extending each to 100% of the original gauge length, the S.R.R. of ST5G64 and ST5G46 were 48% and 86%, respectively. Increased extension ratios gave decreased S.R.R. The curve shape of ST5G64 closely resembles that of ST5G46, showing that S.R.R. of ST5G64 is about half of that of ST5G46.

In the case of ST5G64, the hard segment content of the copolymer is so high that the elongated part of hard segment is fixed and cannot recover

as much as the soft segment rich copolymer (ST5G46) does. A similar observation also reported by Chun et al.,[26] was that the shape recovery ratio was increased with adding polyether to aromatic polyester. These observations reveal that S.R.R. is controlled by the content of the soft segment when the hard segment is fixed. Because a perfect elastomer should show an S.R.R. of 100% with extensions of more than 300%, tested copolymers in this experiment are not good elastomers. However, it is evident that ST5G46 has a reasonable elastomeric property under limited extension.

CONCLUSION

New types of biodegradable segmented block copolymers, with the properties of improved elongation and elasticity, were synthesized by copolymerizing PTMG and PBS–PTMG. The thermal and mechanical properties of copolymers can be controlled by the PTMG content. Initial modulus and breaking stress of copolymer were decreased, but toughness and breaking strain of the copolymers were increased with increasing PTMG content. The shape recovery ratio of copolymer containing 70 wt % PTMG was almost twice that of copolymers containing 40 wt % PTMG.

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