Enhanced Dynamic Mechanical and Shape-Memory Properties of a Poly(ethylene terephthalate)–Poly(ethylene glycol) Copolymer Crosslinked by Maleic Anhydride

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ABSTRACT: Dimethyl terephthalate (DMT) and ethylene glycol (EG) were used for the preparation of poly(ethylene terephthalate) (PET), and poly(ethylene glycol) (PEG) was added as a soft segment to prepare a PET–PEG copolymer with a shape-memory function. MWs of the PEG used were 200, 400, 600, and 1000 g/mol, and various molar ratios of EG and PEG were tried. Their tensile and shape-memory properties were compared at various points. The glass-transition and melting temperatures of PET–PEG copolymers decreased with increasing PEG molecular weight and content. A tensile test showed that the most ideal mechanical properties were obtained when the molar ratio of EG and PEG was set to 80:20 with 200 g/mol of PEG. The shape memory of the copolymer with maleic anhydride (MAH) as a crosslinking agent was also tested in terms of shape retention and shape recovery rate. The amount of MAH added was between 0.5 and 2.5 mol % with respect to DMT, and tensile properties and shape retention and recovery rate generally improved with increasing MAH. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 27–37, 2002

Key words: poly(ethylene terephthalate); poly(ethylene glycol); maleic anhydride; crosslinking; shape memory; modulus; copolymer

INTRODUCTION

Recently, active research has been done on smart materials such as a shape-memory alloy, semiconductors, polymers, and medical materials. Since 1990, smart materials have emerged that can detect an external stimulus, process it, and finally respond.[1–6] A shape-memory polymer, one of these smart materials, was first developed by Nippon Zeon in 1984 under the trade name of polynorbornene.[7] Meanwhile, a shape-memory polymer based on urethane was introduced in 1988 by Mitsubishi and was easily processed by injection, extrusion molding, or solvent coating.

To utilize the shape-memory effect, it is very important to control the structure and physical properties of a shape-memory polymer. Generally, a polymer deforms much easier at temperatures above its glass-transition temperature (T_g) because it is in a rubbery state and has a low modulus. A conventional polymer that has more than 100 times a difference in modulus around T_g tends to retain its deformed shape if the polymer is heated above T_g and cooled below T_g with the load removed. Therefore, a conventional polymer has difficulty recovering its original shape. How-

ever, a shape-memory polymer has fixed points that can prevent the plastic flow of chains and is composed of two phases that can be reversibly changed between soft and hard, depending on the temperature, which help in recovery of its original shape.

In this investigation, poly(ethylene terephthalate) (PET) was selected as the starting material for the development of a basic matrix material that could be applied to smart fabric with vapor permeability control and smart-fiber-reinforced composite material with damping control. PET was copolymerized with poly(ethylene glycol) (PEG) with molecular weights (MWs) ranging from 200 to 1000 g/mol. Among the candidates, an ideal PET–PEG copolymer composition was selected, and maleic anhydride (MAH) was added to the PET–PEG copolymer to crosslink the copolymer chains. Mechanical and shape-memory properties of the PET–PEG–MAH copolymers were compared to find the best composition of PET–PEG–MAH.

EXPERIMENTAL

Materials

Dimethyl terephthalate (DMT) and ethylene glycol (EG) were kindly supplied by SK Chemicals (Suwon, Korea), and PEG and MAH (Formula Weight = 92.10g/mol) were purchased from Duksan Chemical (Ansan, Korea). The MWs of PEG were 200, 400, 600, and 1000 g/mol. Calcium acetate and antimony oxide were from Hayashi Pure Chemical Industry (Osaka, Japan). Phosphorous acid used as a stabilizer was purchased from Kanto Chemical (Tokyo, Japan).

Preparation of Copolymers

PET–PEG copolymers were prepared with DMT by the melt-condensation method with a polymerization reactor custom made by Go Do Engineering Co. (Seoul, Korea). We prepared the copolymers in two different ways by either the changing MW of PEG (soft segment) or the composition of PEG. In addition, MAH was added in various ratios as a crosslinking agent to the copolymer composed of 4 mol % of EG and 1 mol % of PEG.

The polymerization reaction was carried out in two steps; in the first step, oligomers were prepared with DMT, EG, and PEG, and in the second step, the oligomers made in first step were condensed to polymers by an esterification reaction, which required a high temperature, constant stirring, and a high vacuum to shift the reaction equilibrium further to the products.

As a representative example, the synthetic method for the polymer (MAH10) prepared at the ratio of 50:80:20 (DMT:EG:PEG) is shown later; other polymers were made by a similar method. Calcium acetate (0.45 g) as a catalyst was added into a mixture that was heated to 145°C and that contained 142 g (2.28 mol) of EG, 114 g (0.57 mol) of PEG (200 g/mol), and 277 g (1.43 mol) of DMT, and the mixture was further heated to 200°C. Methanol was removed from the reaction mixture by distillation, and the esterification was continued until the methanol was not produced any more; this was followed by the addition of 0.5 g phosphorous acid as a stabilizer and an additional 10 min of stirring. After the oligomer mixture was transferred into the polymerization reactor that was heated to 245°C and 0.5 g antimony oxide was added as a catalyst, the mixture was heated to 270°C and kept under vacuum (45 mmHg) for 30 min to remove unreacted EG and PEG. After the addition of MAH, polymer condensation was carried out under higher vacuum (1mmHg) for 3 h. Finally 350 g of dark brown copolymer was obtained. The synthetic scheme and characterization of the polymers synthesized are shown in Scheme 1 and Tables I and II, respectively.

Intrinsic Viscosity [η]

The [η] of the PET–PEG and PET–PEG–MAH copolymers in 1,1,2,2- tetrachloroethane/phenol (4/6 w/w) was measured with a Ubbelohde viscometer at 35°C and 0.5 g/dL concentration.

Thermal Analysis

T_g and melting temperature (T_m) were measured with a differential scanning calorimeter (TA-2000; TA Instruments, New Castle, DE). Specimens were heated to 300°C at a 10°C/min heating rate, kept at this temperature for 3 min, and then cooled to -50°C at -10°C/min. T_g and T_m were determined from the second heating thermograms.

Spectroscopic Measurements

We prepared NMR samples by dissolving PET–PEG copolymers in CDCl$_3$ and a small amount of CD$_3$OD, and NMR spectra were measured by Fourier Transform-NMR (Avance 600, Bruker, Rheinstetten, Germany). For the IR spectrum, specimens were prepared as thin films on NaCl disks and analyzed with a Fourier transform in-

(a)

(b)

(c)
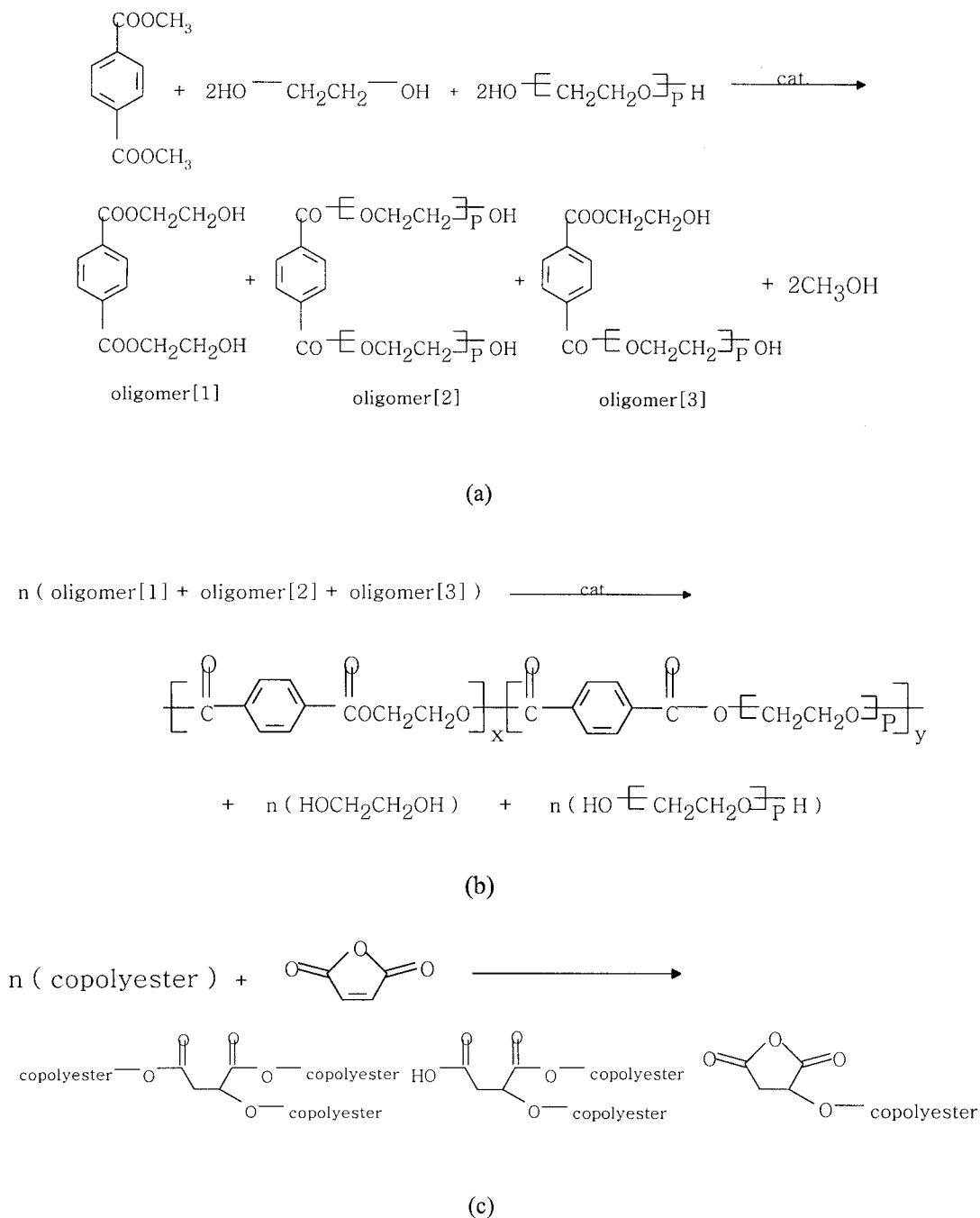
Scheme 1 Synthetic scheme of PET–PEG–MAH copolymer.

frared (FTIR) spectrometer (Michelson MB series 104, Bomem, Quebec, Canada).

Mechanical Properties Analysis

Prepared copolymers were preheated at 60°C for 24 h to prevent hydrolysis from moisture and compression-molded to a sheet 1 mm thick and 5 mm wide at 30°C, which was above its T_m. Tensile tests were performed with a universal testing machine (UTM; Lloyd LR 50K, Fareham, UK), with dumbbell-type specimens prepared according to ASTM D-638 at a crosshead speed of 100 mm/min.

For dynamic mechanical property measurements, a dynamic mechanical thermal analyzer (Mark IV, Rheometric Scientific, Leatherhead,

Table I   Basic Characterizations of the PET–PEG Copolymer

Sample Code	PEG (mol %)	PEG MW (g/mol)	T_g (°C)	T_m (°C)	[η] (dL/g)
PET	0	—	79.1	252.0	0.68
E200-5	5	200	45.8	228.1	0.72
E200-10	10	200	33.5	213.5	0.62
E200-15	15	200	29.8	198.1	0.55
E200-20	20	200	8.1	167.3	0.60
E200-25	25	200	—	—	0.43
E200-30	30	200	11.7	—	0.39
E200-35	35	200	−8.3	—	0.44
E400-10	10	400	−12.9	200.0	0.70
E400-15	15	400	−23.5	173.0	0.60
E400-20	20	400	−26.1	—	0.44
E600-05	5	600	−16.9	225.8	0.69
E600-10	10	600	−32.4	194.6	0.67
E600-15	15	600	−33.2	181.7	0.57
E600-20	20	600	—	—	0.41
E1000-5	5	1000	−42.5	221.2	0.55
E1000-8	8	1000	−46.5	—	0.43
E1000-10	10	1000	−34.9	—	0.41

UK) was employed with a sheet 1 mm thick, and 5 mm wide as the specimen at a 3°C/min heating rate and at 1.1 Hz.

The shape-memory effect was checked by tensile test with a UTM equipped with a temperature-controlled thermal cabinet. For measurement of the shape retention rate, a specimen with length L_0 was strained to 100% above T_g but below T_m (40°C) and kept at that temperature for 1 min. The specimen under the strain was cooled back to below T_g (−30°C) and left at that temperature for 30 min after removal of load; measurement of the deformed length L_1 followed. The specimen was heated again to a temperature above T_g but below T_m, kept at that temperature for 10 min, cooled back to a temperature below T_g, and kept at this latter temperature for 30 min. From the final specimen length L_2, shape reten-

tion and shape recovery rate could be calculated by the following equations:

$$\text{Shaped retention rate (\%)} = (L_1 - L_0)/L_0 \times 100$$

$$\text{Shaped recovery rate (\%)} = (2L_0 - L_2)/L_0 \times 100$$

This whole procedure was repeated three times for the shape-memory test of PET–PEG–MAH copolymers.

RESULTS AND DISCUSSION

NMR and IR Analysis

In Figure 1, the proton NMR spectrum of MAH05 showed that the chemical shift of EG moved from

Table II   Basic Characterizations of the PET–PEG Copolymer Containing MAH

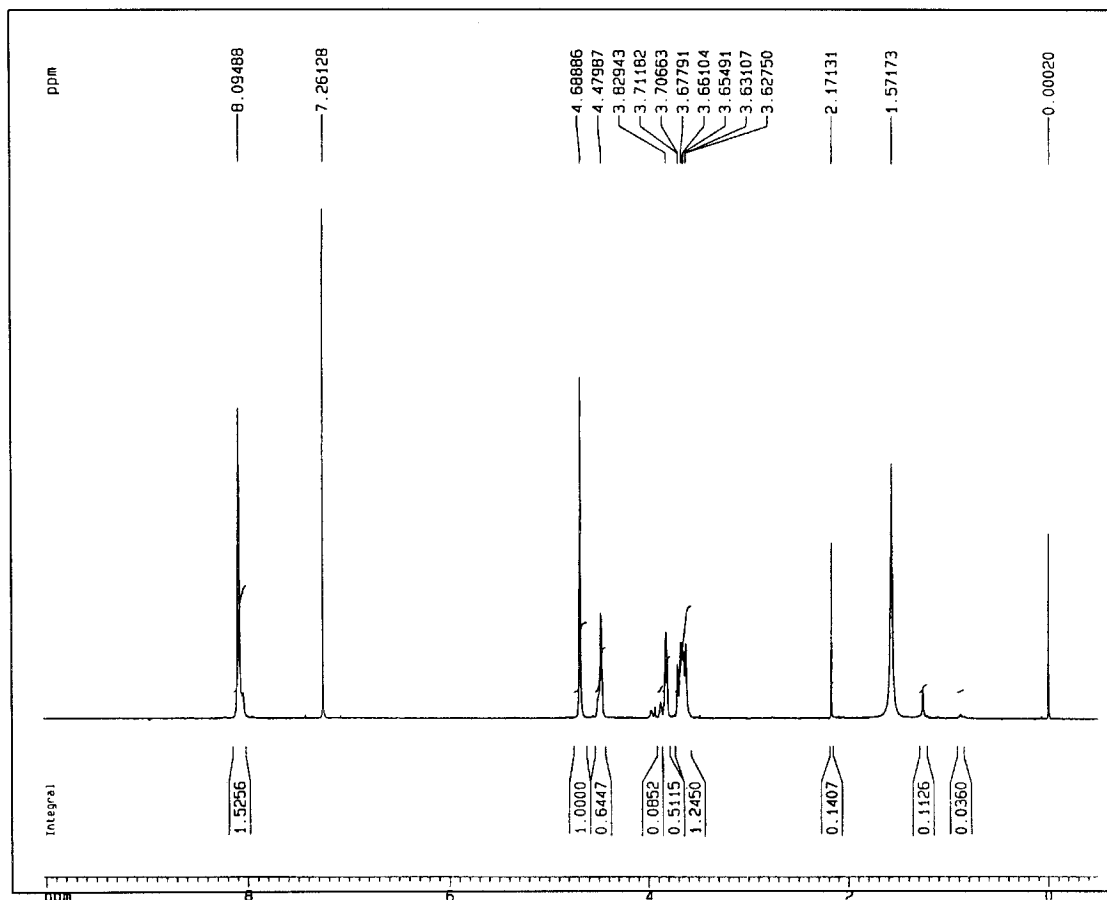| Sample Code	PEG MW (g/mol)	MAH (mol %)	T_g (°C)	T_m (°C)	[η] (dL/g)
E200-20	200	0	8.1	167.3	0.60
MAH05	200	0.5	8.3	165.1	0.62
MAH10	200	1.0	9.8	164.2	0.71
MAH15	200	1.5	11.6	166.3	0.65
MAH20	200	2.0	13.6	164.3	0.79
MAH25	200	2.5	17.7	164.2	0.67

Figure 1 ^{1}H-NMR spectrum of the PET–PEG–MAH copolymer (MAH05).

3.4 ppm of free EG to 4.4–4.7 ppm of the polymer, originating from the electron-withdrawing ester formation during polymerization, and the composition of EG and PEG calculated by the division of the integration ratio between EG and PEG with their number of protons was found to be 4.05:1.00, which was in excellent agreement with the theoretical ratio of 4:1. The peaks appearing at 1.57 and 2.17 ppm came from the trace amount of methanol in the CD_3OD solvent and MAH, respectively. In the FTIR spectrum shown in Figure 2, the complete disappearance of the —OH stretching at 3300 cm^{-1} can be seen, which was found as a broad band for the free EG and PEG. As judged from the NMR and FTIR data, the copolymerization was completed as expected.

Thermal Properties

As shown in Figure 3(a), T_g decreased rapidly at the beginning, but the decrease became slow as more PEG was included. With the same PEG content, PEG with a higher MW showed a larger decrease in T_g, and as shown in Figure 3(b), T_m also decreased linearly with PEG addition. The decrease of T_g and T_m was due to the increased chain flexibility and chain disorder with the addition of PEG.

As shown in Table II, T_m of PET–PEG copolymer crosslinked with MAH was not affected much by the amount of MAH, but T_g was dependent on the amount of MAH. For example, T_g jumped from 8.1 to 17.7°C as 2.5 mol % of MAH was introduced. The observed increase of T_g with MAH incorporation was due to the restricted molecular motion with more crosslinking.[8]

Tensile Properties

As seen in Figure 4(a), where maximum stress of PET–PEG copolymers is shown, the maximum stress increased with the addition of PEG but started to decrease afterward. When the PEG with MW 200 g/mol was used, the highest maximum stress was obtained at 10 mol % of PEG. However, at more than 10 mol % of PEG, the
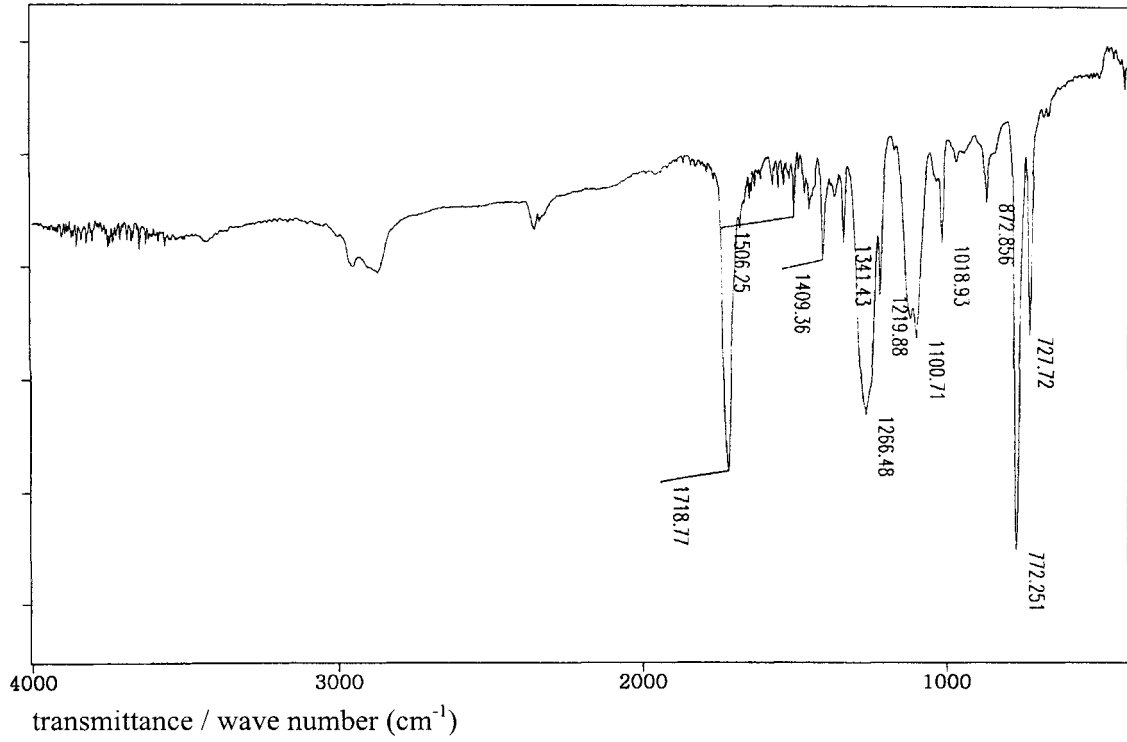
transmittance / wave number (cm⁻¹)

Figure 2 FTIR spectrum of the PET–PEG copolymer (E200-15).
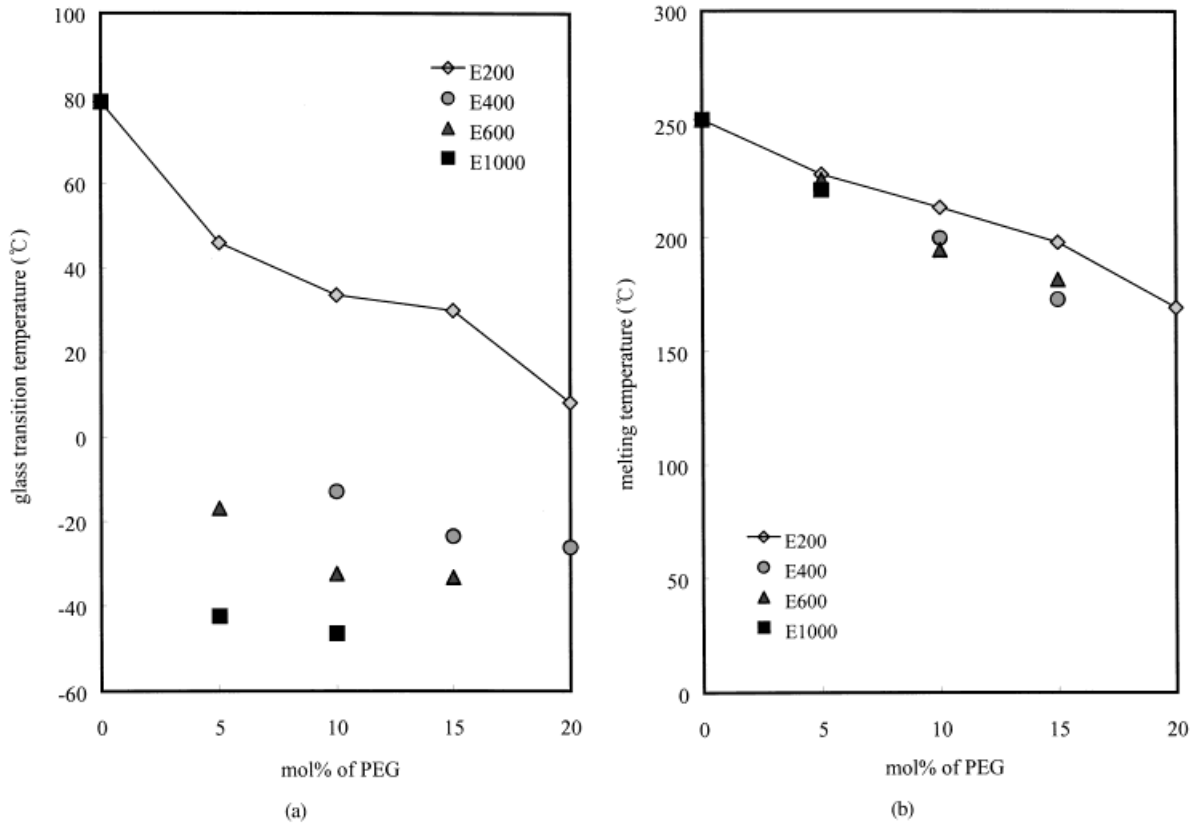

Figure 3 (a) T_g and (b) T_m of PET–PEG copolymers.
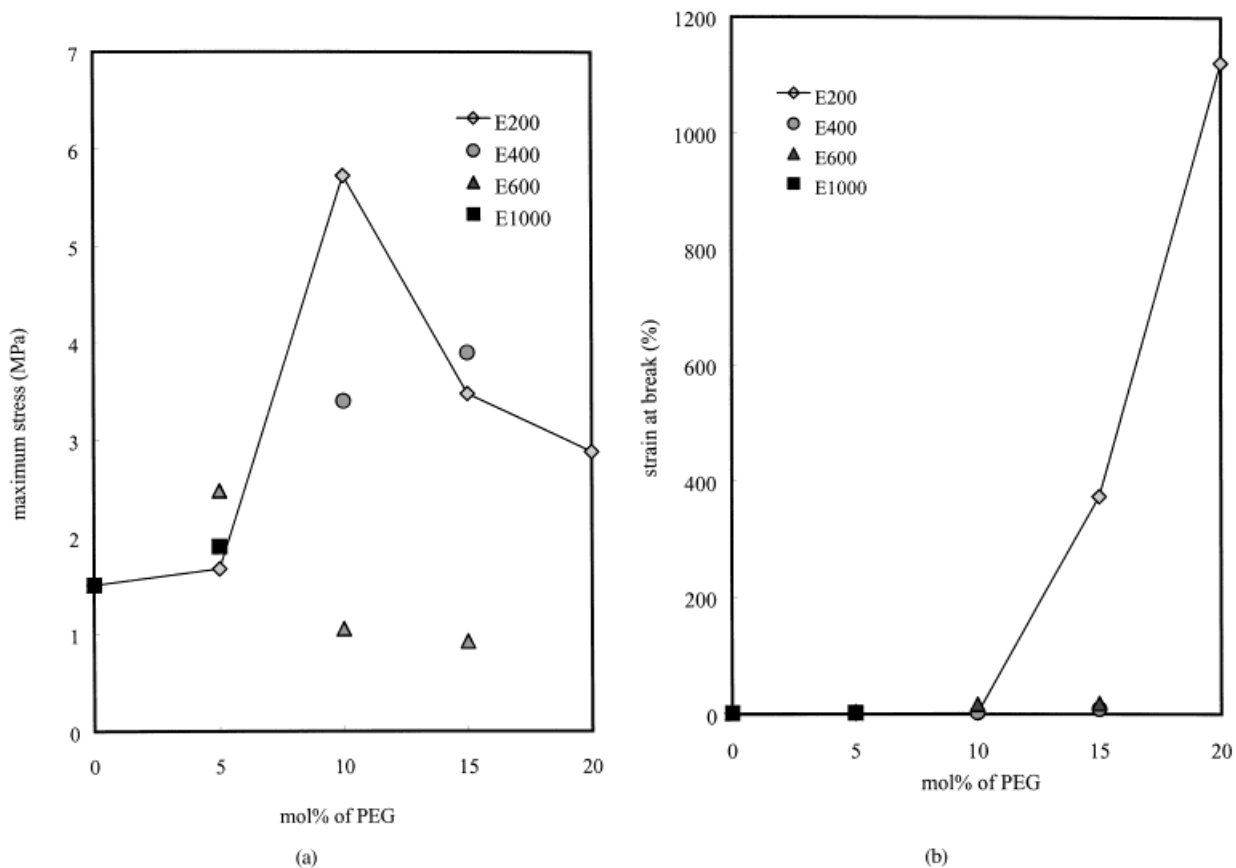
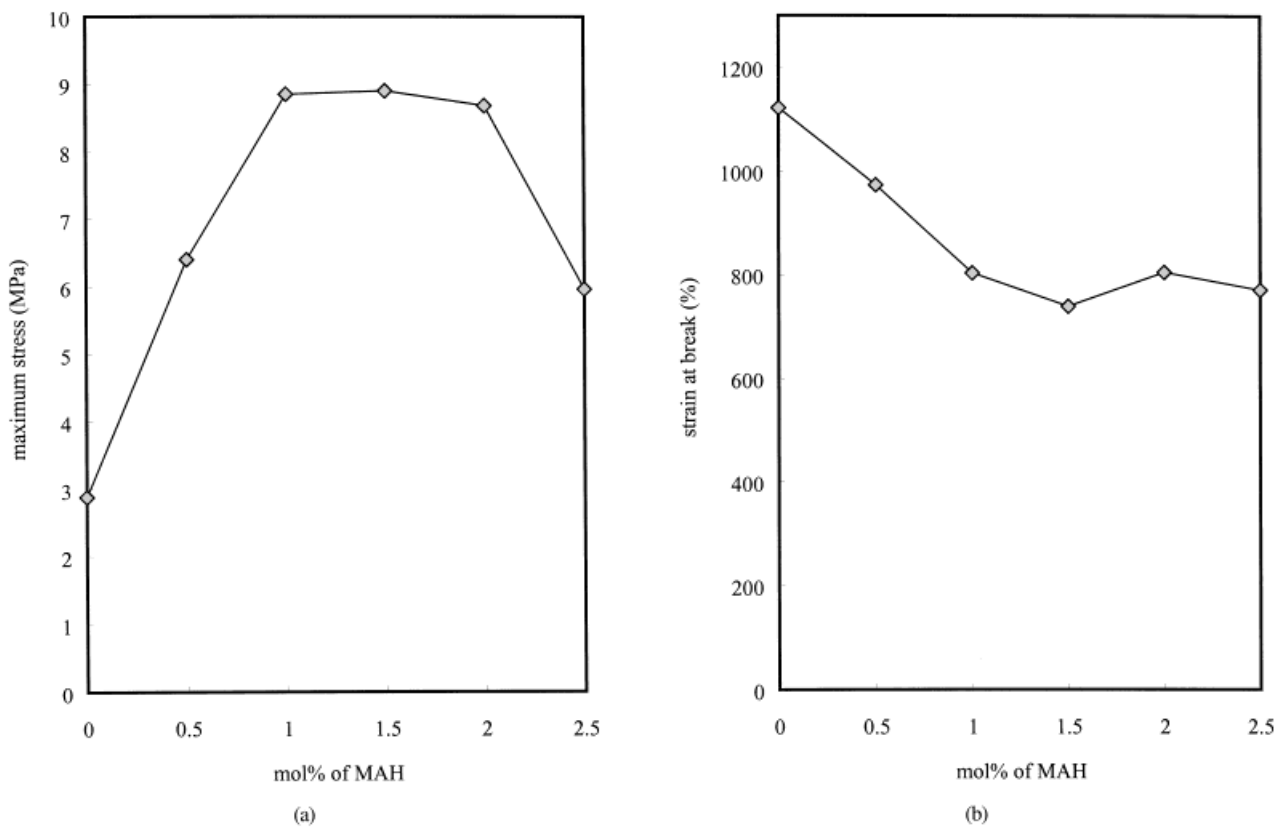**Figure 4** (a) Maximum stress and (b) strain at break of PET–PEG copolymers.

Figure 5 (a) Maximum stress and (b) strain at break of PET–PEG–MAH copolymers
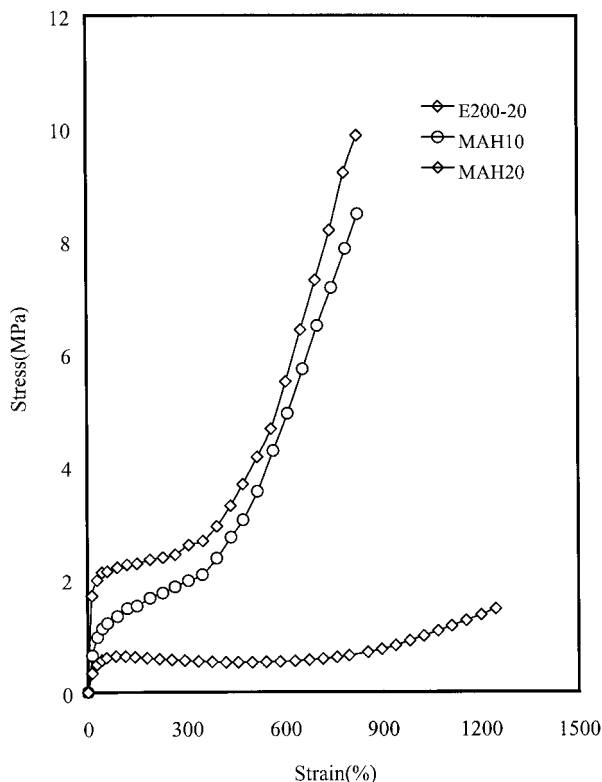
Figure 6 Representative stress–strain curves of PET–PEG–MAH copolymers.

maximum stress started decreasing. As the MW of PEG increased, the maximum stress generally decreased. As shown in Figure 4(b), strain at break showed a very slight increase for PET–PEG copolymers with a PEG MW of 400, 600, and 1000 g/mol. The strain at break of PEG (MW = 200 g/mol) gradually increased up to 10 mol % of PEG, and the increase was accelerated at more than 10 mol % of PEG, reaching over 1,000% at 20 mol % of PEG. The minimum percent strain at break needed for testing the shape-memory effect was 100%; only PET–PEG copolymers with 15–20 mol % of PEG (MW = 200 g/mol) could satisfy these requirements.

Figure 5 shows the maximum stress and percent strain at break of PET–PEG and PET–PEG–MAH copolymers. Maximum stress showed a sudden increase from about 3 MPa of no MAH to 8.8 MPa at 1.5 mol % of MAH and a decrease to about 6 MPa of 2.5 mol % of MAH. All of PET–PEG–MAH copolymers showed higher maximum stresses than PET–PEG copolymers, which was due to more resistance to deformation by the crosslinks within polymer chains. Percent strain at break decreased from 1100% to around 750% as more MAH was introduced, with an initial
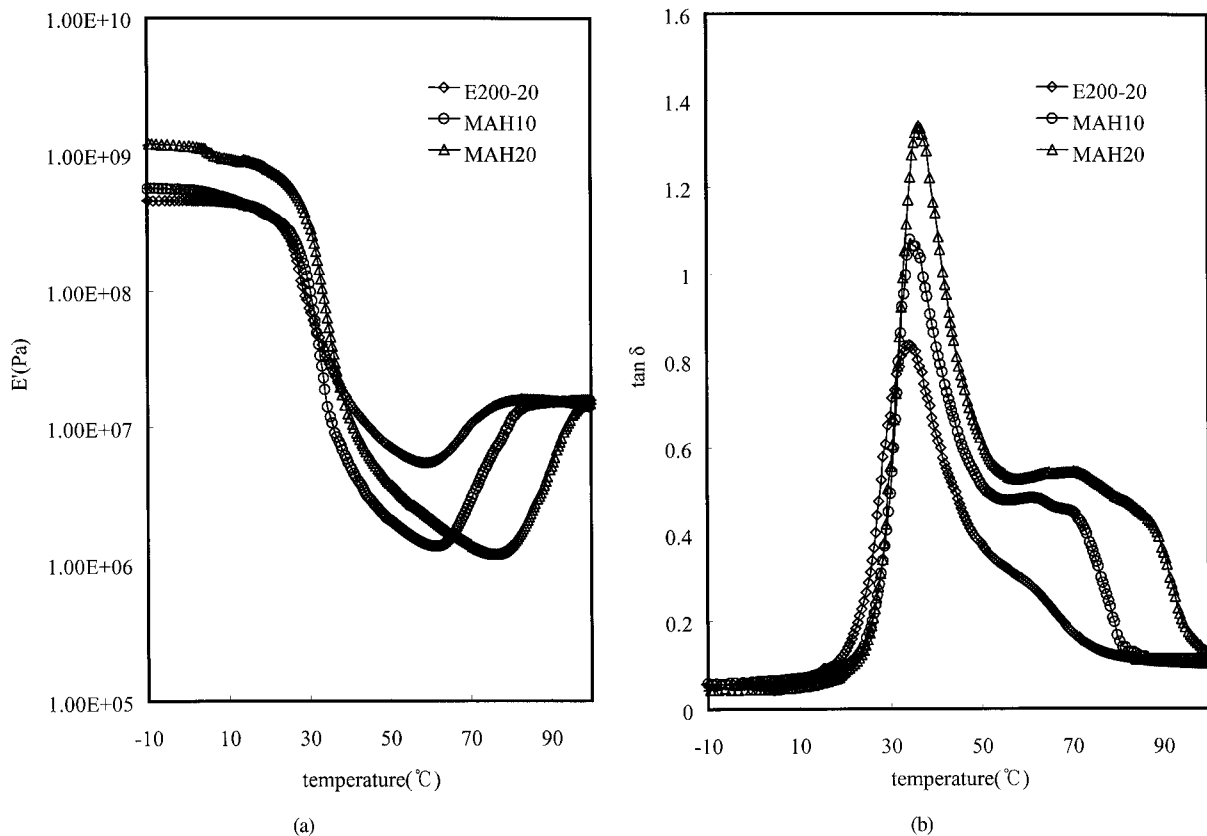

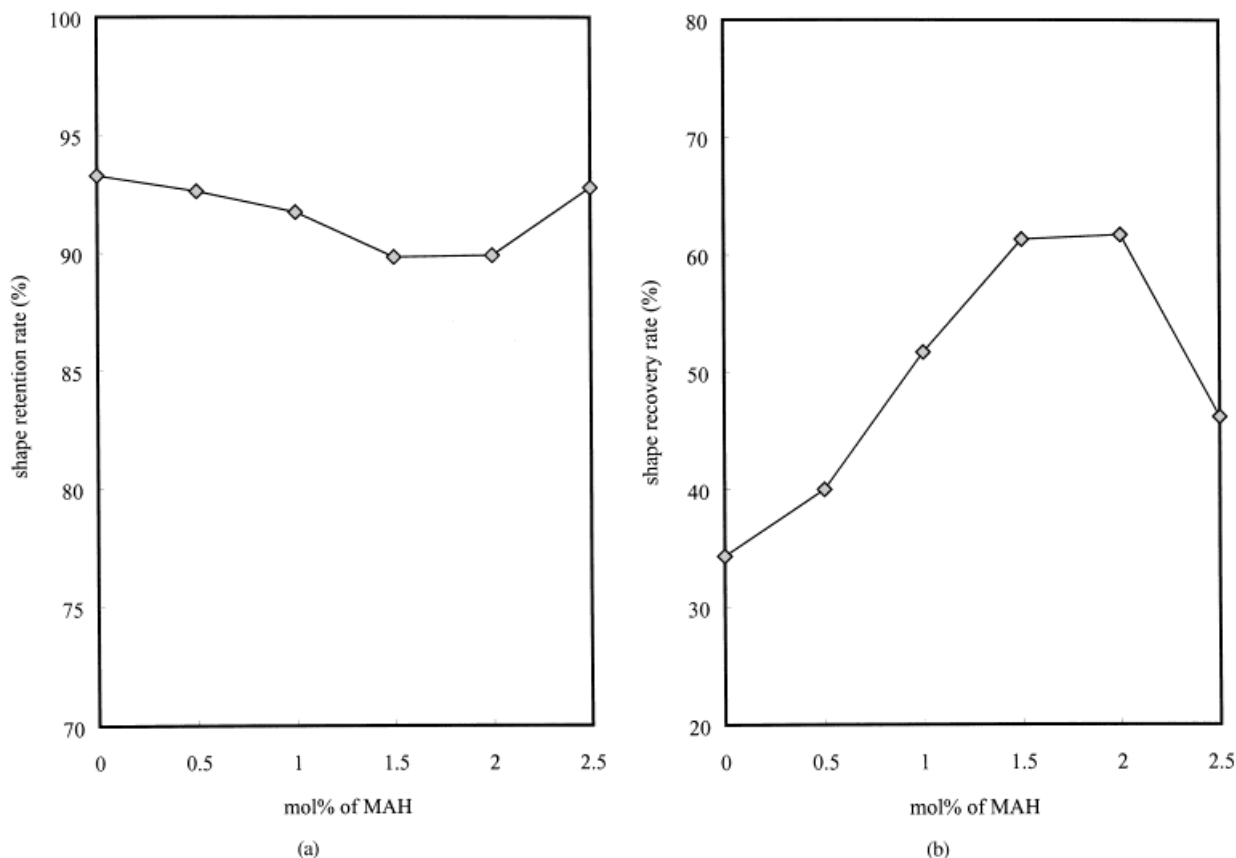**Figure 7**   (a) E′ and (b) loss tangent of PET–PEG–MAH copolymers.

Figure 8 (a) Shape retention rate and (b) shape recovery rate of PET–PEG–MAH copolymers.

drop up to 1.5 mol % of MAH and a plateau region after that [Fig. 5(b)]. This was not unexpected because the added MAH increased the number of crosslinks in the polymer chains, thus reducing the extension of chains.

Figure 6 shows the representative stress–strain curves of PET–PEG–MAH copolymers. As shown in this figure, as the amount of MAH increased, the modulus of elasticity and maximum stress increased. As the MAH agent increased, because of the increased physical crosslink points, it became more brittle and resulted in a lower strain at break. Also, with the increased hard domain, it showed a higher yield stress and lower yield strain.

Dynamic Mechanical Thermal Properties

Figure 7 shows the storage modulus (E′) and loss tan δ of the PET–PEG copolymer with a PEG MW of 200 g/mol along with PET–PEG–MAH copolymers with 1.0 and 2.0 mol % of MAH. All specimens exhibited 2 or 3 orders of decrease in E′ with respect to T_g. E′ below T_g increased as MAH

was introduced to the PET–PEG copolymer, which resulted from reduced chain mobility caused by more crosslinking. If the PET–PEG copolymer was deformed in the rubbery plateau region and cooled back to the temperature below T_g, the deformed shape was maintained. However, if we warmed this specimen to the rubbery plateau region, the original shape was recovered. The fact that the modulus drop at the T_g was about 10–1000,[9] and the E′ drop width (transition width) was narrower for the PET–PEG–MAH copolymers compared to the PET–PEG copolymer suggests possible application as a temperature-sensitive material.

As shown in Figure 7(b), a higher tan δ was observed as more MAH was introduced, and a shift to higher temperature followed as more MAH was introduced. Because better shape recovery could be achieved with a higher tan δ so that the polymers could deform like an elastomer, PET–PEG–MAH copolymers could acquire higher shape recovery rates. The width of the rubbery plateau region above T_g widened with more MAH,

which worked as a chain extender or crosslinking agent, and the result was in accordance with the [η] data of PET–PEG–MAH copolymers (Table II).

Figure 7(a) also shows the increase of E′ in the temperature range above 60°C. It was ascribed to the recrystallization of the PET–PEG copolymer during the measurement, as a similar behavior has been reported in polyesters such as poly(trimethyl terephthalate).[10] In the case of the PET–PEG–MAH copolymers, a larger increase in E′ was observed, and it resulted from the polymer crystallization of the amorphous region subjected to the restriction in chain segments due to the crosslinking of MAH.[11,12] The same phenomenon appeared above 60°C in the loss tangent curve as shown in Figure 7(b). The small relaxational shoulder of the PET–PEG copolymer was seen in that temperature range due to the polymer crystallization, whereas PET–PEG–MAH copolymers represented the double-peak pattern because of the crosslinking of MAH and recrystallization of PET–PEG copolymer. Particularly, the peak intensity of the loss tangent increased relatively as the MAH concentration increased. This indicates that the presence of crosslinked MAH had a large influence on the relaxation of the molecular motions. Such a characteristic may lead to a more superior shape-memory effect in the specimens crosslinked with more MAH content.

Shape-Memory Effect

As shown in Figure 8(a), PET–PEG–MAH copolymers generally exhibited slightly lower shape retention than the PET–PEG copolymer, and all specimens showed shape retentions of more than 90%, which is an exciting result. The overall tendency was a decrease in shape retention with MAH addition, but shape retention increased again at more than 2.0 mol % of MAH. Figure 8(b) shows the shape recovery rate; the maximum shape recovery rate was obtained at 1.5–2.0 mol % of MAH, which was caused by the influence of crosslinks formed by the MAH on the recovery of the soft segment. Physical crosslinking by PET and chemical crosslinking by MAH could be considered as the hard segment. The hard segment was dispersed evenly within the matrix as crosslink points, and this resulted in an improvement of shape-memory effect in PET–PEG–MAH copolymers. This behavior is demonstrated in Figure 9, which shows the shape recovery rate of PET–PEG–MAH specimens after three cycles of shape-memory tests. The lowest reduction in
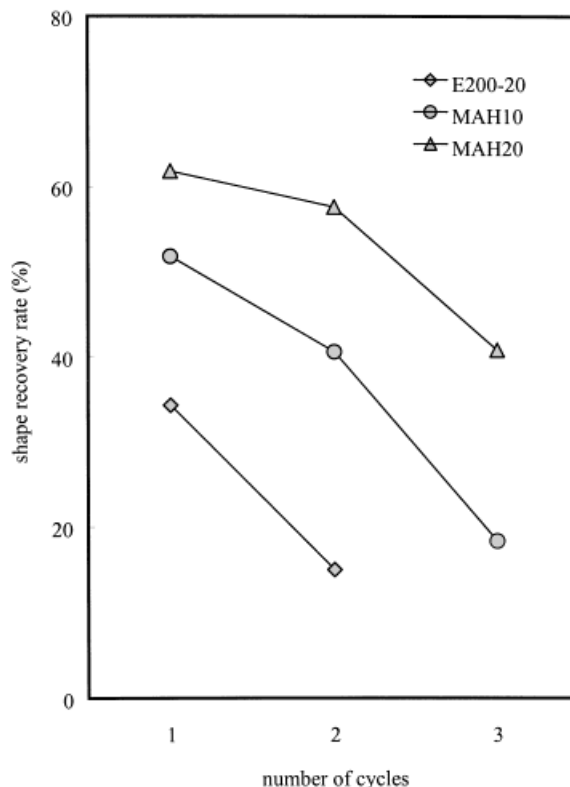

Figure 9 Shape recovery rate of PET–PEG–MAH copolymers after three cycles of the shape-memory test.

shape recovery rate was observed for the PET–PEG–MAH copolymer with 2 mol % of MAH, which was due to the increased resistance against the plastic deformation of the chain segment along the stress direction by chemical crosslinking through MAH. This result agrees with the results show in Figure 7(b); PET–PEG copolymer, shown in Figure 7(b), had the lowest tan δ, and it fractured after only two cycles of shape-memory tests due to the severe plastic deformation of chains along the stress direction, as shown in Figure 9. The PET–PEG–MAH copolymer with 2.0 mol % of MAH showed the best shape recovery rate, and the result shows that hard segment and crosslinking formed by MAH could be good crosslink points for the soft segment.

CONCLUSIONS

PET–PEG copolymers consisting of PEG soft segment and PET hard segment were synthesized along with PET–PEG copolymers crosslinked by MAH. Experimental results show that highest tensile properties were obtained in the case of PET–PEG copolymer with the molar ratio of 80

mol % of EG and 20 mol % of PEG (MW = 200 g/mol). The addition of MAH to crosslink the PET–PEG copolymer resulted in a decrease in strain at break and an increase in maximum stress. In addition, crosslinking improved the even distribution of the hard domain, shape-memory effect, and damping. As a conclusion, the best shape retention and shape recovery were obtained from PET–PEG–MAH copolymers with PEG (MW = 200 g/mol) and 1.5–2.0 mol % of MAH.

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