

Effect of Glucose Crosslinking on Thermomechanical Properties and Shape Memory Effect of PET-PEG Copolymers

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Received 10 December 2007; accepted 26 February 2008

DOI 10.1002/app.28489

Published online 2 June 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Poly(ethylene terephthalate) (PET) and poly(ethylene glycol) (PEG) copolymers crosslinked with glucose as a crosslinker are prepared to improve their mechanical and shape memory properties compared to the one without crosslinking. Composition of PEG and glucose is varied to search for the one with the best mechanical and shape memory properties. The highest shape recovery rate is found in the copolymer composed of 25 mol % PEG-200 and 2.0 mol % glucose. The result that crosslink-

ing by glucose improves the shape recovery rate and supports the high shape recovery rate under the repetitive cyclic test conditions, compared to the one without crosslinking, will be discussed in the points of the structure and shape memory mechanism. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3533–3539, 2008

Key words: shape memory; crosslinking; shape recovery; shape retention; copolymer

INTRODUCTION

It is the special features of shape memory material to detect thermal, mechanical, electrical, or magnetic stimulus, and to respond by changing its shape, location, modulus, damping, and abrasion, in addition to the reproducible shape recovery to original shape after distortion.^{1–3} Because of the advantages such as lightness, high shape recovery rate, easy processing, and high damping, compared to other materials, shape memory polymer (SMP) is used in the development of composite laminate with vibration control.^{4–7} SMP generally has a phase-separated structure in which hard and soft domain is formed due to the difference in intermolecular attraction between hard and soft segments. Interactions such as hydrogen bonding and dipole–dipole interaction bind hard segments to form hard domain, and the hard domain plays an important role in shape recovery mechanism. The soft segment absorbs an external stress by stretching and shrinking along the chain, and keeps the polymer chain resilient even at low temperature. In this study, poly(ethyleneterephthalate) (PET)/polyethyleneglycol (PEG) copolymer is crosslinked with glucose, a multi-way crosslinker,

and the effect of many crosslinking points, compared to other crosslinking agents, on mechanical and shape memory properties is investigated.

EXPERIMENTAL

Materials

Dimethylterephthalate (DMT) and PEG were obtained from Aldrich chemical (Milwaukee, WI). Ethyleneglycol (EG) was from Duksan Chemical (Korea). Calcium acetate and antimony oxide (Hayashi Pure Chemical, Japan) were used as the catalyst for esterification, and phosphorous acid (Kanto Chemical, Japan) was added as a stabilizer.

Preparation of crosslinked copolymer

PET-PEG copolymer was synthesized by melt-condensation method with a custom-made reactor.^{3,8,9} Polymerization was carried out in two steps; oligomer was prepared in the first step with DMT, EG, and PEG-200, and the oligomer from the first step was condensed and crosslinked with glucose in the second step at 250°C and vacuum to shift reaction equilibrium further to product. Detailed synthetic procedure for PET-PEG copolymer can be found in our previous papers.^{3,8,9} Synthetic scheme and characterization of copolymers are shown in the results and discussion section.

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Contract grant sponsor: MOST/KOSEF; contract grant numbers: R11-2005-065, R01-2007-000-20385-0.

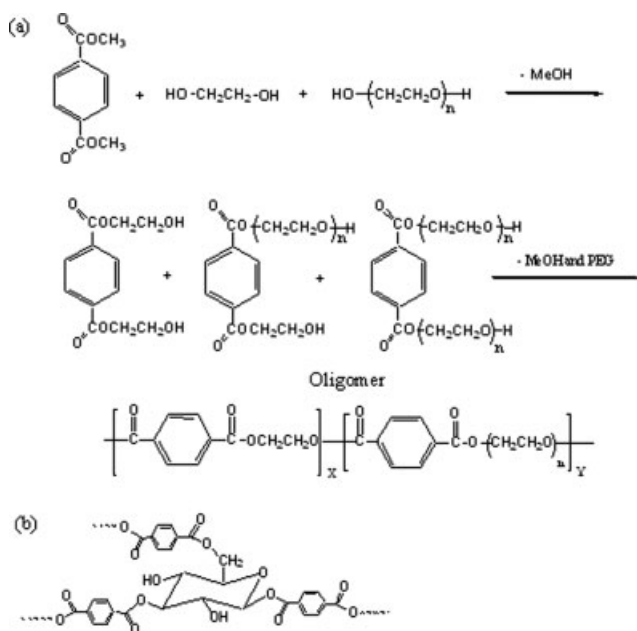


Figure 1 (a) Synthetic scheme, and (b) the proposed glucose crosslinked structure.

General analysis

NMR spectra of the copolymer dissolved in CD₃OD were obtained by a 600-MHz Bruker FT-NMR (Avance 600) at the National Instrument Center for Environmental Management, Seoul National University, Korea. FTIR spectra were taken by a Bomem MB series FTIR spectrophotometer. X-ray diffraction pattern was recorded by a wide-angle X-ray diffractometer (Rigaku) under the conditions of $2\theta = 10^\circ\text{--}30^\circ$, Cu K α , 40 kV, and 30 mA. Intrinsic viscosity $[\eta]$ of the copolymer dissolved in 1,1,2,2-tetrachloroethane/phenol (4/6, w/w) mixture was measured by a Ubbelohde viscometer at 35°C and 0.5 g/dL of concentration.

Thermal analysis

Glass transition temperature (T_g) and melting temperature (T_m) were measured by a differential scanning calorimeter (DSC, Perkin-Elmer Diamond 6). The specimen was heated to 200°C at 10°C/min of heating rate, kept at that temperature for 3 min, and then cooled to -30°C at -10°C/min. T_g and T_m were determined from the second heating scan. Dynamic mechanical property was measured by a dynamic mechanical analyzer (DMA-2980, TA instrument), where storage modulus and loss tangent ($\tan \delta$) were scanned between -20 and 110°C at the heating rate of 3°C/min, and 1 Hz.

Mechanical properties and shape memory analysis

Tensile test was performed by a universal testing machine (UTM, Lloyd LR 50 K) using a dumbbell-type specimen prepared according to ASTM D-638 at

a crosshead speed of 100 mm/min. Shape memory effect was also checked by the tensile test using UTM equipped with a temperature-controlled thermal cabinet. For the measurement of shape retention rate, a specimen with a length L_0 was strained to 100% at above T_g but below T_m , and kept at that temperature for 1 min. The specimen under strain was cooled to below T_g , and left at the temperature for 30 min after the removal of load, followed by the measurement of deformed length (L_1). For the measurement of shape recovery, the specimen was heated again to a temperature above T_g but below T_m with 10-min stay, cooled back to a temperature below T_g , staying at this temperature for 30 min, and the final length (L_2) of specimen was measured (Fig. 2). The whole procedure was repeated three times consecutively. Shape retention and shape recovery rates can be calculated by the following equation.^{3,8-10}

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

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

RESULTS AND DISCUSSION

Synthesis of the copolymer

Synthesis of the copolymer and the proposed crosslinked structure is shown in Figure 1 in which an oligomer made in the first step from the mixture of DMT, EG, and PEG is further polymerized in the second step. In Figure 3, the proton NMR spectra of PET copolymer show that chemical shifts of PEG (3.5–4.0 ppm) and EG (4.4–4.7 ppm) appear as expected, and the proton peaks belonging to glucose are buried in the PEG peaks [compare Fig. 3(a,b)]. The peak at 1.57 ppm is coming from the trace amount of methanol in CD₃OD solvent. FT-IR spectrum, although not shown, shows the complete disappearance of the -OH stretching at 3300 cm⁻¹ which is found as a broad band in the free EG and PEG. Judging from the NMR and FTIR data, the copolymerization is completed as expected.

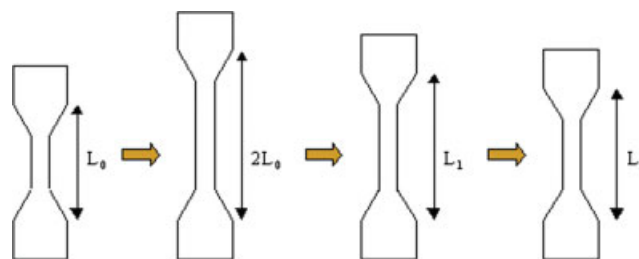


Figure 2 Shape retention and recovery test, where L_0 = initial specimen length, $2L_0$ = length of L_0 strained 100% at above T_m , L_1 = deformed length at below T_m after load removal, and L_2 = final specimen length at above T_m . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

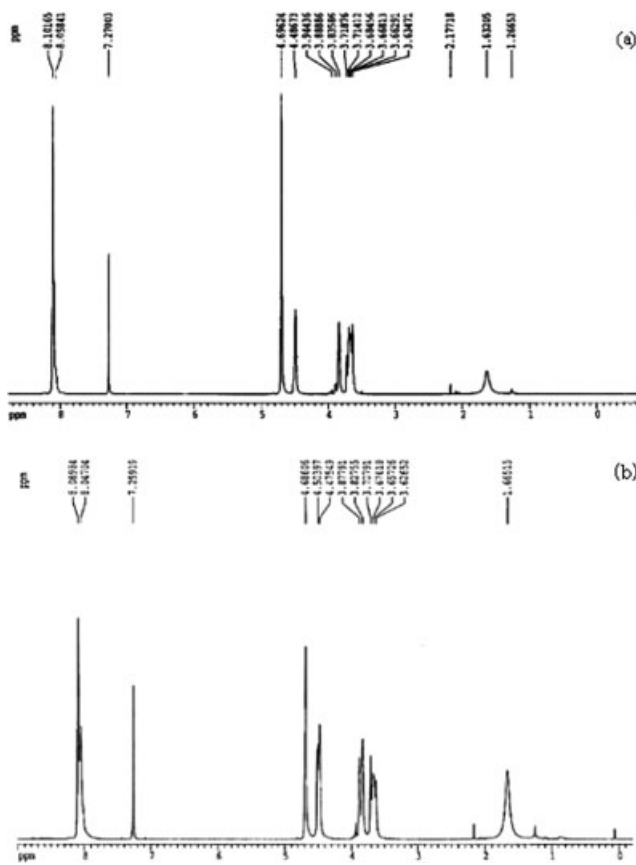


Figure 3 NMR spectra of (a) PET copolymer without glucose crosslinking, and (b) PET copolymer crosslinked with glucose.

Thermal analysis and XRD spectra

T_g of copolymers with a different PEG chain length and PEG-200 content is compared in Table I. All of the copolymers in Table I contain 2.5 mol % glucose. Copolymers with PEG-400 or PEG-600 have too low T_g value to be used as a SMP, because T_g around room temperature is necessary for practical application, based on the results from the previous experiments.^{3,8-10} Therefore, PEG-200 is selected and PEG-200 content is changed from 15 to 40 mol % to search for the right T_g range. E200-15 and E200-20 are set aside as the SMP candidate, because E200-15

fails during tensile test and E200-20 shows a strain at break a little lower than other candidates although T_g is close to room temperature. E200-40 is excluded due to the low T_g . Finally, E200-25 is selected over E200-30 as the SMP candidate, because it has better maximum stress and strain at break, and the T_g is close to room temperature. After selecting E200-25 as the right PEG-200 composition, glucose content is varied from 0.5 to 3.0 mol % (Table II). T_g increases with glucose content, starting from -6.13°C of E200-25-05 (0.5 mol % glucose) to 23.6°C of E200-25-30 (3.0 mol % glucose) (Fig. 4). E200-25-0 (without glucose) and E200-25-5 (0.5 mol % glucose) are not appropriate for SMP because T_g is below 0°C . E200-25-10 (1.0 mol % glucose) and E200-25-15 (1.5 mol % glucose) also show very low T_g as a SMP. E200-25-30 (3.0 mol % glucose) has T_g around room temperature (23.6°C), but the strain at break is very low. E200-25-20 (2.0 mol % glucose) and E200-25-25 (2.5 mol % glucose), although both show a little low T_g , are selected for the shape memory test, because both have enough strain for shape memory test. Glucose content is not raised more than 3.0 mol % due to the hardening of copolymer. The fact that glucose raises T_g and decreases strain suggests that a compromise between T_g and strain should be made in deciding the SMP candidate. T_m of E200-25 series also increases with glucose content, and T_m of E200-25-20 and E200-25-25 stays around 170°C (Fig. 5). T_g of E200-25-25 decreases by about 8°C compared with the similar PET-PEG copolymer crosslinked with 2.5 mol % glycerol (T_g of 23.7°C).⁹ XRD spectra of E200-25 series were compared at the temperatures below T_g and above T_g . The E200-25-0, one without glucose, does not show any peaks at -30°C , but the peaks around $2\theta = 20^\circ$ appear at 25 and 60°C [Fig. 6(a)]. It seems that the hard segment domain, one showing the diffraction peaks, is formed well at high temperature, but a restricted rotation of polymer chains at low temperature prohibits the alignment of hard segment. As the glucose content increases to 0.5 mol % (E200-25-5), the diffraction peaks at -30°C appear and the peaks at higher temperature show a higher intensity [Fig. 6(b)]. The copolymer with

TABLE I
Physical Properties of the PET-PEG Copolymers Crosslinked by 2.5 mol % Glucose

Sample code	PEG (mol %) ^a	Max. stress (MPa)	Strain at break (%)	T_g ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	$[\eta]$ dL/g
E400-20	20	–	–	–20.4	141.0	0.43
E600-20	20	–	–	–29.5	136.9	0.41
E200-15	15	24.9	–	42.3	203.5	0.52
E200-20	20	16.8	196	26.1	178.1	0.54
E200-25	25	3.38	360	15.2	157.2	0.51
E200-30	30	1.73	293	11.2	141.8	0.44
E200-40	40	0.984	561	–10.3	142.9	0.49

^a MW of PEG (200, 400, or 600) is denoted in sample code. The 2.5 mol % glucose is included for all of the copolymers.

TABLE II
Physical Properties of the E200-25 PET-PEG Copolymers Crosslinked by Variable Content of Glucose

Sample code	Glucose content (mol %)	Max. stress (MPa)	Strain at break (%)	T_g (°C)	T_m (°C)	$[\eta]$, dL/g
E200-25-0	0	0.736	3000	-23.3	156.3	0.61
E200-25-05	0.5	0.185	1850	-6.13	156.2	0.59
E200-25-10	1.0	0.695	745	9.4	156.9	0.47
E200-25-15	1.5	2.76	530	13.5	166.7	0.37
E200-25-20	2.0	3.00	330	17.34	167.8	0.45
E200-25-25	2.5	3.38	360	15.2	177.2	0.51
E200-25-30	3.0	12.7	28	23.6	181.0	0.44

1.0 mol % glucose (E200-25-10) shows very high peak intensity compared to the one with 0.5 mol % glucose at both temperatures (-30 and 60°C) [Fig. 6(c)]. In the case of the copolymer with 2.0 mol % glucose (E200-25-20), peaks with the highest intensity for both temperatures (-30 and 60°C) are observed [Fig. 6(d)]. It is found from the XRD spectra that glucose, as a crosslinker, induces the hard segment domain formation even at the temperature below T_g .

Tensile property

Tensile mechanical properties of the crosslinked copolymers (2.5 mol % glucose) with PEG 200, 400, or 600 are compared in Table I. The copolymer with PEG-400 or 600 easily breaks down during tensile test, but the copolymer with PEG-200 shows the high stress and strain results. As PEG content is raised, strain at break increases from 196% (20 mol % PEG) to 561% (40 mol % PEG). Instead, maximum stress decreases with the increase of PEG content: maximum stress decreases from 16.8 MPa (20 mol % PEG) to 0.984 MPa (40 mol % PEG). As mentioned in thermal analysis section, E200-25 is selected and glucose content is varied at 25 mol % of PEG-200. Maximum stress gradually increases with the

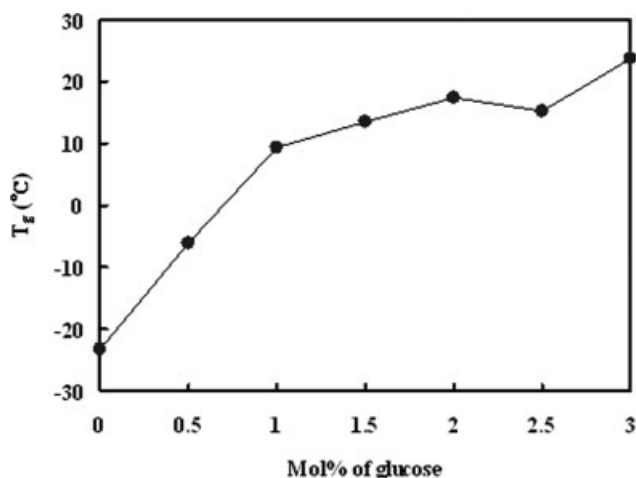


Figure 4 Glass transition temperature versus glucose content profile.

increase of glucose content and reaches the highest one at 3.0 mol % (Fig. 7). Strain at break decreases with the increase of glucose content, showing 1850% at 0.5 mol % glucose and 360% at 2.5 mol % glucose (Fig. 8). However, the strain at break result has improved significantly compared with 48% of the glycerol crosslinked PET-PEG copolymer (2.5 mol % glycerol).⁹ The dependence of mechanical properties on the temperature and glucose content is investigated in the stress-strain curve (Fig. 9). It is obvious from the Figure 9 that the stress improved with glucose content for all of the three temperatures (-30, 25, and 60°C) and was, if compared at the same glucose content, better at higher temperature. Instead, strain was reduced with the increase of glucose and was better, at the same glucose content, at lower temperature. The reason for the above result can be traced to the fact that the increased crosslinking at high glucose content improves the stress but reduces the strain, and the solid hard domain formation at higher temperature, as shown in the XRD spectra, results in high stress and low strain.

Dynamic mechanical property

Storage modulus and $\tan \delta$ of the copolymers are compared in Figures 10 and 11, respectively. In

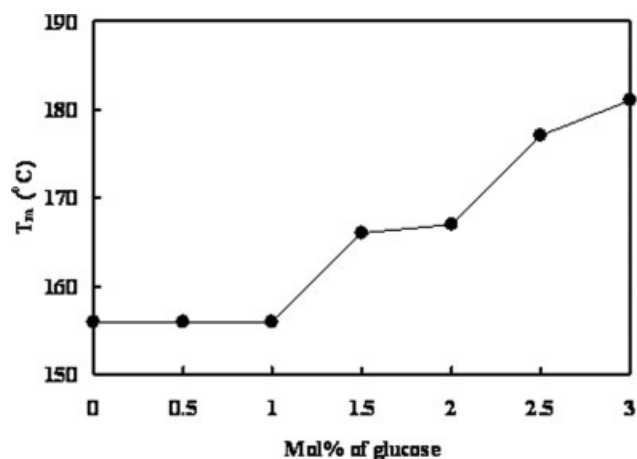


Figure 5 Melting temperature versus glucose content profile.

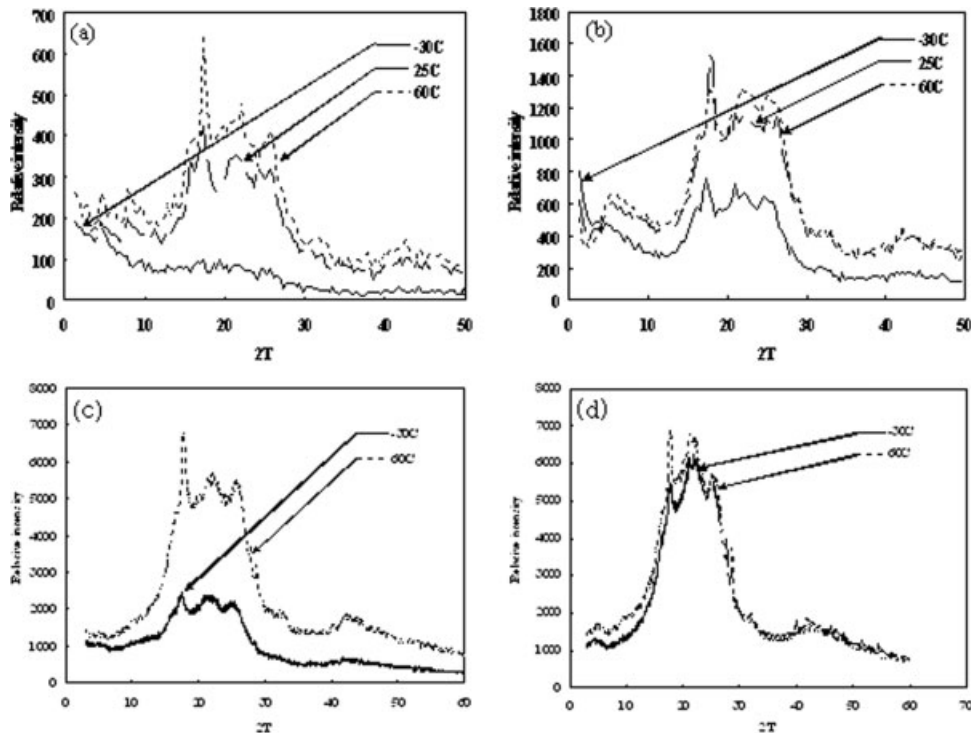


Figure 6 XRD spectra of the copolymer with (a) 0 mol % glucose (-30 , 25 , and 60°C), (b) 0.5 mol % glucose (-30 , 25 , and 60°C), (c) 1.0 mol % glucose (-30 and 60°C), and (d) 2.0 mol % glucose (-30 and 60°C) at various temperatures.

Figure 10, storage modulus of E200-25-20 and E200-25-25 is in high contrast with other E200-25 series; the peak storage modulus of E200-25-20 and E200-30-25 is more than three times higher than other E200-25 series. The high crosslinking content of E200-25-20 and E200-25-25 increases storage modulus below glass transition temperature. In Figure 11, $\tan \delta$ changes around glass transition temperature for all of the E200-25 series copolymers, and the temperature at the peak $\tan \delta$, due to the increased crosslinking content, shifts to a higher temperature as the glucose content increases. Because $\tan \delta$ indi-

cates damping ability, the E200-25 series copolymers can be useful as a candidate for vibration-control material.

Shape memory effect

Shape retention rate of the copolymers generally maintains above 85% of the original shape, but the shape recovery rate is dependent on glucose content. In Figure 12, shape memory rate does not decrease much after three cyclic shape memory tests and the highest shape memory rate is observed at 2.0 mol %

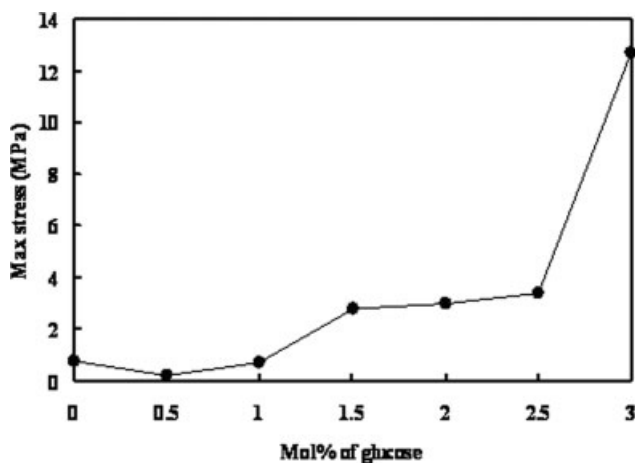


Figure 7 Maximum stress versus glucose content profile.

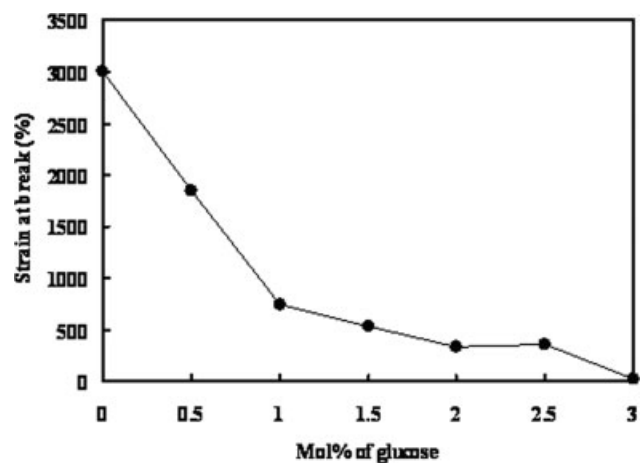


Figure 8 Strain at break versus glucose content profile.

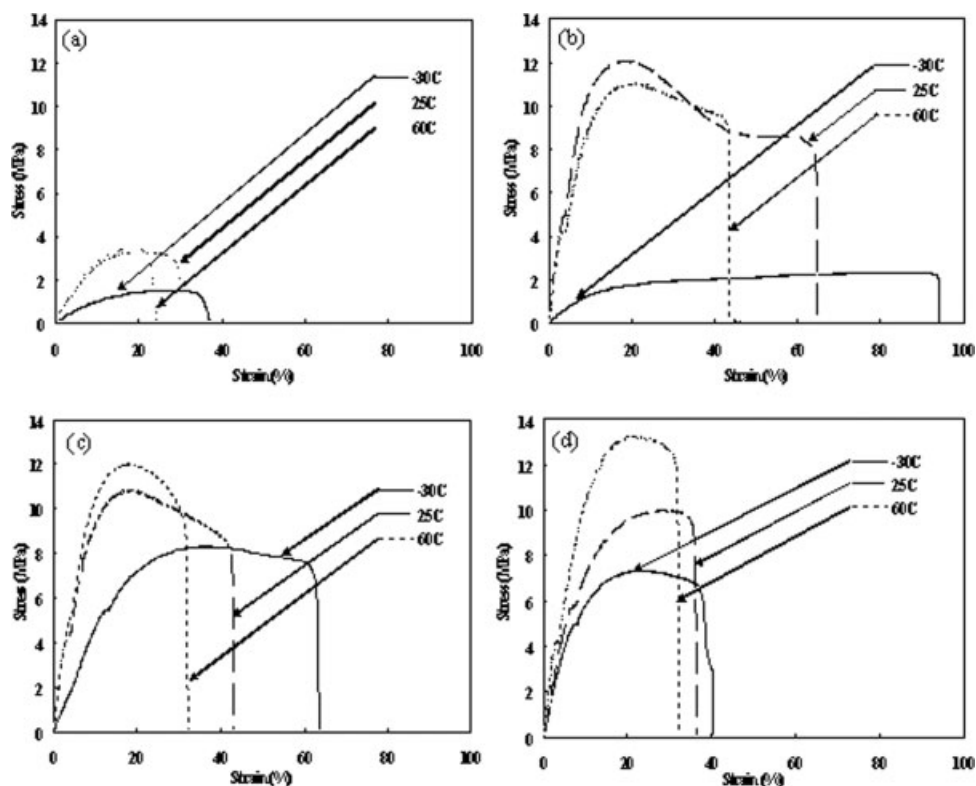


Figure 9 Stress-strain curve of the copolymer with (a) 0 mol % glucose, (b) 0.5 mol % glucose, (c) 1.0 mol % glucose, and (d) 2.0 mol % glucose.

glucose. Shape recovery rate of E200-25-20 is 90% at the first cyclic test and decreases to 67% (second cycle) and 63% (third cycle). The decrease of shape recovery rate is due to the distortion of hard segment interaction after repeated stretch and shrinkage during shape memory test. Previously, we reported the shape recovery rate of PET copolymer cross-linked by glycerol.⁹ Shape recovery rate of the copolymer crosslinked by glycerol, in the best case,

is 85% at the first cycle, 82% at the second cycle, and immeasurable after the third cycle due to break down of the copolymer. Comparing the two types of crosslinked copolymers, E200-25-20 improves the shape recovery rate in the first cycle, and survives the three test cycles. Extra crosslinking site of glucose compared to glycerol is responsible for the higher shape recovery rate. Although the shape recovery rate is satisfactory as a preliminary study, it should stay above 90% after the third cycle to be

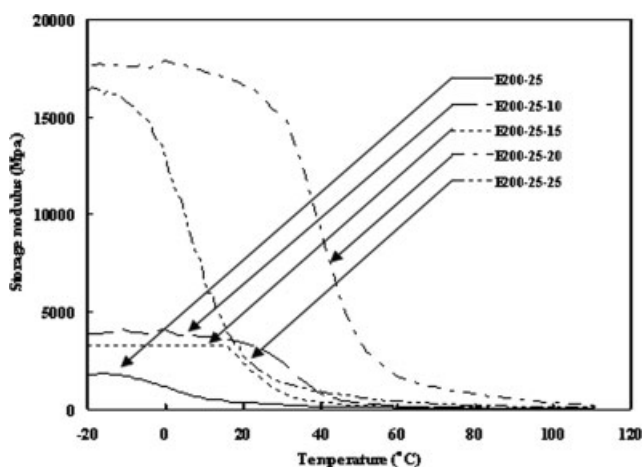


Figure 10 Storage modulus versus glucose content profile.

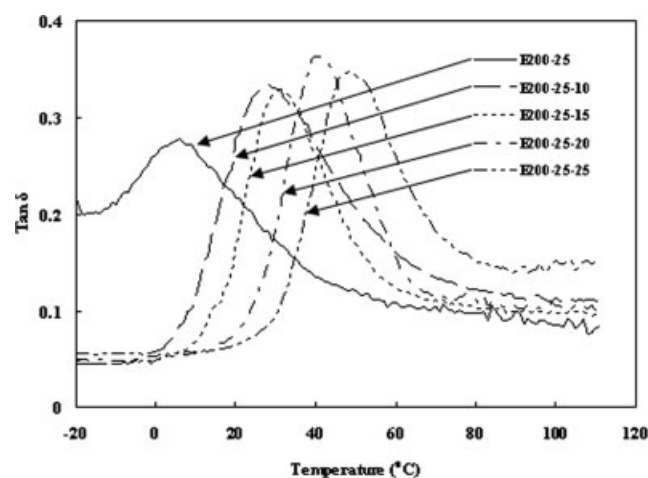


Figure 11 Loss tangent versus glucose content profile.

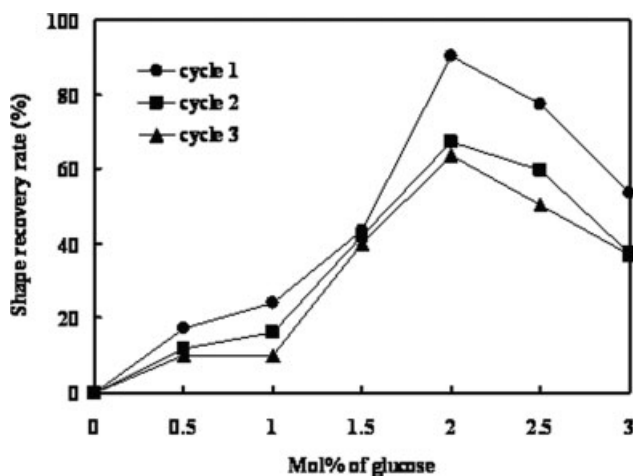


Figure 12 Comparison of shape memory effect of PET copolymers.

useful as a structural material and will be achieved in the next related research.

CONCLUSIONS

Shape memory PET-PEG copolymers crosslinked by glucose are prepared to test the crosslinker effect on shape memory and mechanical properties. PEG-200

is selected as a soft segment due to higher mechanical properties than PEG-400 and PEG-600 at the same crosslinker content (2.5 mol % glucose). Shape recovery rate of E200-25-20 goes up to 90% at the first cycle and decreases after the third cycle. The multi way crosslinking by glucose significantly improves shape recovery rate, compared to the three-way crosslinking glycerol, and extra crosslinking by glucose is responsible for the improvement.

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