

Shape Memory Effect of Poly(ethylene terephthalate) and Poly(ethylene glycol) Copolymer Cross-linked with Glycerol and Sulfoisophthalate Group and Its Application to Impact-Absorbing Composite Material

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ABSTRACT: Poly(ethylene terephthalate) (PET) and poly(ethylene glycol) (PEG) copolymers crosslinked with glycerol and sulfoisophthalate (SP) were prepared to investigate the feasibility of fabricating smart vibration-controlling composite laminate. The composition of glycerol and SP was varied to get a copolymer with the best mechanical and shape memory properties. The highest shape recovery was observed for the copolymer with 2.5 mol % of glycerol and 2.5 mol % of SP. With the high shape-recovery copolymer in hand, sandwich-type copolymer composites were made with epoxy beam laminate, and the copolymer composite, in

the best case, showed improved impact strength (3.5 times) and damping effect (2.6 times) compared to epoxy laminate beam alone. The sandwich-type epoxy composite, together with the advantage of control of glass transition temperature by PET, PEG, or the additives, can be applied to structural composite material requiring vibration control. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 308–316, 2004

Key words: shape memory; composite; crosslinking; vibration control

INTRODUCTION

Materials equipped with previously unknown exceptional functions are always sought, and examples include smart materials used in such areas as shape memory alloy, semiconductor, polymer, and medical supply. Ideally, shape memory material, in addition to shape memory, shape retention, and impact absorption, can detect thermal, mechanical, electrical, or magnetic stimulus and then respond via property changes in shape, location, modulus, damping, and abrasion.^{1–3} Shape memory polymer, being superior to other materials in the points of lightness, high shape recovery, easy processing, and high damping near its T_g , has drawn our attention and is applied to the manufacture of composite laminate with vibration control ability.^{4–7} Poly(ethyleneterephthalate) (PET)/polyethyleneglycol (PEG) copolymer is used as a matrix material, and glycerol and sulfoisophthalate groups were adopted as covalent and ionic crosslinking agents, respectively. The effect of two different

kinds of crosslinker on the mechanical, shape memory, and damping property of the copolymers was compared. Comprehensive mechanical properties of various sandwich-type composite laminates from the above copolymers are examined (Table I), and reasons for such high vibration control are briefly discussed.

EXPERIMENTAL

Materials

DMT, EG, and PEG-200 were commercially obtained. Glycerol (Duksan Chemical) and dimethyl 5-sulfoisophthalate sodium salt (Aldrich) were used as obtained. Epoxy laminate beam with 1.0-mm thickness was supplied by Korea Fiber Co. and used to prepare unidirectional glass-fiber-reinforced composite with 2.7-mm total thickness.

Preparation of cross-linked copolymer

PET/PEG copolymers were synthesized by melt-condensation method with a custommade reactor.^{8,9} Polymerization was carried out in two steps; the oligomer was prepared in the first step with DMT, EG, and PEG-200, and the oligomer made in the first step

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TABLE I
Physical Properties of Cross-linked PET/PEG Copolymers

Sample code	PEG-200 ^a (mol%)	Glycerol (mol%)	SP ^b (mol%)	Max. stress (N/mm ²)	Strain at break (%)	T_g (°C)
E20020	20	0	0	5.9	1122	11.2
G10	20	1.0	0	12.3	423	21.5
G10D05	20	1.0	0.5	11.4	456	24.3
G10D10	20	1.0	1.0	8.2	548	23.6
G10D15	20	1.0	1.5	5.5	623	18.3
G10D20	20	1.0	2.0	10.6	338	25.4
G10D25	20	1.0	2.5	13.7	283	27.7
G15	20	1.5	0	16.5	317	23.3
G15D05	20	1.5	0.5	15.4	324	25.1
G15D10	20	1.5	1.0	13.2	342	24.7
G15D15	20	1.5	1.5	10.4	369	22.4
G15D20	20	1.5	2.0	17.3	264	26.9
G15D25	20	1.5	2.5	18.1	241	28.4
G25	20	2.5	0	19.6	48	23.7
G25D05	20	2.5	0.5	19.8	46	24.4
G25D10	20	2.5	1.0	20.4	41	25.3
G25D15	20	2.5	1.5	21.6	37	26.9
G25D20	20	2.5	2.0	23.1	31	28.2
G25D25	20	2.5	2.5	23.8	29	30.7

^a The mol % of the copolymers is based on that of DMT and 80 mol % of EG is also included for all of the above combinations.

^b SP means the 5-sulfoisophthalate group.

was condensed and crosslinked with glycerol and dimethyl 5-sulfoisophthalate in the second step at high temperature and high vacuum to shift the reaction equilibrium further to the product. A detailed synthetic procedure for PET/PEG copolymer can be found in our previous paper.^{8,9} The synthetic scheme and characterization of copolymers are shown under Results and Discussion.

Intrinsic viscosity

Intrinsic viscosity $[\eta]$ of the copolymer dissolved in 1,1,2,2-tetrachloroethane/phenol (4/6, w/w) mixture was measured with an Ubbelohde viscometer at 35°C and 0.5 g/dL concentration.

Thermal analysis

T_g and T_m were measured by differential scanning calorimeter (DSC, Perkin-Elmer Diamond 6). The specimen was heated to 200°C at 10°C/min 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 at 10°C/min heating rate.

Spectroscopic analysis

NMR of the copolymer dissolved in CDCl₃/CD₃OD mixture or trifluoroacetic acid (TFA) for the crosslinked copolymer was scanned using a 600-MHz

Bruker FT-NMR (Avance 600) at the National Instrument Center for Environmental Management, Seoul National University. FT-IR spectra were taken using a Bomem MB Series 104.

Preparation of laminate beam

Copolymer was preheated at 60°C for 24 h to prevent any hydrolysis from moisture and compression-molded to a sheet with 1-mm thickness and 5-mm width at 30°C above its T_m . Sandwich-type laminate composite was prepared by compressing two 1.0-mm epoxy laminate beams and the above PET/PEG copolymer sheet in the middle layer at 210°C in a heating press.

Mechanical properties and shape memory analysis

Tensile test was performed using a universal testing machine (UTM, Lloyd LR 50K) 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 tensile test using the UTM equipped with a temperature-controlled thermal cabinet. For measurement of shape retention rate, specimen with a length L_0 was strained to 100% above T_g but below T_m and kept at that temperature for 1 min. The specimen under strain was cooled back to below T_g and left at that temperature for 30 min after removal of the load, followed by measurement of the deformed length. For measurement of shape recovery,

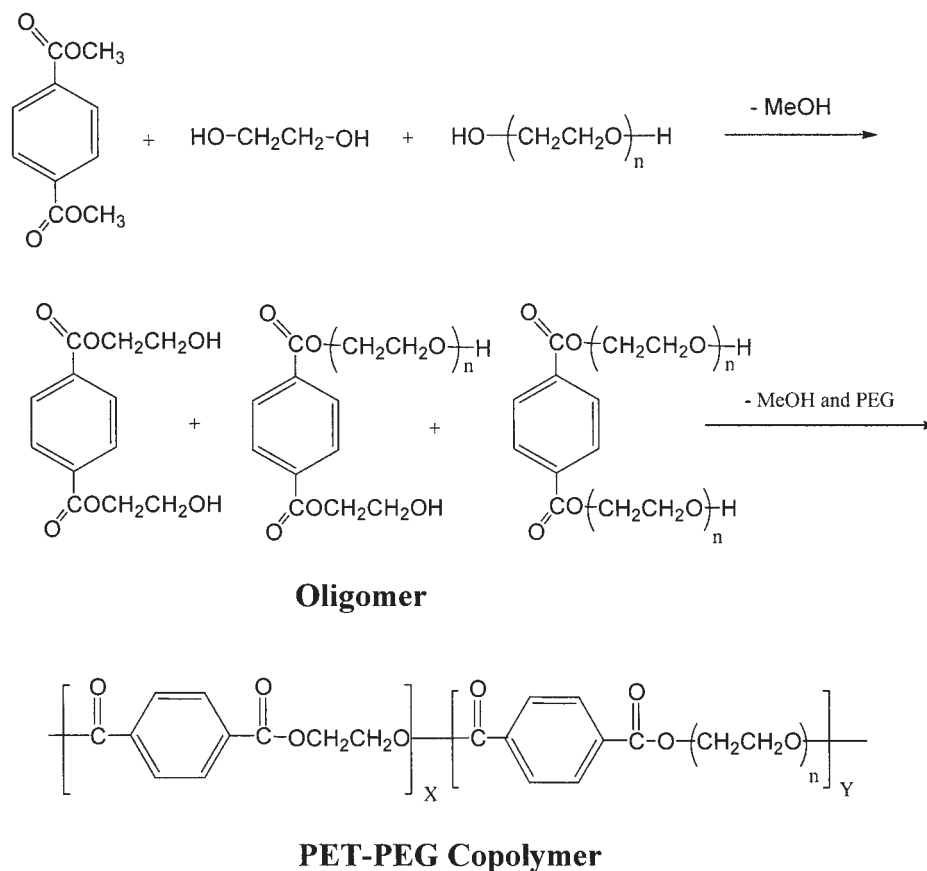


Figure 1 Synthetic scheme of PET/PEG copolymers.

the specimen was heated again to above T_g but below T_m with a 10-min stay and cooled back to below T_g and kept at this temperature for 30 min, and the final specimen was measured. The whole procedure was repeated three times consecutively. Calculation of shape retention and shape recovery rates can be found in our previous paper.^{8,9} As for dynamic mechanical property, a dynamic mechanical thermal analyzer (DMTA, Rheometric Scientific, Mark IV) was employed to test a sheet-type specimen with 1-mm thickness and 5-mm width at a heating rate of 3°C/min and 1.1 Hz. Unnotched Charpy impact strength was measured by impact tester (Testing Machines, Inc., Model 43-02, pendulum 75 kgcm, Charpy type) for composite laminate in 3-point bending mode, respectively.

RESULTS AND DISCUSSION

Spectroscopic analysis of the copolymer

It is clear from FT-IR analysis that the characteristic hydroxyl groups (3300 cm^{-1}) of PEG and EG disappeared after polymerization and, therefore, complete esterification was achieved. Proton NMR peaks of EG, PEG, and DMT were observed at 4.5–4.8, 3.5–3.8, and 8.0–8.2 ppm, respectively, and inclusion of glycerol

generally shifted the above peaks downfield by 0.2–0.3 ppm. The ratio of peak integration between EG and PEG after polymerization shows excellent agreement with the initial molar ratio of EG and PEG used for polymerization: for example, the integration ratio of EG and PEG of copolymer (4.05:1) is quite close to the initial mixing ratio of 4:1.

Tensile property

Synthesis of copolymers is followed according to Figure 1 and the proposed cross-linked structure is shown in Figure 2. Because we know from the previous results that PET/PEG copolymer with 20 mol % of PEG 200 (E200-20) showed the best tensile test result, the composition was used for preparation of cross-linked copolymer and related shape memory test. Maximum stress of glycerol (1.0 and 1.5 mol %) copolymers showed an initial decrease with SP content and a sharp increase at SP content higher than 1.5%; copolymers with 2.5 mol % glycerol content had a gradual increase with SP content (Fig. 3). The strain at break of glycerol (1.0 and 1.5 mol %) copolymers increased with SP contents up to 1.5% and decreased at higher content, but 2.5 mol % glycerol copolymer

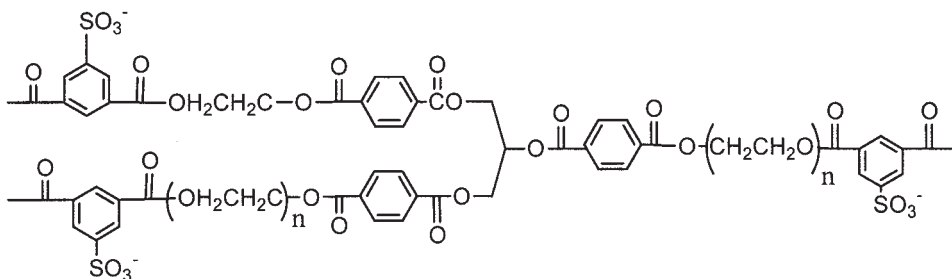


Figure 2 Structures of cross-linked copolymers with glycerol and a sulfoisophthalate group.

showed a slow decrease with the inclusion of SP (Fig. 4). Both maximum stress and strain at break results are similar to T_g data in the next section, and an explanation for the combined results will appear there.

Thermal analysis

Glass transition temperature (T_g) of the copolymers with different combination of glycerol and SP is compared in Figure 5. For the copolymers with 1.0 and 1.5 mol % of glycerol, the addition of SP decreased the transition temperature up to 1.5 mol %, and a steep increase of T_g was observed from the 1.5 to the 2.5 mol % region. Unlike the above series, the copolymers with 2.5 mol % of glycerol showed constant increase of T_g with the content of SP. Such a result can be understood from the fact that the copolymer chain is not tightly crosslinked at lower mol % of glycerol (1.0 and 1.5 mol %) and the presence of SP along the chain hinders ordered

chain packing, thus resulting in reduced T_g . But, as the SP content increases, interchain ionic interaction among sulfonyl sodium salt groups additionally improves interchain attraction and, therefore, T_g value increases at SP content higher than 1.5 mol %. The highest inclusion of glycerol (2.5 mol %) dominates the copolymer crosslinking, and the decrease of T_g at lower mol % of SP observed in the above case does not happen because covalent crosslinking of glycerol can subdue the disrupting effect of SP. As more SP was included, T_g of 2.5 mol % glycerol copolymer also increased due to the additional ionic interchain interaction originating from the sulfonyl groups. The above explanation can be applied to the tensile test results. Such a trend can be consistently observed in the following mechanical and shape recovery data, and the combination of covalent crosslinking by glycerol and ionic interaction by SP can manipulate the desired transition temperature of copolymers.

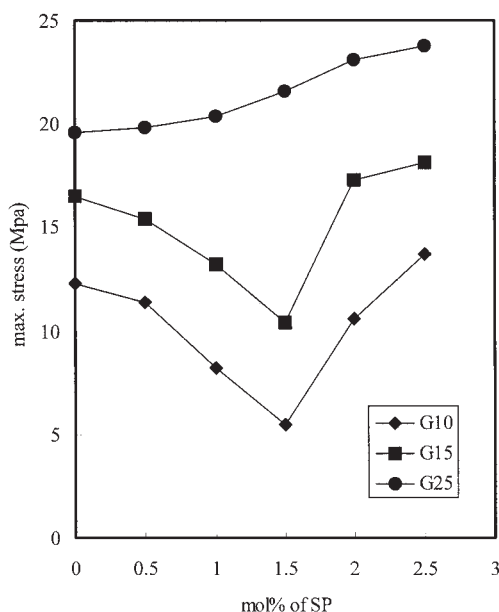


Figure 3 Maximum stress of PET/PEG copolymers crosslinked with glycerol and a sulfoisophthalate group (SP).

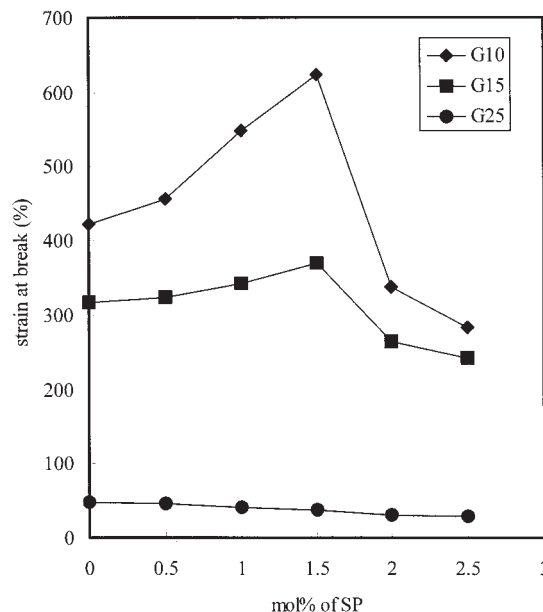


Figure 4 Strain at break of PET/PEG copolymers crosslinked with glycerol and a sulfoisophthalate group (SP).

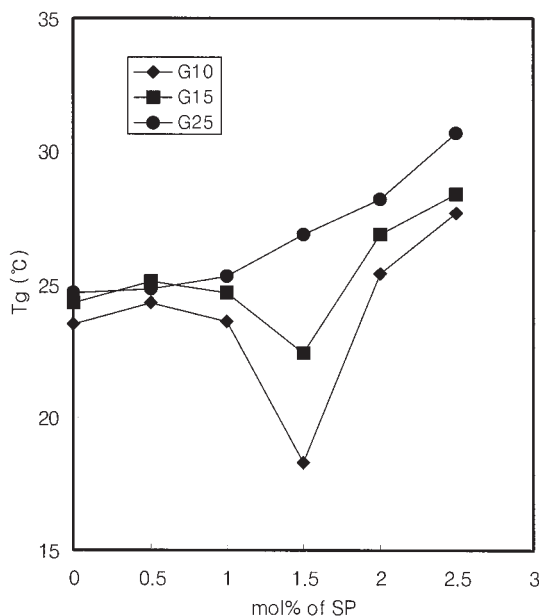


Figure 5 Glass transition temperature (T_g) of PET/PEG copolymers crosslinked with glycerol and a sulfoisophthalate group (SP).

Shape memory effect

Shape retention rates of the copolymers generally maintain 97–99% of the original shape, but shape recovery rates are significantly dependent on cross-linking agents (glycerol and SP). In Figure 6, cyclic shape memory test results of 1.0 mol % glycerol copolymers with various SP contents were compared; shape recovery was getting worse with inclusion of SP up to 1.5% and was substantially improved at 2.5 mol % of SP to a level that was better than the starting one without SP. In Figure 7, cyclic tests were done with 1.5 mol % glycerol copolymers with various SP contents; shape recovery again decreased up to 1.5 mol % of SP and went up at 2.5 mol % of SP, showing a trend similar to that of the 1.0 mol % case. Finally, 2.5 mol % glycerol copolymers were not much affected by the content of SP: there are some drops in shape recovery for the cases of 0.5 and 1.0 mol % of SP, but 1.5, 2.0, and 2.5 mol % of SP all showed higher shape recovery (Fig. 8). From the above results, shape recovery rates of the copolymers at low mol % of glycerol can be controlled by the content of SP, and high glycerol content dominates the shape recovery effect with very minor dependence on SP content. Again, shape memory results remind us of the differences in interchain interactions coming from glycerol and SP as explained above.

Charpy impact strength test

Unnotched Charpy impact strength of composite laminate was compared in Figure 9. Impact strength nor-

mal to the laminate layer of sandwich structure direction was measured with unnotched specimens.¹⁰ Compared to epoxy beam laminate by itself, composite laminate showed higher impact strength; laminate with uncross-linked copolymer (E200–20) had 3.5 times higher impact strength than epoxy laminate; laminates made from the copolymers with glycerol and SP showed 1.3–2.6 times higher impact strength than epoxy laminate. Inclusion of glycerol lowered impact strength of the laminate and the presence of SP additionally decreased the value; the higher rigidity of cross-linked copolymer is mainly responsible for the

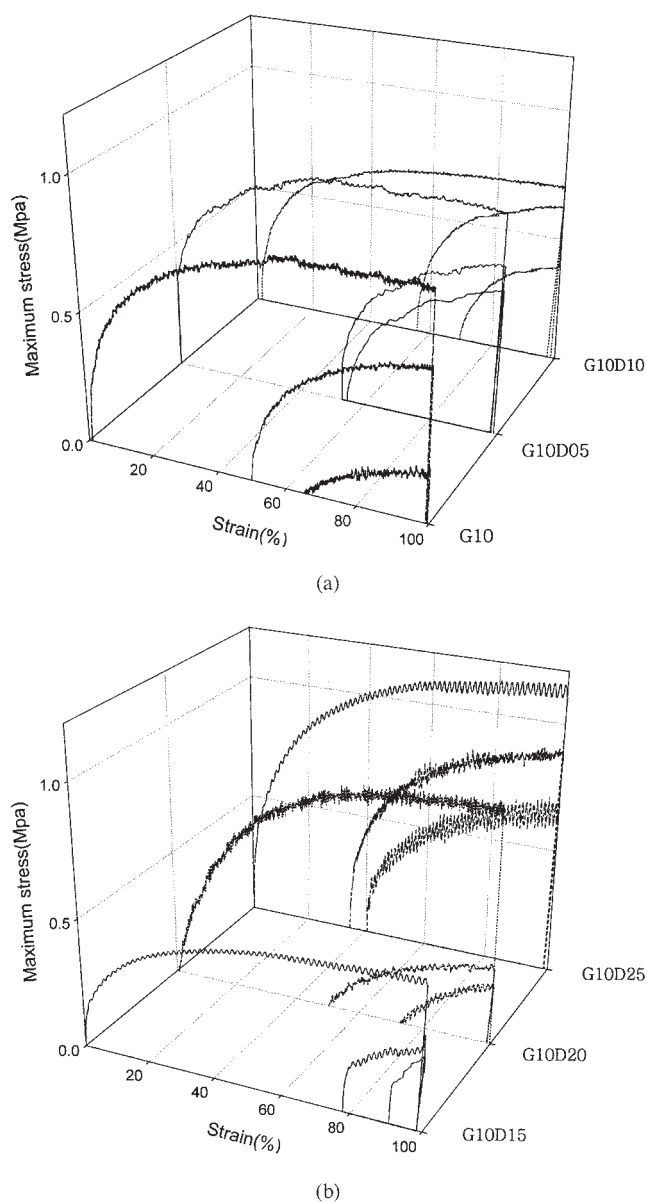


Figure 6 Cyclic shape memory test of PET/PEG copolymers crosslinked with 1.0 mol % glycerol and (a) 0 mol % SP (G10), 0.5 mol % SP (G10D05), or 1.0 mol % SP (G10D10), (b) 1.5 mol % SP (G10D15), 2.0 mol % SP (G10D20), or 2.5 mol % SP (G10D25).

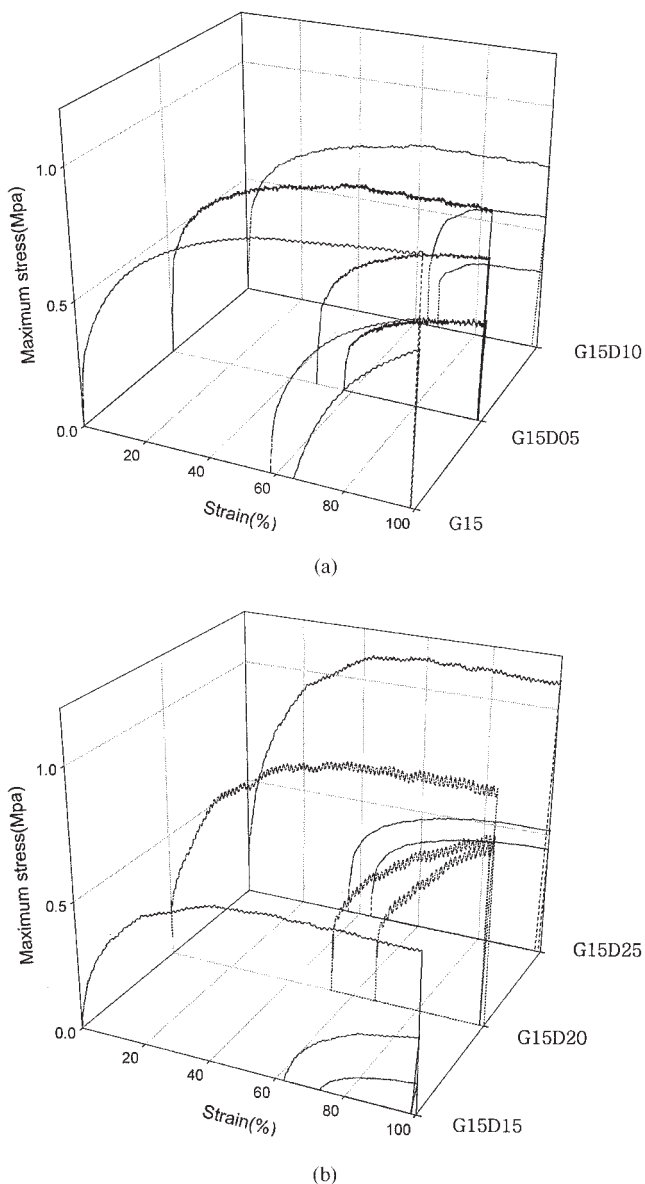


Figure 7 Cyclic shape memory test of PET/PEG copolymers crosslinked with 1.5 mol % glycerol and (a) 0 mol % SP (G15), 0.5 mol % SP (G15D05), or 1.0 mol % SP (G15D10), (b) 1.5 mol % SP (G15D15), 2.0 mol % SP (G15D20), or 2.5 mol % SP (G15D25).

decrease of impact strength and the desired impact strength can be adjusted by control of the composition of glycerol and SP. The impact strength results are closely related to the transition temperature of copolymers (E200–20: 11.2°C, G10D10: 23.6°C, G10D25: 27.7°C, G15D10: 24.7°C, G15D25: 28.4°C, G25D10: 25.3°C, G25D25: 30.7°C); relative softness at room temperature where impact strength is measured should be inversely proportional to transition temperature. Therefore, laminates made of G-25 series get the most solid structure among those compared, but such rigid structure is very weak in absorbing external impact and shows low impact strength. Compromise of shape

memory and impact strength of copolymer is necessary depending on the required property under various surrounding conditions.

Dynamic mechanical property of sandwich laminate beam structure composite

Storage modulus and $\tan \delta$ of sandwich laminate beam composites of G25 series are compared in Figures 10 and 11. In Figure 10 the storage modulus of epoxy laminate beam was in high contrast with all other copolymer laminates; G25 copolymer laminates showed similar shape over the temperature range, a

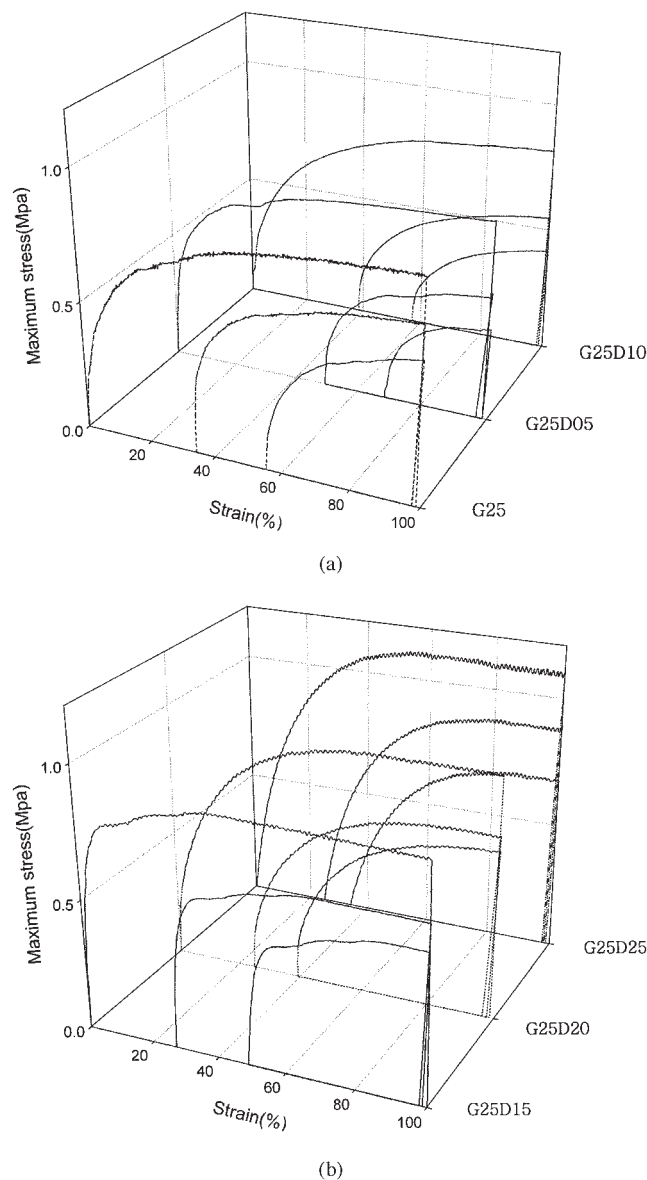


Figure 8 Cyclic shape memory test of PET/PEG copolymers crosslinked with 2.5 mol % glycerol and (a) 0 mol % SP (G25), 0.5 mol % SP (G25D05), or 1.0 mol % SP (G25D10), (b) 1.5 mol % SP (G25D15), 2.0 mol % SP (G25D20), or 2.5 mol % SP (G25D25).

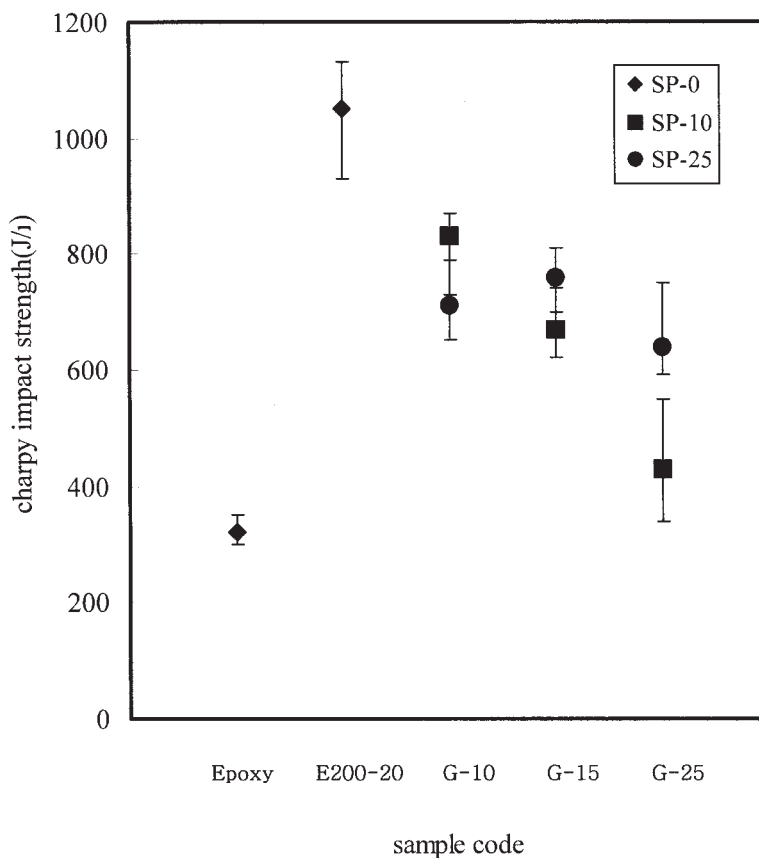


Figure 9 Unnotched Charpy impact strength of composite laminates.

significant drop at transition temperature, and immediate recovery at higher temperature. Additional ionic interaction from SP, together with glycerol crosslinking, increased transition temperature and the increase was proportional to SP content. In Figure 11, $\tan \delta$ sharply changed at the transition temperature for all copolymer laminates; their peak temperatures are in good agreement with the transition temperatures of each copolymer. But epoxy laminate was not responsive over temperature ranges, as expected from the storage modulus results. Because $\tan \delta$ indicates damping ability, high $\tan \delta$ of copolymer laminates around the room temperature range suggests the possibility of developing highly vibration-controlling composite material.¹¹ There is still more room for fine-tuning the copolymer structure through modification of the cross-linking method, PEG chain length, and hard segment structure for the control of transition temperature, vibration absorption, and mechanical properties.

CONCLUSION

Shape memory polyester copolymers are used to develop composite laminate material with vibration

control, and covalent crosslinking by glycerol and ionic interaction from SP were the key features in controlling the shape memory properties of copolymers. The shape retention rate of all copolymers showed very high value (97–99%); shape recovery at low mol % of glycerol showed an initial decrease and a sharp increase with SP content, but the 2.5 mol % glycerol copolymer series had a gradual increase with SP content. Such results originated from the balance between strong covalent crosslinking by glycerol and weak ionic interaction from SP, and the additional fine control of shape recovery by ionic interaction helps us in developing custommade smart materials. A similar trend was observed for the glass transition temperatures of copolymers. Composite laminates prepared with copolymers showed high impact strength and loss tangent δ , and their value can be adjusted with SP content. Finally, physical properties of the sandwich-type laminate with shape memory copolymer can be controlled by proper selection of cross-linking agents, which is very helpful in developing composite materials with controlled T_g and high damping effect.

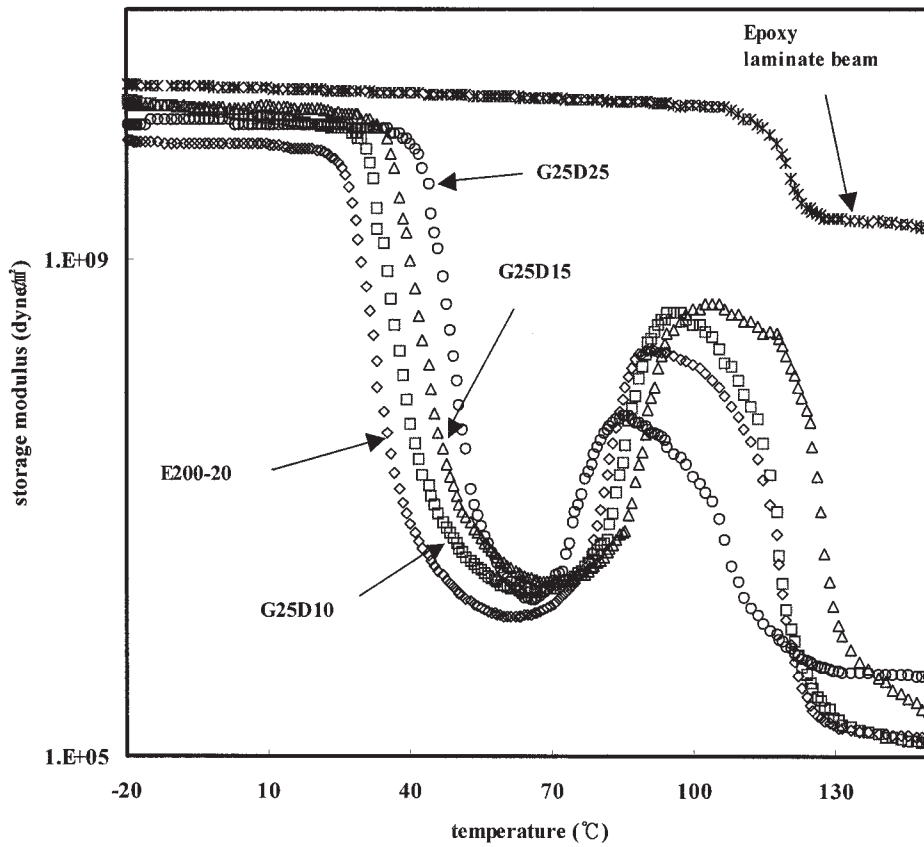


Figure 10 Storage modulus of copolymer composite laminates.

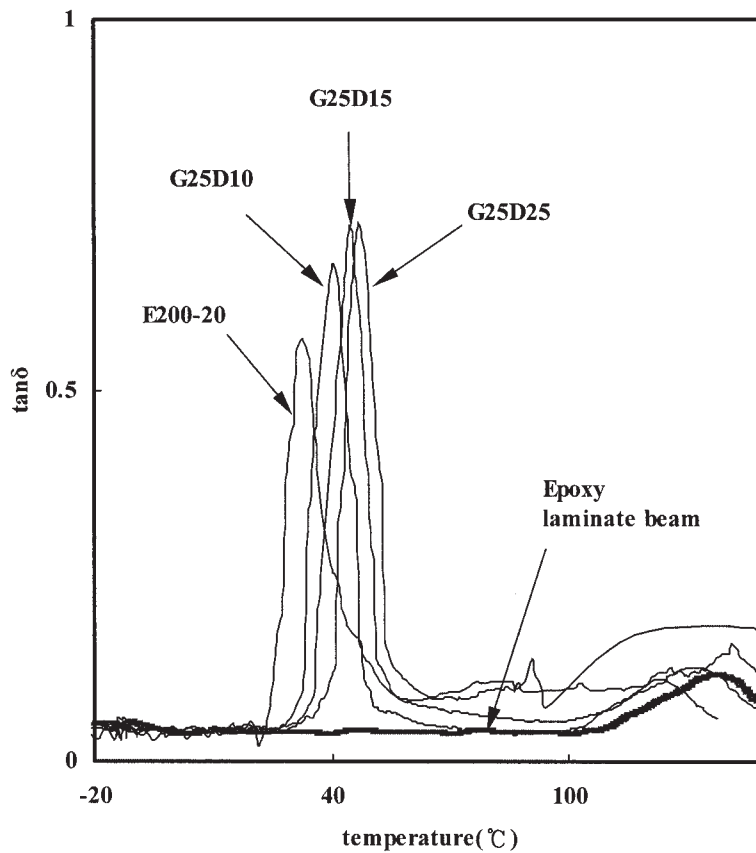


Figure 11 Loss tangent δ of copolymer composite laminates.

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