Dynamic Mechanical Properties of Sandwich-Structured Epoxy Beam Composites Containing Poly(ethyleneterephthalate)/Poly(ethyleneglycol) Copolymer with Shape Memory Effect

Byoung Chul Chun,[1] Sang Hyuk Cha,[1] Chul Park,[1] Yong-Chan Chung,[2] Myung Ju Park,[2] Jae Whan Cho[c]

[1]Department of Polymer Engineering, The University of Suwon, San 2-2, Wawuri, Bongdameup, Hwasungshi, Kyonggi-do, Korea
[2]Department of Chemistry, The University of Suwon, Kyonggi-do, Korea
[3]Department of Textile Engineering, Konkuk University, Seoul, Korea

ABSTRACT: To make smart vibration-controlling composite laminate, a few poly(ethylene terephthalate) (PET) and poly(ethylene glycol) (PEG) copolymers with shape memory ability were prepared. After selecting the best composition of PET–PEG copolymer in mechanical properties, a crosslinking agent such as glycerine, sorbitol, or maleic anhydride (MA) was included for crosslinked copolymer, followed by analysis of its effect on mechanical, shape memory, and damping properties. The highest shape recovery was observed for copolymer with 2.5 mol % of glycerine, and the best damping effect indicating vibration control ability was from copolymer with 2.5 mol % of sorbitol. With the optimum copolymers in hand, sandwich-structured epoxy beam composites fabricated from an epoxy beam laminate and crosslinked PET–PEG copolymer showed that impact strength increased from 1.9 to 3.7 times depending on the type of copolymer, and damping effect also increased as much as 23 times for the best case compared to epoxy laminate beam alone. The resultant sandwich-structured epoxy beam composite can be utilized as structural composite material with vibration control ability, and its glass transition temperature can be controlled by adjustment of PET, PEG, or crosslinking agent composition. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3141–3149, 2003

Key words: composites; crosslinking; shape memory

INTRODUCTION

Active research is undergoing on smart materials such as a shape memory alloy, semiconductors, polymers, and medical supplies. Shape memory material, one of the smart materials, has a few characteristics such as shape memory, shape retention, and impact absorption effect. In addition, it can detect thermal, mechanical, electrical, and magnetic stimulus, and then respond via property changes in shape, location, modulus, damping, and abrasion, which can be applied to various fields.[1–3] Meanwhile, shape memory polymer, because of lightness, high shape recovery, good processability, and high damping near its T_g, was applied to manufacture of laminate composite materials.[4,5]

In this investigation, poly(ethyleneterephthalate) (PET)/polyethyleneglycol (PEG) copolymer is used as matrix material for the ultimate purpose of developing a laminate composite with vibration con-

trol ability. A crosslinking agent such as glycerine, sorbitol, or maleic anhydride (MA) was tried, and its effect on the mechanical, shape memory, and damping property was compared. Comprehensive mechanical properties of various sandwich-structured laminate composites were examined, and reasons for such high vibration control were briefly discussed.

EXPERIMENTAL SECTION

Materials

DMT and EG were generously supplied by SK Chemical, and PEG and maleic anhydride were purchased from Duksan Chemical. Molecular weights of PEG were 200, 400, 600, and 1000 g/mol. Calcium acetate and antimony oxide were from Hayashi Pure Chemical Industry, and the phosphrous acid used as a stabilizer was from Kanto Chemical. The epoxy laminate beam with 0.7 mm thickness was supplied by Korea Fiber Co., and used to prepare unidirectional glass fiber-reinforced composite with 2.1 mm total thickness.
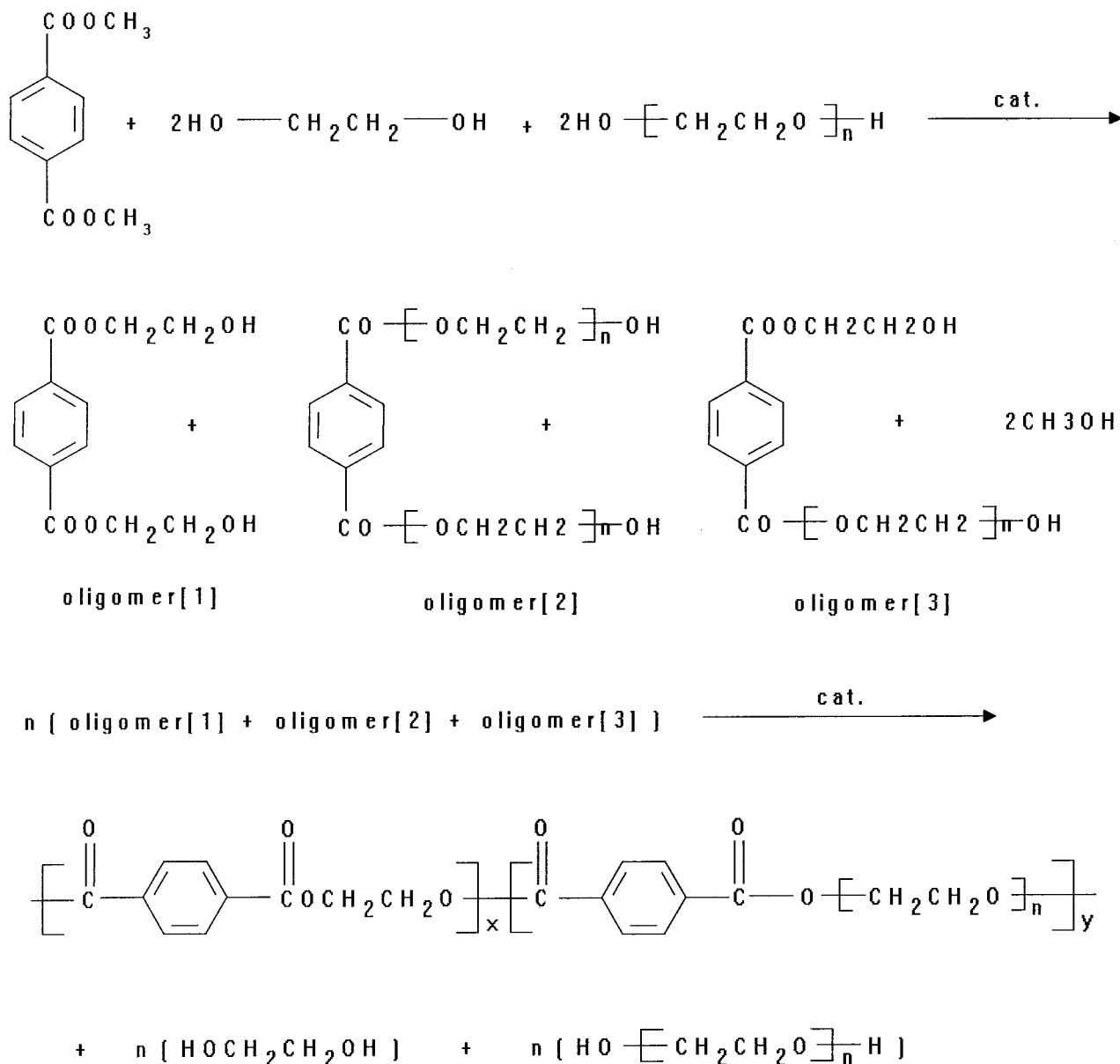
Scheme 1　Synthetic scheme of the PET–PEG copolymer.

Preparation of crosslinked copolymer

PET–PEG copolymers were synthesized from DMT and PEG by a melt-condensation method with a reactor custom made by Go Do Engineering Co. The copolymer composition was varied by either changing molecular weight or percentage of PEG. Polymerization was carried out in two steps; the oligomer was prepared in the first step with DMT, EG, and PEG, and oligomer made in the first one was condensed to polymer in the second step by an esterification reaction, which required high temperature, constant stirring, and high vacuum to shift reaction equilibrium further to the product. A detailed synthetic procedure for PET–PEG copolymer can be found in our previous article.[6] In addition, glycerine, sorbitol, or MA was

added in various ratios as a crosslinking agent into the copolymer. The synthetic scheme and characterization of the copolymers are shown in Schemes 1 and 2, and Tables I and II.
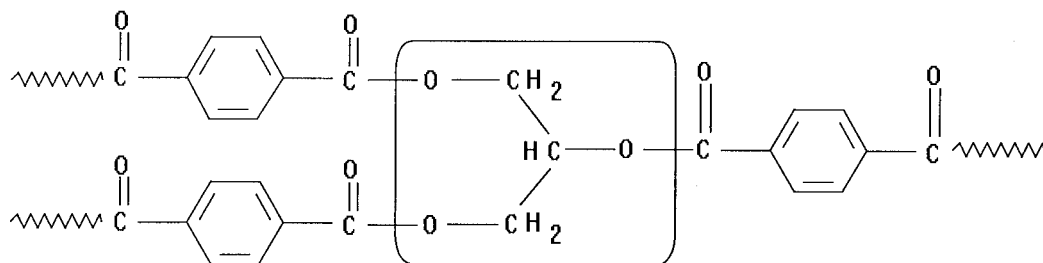
Intrinsic viscosity

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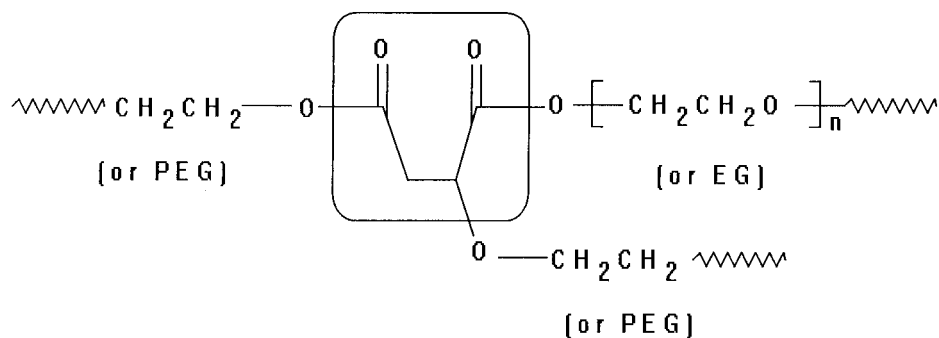
Thermal analysis

T_g and T_m were measured by differential scanning calorimeter (DSC, TA-2000). The specimen was heated
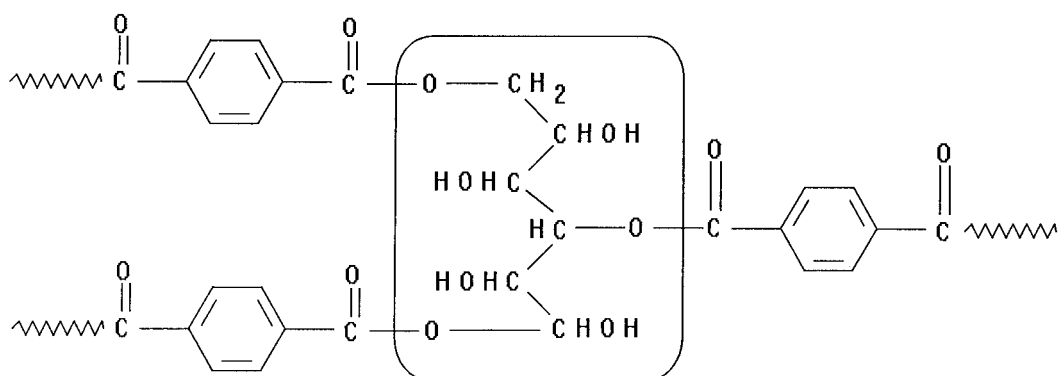
(A)

(B)

(C)

Scheme 2 Schematic of the PET–PEG copolymer crosslinked by (a) glycerine, (b) sorbitol, and (c) maleic anhydride.

to 300°C at 10°C/min of heating rate, and kept at that 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 scan.

Preparation of laminate beam

The sandwich-structured laminate composite was prepared by compressing two 0.7-mm epoxy laminate

TABLE I
Properties of PET–PEG Copolymers

Sample code	PEG (mol %)	PEG M.W. (g/mol)	T_g (°C)	T_m (°C)	$[\eta]$ (dL/g)
PET	0	—	79.1	252.0	0.68
E200-10	10	200	33.5	213.5	0.62
E200-20	20	200	8.1	167.3	0.60
E400-10	10	400	−12.9	200.0	0.70
E600-10	10	600	−32.4	194.6	0.67
E1000-5	5	1000	−42.5	221.2	0.55

TABLE II
Comparison of Crosslinked PET–PEG Copolymers

Sample code	PEG (mol %)	PEG M.W. (g/mol)	Cross-link agent (mol %)	Maximum stress (N/mm^2)	Strain at break (%)	T_g (°C)
E200-20	20	200	—	5.9	1122	11.2
G-15	20	200	Glycerine (1.5)	16.5	317	14.3
G-25	20	200	Glycerine (2.5)	19.6	48	23.7
M-15	20	200	Maleic anhydride (1.5)	9.1	832	13.2
M-25	20	200	Maleic anhydride (2.5)	9.1	770	14.1
S-15	20	200	Sorbitol (1.5)	14.4	805	9.2
S-25	20	200	Sorbitol (2.5)	14.3	632	11.7

beams and one 0.7-mm PET–PEG copolymer sheet in a middle layer at 210°C in a heating press.

Mechanical properties and shape memory analysis

The 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. Tensile test was performed by 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. The shape memory effect was also checked by a tensile test using a UTM equipped with a temperature-controlled thermal cabinet. For measurement of the shape retention rate, the 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. Specimen under strain was cooled back to below T_g, and left at the temperature for 30 min after removal of load, followed by measurement of the deformed length. For measurement of shape recovery, the specimen was heated again to the temperature above T_g but below T_m with a 10-min stay, and cooled back to the temperature below T_g, staying at this temperature for 30 min, and the final specimen was measured. The whole procedure was repeated three times consecutively. 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 an impact tester (Testing Machines Inc., model 43-02, pendulum 75 kgcm, Charpy type) for both the matrix and composite laminate in a tensile mode and three-point bending mode, respectively.

RESULTS AND DISCUSSION

Tensile property

Synthesis of copolymers is followed according to Scheme 1, and the proposed crosslinked structures of them are shown in Scheme 2.[6] Because the PET–PEG copolymer with 20 mol % of PEG 200 (E200-20)

showed the best tensile test result, the composition was used for preparation of a copolymer with a crosslinking agent and related shape memory test (Table I). More information about properties of the copolymer, E200-20, can be found in ref. 6. Tensile test results of the crosslinked copolymers indicated that tensile strength generally increased, but strain at break decreased as more crosslinking agent was included (Table II). Such result undoubtedly originated from higher resistance to deformation by introduction of crosslinking in the copolymer chain, and the concomitant crosslinked solid structure resulted in high tensile strength and low strain at break. Among the crosslinked PET–PEG copolymers, one crosslinked by glycerine showed the highest tensile strength and the lowest strain at break.

Shape memory effect

From the point of shape memory ability, shape retention rate slightly decreased, but shape recovery significantly increased after crosslinking. Especially, the PET–PEG copolymer crosslinked by glycerine showed the highest shape recovery rate (Fig. 1). For example, shape recovery rate of E200-20 decreased from 50.5 to 21.5% after two cycles of the shape memory test, but G-15 and G-25 maintained 51.0 and 79.9%, respectively, under the same condition. The PET–PEG copolymer crosslinked by sorbitol also exhibited high shape recovery rate. The specific shape memory test results are summarized in Table III. As for all crosslinked copolymers, shape retention rate was more than 95%, which told us that the deformed shape of the copolymer could be almost perfectly be kept below the transition temperature.

In addition to chemical crosslinking, the following characteristics can be responsible for high shape recovery of the crosslinked copolymer: (1) molecular interactions among hard segments (PET part), such as hydrogen bonding, dipole–dipole interaction of carbonyl groups of PET, and induced dipole–dipole interaction of aromatic rings, work as a pivoting point for shape memory after several deformation–recovery processes; (2) soft segment (PEG part) effectively and
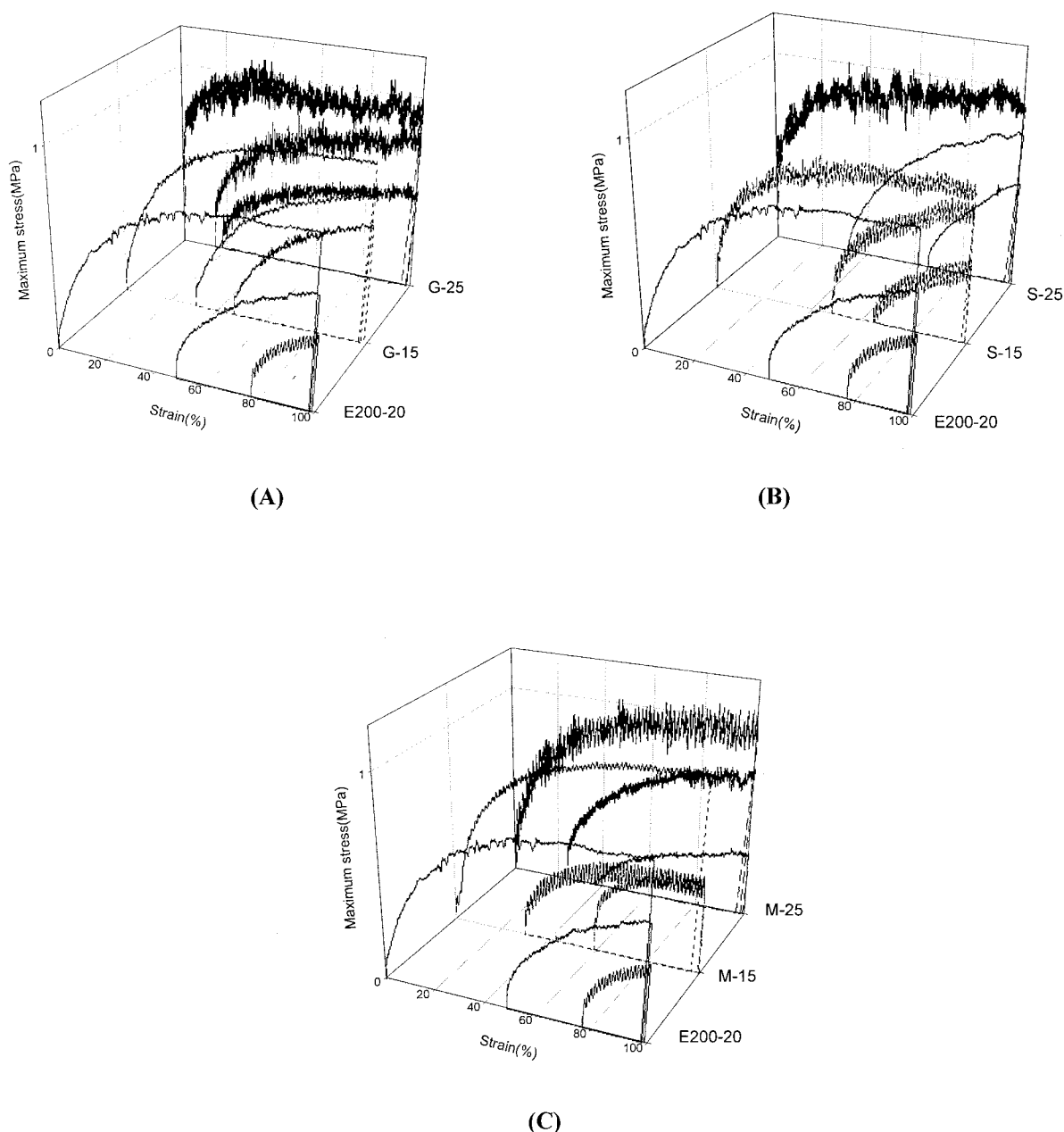
(A)

(B)

(C)

Figure 1 Cyclic shape memory effect of PET–PEG copolymer crosslinked by (a) glycerine, (b) sorbitol, and (c) maleic anhydride.

entirely absorb the applied stress so that the relative position of the hard segment or the original shape of the copolymer can be safely preserved under severe experimental conditions; (3) glycerine, a shorter crosslinking agent than sorbitol, is more effective for shape memory, because, although both are connecting the hard segment, the short and rigid structure of glycerine is more favored for shape retention of the hard segment: (4) MA, which crosslinks the soft segment, is inferior to glycerine or sorbitol, because the soft segment's role in the shape memory copolymer is to absorb external stress, and crosslinking by MA hinders flexible movement of the soft segment. The mech-

anism for the higher shape memory properties of the glycerine crosslinked copolymers can be schematically explained as in Figure 2: the hard segments connected through crosslinking and interchain interactions maintains the original shape, while soft segments reversibly absorb external stress.

Dynamic mechanical thermal property

In Figures 3, 4, and 5, storage modulus and tan δ of various crosslinked PET–PEG copolymers were compared. Storage modulus abruptly decreased around

TABLE III
Shape Memory Test Results of Copolymers

Sample code	First cycle		Second cycle		Third cycle	
	Recovery (%)	Max stress (Mpa)	Recovery (%)	Max stress (Mpa)	Recovery[a] (%)	Max stress (Mpa)
E200-20	51.8	0.85	23.5	0.56	—	0.37
G-15	69.4	0.90	53.7	0.75	—	0.60
G-25	85.8	1.00	82.2	0.85	—	0.52
M-15	70.3	0.97	41.7	0.49	—	0.46
M-25	76.1	1.01	66.0	0.77	—	0.33
S-15	52.3	0.76	36.1	0.68	—	0.42
S-25	68.7	0.92	34.7	0.78	—	0.53

[a] Recovery for the third cycle was not proceeded because of the very low value of E200-20.

T_g, and increased later at about 60°C above their T_gs for all three kinds of crosslinked copolymers, which could be coming from disorganization at T_g and recrystallization at higher temperature of PET-PEG copolymer chains during the heating process in dynamic mechanical property measurement, and such a result was not uncommon, as previously observed for poly(trimethyleneterephthalate).[7–10] As more of a crosslinking agent was included in the copolymer chain, the storage modulus profile generally shifted toward a higher temperature, and thus recrystallization of the copolymer chains occurred at a higher temperature, which originated from combined interactions from additional chemical crosslinking, dipole–dipole interaction of carboxyl groups of PET, and induced dipole–dipole interaction between phenyl rings.[11,12] From this result it can be suggested that variation of dynamic mechanical property over temperature can be overcome by a drawing process of the specimen before heating.

A similar thermomechanical trend was observed in the tan δ profile at around T_g, and a small relaxation shoulder immediately after T_g was probably coming from a temporary disruption of chains during re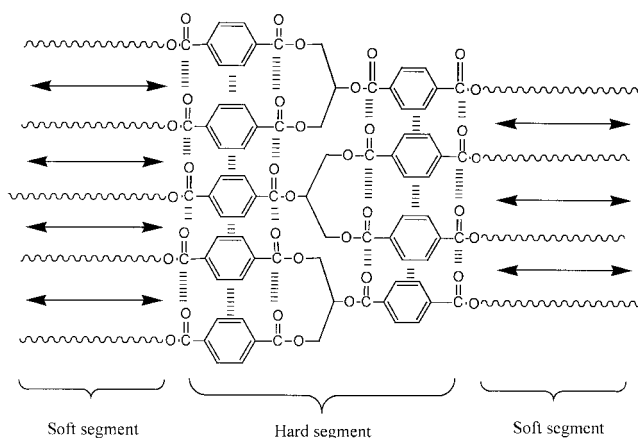crystallization. Addition of the crosslinking agent resulted in a broader tan δ profile, because restricted chain movement by the crosslinking agent made the chain rearrangement a slower and more energy-consuming process than the uncrosslinked copolymer; therefore, both disorganization and recrystallization were observed at a broader temperature range, in addition to broadening of the transition area in tan δ vs temperature profile, and temperature at peak transition shifted toward a higher region, which could be interpreted by the same mechanism. As a high tan δ means better deformation and shape recovery, crosslinked PET–PEG copolymers are promising candidates for shape recovery material based on tan δ results. A
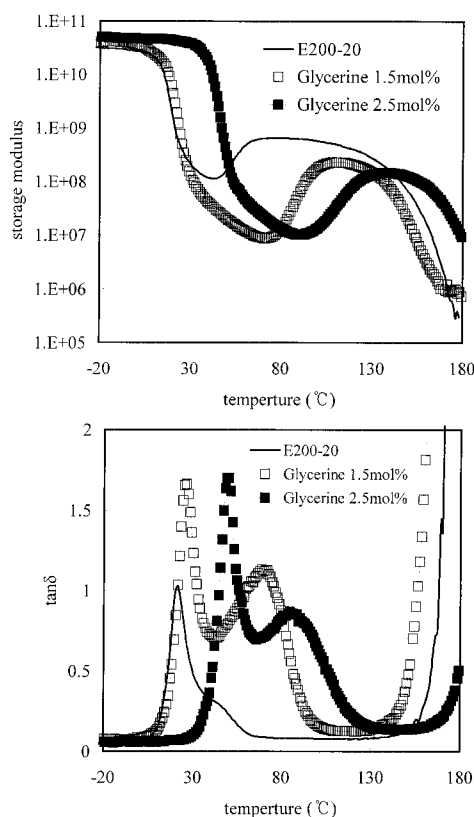

Figure 2 Schematic drawing of hard and soft segments of glycerine-crosslinked shape memory copolymers.

Figure 3 Dynamic mechanical properties of PET–PEG copolymer crosslinked by glycerine.
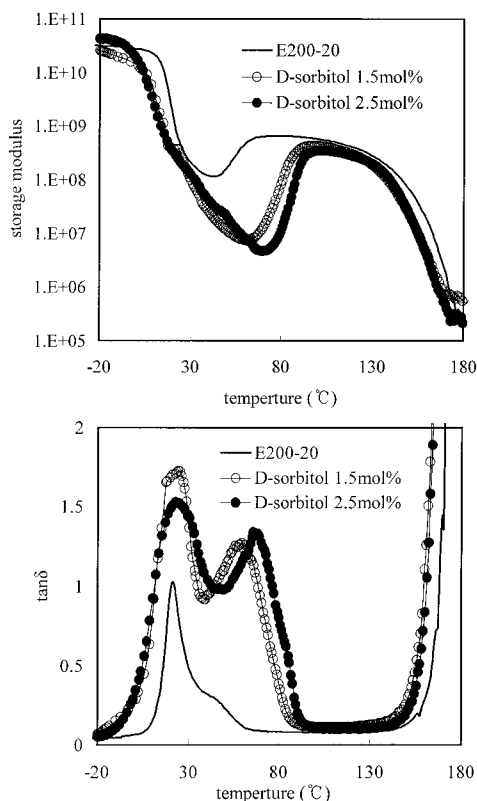
Figure 4 Dynamic mechanical properties of PET–PEG copolymer crosslinked by sorbitol.

rubbery plateau region observed at a higher temperature narrowed with the introduction of a crosslinking agent such as glycerine or sorbitol, but the MA-crosslinked copolymer had a similar width of the rubbery plateau region as the uncrosslinked one; such a difference, which is presumed to be coming from the crosslinking point, hard-segment linking (glycerine and sorbitiol), or soft-segment linking (MA), tell us once again the importance of the selection of the crosslinking agent in developing a highly reliable shape memory copolymer.

It is generally known that a shape memory polymer retains its deformed shape if stressed at the rubbery plateau region, which is above the T_g and then cooled to a temperature below T_g, and it recovers its original shape if heated to the rubbery plateau region again. Therefore, the shape memory polymer has better shape retention property at a temperature below T_g with the resulting high storage modulus, and its deformation becomes easier at a temperature above T_g because of a low storage modulus. From a different perspective, the crosslinked PET–PEG copolymer, especially one by glycerine or sorbitol, showed a significant modulus change around T_g, which was above the necessary modulus change (order of three) as a temperature-sensitive material, resulting in high hope for application in that area. Among the copolymers, a comparatively sharper transition in the glycerine-

crosslinked one suggests that crosslinking at the hard segment (PET), and short and rigid crosslinking agent are also advantageous in developing highly thermosensitive material.[13]

Dynamic mechanical test results of the copolymers with three different crosslinking agents are summarized as follows: (1) crosslinking by glycerine provides higher T_g, storage modulus, tan δ, and apparent change of storage modulus plus sharp transition of tan δ around T_g; (2) crosslinking by sorbitol also shows similar characteristics as glycerine, but transitions for both storage modulus and tan δ are blunt, which comes from the fact that flexible crosslinking of the hard segment by sorbitol may mitigate strong interaction and shape retention among hard segments as observed in shorter glycerine; (3) crosslinking by MA is least successful in obtaining improved thermomechanical properties, and interconnection of soft segments like MA crosslinking is not desirable for our purpose, because soft segment should absorb external stress instead of blocking free movement of PEG chains.

Charpy impact strength test

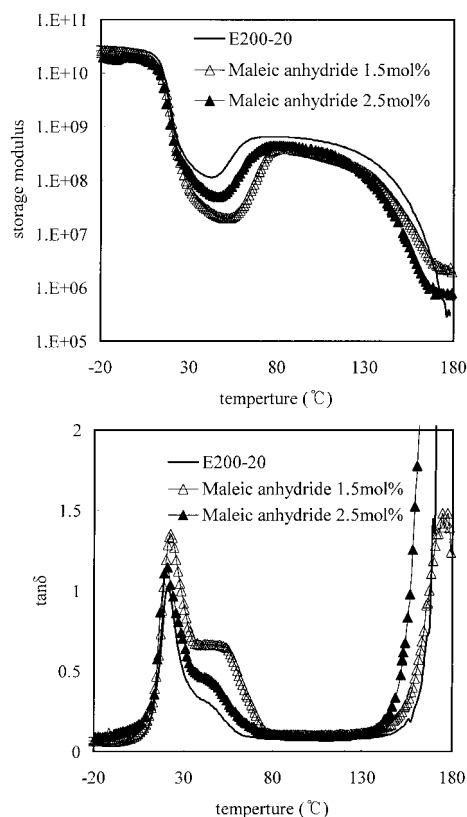Unnotched Charpy impact strength of composite laminate was compared in Figure 6. Impact strength nor-

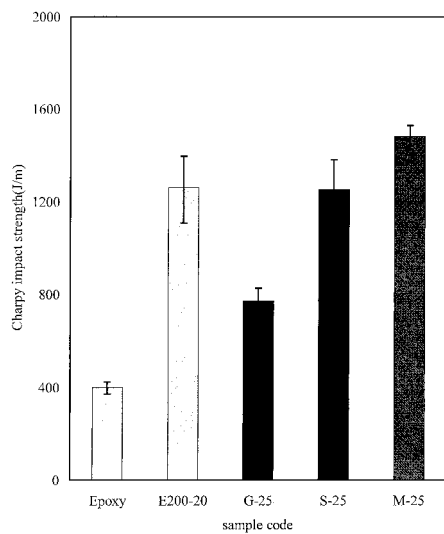**Figure 5** Dynamic mechanical properties of PET–PEG copolymer crosslinked by maleic anhydride.

Figure 6 Unnotched Charpy impact strength of composite laminates.

Figure 7 Storage modulus of composite laminates.

mal to the laminate layer of sandwich structure direction was measured with unnotched specimens.[14] Compared to the epoxy beam laminate by itself, composite laminate showed higher impact strength; laminate with an uncrosslinked copolymer (E200-20) or a crosslinked one by sorbitol (s-25) or maleic anhydride (M-25) had more than four times higher impact strength than the epoxy laminate; laminate with glycerine (g-25) was the lowest in impact strength, but still two times higher than epoxy laminate. The above results are closely related to the stiffness of the copolymer, which differentiates the overall impact strength of the laminate; from the transition temperature of the copolymer (E200-20: 8.1°C, G-25: 23.7°C, S-25: 11.7°C, and M-25: 14.1°C), relative softness at room temperature where impact strength is measured should be reversely proportional to the transition temperature. Therefore, G-25 itself and the laminate made of G-25 get the most solid structure among compared copolymers, but such a rigid structure is very weak in absorbing external impact and shows low impact strength. Compromise of shape memory and impact strength of the copolymer is necessary, depending on what is the required property under various surrounding conditions.

Dynamic mechanical property of a sandwich laminate beam structure composite

Storage modulus and tan δ of the sandwich laminate beam composites were compared in Figures 7 and 8. In Figure 7, storage modulus of the epoxy laminate beam was in high contrast with all other copolymer laminates; all of copolymer laminates except G-25 showed similar shape over the temperature range, significant drop at transition temperature, and imme-
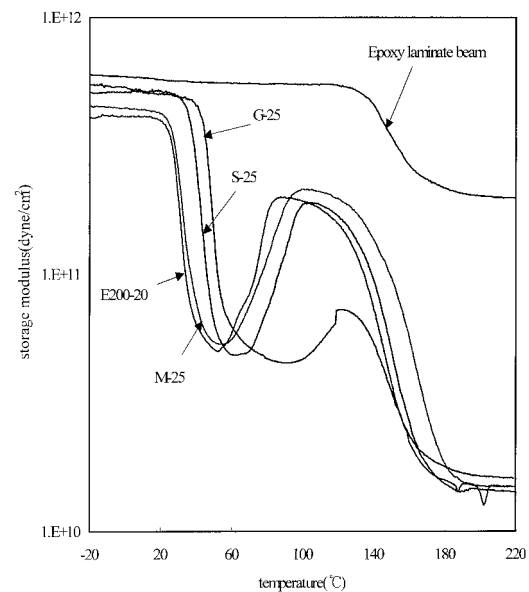
diate recovery at higher temperature. Laminate with G-25 with its rigid and well crosslinked copolymer is hard to rearrange its chains at high temperature once organized structure is dismantled. Deviation of G-25 laminate from other copolymer laminates is in accord with the above Charpy impact strength result. In Figure 8, tan δ sharply changed at transition temperature for all of the copolymer laminate with no exception of the G-25 laminate; their peak temperatures are in good order with transition temperatures of each copolymers. But epoxy laminate was not responsive over temperature ranges as expected from the storage modulus results. Because tan δ indicates damping ability,
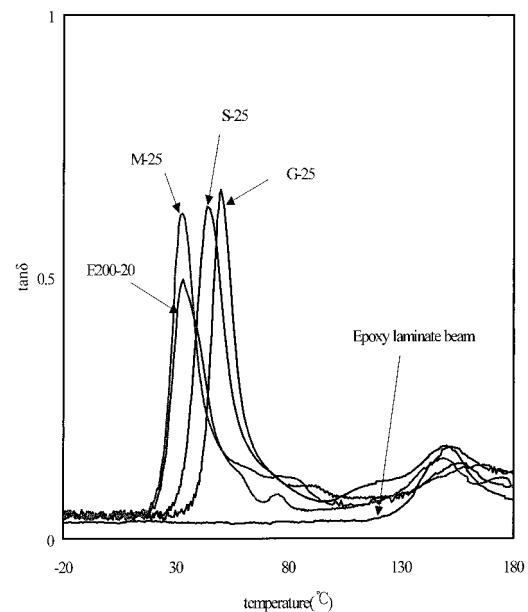

Figure 8 Loss tangent of composite laminates.

high tan δ of copolymer laminates (23 times as high as epoxy laminate for the best case) around the room temperature range suggests the possibility of developing highly vibration-controlling composite material. More fine-tuning of the copolymer structure through modification of the crosslinking method, PEG chain length, and hard segment structure, is still necessary for the control of transition temperature, vibration absorption, and mechanical properties.

CONCLUSION

As a preliminary search for developing composite laminate material with vibration control ability, various crosslinked shape memory copolymers were investigated for a damping effect. Crosslinking agents such as glycerine, sorbitol, and maleic anhydride were tried, and each crosslinked copolymer showed its own merits in different tests. For uncrosslinked copolymer, best mechanical properties were obtained with the copolymer composed of 80 mol % of EG and 20 mol % of PEG-200. Addition of glycerine, sorbitol, or maleic anhydride as a crosslinking agent into the above copolymer improved both the shape memory and damping effect. The highest shape recovery rate was obtained with 2.5 mol % of glycerine, and highest tan δ was from 2.5 mol % of sorbitol. When a sandwich-type composite laminate was prepared with a glass fiber-reinforced epoxy beam and crosslinked copolymer, Charpy impact strength increased 1.9–3.7 times and damping effect also increased 23 times for the best case at room temperature compared to the pure epoxy beam. Thus, from this investigation, the crosslinked PET–PEG copolymer sandwiched to a laminate composite, enables developing composite materials with controlled T_g and a high damping effect.

References

1. Gandhi, M. V.; Thompson, B. S. Smart Materials and Structures; Chapman and Hall: New York, 1992.
2. Takahashi, T.; Hayashi, N.; Hayashi, S. J Appl Polym Sci 1996, 60, 1061.
3. Wei, Z. G.; Sandstrom, R. J Mater Sci 1998, 33, 3743.
4. Liang, C.; Rogers, C. A.; Malafeew, E. J Intell Mater Syst Struct 1991, 8, 380.
5. Takagil, T. J Intell Mater Sys 1990, 1, 149.
6. Chun, B. C.; Cha, S. H.; Chung, Y. C.; Cho, J. W. J Appl Polym Sci 2002, 83, 27.
7. Oh, P. R.; Kim, K. J.; Kim, Y. H. J Korean Fiber Soc 1999, 36, 132.
8. Hoffman, D. M. J Appl Polym Sci 2002, 83, 1009.
9. Wu, C.; Yanagishi, T.; Makamoto, Y.; Ishida, S.; Nitta, K.; Kubota, S. J Polym Sci 2000, 38, 2285.
10. Cascone, M. G. Polym Int 1997, 43, 55.
11. Cho, D.; Choi, Y.; Drzal, L. T.; Polymer 2001, 42, 4611.
12. Krumova, M.; Lopez. D.; Benavente, R.; Mijangos, C. Polymer 2000, 41, 9265.
13. Lee, S. Y.; Kim, B. K.; Xu, M. Polymer 1996, 37, 5781.
14. Dutra, D.; Soares, B.; Campos, E.; Silva, J. Polymer 2000, 41, 3841.