

Vibration Control Ability of Multilayered Composite Material Made of Epoxy Beam and Polyurethane Copolymer with Shape Memory Effect

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Received 9 February 2004; accepted 5 April 2004

DOI 10.1002/app.20902

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

ABSTRACT: Sandwich-type layered composite material was prepared with epoxy beam and polyurethane copolymer that was synthesized from 4,4-methylene bis (phenylisocyanate), poly(tetramethyleneglycol), and 1,4-butanediol as a chain extender. As for the polyurethane, shape recovery was improved with higher content of hard segment, and the highest damping effect as judged by $\tan \delta$ was observed at 30–35% hard segment. The composite material had better

impact strength and higher $\tan \delta$ than epoxy beam alone, but the superiority became less as more hard segment was incorporated. The interfacial binding force between polyurethane and the epoxy beam also decreased in proportion to the hard segment content. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 302–307, 2004

Key words: sandwich; layered structure; smart material

INTRODUCTION

These days, a lot of smart materials that can be applied to controlling vibration have been reported. For example, sandwich-type composite material made of shape memory polymer with elastic properties was tested for the potential application to mechanical parts that required high vibration control ability.^{1,2} Shape memory polymer, one of the smart materials, is known to sense thermal, mechanical, electrical, or magnetic change in its surroundings and respond effectively by utilizing its distinct properties such as shape memory, shape recovery, shape retention, or shock absorption. Additional merits such as lightness ($d = 1.0\text{--}1.3 \text{ g/cm}^3$), high shape recovery ratio (more than 400%), and ease of processing render shape memory polymer more attractive. Shape memory polyurethane, which we have chosen for this study, was introduced in 1988 by the Nagoya Research and Development Center of the Mitsubishi company and is composed of a hard segment and a soft one, showing a range of glass transition temperature ($-30\text{--}60^\circ\text{C}$) and complete recovery from distortion.³ Specifically, 4,4'-diphenylmethanediisocyanate (MDI) and polytetramethyleneglycol (PTMG, MW = 2000 g/mol) were used for

polymerization with 1,4-butanediol (BD) as chain extender (Fig. 1). The fact that the hard segment and the soft one in shape memory polymer can realign to form a hard domain and a soft one through various interactions such as hydrogen bonding and dipole–dipole interaction seemed to provide the momentum necessary for recovering the original shape.⁴

It was already reported that composite material that has a shape memory polymer layer sandwiched between two carbon fiber layers shows higher $\tan \delta$ and better damping effect than carbon fiber alone.⁵ We were intrigued by the remarkable shape recovering properties of polyurethane and decided to apply it to the preparation of composite material with an epoxy beam for carbon fiber. Although the epoxy beam has a few advantages such as high strength and robustness considering its weight and cost, it easily breaks upon external impact because the energy is not effectively absorbed by itself. Thus, if another material that can reduce the impact is combined with the epoxy beam, an ideal composite that can resist external impact can be developed. Shape memory polyurethane with its high damping effect and $\tan \delta$ is a highly plausible candidate for the impact-absorbing material. From the polyurethanes with different compositions of hard and soft segments, we selected the one with the best physical properties and used it for the preparation of composite material with epoxy beam, together with characterization in the points of shape memory and damping effects.

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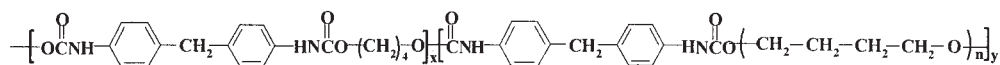


Figure 1 Structure of polyurethane block copolymer.

EXPERIMENTAL

Materials

MDI from Junsei Chemical and PTMG (MW = 2000 g/mol), a generous gift from Cheil Chemical, were dried in a vacuum oven for 5 h before use, and BD from Duksan Chemical was dried and stored over a 4-Å molecular sieve. Epoxy beam with 0.5 mm thickness that was fortified with glass fiber was obtained from Korea Fiber Co.

Polymerization

MDI and PTMG at the equivalent ratio specified in Table I were placed in a four-neck reaction vessel equipped with a stirrer, nitrogen purge, and oil bath, and then BD as a chain extender was added depending on the molar ratio of NCO/OH. Polymerization went on further until the remaining isocyanate group disappeared as detected by a separate amine titration method. After polymerization, the sticky polyurethane was completely dried in an oven for 3 days and spread in a mold to prepare a sheet. Molecular weight of the polymer was determined by GPC (Younglin Model M930).

Preparation of test specimen

Synthesized polyurethane after additional drying at 100°C for 24 h was used for preparing mechanical test specimens by a mini-max molder (Bautech Model BA-915); the molding temperature was adjusted between 160 and 230°C depending on the composition of hard and soft segments and the thickness was set to 3 mm. To prepare a multilayered composite sheet, polyurethane was melted at 160–230°C and pressed by hydraulic force to a sheet (150 × 100 × 0.1 mm); the polyurethane sheet was sandwiched between two epoxy beam sheets with 0.5-mm thickness and the combined sheets were again pressure molded (see Fig. 2).

Thermal analysis

Glass transition temperature (T_g) and melting temperature (T_m) were detected by DSC (Du Pont DSC-2000). After being melted at 250°C for 5 min and quick cooled to -50°C, the specimen was warmed to 250°C at 10°C/min, while phase transition was monitored. To find the heat of crystallization the specimen was melted at 250°C at the start and cooled to -50°C at a rate of -10°C/min.

Mechanical analysis

Tensile strength was measured according to ASTM D638 by UTM (Lloyd Instrument, Model LR50K) with a dumbbell-type specimen under the following conditions: gauge length = 25 mm; crosshead speed = 10 mm/min; load cell = 2.5 kN. Shear test was also measured by UTM for the specimen shaped like the one in Figure 3 and the conditions were 1 mm/min of crosshead speed and 2.5 kN of load cell. Impact strength was measured by Impact Tester (Testing Machine, Inc., Model TMI 43-02, pendulum 75 kg/cm) by unnotched Charpy method.

Thermomechanical analysis

The above-mentioned UTM equipped with a temperature-controlled chamber was used to measure stress and strain at various temperatures for the investigation of shape memory: for shape retention, L_1 was measured by drawing the specimen 100% at 20°C above T_g for 5 min and letting it shrink at 20°C below T_g for 30 min; for shape recovery, L_2 was measured after the specimen was incubated at 20°C above T_g for 10 min and cooled at 20°C below T_g . The measurements were repeated three times, and shape retention rate and shape recovery rate could be calculated with L_1 and L_2 from the following equations.

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

TABLE I
Composition of Polyurethane Block Copolymers

Sample code	Molar ratio			Hard segment (wt %)	MW	T_g
	MDI	PTMG	BD			
PU55	5.0	1.0	4.0	45	82,000	-7.8
PU60	4.0	1.0	3.0	40	131,000	-8.0
PU65	3.5	1.0	2.5	35	97,000	-8.5
PU70	3.0	1.0	2.0	30	145,000	-9.0

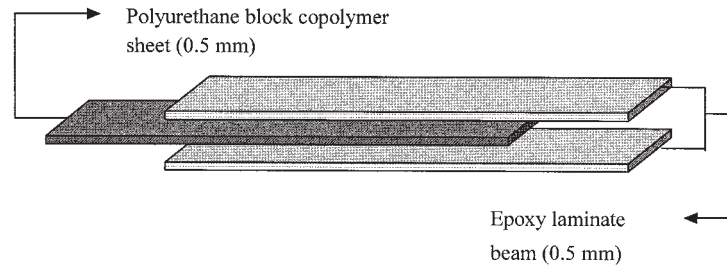


Figure 2 Sandwich-structure of composite laminate.

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

Dynamic mechanical analysis

Vibration control and damping effects were investigated by a Dynamic Mechanical Analyzer (Rheometric Scientific, Mark IV, UK), and loss $\tan \delta$ for the specimen sized $5 \times 8 \times 1$ mm ($l \times w \times d$) was tested at a heating rate of $3^\circ\text{C}/\text{min}$ between -60 and 65°C . Polyurethane was measured in tension mode, but composite material was done in 3-point bending mode.

RESULTS AND DISCUSSION

Mechanical analysis

Tensile strength

Figures 4-6 show tensile results of polyurethane block copolymers at various hard segment contents: maximum stress and elasticity increased as more hard segment content was included (Figs. 4 and 5), but elongation at break decreased (Fig. 6). Polyurethane has two different phases, a glassy hard segment with high T_g and a rubbery soft segment with low T_g , which are immiscible and contribute to shape recovery through interchain interactions such as hydrogen bonding and Van der Waals interaction. As the percentage of hard segment goes up, stronger interactions among chains lead to crystallinity of the hard segment, high tensile strength, and high modulus, but elongation at break decreases due to the interactions.

Impact test

An unnotched specimen was used (Fig. 7) because a notch may change the surrounding composite structure where the impact was delivered, especially for a fiber-reinforced composite, for which the mechanical properties were strongly affected by the volume change of component material, which may thus affect its tensile results.⁶ The composite composed of epoxy beam and shape memory polyurethane showed as much as 4 times higher impact strength than epoxy beam alone, and the impact strength slowly decreased with high hard segment content. The high impact strength of the composite compared to the epoxy beam originated from the inclusion of impact-absorbing polyurethane and the small decrease of impact strength at high hard segment content resulted from the growing interchain interactions of hard segments and the resultant rigid nature of the polyurethane layer, together with the weak interfacial binding of the composite due to the rigidity of the polyurethane layer.⁷

Lab shear test

Composite material, especially including shape memory polymer, was applied for vibration control and noise reduction, and the outstanding performance was traced to high interfacial contact among each components.^{8,9} In Figure 8, the interfacial binding forces were measured for the composite by the lab shear test. Lab

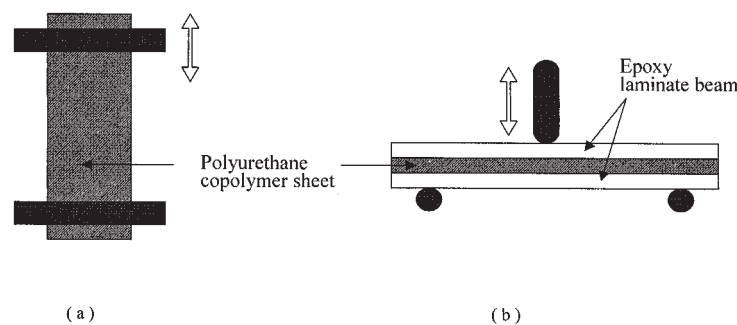


Figure 3 Testing method of dynamic mechanical thermal analysis. (a) Tension mode and (b) 3-point bending mode.

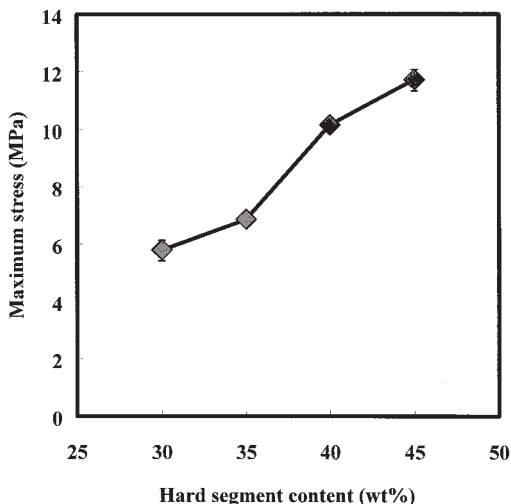


Figure 4 Maximum stress profile at various hard segment contents (bar indicates 95% confidence limit).

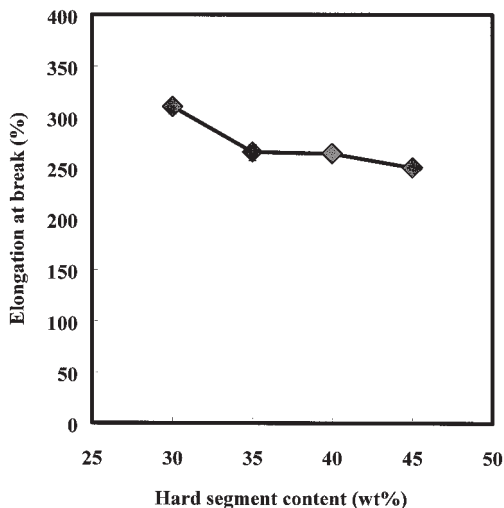


Figure 6 Percentage elongation at break profile at various hard segment contents (bar indicates 95% confidence limit).

shear stress decreased as the hard segment content increased, which could be understood from the fact that polyurethane layer became rigid at high hard segment content and interfacial binding at the contact area accordingly weakened, thus resulting in the bound layer peeling off easily.

Thermomechanical analysis

Shape recovery and retention results from three independent experiments are shown in Figures 9 and 10. In order for the shape memory polymer to work, glassy hard segments should maintain their shape through inter- or intramolecular attractions such as hydrogen bonding or dipole-dipole interaction, together with the physical crosslinking, but soft segments could freely absorb external stress by unfolding or extending

their molecular chains. If stress exceeds and breaks the interactions among hard segments, shape memory will be lost and the original shape cannot be restored.^{10,11} Therefore, precise control of the composition and structure of hard and soft segments is very important to satisfy the conditions required for various composite smart materials. Polyurethane with 30–45% hard segment recovered 80% of the initial shape after the first elongation-recovery cycle, but the recovery ratio was slowly reduced as more cyclic tests were tried, suggesting that some hard segments were not properly oriented for the attractions after repeated deformation. However, shape recovery was better for those with higher hard segment content, and shape retention was still maintained at greater than 85%.

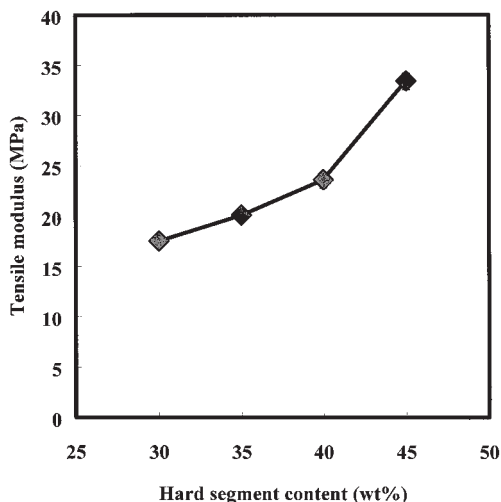


Figure 5 Tensile modulus profile at various hard segment contents (bar indicates 95% confidence limit).

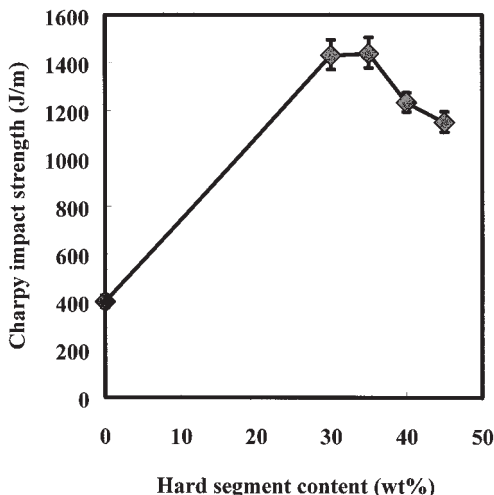


Figure 7 Unnotched Charpy impact strength profile at various hard segment contents (bar indicates 95% confidence limit).

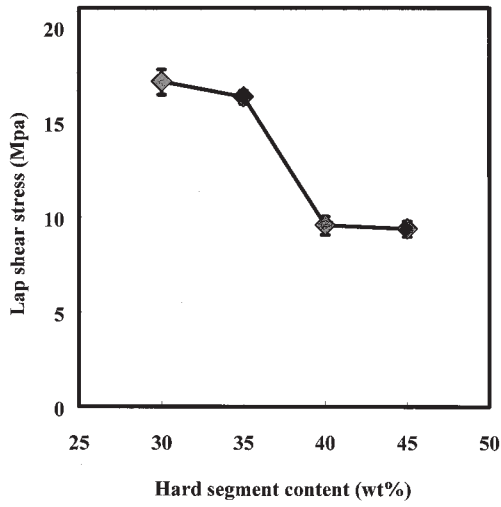


Figure 8 Lap shear stress profile at various hard segment contents (bar indicates 95% confidence limit).

Dynamic mechanical analysis

In Figure 11 where the plot of storage modulus versus temperature for the polyurethane with hard segment contents between 30 and 45% is shown, storage modulus increased with hard segment content because additional interactions among hard segments due to the above-mentioned intermolecular forces resulted in interchain attraction and crystallization. The soft segment partially contributed to storage modulus through the entropy effect by uncoiling its entangled chain while the polymer was stretched.^{12,13} Loss $\tan \delta$ versus temperature at various hard segment contents is shown in Figure 12; the highest loss $\tan \delta$ was observed at 30% hard segment and a significant reduction in loss $\tan \delta$ was found around the glass

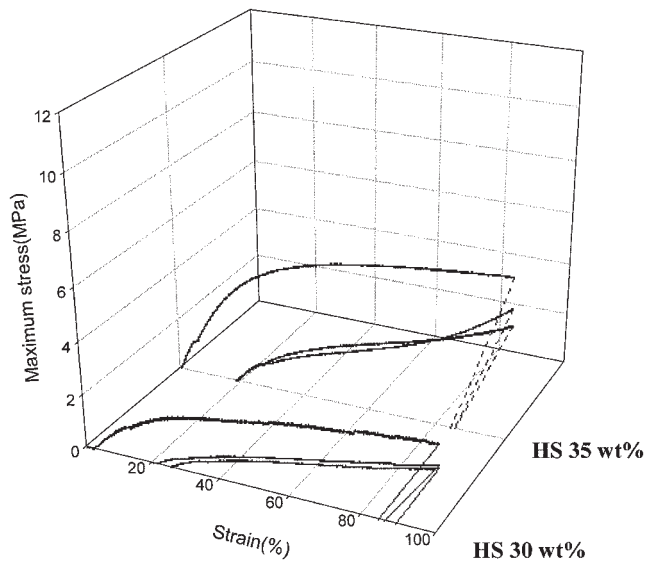


Figure 9 Cyclic shape memory test of polyurethane with 30 or 35% hard segment content.

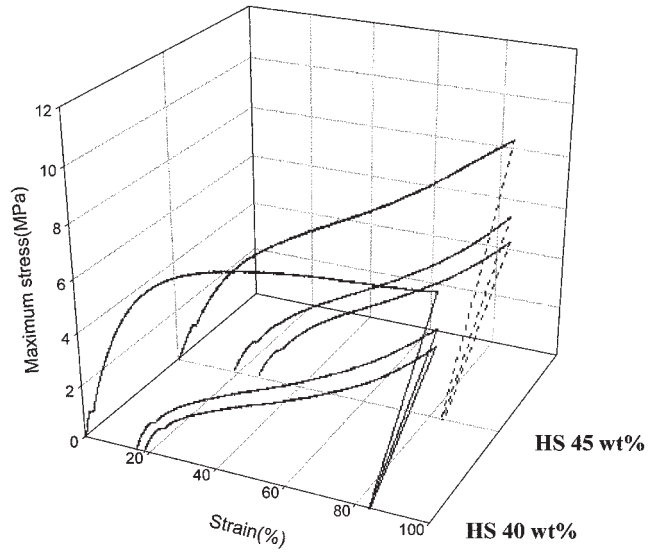


Figure 10 Cyclic shape memory test of polyurethane with 40 or 45% hard segment content.

transition temperature, which depended on the phase separation of hard and soft segments and crystallization of soft segments.

In Figure 13, composite material generally showed lower storage modulus than that of epoxy beam alone and storage modulus increased with hard segment content as with other previously observed properties.^{11,12} Although phase transition was not clearly observed for the composite material, a slight change in storage modulus could be detected around the transition temperature. Loss $\tan \delta$ of the composite material is shown in Figure 14. The shape memory polymer that was used for the preparation of smart material is known to absorb vibration most effectively around T_g , because of its high damping effect at that temperature,

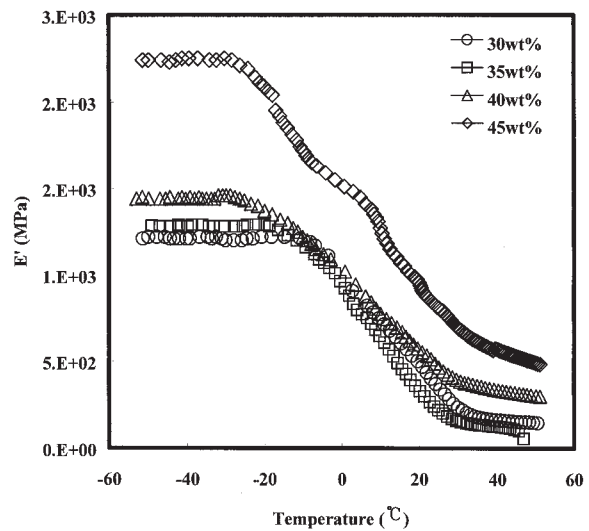


Figure 11 Tensile storage modulus versus temperature profile of polyurethane with various hard segment contents.

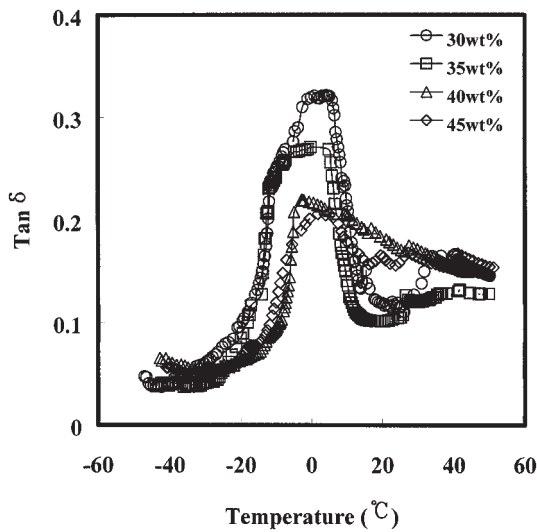


Figure 12 Loss tan δ versus temperature profile at various hard segment contents.

which paved the way for developing a new smart fabric that can absorb vibrational shock.¹⁴⁻¹⁷ Although composite material is quite rigid due to the inclusion of the epoxy beam, loss tan δ can be raised by reducing the hard segment content and the maximum of 5 times the difference is observed at 30% hard segment. Overall, careful control of the phase transition temperature of the composite material will make it possible to develop a composite material with enhanced vibration control.

CONCLUSION

Shape memory polyurethane copolymers with various hard segment contents between 30 and 45% were syn-

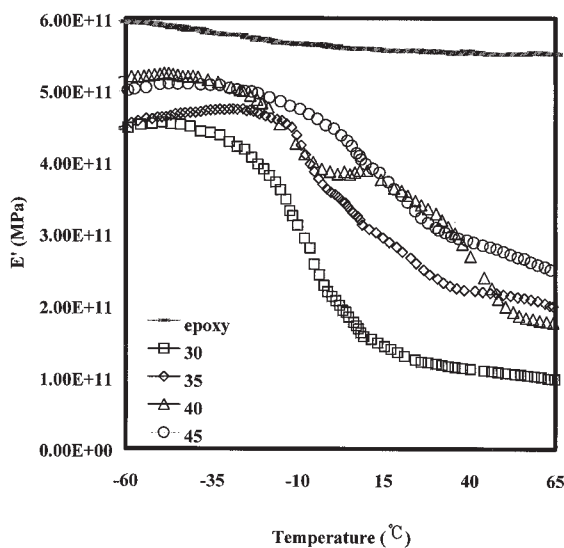


Figure 13 Storage modulus versus temperature profile of composite (polyurethane/epoxy beam) with various hard segment contents.

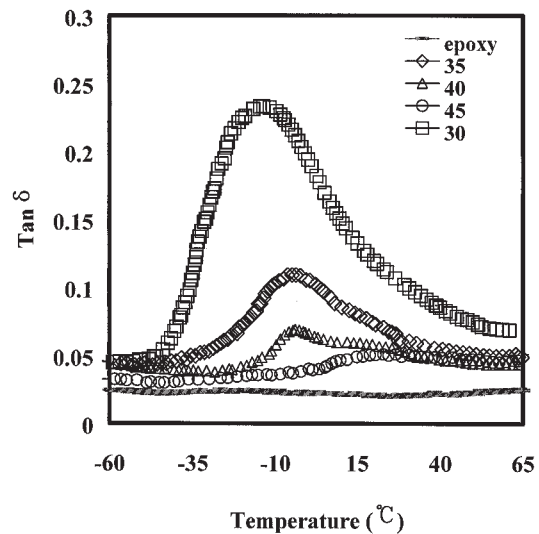


Figure 14 Loss tan δ versus temperature profile of composite (polyurethane/epoxy beam) with various hard segment contents.

thesized in two steps and were used for the preparation of layered composite materials that were characterized in the points of mechanical properties, shape recovery, and damping effect. As the hard segment content in the polyurethane increased, higher shape recovery was observed; especially, 30% hard segment showed the best damping effect. The composite material made of the shape memory polyurethane attained 5 times higher impact strength and 4 times better damping effect than epoxy beam alone. Therefore, it is quite feasible for the shape memory polyurethane to be utilized as a layered composite material in fields that demands high vibration control ability.

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