Damping Properties of Interpenetrating Polymer Networks of Polyurethane-Modified Epoxy and Polyurethanes

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ABSTRACT: Interpenetrating polymer networks (IPNs) were prepared from polyurethane (PU)-modified epoxy with different molecular weight of polyol and polyurethanes based on the mixture of polydiol and polytriol by a one-shot method. Two types of PU-modified epoxy: PU-crosslinked epoxy and PU-dangled epoxy were synthesized, and the effects of the different molecular weights of polyol in the PU-modified epoxy/PU IPNs on the dynamic mechanical properties, morphology, and damping behavior were investigated. The results show that the damping ability is enhanced through the introduction of PU-modified epoxy into the PU matrix to form the IPN structure. As the molecular weight of polyol in PU-modified epoxy/PU IPNs exhibit much higher damping property than that of the PU-crosslinked epoxy/PU IPNs with 20 wt % of PUcrosslinked epoxy. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 328–335, 1999

Key words: IPNs; polyurethane-modified epoxy; one-shot method

INTRODUCTION

Viscoelastic polymeric materials are used for attenuating the sound and damping the vibration. In the views of the macrostructure of the polymer, the capability of the polymer to dissipate the sound or the vibrational mechanical energy into heat depends on the intensity and broadness of the loss modulus or tan δ peaks at the applying temperature. As the temperature or frequency varies, the loss modulus (E'') and loss tangent (tan δ) show a peak value, where damping reaches a maximum.¹ Generally, the damping peaks of known homopolymers ranges between 20–30°C,² which is rather narrow for practical applications. To obtain material useful in the damping application, the damping peaks should be broadened, and thereby improve the damping property. On

the other hand, the damping behavior of polymers is due to (a) intramolecular friction and molecular relaxation, (b) friction between polymer chain and filler, (c) friction between filler and filler, and (d) deformation of microbulbs in cellules and the nature of polymers;³ therefore, the damping properties of the polymer can be tunneled by varying the microstructure of the polymers such as the formation of the copolymer polymeric blends or the interpenetrating polymer networks (IPNs).⁴⁻¹³ According to our previous work,^{14,15} Epoxy/polyurethane (PU) interpenetrating polymer networks exhibit excellent damping properties.

The characterization values for damping property were proposed with LA (the area under the loss modulus vs. the temperature curve) and TA (the area under the tan δ vs. the temperature curve).^{16–18} The LA value is related to the molecular structure of the polymer and affected by the crosslinking density, morphology, and miscibility, but it is independent of decrosslinking or annealing of the IPNs.^{19,20}

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Designation	Description	Source
PPG400	Poly(oxypropylene) glycol MW = 400	ACRO Chem. Taiwan Co. Taiwan.
PPG1000	Poly(oxypropylene) glycol MW = 1000	ACRO Chem. Taiwan Co. Taiwan.
PPG2000	Poly(oxypropylene) glycol MW = 2000	ACRO Chem. Taiwan Co. Taiwan.
PPG4000	Poly(oxypropylene) glycol MW = 4000	ACRO Chem. Taiwan Co. Taiwan.
PPG3000	Poly(oxypropylene)triol, ethylene oxide capped	ACRO Chem. Taiwan Co. Taiwan.
MDI	4,4'-diphenyl methane diisocyanate. Eq. wt = 125.	BASF Wyandotte Co. Switzerland
EPOXY	Diglycidyl ether of bisphenol A EEW = 186, n =	-
	0.11267.	Dow-Chemical Co. USA
TDMP	2,4,6, tri(dimethyl aminomethyl) phenol.	Ciba-Geigy Co., Switzerland
DBTDL	Dibutyltin dilaurate(catalyst $SnO/o = 18$)	Merk Co. Germany

 Table I
 Materials Used in This Study

In this study, two types of IPNs of PUcrosslinked epoxy or PU-dangled epoxy where one of ends of the PU chain is bonded on epoxy and the other is free, and PU based on polyether polyol with different molecular weights were prepared for application as a damping material. The LA and TA were measured to characterize damping property of these IPNs. The effect of the molecular weight of polyol of PU-modified epoxy in the IPNs and structure of different PU-modified epoxy in the IPNs on the damping behavior and dynamic mechanical properties were investigated.

EXPERIMENTAL

Materials

The materials used and their designations are listed in Table 1. Poly(oxypropylene) glycol (PPG400, PPG1000, PPG2000, PPG4000), Poly-(oxypropylene)triol(PPG3000), and epoxy (DGEBA) were degassed at 80°C for at least 12 h. The 4,4'diphenylmethane diisocyanate (MDI) was melted at 70°C before it was used. The 2,4,6-tri(dimethyl aminomethyl)phenol (TDMP) was used as received without further purification.

Preparation of the Polyurethane Prepolymer

The polyurethane prepolymer was prepared by two equivalents of MDI and one equivalent of polyol. The reaction of MDI and polyol was carried out at 70°C under nitrogen. The reaction was stopped when the —NCO content, which was determined by the di-n-butylamine titration method,²¹ reached the theoretical value.

Preparation of Polyurethane-Crosslinked Epoxy²²

The PU prepolymer was put into a reaction kettle that was maintained at about 68°C under nitrogen. A suitable amount of epoxy (the equivalent ratio of the —NCO group of the PU prepolymer and hydroxyl group of the epoxy is 1.05) was then poured into the kettle under vigorous mixing. The crosslinking reaction occurred between the pendant hydroxyl groups of the epoxy resin and the isocyanate groups of the PU prepolymer. A few drops of dibutyltin dialurate (DBTDL) were added and vigorously agitated for several hours.

Preparation of Polyurethane Dangling in Epoxy

PU prepolymer was put into a reaction kettle that was maintained at about 68°C under nitrogen. A suitable amount of epoxy (the equivalent ratio of the —NCO group of the PU prepolymer and hydroxyl group of the epoxy is 2.1) was then poured into the kettle under vigorous mixing. The grafting reaction occurred between the pendant hydroxyl groups of the epoxy resin and the isocyanate groups of the polyurethane prepolymer. When the grafting reaction was completed, alcohol was added to the reaction system. The remaining isocyanate groups of the PU prepolymer in the system were terminated with the hydroxyl group of alcohol.

Preparation of PU-Modified Epoxy/PU IPNs

The preparation of PU-modified epoxy/PU IPNs was carried out with the polyurethane (PU) synthesized via a one-shot method. The IPNs were prepared by mixing two components together; one component being PU-crosslinked epoxy or PUdangled epoxy and MDI, and the other being the



Figure 1 Infrared spectra during progress of the reaction between isocyanate of the PU prepolymer and the pendant hydroxyl group of epoxy.

mixture of the PPG400, PPG3000, and TDMP. The mixture was vigorously stirred for 60 s with a high torque mechanical stirrer at about 60°C. It was then poured into a hot mold at 90°C and cured in a hot press under pressure of 13.7 MPa for 2 h. The sample was then postcured at 110°C for 24 h. Finally, the samples were removed from the mold and placed in a desiccator, where the relative humidity was maintained at 50%, for at least 3 days before they were tested.





Figure 2 Infrared spectra during progress of the reaction between isocyanate of the PU prepolymer and the pendant hydroxyl group of epoxy. (a) End of reaction; (b) beginning of reaction.

Testing Methods

The tensile strength and modulus were measured by using Tensilon (Model:TCF-RC, Yashima Works Ltd., Japan). The test procedure using the specifications of the ASTM D412-Die C type was followed with a strain rate of 100%/min, and at least five specimens were taken for the test.

The dynamic mechanical analysis (DMA) was carried out on a Perkin-Elmer DMA-7 from -100 to 150° C, with a heating rate of 3° C/min. The



Structure of PU(PPG1000)-dangled epoxy

Figure 3 1 H-NMR spectra of PU-dangled epoxy. (a) Without D_2O exchange; (b) with D_2O exchange. Structural formula of PU (PPG1000) dangled epoxy is also shown along with peak assignments.

measurement was performed on the extension mode with fixed dynamic and static stress with a force control. The frequency was set at 1Hz. The dimensions of the specimens were approximately $5 \times 1.5 \times 1$ mm.

The loss modulus area (LA) under the curve of loss modulus vs. temperature and the tan δ area

(TA) under the curve of tan δ vs. the temperature are calculated by integrating from -70 to 60° C.

Morphological studies were performed by using scanning electron microscopy (SEM). Microphotographs were taken on the surface, which was made by breaking the specimen in liquid nitrogen and then coating with gold powder.



Figure 4 Loss modulus (E'') vs. temperature for various PU (PPG)-crosslinked epoxy/PU IPNs at 20 wt % epoxy contents. (_____) PU (PPG1000), (---) PU(PPG2000), (---) PU (PPG4000).

RESULTS AND DISCUSSION

Reaction of PU-Modified Epoxy

The progress of the reaction between the isocyanate group of the PU prepolymer and the pendant hydroxyl group of the epoxy resin was followed by IR (Fig. 1). The disappearance of the —NCO peak at 2270 cm⁻¹ indicated the completion of reaction. The reaction scheme of the PU-crosslinked epoxy/PU IPN is shown in Scheme 1.

The intensity of the IR (Fig. 2) absorption peak at 915 cm⁻¹ for the epoxide groups did not change during the grafting reaction of the PU-modified epoxy system. It indicates that the group does not react with the isocyanate during the reaction at 68° C. The intensity ratio of the isocyanate peak (2270 cm⁻¹) to the epoxide peak (915 cm⁻¹) was



Figure 5 Loss modulus (E'') vs. temperature for various PU(PPG)-dangled epoxy/PU IPNs at 20 wt % epoxy contents. (_____) PU (PPG400), (---) PU (PPG1000), (---) PU (PPG2000).



Figure 6 Loss tangent $(\tan \delta)$ vs. temperature for various PU (PPG)-crosslinked epoxy/PU IPNs at 20 wt % epoxy contents. (——) PU (PPG1000), (--) PU (PPG2000), (--) PU (PPG4000).

employed as an indication of the degree of grafting reaction between the isocyanate groups of the PU prepolymer and the pendant hydroxyl groups of the epoxy resin. As shown in Figure 2, the intensity ratio was high at the beginning of the grafting reaction; as the reaction proceeded, it decreased and reached a constant value, indicating that the pendant hydroxyl groups of the epoxy had reacted completely with the isocyanate groups of the PU prepolymer. After the grafting reaction, the remaining isocyanate groups in this system were then terminated with the hydroxyl group of alcohol. Accordingly, the intensity ratio of the isocyanate absorption peak at 2270 cm^{-1} to the epoxide peak at 915 cm^{-1} was further reduced, finally approaching zero. This indicates that the PU was dangled in the epoxy chain. The reaction scheme of the PU-dangled epoxy/PU IPN



Figure 7 Loss tangent $(\tan \delta)$ vs. temperature for various PU (PPG)-dangled epoxy/PU TPNs at 20 wt % epoxy content. (_____) PU (PPG400), (---) PU (PPG1000), (---) PU (PPG2000).

Polyol M.W.	Tan δ Maximum	${ m Tan} \; \delta > 0.3$ Temperature Range (°C)	Tan δ at 20°C	${ m TA} { m Height} imes { m K}$	${ m LA} { m GPa imes K}$
1000 2000 4000	$0.53 \\ 0.54 \\ 0.70$	$-22 \sim 69 \ -30 \sim 67 \ -41.7 \sim 77$	0.44 0.52 0.69	$41.0 \\ 47.8 \\ 66.3$	$10.5 \\ 12.0 \\ 17.2$

Table II Damping Properties of PU-Crosslinked Epoxy/PU IPNs at 20 wt % Epoxy Content

is shown in Scheme 2. The dangling fraction of the PU-dangled epoxy calculated from the ratio of peak c to peak a in the NMR spectra (Fig. 3) and initial ratio of NCO/OH(=1.1) was about 91%.

Dynamic Mechanical Properties

Figure 4 shows the loss modulus of the PUcrosslinked epoxy/PU IPNs with different molecular weights of polyol at 20 wt % epoxy content. As can be seen from the width and intensity of the loss modulus peaks of the IPNs, the transition peaks are significantly affected, becoming broader and more intense by the PU-crosslinked epoxy having different molecular weights . In addition, the peak shifts to a low temperature as the molecular weight of polyol in the PU-crosslinked epoxy increases. This is due to the PU chain of the PU-crosslinked epoxy networks dissolving into the PU matrix and the epoxy, forming a microheterogeneous domain dispersed in the PU matrix. Another reason for peak shifting and broadening could be the decrease of the crosslinking density of the epoxy, and as a result of more PU chain in the PU-crosslinked epoxy of IPN and the distribution of relaxation times of molecules in the IPN becoming broader.

The loss modulus of the PU-dangled epoxy/PU IPNs with various PU-dangling chain lengths (Fig. 5) shows a similar tendency, as observed in Figure 6. The peak of the loss modulus of these IPNs shifted to lower temperatures as the PUdangling chain length increased in the epoxy. This is due to the introduction of the more flexible and branched PU-dangling chain into the epoxy of the IPN system. Because the dangling chain with a free chain end possess more effective molecular motion and energy loss, the intensity of the loss peak of PU-dangled epoxy/PU IPN increased, and the peak broadened as an increase of the molecular weight of polyol in PU-dangling chain of the epoxy.

The tan $\delta(E''/E')$, which indicates the damping ability of the material, is the ratio of mechanical dissipation energy to the storage energy. Therefore, a high tan δ value of the IPN is essential for damping material. The tan δ values of the PUcrosslinked epoxy/PU IPNs with a high molecular weight PU in the PU-crosslinked epoxy are larger than those of PU-crosslinked epoxy with a low molecular weight PU (Fig. 6). The tan δ peak broadens and increases in height as the molecular weight of the PU in the PU-crosslinked epoxy increases. The tan δ peaks of PU-dangled epoxy/PU IPNs (Fig. 7) show the same behavior as those in Figure 6. At 20 wt % epoxy composition in the IPN system, the tan δ curve exhibits a plateau at high values with large temperatures range from -30 to 60° C.

Damping Behavior

The area under the loss tan δ curve (TA) (integrated from -70 to 60° C) and the temperature ranges for the tan δ value higher than 0.3 are listed in Tables II and III. It is observed that the

Table III Damping Properties of the PU-Dangled Epoxy/PU IPNs at 20 wt % Epoxy Content

Polyol MW	Tan δ Maximum	${ m Tan}~\delta>0.3$ Temperature Range (°C)	Tan δ at 20°C	${ m TA} { m Height} imes { m K}$	$\begin{array}{c} \text{LA} \\ \text{GPa} \times \text{K} \end{array}$
400	0.64	$-15\sim >\!65$	0.64	45.0	6.6
1000	0.64	$-23\sim 69$	0.59	47.4	11.1
2000	0.67	$-31.2\sim>\!64$	0.65	56.7	15.2



Figure 8 Loss areas (LA) of IPNs at 20 wt % epoxy content. —□— PU (PPG)-crosslinked epoxy/PU IPNs, –▲– PU (PPG)-dangled epoxy/PU IPNs.

IPNs based on the PU-modified epoxy with the high molecular weight polyol in the PU have large TA and LA values. As the molecular weight of polyol in PU increases in these IPNs, the LA value increases. This effect is attributed to the long-chain molecule of the PU in the PU-modified epoxy, which decreased the crosslinking density in the PU-modified epoxy matrix. The TA and LA values of the PU-dangled epoxy/PU IPNs are larger than those of the PU-crosslinked epoxy/PU IPNs. This indicates that the PU-dangled in epoxy/PU IPNs have higher damping properties than the PU-crosslinked epoxy/PU IPNs. In both the IPNs system, the maximum tan δ value and the tan δ value at 20°C increase as the molecular weight of the PU in the epoxy increases.

The change in LA value with the increase in the molecular weight of the PU in the PU-modified epoxy is shown in Figure 8. As can be seen from the figure, the LA values of the PU-dangled epoxy/PU IPNs are larger than those of the PUcrosslinked epoxy/PU IPNs when the molecular weight of the PU in the PU-modified epoxy is higher than 1000. For the IPNs of the PU-modified epoxy with the polyol of a molecular weight of 400 in the PU, the LA value of the PU-dangled epoxy/PU IPN is lower compared with that of the PU-crosslinked epoxy /PU IPN. This can be attributed to the PU free chain end of the PUdangled epoxy in the system with higher molecular motion than the other PU-crosslinked system. The LA value indicates the ability of converting mechanical energy into heat through molecular motion. Therefore, the materials of the higher LA value have high damping properties in those selected temperatures or frequency ranges.

Morphology

The micrographs of the fractured surface of the PU-crosslinked epoxy/PU IPNs with various molecular weights of the polyol in the PU are shown in Figure 9. Small particles separate out from the matrix of these IPNs on the fractured surface. It reveals that heterogeneous microstructures are formed in the IPNs. This particle-matrix morphology of the material corresponding to high values of LA and TA is responsible for the excellent damping property. This is consistent with our earlier observation.

CONCLUSIONS

We have shown in this article that the damping properties are significantly improved by introduc-



е ×10к 0075 20кV 5µm

(b)

Figure 9 Microphotographs of PU (PBA)-crosslinked epoxy/PU IPNs at 20 wt % epoxy contents. (a) PU (PPG2000), (b). PU (PPG 4000).

ing PU-modified epoxy (PU-crosslinked epoxy or PU-dangled epoxy) into the PU matrix to form IPNs. PU-dangled epoxy/PU IPNs show broader loss modulus peaks than those of the PUcrosslinked epoxy/PU IPNs. The damping study of these two IPN types through the dynamic mechanical analysis indicates that the PU-dangled epoxy with a longer chain of the PU in the IPN system has a higher LA, TA, and broadened loss peak, which results in a higher damping ability.

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