

Studies on the Dynamic Mechanical and Vibration Damping Properties of Polyether Urethane and Epoxy Composites

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SYNOPSIS

The dynamic mechanical and vibration damping properties of polyether urethane and epoxy composites have been studied. The experiment results show: the crosslink density is an important factor that influences the loss factor of polyether urethane damping materials; increasing the amount of pendant methyl of the backbone contributes to raising the value of the loss factor ($\tan \delta$) and broadens the damping temperature range; adding the planar filler can increase the shear motion and the internal dissipation in polyurethane materials. As the thickness ratio and the Young's modulus of the constraining layer increase, the composite loss factor (η) increases significantly. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Damping for suppression of sound and vibration has become dramatically topical. There are an increasing number of high-payoff applications, both military and civilian. Polymers are often used in sound and vibration damping areas. In general, one of the most important polymer properties for these application is the glass transition. At the glass transition, a polymer is most efficient in converting sound and mechanical vibrational energy into heat that results in absorption. Early in the automobile industry the utility of a mastic deadener composed of asphalt filled with inorganic filler or fibers was recognized. Soon viscoelastic damping materials appeared.¹ Oberst² studied the extensional type damping composites composed of a viscoelastic layer on an elastic substrate (e.g., steel). Later the constrained layer damping configuration appeared.² This sandwich structure is composed of the substrate, a viscoelastic layer, and a second stiff elastic layer that may be metallic or plastic. It yields better damping than the extensional type. Oberst outlined the basic principles related to thickness ratios. The theory was developed by Kerwin³ and Ungar.⁴ It was noted in particular

that the composite loss factor (η) was related to the loss factor ($\tan \delta$) of the viscoelastic layer.⁴ By tailoring the polymer structure so that the glass transition is in the required temperature and frequency range, the polymer becomes an effective damper.⁵⁻⁷

Usually, the width of the glass transition region in terms of the temperature range of a polymer is narrow and not practical in sound and vibration damping. Many methods were utilized to broaden the temperature range and enhance the loss factor,^{5,7,8} such as blend, copolymerization, and forming IPNs, etc. The mechanical damping of polymeric material was contributed from:⁹

1. internal friction among macromolecules;
2. interaction between macromolecules and fillers;
3. mutual friction among fillers.

In this paper, a series of polyether urethane compositions with varying crosslink density, pendant methyl group amount, and fillers were prepared. The dynamic mechanical properties of these materials were studied and characterized.

The polyether urethane and epoxy composites is a kind of a constrained layer damping configuration (see Fig. 1). The damping layer is composed of polyether urethane and the constraining layer is composed of epoxy resin. The composite loss factor

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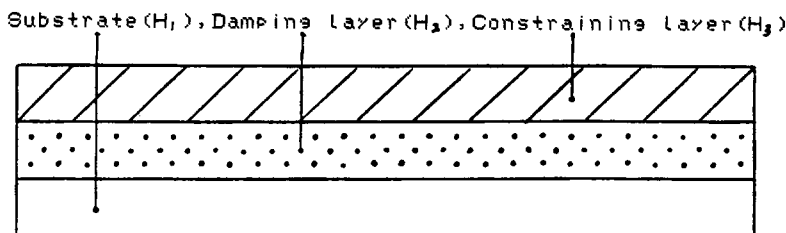


Figure 1 Constrained layer damping configuration.

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is related to the loss modulus of the damping layer divided by the elastic modulus of the substrate and to the square of the thickness ratio.³ Both the damping layer and the constraining layer are easy to apply by trowel, brush, or spray. It was found that the composite loss factor increased as the thickness ratio or the Young's modulus of the constraining layer increased.

EXPERIMENTAL

Materials

1. Poly(propylene oxide) glycol (PPG), equivalent weight 1000, Tianjin Third Petrochemical Factory.
2. Toluene-2,4-diisocyanate (TDI), Dalian Dyestuff Plant.
3. 1,4-Butandiol (1,4-BDO), No. 1 Chemical Agents Factory, Shanghai.
4. 1,6-Trimethyl-hexanediol (1,6-THO), Hüls Co., Germany.
5. Dibutyl tin dilaurate (T-12), Tianjin Chemical Agents Factory.
6. Epoxy resin (E-44), Jinan Resin Factory.
7. Epoxy curing agent (TF-1), Kunshan Auxiliary Factory.
8. Planar mica (PM), 160–200 mesh, Yaan Mica Co.
9. Mica (M), 320 mesh, Zhaoyuan Mica Factory.
10. No. 8 anti-corrosion primer (8#), Marine Coatings Research Institute, Qingdao.
11. Galvanized steel (Fe) and aluminum foil (Al), Qingdao Aluminum Products Factory.
12. Steel beam, A3 gauge, Jinnan Steel & Iron Factory, degreased with xylene, immersed in dilute nitric acid 1 : 10 for 15 min at 60°C, rinsed with distilled water, then acetone, dried and coated with 8# primer, dried, and stored in a desiccator until used.

Synthesis of PU

Prepolymer was prepared from PPG having nominal equivalent weight 1000 and TDI. When the diisocyanate was used, the process was suitable with a nitrogen atmosphere. The polyol, which was added to the stoichiometric amount of TDI at 50–55°C, produced an exothermic reaction that raised the temperature to 80°C. The mixture was held at 85–90°C for 1–2 h and the mixture was then degassed, cooled, and sealed under nitrogen. The percent isocyanate was determined by the dibutyl amine method. The prepolymer (PPG-TDI, TDI/PPG stoichiometrical ratio 2 : 1), was chain extended with 1,4-BDO and 1,6-THO.

Constraining Beam Preparation

The steel beam was coated with the polyether urethane (PU), dried and then coated with the epoxy resin (EP). The thickness of the damping layer H_2 to the thickness of the substrate H_1 is defined as h_2 . Likewise, the thickness of the constraining layer H_3 to the thickness of the substrate H_1 is defined as h_3 ; and the thickness of the total layers (both H_2 and H_3) to the thickness of the substrate H_1 is defined as h_{23} .

Measurements

Dynamic Mechanical Property

The prepolymer was mixed with the chain extender, the filler, and the catalyst in appropriate proportion. The mixture was heated to 90°C and degassed under -0.1 MPa vacuum, then poured into PTFE molds and cured at room temperature for 24 h and post-cured for 72 h before testing. The samples were cut into thin sheets. A Rheovibron model DDV-III-EA direct reading viscoelastometer was used to measure the dynamic mechanical properties at 110 Hz over the temperature range -60 to $+100$ °C. The complex (E), storage (E'), and loss (E'') moduli were cal-

culated and tangent of the phase angle (δ) recorded. The $\tan \delta$ was defined as the loss factor.

Vibration Damping Property

The vibration damping property in terms of the composite loss factor (η) were measured with a Brüel and Kjaer Complex Modulus Apparatus Type 3930 in connection with a Brüel and Kjaer Sine/Noise Generator Type 1024 and Level Recorder Type 2317.

The samples were steel beams coated with the PU/EP composites as mentioned above. The resonant beam test technique formed the basis of the ASTM Standard E756-83 for measuring the composite loss factor. The samples were placed in an environmental chamber operated over the temperature range -10 to $+50^\circ\text{C}$. The composite loss factor was determined from the sharpness of the resonance curves $\eta = \Delta f/f_n$ in which f_n is the undamped resonance frequency of resonance mode n and Δf is the band width 3 dB down from the n th resonance peak.

RESULTS AND DISCUSSION

PU Damping Layer

Crosslink Density

Polyurethanes are alternating block copolymers made of soft segments derived from polyester or polyether diols and hard segments derived from the

diisocyanate and diol chain extender.¹⁰ Because the soft and hard segments are chemically dissimilar, they tend to be incompatible and separate into different phases. In order to improve the phase mixing and coordination of the segments motion, the crosslink density of polyurethanes was varied. This was one of the modifying methods to improve the compatibility.¹¹

It is a simple method to change the equivalent ratio of isocyanate (NCO) and hydroxyl (OH) because the compositions are constant for studying the effect of crosslink density on the dynamic mechanical properties. The equivalent ratio of NCO/OH was defined as value α . The PPG-TDI prepolymer was chain extended with 1,4-BDO as the value α was 0.6, 0.7, 0.8, and 1.0, respectively. Their dynamic mechanical spectroscopies are shown in Figure 2. The value of $\tan \delta$ of these polyurethane materials increased as the crosslink density decreased (i.e., value α decreased) in the interesting temperature range -20 to $+80^\circ\text{C}$. This is caused by the fact that the compatible degree of soft and hard segments increased as the crosslink density decreased. In this way, the "fettering effect" caused by crosslinking was weakened, and the motion resistance of the hard segments was decreased simultaneously. Then the coordinative motion of soft and hard segments was increased. More and more macromolecules were joined to transform the configuration when the material was applied by external force. The internal friction among macromolecule segments was increased to convert the mechanical en-

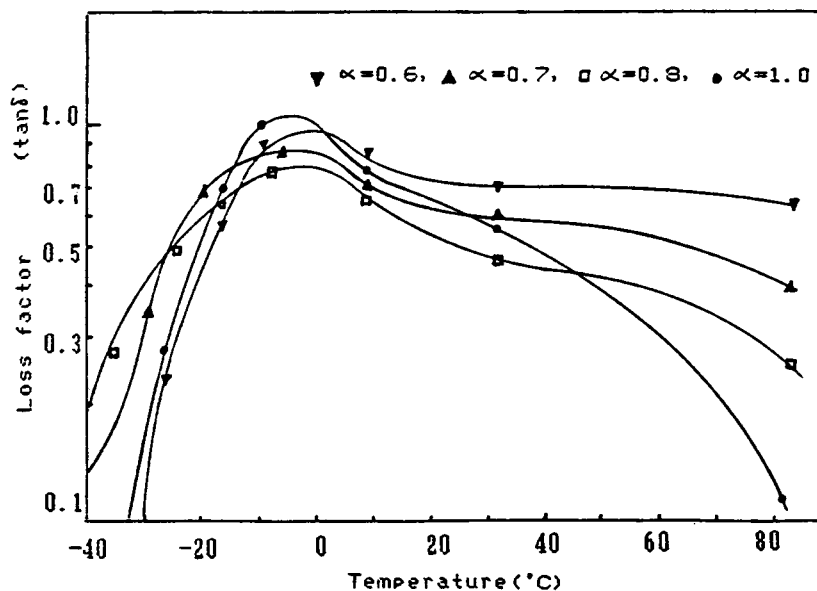


Figure 2 The effect of crosslink density on the loss factor.

ergy into heat. Meanwhile, the interaction between macromolecules and fillers became violent. The increment of the internal friction and the interaction increases the mechanical dissipation and enhances the vibration damping.

Pendant Methyl

The amount of pendant methyl had a significant effect on the mechanical damping of polymeric materials.¹² In this paper, the diol chain extenders of 1,4-BDO and 1,6-THO containing pendant methyls were selected. The crosslink density was constant when the 1,4-BDO and 1,6-THO were reacted. The dynamic mechanical spectroscopy of the PPG-TDI prepolymer chain extended with this two agents is shown in Figure 3. The major morphological difference between 1,4-BDO extended polymer and 1,6-THO containing pendant groups extended polymer yielded significant differences in the loss factors of the polymer system. Very wide ranges of temperature, $\tan \delta$ greater than 0.7, fell within the damping region broadened from -25 to $+50^\circ\text{C}$ of 1,4-BDO to as much as -45 to $+80^\circ\text{C}$ of 1,6-THO. It appeared that the increment of pendant methyl in the long-range structure of polymer would increase the internal friction resistance during the configuration transformation. Interfriction resistance between segments and fillers increased. It dissipated much more external energy when the material was applied. Therefore, the damping temperature range was broadened.

Planar Filler

Fillers have the same effect as hard segments providing there is adequate adhesion between the phases. Fillers often increase the Young's modulus and the loss factor yielding an apparently higher glass-transition temperature for the matrix.

In our research, PM, M, and their mixture were dispersed in the polyurethane binder, respectively. Their dynamic mechanical spectroscopies are plotted in Figure 4. The values of $\tan \delta$ of the samples adding PM, M, and the mixture were higher, lower, and in the middle, respectively. It showed that planar fillers had the property to increase the loss factor.¹³ The planar fillers tended to lie parallel in the plane of the polyurethane layer. They could be considered as a microconstraining layer. On calculating the vibration damping effectiveness from the loss factor, the data calculated for the constrained configuration closely approximated the actual data than did the values calculated for the extensional mode. In this way, the shear deformation in the microcosm took place among planar fillers instead of the extensional deformation in the macrocosm. This shear motion would increase the mutual friction among fillers, and the external energy would be converted into heat. Then the vibration damping property was increased notably.

PU-EP Composites Layer

In this study, the steel beam was coated with the PU damping layer and then a layer of galvanized

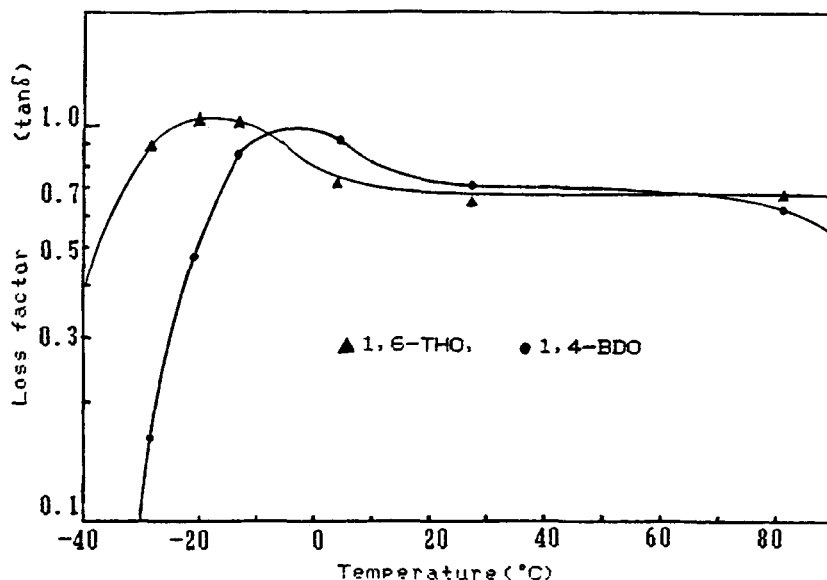


Figure 3 The effect of pendant methyl on the loss factor.

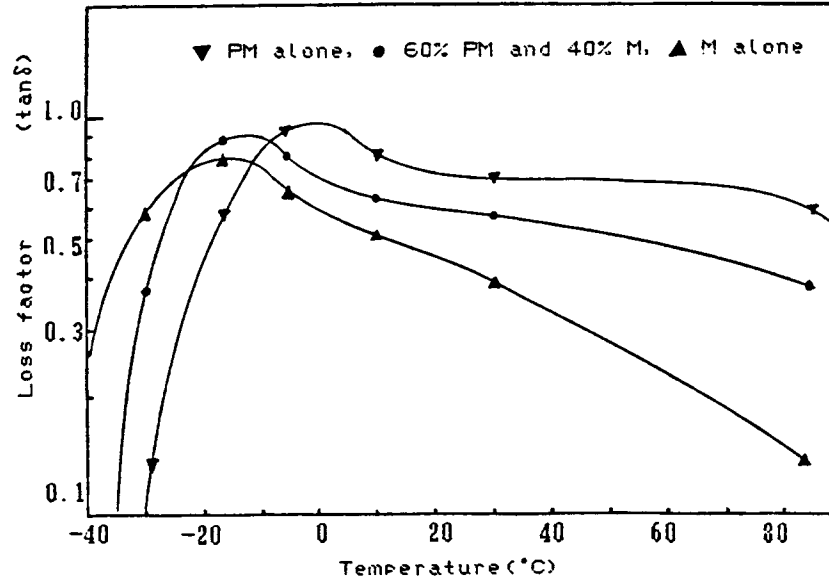


Figure 4 The effect of planar filler on the loss factor.

steel (Fe) and aluminum foil (Al) or epoxy resin was added as the constraining layer. The moduli of the steel, aluminum, and epoxy were, respectively, 2×10^{11} , 7.2×10^{10} , $1.5-7.5 \times 10^9$ Pa.

Thickness Ratio

Here the constraining layer was epoxy resin filled with fillers and fibers. When H_2 was constant, the composite loss factor increased as the H_3 increased because the composite loss factor of the constrained

layer configuration was related to the h_{23} (Fig. 5). But this was not practical to increase the composite loss factor by increasing the H_3 . When h_{23} was 2, the best result was the thickness ratio of $H_3/H_2 = 1 : 1$ varying the thickness ratios¹⁴ (Fig. 6). In addition, we found that the curve shapes all decreased as the temperature increased. This is because

1. the loss factor of the damping layer decreased as the temperature increased;

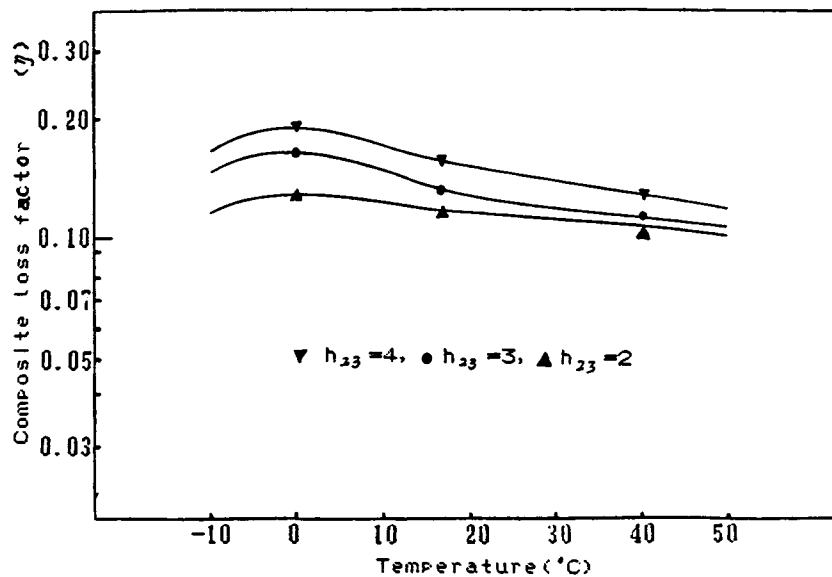


Figure 5 The effect of thickness ratio on the composite loss factor.

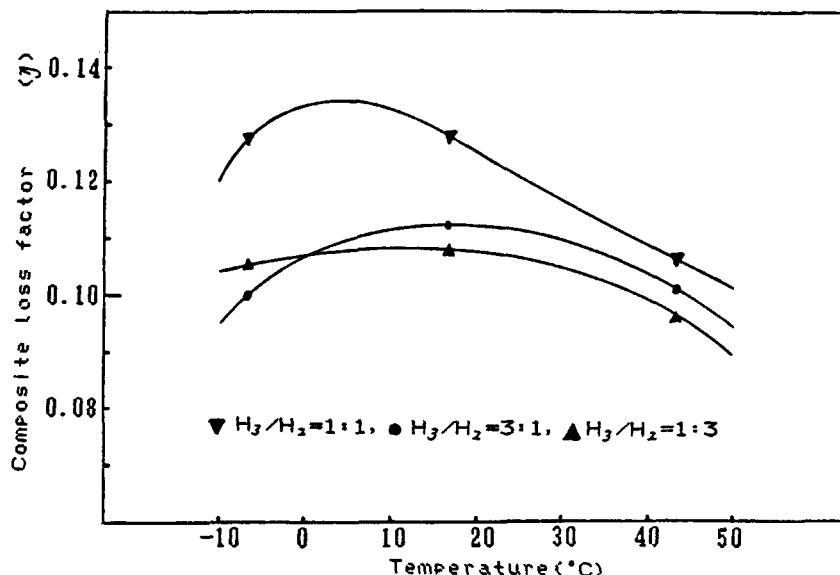


Figure 6 The effect of thickness ratio on the composite loss factor ($h_{23} = 2$).

- 2. the Young's modulus of the constraining layer decreased as the temperature increased, too.

Modulus

For the constrained layer system, the composite loss factor can be calculated by the following formula¹⁵:

$$\eta = \beta XY / [1 + (2 + Y)X + (1 + Y)(1 + \beta^2)X^2]$$

where β is the loss factor ($\tan \delta$), X is the shear parameter, and Y is the geometric parameter. Under otherwise identical conditions, Y depended on the modulus (E) and the thickness of the constraining layer. The lower modulus epoxy constraining layer, even at a greater thickness, was less effective as dis-

cussed above. Another effective method to increase the modulus of the constraining layer was to inlay the higher modulus Fe or Al foil to the epoxy constraining layer. The results are shown in Figure 7. This is because the higher modulus constraining layer containing Fe or Al foil will increase the effective value of shear motion of the damping layer and have a greater dissipation.

CONCLUSIONS

Based on the dynamic mechanical and vibration damping measurements reported here, the following specific conclusions were reached:

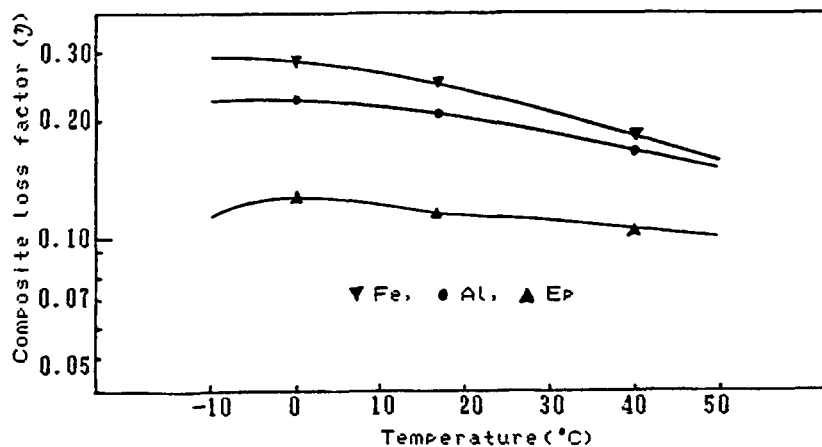


Figure 7 The effect of modulus of the constraining layer on the composite loss factor.

1. The proper crosslink density is conducive to increasing the internal friction among macromolecules and the interaction among macromolecules and fillers.
2. Pendant methyl groups of the hard segment can increase the internal friction resistance during the molecular configuration transformation.
3. Planar fillers behaved like microconstraining layers to increase the interaction between macromolecules and fillers, the mutual friction among fillers.
4. Increment of the thickness ratio and the Young's modulus of the constraining layer yields better damping.

REFERENCES

1. C. Zwikker and C. W. Kosten, *Sound Absorbing Materials*, Elsevier, New York, 1949.
2. H. Oberst, *Acustica, Akust. Beih.*, **2**, 181 (1952).
3. E. M. Kerwin, Jr., *J. Acoust. Soc. Am.*, **31**, 952 (1959).
4. E. E. Ungar, *Noise and Vibration Control*, L. L. Beranek, ed., McGraw-Hill, New York, 1971.
5. T. Hur, J. A. Mason, and L. H. Sperling, *J. Polym. Sci., Polym. Phys.*, **27**, 2251 (1989).
6. D. Klepner, L. Berkowski, K. C. Frisch, K. H. Hsieh, and R. Ting, *Polym. Mater. Sci. Eng.*, **52**, 57 (1985).
7. B. Hartmann, *Polym. News*, **16**, 134 (1991).
8. J. A. Manson and L. H. Sperling, *Polymer Blends and Composites*, Plenum Press, New York, 1976.
9. He Tianbai, Liu Jingjiang, and Yu Fusheng, *Polym. Commun.*, **1**, 30 (1986).
10. S. L. Cooper and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **10**, 1837 (1966).
11. Huang Weibo and Zhan Fengchang, *Polym. Mater. Sci. Eng.* **4**, 42 (1992).
12. He Manjun, Chen Weixiao, and Dong Xixai, *Polymer Physics*, Fudan University Press, Shanghai, 1983.
13. G. L. Ball and I. O. Salyer, *J. Acoust. Soc. Am.*, **39**, 663 (1966).
14. Huang Weibo and Zhan Fengchang, *Proceedings of The 3rd Chinese Youth Symposium on Material Science*, **2**, 56 (1991).
15. Dai Depei, *Sound and Vibration Damping Technology*, Xian Jiaotong University Press, Xian, 1986.

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