Investigation on Damping Behavior and Morphology of Polyurethane/Polymethacrylates and Polyacrylates Interpenetrating Polymer Networks

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SYNOPSIS

Simultaneous Interpenetrating Networks (SINs) were synthesized based on polyepichlorohydrin glycol (PECG), toluene diiocyanate (TDI), and trihydroxymethyl propane (TMP) as network I; and methyl methacrylate (MMA), ethyl methacrylate (EMA), methyl acrylate (MA), ethyl acrylate (EA), and ethyleneglycol dimethylacrylate (EGLM), respectively as network II. Damping behavior of the SINs was studied by a dynamic viscoelastometer. It was found that loss factor, tan δ, of PU/PEMA and PU/PEA is much higher than that of PU/PMMA and PU/PMA. The present authors consider that the length of pendant groups has an influence on the height of tan δ in the interpenetrating structure. Transmission electron microscopy (TEM) photos show that the SINs possess multiphase structures. These two networks are dispersed in a system microheterogeneously. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Interpenetrating polymer networks (IPNs) have been widely used as damping material with excellent results. Their structure and properties have been investigated.[1-4] The damping properties of a polymer are dominated by its glass transition. When the chain segments in a polymer backbone make de Gennes[5,6] reptation motions, molecular vibrational energy converts into heat energy and a loss peak appears in a certain temperature range. Usually, the glass transition region of a homopolymer is about 20-30°C. On the basis of the time–temperature superposition principle, this temperature region corresponds to two to four orders of frequency range. However, this range can hardly be met practically. The use of an IPN structure is the most effective way to widen the loss peak.

An IPN may be defined as a combination of two polymers or more in network form. If two polymers are miscible, the IPN obtained is homophase. However most IPNs exhibit a limited phase-separation multiphase structure. To obtain a material with a wide loss peak, two partly miscible polymers can be selected with not too great an interval in the glass transition temperature. The damping property of a material is related to the structure of the material. The height and width of the loss peak are mutually linked. Therefore, obtaining a loss peak which is both high and wide is impossible at the same time.[4] However, J. J. Fay et al.[7,8] considered that the area under linear loss modulus temperature curves related mainly to the chemical composition of the polymer, and was affected by morphology, crosslink density, and miscibility in multicomponent polymer systems. Hence selection of a suitable monomer and control of network density may make the loss peak reach an optimum.

The present authors synthesized simultaneous interpenetrating networks (SINs) consisting of a pair of polymers which have similar structure, and studied their structure and properties.[9,10] In Yu et al.,[9] the tan δ peaks of the IPNs are not high for the polymers not having enough good damping, and in Chen et al.,[10] the tan δ peaks are relatively wide and high for the polymers possessing good damping.

In this work, a series of SINs were synthesized

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with PECG–polyurethane as network I, and with PMMA, PEMA, PMA, and PEA as network II. Their dynamic mechanical properties were studied. It was found that loss tan δ peaks of PEMA and PEA are significantly higher than those of PMMA and PMA. There are no distinct differences in loss moduli of the four samples. The present authors consider that the length of pendant chains has an influence on the damping factor, tan δ. TEM shows that the SINs possess a multiphase structure. These two networks are dispersed in a system microheterogeneously. The domains of network I within PU/PMMA and PU/PEMA are about 40–120 nm in size. In PU/PMA and PU/PEA, the two networks occur in the form of a diffuse area. The appearance of local aggregation of network I chains about 100 nm in size, however, is presumed to be relative to the reaction rate of polymerization of network II.

EXPERIMENTAL

Synthesis

Toluene diiocyanate, methyl methacrylate, ethyl methacrylate, methyl acrylate, and ethyl acrylate were distilled under vacuum. Trihydroxymethyl propane was dried at 60–70°C for 4–6 h under a vacuum of 2 mmHg. Ethyleneglycol dimethacrylate was prepared by the present authors and its purity determined by IR. Polyepichlorohydrin glycol was also synthesized by the authors. The molecular weight was determined by GPC and VPO. $\bar{M}n$ = 1007. $\bar{M}w/\bar{M}n$ = 1.73.

Simultaneous interpenetrating networks were prepared based on PECG, TDI, and TMP as net-

work I; and MMA, EMA, MA and EA, and EGLM, as network II. Network II was initiated with benzoin. All components were weighed and added to the beaker, then homogeneously mixed (the monomer of network II should be in moderate excess). The air entrapped during mixing was removed by applying a vacuum for 1–2 min. The mixture was poured into a polytetrafluoroethylene mold and allowed to react for 20 h at room temperature, then heated to 60°C, holding at this temperature for 4 h. The reactant was irradiated with an ultraviolet lamp for 20 min. All samples were transparent films. The films were held at 60°C under a vacuum of 2 mmHg for 48 h, then weighed; the ratio of network I to network II was calculated with an error of ±2%. The samples were put in a desiccator. The components and appearance of samples are listed in Table I.

Dynamic Mechanical Properties

Dynamic mechanical properties were determined by a Rheovibron DDV–II–EA dynamic viscoelastometer. The samples were measured at a frequency of 110 Hz from –50 to 150°C at a heating rate of 2°C/min.

TEM

The samples were cut 0.5 × 0.5 × 10 mm, and then were embedded in epoxy resin and cured at 60°C for 24 h. The final specimens were cut to a thickness of about 100 nm using an LKB Ultratome at 0°C.

The samples were vapor stained in 0.2% aqueous solution of ruthenium tetraoxide (RuO_4) for 10–20 min[11] at room temperature. The stained samples were vacuum-dried for 24 h. Electron micrographs

Table I   The Components and Appearance of Samples

Samples	I Component PECG : TMP : TDI (mol)	II Component Acrylate : EGLM (mol)	I/II wt %	Appearance of Samples
PECG-PU	1.7 : 1.0 : 3.2	16 : 1	100/0	transparent film
PU/PMMA	1.7 : 1.0 : 3.2	16 : 1	70/30	transparent film, brittle
PU/PEMA	1.7 : 1.0 : 3.2	16 : 1	70/30	transparent film, tough
PU/PMA	1.7 : 1.0 : 3.2	16 : 1	70/30	transparent film, tough, local wrinkle and split after irradiating UV light
PU/PEA	1.7 : 1.0 : 3.2	16 : 1	70/30	transparent film, tough, local wrinkle and split after irradiating UV light

were taken with a Hitachi H–800 electron microscope at an accelerating voltage of 200 KV.

RESULTS AND DISCUSSION

Control of Synthesis Conditions

The present authors selected PU as network I and MMA, EMA, MA, and EA as network II. The above-mentioned four monomers are the same in the backbone chains, with slight differences in pendant groups. Their solubility parameters are similar and are shown in Table II.[12] These two networks are regarded as having partial miscibility, the structure of interpenetrating networks causing them to be more miscible.

The SINs were synthesized by two procedures. When all the reactants were mixed together, network

Table II   Solubility Parameters and Tg of Homopolymer (12)

polymer	δ (Cal/Mol.K)	Tg (°C)
PMMA	9.5	105
PEMA	8.9	65
PMA	10.15	10
PEA	9.4	−24
PECG-PU*	10.14	−15 (E″)

* Values available in this paper

I of PU was formed first and then network II was formed, because the condensation polymerization of network I and the addition polymerization of network II have different reaction rates at the temperature chosen. It is important to control reaction time and temperature. Network II should not be initiated
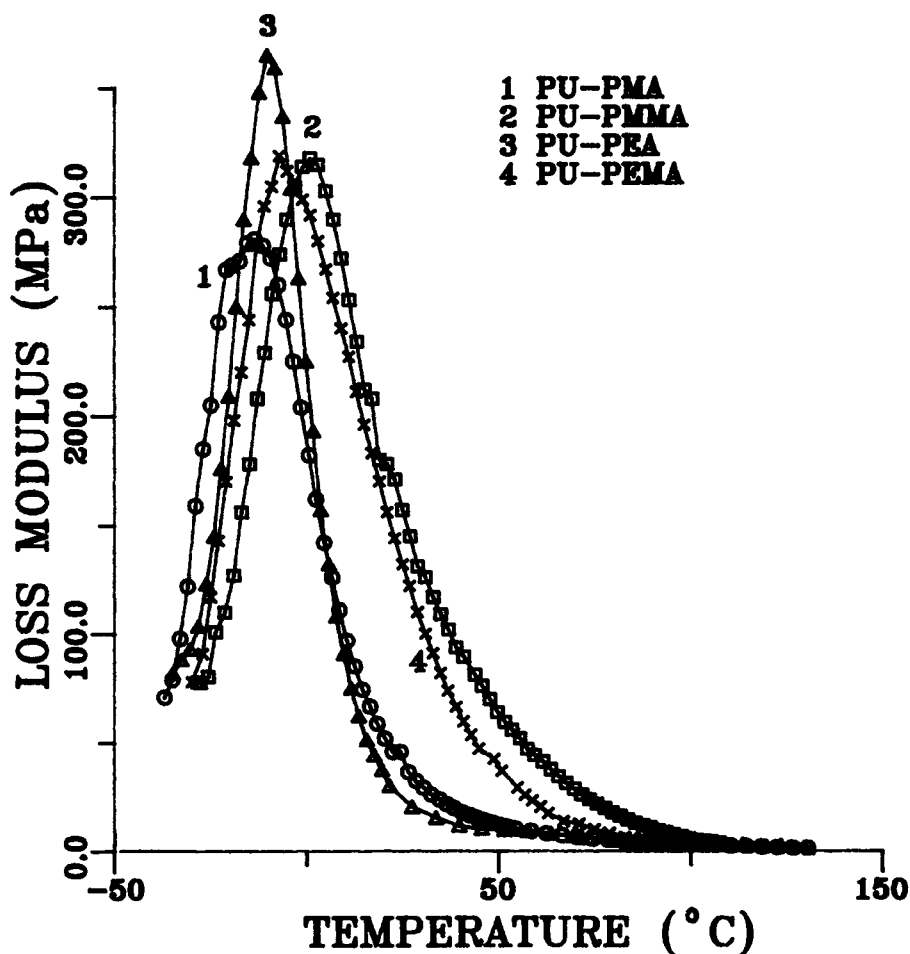

1 PU–PMA
2 PU–PMMA
3 PU–PEA
4 PU–PEMA

Figure 1   Linear modulus vs. temperature curves for SINs.

until network I has basically formed. It is done in this way because network II is not as easy to swell as network I because of its high viscosity. A good interpenetrating structure was formed under conditions where the monomer of network II was fully swelled in network I.

Making a comparison between the solubility parameters of the two polymers (see Table II), it can be seen that the solubility parameter of network I is similar to that of the four polymers. Therefore they should have good miscibility. The large diffuse area of the two networks shown in TEM pictures agrees with this observation.

All the samples were made under the same reaction conditions. However, the results were more or less different, the films of PU/PMMA and PU/PEMA being transparent and those of PU/PMA and PU/PEA being wrinkled or cracked after irradiation with UV light. The authors consider that the wrinkles and cracks may result from a high rate of polymerization.

The Dynamic Mechanical Properties

Dynamic mechanical experimental results for the four SINs are shown in Figures 1 and 2. These figures exhibit broader glass transition peaks, as shown by the linear loss modulus, E'', or tan δ versus temperature curves. For the E''–T curves, the peaks of all samples are symmetrical. Fay et al.[7] and Chang et al.[13] suggested that the integral value of the loss modulus versus temperature curve, which was called loss area, displays the properties of materials which were related to its structure. Every group within the polymer contributes to the loss, respectively. The main chain and the pendant chain linked directly with the main chain make chief contributions to the damping property in the glass transition region. Table III gives the integral area for E'' to T. As seen from the integral values, neither methyl nor ethyl has an influence on the loss area, as is consistant with Sperling's[3] and Chang's[13] observations. However another important property, the tan δ curve,

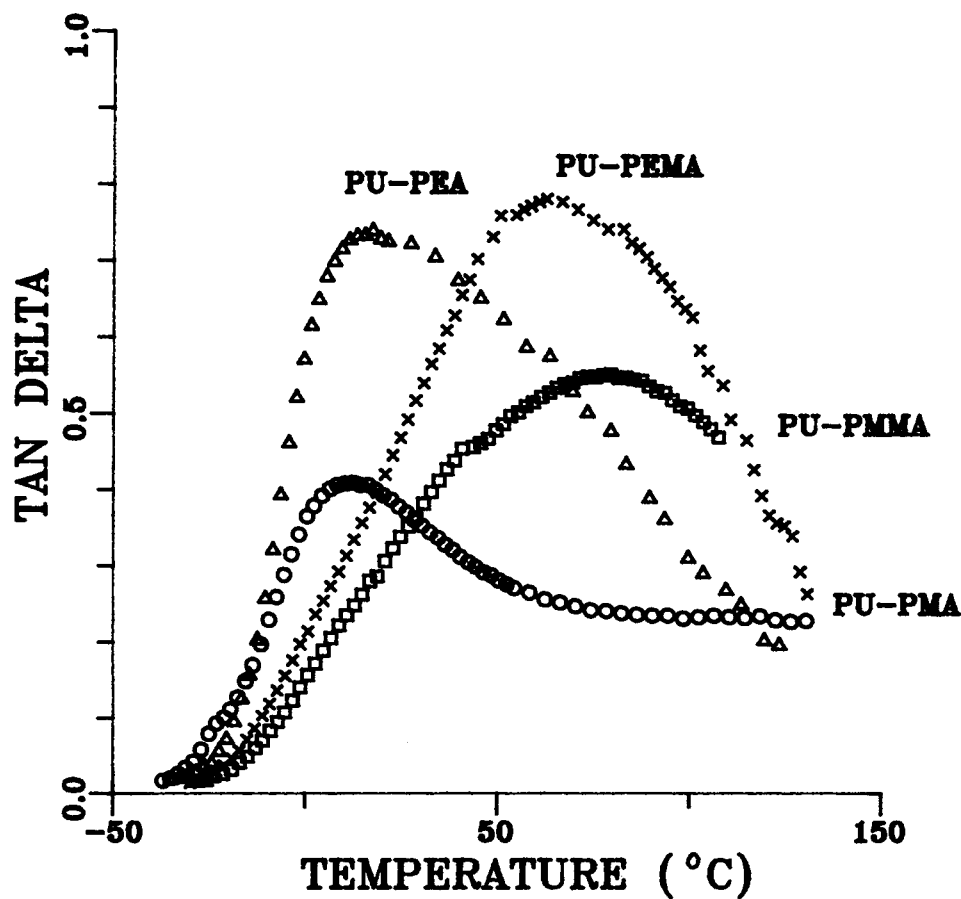

Figure 2   Tan δ vs. temperature curves for SINs.

corresponding to E″, was not found to obey a group contribution analysis.[8] On the other hand, the area under the curve (loss tan δ vs. temperature) has been shown to be related to the activation energy of the backbone motion in magnitude.[4] The tan δ curve available in this paper exhibits a broader peak (Fig. 2), and the curves for the four samples show greater differences in their height and area. As listed in Table III, the temperature ranges of tanδ > 0.3 of the samples except PU/PMA extend over a range of 100°C, and the tan δ peaks of PU/PEMA and PU/PEA are greater than those of PU/PMMA and PU/PMA in height. The structure of the main chain of the four SINs is the same, while that of the pendant chain is slightly different. The long chain side groups are more flexible than the short ones, act as diluents, and make the motion of the main chain easier. Therefore, Tg of the polymers with a long pendant chain is lower than that of the polymers with a short pendant chain (see Tables II and III). For example, the glass transition range temperature of PU/PEMA is lower than that of PU/PMMA, and the temperature of PU/PEA is lower than that of PU/PMA, as shown in Table III and Figure 2. The tan δ peak and the integral areas in PU/PEMA and PU/PEA are larger than those in PU/PMMA and PU/PMA. This fact indicates that the frictional damping is heavy when the backbone underwent de Gennes reptation motions for PU/PEMA and PU/PEA. The ethyl group in the side group of the polymer is not directly linked with the backbone. Therefore, the ethyl group possesses a greater free degree of motion. The backbone motion is greater due to the moving pendant chain. The chains in tangle lose a large amount of energy, which is indicated by a higher peak. The height and width of the peak are relative not only to the properties of the selected material but also to the miscibility and the phase separation of the IPNs. For most of the IPNs, there exist certain miscibility in structure and forced mis-

cible action. Usually, a broader glass transition indicates that the phases are not completely homogeneous. The width of the peak depends on the Tgs of the two homopolymers. If the system is partially miscible and the difference of the Tg of the two homopolymers is about 50°C, the temperature range of tan δ > 0.3 can approach 100°C. If ΔT is too great, the width of the peak is great, but the height must be lower. As a result the damping power is poor. The height and width of the damping peak cannot be adjusted independently. The area under the peak is essentially constant.[3,4] The damping peak must be maximized so that requirements for the application are met.

Morphology of the IPNs

Morphology of the PU/PMMA IPN was studied by Kim et al.[14] and Allen et al.[15] Their experiments show that the IPNs have a two-phase structure, regardless of the proportion of network I to network II. The degree of phase separation and the domain size depend, however, on the synthesis method and proportions of the two compositions.

The morphology of the SINs herein was observed using TEM. TEM photos are shown in Figure 3. The black area on the photos is network I, and the white area is network II. The samples were stained by RuO_4, an effective staining agent for polyether.[11] It is important to control the time of staining. The samples were vapor-stained in RuO_4 for 15 min.

As seen from the photos, pure network I is homogeneous in structure. Network I is mainly linked up by polyether and TDI alternately. When interpenetrating networks were formed, the phase separation was dependent on the miscibility of those two networks and polymerization condition. Network I and PMA have almost the same solubility parameters so the miscibility is quite good between the two networks. The solubility parameters of network I and PEMA are more different and their phase separation is obvious. The other two lie between them. As seen from Figure 3, these four samples all have two–phase structures. The better the miscibility, the bigger the diffuse area. Within PU/PMMA and PU/PEMA, the domain size of network I has a range of 40–120 nm. Networks present a relatively uniform distribution. PU/PMA and PU/PEA dominate the diffuse area, however the dispersion of the networks is not uniform enough. The partial aggregation of the segments of network I, about 100 nm in size, may relate to the polymerization rate of these two networks. Under the condi-

Table III Tan δ and loss area of Experimental for the Samples

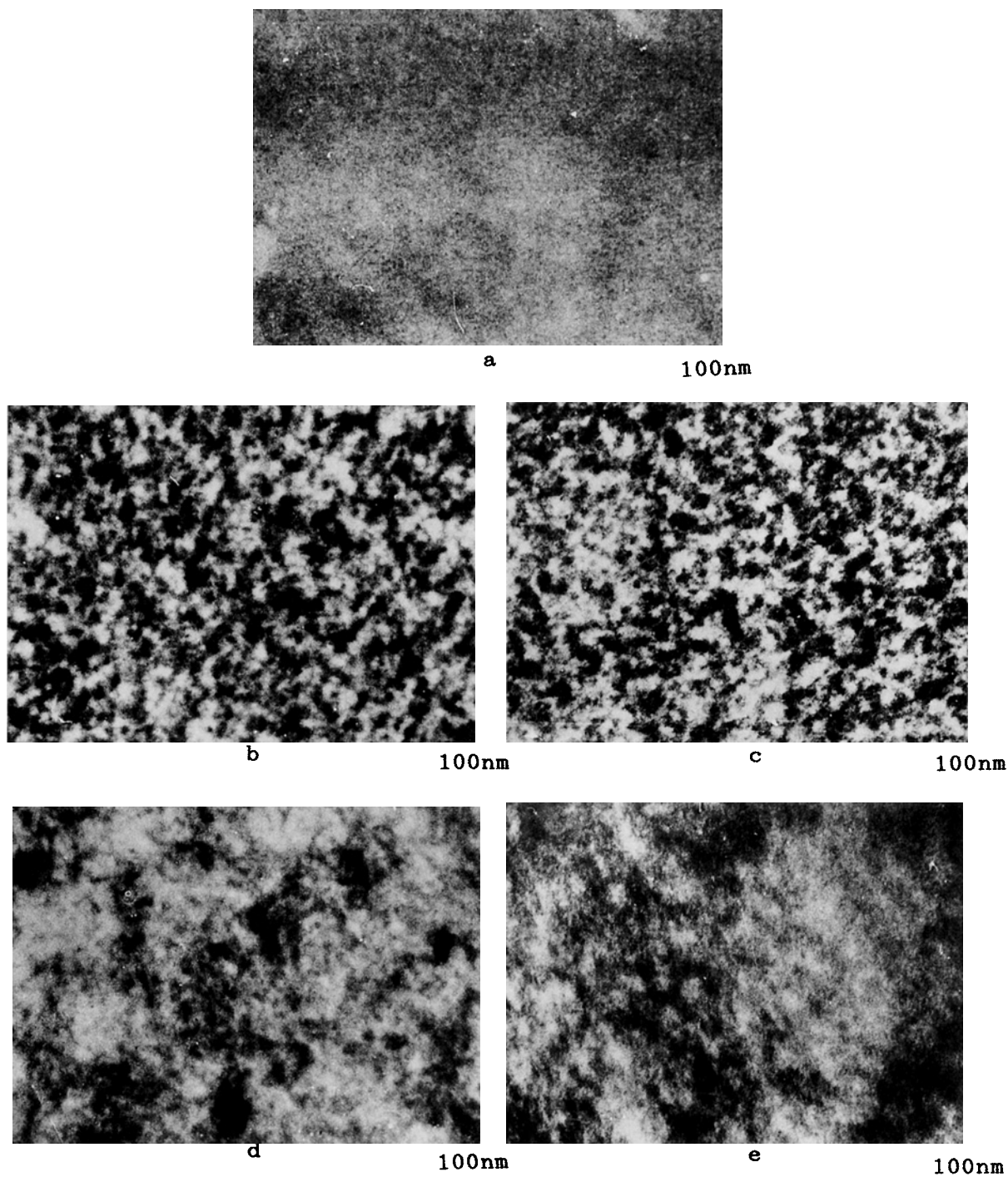| Samples	Tan δ max	tan δ > .3 Temp. ranges	Area of E″ GPa∗K	Area of tan δ Height∗K
PEGC-PU	/	−7—60	14.4	/
PU/PMMA	.55	20–> 125	11.3	54.4
PU/PEMA	.78	12—127	11.0	69.6
PU/PMA	.41	−4—46	7.8	38.8
PU/PEA	.74	−9—100	8.0	67.5

Figure 3   TEM photograph of SINs. (a) network I; (b) PU/PMMA; (c) PU/PEMA; (d) PU/PMA; (e) PU/PEA.

tions herein, the polymerization rate of network I and methyl acrylate match comparatively with each other with a uniform distribution of networks. If

other acrylates take the place of methyl acrylate within network II, networks I and II fail to match because of a big difference in their polymerization

rate. When the polymerization of network II occurs, the very rapid reaction causes quick aggregation of the network II monomer. Consequently, the partial chain segments of network I are excluded.

CONCLUSION

1. A microphase–multiphase structure and the widening of the glass transition peak which is shown by DMS and TEM demonstrate that the SINs under study possess good interpenetrating network structures.
2. The length of the pendant group, without direct link to the backbone, has an effect upon the value of tan δ. The role played by $COOC_2H_5$ is higher than that of $COOCH_3$ in this aspect.
3. The damping properties of PU/PEMA and PU/PEA are better than those of PU/PMMA and PU/PMA.
4. Damping materials suitable for different frequencies may be prepared for satisfying specific needs in application.

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