

Studies on Damping Properties of P(MMA-AN)/P(EA-nBA) LIPNs

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ABSTRACT: Using a two-stage emulsion polymerization method, a series of poly(methyl methacrylate-acrylonitrile)/poly(ethyl acrylate-*n*-butyl acrylate) [P(MMA-AN)/P(EA-nBA)] latex interpenetrating polymer networks (LIPNs) were synthesized by varying AN content, ratio of network I/network II, crosslinker content, and introducing chain transfer agent. The damping properties of the LIPNs were investigated using a Rheovibron Viscoelastometer. The results indicate that a suitable content of AN can improve the damping properties of the LIPNs. Three kinds of fillers were incorporated into the LIPNs, respectively, to measure the change in the damping properties. Mica and TiO₂ both increased the damping properties of the LIPNs over the wide temperature range. For TiO₂-filled LIPNs, it was observed that the tan δ values exceeded 0.4 over 112.6°C temperature range from -50 to 72.6°C. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 722–727, 2000

Key words: latex; interpenetrating polymer networks (IPNs); damping properties; P(MMA-AN)/P(EA-nBA), filling

INTRODUCTION

Research on damping polymer materials that are used for the control of sound and vibration damping has become more and more urgent with the development of modern industry. Based on the damping theory, the damping properties of polymers are dominated by their glass transition. Polymers form especially useful vibration damping materials near their glass transition temperature, T_g , as a result of the onset of coordinated chain molecular motion, maximizing dissipation of the mechanical energy as heat.^{1,2} Usually, homopolymers have efficient damping in a temperature range of only 20–30°C around the T_g . How-

ever, good damping materials for outdoor or machinery application should exhibit a high loss factor over a temperature range of at least 60–80°C.^{3,4} A very effective method to broaden the temperature range is through the use of interpenetrating polymer networks (IPNs).^{5,6} LIPNs, which is an important type of IPNs produced by the two-stage emulsion polymerization, has been used in the field of sound and vibration damping in recent years, especially in the form of coating. The effectiveness of vibration damping of LIPNs depends on such factors as backbone flexibility, steric effects, interaction between components, and extent of crosslinking, among others.⁷ In this article, at first, PMMA/P(EA-nBA) LIPNs were synthesized, and the LIPNs exhibits the loss factors (tan $\delta > 0.3$) over a temperature range from -30 to 70°C. To further improve the damping properties over the wide temperature range, we

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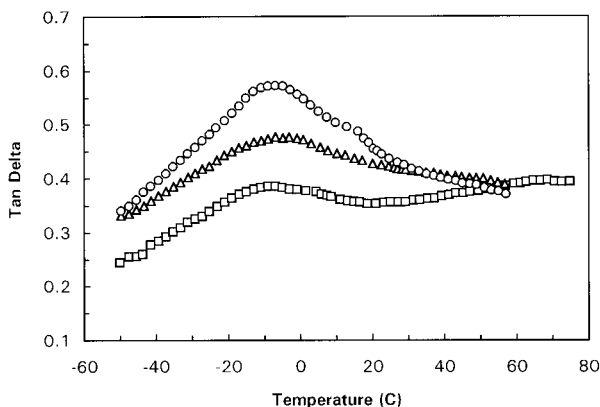


Figure 1 Dynamic mechanical spectra of P(MMA-AN)/P(EA-nBA) LIPNs at various ratios of MMA/AN: (□) 100/0, (△) 90/10, (○) 80/20.

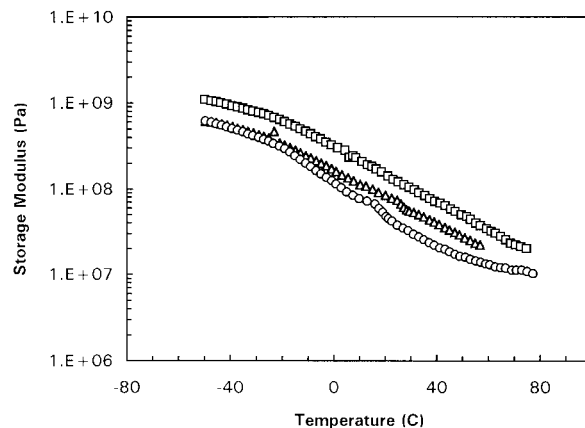


Figure 2 Storage modulus vs. temperature curves for P(MMA-AN)/P(EA-nBA) LIPNs at various ratios of MMA/AN: (□) 100/0, (△) 90/10, (○) 80/20.

synthesized a series of P(MMA-AN)/P(EA-nBA) LIPNs by introduction of an acrylonitrile (AN) in network I. The effects of AN content, the composition of two networks, crosslinker content, chain transfer agent, and fillers on the damping properties of the LIPNs were studied.

EXPERIMENTAL

Materials

In this study the following materials were used: methyl methacrylate (MMA), acrylonitrile (AN), ethyl acrylate (EA), and *n*-butyl acrylate (nBA) were used as the monomers, and the monomers were distilled under reduced pressure to remove inhibitor before use; trimethylpropane triacrylate (TMPTA) as the crosslinking agent (0.4 wt % crosslinking agent was used except as indicated); $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as the initiator; lauryl mercaptan as the chain transfer agent; and sodium lauryl sul-

fate (SLS) as the emulsifier. Mica, TiO_2 , and CaCO_3 served as the fillers.

P(MMA-AN)/P(EA-nBA) LIPNs were prepared by a two-stage emulsion polymerization technique. First, the emulsifier was dissolved into the deionized water at 60°C in the reaction bottle, then a part of a monomer I (MMA, AN) containing a crosslinker and an initiator were added by a dropping funnel, respectively. The bottle was heated to 80°C after the temperature was maintained for a one-half hour, and then the rest of the monomer I, the crosslinker, and the initiator were added. After 2 h of heat preservation it was cooled to 60°C, resulting in the seed latex for the second stage. The next a part of monomer II (EA and

Table I Damping Properties with Changing AN Content

MMA/AN	Peak Height or $\tan \delta_{\max}$	Temperature Range of $\tan \delta > 0.4$ (°C)		
		T1	T2	ΔT
100/0	0.385	—	—	—
90/10	0.477	-32.0	50.7	82.7
80/20	0.572	-37.3	40.0	77.3

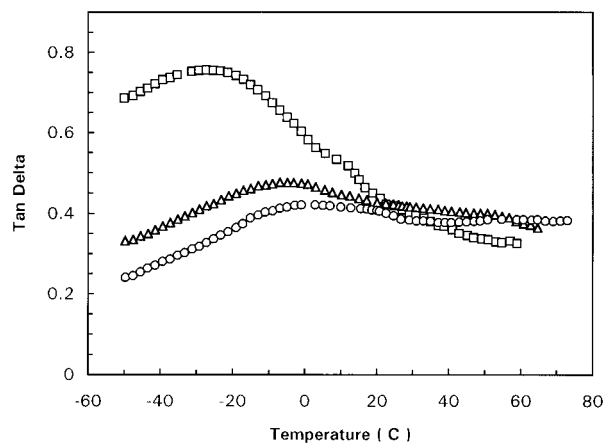


Figure 3 Dynamic mechanical spectra of P(MMA-AN)/P(EA-nBA) LIPNs at various ratios of network I/network II: (□) 30/70, (△) 40/60, (○) 45/55.

Table II Influence of Ratio of Monomer I/Monomer II on Damping Properties

P(MMA-AN)/ P(EA-nBA)	T_g (°C)	Peak Height or $\tan \delta_{\max}$	Temperature Range of $\tan \delta > 0.4$ (°C)		
			T_1	T_2	ΔT
30/70	-27.2	0.755	-50.0	29.0	79.0
40/60	-5.0	0.477	-32.0	50.7	82.7
45/55	0.8	0.420	-11.0	22.6	33.6

Ratio of MMA/AN in networks I is 90/10.

nBA in a ratio of 50 : 50) containing a crosslinker, and an initiator was added into the seed latex at 60°C. The following reaction was completed under the same conditions as the first stage, and the resulting sample was the LIPNs.

Measurement

The dynamic mechanical properties were detected by an Autovibron Dynamic Viscoelastomer (Rheovibron DDV-III-EA type, Toyo Baldwin Co. Ltd.) at a heating rate of 2°C/min and a frequency of 35 Hz. The temperature range measured was from -50 to 80°C.

RESULTS AND DISCUSSION

Influence of AN Content on Damping Properties

Figure 1 shows dynamic mechanical spectroscopy of P(MMA-AN)/P(EA-nBA) LIPNs at varying AN contents of network I and a fixed ratio of 40/60 network I/network II. Without an AN component

in network I, the LIPNs, i.e., PMMA/P(EA-nBA) LIPNs, exhibit a plateau peak, and damping values are smaller than 0.4 over the temperature range studied. It is obvious that the introduction of AN improves the damping properties over a wide temperature range, for example, the temperature range of $\tan \delta > 0.4$ is 82.7°C when the AN content in network I is 10 wt % (as shown in Table I). Above 50°C, the damping properties decrease with an increase of the AN content. The relaxation of the LIPNs below 50°C is mainly contributed to network II, which is an EA-nBA copolymer. Substituting for a part of MMA, the introduction of the AN component with strong polar group of CN is favourable for enhancing interaction between the two networks; therefore, the damping values increase with increasing the AN content, although the relaxation of the LIPNs in a higher temperature region is mainly contributed to network I. The irregular arrangement of the molecular chain due to copolymerization of MMA and AN reduces interaction between the chain in

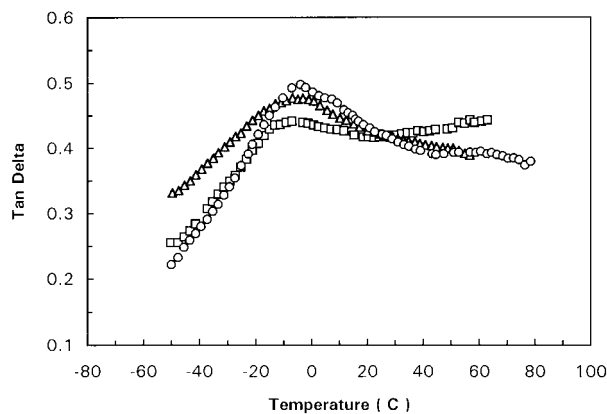


Figure 4 Dynamic mechanical spectra of P(MMA-AN)/P(EA-nBA) LIPNs at different crosslinker contents (wt %): (□) 0.2, (△) 0.4, (○) 0.8.

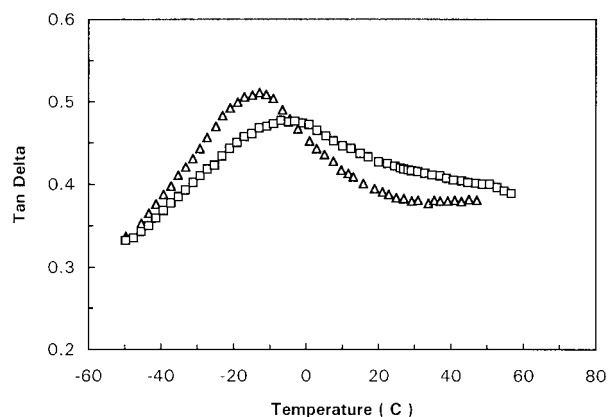


Figure 5 Influence of chain transfer agent on dynamic mechanical spectra of P(MMA-AN)/P(EA-nBA) LIPNs: (□) without lauryl mercaptan, (△) 0.2 wt % lauryl mercaptan.

Table III Damping Properties with Changing Crosslinker Content

Content ^a (wt %)	T_g (°C)	Peak Height or $\tan \delta_{\max}$	Temperature Range of $\tan \delta > 0.4$ (°C)		
			T_1	T_2	ΔT
0.2	-7.0	0.441	-19.1	63.1	82.2
0.4	-5.0	0.477	-32.0	50.7	82.7
0.8	-3.9	0.497	-21.1	34.9	56.0

^a The crosslinker content of the two networks is changed in the same level.

the network I; therefore, the storage modulus of the LIPNs decreases with increasing the AN content, as showed in Figure 2. The negative effect on damping properties in the temperature region exceeds the positive role contributed by the increasing interaction between the two networks due to the introduction of AN, resulting in lower damping values as the AN content increases, beyond 10%.

In the $\tan \delta$ - T curve of the LIPN without the AN component, two transitions are observed. One transition locates at -8°C , another appears at 65°C . Moreover, the valley between the two transitions is shallow. These reveal that PMMA/P(EA-nBA) LIPN is partially miscible. As the AN content increases, the height of a lower temperature peak enhances and a higher temperature peak disappears, which is an indication of a semi-miscible polymer blend.

Influence of Ratio of Monomer I to Monomer II on Damping Properties

The influence of ratio of monomer I/monomer II on the dynamic mechanical properties is shown in Figure 3 and Table II. When the content of the P(EA-nBA) network decreases from 70 to 55%, there is obviously a tendency to shift glass transition to a higher temperature, which corresponds to that of the P(MMA-AN) network; the damping values in the low-temperature region notably decrease, but the ones in the high-temperature re-

gion increase slightly. The result indicates that the damping properties of P(MMA-AN)/P(EA-nBA) LIPNs is mainly dominated by the glass transition of the P(EA-nBA) network. This is due to the special "core-shell" structure^{8,9} of LIPNs. During the synthesis of P(MMA-AN)/P(EA-nBA) LIPNs, P(EA-nBA) is polymerized later, leading to a P(EA-nBA)-rich shell and a P(MMA-AN)-rich core. After the LIPNs are dried and form film, the P(EA-nBA) component is more liable to form a continuous phase. Therefore, the variation of the content of the P(EA-nBA) network has more obvious influence on the damping properties than that of the P(MMA-AN) network.

Influence of Crosslinker Content on Damping Properties

Figure 4 and Table III illustrate the influence of crosslinking on damping properties for P(MMA-AN)/P(EA-nBA) LIPNs containing a 40% network I (ratio of MMA/AN in the network is 90/10). When increasing the crosslinker content from 0.2 to 0.8%, the plateau peak disappears, the curves show a single transition, and the T_g shifts to a high temperature. This is due to the fact that the increasing crosslinker content tends to improve molecular mixing and, hence, decrease domain size, indicating that an appropriately increasing crosslinker content of network II can improve the damping properties in the lower temperature region. However, when the crosslinker content in

Table IV Influence of Chain Transfer Agent on Damping Properties

Content (wt %)	T_g (°C)	Peak Height or $\tan \delta_{\max}$	Temperature Range of $\tan \delta > 0.4$ (°C)		
			T_1	T_2	ΔT
0	-5.0	0.477	-32.0	50.7	82.7
0.2	-12.5	0.511	-37.3	15.8	53.1

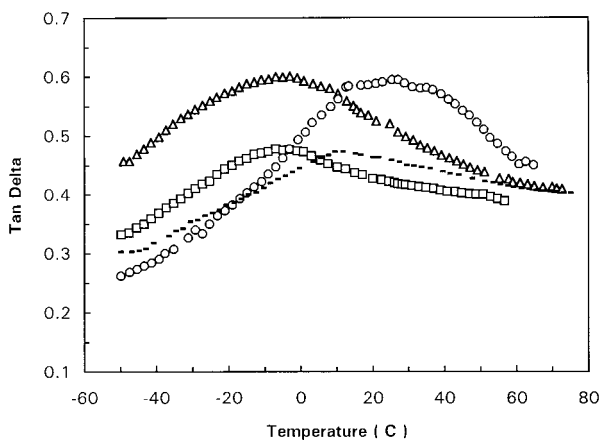


Figure 6 Dynamic mechanical spectra of P(MMA-AN)/P(EA-nBA) LIPNs with different types of fillers: (□) Unfilled, (△) TiO_2 , (○) Mica, (—) CaCO_3 .

network I exceeds 0.2%, the damping properties in the higher temperature region reduce. This is because of a sharper core-shell structure in the LIPNs, for a high crosslinking in network I restricts the permeation and interpenetration of network II.

Influence of Chain Transfer Agent on Damping Properties

Lauryl mercaptan (0.2%) as the chain transfer agent was added into the monomers before polymerization. Influence of the chain transfer agent on the damping properties is presented in Figure 5 and Table IV. Compared with the LIPNs without the chain transfer agent, addition of the chain transfer agent causes the damping peak shift toward the low temperature; the damping values by the low-temperature side of the peak increases, and decreases by the high-temperature side of the peak. During polymerization, some of the chain free radicals can transfer to the chain transfer

agent, resulting in the decreasing of the molecular weight of the polymer. In this study, the chain transfer agent was added in one lump before polymerization. Therefore, the chain transfer agent added affected the molecular weight of network I more than that of network II, for it was almost used up after the seed latex was produced. The lowering of the molecular weight of network I results in the decreasing of the glass temperature and damping values due to weakening of the interaction force among the chains. However, when network II was synthesized, monomer II was easy to permeate into network I due to lowering the molecular weight of network I, causing a rise in the damping properties of network II.

Influence of Various Fillers on Damping Properties

In this study, three kinds of inorganic fillers were incorporated into 40/60 P(MMA-AN)/P(EA-nBA) LIPNs, respectively; content of the filler is 10%. The dynamic mechanical properties of the unfilled and filled LIPNs are shown in Figure 6 and Table V. From the data, it can be seen that mica and TiO_2 have good effects on the damping properties. In the system studied, mica markedly improves the damping properties in the high-temperature region. The most pronounced effect of TiO_2 is the broadening of the damping temperature range; obviously increasing of the damping values over the temperature range, especially in the low-temperature region. The general mechanisms, where some fillers can improve the damping properties of polymer over the glass transition, include¹⁰ particle-polymer friction and particle-particle friction. Besides the probable mechanisms mentioned above, mica also has shown the microconstrained layer damping mechanism due to the platelet structure of mica. Therefore, in the mica-filled LIPN, the platelet at one side of the LIPN damping layer can be con-

Table V Influence of Various Filler on Damping Properties

Sample	T_g (°C)	Temperature Range of $\tan \delta > 0.4$ (°C)			Temperature Range of $\tan \delta > 0.5$ (°C)		
		T_1	T_2	ΔT	T_1	T_2	ΔT
Unfilled	-5.0	-32.0	50.7	82.7	—	—	—
TiO_2	-3.0	-50.0	72.6	112.6	-37.4	26.9	64.3
Mica	26.4	-14.9	64.8	79.7	1.3	50.9	52.2
CaCO_3	10.0	-15.1	74.5	89.6	—	—	—

sidered as a vibrating substrate, while the platelet at the other side of the damping layer acts as a constrained layer. The shear takes place in the damping layer between the platelets when the specimen is vibrating, which increases the mechanical loss of energy being converted into heat. For the TiO₂-filled LIPN system, more study will be needed to explain the reason for increasing the damping properties.

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