

# Studies on Damping Behavior of PS/P(EA-*n*BA) LIPNs

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## SYNOPSIS

A series of polystyrene/poly(ethyl acrylate-*n*-butyl acrylate) [PS/P(EA-*n*BA)] latex interpenetrating polymer networks (LIPNs) were synthesized by the two-stage emulsion polymerization method. The influence of composition, crosslinker content, chain transfer agent, polar group, and feeding sequence on the damping properties of the LIPNs were investigated with a Rheovibron Viscoelastometer. The results show that the PS/P(EA-*n*BA) LIPNs are a partially miscible system, and that LIPNs favor the broadening of the damping temperature range. The influence of crosslinker content of network I on the damping properties of the LIPNs is not the same as that of network II. The damping properties of the PS/P(EA-*n*BA) LIPN is superior to that of P(EA-*n*BA)/PS LIPN. Moreover, the introduction of polar groups into the system can increase the damping properties, and adding chain transfer agent can broaden the damping temperature range. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

There has been an increased interest in polymers for sound and vibration damping in recent years.<sup>1</sup> Polymers are useful vibration damping materials near their  $T_g$  as a result of the onset of coordinated chain molecular motion that dissipates the mechanical energy as heat.<sup>2</sup> Homopolymers generally have narrow glass transition regions (20–30°C). However, when temperature becomes a significant variable, the narrow temperature range of the glass transition causes most homopolymer damping materials to fail. One solution to the problem lies in selecting a multicomponent polymer system with controlled degrees of miscibility. In this multicomponent system, such as copolymers and mechanical blends have been used, but in many cases dynamic mechanical spectroscopy shows limited damping capability as indicated by two narrow peaks. Another method to broaden the damping peaks is through use of interpenetrating polymer networks (IPNs).<sup>3</sup> Since Sperling and Frich developed the concept of Miller's LIPNs in 1969, latex IPNs (LIPNs), as an important type of IPNs has drawn the attention of many investigators. Early in 1970s, Sperling et al. pointed out that the semicompatible LIPNs have

potential practical value for noise and vibration damping.<sup>4</sup> Most recently, work was done to determine quantitatively the relationship between molecular structure and damping. Chang et al. developed a group contribution analysis of the loss area, LA, which is a valuable tool to help design polymeric damping materials based on chemical composition.<sup>5</sup>

We synthesized a series of polystyrene/poly(ethyl acrylate-*n*-butylacrylate) [PS/P(EA-*n*BA)] LIPNs by varying composition, crosslinker content, feeding sequence of monomers, and introducing polar monomers and chain transfer agent. The damping behavior of the LIPNs was investigated by means of a Rheovibron Viscoelastomer.

## EXPERIMENTAL

### Materials

The LIPNs were synthesized using the following materials: styrene (St), *n*-butyl acrylate (*n*BA), ethyl acrylate (EA), acrylic acid (AA), trimethylpropane triacrylate (TMPTA),  $K_2S_2O_8$ , sodium lauryl sulfate (SLS), and lauryl mercaptan. The monomers were distilled under reduced pressure to remove inhibitor before use.

### Synthesis

LIPNs were synthesized by a two-stage emulsion polymerization technique. First the deionized water

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**Table I** Influence of Ratio of EA/*n*BA on Damping Behavior

EA/ <i>n</i> BA	20/80	50/50	70/30
$T_g$ shifting value (°C)	25.0	29.6	23.4
Peak height	0.361	0.412	0.381
Peak width (tan $\delta >$ 0.3, °C)	22.2	38.1	26.0

was introduced into a bottle along with the emulsifier (SLS) at 60°C, then a part of monomer I (St) containing crosslinker was added, followed by the addition of the initiator (0.5%  $K_2S_2O_8$ ). The bottle was heated to 80°C, then the rest of monomer I was added. After standing at 80°C for 2 h, it was cooled to room temperature resulting in the seed latex for the second stage. Next, a part of monomer II (EA-*n*BA), also containing crosslinker and initiator, were added. The reaction was completed under the same conditions as the first stage, and the resulting product was LIPNs.

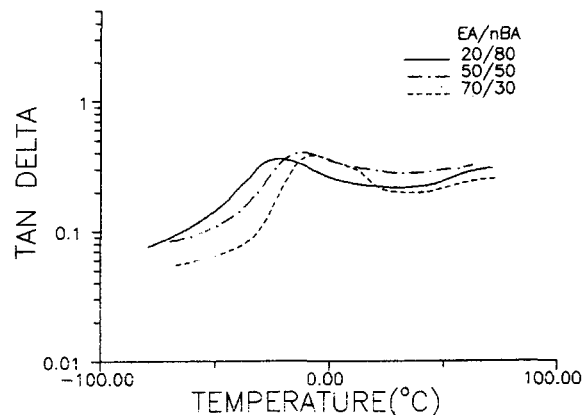
#### Measurement of Dynamic Mechanical Properties

The dynamic mechanical properties of the LIPNs were determined with an Autovibron Dynamic Viscoelastomer (Rheovibron DDV-III-EA type, Toyo Baldwin Co. Ltd.), and the dynamic mechanical spectra (DMS) was obtained. The heating rate was 2°C/min from -60° to 100°C (using the temperature range of the LIPNs) and the frequency was 35 Hz.

## RESULTS AND DISCUSSION

### Influence of Composition of Network II on Damping Behavior

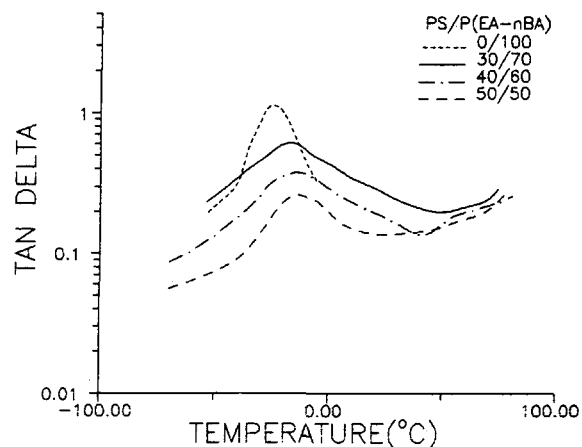
Variation of the composition of network II of PS/P(EA-*n*BA) LIPNs was achieved by changing the ratio of EA to *n*BA, the ratio of monomer I/monomer II being 40/60. The effect of this variation on the damping properties is illustrated in Table I and Figure 1. It can be seen that, as the content of EA increases, the glass transition temperature of network II shifts toward the high temperature as predicted by the Fox equation. Compared with the  $T_g$  of the pure components, it is noted that the  $T_g$  of network II shifts toward the midrange indicating that the PS/P(EA-*n*BA) LIPNs are partially miscible,<sup>6</sup> resulting in broadening of the damping peak. The resulting tan  $\delta - T$  curve shows a transition peak with a higher tan  $\delta$  value in the wide temper-

**Figure 1** Influence of the composition of network II on the damping properties of PS/(PEA-*n*BA) LIPNs.

ature range when the EA content was 50%, due to the synergisms of microheterogeneous morphology in the partially miscible LIPNs system possibly being more obvious when EA content is 50%. More studies are needed.

### Influence of Ratio of Monomer I to Monomer II on Damping Behavior

A series of PS/P(EA-*n*BA) LIPNs were synthesized by varying the ratio of monomer I to monomer II. The resulting tan  $\delta - T$  curves are illustrated in Figure 2. Table II summarizes the data for these LIPNs. Compared with the  $T_g$  of the pure components, it should be noted that the transition temperature shifts toward the midrange gradually with the increase of PS content. This might be attributed to the PS component existing in P(EA-*n*BA) phase due to interpenetration between network I and network II during polymerization, which confines the

**Figure 2** Influence of the ratio of network I to network II on the damping properties of PS/P(EA-*n*BA) LIPNs.

**Table II** Influence of Ratio of PS/P(EA-*n*BA) on the Damping Properties

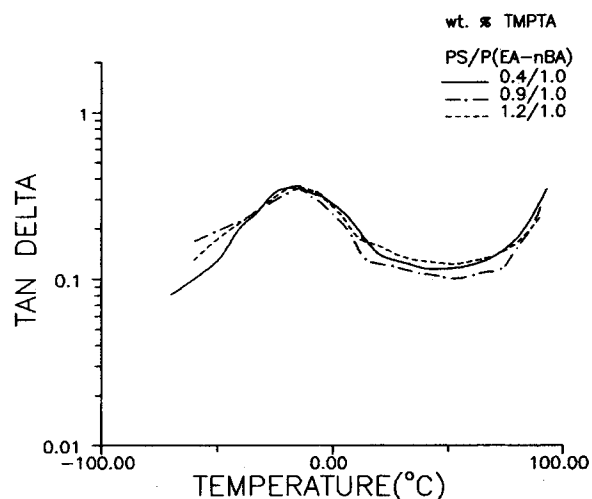
	PS/P(EA- <i>n</i> BA)			
	0/100	30/70	40/60	50/50
$T_g$ (°C)	-24.7	-17.4	-15.4	-13.0
Peak height	1.128	0.617	0.378	0.262
Peak width (tan $\delta$ > 0.3, °C)	30	60.8	21.9	—

segment motion of P(EA-*n*BA). Figure 2 shows that the damping behavior of PS/P(EA-*n*BA) LIPNs is dominated by the glass transition of the P(EA-*n*BA) phase. The height of the damping peak decreases as the content of PS increases. It can be seen that as the content of P(EA-*n*BA) increases, it makes more contribution to the damping of the system. The 30/70 composition has better damping properties; its tan  $\delta$  values between 0.3–0.6 extend over the 61°C temperature range.

### Influence of Crosslinker Content on Damping Properties

The damping properties were determined for PS/P(EA-*n*BA) LIPNs containing 40% PS with the crosslinker content being changed. The variation and results are illustrated in Table III and Figures 3 and 4.

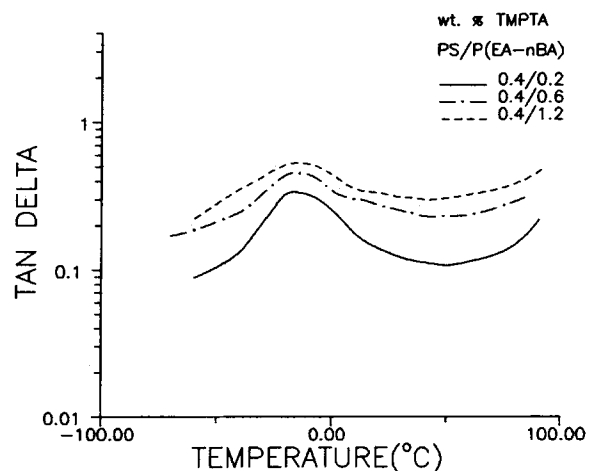
It is noted that as the crosslinker content of the PS network increases with the crosslinker content of the P(EA-*n*BA) network, being set constant as 1.0% by weight, the tan  $\delta$  -  $T$  curves do not appear to be sufficiently different although the variation of  $T_g$  and tan  $\delta$  is not regular. However, the influence of the crosslinker content of the P(EA-*n*BA) network on the damping behavior is not the same as that of the PS network. When the crosslinker content of the P(EA-*n*BA) network is gradually increased while the crosslinker content of PS network is fixed at 0.4% by weight, the  $T_g$  shifts toward the high temperature gradually and the height and width

**Figure 3** Influence of crosslinker content of network I on the damping properties of PS/P(EA-*n*BA) LIPNs.

of the glass transition peak increases progressively. The damping properties of the LIPNs are improved. Generally, for sequential IPNs it is thought that the continuance of the first network is superior to that of the second network, so the variation of crosslinker content of the first network has great influence on the dynamic mechanical properties. As the crosslinker content of the first network increases, the glass transition temperature shifts toward the mid-range, and the transition region broadens, the miscibility and damping properties increase. On the contrary, the variation of the crosslinker content of the second network has little influence on the dynamic mechanical properties. Although LIPNs can be seen as sequential IPNs, the influence of crosslinker content on the dynamic mechanical properties is not the same as that of sequential IPNs. This is due to the special “core-shell” structure<sup>7,8</sup> of LIPNs and the variation of their morphology after drying. During the synthesis of PS/P(EA-*n*BA) LIPNs, P(EA-*n*BA) is polymerized later, leading to a P(EA-*n*BA) rich shell and a PS rich core. After the LIPNs are dried and form film, P(EA-*n*BA) component is more liable to form a continuous phase. Therefore, the variation of crosslinker content of

**Table III** Influence of Crosslinker Content on Damping Behavior

	PS/P(EA- <i>n</i> BA)					
	0.4/1.0	0.9/1.0	1.2/1.0	0.4/0.2	0.4/0.6	0.4/1.2
$T_g$ (°C)	-15.3	-14.8	-16.0	-17.0	-15.1	-13.3
Peak height	0.362	0.346	0.354	0.340	0.460	0.532
Peak width (tan $\delta$ > 0.3, °C)	24.0	16.0	20.3	18.4	44.9	85.8



**Figure 4** Influence of crosslinker content of network II on the damping properties of PS/P(EA-*n*BA) LIPNs.

P(EA-*n*BA) network has more obvious influence on the dynamic mechanical properties than that of the PS network, which was polymerized previously with poor continuity.

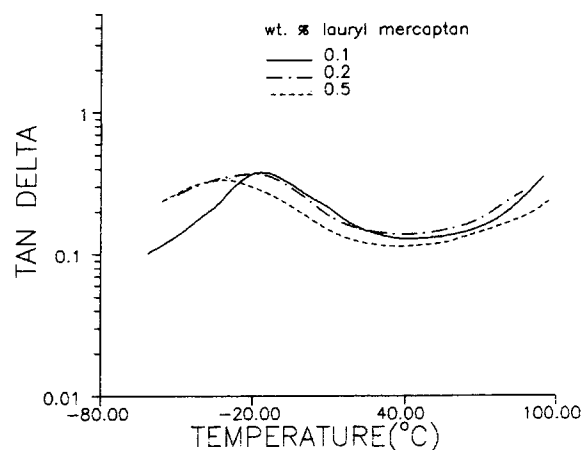
#### Influence of Chain Transfer Agent on Damping Properties

Before polymerization, different amounts of lauryl mercaptan were added into the monomers as chain transfer agent. Table IV and Figure 5 show the effect of chain transfer agent on the damping properties. It can be seen that the damping peak shifts toward the low temperature, and the width of the peak increases; but the height of the damping decreases as the content of chain transfer agent increases. A comprehensive study of the  $\tan \delta$  value and the damping temperature range shows that the system with 0.2% lauryl mercaptan has better damping properties.

Because of the introduction of the chain transfer agent into the system, some of the chain free radical can transfer to the chain transfer agent during po-

**Table IV** Influence of Chain Transfer Agent on Damping Properties

	Content of Chain Transfer Agent (wt %)		
	0.1	0.2	0.5
$T_g$ (°C)	-15.4	-20.2	-33.5
Peak height	0.372	0.369	0.333
Peak width ( $\tan \delta > 0.3$ , °C)	21.9	34.5	21.8

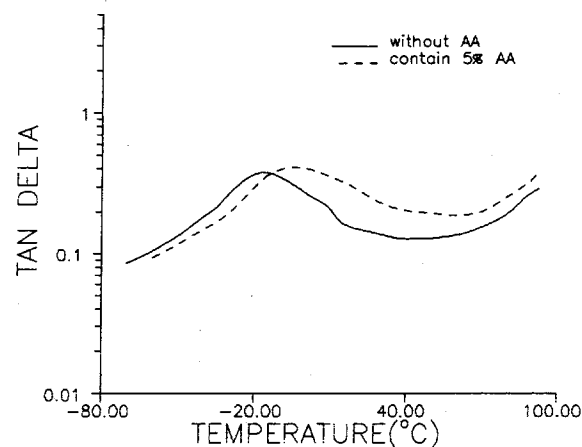


**Figure 5** Influence of chain transfer agent on the damping properties of PS/P(EA-*n*BA) LIPNs.

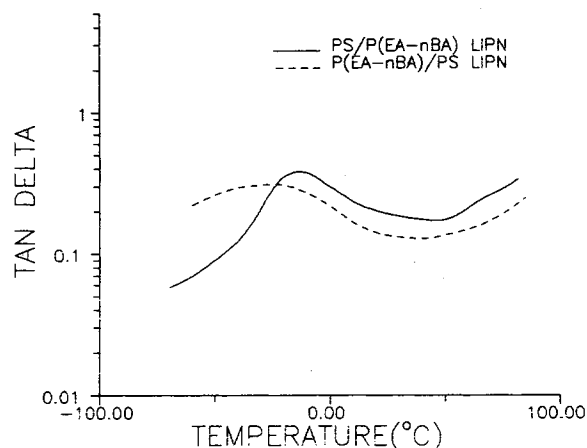
lymerization, and the growth rate of the chain is controlled. This causes the decrease of the molecular weight of the polymer, leading to the decrease of the glass transition temperature. On the other hand, the feeding method of the chain transfer agent affects the molecular weight distribution of the polymer. In this study the chain transfer agent was added in one lump, and the molecular weight of the polymer is in inverse proportion to the concentration of the chain transfer agent in the lower conversion. As the conversion increases, the chain transfer agent is consumed gradually, such that the molecular weight of the polymer increases dramatically in the higher conversion. This results in the broadening of the molecular weight distribution, the  $\tan \delta - T$  curve, and the glass transition.

#### Influence of Polar Group on Damping Behavior

The ratio of monomer I to monomer II was fixed at 40/60. When 5 wt % polar monomer, AA, was in-



**Figure 6** Influence of polar group on the damping properties of PS/P(EA-*n*BA) LIPNs.



**Figure 7** Influence of feeding sequence on the damping properties of PS/P(EA-*n*BA) LIPNs.

roduced into the monomer II, a change was observed in the damping behavior as reflected by Figure 6 and Table V. Compared with the sample without AA, the  $\tan \delta$  increases, the transition peak shifts toward high temperature, and the damping range is broadened. This indicates that introduction of the polar group improves the damping properties of the system. It is known that polarity can increase the interchain attraction, which favors the permeation of the molecular chain, enhances the mutual entanglement between the networks, and increases the friction between the polymer molecular chains. Consequently, the damping properties of the system are improved.

#### Influence of Feeding Sequence on Damping Behavior

Keeping the composition at 40/60, two types of LIPNs, i.e., PS/P(EA-*n*BA) and P(EA-*n*BA)/PS, were synthesized by changing the feeding sequence of the monomers. The result is illustrated in Figure 7 and Table VI. It is obvious that the miscibility and damping properties of PS/P(EA-*n*BA) are superior to that of P(EA-*n*BA)/PS. This is due to the different level of the interpenetration and entanglements between the networks, which is caused by the feeding sequence. In PS/P(EA-*n*BA) LIPNs, PS networks are synthesized first; and, because the PS molecular chain is rigid, its movement capability is poor, the chains pile up loosely, and the space between the molecular chains is bigger. EA and *n*BA molecules diffuse easily while the PS networks are

**Table V** Influence of Polar Group on Damping Behavior

	AA Content (wt %)	
	0	5
$T_g$ (°C)	-15.4	-5.0
Peak height	0.378	0.421
Peak width ( $\tan > 0.3$ , °C)	21.9	36.8

**Table VI** Influence of Feeding Sequence on Damping Behavior

	PS/P(EA- <i>n</i> BA) LIPN	P(EA- <i>n</i> BA)/PS LIPN
$T_g$ (°C)	-13.6	-32.2
Peak height	0.385	0.304
Peak width ( $\tan > 0.3$ , °C)	25.0	19.0

swelled with monomer II. Consequently, the molecular mixing level is higher, leading to better miscibility and damping properties for PS/P(EA-*n*BA) LIPNs. For P(EA-*n*BA)/PS LIPNs, the condition is contrary.

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