

Effect of Crosslinker, Buffer, and Blending on Damping Properties of Poly(styrene-acrylonitrile)/Poly(ethyl acrylate-*n*-butyl acrylate) Latex Interpenetrating Polymer Networks

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ABSTRACT: A series of poly(styrene-acrylonitrile)/poly(ethyl acrylate-*n*-butyl acrylate) latex interpenetrating polymer networks (LIPNs) are synthesized by changing the kind of crosslinker and introducing a buffer. The results show that the crosslinker has an important effect on the damping properties of the LIPNs; divinylbenzene is the best crosslinker in the study. Moreover, introducing a buffer into LIPNs leads to an increase of the damping values over the temperature range where the damping value surpasses 0.5. The LIPN blend prepared by mixing LIPNs results in broadening of the damping peak, therefore improving the damping properties. Tests of the damping properties show that the LIPNs have good practical value. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2347–2351, 2002

Key words: latex interpenetrating polymer networks; poly(styrene-acrylonitrile)/poly(ethyl acrylate-*n*-butyl acrylate); crosslinker; buffer; blend

INTRODUCTION

Among the different types of polymeric materials for sound and vibration damping, interpenetrating polymer networks (IPNs) are useful because of their broad glass-transition region.¹ Of the IPN damping materials, the latex IPNs (LIPNs) prepared by two-stage emulsion polymerization methods have a special advantage of causing no environmental pollution in their preparation. In general, the damping properties of LIPNs are associated with their microheterogeneous morphology,^{2,3} the interaction, and the miscibility^{4,5} among the components for the multicomponent polymeric material, which is defined by important variables such as the structure of the respective components, the composition of the two networks, the crosslinking density, the synthesis conditions, and others.⁶

In our previous article⁷ poly(styrene-acrylonitrile)/poly(ethyl acrylate-*n*-butyl acrylate) [P(St-AN)/P(EA-*n*BA)] LIPNs were synthesized, and the effect of AN and acrylic acid (AA) on the damping properties was discussed. The addition of AN and AA to the LIPNs obviously broadened the damping temperature region and increased the damping values over the region. Further studies were carried out on the LIPNs in the present work by varying the types of crosslinkers, introducing buffers into the LIPN, and blending two different P(St-AN)/P(EA-*n*BA) LIPNs with different AA and crosslinker concentrations in order to investigate the effect of those factors on the damping properties.

EXPERIMENTAL

Materials

The St, AN, *n*BA, EA, and AA were used as monomers. Inhibitors of the monomers were removed

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by distilling under reduced pressure before use. Ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$, sodium lauryl sulfate, nonylphenol polyoxyalkylene ether (NPPOE), sodium bicarbonate (NaHCO_3), trimethylolpropane triacrylate (TMPTA), divinylbenzene (DVB), and diethylene glycol diacrylate (DEGDA) were the initiator, anionic surfactant, nonionic surfactant, buffer, and three crosslinkers, respectively.

Syntheses

Deionized water and emulsifier were stirred and gently warmed in a bottle. Monomer I mixture, which contained crosslinkers, was added under stirring at a constant speed at 60°C . A part of the initiator was added dropwise at 80°C . After the exotherm was complete, the temperature was maintained at 80°C for 2 h and then gradually cooled to 60°C , followed by the dropwise addition of the monomer II mixture, which also contained crosslinkers. The seed latex plus monomer II was then allowed to stand while stirring at 60°C for a time interval of 1 h. The polymerization procedure that was followed was the same as that of monomer I. Except as specified, in the study (samples F and G) the ratio of network I/network II was fixed at 40/60 and the ratio of St/AN in the network I was 90/10.

Measurement

The dynamic mechanical spectra of the LIPNs were obtained by employing an Autovibron dynamic viscoelastomer instrument (Rheovibron DDV-III type, Tokyo Baldwin Co. Ltd.). The temperature range was -50 to 150°C at a heating rate of $2^\circ\text{C}/\text{min}$, and the vibration frequency was

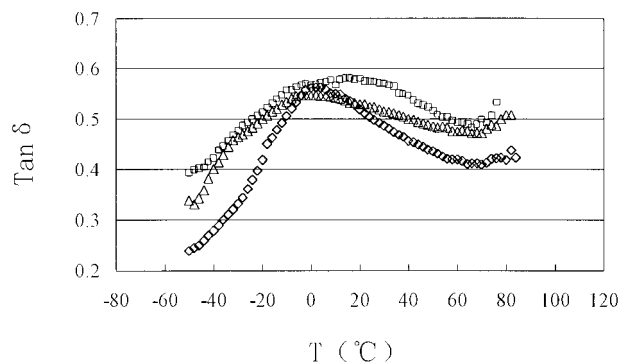


Figure 1 The influence of the kind of crosslinker on the damping properties of P(St-AN)/P(nBA-EA) LIPNs (\diamond) A-1, (\square) D-1, and (\triangle) D-2.

Table I Effects of Different Crosslinkers on Damping Properties

	No.		
	A-1	D-1	D-2
Crosslinker	TMPTA	DVB	DEGDA
T_g ($^\circ\text{C}$)	4.1	16.8	6.8
$\text{Tan } \delta_{\text{max}}$	0.562	0.581	0.547
Peak width $\text{tan } \delta > 0.5$			
T_1 ($^\circ\text{C}$)	-8.9	-23.2	-18.6
T_2 ($^\circ\text{C}$)	24.8	59.9	40.6
ΔT ($^\circ\text{C}$)	33.7	83.1	59.2

35 Hz. There are probably two glass-transition temperatures (T_g) for the composition studied, and the P(St-AN) is probably close to 100°C . The length of the sample increases with the temperature during the measurement, and the viscoelastomer stops working as soon as the length increment reaches 0.5 cm. Therefore, in the measurement the peak for the P(St-AN) network could not be obtained because the length increment surpassed 0.5 cm in the corresponding transition temperature region; the T_g in that study is contributed by the P(EA-nBA) network.

RESULTS AND DISCUSSION

Influence of Crosslinker

Figure 1 and Table I show the dynamic mechanical properties for a series of P(St-AN)/P(EA-nBA) LIPNs synthesized by using three crosslinkers (DVB, TMPTA, and DEGDA) at the same ratio of monomer I/monomer II; each LIPN has 0.4 wt % crosslinker. It is very clear that the structure of the crosslinker has an obvious influence on the damping properties. In the $\text{tan } \delta$ and temperature (T) curves, the temperature where the damping value surpasses 0.5 is 83.1°C for the LIPNs with DVB and the ones for the LIPNs with TMPTA and DEGDA are only 33.7 and 59.2°C , respectively. On the other hand, the T_g for the P(EA-nBA) network with TMPTA is 4.1°C . The addition of DVB leads to an obvious increase in the T_g of the network. The results indicate that DVB can significantly improve the damping properties of the LIPNs over a broad temperature region compared to TMPTA and DEGDA, which could be attributed to the rigidity and steric effect of DVB due to the phenyl of the molecule.

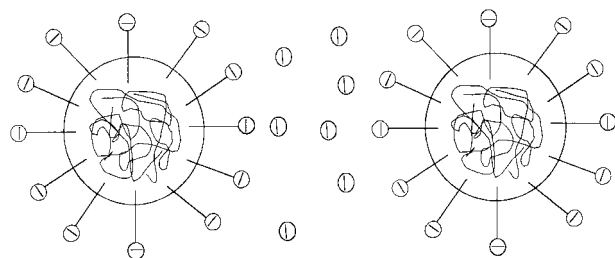


Figure 2 The sketch map of the stabilization of latex particles under alkaline conditions.

Although the three samples contain the same weight percentage of crosslinker, the three crosslinkers have different molecular weights (DVB = 130, DEGDA = 236, TMPTA = 296). At the same weight percentage, the molecular number of DVB is the most and TMPTA the least. Therefore, the crosslinked point density of the LIPNs with DVB or DEGDA is higher than TMPTA, which favors decreasing the size of the phase domains, resulting in the enhancement of the damping values.

Influence of Buffer

When $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was used as the initiator, it tended to decrease the pH value of the emulsion. The change of the pH affects the stabilization mechanism of latex particles and the dynamic mechanical properties of LIPNs. Therefore, NaHCO_3 (10 wt %) was introduced into the emulsion system as a buffer before polymerization and the pH values of all systems were adjusted to 8; buffer was used to help stabilize the LIPN systems.

Stabilization Mechanism of Latex Particles

The surface of the latex particles was covered by the anions when anion emulsifier was used. Keeping the latex particles stable was mainly derived from the interaction among anions, which provided the mechanical stabilization of the latex particles. After the addition of the buffer, the LIPNs system showed weak alkalinity. Some OH^- in the emulsion were dissociated, which could act to repel the negative ion at the surface of the latex particles. An isolation layer was thereby formed between two latex particles, so that they could not approach each other, as shown in Figure 2.

Without the buffer the pH value of the emulsion was about 3–4 when using a part of the

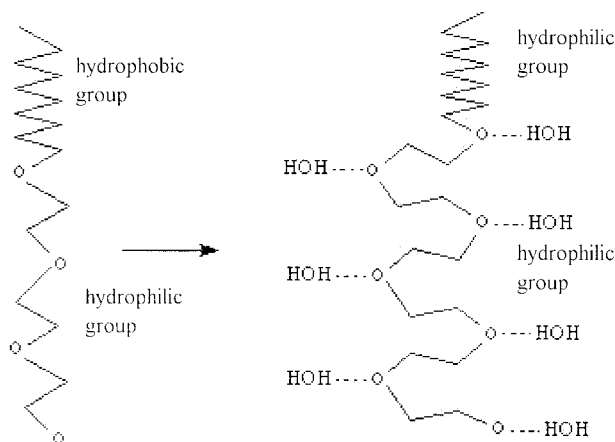


Figure 3 The sketch map of the stabilization of latex particles under acidic conditions.

nonionic emulsifier (NPPOE), and it showed moderate acidity. Latex particles could also maintain stability throughout the hydration layer (as shown in Fig. 3) formed by the nonionic emulsifier inserting itself into the ionic emulsifier. It also stabilized the latex particles. However, buffer must be used when the solid content is higher because of the low efficiency of the nonionic emulsifier.

Effects of Buffer on Damping Properties

It can be seen from Table II and Figure 4 that the glass-transition temperature range was little changed by the introduction of the buffer, but the damping value rapidly increased in this range. A possible reason is that there were differences in the course of the formation of latex particles when polymerizing. The initiator was $(\text{NH}_4)_2\text{S}_2\text{O}_8$, which was heated and decomposed to $\text{SO}_4^- \cdot$ con-

Table II Effects of Buffer on Damping Properties

	No.	
	D-3	E-1
T_g (°C)	3.7	1.9
$\text{Tan } \delta_{\text{max}}$	0.624	0.776
Peak width $\text{tan } \delta > 0.5$		
T_1 (°C)	35.3	37.5
T_2 (°C)	51.6	41.1
ΔT (°C)	86.9	78.6

D-3, without buffer; E-1, with buffer.

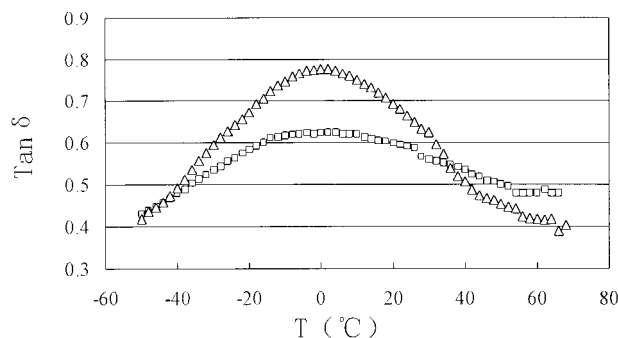


Figure 4 The influence of the introduction of buffer on the damping properties of P(St-AN)/P(nBA-EA) LIPNs (□) D-1 and (△) E-1.

taining a negative electric charge. By introducing the buffer into LIPN systems, the latex particles were stabilized and their surface was overlaid by a negative charge. When polymerization began, the active chains were wrapped into the emulsifier to form latex particles. Because of mutual repulsion, other radicals found it difficult to penetrate into the growing particles to terminate the polymerization. With no buffer the negative ions on the surface of the latex particles were neutralized by H^+ (because the pH value of latex is <7), and it was easier for free radicals to enter into the latex particle to end the polymerization. The time of polymerization was prolonged with the introduction of the buffer, so the average length of the polymer chains in the latex particles was comparatively long and the degree of entanglement was larger. The internal friction resistance of the molecule was enhanced at the glass transition, causing the increase of the damping value. On the other hand, longer chains and larger entangle-

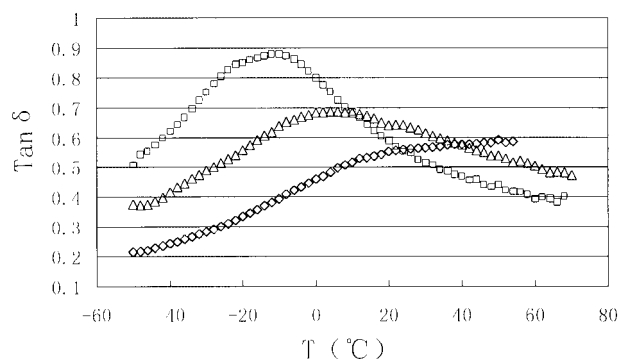


Figure 5 The influence of blending on the damping properties of P(St-AN)/P(nBA-EA) LIPNs (□) F, (◇) G, and (△) the blend.

Table III Effects of Blending on Damping Properties

	No.		
	F	G	Blend
T_g (°C)	-10.9	50.3	23.6
Tan δ_{max}	0.881	0.592	0.643
Peak width tan $\delta > 0.5$			
T_1 (°C)	-50	8.2	-27.3
T_2 (°C)	30.6	>54	60.7
ΔT (°C)	80.6	>62.2	88

ments worked against the interaction between the two networks, which led to the decrease of forced interpenetration; with no buffer the polymerization ended rapidly, which caused the polymer chains to be shorter, the chain segments to move easily, and the damping value to be lower. Shorter chains are good to increase interactions between networks and enhance forced interpenetration. The decrease in the depth of the trough between the two glass transitions was also much smaller.

Influence of Blending

The dynamic mechanical data of the blend prepared by mixing sample F with sample G are shown in Figure 5 and Table III. Sample F is 30/70 P(St-AN)/P(nBA-EA) LIPNs with a St/AN ratio of 90/10 in network I and a nBA/EA/AA ratio of 50/45/5 in network II; sample G is 40/60 P(St-AN)/P(nBA-EA) LIPNs with a St/AN/AA ratio of 85/10/5 in network I and a nBA/EA/AA ratio of 50/45/5 in network II. In the tan δ - T curve of sample F the damping peak is located at -10.9°C and the tan δ values exceed 0.5 over the 80.6°C temperature range between -50 and 30.6°C . The damping values are higher in the lower temperature region but lower in the room temperature region. The damping peak of sample G appears at

Table IV Effects of Decreasing Noises

Operating Mode	Before Damped (dB)	After Damped (dB)
Low blower speed	44.28	42.98
High blower speed	45.57	39.87
High cooling	46.68	42.83
Low cooling	49.00	47.38

Table V Effects of Decreasing Vibration

Operating Mode	Before Damped (mV)	After Damped (mV)
Low blower speed	6.78	6.06
High blower speed	8.10	7.50
High cooling	7.90	7.58
Low cooling	7.91	6.64

50.3°C, and the damping values exceed 0.5 beyond 8.2°C. The blend of sample F with sample G results in a broader and well-distributed damping peak. $\tan \delta$ values between 0.5 and 0.643 are noted over 88°C, which is consistent with the results on two LIPN blends reported by Satgurunathan and Campbell.⁸

Application

Plates of about 1-mm thickness, which were produced using the LIPNs, were bonded on the top of an air conditioner. A microphone and millivoltmeter were used to collect the noises at standard points. Eight characteristic points were selected on the top of the air conditioner by using a transistor vibration meter and a piezoelectricity sensor, and the vibration data were collected under four operating modes. These data were used to analyze the actual damping properties.

The noise collected from each standard point was the composite noise of the whole machine. Only the top of the air conditioner was covered by the damping layer, so the disturbance of other noise sources in the middle of the air conditioner must be removed to express the real effect of the damping layer on the top of the shell. The following equation was used to calculate the noises in different operating conditions after damping:

$$L_1 = 10 \log(10^{L/10} - 10^{L_2/10})$$

where L are the composite noises produced by components 1 and 2, and L_1 and L_2 are the respective noises produced by components 1 and 2. It can be seen from Table IV that the effects of

decreasing noise were significant, especially on high blower speed noises diminished by 5.7 dB. Table V shows that the extent of vibration at the top of the shell was also weakened. In the low cooling mode the most obvious effect was that vibration was attenuated 16%.

CONCLUSIONS

1. A series of P(St-AN)/P(EA-nBA) LIPNs was synthesized by using three crosslinkers (DVB, TMTPA, and DEGDA). The results indicate that DVB can specifically improve the damping properties of the LIPNs over a broad temperature region compared to TMTPA and DEGDA.
2. The NaHCO_3 introduced into the emulsion system as a buffer before polymerization helped to keep the LIPN systems stable and caused an increase of the damping value.
3. The LIPN blends prepared by mixing LIPNs resulted in a broader and well-distributed damping peak.
4. The tests of the damping properties on an air conditioner show that these LIPNs gave some improvement in reducing noise and attenuating vibration.

REFERENCES

1. Fay, J. J.; Murphy, C. J.; Thomas, D. A.; Sperling, L. H. *Polym Eng Sci* 1991, 31, 1731.
2. Corsaro, R. D., Sperling, L. H., Eds. *Sound and Vibration Damping with Polymers*, ACS Symposium Series 424; American Chemical Society: Washington, DC, 1990.
3. Sperling, L. H. *Interpenetrating Polymer Networks and Related Materials*; Plenum: New York, 1981; Chapter 8.
4. Li, S.; Qiu, Q.; Jarvela, P. *J Appl Polym Sci* 2000, 76, 722.
5. Hu, M.; El-Aasser, S.; Dimonie, V. L.; Sperling, L. H. *Colloids Surfaces* 1999, 153(1–3), 241.
6. Kim, S. D.; Boczar, E. M.; Klein, A.; Sperling, L. H. *Polym Mater Sci Eng* 1999, 80, 569.
7. Li, S.; Zeng, W. *J Appl Polym Sci*, to appear.
8. Satgurunathan, R.; Campbell, A. M. *Polym Mater Sci Eng* 1991, 63, 674.