

# Effect of Components (Acrylonitril and Acrylate Acid) on Damping Properties of Poly(styrene-acrylonitril)/Poly(ethylacetate-*n*-butylacrylate) Latex Interpenetrating Polymer Networks

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**ABSTRACT:** A series of poly(styrene-acrylonitril)/poly(ethylacetate-*n*-butylacrylate) latex interpenetrating polymer networks (LIPNs) have been synthesized by varying the content of AN and the distribution of acrylate acid. The damping temperature range of the LIPNs was broadened and the damping value increased distinctly when the content of acrylonitril was 10%. In low or high temperature range, the damping value of the LIPNs would have a different level of increase with the different distribution of AA in both the networks. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 821–826, 2002; DOI 10.1002/app.10350

**Key words:** latex; damping; latex interpenetrating polymer networks (LIPNs); P(St-AN)/P(EA-*n*BA)

## INTRODUCTION

Interpenetrating polymer networks (IPNs) contain an especially intimate mixture of two polymeric components<sup>1</sup> synthesized by swelling network polymer I with monomer II plus crosslinkers and polymerize *in situ*.<sup>2</sup> Through the resulting two-component system tends to produce the phase separately, the double-network structure restricts the resulting phase size, prevents gross phase separation and macroscopic layering effects, and provides excellent properties. Since Sperling<sup>3</sup> and Frich<sup>4</sup> developed the concept of Millar's IPNs in 1969, latex IPNs (LIPNs), an important type of IPNs, have drawn a great deal of attention from many investigators. Early in 1970s, Sperling pointed out that semicompatible LIPNs have a potential practical value for noise

and vibration damping. Polystyrene/polyacrylate (PS/PACE) LIPNs comprise one of the latex systems that has been commonly investigated. In this article, a series of poly(styrene-acrylonitril)/poly(ethylacetate-*n*-butylacrylate) [P(St-AN)/P(EA-*n*BA)] have been synthesized by introducing AN in the monomer I mixture and changing the distribution of acrylate acid (AA). The damping behavior of the LIPNs was studied using a Rheovibron Viscoelastomer.

## EXPERIMENTAL

### Materials

The following materials were used in the studies: styrene (St), acrylonitril (AN), *n*-butyl acrylate (*n*BA), ethyl acrylate (EA), acrylic acid (AA), trimethylpropane triacrylate (TMPTA), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and sodium lauryl sulfate (SLS). The monomers were distilled under reduced pressure to remove inhibitors before use.

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**Table I** The Variation of Ratio of Acrylonitril/Styrene in Polymer Network I

Sample	A-0	A-1	A-2
Acrylonitril (%)	0	10	20
Styrene (%)	100	90	80
$T_g$ (°C)	-19.2	4.1	-1
$\tan \delta$ max	0.446	0.562	0.449
Temperature range of $\tan \delta > 0.4$			
$T_1$ (°C)	-41.5	-21	-19
$T_2$ (°C)	-3.2	> 85.2	> 80
$\Delta T$ (°C)	38.3	> 106.2	> 99
Temperature range of $\tan \delta > 0.5$			
$T_1$ (°C)	—	-8.9	—
$T_2$ (°C)	—	24.8	—
$\Delta T$ (°C)	—	33.7	—

### Synthesis

LIPNs were synthesized by a two-staged emulsion polymerization technique. First the deionized water was introduced into a bottle along with the emulsifier (SLS) and stirred at 60°C, then monomer I (St, AN) containing crosslinker was added. The flask was heated to 80°C, and then the initiator [2% (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] was dropped. It was cooled to room temperature after reacting at 80°C for 2 h, resulting in the seed latex for the second

stage. Next, monomer II (EA, nBA), also containing crosslinker, was added, using a dropwise addition. The second monomer (II) was allowed to be in contact with the seed polymer for 1 h before the second stage of polymerization was carried out. Finally, the reaction was completed under the same conditions as the first stage, and the resulting product was LIPNs. In the experiment, the ratio of monomer I to monomer II was fixed at 40/60.

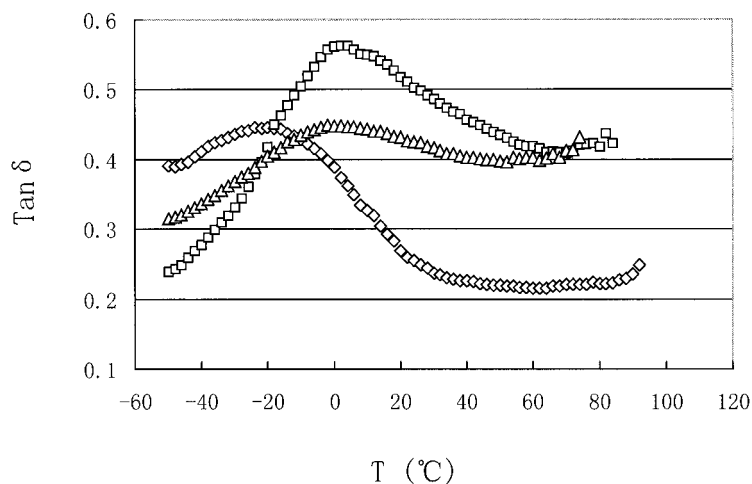
### Tests of Dynamic Mechanical Properties

The dynamic mechanical spectrum (DMS) of LIPNs was measured by employing a Rheovibron directreading viscoelastometer, Model DDV-III (Vibron, Tokyo Measuring Instrument Co., Ltd., Tokyo, Japan). The temperature range investigated ranged from -50°C to 150°C, with a heating rate of 2°C per minute, and the vibration frequency employed was 35 Hz. The dynamic mechanical data were automatically reported every 2 min.

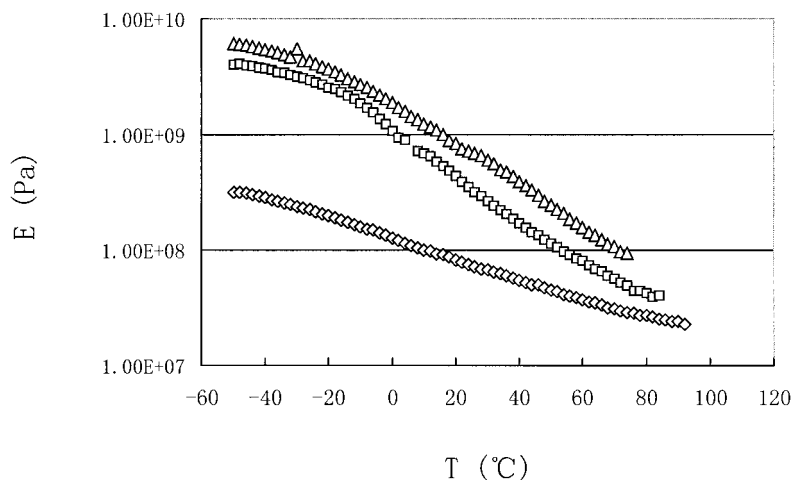
## RESULTS AND DISCUSSION

### Influence of AN in Network Polymer I

Table I and Figure 1 show the effect of the AN component on the damping properties of P(St-AN)/P(nBA-EA) LIPNs. It can be seen that when AN content in the network I is zero, the resulting



**Figure 1** Influence of the content of acrylonitril on the damping properties of the poly(styrene-acrylonitril)/poly(ethylacetate-*n*-butylacrylate) latex interpenetrating network ( $\diamond$  A-0,  $\square$  A-1,  $\triangle$  A-2)



**Figure 2** Influence of the content of acrylonitril on the storage modulus of poly(styrene-acrylonitril)/poly(ethylacetate-*n*-butylacrylate) latex interpenetrating network ( $\diamond$  A-0,  $\square$  A-1,  $\triangle$  A-2)

LIPN, that is, PS/P(*n*BA-EA) LIPN, is a partially miscible system.<sup>5</sup> St contains a phenyl group. The steric hindrance of this phenyl group makes chain segments of polymer network I tend to pile up loosely, which is favorable for the interpenetration of two networks, whereas the degree of interpenetration is limited because of the difference of polarity between St and EA or *n*BA. Therefore, the PS/P(*n*BA-EA) LIPNs have two main transitions, and the valley between the two transition regions is deep relatively (the peak in Fig. 1 belongs to polymer network I, namely, PS). It is very clear that the damping values of the two transition regions have obvious differences. The values in the high-temperature region are low, even smaller than 0.25, while the maximum value in the low-temperature region is 0.446. For the temperature range where  $\tan \delta$  is more than 0.4 is only 38.3°C, the damping properties of the PS/P(EA-*n*BA) LIPN are not ideal. However, the damping properties were visibly improved after introducing AN into network I. Not only did all the damping values in the temperature range

measured surpass 0.3 but the temperature range of  $\tan \delta > 0.4$  is about 100°C, the effective damping temperature range in which the  $\tan \delta$  value is bigger than 0.3<sup>6,7</sup> is broadened. AN is a strong polar molecule; therefore, the copolymerization of St and AN improved the polarity of network I and the interaction between two networks. The miscibility of the P(St-AN)/P(EA-*n*BA) LIPNs rises, and the glass transition peak shifts inward compared with the PS/P(EA-*n*BA) LIPN. The DMS indicates that P(St-AN)/P(EA-*n*BA) LIPNs are a semimiscible polymer blend.

Figures 1 and 2 also show the effect of the amount of AN on the properties of the LIPNs system. With an increased amount of AN, the temperature range of  $T_g^\delta > 0.4$  decreases from 106.2°C to 99°C and damping values in that temperature range fall slightly. AN can increase the degree of interpenetration of the LIPNs because of raising miscibility, but the increase of AN would produce counteraction on the interpenetration of the system due to the increase of interaction among molecules. The greater the content of

**Table II** The Glass Transition Temperature of Polymer Network II

Sample	P( <i>n</i> -butyl acrylate-ethyl acrylate)	A-0	A-1	A-2
Measuring value (°C)	-24.7	-19.2	4.1	-1
Theoretical value (°C)	-39.7	-34.2	-10.9	-16

**Table III** Volume Variation of Polymer I inside Polymer Network II

Sample	A-0	A-1	A-2
$\phi_1$ (%)	3.8	19.7	16.0

AN is, the stronger the interaction among AN is. Therefore, the structure of polymer network I would have a greater effect (as shown in Fig. 2, the modulus also rises with an increase of AN), which could prevent monomer II from penetrating into polymer network I and thus restrict the degree of interpenetration. The damping properties of the LIPNs were controlled by the two factors. The first factor is most important when the content of AN is 10 wt %. As the content of AN increases from 10 to 20 wt %, the later factor gradually increases and was stronger than the former factor. So the glass transition temperature of sample A-1 is higher than that of A-2, which indicates that the degree of interpenetration of A-1 is a little higher than that of A-2.

According to the Giffs–Dimarzio equation,

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}, \quad (1)$$

where  $T_g$  represents the glass transition temperature of copolymers;  $T_{g1}$  and  $T_{g2}$  represent the glass transition temperature of component I and component II, respectively; and  $W_1$  and  $W_2$  are the respective weight fractions. The glass transi-

tion temperature of P(EA-nBA) can be calculated and is called the theoretical value (as shown in Table II). The discrepant value between the theoretical value and the measuring value of P(EA-nBA) is the revised value. Therefore, the theoretical value of polymer network I in A-0, A-1, and A-2 was roughly considered to be equal to the corresponding measured value plus the discrepant value. Using the theoretical value, the volume fractions of polymer network I in polymer network II can be calculated by means of eq. (2):

$$T_g = \phi_1 T_{g1} + \phi_2 T_{g2}, \quad (2)$$

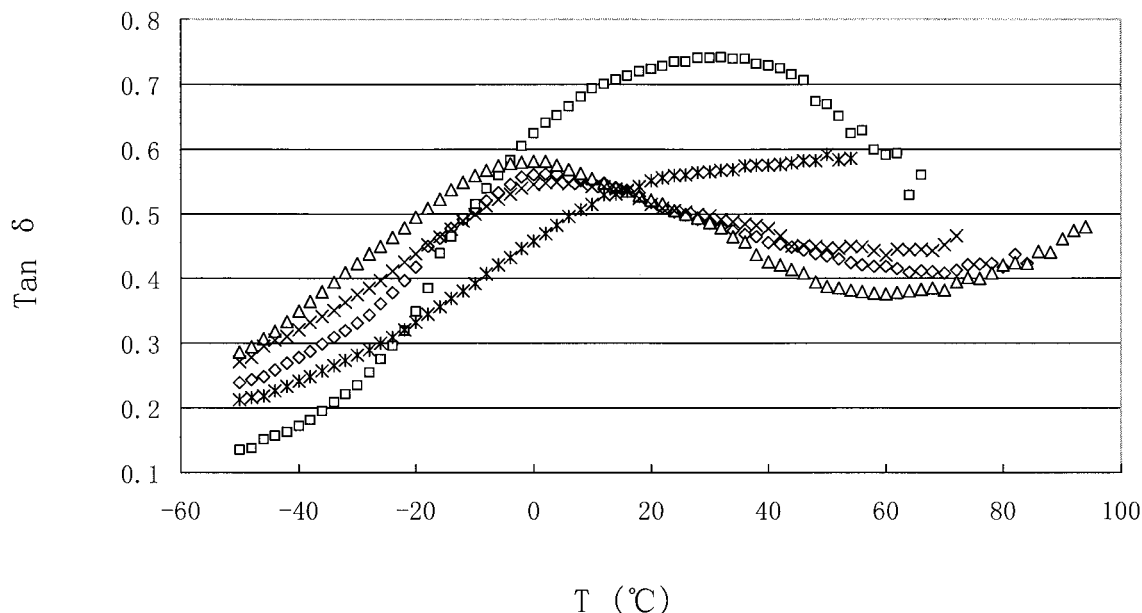
where  $T_{g1}$  and  $T_{g2}$  represent the theoretical values of P(EA-nBA) and P(St-AN), respectively [the theoretical values of P(EA-nBA) and P(St-AN) (100/0), (90/10), and (80/20) are 39.7°C, 105°C, 106.5°C, and 108°C, respectively];  $\phi_1$  and  $\phi_2$  are the respective volume fractions in the polymer network II; and  $T_g$  is the theoretical value of polymer network II.  $\phi_2$  was an estimated value of network I content in network II. The results (as shown in Table III) indicated that the extent of interpenetration of A-1 is surely higher than that of A-2.

#### Influence of the Distribution of AA

The ratio of monomer I to monomer II was fixed at 40/60. AA (5 wt %) as a functional monomer was introduced into the monomer I or/and monomer II. The effect on the damping properties of the distribution of AA in the two networks is illus-

**Table IV** Influence of AA Distribution on the Damping Properties

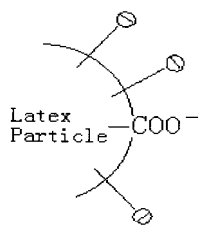
NO.	A-1	B-1	B-2	B-3	B-4
AA content (wt%):					
Network I	0	5	0	1.5	3.5
Network II	0	0	5	3.5	1.5
$T_g$ (°C)	4.1	32.3	4.9	4.7	50.3
$\tan \delta$ max	0.562	0.743	0.581	0.549	0.592
Temperature range $\tan \delta > 0.4$					
$T_1$ (°C)	-21	-18	-33	-25	-8
$T_2$ (°C)	> 85.2	> 69.1	48	> 77.7	> 54
$\Delta T$ (°C)	> 106.2	> 87.1	81	> 102.7	> 62
Temperature range $\tan \delta > 0.5$					
$T_1$ (°C)	-10	-12	-19	-9.3	8
$T_2$ (°C)	25	> 69.1	26	28.7	> 54
$\Delta T$ (°C)	35	> 81.1	45	38	> 46



**Figure 3** Influence of the distribution of acrylate acid in both networks on the damping properties of poly(styrene-acrylonitrile)/poly(ethylacetate-*n*-butylacrylate) latex interpenetrating network ( $\diamond$  A-1,  $\square$  B-1,  $\triangle$  B-2,  $\times$  B-3,  $*$  B-4)

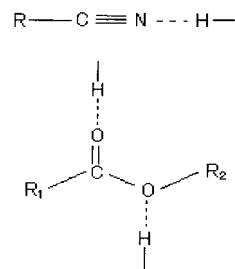
trated in both Table IV and Figure 3. It can be seen that the glass transition peak varies significantly and with complexity. Containing a polar group ( $-\text{COOH}$ ), AA can affect the damping properties of the LIPN system as well as AN. In addition, the active H of the carboxy could produce a hydrogen bond with other groups, like  $-\text{COO}-$ ,  $-\text{C}\equiv\text{N}$ , and so on, which would increase the damping properties of LIPNs.

AA, as a hydrophilic monomer, tends to be distributed at the surface of the latex particles in the process of polymerization, which means that it could act as emulsifier and improve the stabilization of latex particles (as shown in Fig. 4). When polymerization had been completed, part of the AA molecules introduced into polymer network I was distributed near the boundary between polymer network I and II (core and shell), while the



**Figure 4** Sketch of the latex particles.

AA introduced into polymer network II was distributed near the surface of latex particles, which would be incorporated in the polymer network II after forming the films. Both  $-\text{COO}-$  and  $-\text{C}\equiv\text{N}$  could form hydrogen bonds with hydrogen, but the ability to form a hydrogen bond is different. As shown in Figure 5, the group  $-\text{COO}-$  could form two hydrogen bonds, but the group  $-\text{C}\equiv\text{N}$  could form only one. In addition, the electronegativity of oxygen is stronger than nitrogen. The bond strength of  $\text{O}\cdots\text{H}$  is also stronger than that of  $\text{N}\cdots\text{H}$ . So it can be assumed that the active H in the boundary layer would form a hydrogen bond with group  $-\text{COO}-$ , which means that the hydrogen bond was formed between two polymer networks; the active H near



**Figure 5** Sketch of the hydrogen bond.

the surface of latex particles would form hydrogen bond inside polymer network II. When AA was part of the monomer I mixture, the hydrogen bond formed was located between two networks of the LIPN, which means that the interaction between two networks was enhanced, the degree of interpenetration was improved, and the damping value in the high-temperature range was increased. The hydrogen bond would be situated inside the polymer network II when AA belonged to monomer II mixture. It could make the structure of polymer network II compact, which resulted in the enhancement of the damping properties in the low-temperature range because of the increase of the kinetic resistance to the chain-segment motion of polymer network II. So the  $\tan \delta$ - $T$  curves of B-1, B-4 shifted toward high temperatures and the damping value in the high temperatures increased because of the hydrogen bond between the two polymer networks. In contrast, while the  $\tan \delta$ - $T$  curves of B-2, B-3 also slightly

shifted toward high temperatures, the damping value in the low temperatures increased because of the hydrogen bond inside the polymer network II.

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