Dynamic Mechanical Properties in Blends of Poly(styrene-*b*-isoprene-*b*-styrene) with Aromatic Hydrocarbon Resin

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ABSTRACT: The damping properties in blends of poly (styrene-*b*-isoprene-*b*-styrene) (SIS) and hydrogenated aromatic hydrocarbon (C_9) resin were investigated by dynamic mechanical analysis. SIS exhibited two independent peaks of loss factor (tan δ) corresponding to the glass transition of polyisoprene (PI) and polystyrene (PS) segments, respectively. The addition of hydrogenated C_9 resin had a positive impact on the damping of SIS. With the increasing softening point and content of the resin, the main tan δ peak shifted to higher temperatures and the useful damping temperature range was broadened. Addition of mica or PS was found to widen the effective damping range evidently in the high-temperature region, especially when PS was mixed in the solid state. It was concluded that the dispersed PS domains played a role of reinforcing fillers at low temperatures and served as a polymer component with a tan δ peak due to its glass transition at the high temperature. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4157–4164, 2006

Key words: poly(styrene-*b*-isoprene-*b*-styrene); hydrocarbon resin; dynamic mechanical properties; damping

INTRODUCTION

Vibration often causes undesirable consequences[1–3] such as unpleasant motions, noises, and dynamic stresses that lead to fatigue and failure of structures, decreased reliability, and degraded performance. Polymers have been widely applied for achieving acoustic and vibration damping and isolation because of a unique combination of low modulus and inherent damping.[2,4] Damping in either free or constrained layer configurations is reflected by dynamic mechanical properties, the temperature dependence of storage modulus E', loss modulus E'', and the ratio E''/E' as loss factor tan δ.[5,6] Usually, it is desirable to have high values of tan δ or E'' over wide temperature and frequency ranges. For instance, tan δ above 0.30 is often required over a temperature range of at least 60–80°C for outdoor or machinery applications in the constrained layer damping of structure vibrations.[7]

However, homopolymers usually exhibit narrow effective damping temperature ranges of only 20–30°C around their glass transition temperatures (T_g), among which the polymers have pronounced dissipation of the mechanical energy as heat,[1–7] based on the onset of coordinated chain molecular motions. Traditional methods of modification and broadening of the damping range often involve use of a multicomponent polymer system with partial compatibility, such as copolymer,[8] mechanical blends,[9] interpenetrating polymer networks,[10–13] or other additives as modified crosslinking agents, plasticizers, fillers,[14] and low-molecular-weight organic compounds.[1,7,15,16]

In most of the current studies, the materials have been shown to exhibit useful damping behaviors in the temperature ranges around room temperature. In the case of our work, it is identified that blends of poly(styrene-*b*-isoprene-*b*-styrene) (SIS), a kind of block copolymer, with aromatic hydrocarbon resin may be good candidates for damping applications, especially in the high-temperature region.

SIS consists of two incompatible blocks in the solid state, the isoprene segments with lower T_g and the styrene segments with upper T_g, which form a microphase-separated structure at room temperature.[17–19] The material can be considered as an elastermeric matrix physically vulcanized by the aggregation of polystyrene (PS) end blocks, which also act as reinforcing filler.[20–22] It provides opportunities for improvement of damping over a wide range at high temperatures, since phase separation behavior has a positive impact on damping.

Hydrocarbon resins are amorphous polymers of low molecular weights, synthesized from molecular species isolated from petroleum feedstreams. These resins, for

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TABLE I
Characteristics and Acronyms of SIS Used

Code	Commercial name	Diblock SI (wt %)	PS blocks (wt %)	Hardness (Shore A)	Melt index (g/10 min)
SIS-A	Quintac3460	42	25	55	11
SIS-B	Quintac3520	78	15	35	7
SIS-C	Quintac3620	12	14	42	9

instance, aliphatic C_5 resins, aromatic C_9 resins, hydrogenated derivatives of C_5 and C_9 resins, and rosin derivatives, have molecular weights ranging from 300 to 3000 and usually exhibit a glassy state at room temperature. Here, C_5 and C_9 resins represent the aliphatic hydrocarbon resins of five carbon atoms per monomer, and the aromatic hydrocarbon resins of nine carbon atoms per monomer, respectively. These resins are commonly referred to as tackifying resins and added to elastomers to improve the wettability and the contact strength on the surface. Hydrogenated C_9 resins can have better compatibility with elastomers than unsaturated C_9 resins can. This is because hydrogenation of C_9 resin gives rise to alicyclic compounds to exhibit more favorable interaction with the elastomers than the latter.[17–24]

Earlier reports of SIS blended with hydrocarbon resin have mainly focused on the miscibility and properties as adhesives.[17–22,25–27] However, the blends are also found to have great potential in practical damping application through our studies on dynamic mechanical properties of the systems. In this article, we have investigated the effects of hydrogenated C_9 resins with various softening points and different loading on the damping of SIS, aiming at a new material of excellent damping over a broad temperature range. Ternary systems, with addition of mica or homopolymer PS, are also under further discussion to optimize the damping performance at the high temperature.

EXPERIMENTAL

Materials and sample preparation

Three types of SIS (Nippon Zeon, Japan) were used as the matrix copolymers. The characteristics of the block copolymer are given in Table I. Hydrogenated C_9 resins with various softening points were supplied by Arakawa Chemicals, Japan. Table II lists the softening points and the molecular weights of the resins, all of which are fully hydrogenated. Mica (Hebei Xuexing, China) is in 10–20 mesh. PS (PG-33) was provided by Chimei (Taiwan), with the softening point of 94 °C and melt index of 75 g/10 min (ISO-1133).

Compositions were kneaded for 10 min to ensure homogeneity of the mixture and then sheeted out by two-roll mill at room temperature unless otherwise mentioned. The stock was compression-molded into sheets of 2.0 mm thickness at 150°C for 10 min under 10 MPa. At the end of molding, the samples under compression were cooled to about 50°C by circulating water at ambient temperature through the platens.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out on a UBM Dynamic Mechanical Analyzer Rheogel E-4000. Strips were cut in dimensions of $23 \times 6 \times 2$ mm³. All the measurements were performed at a fixed frequency of 11 Hz in tension mode with a strain amplitude of 3 μm and at temperatures from −60 to 180°C with a heating rate of 3°C/min under liquid nitrogen.

Scanning electron microscopy

The morphology was conducted with a JEOL JSM-6360LV series scanning electron microscope (SEM). All the samples were immersed in liquid nitrogen for 5 min and broken. And the cryogenically fractured surfaces were sputter-coated with gold before examination.

RESULTS AND DISCUSSION

Dynamic mechanical analysis of SIS

Dynamic mechanical testing is a versatile and sensitive tool enabling a complete exploration of relaxational mechanisms in viscoelastic materials. E', E'', and tan δ are the most common information from DMA. E' is a measure of the recoverable strain energy in a deformed specimen. E'' is related to the dissipation of the material. Tan δ, the ratio E''/E', is the ratio of energy lost per cycle to the maximum energy stored per cycle.[28]

Figures 1–3 illustrate the temperature dependence of the tan δ and the dynamic E'' and E' of the SIS materials. The data are also recorded in Table III. The three types

TABLE II
Typical Properties of Hydrogenated C_9 Resins

Code	Softening point (°C)[a]	Glass transition temperature (°C)[b]	Molecular weight[c]		
			M_n	M_w	MWD
P90	90	48.0	670	1160	1.74
P125	125	81.0	870	1730	1.99
P140	140	86.0	1060	2220	2.10

[a] ASTM E28-67.
[b] Measured by DSC.
[c] Measured by GPC.

TABLE III
Details of Dynamic Mechanical Analysis for SIS

Sample	SIS-A	SIS-B	SIS-C
Tan δ_{max}/T_{max}			
T_{low}	0.44/−40	1.31/−45	1.91/−46
T_{high}	1.09/114	0.60/115	−
Plateau modulus (Pa)			
E'	$1.2 \times 10^8 - 1.5 \times 10^7$	$1.2 \times 10^7 - 1.6 \times 10^6$	$8.7 \times 10^6 - 9.7 \times 10^5$
E''	$3.6 \times 10^7 - 6.2 \times 10^6$	$7.2 \times 10^6 - 7.2 \times 10^5$	$7.9 \times 10^6 - 2.5 \times 10^5$
Plateau temperature range (°C)	−25–101	−30–105	−36–118
Flowing temperature (°C)	175	166	150

of SIS exhibit similar tendency of dynamic mechanical properties. As shown in Figure 1, the maxima in tan δ near −40 and 115°C reflect glass transitions for the PI and PS domains, respectively. The two independent tan δ peaks stay in the same location despite the alternate block content of different SIS, indicative of the separate microdomains for the PI and PS blocks. Nevertheless, the height of tan δ peak is dependent on the content of corresponding blocks. According to the details listed in Table III, SIS-C, with the highest content of PI blocks, gives a tan δ peak approaching to 1.91 at −46°C and an indistinct transition at the high temperature, while SIS-A gets the sharpest peak at 114°C as a result of the highest content of PS blocks.

In Figure 2, the E'' curves provide more information for the relaxation of the PI and PS segments, consistent with the tan δ peaks in Figure 1. In the E' spectra in Figure 3, there are wide modulus plateaus between the two T_g of the soft and hard blocks for SIS due to the glassy styrene domains acting as physical crosslinkers. Moreover, the plateau modulus and flowing temperature goes up with the increasing content of PS blocks. The flowing temperature is determined by the point of E' equal to 10^4 Pa.

It is noticeable that the hard blocks have a significant impact on the tan δ peak at the upper temperature and the flowing temperature of SIS. In our study, SIS-A with the highest content of PS is considered to be the most suitable base polymer to obtain the good damping in the high-temperature region.

Effects of hydrogenated C$_9$ resins

Although SIS-A shows more advantages for the damping properties at high temperatures than SIS-B and SIS-C, it is indispensable to take an effort to widen the useful damping temperature range. P140, which is of the highest softening point among the three hydrogenated C9 resins, is blended with SIS-A to attempt an improvement of damping properties. Figures 4 and 5 show the temperature dependence of tan δ and E'' for SIS-A/P140 as a function of blend ratio. Great changes take place for the tan δ and E'' curves with the addition of P140.

In Figure 4, P140 of content below 30 wt % exhibits compatibility with both the PI and PS domains, and its incorporation in SIS-A shifts the T_g for PI blocks to higher temperatures and reduces the thermal location
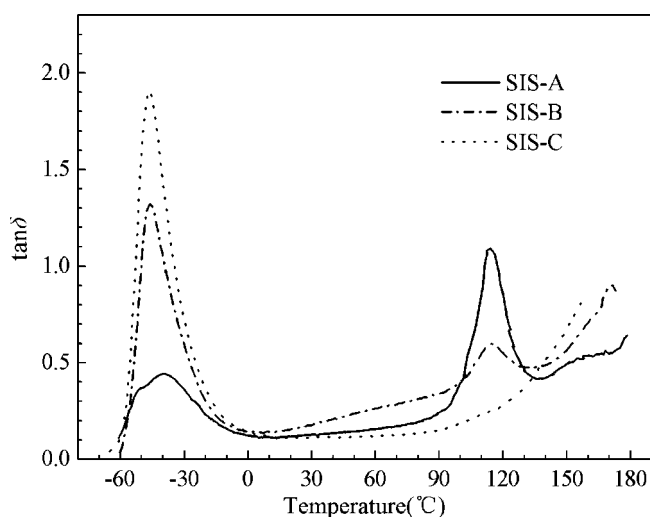

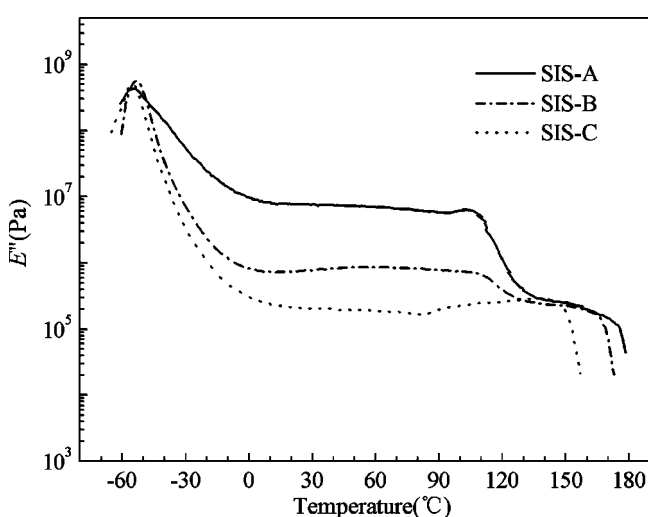**Figure 1** Temperature dependence of tan δ at 11 Hz for various SIS.

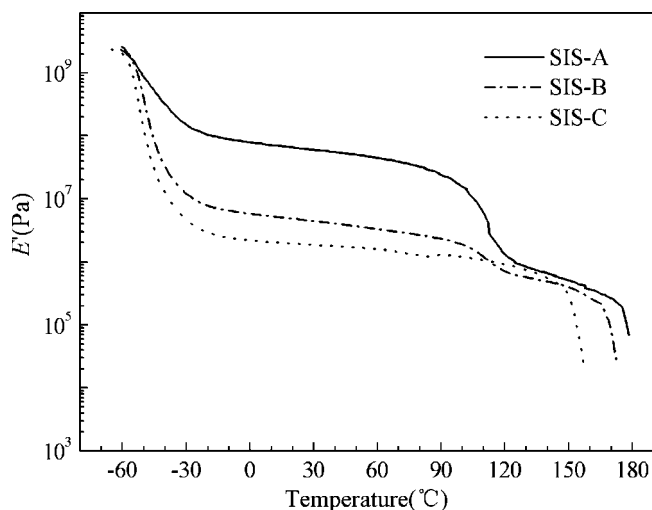**Figure 2** Temperature dependence of E'' at 11 Hz for various SIS.

Figure 3 Temperature dependence of E' at 11 Hz for various SIS.

Figure 5 Temperature dependence of E'' at 11 Hz for SIS-A/P140 as a function of blend ratio.

of the transition related to the PS blocks. The former moves more than the latter, and the tan δ peak at the lower temperature is intensified, but the tan δ peak at the upper temperature is weakened. As P140 is added by 30–40 wt %, the tan δ peak for the tackified PI blocks is split into two parts, and the transition at the upper temperature becomes inconspicuous. When the P140 content is above 40 wt %, the main tan δ peak moves to higher temperatures and increases remarkably, while the shoulder peak on the left decreases gradually without displacement.

Similar results are from the evolution of E'' curves in Figure 5. With the P140 content less than 30 wt %, the E'' peaks move with agreement with the tan δ peaks. As the P140 content reaches 40 wt %, a new transition emerges between the two original transitions at the

lower temperature and upper temperature, respectively. The new E'' peak shifts to higher temperatures and is strengthened with the addition of P140, whereas the other two transitions keep in the same positions. The related E' spectra are plotted in Figure 6. With the addition of P140, the flowing temperature declines all along, while the E' decreases drastically in the whole temperature region at the beginning and then has a slight promotion at low temperatures.

On the basis of the results, it is interesting to define the addition of resin as a two-step course. With the small content of resin, the resin disperses in the PI and PS domains, and P140 seems to have better compatibility with the PI blocks than with the hard blocks. This kind of dispersion is baffled at certain content when the domains of SIS are saturated with the resin. Once the

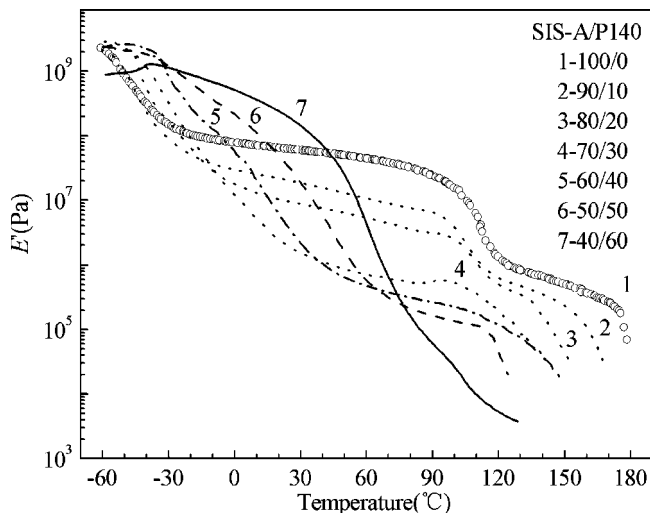**Figure 4** Temperature dependence of tan δ at 11 Hz for SIS-A/P140 as a function of blend ratio.

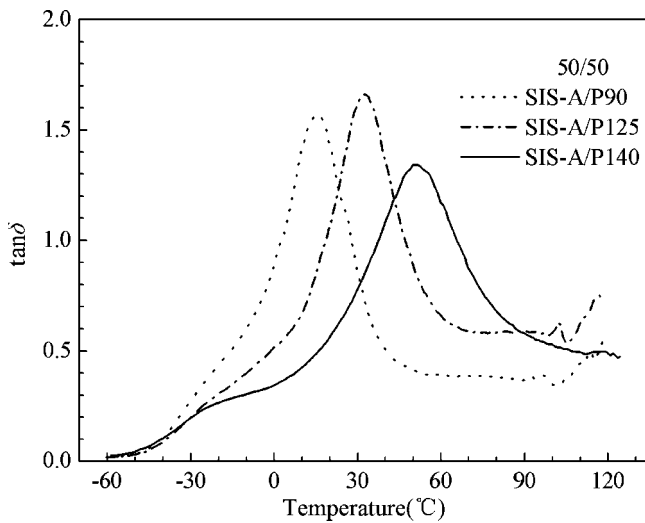**Figure 6** Temperature dependence of E' at 11 Hz for SIS-A/P140 as a function of blend ratio.

Figure 7 Temperature dependence of tan δ at 11 Hz for blends of SIS-A and hydrogenated C_9 resin with different softening points.

content of resin exceeds the critical point, the surplus resin will accumulate to form its own rich domains with a few PI segments dispersed. Therefore, it is identified that the resin acts as tackifying resin to dilute the physical entanglement network of SIS-A with small content and its excess portion becomes a kind of reinforcing fillers above a critical content.[19]

As regards the damping properties, the effective damping temperature range is broadened and moves to higher temperatures evidently resulted from the addition of P140. It is found that SIS-A/P140 (40/60) shows a tan δ peak centered at 76 °C and an effective temperature range of tan δ above 0.30 from 25 to 129°C and tan δ above 1.00 from 57 to 109°C.
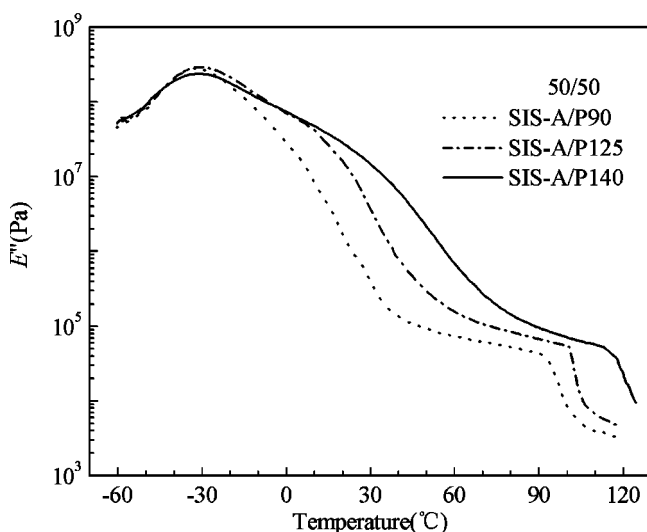

Figure 8 Temperature dependence of E'' at 11 Hz for blends of SIS-A and hydrogenated C_9 resin with different softening points.
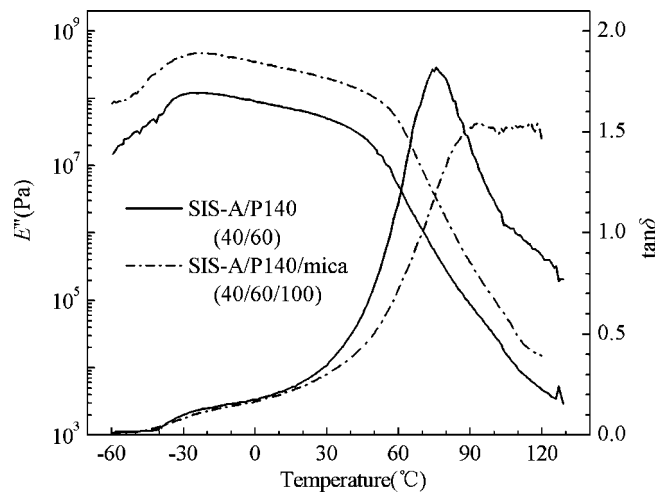

Figure 9 Effects of mica (100 phr) on temperature dependence of tan δ and E'' at 11 Hz for SIS-A/P140 (40/60).

Besides P140, the addition of P90 and P125 is also discussed. Figures 7 and 8 show the additive effects of three kinds of hydrogenated C_9 resins with 50 wt % content on the tan δ and E'' spectra of SIS-A. The dynamic mechanical curves for the three binary systems are analogous to each other with the transitions of the tackified PI and PS domains and the rich resin domains. It should be mentioned that the main tan δ peak owing to the relaxation of the resin itself and the effective damping temperature region move to higher temperatures with the increasing softening point of the resin, which is consistent with the increasing T_g.

It is concluded that the dynamic mechanical properties and the damping capacity of the blends could be manipulated by the resin type and concentration conveniently. System with the hydrogenated C_9 resin of higher softening point and content will have better damping performance in the high-temperature region.
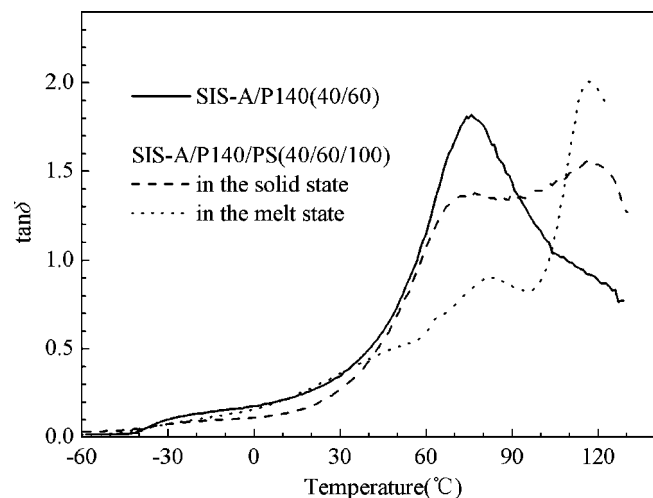

Figure 10 Effects of PS (100 phr) on temperature dependence of tan δ at 11 Hz for SIS-A/P140 (40/60).
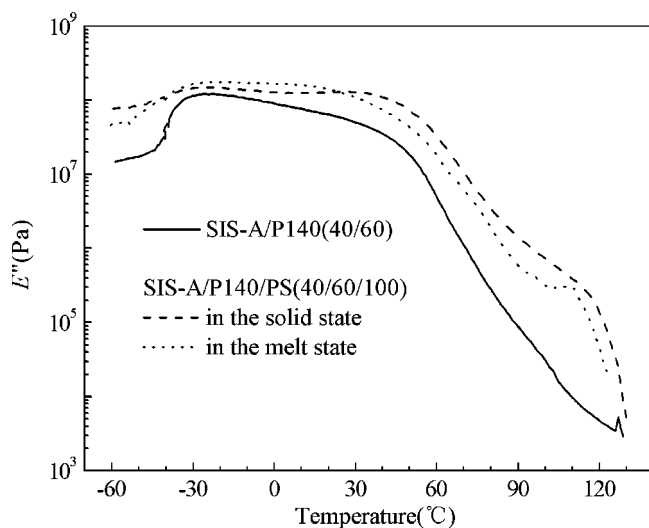
Figure 11 Effects of PS (100 phr) on temperature dependence of E'' at 11 Hz for SIS-A/P140 (40/60).

Of course, it is not always rewarding with too much resin in the blends because the samples will become much more brittle and the flowing temperature drops with the addition of the resin. Hence, the system of SIS-A with 60 wt % content of P140 is appropriate for our target to have a wide effective damping range particularly at high temperatures.

Ternary system of SIS-A/P140 (40/60) with mica

Mica, a kind of inorganic filler, has been reported to improve the damping properties of polymer over the glass transition because of the platelet structure, especially in the high-temperature region.[14] Figure 9 presents effects of 50 wt % content of mica on the dynamic mechanical properties of SIS-A/P140 (40/60). The original main tan δ peak turns into a platform at higher temperatures and the temperature of tan δ above 1.00

expands into the range from 70 to 120°C, with displacement of over 10°C compared with the unfilled system. Apart from general particle-polymer friction and particle-particle friction, platelets of mica and polymer damping layer form the unique structure of microconstrained layer damping, which may be greatly attributed to the high damping effect.[14] At the same time, the enhancement of E'' also offers possibility for the sample to be a kind of free-layer damping, where energy is dissipated because of direct strains, such as alternate extension and compression of the viscoelastic layer.[5]

Only one problem is found that the addition of mica leads to a more difficult mixing process and the tough technique will limit the practical application. It is necessary to find another component to take the place of mica.

Ternary system of SIS-A/P140 (40/60) with PS

As the PS domains of SIS-A embodies great significance on the damping properties at high temperatures referred earlier, homopolymer PS is incorporated into SIS-A/P140 (40/60) with the same loading as mica, in the hope of expanding effective range into higher temperatures. The introduction of PS is carried out at room temperature and at 120°C, where PS is in the solid state and in the melt state, respectively.

The process of adding PS gets much easier than that of mica. Figures 10 and 11 show the effects of PS added in the solid state and in the melt state on the dynamic mechanical properties of SIS-A/P140/PS (40/60/100). For the sample mixed at room temperature, it is found that the tan δ maximum at 76°C has a little reduction and another new peak appears at 115°C. The ternary system gives excellent damping with tan δ above 1.00 from 59°C to even 129°C, 20°C wider than the system with mica mentioned earlier. Unexpectedly, the specimen mixed at 120°C takes on the different tan δ curve from the unheated one, although the strengthened modulus is close to each other. An evident degradation

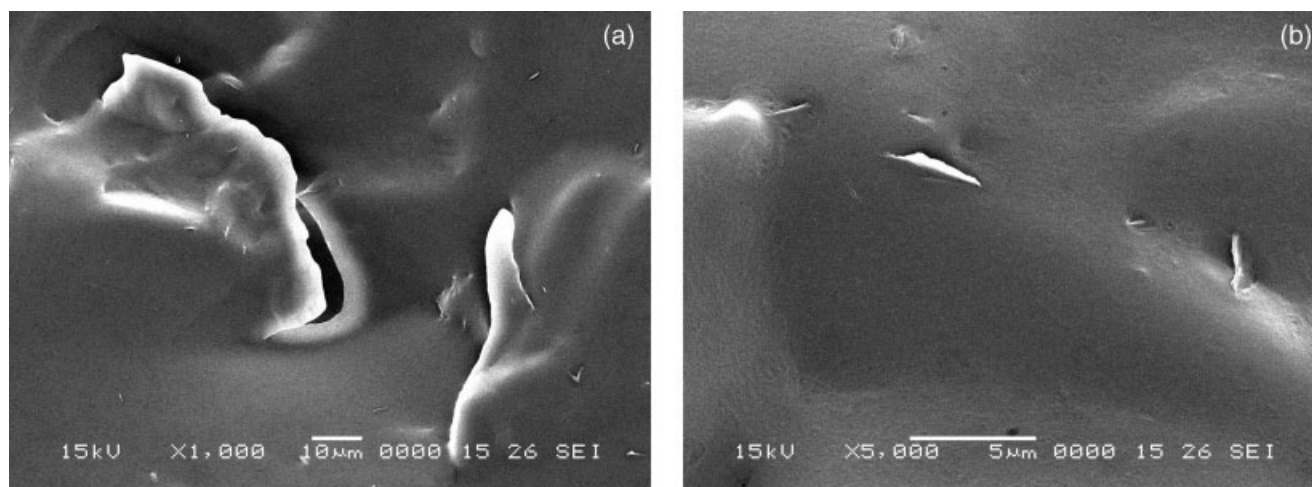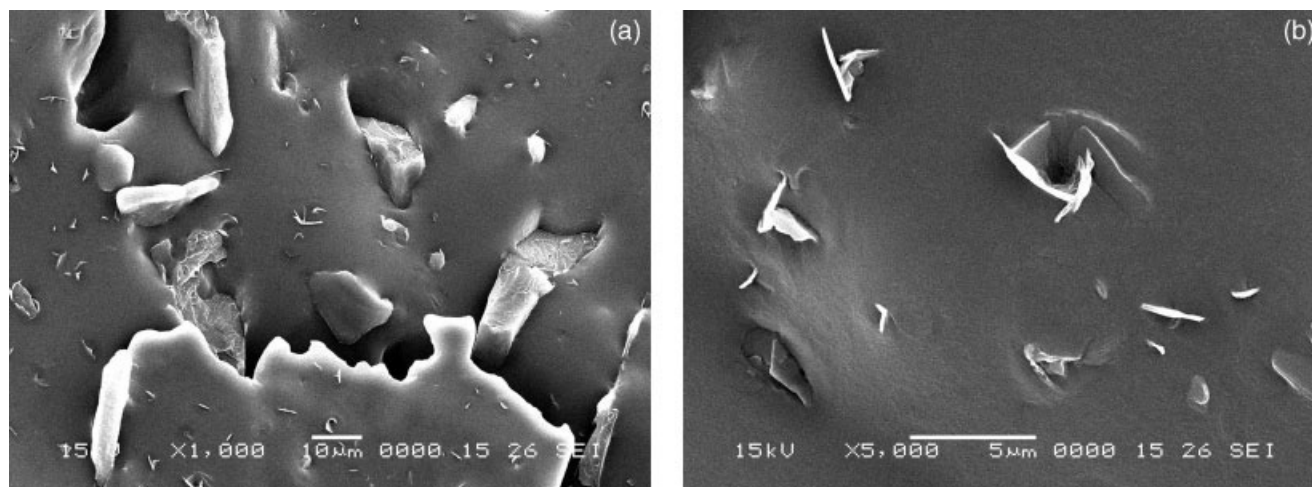**Figure 12** SEM images of SIS-A/P140 (40/60) (a) ×1000 (b) ×5000.

Figure 13 SEM images of SIS-A/P140/PS (40/60/100) with PS mixed in the solid state. (a) ×1000 (b) ×5000.

is for the main tan δ peak centered at 76°C, and a prominent tan δ peak exceeding to 2.00 emerges at 116°C. Moreover, the temperature range with tan δ above 1.00 shrinks to only 19°C, from 104 to 123°C. Intensity and

location of the tan δ peak always provide interaction and morphological properties in the blends. The new tan δ peak near 115°C is deduced to be caused by the glass transition of the newly added PS, which has few
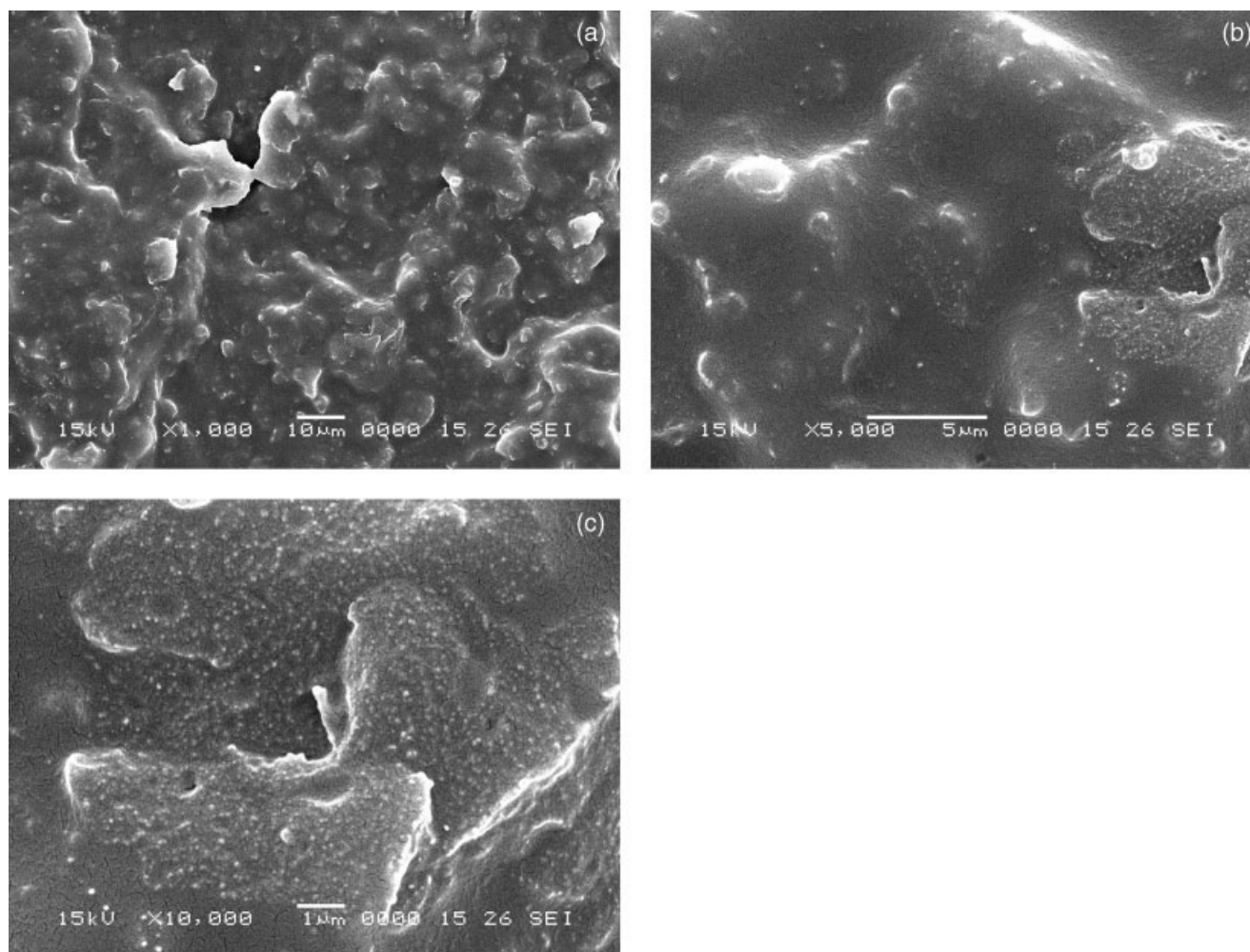

Figure 14 SEM images of SIS-A/P140/PS (40/60/100) with PS mixed in the melt state. (a) ×1000 (b) ×5000 (c) ×10,000.

impacts on the location of the transition associated with the rich resin domains. It is observed that the resin has little compatibility with PS for the invariant locations of the two independent tan δ peaks in spite of the different mixing temperatures. And the change of the tan δ peak maxima indicates the transformation of dominant phase in the blends.

SEM is further applied to detect the morphological structure of the multicomponent systems of SIS-A/P140 (40/60) and SIS-A/P140/PS (40/60/100) mixed at different temperatures. As shown in Figure 12, a uniform mixture is produced by the mechanical blending of SIS-A and P140, except that a spot of P140 exists as small flakes, which is not milled entirely in the matrix. The phase-separation morphology of SIS-A/P140 (40/60) is hard to observe by the use of SEM, although DMA spectra exhibit three glass transitions corresponding to the tackified PI and PS blocks and the rich resin phase. For the ternary system of SIS-A/P140/PS (40/60/100), Figure 13 clearly represents that SIS-A/P140 forms the continuous matrix and PS mixed in the solid state forms the dispersed phase. On the other side, the results are reversed for the system with PS mixed in the melt state in Figure 13. Figure 14(a) and 14(b) shows the mixture without distinct interface, but the magnified picture in Figure 14(c) reveals that SIS-A/P140 disperses in the continuous phase of PS. The occurrence of phase-conversion gives an explanation that the broad effective damping temperature range is contributed to the PS added in the solid state as the dispersed phase, which serves as reinforcing fillers like mica to increase friction at low temperatures and also exhibits a distinguished tan δ peak for the glass transition at the high temperature.

CONCLUSIONS

Blends of SIS with hydrogenated C_9 resin demonstrated great potential for mechanical damping applications. SIS with a phase separate microstructure exhibited two tan δ peaks and a modulus plateau over a wider temperature range. The value of tan δ peak was dependent on the content of corresponding segments in the copolymer. Hydrogenated C_9 resin with small content is compatible with the PI and PS domains of SIS. The rich resin domains emerge when SIS is saturated with the resin of critical content. With the increasing softening point and content of resin, the main tan δ peak shifted to higher temperatures and the effective damping temperature range was broadened remarkably. PS added in the solid state improved the damping of SIS-A/

P140(40/60) with tan δ above 1.00 from 59°C to even 129°C, much more than mica of the same content. The excellent damping performance of the ternary system lied in the role of dispersed phase of PS, which acts as reinforcing fillers at low temperatures and showed a distinguished tan δ peak because of its glass transition at the high temperature. Therefore, the blends of SIS with hydrogenated C_9 resin and PS could be considered as a competent candidate for damping materials, especially in the high temperature region.

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