

Polystyrene/Sn–Pb Alloy Blends. I. Dynamic Rheological Behavior

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ABSTRACT: The dynamic rheological behavior of polystyrene filled with low-melting-point (T_m) Sn–Pb was investigated at temperatures below and above the T_m of the alloy, 183°C. In the whole temperature range of interest, there existed a secondary plateau in the plot of the dynamic storage modulus versus frequency (ω) at low ω s, and the influences of alloy content and temperature on the plateau were related to the matter state (liquid or solid) of the alloy. We believe that the secondary plateau observed below the alloy T_m was due to the network-type structure formed by the agglomeration of solid filler particles, whereas the plateau above T_m was due to the deformability and relaxation

of the liquid alloy droplets. By analyzing the Cole–Cole diagrams, we suggest that the alloy fillers retarded the relaxation processes for polystyrene melt when the temperature was lower than the T_m . However, there existed two separated relaxation processes when the temperature was higher than the T_m , that is, the high- ω relaxation of the phases and low- ω relaxation of the droplets. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3166–3172, 2002

Key words: rheology; polystyrene; composites; melting point; alloys

INTRODUCTION

Polymer composites prepared by the incorporation of additives into polymer matrices have been increasingly applied in many fields.^{1–3} When the main technologies used for the preparation/processing of these composites, such as extrusion, injection, and molding, are considered, the rheological behavior of filled polymer melts has become a subject of great importance due to the increasing use of polymer composites.⁴ It is well known that for homopolymers and in low-frequency (ω) regions, the dynamic storage modulus (G') and the dynamic loss modulus (G'') are proportional to ω^2 and to ω ; that is, $G' \propto \omega^2$ and $G'' \propto \omega$, respectively. For filled polymer melts, the rheological behavior is much more complicated than for homopolymers. The rheological properties depend strongly on the composition and the respective viscoelastic properties of the components. It is generally observed that filled polymer composites show pronounced elastic properties at

low ω s and have very long relaxation time processes.^{5–8} Besides, the rheological behavior of filled polymer composites is also affected by the matter state (solid or molten) of the fillers.^{9–11}

The variation of rheological behavior induced by the incorporation of the fillers often leads to other important properties. An example of academic importance and applied value is the positive temperature coefficient (PTC) of composites that display a remarkable increase in electrical resistance with increasing temperature and are mass produced for their great usage as *thermistors*, or temperature-dependent resistors.^{12,13} It is well known that the negative temperature coefficient effect following the PTC transition is harmful to the application of such composites.¹⁴ To overcome such a disadvantage, we developed a novel electrical composite whose PTC transition is achieved by the addition of a low-melting-point (T_m) alloy filler.¹⁵ Furthermore, a new composite possessing double PTC transition was also developed according to the same principle.¹⁶ The performance of these composites can be controlled by the change of the matter state during the melting of fillers. The rheological behavior of both polymer matrix and fillers are believed to play an important role in the ultimate morphology and properties of the composites.^{15,16} Hence, the study of the effects of the low- T_m alloy, which can change from the solid to the liquid state, on polymer rheological behavior is also a requirement of research and application of PTC composites. To our knowledge, few

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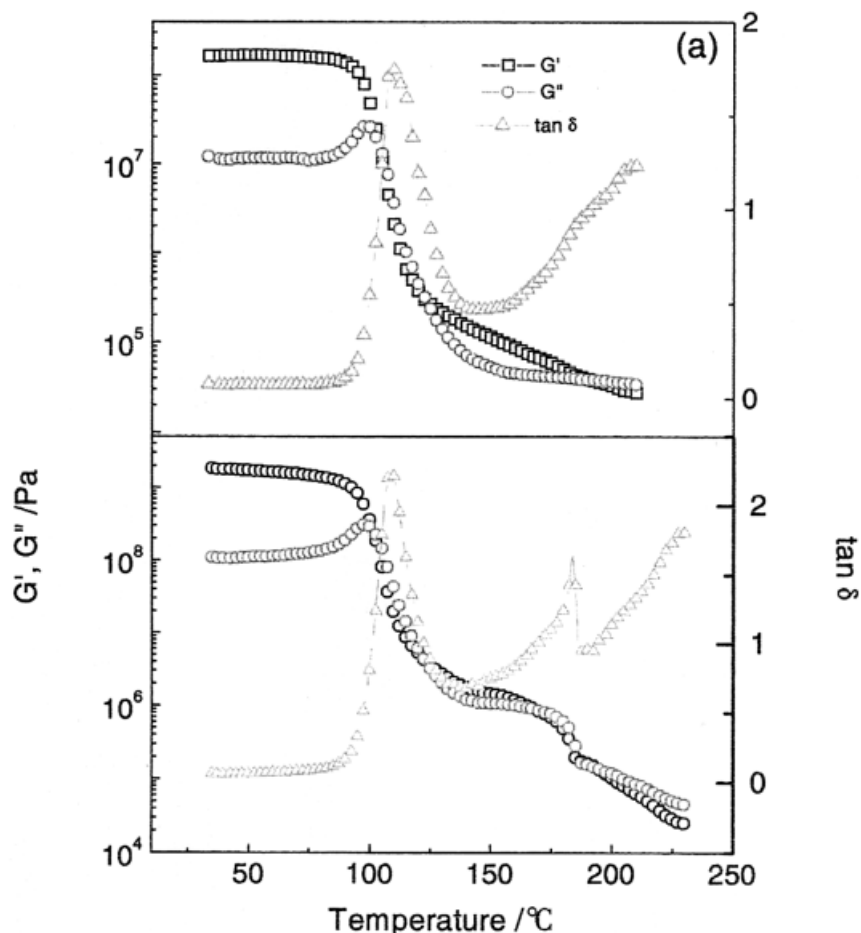


Figure 1 Temperature dispersion curves of dynamic viscoelastic functions for (a) PS and (b) PS filled with 35 vol % Sn-Pb alloy at a ω of 10 rad/s.

articles dealing with polymer composites containing a low- T_m alloy filler, together with PTC transition, have been published to date.

In this study, the rheological behavior of polystyrene (PS) composites filled with a Sn-Pb alloy, a kind of low- T_m alloy, was investigated. The reason we selected the Sn-Pb alloy was its T_m ; that is, the transition temperature from rigid particles to deformable droplets of the alloy was within the processing temperature range of the PS matrix.

EXPERIMENTAL

The low- T_m alloy used was powdered solder at a composition of 70 wt % Sn and 30 wt % Pb and was provided by the Institute of Powder Metallurgy of Zhongnan Technology University of China. The alloy T_m was 183°C according to the phase diagram, and the mean particle size was about 11 μm . The polymer matrix used was PS with a melt flow index of 8 g/10 min. The Sn-Pb alloy and PS mixtures, which varied only in Sn-Pb alloy concentration, were mixed in a satellite ball miller (QM-1SP, Nanjing University In-

struments, Nanjing, China) at 200 rpm for 11 h. These mixtures were molded into disks with diameters of 25 mm at 165°C.

Dynamic rheological measurements were carried out with the Advanced Rheology Expansion System (Rheometrics Inc., USA) in a parallel-plate mode. Temperature sweeps were done at a constant ω of 10 rad/s for the composites of different filler concentrations, whereas ω sweeps from 10^{-1} to 10^2 rad/s were conducted at 140, 165, 175, 180, 190, 200, 210, and 230°C, respectively. The strain amplitude used was small (5%) to ensure that the rheological behavior was located in the linear viscoelastic range.

RESULTS AND DISCUSSION

Dynamic viscoelastic transition for virgin PS and composites

Figure 1 gives the temperature dispersion curves of the G' , G'' and loss tangent ($\tan \delta$) of virgin PS and PS filled with 35 vol % Sn-Pb alloy over a temperature range of 35–210°C. As shown in Figure 1(a), the tran-

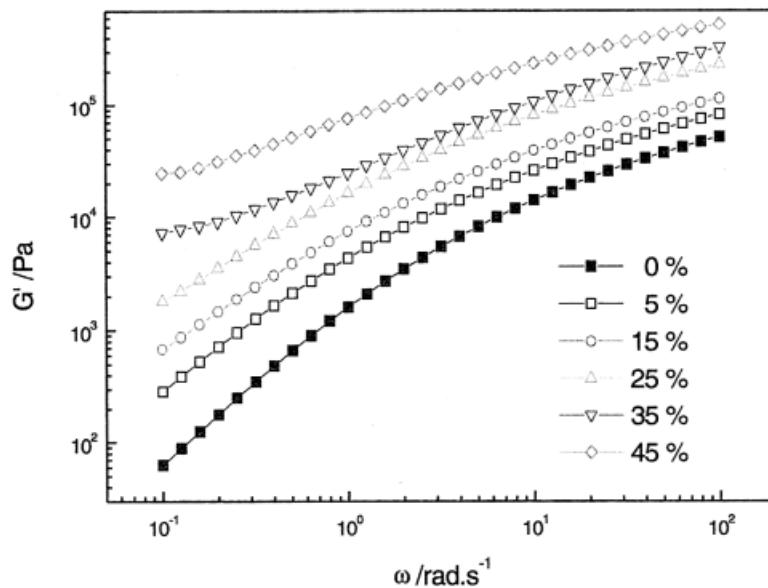


Figure 2 ω dependence of G' for PS filled with various amounts (in volume percent) of Sn-Pb alloy at 175°C.

sition of dynamic viscoelastic functions occurred in the temperature range of 95–110°C and was thus reasonably attributed to the glass transition of PS. Correspondingly, the transitions around 100 and 183°C, as shown in Figure 1(b), were derived from the glass transition of PS and the melting of the Sn-Pb alloy in the composites, respectively. Therefore, the dynamic viscoelasticity of PS in the composite system was almost unchanged, indicating the immiscibility of PS with the Sn-Pb alloy.

Dynamic rheological behavior for the composites below the T_m

When the temperature was lower than the T_m of the Sn-Pb alloy, the alloy filler existed in the form of rigid particles. The ω dependence of the G' for PS filled with various amounts of Sn-Pb alloy is shown in Figure 2. The G' increased with increasing Sn-Pb alloy content, which has been attributed to the solidification of polymer chains on particle surfaces, resulting in a high modulus layer of polymer matrix surrounding filler particles.^{17–19} It was also due to the intrinsic presence and rigidity of the filler.

At low ω s, a secondary plateau, or so-called terminal shoulder-like trend, emerged for the composites containing more than 25 vol % Sn-Pb alloy, which could be attributed to the network-type structure formed by the agglomeration of filler particles at these filler contents.^{6,9–11,20} The formation of a network has also been confirmed by a test of electrical properties.^{15,21} The ω dependence of G' for PS filled with 35 vol % Sn-Pb alloy at various temperatures is presented Figure 3. As the temperature increased, the relaxation time of the composites decreased; therefore,

the G' decreased, and the second plateau appeared more obvious.

It is well known that the relationship between the dynamic viscosity (η') and loss viscosity (η''), namely the Cole-Cole diagram, indicates the existence of various groups of relaxation times and gives detailed information on the relaxation processes for the filled polymer melts. Figure 4 shows the Cole-Cole diagrams of the virgin PS and PS filled with various contents of Sn-Pb alloy at 175°C. The Cole-Cole diagrams of the composites containing Sn-Pb alloy less than 25 vol % demonstrated the form of a semicircle, which was similar to that of virgin PS. With the increasing content of Sn-Pb alloy in the composites (>25 vol %), η'' ($= G'/\omega$, meaning the elasticity part) in the region of long relaxation times (i.e., the low ω region) increased, and the form of the Cole-Cole diagram

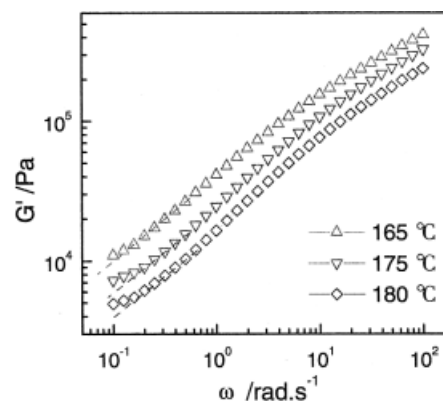


Figure 3 ω dependence of G' for PS filled with 35 vol % Sn-Pb alloy at various temperatures below the T_m of the alloy.

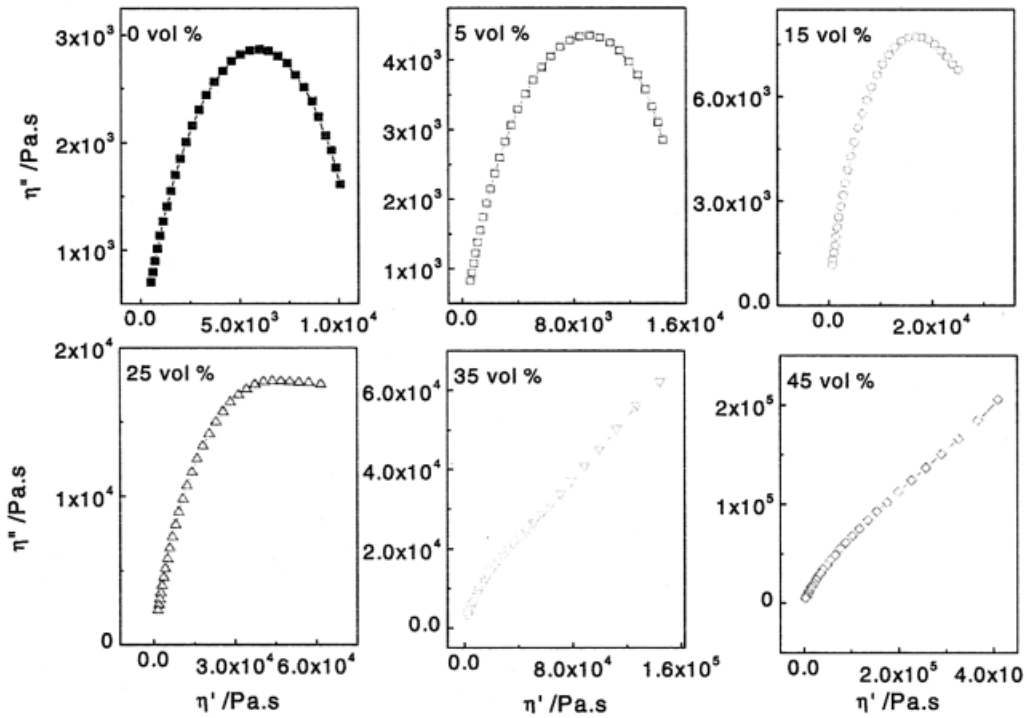


Figure 4 Cole-Cole diagrams of PS and PS filled with various amounts of Sn-Pb alloy at 175°C.

changed from semicircular to linear. As the rigid particles retarded the relaxation process of polymer melt, the incorporation of Sn-Pb alloy increased the elasticity to viscosity ratio of the composites. The network-type structure formed by the agglomeration of filler particles made the retardation more serious, which was believed to be the intrinsic factor resulting in the change of Cole-Cole diagrams and the emergence of secondary plateau as presented in Figure 2.

On the basis of the effect of temperature on the Cole-Cole diagrams as shown in Figure 5, we found a

transformation of the region of long relaxation times from semicircle to linear diminishes with the increase in temperature. In other words, the composites dominantly exhibited viscous properties resulting from the PS matrix with an increase in temperature, suggesting that the retardation of the relaxation processes induced by the rigid particles was lowered as the temperature increased.

Dynamic rheological behavior for the composites above the T_m

In the composites, the Sn-Pb alloy filler melted and changed from the rigid particles to deformable droplets when the temperature increased beyond the alloy

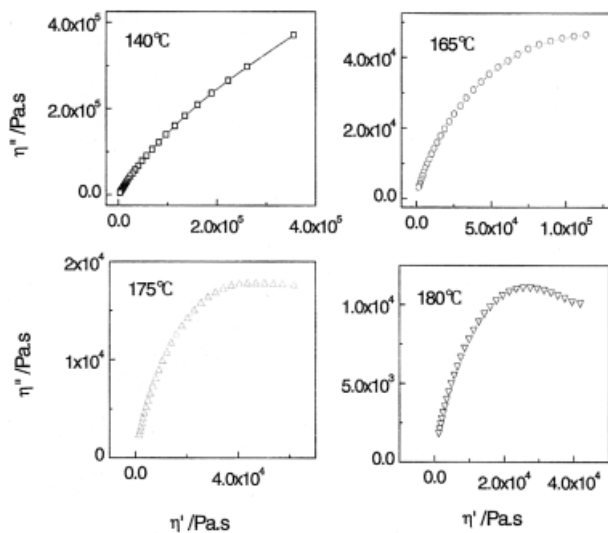


Figure 5 Cole-Cole diagrams of PS filled with 25 vol % Sn-Pb alloy at various temperatures before the alloy melted.

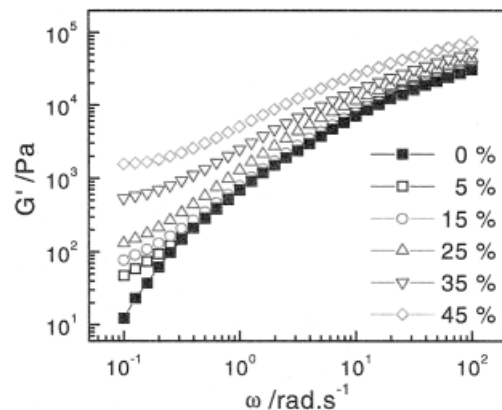


Figure 6 ω dependence of G' for PS filled with various amounts (in volume percent) of Sn-Pb alloy at 200°C.

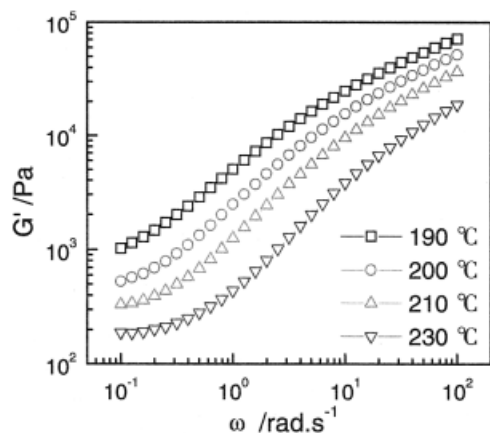


Figure 7 ω dependence of G' for PS filled with 35 vol % Sn-Pb alloy at temperatures above the alloy T_m .

T_m , leading to a pronounced change of the rheological behavior of the filled system. The ω dependence of G' for PS filled with various amounts of the Sn-Pb alloy at 200°C is shown in Figure 6. The G' also increased with the increase in filler content, which was similar to the dynamic viscoelasticity at temperatures lower than the T_m . However, the secondary plateau appeared over the whole range of alloy contents studied, instead of more than 25 vol % for the composites at temperatures lower than the T_m , as demonstrated in Figure 2. The ω dependence of G' for PS filled with 35 vol % Sn-Pb alloy at temperatures greater than T_m is given in Figure 7. Compared with Figure 3, the secondary plateaus here were more typical than those appearing at temperatures lower than the T_m . The

plateau also became more obvious with the increase in temperature.

According to the previous discussion, in the case that the incorporated fillers existed in the form of rigid particles, the occurrence of a secondary plateau was the result of the formation of a network-type structure by the agglomeration of filler particles. However, when the alloy melted from rigid particles to deformable droplets and the viscosity of the molten alloy became much lower than that of the polymer matrix, the plateau observed could by no means be attributed to the formation of a network-type structure in the composites. The secondary plateau here was believed to be due to the deformability and relaxation of the alloy droplets under the action of applied force.^{6-8,10} For the composites with any content of Sn-Pb alloy, the deformation of alloy droplets existed. Hence, the secondary plateau emerged even for the composites with low alloy contents, such as 5 vol %, as demonstrated in Figure 6. As the viscosity of the polymer matrix decreased with the increase in temperature, the deformation of alloy droplets became easier, resulting the secondary plateau appearing more obvious.

The Cole-Cole diagrams of virgin PS and PS filled with various contents of Sn-Pb alloy at 200°C are shown in Figure 8. The incorporation of the Sn-Pb alloy changed the Cole-Cole diagrams of PS greatly, especially at low ω s. For the virgin PS, the relaxation diagram had the form of semicircle. However, after the incorporation of the Sn-Pb alloy, η'' at low ω s increased, and the semicircle transformed into an irregular shape; that is, a "tail" appeared at low ω s. This

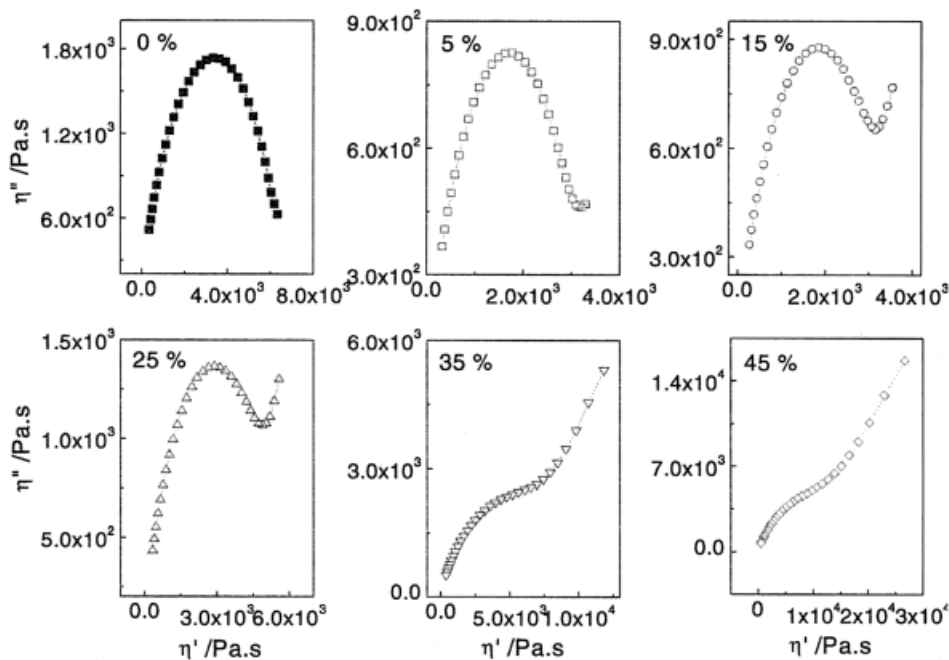


Figure 8 Cole-Cole diagrams for PS filled with various amounts of Sn-Pb alloy at 200°C.

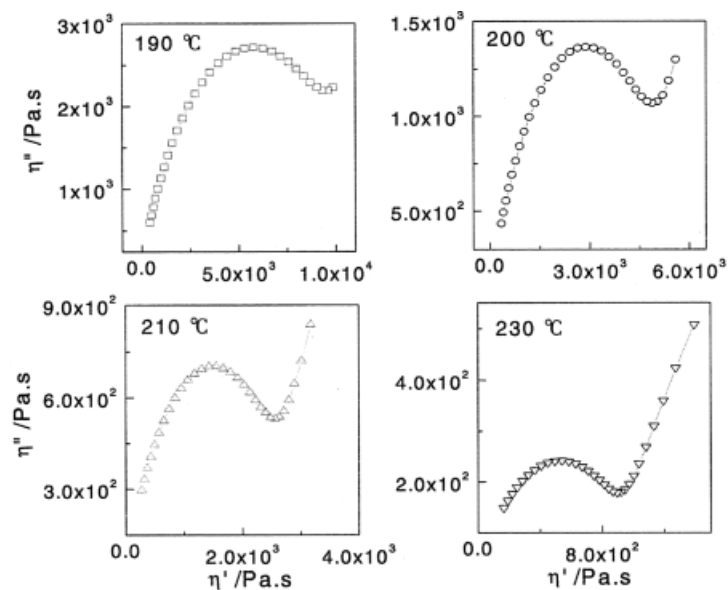


Figure 9 Cole-Cole diagrams for PS filled with 25 vol % Sn-Pb alloy at temperatures above the alloy T_m .

tail became longer with increases in the alloy content and predominated over the semicircle when the alloy content increased over 25 vol %. These changes imply that two relaxation mechanisms coexisted for the composites containing the deformable alloy droplets, that is, the high- ω relaxation of the phases and the low- ω relaxation of the droplets.^{5,8} The low- ω relaxation of the droplets was believed to be due to the deformability and relaxation of the alloy droplets, which was also the reason of the emergence of the secondary plateau. Similar to the secondary plateau that appeared for the composites with any alloy content as shown in Figure 6, the tail of the Cole-Cole diagrams also emerged over the whole content range. Besides, when the secondary plateau, as shown in Figure 6, became more obvious, when the Sn-Pb alloy content reached 35 vol %, the tail predominated over the semicircle in the Cole-Cole diagrams. It was clear that the transformation of the Cole-Cole diagram was more distinct than that of second plateau. Thus, it is suggested that the Cole-Cole diagram was more sensitive for reviewing the structure information, such as the deformability and relaxation of the alloy droplets in our study.

The Cole-Cole diagrams for PS filled with 25 vol % Sn-Pb alloy above the T_m are presented in Figure 9. With increases in temperature, the tail at low ω s became more apparent and dominated over the semicircle at 230°C. It may have been because the deformability and relaxation of the alloy droplets became easier when the viscosity of PS matrix decreased with the increase in temperature.

CONCLUSIONS

G' and G'' of PS filled with Sn-Pb alloy decreased rapidly at the alloy T_m . Because the relaxation process

of the composites was affected by the matter state (solid or molten) of the incorporated fillers, the composites exhibited different dynamic viscoelastic behaviors at temperatures below, near, and above the T_m of the Sn-Pb alloy.

At low ω s, the correlation between the G' and ω presented a secondary plateau both below and above the alloy T_m . At the same time, the influence of alloy content and temperature on the plateau was mainly determined by the matter state of the alloy. Below the alloy T_m , the secondary plateau was attributed to the network-type structure formed by the agglomeration of filler particles, whereas above the alloy T_m , the plateau indicated easier deformability and relaxation of the alloy droplets.

The difference in dynamic viscoelastic behavior of the composites below and above the alloy T_m was verified by the Cole-Cole diagrams. It is believed that the alloy fillers retarded the relaxation processes in the molten state for PS when the temperature was lower than the alloy T_m , although they endowed the composites with a low- ω relaxation of the alloy droplets when the temperature was higher than the alloy T_m .

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