Polystyrene/Sn–Pb Alloy Blends. II. Effect of Alloy Particle Surface Treatment on Dynamic Rheological Behavior

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ABSTRACT: The effect of filler surface treatment on the dynamic rheological behaviors of polystyrene filled with Sn–Pb alloy particles was tested below and above the melting temperature (T_m) of the alloy. The mechanical relaxation relevant to the T_m of the alloy in the composite was diminished by the filler surface pretreatment. In the whole temperature range of interest, there existed a secondary plateau of the storage modulus at low frequencies. The effect of alloy particle surface treatment on the plateau was related to the matter-state change (from solid to liquid) of the alloy. Above the T_m of the alloy, the surface treatment of the alloy affected the secondary plateau, but below the T_m, it did not. The analyses of Cole–Cole diagrams of the systems suggested that untreated and pretreated alloy fillers all retarded the relaxation processes in the molten state of polystyrene below the T_m of the alloy and that the relaxation process was separated into the high-frequency relaxation of the phases and the low-frequency relaxation of the droplets above the T_m. The surface treatments of the alloy filler further enhanced this action. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3173–3179, 2002

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

INTRODUCTION

The rheological behavior of filled polymer composites has become of great interest because of the increasing applications of the polymer composites. Compared with the rheological behavior of the pure polymer matrix, polymer composites generally exhibit pronounced elastic properties and long relaxation times.[1–4] The rheological behavior of a filled polymer composite is governed first by the properties of both the polymer matrix and incorporated fillers and is then influenced by the volume fraction and agglomerations of the filler particles and the interfacial adhesion between the filler and matrix.[5–8]

On the other hand, dynamic rheological measurement is an effective method to characterize the morphological and structure of the multicomponent and/or multiphase polymer composites.[9–16] The rheological property change of a polymer matrix induced by filler incorporation are thought to be caused by two factors. One is the mechanical coupling between filler and polymer matrix,[7,8] The other one is the interface morphological structure depending on the interfacial adhesion or adsorption between the phases.[6,7,15,16] Besides the previously mentioned causes, the matter state (solid or liquid) of fillers also has a significant influence on the rheological behavior of composites; little attention was paid to this behavior until recently. In previous research,[17–20] rigid particles, such as mineral fillers, and deformable droplets, such as rubber fillers, softeners, and lubricants, have been two main kinds of fillers. Rigid particles are the reinforcements of composites, but deformable droplets usually act as a polymer processing promoters. In processing temperatures of the previous systems, however, matter-state changes did not occur.

Incorporation of a filler in a polymer matrix often brings about some important properties to the composite. An example of academic and application importance is the positive temperature coefficient (PTC) composites made of electrical conductive particles and a polymer matrix by blending. These kinds of composites, exhibiting a remarkable increase in electrical resistance in a narrow range during a temperature increase, have been successfully used as *thermistors*, or temperature-dependent resistors.[21,22] However, a negative temperature coefficient (NTC) effect following the PTC transition limits the applications of such com-

posites.[23] To solve this problem, we developed a new type of PTC polymer composite by mixing low-melting alloy (Sn–Pb) particles and polymer.[24,25] A so-called double PTC effect was termed for the PTC transitions occurring twice at the melting temperatures (T_m's) of both low-melting alloy and the polymer matrix, respectively. More important, the NTC effect was restrained by the double PTC transitions. It is obvious that the performance of these polymer composites was controlled by not only the matter-state change of matrix but also of the filler. The unique properties of the composites were due to the special structure changes resulting from the two matter-state changes during heating. For the purpose of understanding, the dynamic rheological behavior of polystyrene (PS) and Sn–Pb alloy composite was studied in terms of the changes of the matter state of both components and consequent electrical conductive network structure and was reported in our previous article.[26]

Furthermore, the cycling stability of PTC transitions of PS/Sn–Pb composites was found to be considerably improved by surface modification of Sn–Pb alloy particles before blending with PS.[24,25] As a continuation of refs. 24–26, this article reports on the rheological behavior of PS filled with surface-modified Sn–Pb alloy particles. The three surface modifiers used in this study were pyltrimethoxysilane, titanate coupling agent, and stearic-acid. The dynamic rheological properties of the composites were measured and compared with each other. Significant effects of the interfacial modifiers on the rheological behavior of the filled polymer composites were found. Possible mechanisms behind the effects are discussed.

EXPERIMENTAL

Materials

The low-T_m alloy used was powdered solder (mean particle size = 11 μm) with a composition of 70 wt % Sn and 30 wt % Pb and was provided by Institute of Powder Metallurgy in Zhongnan Technology University of China, Changsha. The T_m of the alloy was assumed around 183°C according to most metallic system phase diagrams. The PS used as the matrix of our composite was obtained from Yan-Shan Petrochemicals Co., Beijing, China. Its density was 1.05 g/cm³, and the melt flow index was 8 g/10 min.

To improve the interfacial adhesion between the filler and polymer matrix, we performed modifications of the surfaces of Sn–Pb particles. Three domestic interfacial modifiers were used: pyltrimethoxysilane [$CH_2{=}C(CH_3)COO(CH_2)_3Si(OCH_3)_3$; KH-570, Shanghai Reagent Co., China], titanate coupling agent {$(CH_3)_2CHOTi[OOC(CH_2)_7CH{=}CH(CH_2)_7CH_3]_3$; Nanjing Plastic Plant, China}, and stearic-acid [$CH_3(CH_2)_{16}COOH$; Wenzhou Chemical Plant, Zhejiang, China).

Sample preparation

The following pretreatments were performed on the Sn–Pb powder. Each interfacial modifier (15 mL) was added into a suspension of 40 g of Sn–Pb alloy powder in 100 mL of methanol (for titanate coupling agent, petroleum ether was used instead of methanol), and then the mixture was stirred for 1 h. Centrifugal sedimentation of Sn–Pb alloy powder was then performed on a centrifugal machine. The sediment was washed with 100 mL of methanol (or petroleum ether for titanate), followed by a second centrifugal sedimentation. The treated Sn–Pb alloy powder was predried at room temperature for 1 day and further dried at 130°C for 1 h in a vacuum.

The Sn–Pb alloy powder (as-received or pretreated) and PS powder mixtures, which varied only in Sn–Pb alloy concentration (in weight percentage), were ball milled at 200 rpm for 11 h in a satellite ball miller (QM-1SP, Nanjing University Instruments, Nanjing, China). These mixtures were then molded at 165°C in the form of 25-mm diameter disks.

Test procedure

Small-amplitude oscillatory shear tests were carried out on a Rheometrics dynamic spectrometer (Advanced Rheology Expansion System, Rheometrics Inc., USA) in the parallel-plate mode. The testing conditions were that the frequency (ω) of 10 rad/s maintained with varying temperature and that a temperature of 140, 165, 175, 180, 190, 200, 210, or 230°C was kept but ω swept from 0.1 to 100 rad/s. The strain amplitude used was small (5 vol %) to ensure the rheological behavior in the linear viscoelasticity range.

RESULTS AND DISCUSSION

Glass transition and melting transition

To simplify the description, the Sn–Pb alloy powders pretreated with modifiers of KH-570, titanate, and stearic-acid are abbreviated as s-Sn–Pb, t-Sn–Pb, and a-Sn–Pb, respectively. u-Sn–Pb stands for the nonpretreated Sn–Pb alloy. Figure 1 gives the temperature dispersion curves of the storage modulus (G') for virgin PS and PS filled with 25 vol % of Sn–Pb alloy powders pretreated and untreated over a temperature range of 35–210°C. Clearly, each of the three curves showed a sharp decease in G' within 90–120°C, corresponding to the glass-transition temperature (T_g) of PS according to most textbooks of polymer physics. These curves for PS filled with the u-Sn–Pb alloy and s-Sn–Pb alloy exhibited a second drop in the temperature range of 180–185°C, consistent with the T_m of the Sn–Pb alloy. The second drop was thus reasonably attributed to the melting of the Sn–Pb alloy.
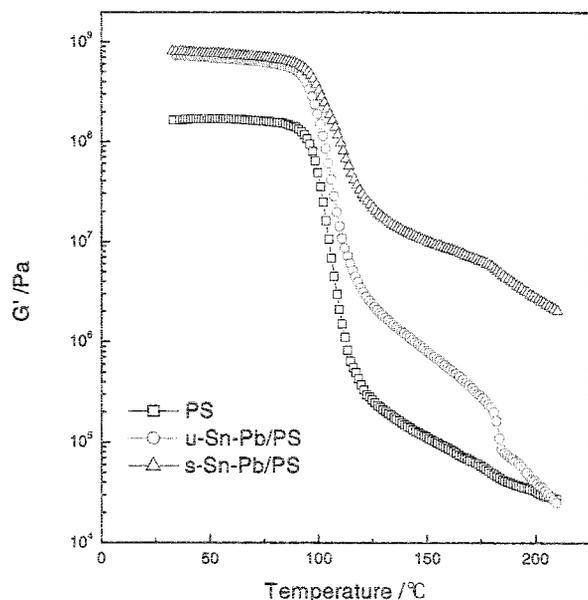
Figure 1 Temperature dispersion curves of G' for PS and PS filled with 25 vol % various Sn–Pb alloys at 10 rad/s.

Sn–Pb loading at 25 vol %, either stearic-acid pretreated or untreated, gave rise to G' over all the temperature range. A similar phenomenon was also found by Vollenberg and Heikens.[27,28] They explained it by the solidification of polymer chains on particle surfaces, which formed high modulus layers. Moreover, G' of PS filled with the s-Sn–Pb alloy was higher than those of PS filled with the u-Sn–Pb alloy at temperatures above 100°C, and the difference got larger as the temperature further increased. In other words, G' of PS filled with the u-Sn–Pb merged with that of PS filled with the s-Sn–Pb at temperatures below 100°C, equally higher than that for virgin PS but approaching the G' of virgin PS at temperatures above 150°C. The difference could be explained by the pretreatment of the alloy particles. When the temperature was lower than the T_g of the PS matrix, the molecular chains of PS were frozen and tightly wrapped the Sn–Pb alloy particles because of contraction during previous cooling so that the influence of the surface treatment of the Sn–Pb alloy on G' was insignificant. Only when the temperature reached and went over the T_g of PS did the molecular chains of PS start to move. However, the s-Sn–Pb particles had stronger joints with PS chains than the u-Sn–Pb because the surface modification. The dependence of G' on the surface treatment thus became significant at high temperatures.[7] Also, for the PS filled with the s-Sn–Pb alloy, the second drop of G' at the T_m of the alloy was not as sharp as that for the PS filled with the u-Sn–Pb alloy, indicating again the better bonding of PS chains with Sn–Pb alloy particles.

Figure 2 shows the loss tangent (tan δ) variations of PS and PS filled with 25 vol % of Sn–Pb alloy pretreated and untreated with temperature. For all the

samples, the tan δ exhibited a peak in the temperature range of 90–130°C, corresponding again to the T_g of PS. The tan δ value at the first peak for PS filled with the s-Sn–Pb alloy was obviously less than those of virgin PS and PS filled with the u-Sn–Pb alloy. For the PS filled with the u-Sn–Pb alloy, there was only feeble mechanical coupling between the u-Sn–Pb alloy and PS because of the large difference between the surface characteristics of the u-Sn–Pb particles and PS.

As a result, it was difficult for the applied force to be transferred between the u-Sn–Pb particles and the PS matrix, leading to the higher energy dissipation than the stored energy after PS was incorporated with the u-Sn–Pb alloy. However, when the Sn–Pb was pretreated with KH-570 (i.e., s-Sn–Pb), the interfacial adhesion was greatly enhanced, resulting in an increase in storage energy with respect to energy dissipation. Also, PS filled with the u-Sn–Pb alloy and PS filled with the s-Sn–Pb, the peak temperatures (corresponding to T_g) of tan δ were 109, 111, and 115°C, respectively. This was the result of the lower mobility of polymer chains by the higher interfacial adhesion caused by KH-570 pretreatment.[29] In Figure 2, a small peak was seen at the alloy T_m for the system of u-Sn–Pb/PS but not for the virgin PS or for s-Sn–Pb/PS. The relatively weak adhesion in u-Sn–Pb/PS led to a second relaxation during alloy melting.

Secondary plateau

Figure 3 illustrates the ω dependence of G' for PS filled with 25 vol % Sn–Pb alloy pretreated in various ways at 180°C. For comparison, the $G'(\omega)$ curve of virgin PS was also plotted. The G' was enhanced by the loading
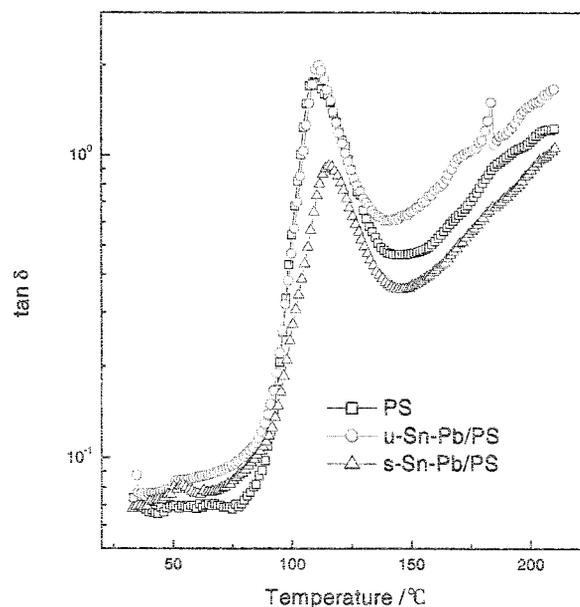
Figure 2 Temperature dispersion curves of tan δ for PS and PS filled with 25 vol % various Sn–Pb alloys at 10 rad/s.

Figure 3 ω dependence of G' for PS and PS filled with 25 vol % various Sn–Pb alloys at 180°C.
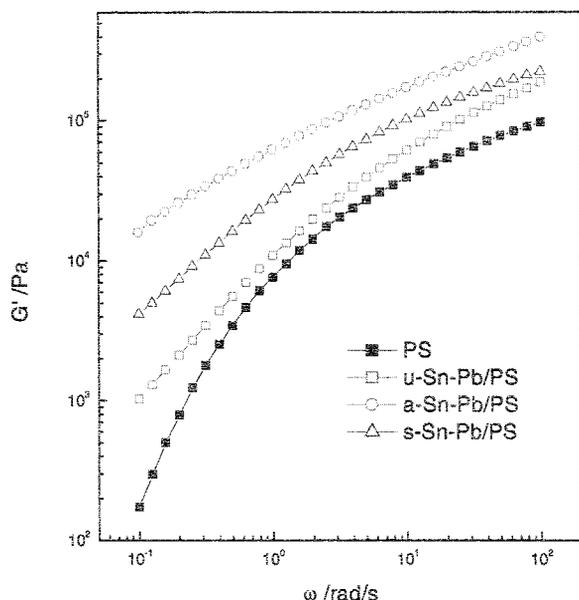
Figure 4 ω dependence of G' for PS and PS filled with 25 vol % various Sn–Pb alloys at 200°C.

of the Sn–Pb alloy (nonpretreated or pretreated with the interfacial modifiers). The enhancement of G' at a low ω was more significant than that at a high ω, which is referred to the secondary plateau phenomenon, or the terminal shoulder-like trend.[30] Moreover, the increase of G' by pretreatment of the Sn–Pb alloy was larger than that of the nonpretreated Sn–Pb alloy, but the trends to show the secondary plateau were similar. Because the test temperature (180°C) was lower than the T_m of the Sn–Pb alloy, the alloy filler acted as rigid particles, and the appearance of the secondary plateau was due to the network-type structure formed by the particles and/or agglomerates of filler particles. Figure 3 also indicated that the formation of such network-type structure was not obviously affected by the surface treatment of the filler in our study.[31–33]

In Figure 4 is plotted the ω dependence of G' at 200°C for the same group of materials. At this temperature, the Sn–Pb alloy filler melted and became deformable droplets. Figure 4 again shows that the incorporation of Sn–Pb alloy led to a secondary plateau, but the plateau was more distinct at 200°C than at 180°C in Figure 3 [i.e., the slope of $G'(\omega)$ in Fig. 4 is much lower than in Fig. 3]. The more distinct secondary plateau was believed to be due to the deformability and relaxation of the liquid filler droplets.[2–4,32] Pretreatment with interfacial modifiers even further flattened the G' versus ω curve and made the secondary plateau more obvious than no pretreatment (Fig. 3). This was because the interfacial adhesion produced by the interfacial modifiers transferred the force from the matrix to the droplets facilely, and the deformation
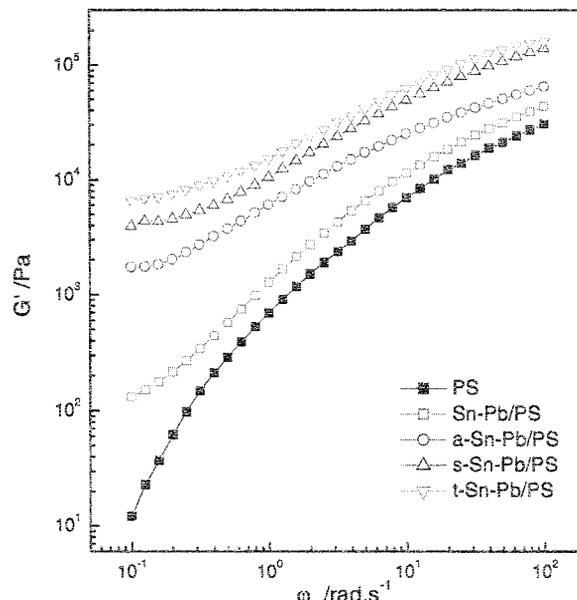
was easily realized at 200°C, but this did not occur at 180°C.

Figure 5 presents the ω dependence of the tan δ at 200°C of PS and PS filled with 25 vol % of the Sn–Pb alloy. The tan δ of virgin PS monotonically decreased with decreasing ω. However, u-Sn–Pb, s-Sn–Pb, and a-Sn–Pb had mild peaks and flattened sections at ωs below 10 rad/s, respectively, indicating again the relaxation of the deformable droplets. In the entire region of ω, the tan δ value decreased in the order from u-Sn–Pb/PS to s-Sn–Pb/PS to a-Sn–Pb/PS.
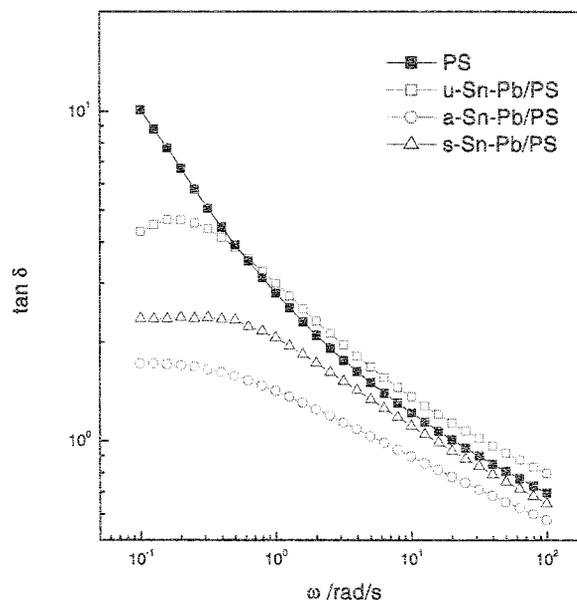
Figure 5 ω dependence of tan δ for PS and PS filled with 25 vol % various Sn–Pb alloys at 200°C.
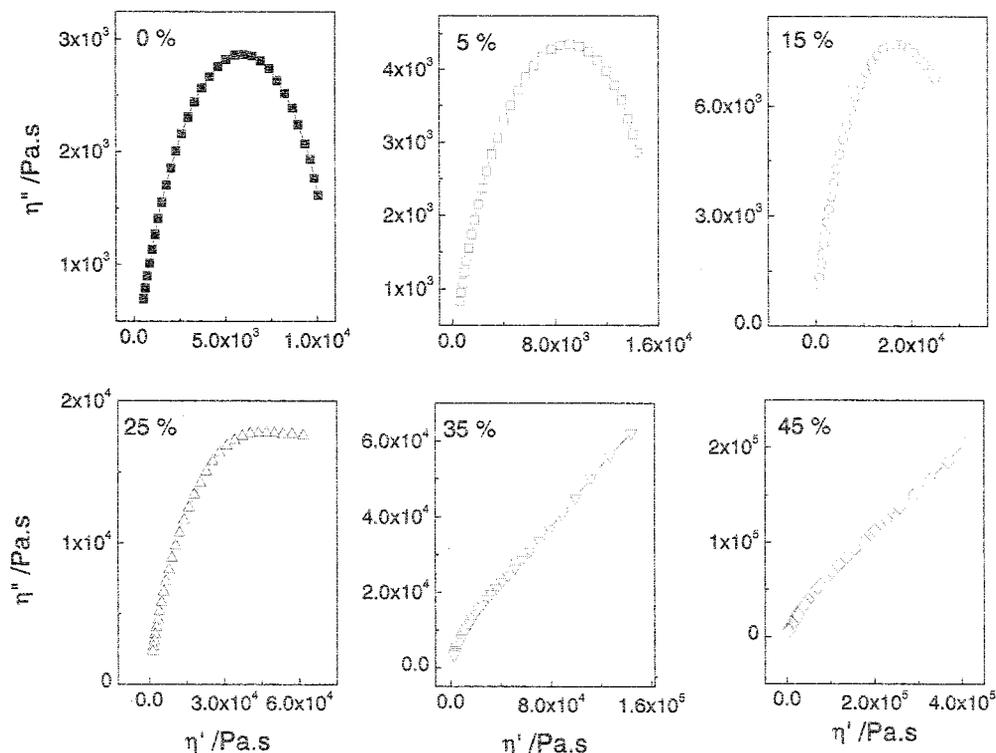
Figure 6 Cole–Cole diagrams of PS and PS filled with various contents of the u-Sn–Pb alloy at 175°C.

Cole–cole diagram

It is well established that the relationship between the dynamic viscosity (η') and loss viscosity (η''), namely, the Cole–Cole diagram, reflects the existence of various groups with different relaxation times and gives detailed information about the relaxation processes for the filled polymer melts. Figure 6 summarizes the Cole–Cole diagrams of PS and PS filled with various contents of the u-Sn–Pb alloy at 175°C, at which the Sn–Pb alloy particles were rigid particles. The relaxation diagram of virgin PS was nearly a semicircle, but the incorporation of the alloy fillers into the polymer considerably transformed the region of long relaxation times, that is, low ωs in the right-hand side of the plots in Figure 6. Therefore,

it was believed that the rigid particles retarded the relaxation processes in the region of the molten state of polymers; namely, the rigid solid filler particles existing in the polymer matrix reduced the ability for the system to relax to some extent, depending on the content of the filler.

Figure 7 shows again a group of the Cole–Cole diagrams measured also at 175°C of PS filled with 25 vol % of Sn–Pb alloy particles differently pretreated. The surface pretreatment of the Sn–Pb alloy further transformed the region of long relaxation times, equivalent to the effect induced by the increase in the alloy content (Fig. 6). This phenomenon suggests that the surface treatment of the Sn–Pb alloy at solid state
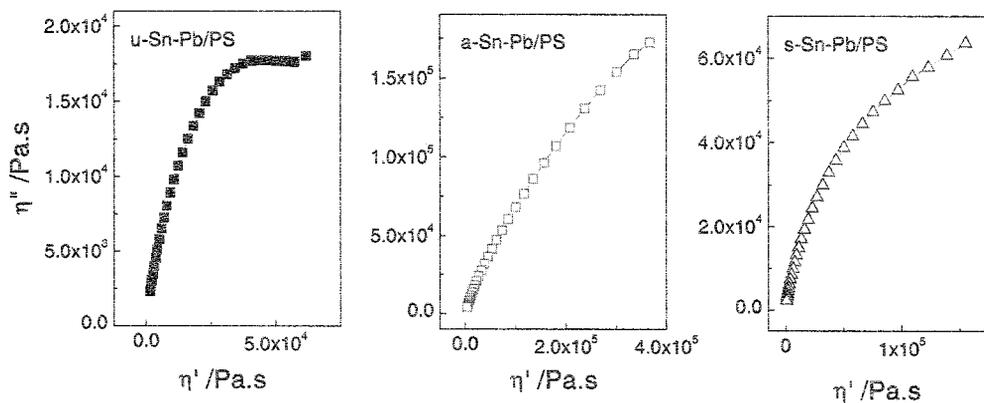
Figure 7 Cole–Cole diagrams of PS filled with 25 vol % various Sn–Pb alloys at 175°C.
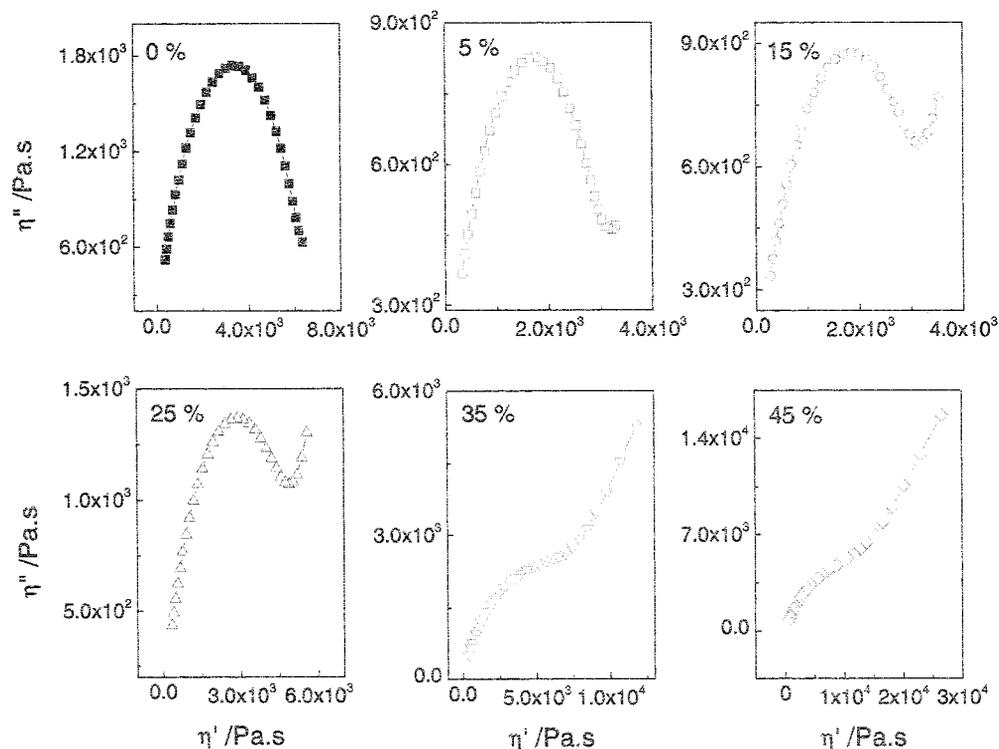
Figure 8 Cole–Cole diagrams of PS and PS filled with various contents of the u-Sn–Pb alloy at 200°C.

improved the interfacial adhesion between the filler and the matrix and retarded the relaxation processes of the molten PS.

The Cole–Cole diagrams obtained at 200°C of PS and PS filled with various contents of the u-Sn–Pb alloy are shown in Figure 8. The existence of liquid alloy droplets in PS matrix at 200°C changed the Cole–Cole diagrams differently from Figure 6. For the virgin PS, the relaxation diagram had a more regular shape of a semicircle than that in Figure 6. However, with the increase in the content of the u-Sn–Pb alloy, the η'' at low ωs increased, and the semicircle transformed into an irregular shape, namely, an upward tail appearing at low ωs. Furthermore, this tail became

longer with the increase in alloy content, and finally, the whole curve turned to be a single tail. This may imply that two relaxation mechanisms, the relaxation of the two deformable phases coupling and the relaxation of the droplets, dominated at high and low ωs, respectively.[1,4] The low-ω relaxation of the droplets was believed to be due to the deformability and relaxation of the shape of the filler droplets, which was also the reason of the emergence of the secondary plateau.

Figure 9, similar to Figure 7, shows the Cole–Cole diagrams of PS filled with 25 vol % of Sn–Pb alloy pretreated with designated agents but obtained at a temperature of 200°C, above the T_m of the Sn–Pb alloy. Compared to Figure 7, a semicircle with a little tail
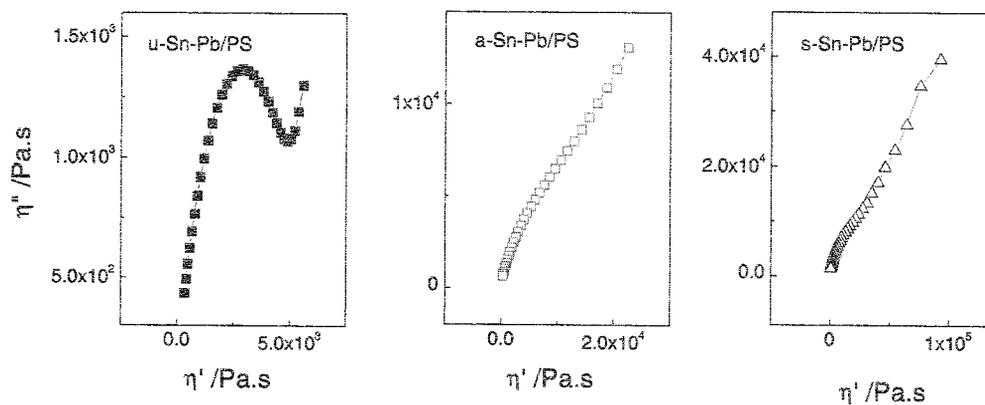
Figure 9 Cole–Cole diagrams of PS filled with 25 vol % various Sn–Pb alloys at 200°C.

attached was seen for the system of 25 vol % u-Sn–Pb/PS. However, for the same content of surface-pretreated Sn–Pb alloy-loaded samples, the whole diagram transformed, becoming a single upward tail. This suggests that the adhesion between molten PS and Sn–Pb at 200°C still existed and retarded the relaxation process.

CONCLUSIONS

As a function of temperature, the G' of PS filled with the Sn–Pb alloy powder dropped twice at the T_g of PS and the T_m of the alloy, respectively, whereas tan δ exhibited two peaks correspondingly. The relaxation processes of the composites were affected by the state change (from solid to liquid) of the fillers, with different viscoelastic behaviors before and after the alloy melted. However, the surface treatment of the alloy fillers diminished the change happening at the T_m of the alloy. The $G'(\omega)$ at low ωs presented a secondary plateau both below and above the T_m of the alloy. The surface treatment of the alloy fillers, however, did not obviously affect the secondary plateau below the T_m but caused the plateau behavior to be more distinct above the T_m. The secondary plateau observed below the T_m was attributed to the network-type structure formed by the agglomeration of filler particles, whereas the plateau above the T_m was due to the deformability and relaxation of the shape of the alloy droplets. The change of tan δ (ω) curves at low ωs by the surface treatment indicated the presence of the structure formed by the fillers in the polymer melts.

The difference of the viscoelastic behavior below and above the T_m of the alloy could also be verified by plotting the Cole–Cole diagrams. The alloy fillers retarded the relaxation processes in the region of the molten state of PS below the T_m of the alloy, although they endowed the composites with a low-ω relaxation of the filler droplets when the alloy melted. The surface treatment of the alloy fillers enhanced the action of fillers and had the same effect as the increase in alloy content without surface treatment.

References

1. Graebling, D.; Muller, R. Colloids Surf 1991, 55, 89.
2. Bousmina, M.; Muller, R. J Rheol 1993, 37, 663.
3. Graebling, D.; Benkira, A.; Gallot, Y.; Muller, R. Eur Polym J 1994, 30, 301.
4. Graebling, D.; Muller, R.; Palierne, J. F. Macromolecules 1993, 26, 320.
5. Memon, N. A. J Polym Sci Part B: Polym Phys 1998, 36, 1095.
6. Chazeau, L.; Paillet, M.; Cavaille, J. Y. J Polym Sci Part B: Polym Phys 1999, 37, 2151.
7. Liang, J. Z.; Li, R. K. Y.; Tjong, S. C. Polym Int 1999, 48, 1068.
8. Alberola, N. D.; Fernagut, F.; Mele, P. J Appl Polym Sci 1997, 63, 1029.
9. Zheng, Q.; Du, M.; Yang, B. B.; Wu, G. Polymer 2001, 42, 5743.
10. Zheng, Q.; Yang, B. B.; Wu, G.; Li, L. W. Chem J Chin Univ 1999, 20, 1483.
11. Zheng, Q.; Zhao, T. J. Chin J Mater Res 1998, 12, 225.
12. Zheng, Q.; Takahashi, M.; Masuda, T. Chem J Chin Univ 1998, 19, 1339.
13. Peng, M.; Zheng, Q. Chin J Polym Sci 2000, 18, 565.
14. Han, C. D. J Appl Polym Sci 1986, 32, 3809.
15. Li, R. K. Y.; Liang, J. Z.; Tjong, S. C. J Mater Process Technol 1998, 79, 89.
16. Lipatov, Y. S. Adv Polym Sci 1977, 22, 1.
17. McCabe, C. C.; Mueller, N. Trans Soc Rheol 1961, 5, 329.
18. White, J. L.; Crowder, J. W. J Appl Polym Sci 1974, 18, 1013.
19. Maiti, S. N.; Mahapatro, P. K. Polym Compos 1988, 9, 291.
20. Taylor, G. I. Proc R Soc London Ser A 1934, 146, 501.
21. Shrout, T. R.; Moffatt, D.; Huebner, W. J Mater Sci 1991, 26, 145.
22. Moffatt, D. M.; Runt, J. P.; Halliyal, A.; Newnham, R. E. J Mater Sci 1989, 24, 609.
23. Narkis, M.; Ram, A.; Stein, Z. Polym Eng Sci 1981, 21, 1049.
24. Zhang, X. W.; Pan, Y.; Shen, L.; Yi, X. S. J Appl Polym Sci 2000, 77, 1044.
25. Zhang, X. W.; Pan, Y.; Zheng, Q.; Yi, X. S. J Appl Polym Sci 2000, 78, 424.
26. Zheng, Q.; Zhang, X. W.; Pan, Y.; Yi, X. S. J Appl Polym Sci 2002, 86, 3166.
27. Vollenberg, P. H. T.; Heikens, D. Polymer 1989, 30, 1656.
28. Vollenberg, P. H. T.; Heikens, D. J Mater Sci 1990, 25, 3089.
29. Sato, K. Prog Org Coat 1976, 4, 271.
30. He, L.; Ding, R.; Leonov, A. I.; Dixon, H.; Quirk, R. P. J Appl Polym Sci 1999, 71, 1315.
31. Aoki, Y. Macromolecules 1987, 20, 2208.
32. Cassagnau, P.; Espinasse, I.; Michel, A. J Appl Polym Sci 1995, 58, 1393.
33. Yanovsky, Y. G. Polymer Rheology: Theory and Practice; Chapman & Hall: London, 1993; p 212.