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The influence of low-melting-point alloy on the rheological properties of a polystyrene melt

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The rheological behavior of polystyrene melts filled with different loadings of Sn-Pb alloy has been studied. The filled polystyrene melts showed a pseudoplastic behavior, and the viscosity varied dramatically at the melting point of the alloy. The temperature dependence of the viscosity has been found to follow two separate Arrhenius equations for high and low temperatures, respectively. The presence of alloy filler was found to increase melt viscosity below the melting point of the alloy, but decreased it on reaching the alloy melting point. The melt elasticity was found to decrease with increase of alloy concentration, and increase abruptly at the alloy melting point. However, viscous flow was the dominant mechanism of deformation over the entire range of temperature studied.

1. Introduction

Polymer composites prepared by incorporating additives into a polymer matrix have been increasingly applied in many fields [1–3]. Some additives, such as mineral fillers, can act as reinforcements to enhance the mechanical properties including modules, hardness, strength, and high-temperature creep resistance, etc. Other additives, such as softeners, pigments, lubricants, and stabilizers, etc., can improve the polymer processing conditions by modifying polymer characteristics over a wide range. Since most of the processing technologies, such as extrusion, injection, and molding, in the modern polymer industry involve flow of polymer melts, the influence of additives on the rheological properties of molten polymers is of great importance from both scientific and engineering points of view [4]. The variety of the rheological behavior of polymer composite melts provides possibilities to optimize the processing conditions and to control the morphology and the performances of the final product.

For polymers filled with mineral fillers in the form of rigid particles, studies of filler influences on rheological properties of polymer melts have been so far centered on two fundamental problems, i.e., viscous and elastic properties, but mostly viscous properties. Most of these studies have been concentrated on the system of carbon black and rubber [5–7], and a few studies have appeared on other fillers such as calcium carbonate [8], titanium dioxide [9], magnesium silicate [1], and nickel [10] in polymer melts or solutions. Generally, fillers increase the level of the viscosity, but the extent differs from system to system and decreases with increasing shear rate. Only a limited number of studies of filler effect on the elastic properties of polymer melts or solutions have been reported, in which filler loading level, particle size and structure influencing the elastic properties of polymer were addressed [5, 7].

Other additives, especially those that can be distorted during processing, are also used widely in polymer industry. The influence of deformable droplets on rheological properties of polymer melts or solutions have also been the subject of many investigators for many years [11]. Taylor [12, 13] first made a prediction of the viscosity (η) of the system in which spherical droplets are contained:

$$\frac{\eta}{\eta_0} = 1 + 2.5\left(\frac{\eta_s + \frac{2}{3}\eta_0}{\eta_s + \eta_0}\right)\phi \qquad (1)$$

where η_s is the viscosity of the deformable droplets, η_0 is the viscosity of the suspending medium, and ϕ is the volume fraction of the droplets. Note that as η_s approaches infinity (i.e., for rigid particles), Equation 1 reduces to

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi \qquad (2)$$

which is generally used to estimate the viscosity of the system containing rigid particles.

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The influences of rigid particles and deformable droplets on the rheological properties of polymer melts differ in many ways such that almost all of the polymer composites in existence can be classified into two categories according to the filler properties. For further study of the effects of both rigid particles and deformable droplets on polymer viscosity, it would be valuable to have a system in which the filler could convert automatically between rigid particles and deformable droplets under some conditions. Reported in this paper is the rheological behavior of a polymer filled with low-melting-point alloy (Sn-Pb alloy) because this system may meet this requirement. As the low-melting-point alloy is melted, the rigid alloy particles may turn into deformable droplets. The melting temperature of the alloy is chosen so that the conversion from rigid particles to deformable droplets is within the range that the polymer matrix can be always kept in a visco-flow state. As a result, the filled polymer has exhibited some special behavior manifesting both scientific and engineering merits.

2. Experimental

The low-melting-point alloy used was powdered solder of composition 70 wt% Sn and 30 wt% Pb provided by Institute of Powder Metallurgy in Zhongnan Technology University of China. The melting temperature range of the alloy is approximately from 183°C to 188°C according to phase diagram, and the mean particle size is about 11 μm. The polymer matrix used was polystyrene (PS) with melt flow index of 6–10 g/10 min. The Sn-Pb alloy and PS mixtures, which varied only in Sn-Pb alloy concentration, were mixed in a satellite ball mill (QM-1SP) at 200 rpm for 11 hrs. These mixtures were moulded into small flakes that were fed into the capillary rheometer for rheological studies.

Rheological measurements were undertaken on a capillary rheometer (XLY-1) at seven temperatures (165°C, 175°C, 180°C, 185°C, 190°C, 200°C, and 210°C) for the composites of different filler concentrations. A capillary of 1 mm in diameter with the aspect ratio $L/D = 40$ was selected for the measurements. The wall shear stress ranged from 18375 to 183750 Pa for all the measurements.

3. Results and discussion

3.1. Viscous property

Rheology data were evaluated from the data at a fixed temperature and various pressures. The true wall shear stress τ_w was calculated as [14]

$$\tau_w = \frac{PR}{2L} \tag{3}$$

where τ_w is the shear stress at the wall of the capillary, P is the pressure drop, L is the length of the capillary, and R is the radius of the capillary. The end correction terms for these data have been neglected as the L/D ratio of the capillary is very large (=40). The apparent shear rate $\dot{\gamma}$ was determined using

$$\dot{\gamma} = \frac{32Q}{\pi D^3} \tag{4}$$

where $\dot{\gamma}$ is the apparent shear rate, Q is the volume flow rate, and D is the diameter of the capillary. The shear rate at the wall was determined from the apparent shear rate after applying the Rabinowistch correction:

$$\dot{\gamma}_w = \left\{\frac{(3n'+1)}{4n'}\right\}\dot{\gamma} \tag{5}$$

where $\dot{\gamma}_w$ is the shear rate at the wall, and n' is the flow behavior index obtained as the slope of the linear plot of $\log \tau_w$ vs. $\log \dot{\gamma}_w$. The melt viscosity η was then estimated as:

$$\eta = \frac{\tau_w}{\dot{\gamma}_w} \tag{6}$$

Fig. 1 shows the typical flow curves at 175°C and 190°C which are linear over the shear rate range of interest. It is clearly seen that the viscous behavior of Polystyrene filled with Sn-Pb alloy also obeys the power law as other filled polymers [14], which is

$$\tau_w = K\dot{\gamma}_w^n \tag{7}$$

As shown in Fig. 1, the power law exponents (n) are always less than unit, indicating a pseudoplastic behavior of all these composites. The values of the power law exponents calculated from Fig. 1 are shown in Table I. It can be seen that all the power law exponents of the pure polystyrene melts vary from 0.31 to 0.37 over the entire range of temperature studied, while those values after incorporating with Sn-Pb alloy are larger than 0.40, suggesting that the deviation of the flow behavior of the incorporated melts from the Newtonian flow diminishes. However, The variation of n is small within the ranges of alloy concentration and temperature, indicating that the pseudoplasticity of these filled polystyrene melts changes inappreciably.

Fig. 2 gives plots of melt viscosity with shear stress for the filled polymers at 175°C and 190°C, respectively. The melt viscosity decreases with increase of shear stress, and changes intricately with the increasing alloy concentration and temperature.

3.2. Effect of alloy concentration on viscous property

Fig. 3 shows the variation of the relative viscosity (η/η_0, where η_0 is the viscosity of pure polystyrene melt) with volume fraction of the Sn-Pb alloy at 175°C, a temperature lower than the melting point of the alloy. It can be seen in Fig. 3 that the relative viscosity first decreases with increase of alloy concentration to a minimum at some critical concentration and then increases with further increase of the concentration. The solid Sn-Pb alloy particles apparently do not exhibit obstruction to the flow of the melts until the volume fraction of Sn-Pb alloy reaches the critical value. Such an obstruction becomes stronger as the volume fraction is further increased over the critical value. In order to understand the critical value a curve of resistivity vs. volume fraction of Sn-Pb alloy is also plotted in Fig. 3. At about 20 vol% where the resistivity drops sharply can then be defined as a critical volume fraction at which a continuous conductive filler network starts to be formed [15].

TABLE I Values of power law exponent (*n*) for the various samples at different temperatures

	165°C	175°C	180°C	185°C	190°C	200°C	210°C
PS	0.33	0.31	0.33	0.32	0.36	0.37	0.37
PS/Sn-Pb 5%	0.46	0.42	0.42	0.43	0.45	0.46	0.46
PS/Sn-Pb 15%	0.42	0.46	0.45	0.42	0.45	0.42	0.43
PS/Sn-Pb 25%	0.47	0.46	0.43	0.46	0.48	0.48	0.49
PS/Sn-Pb 35%	0.43	0.42	0.42	0.44	0.46	0.43	0.47
PS/Sn-Pb 45%	0.43	0.44	0.43	0.48	0.50		

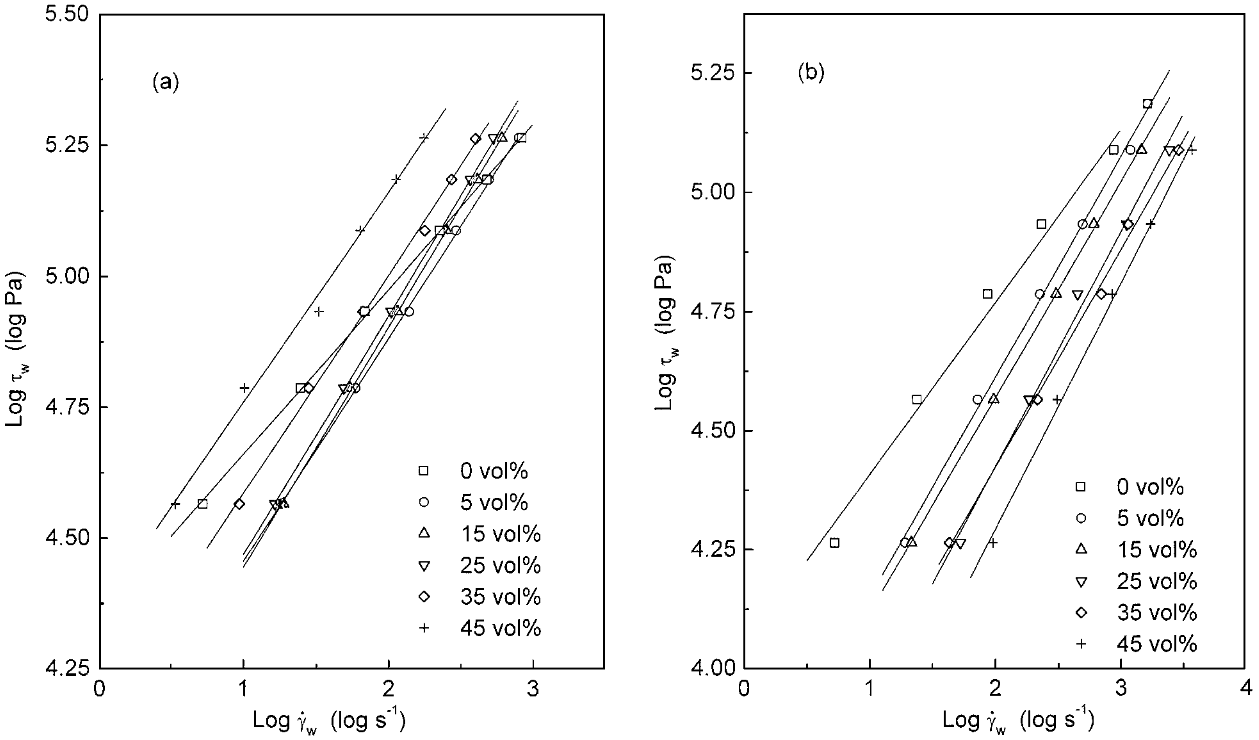

Figure 1 Flow curves of Sn-Pb alloy filled polystyrene at the temperature of: (a) 175°C; (b) 190°C.

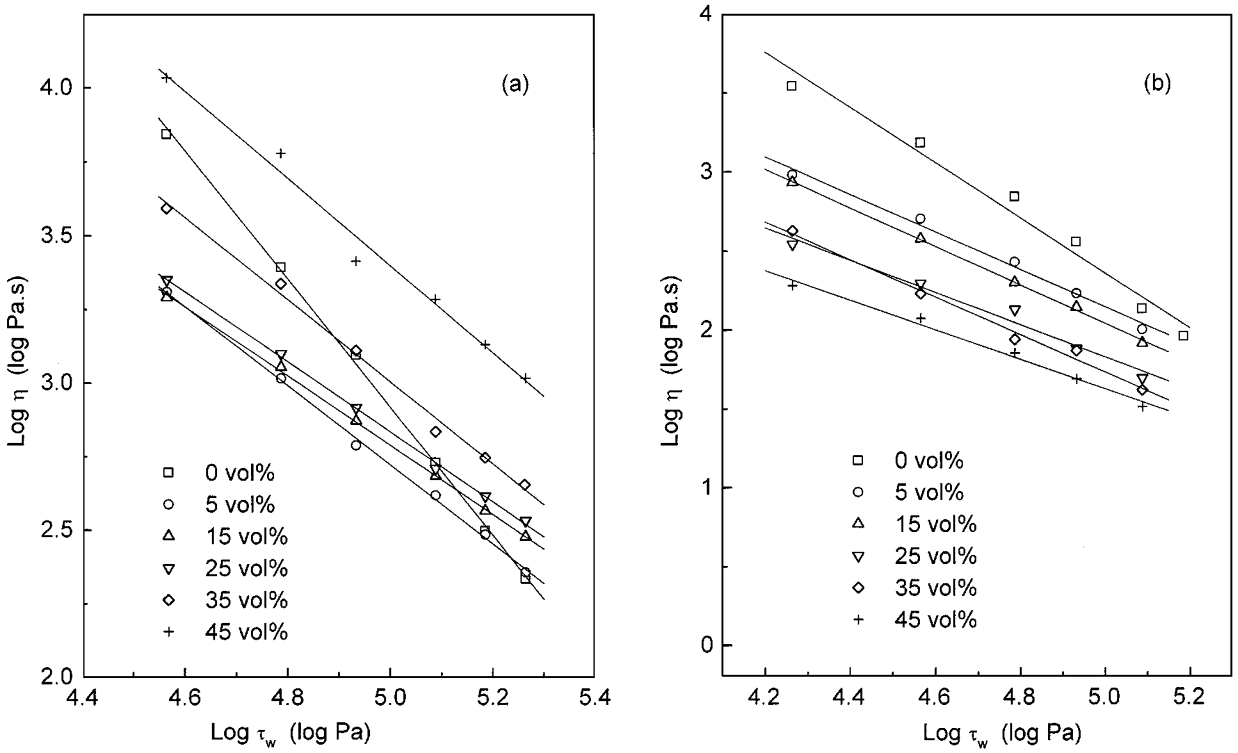

Figure 2 Variation of melt viscosity (*η*) with shear stress for Sn-Pb alloy filled polystyrene of different filler concentration at the temperature of: (a) 175°C; (b) 190°C.

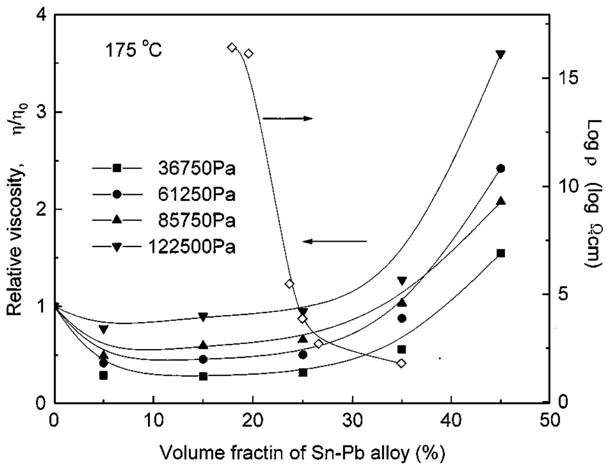

Figure 3 Variation of relative viscosity (η/η_0) with alloy concentration for Sn-Pb alloy filled polystyrene at 175°C at constant shear stresses.

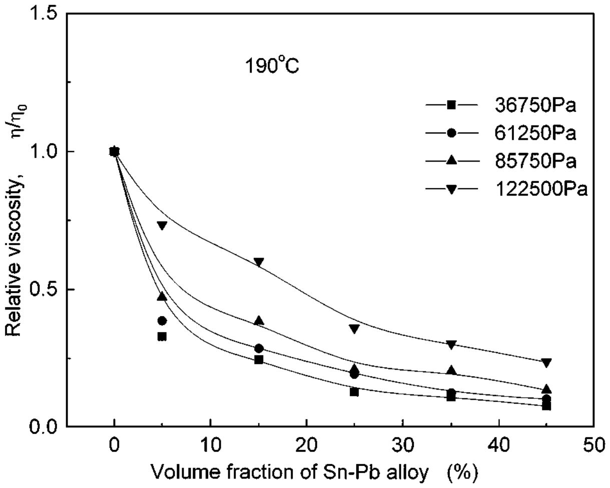

Figure 4 Variation of relative viscosity (η/η_0) with alloy concentration for Sn-Pb alloy filled polystyrene at 190°C at constant shear stresses.

It is interesting that the critical volume fraction determined by the resistivity-volume fraction curve happens to be the same one at which the viscosity starts increasing. Therefore, it may be concluded that the obstruction of the alloy particles to flow appears only after the particles are densely populated to form continuous networks in the melts.

The variation of the relative viscosity with volume fraction of alloy under different shear stresses at 190°C, a temperature above the melting point of the melt, are shown in Fig. 4. Being different from the curves obtained at 175°C, the relative viscosity decreases monotonically with the increase of alloy volume fraction over the whole range of alloy concentration. At 190°C the alloy filler is melted from rigid particles to deformable droplets. It is generally believed that the viscosity of the melted alloy is much lower than that of polymer melts. The alloy droplets in the melts will be distorted and torn to become fiber shaped inclusions within the polymer melts oriented along the shear stress direction. As a result, the overall viscosity of the composite will obey a mixtures rule of the component properties, and dramatically decreases with the increase of incorporated alloy content at temperatures above the alloy melting point.

3.3. Effect of temperature on viscous property

As usual, the temperature dependence of the melt viscosity of different loading levels was assessed by plotting $\log\eta$ vs $1000/T$ in Fig. 5a and b for constant shear rate and constant shear stress, respectively. As the free volume available for molecular motion is greater at higher temperature, the viscosity decreases with increase of temperature. In general, the temperature dependence of the viscosity of filled polymer melt can be represented by the Arrhenius equation [10]:

$$\eta = A\exp\left(\frac{\Delta E}{RT}\right) \tag{8}$$

where ΔE is the activation energy of flow and R is the universal gas constant. This rule basically holds for polystyrene filled with low-melting-alloy but in different manners (different ΔE & A) for the temperature ranges above and below the melting point of the alloy, respectively.

The activation energies at constant shear rates, ($\Delta E_{\dot\gamma}$) and constant shear stresses (ΔE_τ), for the two different temperature ranges are calculated from Fig. 5, and are shown in Fig. 6a and b, respectively. For low temperatures (below the melting point), $\Delta E_{\dot\gamma}$ at a certain shear rate increases and then slightly decreases with increasing alloy concentration, and a higher shear rate leads to higher increasing and decreasing rates. For high temperatures (above the melting point) $\Delta E_{\dot\gamma}$ varies little with either increasing concentration or increasing shear rate. As a result, the temperature sensitivity of the viscosity of alloy filled polystyrene melts alters a lot before and after the alloy filler is melted. From Fig. 5b, where the activation energies at different shear stresses (ΔE_τ) are shown, similar results but no decreases in ΔE_τ are obtained. Furthermore, at any alloy concentration a relation which is:

$$\Delta E_{\dot\gamma} = n\Delta E_\tau; \quad 0 \le n \le 1 \tag{9}$$

seemingly holds. Where $n = 0.40$–0.50 is the power term exponent shown in Table I. The effect of alloy concentration on $n\Delta E_\tau$ is shown Fig. 6c, suggesting similarities both in values and curve shapes of $n\Delta E_\tau$ (Fig. 6c) to $\Delta E_{\dot\gamma}$. Eq. (9) proves to be a good description of the observed behavior.

3.4. Elastic property

The die-swell ratio is defined as:

$$B = \frac{\mathrm{Di}}{D} \tag{10}$$

where Di and D are the diameters of extrudates and die respectively. The die swell ratio of a given filled polymer after extrusion through long die, designed B_∞, is only proportional to the applied shear stress no matter what shape the die has. At a constant shear stress, B_∞ depends only on the anisometry of filler particles and loading level. According to Cotton [16] B obtained at

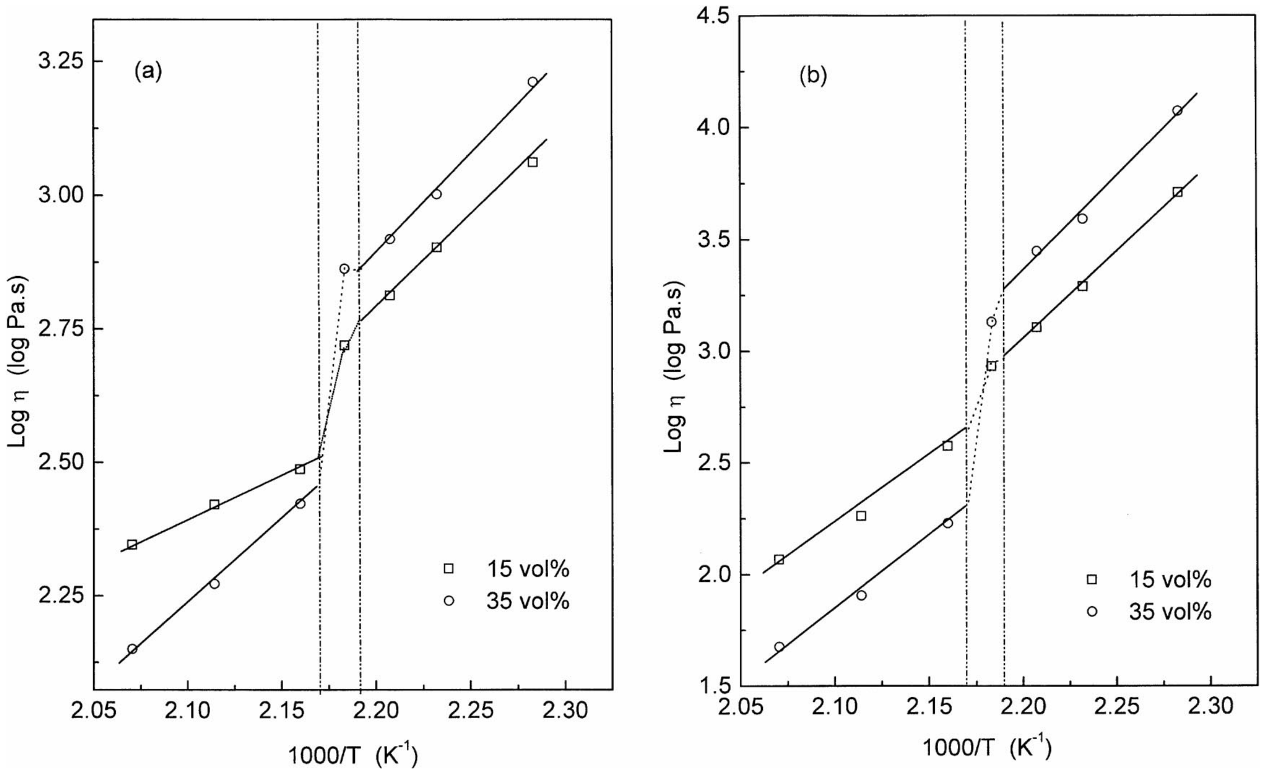

Figure 5 Effect of temperature on melt viscosity of Sn-Pb alloy filled polystyrene at constant: (a) shear rate; (b) shear stress.

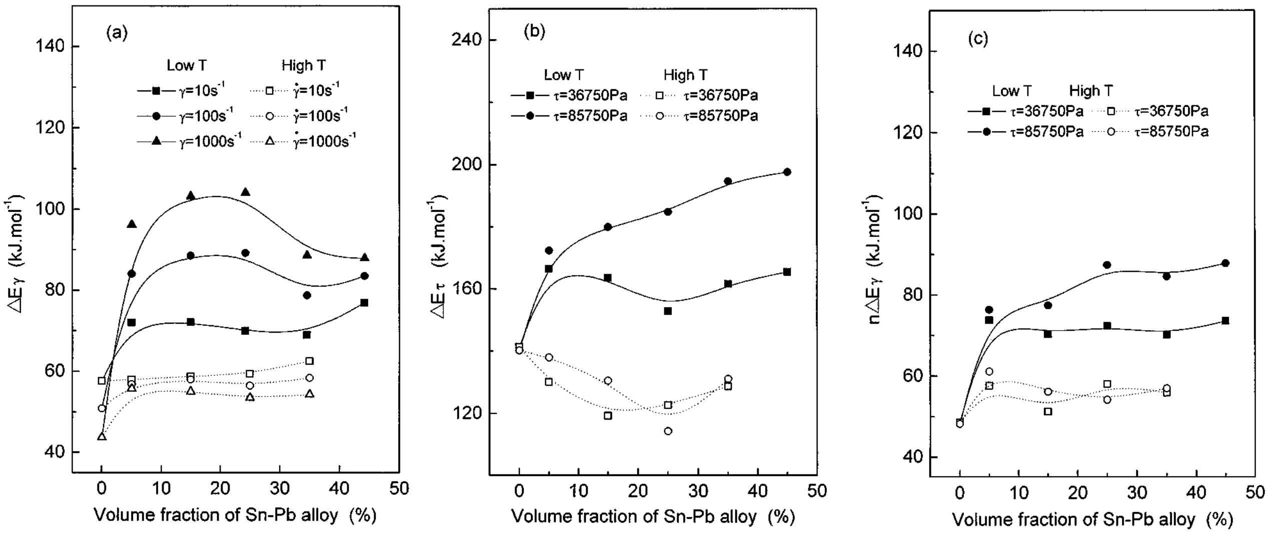

Figure 6 Active energy for Sn-Pb alloy filled polystyrene. (a) $\Delta E_{\dot{\gamma}}$; (b) ΔE_{τ}; (c) $n\Delta E_{\dot{\gamma}}$.

$L/D = 40$ (≥ 16.5) used in this study may be treated as B_∞, reflecting the intrinsic behavior of the melts. Other parameters characterizing the melt elasticity are the primary or first normal stress difference ($\tau_{11} - \tau_{22}$), recoverable shear strain (S_R), and apparent shear modulus (G). In this study, the die swell ratios were measured at various shear stresses for the melts with different alloy concentrations. The primary normal stress difference, recoverable shear strain, and apparent shear modulus were calculated according to the following relations based on the assumption that the melts obeys Hooke's law in shear [11]:

$$\tau_{11} - \tau_{22} = 2\tau_w \left[2\left(\frac{\mathrm{Di}}{D}\right)^6 - 2 \right]^{1/2} \tag{11}$$

$$S_R = \frac{(\tau_{11} - \tau_{22})}{2\tau_w} \tag{12}$$

$$G = \frac{\tau_w}{S_R} \tag{13}$$

Variations of die swell ratio with volume fraction of Sn-Pb alloy at 175°C and 190°C are shown in Fig. 7. The die swell ratio decreases with increasing alloy concentration and increases with the increasing shear stress. The lower elasticity of the polymer melts with higher alloy concentration is due to the enhancement of the rigidity of the polymer in the presence of filler, which implies the lower mobility of the macromolecular chain at the applied shear stress [9]. It can also be seen that the die swell ratios at 175°C at different

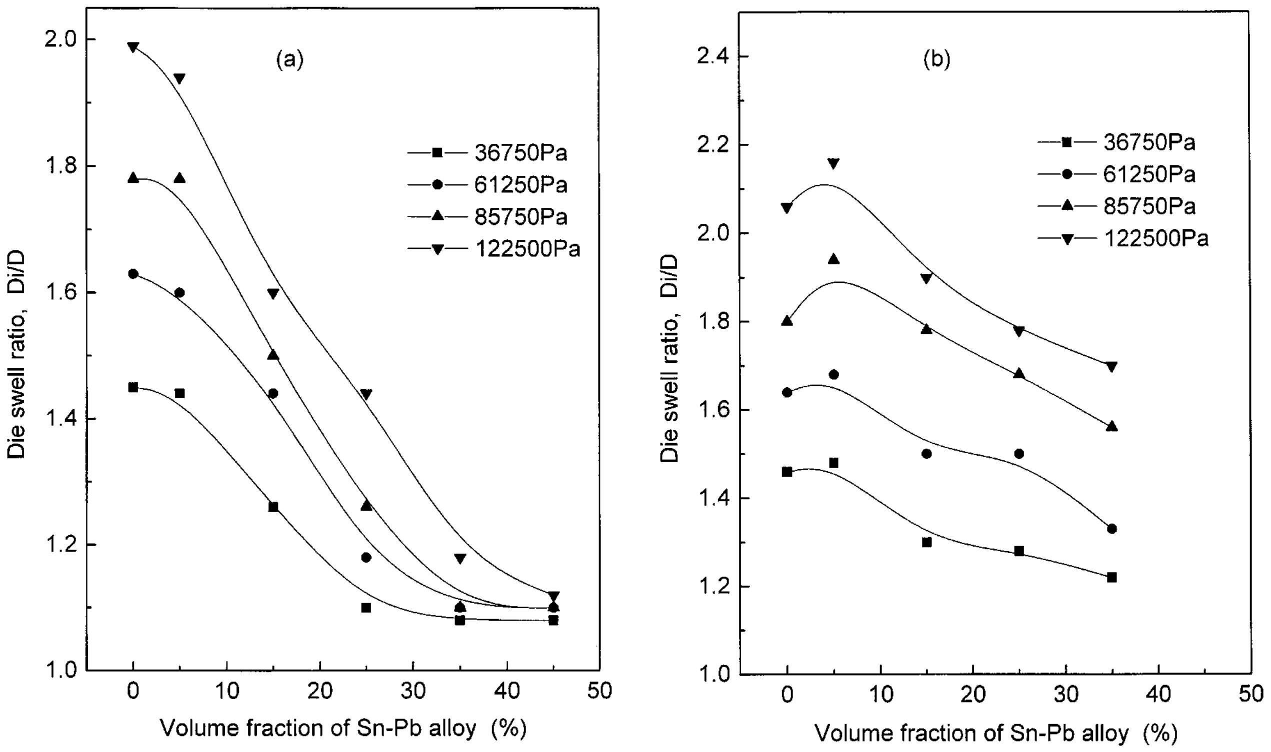

Figure 7 Variation of die swell ratio with alloy concentration for Sn-Pb alloy filled polystyrene at the temperature of: (a) 175°C; (b) 190°C.

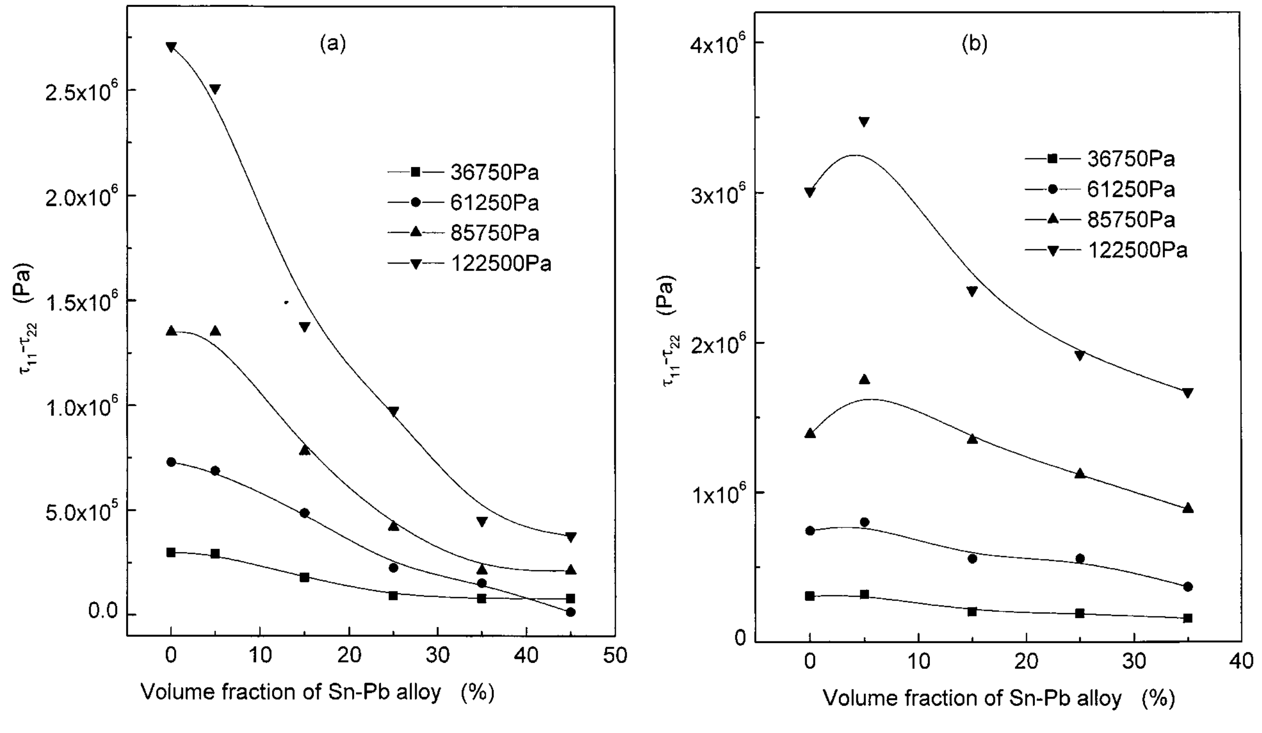

Figure 8 Variation of primary normal stress difference with alloy concentration for Sn-Pb alloy filled polystyrene at the temperature of: (a) 175°C; (b) 190°C.

shear stresses converge to almost the same value at about 45 vol%, but this phenomenon does not appear at 190°C. It may be concluded that the elasticity of the system alters after the Sn-Pb alloy changes from rigid solid particles to deformable droplets. Similar results are also obtained from Fig. 8, where the variations of primary normal stress difference are shown as functions of volume fraction of alloy at different shear stresses.

Effects of shear stress on the recoverable shear strain at various alloy concentrations are represented in Fig. 9. The recoverable shear strain increases with increase of shear stress, indicating an increase of melt elasticity. The differences between the plots for 175°C and those for 190°C are inappreciable. Fig. 10 shows the variations of apparent shear modulus with shear stress. The apparent shear modulus increases with increase of shear stress at 175°C, but does not vary much at 190°C. As compared with Fig. 9 the differences of apparent shear modulus between 175°C and 190°C are quite large. The increase of recoverable shear strain with increasing

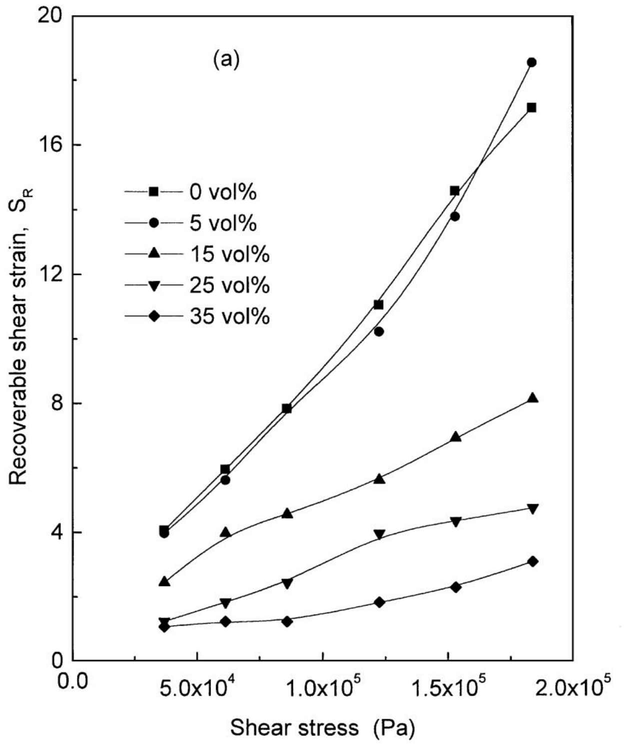

Figure 9 Effect of shear stress on recoverable shear strain of Sn-Pb alloy filled polystyrene at the temperature of: (a) 175°C; (b) 190°C.

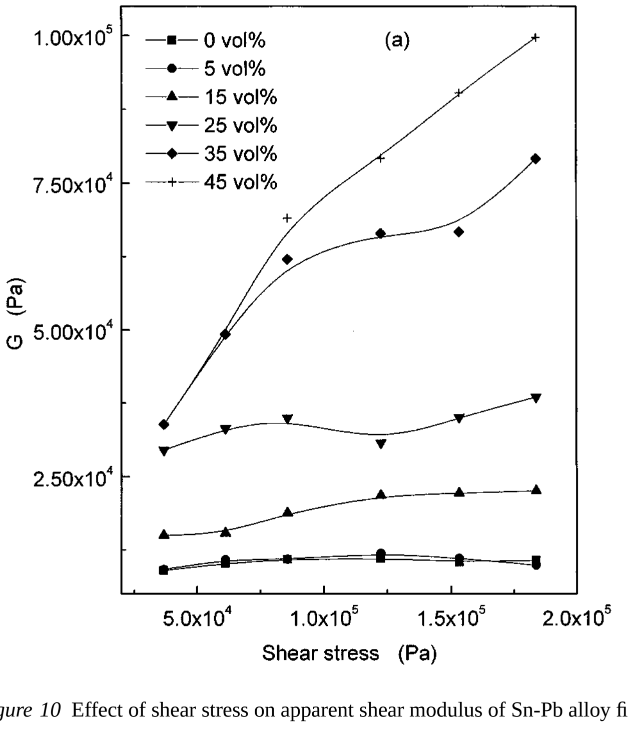

Figure 10 Effect of shear stress on apparent shear modulus of Sn-Pb alloy filled polystyrene at the temperature of: (a) 175°C; (b) 190°C.

shear stress shown in Fig. 9a and b implies that the macromolecular chains are more moveable at higher shear stress, and the mobility increase is mainly attributed to the polymer properties and the alloy concentration, but not much to the state of the alloy. However, the change of the melt rigidity does not exactly follow the change of macromolecular chain mobility, losing the coherence between them as usual. The melt rigidity increases with increasing shear stress before the melting point of the alloy, and does not change much after the alloy melts. It can also be obtained from Fig. 9 and Fig. 10 that the recoverable shear strain decreases and apparent shear modulus increases with increase of alloy concentration at constant shear stress.

3.5. Effect of temperature on elastic property

In order to investigate the effect of alloy state on the elastic property, variations of die swell ratio, primary normal stress difference and recoverable shear strain as functions of temperature at different constant alloy

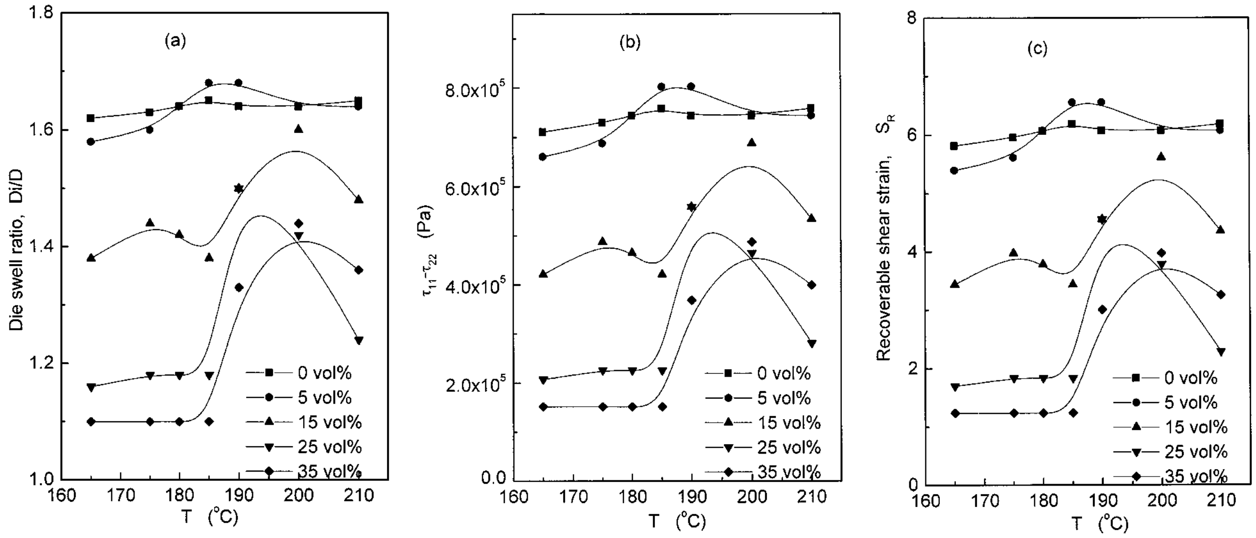

Figure 11 Effect of temperature on the: (a) die swell ratio; (b) primary normal stress difference; and (c) recoverable shear strain.

concentrations are shown in Fig. 11. The same values of these elasticity parameters of the pure polystyrene are almost held over the whole range of temperature studied. However, the die swell ratio, primary normal stress difference, and recoverable shear strain of the filled melts at any alloy concentration vary little before the alloy melts, but increase abruptly and then decrease with further increase of temperature when the alloy melts. The presence of the alloy rigid particles reduces the mobility of the macromolecular chains, and thus enhances the rigidity of the polymer. Furthermore, the enhancement of the polymer rigidity is independent of the temperature, so the elasticity does not change much within the temperature range before the alloy melts. However, when the temperature reaches the melting point of the alloy, the rigid alloy particles are melted into deformable droplets, and the deformability of alloy droplets enhances the mobility of macromolecular chains instead of decreasing it, resulting in the abrupt increase of the elasticity at the melting point. However, when the temperature keeps rising continuously, the elasticity decreases. In Fig. 12 the effect of temperature on the apparent shear modulus is shown. It can also be seen that the apparent shear modulus varies little before reaching the melting point of the alloy, but first decreases abruptly and then slightly increases with further increase of the temperature after the alloy melts.

3.6. Relaxation time

The elastic deformation of a polymer melt is usually caused by the movements of the macromolecular segments, and the moving capability of the segments (i.e., the speed of the relaxation) is characterized by the relaxation time ($\tau = \eta/G$). If the τ is very little, less than the observation time t, viscous flow is the dominant mechanism of the polymer melt deformation. However, if the relaxation time is very large (i.e., $t \ll \tau$), melt elastic deformation instead of viscous flow will be dominant. The relaxation times of filled polymer melts with various alloy concentrations are plotted against the temperature in Fig. 13. Contrasting with the observation time, the relaxation time of the samples studied is relatively short, and even shorter with the increase of temperature. Therefore, viscous flow is the dominant mechanism of the deformation as compared with the elastic one,

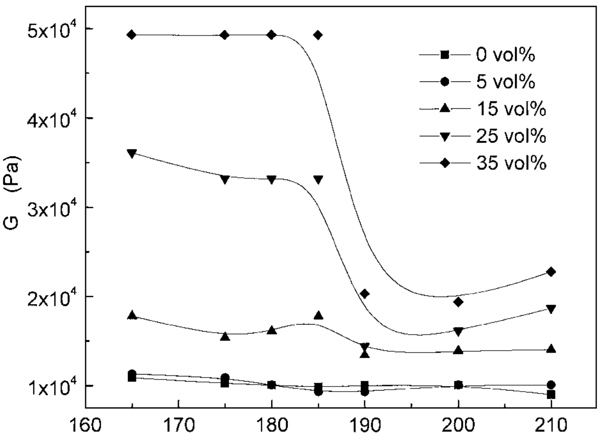

Figure 12 Effect of temperature on apparent shear modulus of Sn-Pb alloy filled polystyrene.

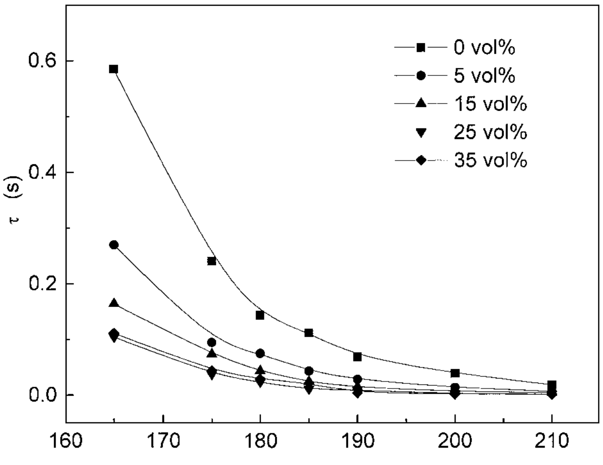

Figure 13 Variation of relaxation time with temperature for Sn-Pb alloy filled polystyrene.

and the domination of viscous flow is more obvious when the temperature rises. The relatively small elasticity of polystyrene melts in the presence of Sn-Pb alloy filler is advantageous from the processing point of view since this will increase the critical shear stress for melt fracture.

Despite the abrupt increase of elasticity at the melting point of the alloy (Figs 11 and 12), the relaxation time keeps decreasing at that temperature, suggesting that the increase of elasticity can be balanced by the increase of viscous flow, and a considerable output increase of the melt can be brought about. From Fig. 13, it can also be seen that the relaxation time decreases with the increase of alloy concentration, indicating that the presence of Sn-Pb alloy promotes the domination of the viscous flow over the studied temperature range.

4. Conclusions

The influences of Sn-Pb alloy on the rheological properties of polystyrene melts have been studied. The power law relationship between shear stress and shear rate is obeyed over the entire range of shear stress studied, and the pseudoplasticity of polystyrene is retained in the presence of Sn-Pb alloy. The alloy filler increases the melt viscosity at temperatures lower than the melting point of the alloy, but decreases the viscosity at temperatures above the melting point. The temperature dependence of the viscosity follows two separate Arrhenius equations at the high and low temperatures, respectively. The melt elasticity represented by die swell ratio, primary or first normal stress difference, and recoverable shear strain, etc., increases abruptly when the temperature reaches the alloy melting point, but decreases with increasing alloy concentration. However, the viscous flow is the main mechanism of deformation over the studied range of temperature in spite of the abrupt increase of elasticity at the melting point.

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