

A New Polymer Composite Thermistor Having Double PTC Transitions

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ABSTRACT: The electrical resistivity of the Sn-Pb alloy filled high density polyethylene composites has been studied as a function of temperature. Two positive temperature coefficient (PTC) transitions, named double PTC of resistance, were found and are thought to be related to the melting points of the polymer matrix and alloy filler, respectively. The two PTC transition temperatures increase with the increase of the alloy volume fraction. With the increasing volume fraction of the alloy, the first PTC intensity decreases, the second PTC intensity increases and then decreases after the volume fraction reaches 38 vol %, and the total PTC intensity decreases. The double PTC effect is reversible and reproducible. The mechanisms for both the first and the second PTC transitions are also proposed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 424–429, 2000

Key words: low-melting-point alloy; high density polyethylene; composite; double positive temperature coefficient; electrical property

INTRODUCTION

Intelligent materials are capable of detecting a change in the environment and respond to it by performing both sensing and actuating functions. The usual stimuli are temperature, pressure, electrical, vibration, etc. The useful responses are changes of resistance, heating, mechanical damping, or acoustic damping.^{1,2} One of the most used intelligent materials is the thermistor, or temperature-dependent resistor, which can display a stronger increase in electrical resistance with increasing temperature.

Positive temperature coefficient of resistance (PTC) has been widely observed in ceramic mate-

rials such as doped BaTiO₃ or V₂O₃ based compounds, which exhibit a change in resistivity of four to six orders of magnitude from the ferroelectric to paraelectric state at the Curie temperature.^{3,4} But the application of ceramic materials as PTC thermistor is limited by the relatively high room temperature resistivities ($\approx 100 \Omega \cdot \text{cm}$) and high manufacturing costs. Conductive powder filled polymer composites also have PTC effects, and are used as thermistors.^{5,6} The most common thermistor of this type is the carbon black filled semi-crystalline polymer (e.g., high density polyethylene), which has high PTC effects and low room temperature resistivities ($1\text{--}10 \Omega \cdot \text{cm}$).^{7–9} For this type of thermistors, the PTC transition takes place in the melting point of the semi-crystalline polymer matrix [see Fig. 1(a)]. The carbon black filled semi-crystalline polymers are cheaper and easier to prepare, but they have disadvantages, such as the negative temperature coefficient (NTC) effect following the PTC transi-

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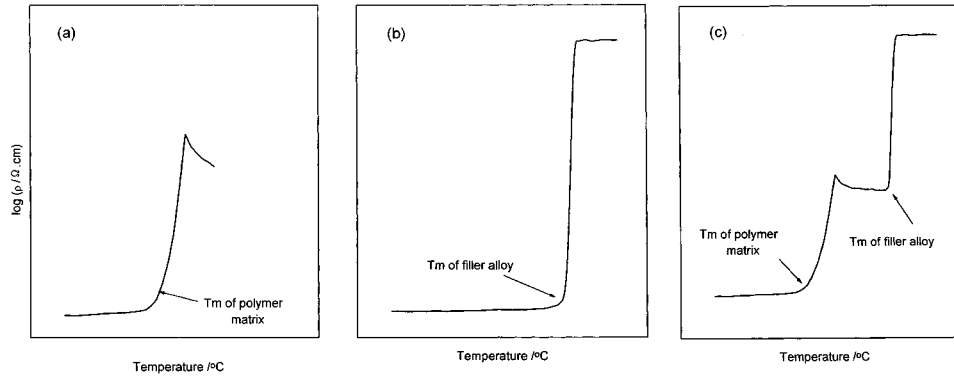


Figure 1 Temperature dependence of resistivity of (a) carbon black filled semi-crystalline polymer composites; (b) low-melting-point alloy filled amorphous polymer composites; and (c) low-melting-point alloy filled semi-crystalline polymer composites.

tion, which limits the application of such composites. Though the NTC effect can be alleviated by crosslinking of the polymer,¹⁰ there is still practical need and theoretical interest to seek easier solutions.

Another new polymer composite thermistor, exhibiting a PTC transition near the melting point of the incorporated conducting filler instead of the polymer matrix [Fig. 1(b)], has been found by the authors.¹¹⁻¹³ This new type of polymer composite thermistor was made by mixing the low-melting-point alloy and amorphous polymer composite. The thermistor made of low-melting-point alloy filled amorphous polymer composites has many advantages as compared with the ceramic materials and carbon black filled semi-crystalline polymers: 1. high PTC intensity; 2. abrupt PTC transition behavior; and 3. adjustable PTC transition temperature by easily selecting the filler alloys with different melting points. However, because the polymer matrix used in the previous investigations is polystyrene in which viscosity is already very low at PTC transition temperature, i.e., T_m of the low-melting-point alloy, the composite is usually distorted and the reproducibility is relatively poor. As a result, the practical application of this thermistor can only be achieved after the reproducibility is solved.

This report presents a new approach by incorporating the low-melting-point alloy in the semi-crystalline polymer. The PTC effect has been found not only at the melting point of the alloy filler but also that of the semi-crystalline polymer matrix [see Fig. 1(c)]. The double positive temperature coefficient (double PTC, or d-PTC) of resistance effects have been thus termed. The NTC effect, which often appears after the PTC transi-

tion, will be restricted to some extent because of the second PTC transition after the first one for the low-melting-point alloy filled semi-crystalline polymer composites. At the same time, the viscosity of the semi-crystalline polymer used in our study is much higher than that of polystyrene used in the previous study, so the distortion is limited and the reproducibility of the composite is improved considerably.

The d-PTC effect of polymer composites found for the first time is significant from both theoretical and application points of view. For example, one can utilize the first PTC effect to make a self-regulating heating element, where only a feeble PTC transition is needed. The second PTC effect can then be used as a circuit protection device for the heating element. As a result, a new thermistor, which contains both the self-regulating heating and circuit protection functions, is brought out by simply compounding the semi-crystalline polymer and low-melting-point alloy. This kind of thermistor is especially important in the application in which both the low room temperature resistivity and strong PTC effect are needed, but these two properties are not easily obtained for many other polymer composite thermistors.

EXPERIMENTAL

Materials

The low-melting-point alloy used in this study was Sn-Pb alloy. It was powdered solder of composition 60 wt % Sn, 40 wt % Pb provided by the Institute of Powder Metallurgy in Zhongnan

Technology University of China. The melting temperature range of the alloy is approximately 183 to 188°C according to phase diagram, and the mean particle size is about 11 μm . The polymer powder used was high density polyethylene (HDPE) which was supplied by Maoming Petrochemicals Co. of China.

Preparations of Composites

The Sn-Pb alloy and HDPE mixtures, which varied only in Sn-Pb alloy concentration, were mixed in a satellite ball mill (QM-1SP) at 200 rpm for 11 h. Then the powder mixtures were hot pressed in a matched metal die at 170°C for 20 min to form the composites.

Measurement

The resistivity of the composites varied over a wide range from 1 to $10^{18} \Omega \cdot \text{cm}$. High resistivity composites were measured on a ZC36 High Resistance Electrometer, whereas low resistivity composites were measured on an M890D Digital Electrometer.

The resistivity-temperature curve was obtained by using a Resistivity-Temperature Tester that was designed by our laboratory, and the sample size was $1.5 \times 1.5 \times 0.1 \text{ cm}$. The heating rate adopted was $1.5^\circ\text{C}/\text{min}$.

The relative thermal expansion was measured on the Volume-Resistance-Temperature on-line Tester designed by Yi.¹⁴ The heating rate used was also $1.5^\circ\text{C}/\text{min}$.

Rheological measurements were undertaken on a capillary rheometer (XLY-1), and 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 18,375 to 183,750 Pa for all the measurements. However, only the data measured at 73,500 Pa are shown in this report.

RESULTS AND DISCUSSION

Resistivity-Temperature Behavior

Figure 2 shows the resistivity of the Sn-Pb alloy filled HDPE as a function of temperature. There exist double PTC transitions for all the composites with various alloy volume fractions of interest. The location of the first PTC effect is closely related to the melting point of the HDPE, whereas the second PTC effect occurs at the melting point of the alloy. The very interesting and

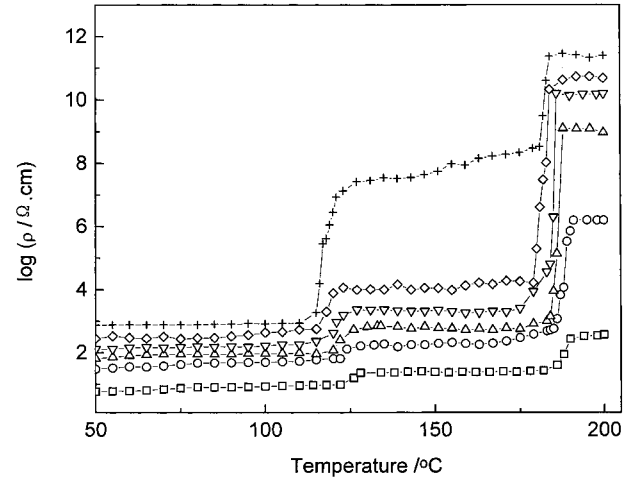


Figure 2 Temperature dependence of resistivity of Sn-Pb/HDPE composites filled with different volume fractions of Sn-Pb alloy: □, 45 vol %; ○, 42 vol %; △, 40 vol %; ▽, 38 vol %; ◇, 36 vol %; +, 34 vol %.

important phenomenon is that there is no evidence of NTC transition after the first PTC transition, which is usual in the carbon black filled HDPE.⁸

For the application as a temperature sensor, an essential parameter is the PTC transition temperature (T_c). For simplification, T_c is defined as the temperature at which half of the resistivity change on a logarithmic scale is reached.² From Figure 2, it can be obtained that the PTC transition temperatures of both the first and the second PTC transitions increase with the increase of the alloy volume fraction.

Besides the T_c , another important aspect of the PTC effect for the polymer composite thermistors is the PTC intensity, which reflects how sensitive and to what extent the resistance response will be after being stimulated by the change of the temperature or electrical current. The PTC intensity is defined as:

$$I_{\text{PTC}} = \log\left(\frac{\rho}{\rho_0}\right) \quad (1)$$

where ρ is the maximal resistivity just over the PTC transition, and ρ_0 is the resistivity before the PTC transition. The effect of alloy volume fraction on the PTC intensity is shown in Figure 3. As shown in Figure 3, the PTC intensity for the first PTC transition decreases with the increase of the alloy volume fraction, which is common for the conducting particle filled polymer composites.¹⁵

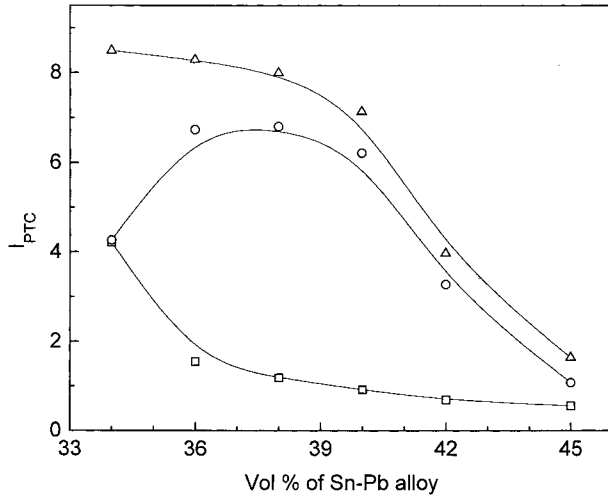


Figure 3 PTC intensity as a function of the alloy volume fraction for the Sn-Pb alloy filled HDPE composites. □, Intensity of the first PTC transition; ○, intensity of the second PTC transition; △, total PTC intensity.

However, the second PTC intensity first increases with the increasing alloy volume fraction, and then decreases after the volume fraction reaches 38 vol %. It can also be seen that the total PTC intensity, i.e., the sum of the above two values, decreases with the increasing alloy volume fraction.

Reversibility and Reproducibility

The thermistors have practical usage only when their PTC effects are reversible and reproducible. The main objective of this section is to investigate the reversibility and reproducibility of the d-PTC of Sn-Pb alloy filled HDPE composites.

Figure 4 shows both the heating and cooling curves of the resistivity-temperature behavior for three Sn-Pb alloy filled HDPE composites with different alloy volume fractions. For all three composites, d-PTC effect appears during heating, which has been discussed in the above section. The shapes of the three cooling curves are similar to each other. The resistivity varies little before cooling to 90°C, and then transits from high-resistive state to low-resistive state at the temperature range of 90–75°C. Although there is only one transition in the cooling curve, the total resistivity mutation is reversible, which indicates that the conducting pathways that have been broken during heating can be re-formed after being cooled.

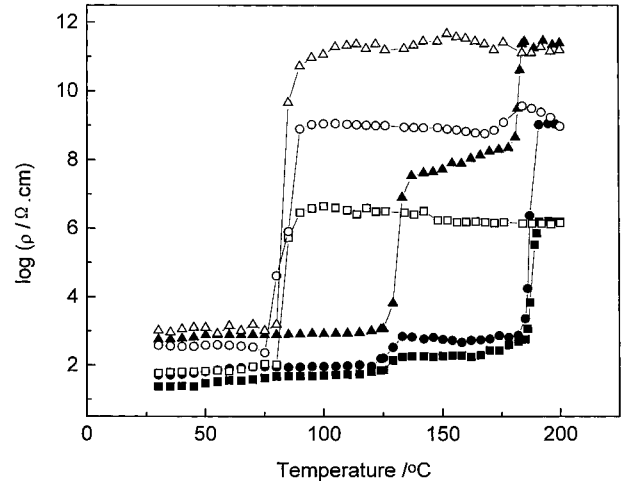


Figure 4 Temperature dependence of resistivity of Sn-Pb/HDPE composites filled with different volume fractions of Sn-Pb alloy: □,■, 42 vol %; ○,●, 40 vol %; △,▲, 34 vol % for the heating (solid symbols) and cooling (hollow symbols) cycles.

The reproducibility of the d-PTC effect for the Sn-Pb alloy HDPE is shown in Figure 5. It can be obtained that the d-PTC effect reoccurs for all three heating cycles studied and the PTC intensity for both PTC transitions almost does not change. Though the room temperature resistivity increases after every temperature run, the increment greatly diminishes after the second temperature run. Furthermore, the resistivity-temperature curves of the successive heating cycles become more adjacent after the first temperature

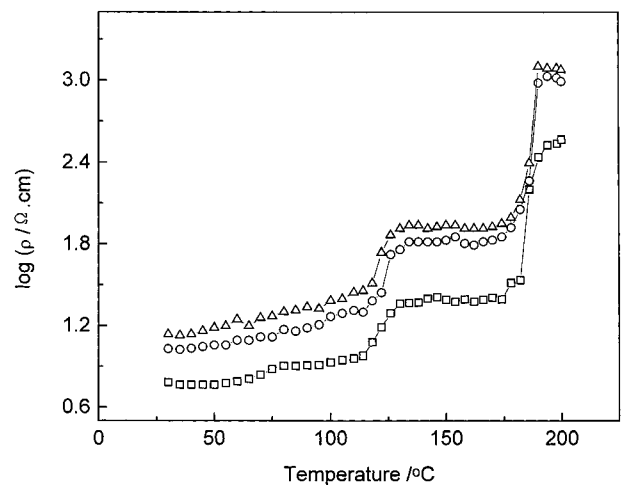


Figure 5 Temperature dependence of resistivity of Sn-Pb/HDPE composites during three successive cycles: □, first cycle; ○, second cycle; △, third cycle.

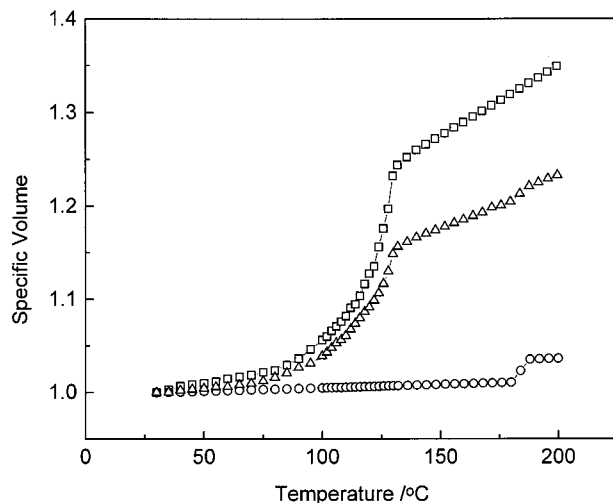


Figure 6 Thermal expansion of \square HDPE, \circ Sn-Pb alloy, and \triangle Sn-Pb/HDPE composite filled with 38 vol % Sn-Pb alloy. The data of Sn-Pb were calculated from that of ref. 19.

run. Therefore, the microstructure of the composites becomes steadier after the temperature run, indicating that the reproducibility can be improved further by heat treatment of the composites.

Possible Mechanism of the d-PTC Effect

The first PTC transition of the d-PTC effect occurs near the melting point of the polymer matrix (HDPE), therefore the thermal expansion of HDPE should be responsible for this PTC transition. Figure 6 shows the relative thermal expansion of the HDPE, Sn-Pb alloy, and Sn-Pb alloy filled HDPE over a wide range of temperatures. The relative thermal expansion of HDPE is much larger than that of Sn-Pb alloy, and there is quite a large change in the relative thermal expansion of HDPE at the melting point of the polymer, which leads to a large change in the relative thermal expansion of the composite. As the thermal expansion of the alloy particles is much less than that of the polymer, the large thermal expansion of HDPE at its melting point results in the break of the conducting pathways, leading to a significant increase in the electrical resistivity of the composite, i.e., the first PTC transition. The thermal expansion of the polymer matrix can also be used to explain some other aspect of the first PTC transition. For example, the change of T_c and PTC intensity with the change of alloy volume fraction (see Figs. 2 and 3) can be explained by the follow-

ing. There are more conducting pathways in the composites with high alloy volume fraction than in those with low volume fraction, so they need larger thermal expansion of the polymer matrix to separate the alloy particles; thus, the T_c increases and PTC intensity decreases with the increase of volume fraction.

Because the location of the second PTC effect is closely related to the melting point of the Sn-Pb alloy, the original of the second must be some characteristic change of the alloy that also results in the break of the conducting pathways. It is noted that the surface energy of solid metal (including alloy) near the melting point is about 10–20% higher than that of the corresponding liquid.¹⁶ As a result, the surface energy of the Sn-Pb alloy is reduced and approaches that of the HDPE to some extent after reaching the melting point of the alloy. The convergence of the surface energies of the alloy and the polymer leads to the improvement of the wettability of the alloy for HDPE. Though the improvement is not very large, its influence on the resistivity is apparent as the electrical property of the composites is very sensitive to the wettability of the filler for the polymer matrix.¹⁷ When the wettability increases, the polymer has a tendency to wet or enwrap the surface of the alloy particles, the particles will be separated from each other and the conducting pathways are thus broken. As a result, the second PTC transition is caused by the surface energy change of the alloy at the melting point. Figure 7 shows the effect of temperature on

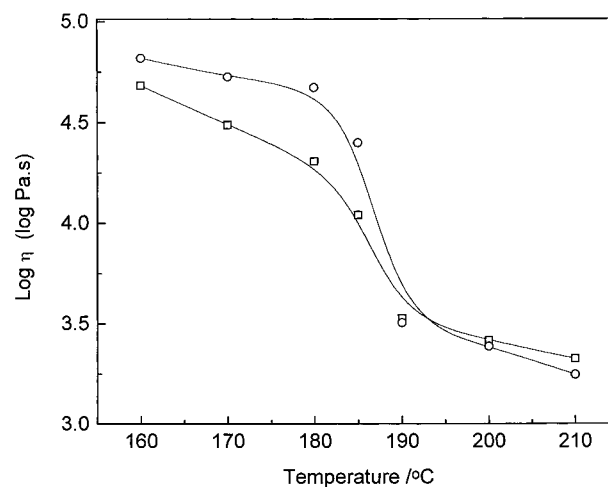


Figure 7 Temperature dependence of viscosity of Sn-Pb/HDPE composites filled with different volume fractions of Sn-Pb alloy: \square , 35 vol %; \circ , 45 vol %.

the viscosity of the composites. It can be seen that there is an abrupt decrease of viscosity at the melting point of the alloy, indicating that the wetting and movement of the alloy particles become easier by the lower viscosity. In short, the sudden change of the surface energy of the alloy at the melting point provides the possibility of thermodynamics for the break of the conducting pathways,¹⁸ whereas the sharp drop of the viscosity promotes that procedure from the dynamics points of view.

CONCLUSIONS

A new polymer composite thermistor consisting of low-melting-point alloy and semi-crystalline polymer has been fabricated. This kind of thermistor exhibits two PTC transitions, namely d-PTC effect. The location of the first PTC transition is a function of the polymer, whereas the second PTC transition appears at the melting point of the alloy. The PTC transition temperatures increase with the increase of alloy volume fraction for both the first and second PTC transitions. With the increasing volume fraction of the alloy, the first PTC intensity decreases, the second PTC intensity increases and then decreases after the volume fraction reaches 38 vol %, and the total PTC intensity decreases.

For all the composites studied, the resistivity transits to low-resistive state after cooling to about 90°C, indicating that the d-PTC effect is reversible. The more important point is that the d-PTC effect is reproducible, which is important in practical application.

The possible mechanism of the d-PTC effect has also been studied. It is found that the first PTC transition is attributed to the relatively large change in volume expansion of the HDPE at its melting point. However, the origin of the second PTC transition may be the sudden change in the surface energy of the alloy at its melting point

from thermodynamics points of view, and the sharp drop of the viscosity of the composites from dynamics points of view.

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