

# A Novel Low-Melting-Point Alloy-Loaded Polymer Composite. I. Effect of Processing Temperature on the Electrical Properties and Morphology

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**ABSTRACT:** Sn–Pb alloy-loaded polystyrene (PS) composites were processed by powder mixing and hot pressing. For the composites hot-pressed at the temperatures below the melting point of the alloy, the resistivity dropped sharply if the alloy volume fraction reached 20 vol %. When the composites were processed at temperatures above the melting point, such phenomenon disappeared. According to the SEM and energy dispersive analysis X-ray (EDAX) analyses, the size and dispersion of Sn–Pb alloy particles in composites changed when the hot-pressing temperature reached the melting point of the alloy, which resulted in the different forms of resistivity–filler volume fraction curves. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1044–1050, 2000

**Key words:** low-melting-point alloy; processing temperature; electrical property; morphology; dispersion

## INTRODUCTION

Composites with conductive filler powder dispersed in a flexible, insulating polymer matrix have found widespread applications in the electronic industry for many years. The most common applications of these conductive composites include die-attach adhesives, electromagnetic interference (EMI) shielding, electrical heating, and connectors.<sup>1–5</sup> The properties of these composite systems are understood in terms of percolation phenomena (i.e., at a critical volume fraction of conductive filler powder in the insulating polymer matrix, the powder particles form a continuous chain, thereby drastically decreasing the composites resistivity).<sup>6,7</sup> Besides the filler-volume frac-

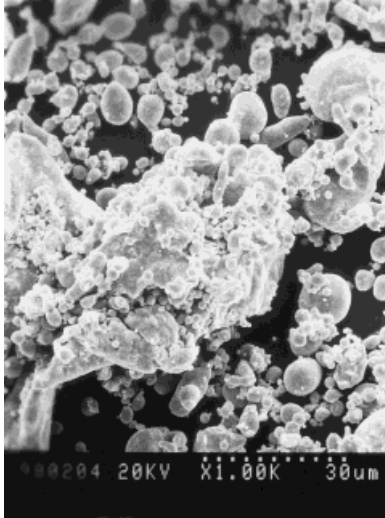
tion, other factors that also affect the electrical properties of the composites are the filler size, sharpness, and structure, among others.

Metal powders, such as iron,<sup>8</sup> aluminum,<sup>8,9</sup> and copper,<sup>10</sup> were mostly used as conductive fillers in conductive polymer composites. However, these fillers suffer from the presence of the oxide layer on their surfaces, which greatly increases the electrical resistivity of the composites. This article presents a new approach to fabrication by mixing and hot-pressing polymer composites with low-melting-point alloy loading. If the hot-pressing temperature is higher than the melting point of the alloy, the alloy melts and the morphology of filler particles changes *in situ* during processing. At the same time, because of the fusing of the alloy particles, the conductive network formed by the filler particles does not have an oxide film between the particles and low resistivity can easily be gained.<sup>11</sup> Upon the filler dispersion, the composite also has many advantages such as low-

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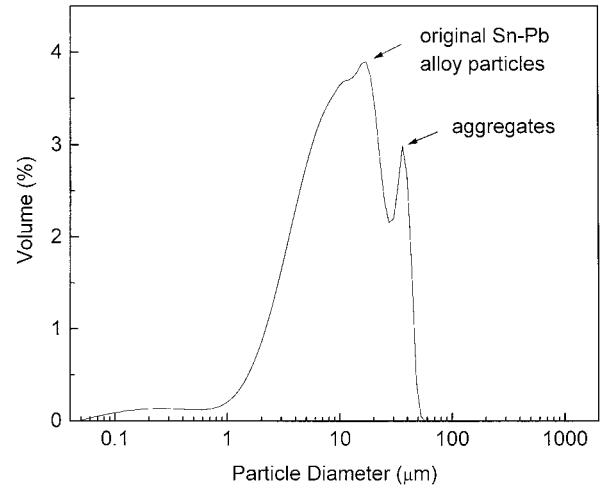
**Figure 1** Powder morphology of Sn-Pb alloy.

room-temperature resistivity and excellent processibility.<sup>12</sup>

As the processing temperature is close to the melting point of the alloy, the effect of processing temperature on the properties of the low-melting-point alloy-loaded polymer composites is drastic. However, little work has been done to study the effect of processing temperature on the electrical properties of these composites, which is the main purpose of this paper.

## EXPERIMENTAL

The low-melting-point alloy powder used in this study was Sn-Pb alloy (60 wt % Sn, 40 wt % Pb) provided by Institute of Powder Metallurgy in Zhongnan Technology University of China (Wuhan City, Hubei Province, China). The melting-temperature range of the alloy is approximately from 183 to 188°C according to phase diagram. The scanning electron micrograph of the alloy powder is presented in Figure 1, which shows that the alloy particles are small and some particles aggregate. The particle-size distribution of the alloy was measured by laser-particle-size analyzer (Coulter LS 230) and is shown in Figure 2. It was found that the mean particle size of the alloy is about 11  $\mu\text{m}$  and the aggregates about 45  $\mu\text{m}$ . The polymer powder used was polystyrene (PS) with a melting index of  $\sim 6$ –10. It was obtained from Yan-Shan Petrochemicals Co. (Shijiazhuang City, Hebei Province, China) and the

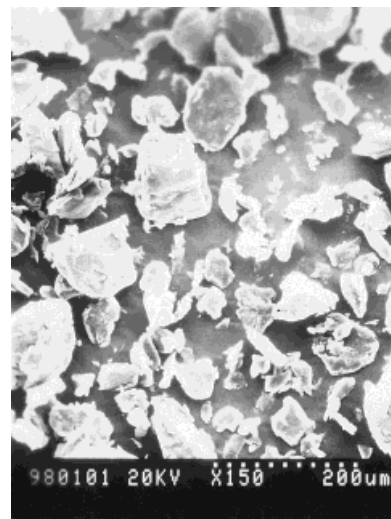


**Figure 2** Particle size distribution of Sn-Pb alloy.

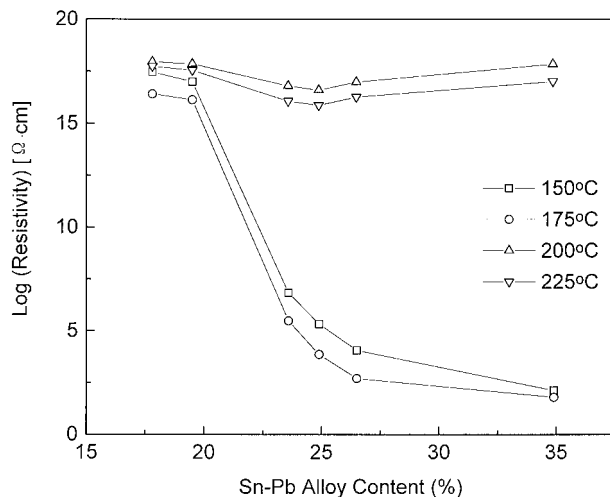
mean particle size is about 60  $\mu\text{m}$  revealed by scanning electron microscope (Fig. 3).

Composites were fabricated by mixing the Sn-Pb alloy powder and PS powder for 11 h at room temperature in a QM-1SP ball mill and then by hot-pressing the mixture in a matched metal die at various processing temperatures for 20 min.

The resistivity data were obtained from samples with a size of 80 mm in diameter and 1 mm in thickness. The resistivity of the samples varied over a wide range from 1 to  $10^{18}$   $\Omega$  cm. High resistivity was measured on a ZC36 high-resistivity meter, while low-resistivity measurement was conducted by using a M890D digital electrometer.



**Figure 3** Powder morphology of PS.



**Figure 4** Resistivity-filler volume fraction plots for Sn–Pb alloy-loaded PS composites processed at various temperatures.

The fracture surfaces of composites were examined under a scanning electron microscope (S-570) after being sputter-coated with platinum, and the Sn element dispersions were detected and imaged by using an energy dispersive analysis X-ray spectrometer (EDAX PV9900).

## RESULTS AND DISCUSSION

### Room-Temperature Resistivity

For the composites processed (hot-pressed) at different temperatures, the room-temperature resistivity is plotted against Sn–Pb volume fraction in Figure 4. It is found that the curves vary dramatically with the processing temperatures. For the composites hot-pressed at temperatures below the melting point of the alloy, such as 150 and 175°C, the resistivity drops sharply at about 20 vol %. At an average fraction of 23 vol %, the composite changes from an insulator to a conductor. This point is usually defined as the critical threshold.

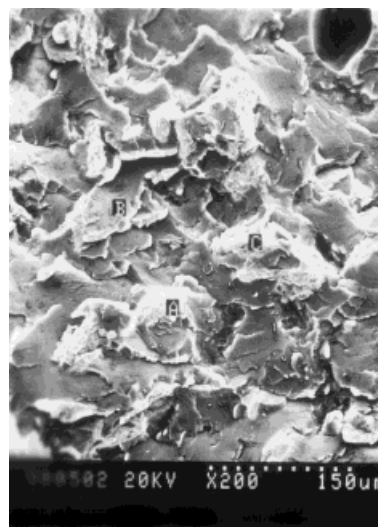
The same phenomenon was also observed for other systems such as carbon-black-loaded polyethylene.<sup>1,4,13</sup> This percolation effect is believed to be due to a sudden change in the dispersion state of conductive particles (i.e., the cluster of particles to form conductive network that facilitate the electrical conduction through the composites).<sup>13</sup> The percolation effect in carbon-black-loaded high-density polyethylene composites was

not found to obviously link with its processing temperature. However, for the Sn–Pb alloy-loaded PS composites processed at 200 or 225°C (i.e., above the melting point), the resistivity varies little, and no percolation effect appears.

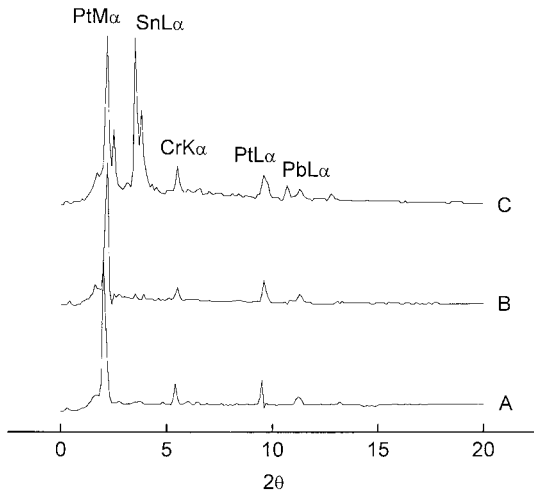
At present, it can be found that the effect of processing temperature on the room-temperature resistivity is drastic.<sup>14</sup> However, there were few studies concerning the effect of processing temperature, and such great influence has never been found before. In the section below, the mechanism on how the processing temperature affects the resistivity will be studied by investigating the morphology and dispersion of the alloy particles in the composites processed at different temperatures.

### Morphology of Alloy Particles in Composites

The morphologies of the fracture surfaces of the composites (23.6 vol % Sn–Pb alloy) processed at 175°C, 14°C lower than the melting point of the alloy, were observed many times, and Figure 5 typically shows the scanning electron micrograph of these composites. The particle size of the alloy in the composites is about 45 μm, which agrees with the size of aggregates of the alloy particles (Figs. 1 and 2) and means that the aggregates are the main form of alloy particles in the composites studied. According to the morphologies, A and C in Figure 5 are believed to be the alloy particle aggregates, and B is a typical area of PS matrix.



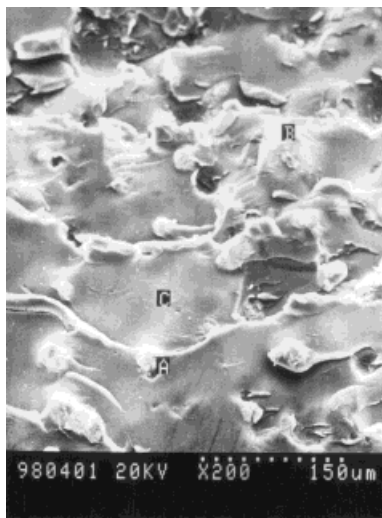
**Figure 5** Scanning electron micrograph for the fracture surface of the composite (23.6 vol % Sn–Pb alloy) processed at 175°C.



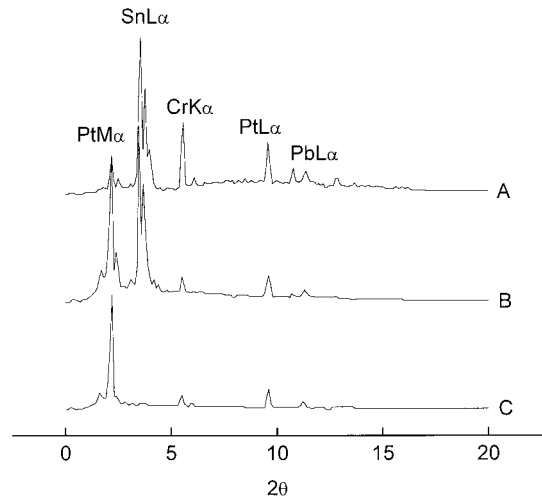
**Figure 6** X-ray microscopical analyses for the point A, B, and C in Fig. 5.

To get more information about the morphology of the composites, the X-ray microscopical analyses of point A, B, and C are shown in Figure 6. Sn and Pb elements were detected on the surface of C, but not detected on A, indicating that PS matrix sometimes adheres, sometimes does not adhere, on alloy-particle aggregates.

The morphologies of the fracture surfaces of the composites processed at 225°C, above the melting point, were observed many times too. It is found that the particle size of the alloy is about 18 μm in many samples. Being different from the composites processed below the melting point, the



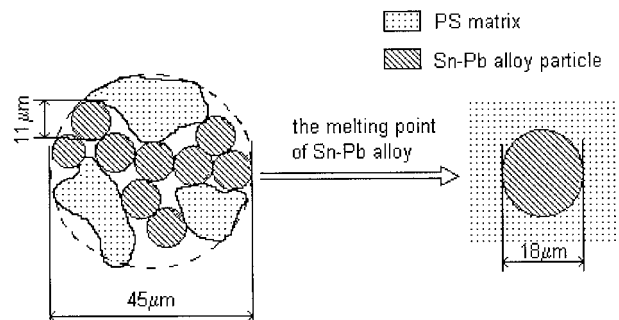
**Figure 7** Scanning electron micrograph for the fracture surface of the composite (23.6 vol % Sn-Pb alloy) processed at 225°C.



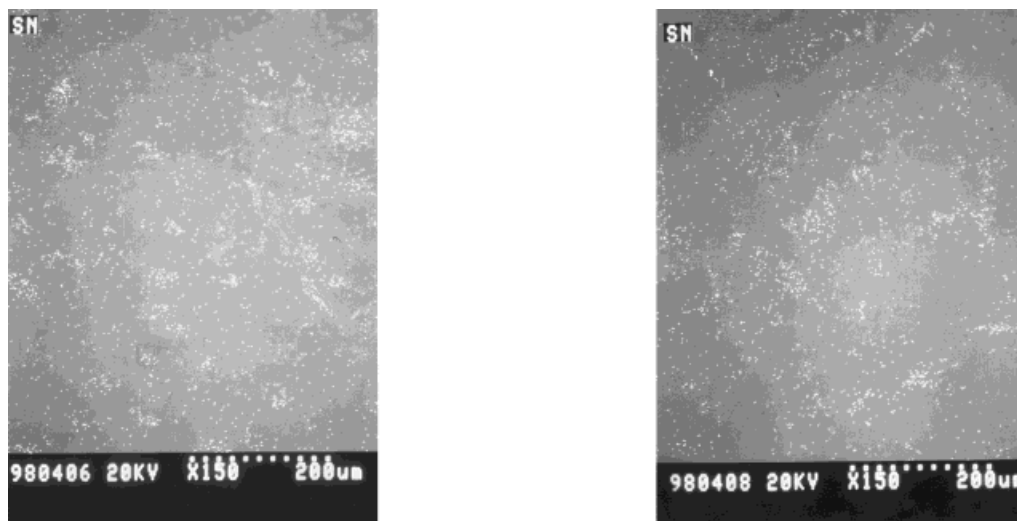
**Figure 8** X-ray microscopical analyses for the point A, B, and C in Fig. 7.

alloy particles in these composites were not found to be coated by PS matrix. Figure 7 is a typical morphology of these composites, in which A and B are the alloy particles (18 μm), and C is PS. Figure 8 shows the X-ray microscopical analyses of point A, B, and C in Figure 7. It can be seen that Sn and Pb elements are detected in both particle A and B, which indicates that little PS matrix adheres on the surface of the alloy particles as compared to the composite processed at the temperature lower than the melting point.

By analyzing the morphologies of the fracture surfaces of composites processed at various temperatures, the evolution of Sn-Pb alloy morphology is suggested in Figure 9. If the composites were processed at the temperature below the melting point of the alloy, the original alloy particles (about 11 μm) aggregate and the aggregates may have some PS particles adhering because of the long-time ball milling. The average size of



**Figure 9** Evolution of Sn-Pb alloy particle morphology in composites.



**Figure 10** Sn X-ray maps for composites (35 vol % Sn–Pb alloy) processed at (a) 225°C, (b) 175°C.

aggregates is about 45  $\mu\text{m}$  (Fig. 5). However, if the composites were processed at the temperature above the melting point, the aggregates of the original particles fuse into relatively larger particles (compared with the original particles) by virtue of the surface tension of the alloy under the action of processing pressure (i.e., the size of conductive particles increases from 11 to 18  $\mu\text{m}$ ) (Fig. 9). At the same time, the surfaces of particles are glossy (compared to the aggregates) and little PS matrix adheres to them (Figs. 7 and 8).

Now, the course of how the processing temperature affects the room-temperature resistivity can be inferred as below. At the temperature above the melting point of the alloy, the alloy aggregates fuse into large particles, which reduce the movement of the particles, and the cluster of particles thus becomes more difficult. As a result, it will be hard for the alloy particles to form the conductive network even at high-alloy volume fraction, and no percolation effect appears.<sup>15</sup>

### Dispersion of Alloy Particles

In the above sections, it is considered that the conductive network can only be easily formed in the composites processed below the melting point of the alloy. To test this inference, the dispersion of alloy particles in the composites were studied. As the particle dispersion in composites can be characterized by the spatial arrangement of particles (point pattern), the digital image analysis

(DIA) developed by Tanaka et al.<sup>16</sup> is applied in our study. The Sn element distribution (X-ray map) of the composites (35 vol % Sn–Pb alloy) processed at various temperatures were first detected and imaged through EDAX (Fig. 10).

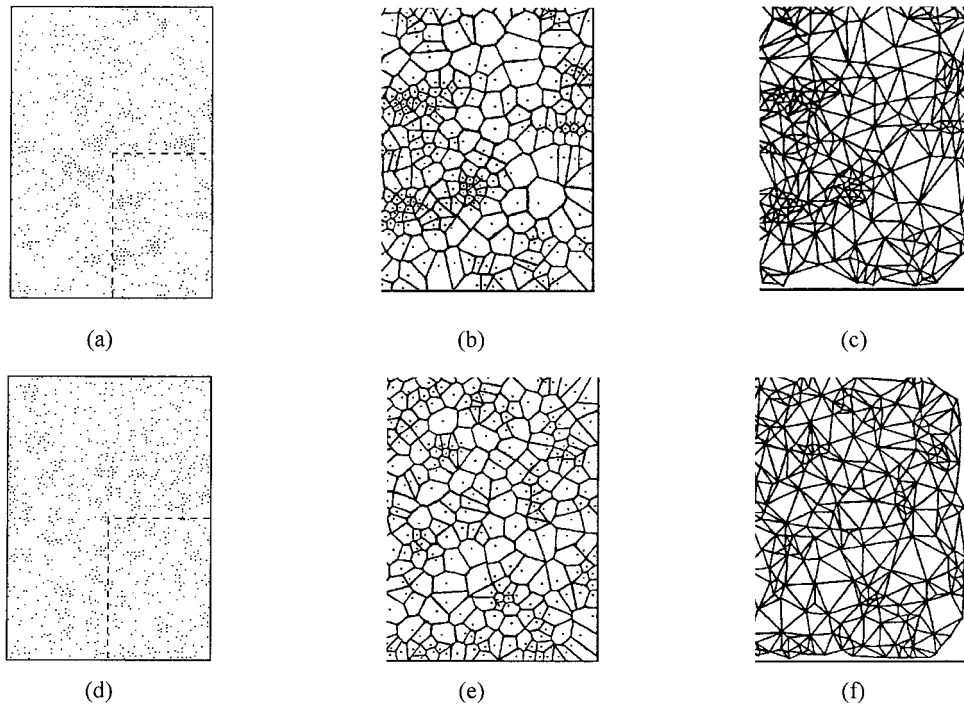
To study the Sn element distribution, these X-ray maps are first converted to the corresponding point patterns [Fig. 11(a,d)]. The corresponding Voronoi polygons and Delauney triangles drawn according to Ref. 16 are also shown in Figure 11 (to make the patterns clearer, only right bottom parts of each patterns are shown). The cluster of points is clearly seen, which is common in the conductive composites.

There are a few kinds of special functions that give us information on the spatial distribution of points.<sup>16</sup> Two of the functions (i.e., the so-called  $p$  function and  $q$  function) are used in our study. The  $p$  function is a cumulative distribution function of the distance between random point and the nearest object  $r_1$ , and it is defined by

$$p(t) = \text{Pr}(r_1 < t) \quad (1)$$

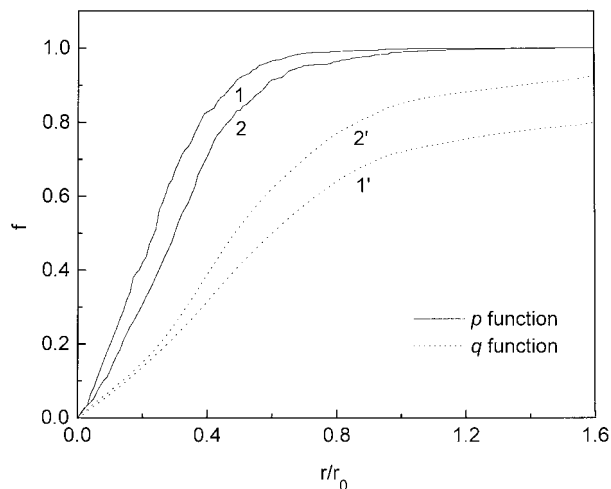
where Pr is the probability. The  $q$  function is a cumulative distribution function of the distance between two nearest neighbor points  $r_2$  and is defined by

$$q(t) = \text{Pr}(r_2 < t) \quad (2)$$



**Figure 11** The point patterns for the composites processed at (a) 175°C, and (d) 225°C, respectively, and the two corresponding Voronoi polygons (b, e) and Delauney triangles (c, f).

The behavior of  $p(t)$  and  $q(t)$  for the pattern is shown in Figure 12, where  $t$  is defined as  $t = r/r_0$ , and  $r_0 = (S/N)^{1/2}$  (where  $S$  is the total area and  $N$  is the number of the points). Both the  $p(t)$  and  $q(t)$  increase with the increasing  $r/r_0$ ; however, the



**Figure 12**  $p$  and  $q$  function for the point pattern of composites processed at (1, 1') 175°C and (2, 2') 225°C, respectively.

increase of the  $p(t)$  is sharp and that of  $q(t)$  is relatively flat, which is characteristic of the aggregated system with many clusters.<sup>16</sup> From Figure 12, it can also be seen that the deviation between the  $p(t)$  and  $q(t)$  for the composite processed at 225°C is less than that processed at 175°C, which means that the Sn element in this situation is less clustered.<sup>16</sup>

Through the study of Sn element distribution, the difference of alloy particle dispersion in the composites processed at various temperatures is known. In the composite processed below the melting point of the alloy, the alloy particles form clusters (see curves 1 and 1' in Fig. 12), which is the essential factor for the establishment of conductive network, and the resistivity is very low. When the processing temperature is higher than the melting point of the alloy, the alloy particles tend to be dispersed more uniformly (see curves 2 and 2' in Fig. 12). As a result, the conductive network is more difficult to be formed, and the resistivity stays very high even at high-alloy volume fraction. Therefore, through the dispersion analyses of the alloy particles, it can be affirmed that the difference of the processing temperature

can determine the formation of the conductive network in the composites studied.

## CONCLUSION

The electrical properties, morphology, and particle dispersion of Sn–Pb alloy-loaded PS were studied with reference to the effect of processing temperature. The resistivity of composites, which were processed at the temperature below the melting point of the alloy, is found to drop sharply at some critical filler content, while such critical threshold disappears when the composites were processed at the temperature above the melting point.

It is observed that the alloy aggregates, which are made up of the original alloy particles, fuse into larger particles when the processing temperature reaches the melting point of the alloy. At the same time, the alloy particles are found to disperse more uniformly and to cluster harder when the composites were processed at the temperature above the melting point. Therefore, the size change of the alloy particles leads to the change of particle dispersion in composites, which results in the break-up of conductive networks and the change of resistivity-filler volume fraction curve.

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