

# Highly Electrically Conductive and Injection Moldable Polymeric Composites

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**ABSTRACT:** Highly electrically conductive polypropylene (PP) composites were prepared by melt mixing using tin-lead (Sn-Pb) alloy as conducting fillers. Two Sn-Pb alloys, Sn-Pb (20/80) and Sn-Pb (40/60), were used for comparison. The effects of Sn-Pb loading and molding temperature on electrical conductivity and mechanical properties of composites were investigated. It was found that both factors had significant effect on electrical conductivity of the final Sn-Pb/PP composite. It was interesting to observe that the

molding temperature could control the formation of long-range conducting paths. The mechanism has been explored through the nonequilibrium phase behavior of Sn-Pb alloy. The influence of Sn-Pb loading on mechanical properties of Sn-Pb/PP composites was also investigated. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2969–2975, 2011

**Key words:** poly(propylene) (PP); composites; injection molding; electrical properties; mechanical properties

## INTRODUCTION

When an electrically conducting material is dispersed in sufficient quantity in a polymeric matrix, an electrically conductive composite may be formed. To prepare a desired conductive composite, many factors such as filler type, particle size and distribution, degree of mixing, polymer matrix, and its crystallinity have to be considered.<sup>1–5</sup> Polymeric composites have been adapted to a variety of applications according to their electrical conductivity and temperature coefficient of resistance. Many studies have been conducted with the intent of reducing the percolation threshold. This approach was successful in developing materials for applications requiring low conductivities, such as antistatic application ( $>10^{-12}$  S·cm<sup>-1</sup>), electrostatic painting ( $>10^{-6}$  S·cm<sup>-1</sup>), and electromagnetic interference shielding ( $>0.1$  S·cm<sup>-1</sup>).<sup>6–8</sup>

Composites with high conductivity ( $>10$  S·cm<sup>-1</sup>) are very useful for applications in conductive circuit elements. To achieve high conductivity, filler contents in those composites have to be much high and greatly exceed percolation thresholds, and in some cases even approach and surpass the critical pigment volume concentration.<sup>1</sup> Various types of thermosetting resins such as epoxies and vinyl esters have been studied as possible materials for making

highly electrically conductive (HEC) composites.<sup>9–13</sup>

It was reported that the bulk conductivity of epoxy composites containing 70% compressed expanded graphite could achieve about 120 S·cm<sup>-1</sup> (Ref. 12). Busick and Wilson reported that the bulk conductivity of vinyl esters composites containing 75% graphite was 85 S·cm<sup>-1</sup> (Ref. 13). A major drawback in using thermosets is the long curing time. Therefore, HEC composites based on thermoplastics like polypropylene (PP), nylon, polyvinylidene fluoride, polyethylene terephthalate, and polyphenylene sulfide have been developed for industrial interests.<sup>6,14–25</sup> These polymeric composites showed high electrical conductivities in the range from 10 to 100 S·cm<sup>-1</sup>. Because of the high loading (usually 50–70 vol %), which resulted in poor flow properties and mechanical properties, most of these HEC polymeric composites typically required compression molding, and injection molding was used with limited success.<sup>14,19,22,23</sup> When compared with compression molding, injection molding is the most promising and cost-effective production method.<sup>26</sup> Therefore, our work is focused on HEC polymeric composites that can be injection molded.

Injection molding requires appropriately low melt viscosity. To reduce the high melt viscosity caused by high filler loading, one kind of fillers is needed, which is liquid with a low melt viscosity at the mixing temperature but is solid with high electrical conductivity at the working temperature. Low-melting-point (LMP) metallic alloys, such as In-Bi, Sn-Pb, Bi-Sn, and Sn-Cu, are potential candidates for this kind of fillers. Sn-Pb (60/40) alloy (60 wt % Sn and 40 wt % Pb)/polymer composites have been reported

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in previous literature, but their electrical conductivity was not high. For example, Sn-Pb/polystyrene composites just had an electrical conductivity of  $0.01 \text{ S}\cdot\text{cm}^{-1}$  with 35 vol % of Sn-Pb (60/40).<sup>27</sup> The electrical conductivity of Sn-Pb/high-density polyethylene composites was  $0.5 \text{ S}\cdot\text{cm}^{-1}$  at a filler loading of 45 vol % Sn-Pb (60/40).<sup>28</sup> The low conductivity was because that those Sn-Pb (60/40) particles were discretely dispersed in the polymeric matrix and could not efficiently form a long-range conducting network. The conductivity of the composites was limited by the high resistance of the polymer present between neighboring alloy particles. To improve the electrical conductivity of LMP metallic alloy/polymer composites to  $10 \text{ S}\cdot\text{cm}^{-1}$  and above for potential applications in the field of electronic elements, an interpenetrating network in composites must be achieved.<sup>29–31</sup> Michaeli and Pfefferkorn reported a novel material combining fiber-filled polymer blends with low-melting metal alloys.<sup>32,33</sup> These alloys had the advantage of being already molten during processing and of not solidifying before the cooling phase, and they serve as the connector in the final interpenetrating network.

In this study, Sn-Pb (40/60) and Sn-Pb (20/80) were used as the conducting fillers, because their melting temperatures range from 183 to 240°C and from 183 to 265°C, respectively, which are within the typical processing temperature window (200–250°C) for PP. This great match has allowed us to use a common molding temperature to prepare highly conductive PP-based composites. We prepared a Sn-Pb/PP binary system to study the nonequilibrium thermodynamics of the formation of interpenetrating networks during injection molding process. The relation between electrical conductivity and phase structures, and the influence of Sn-Pb loading on mechanical properties have been studied in detail. The effect of molding temperature on electrical conductivity was also investigated. It was found that molding temperature was one key to prepare HEC polymeric composites, and its mechanism has been discussed.

## EXPERIMENTAL

### Materials

Polypropylene (PP, MB3020-01) was purchased from Aldrich with a melt index of 4.0 g/10 min (230°C/2.16 kg). Tin-lead (Sn-Pb) (20/80) alloy solder wires with a diameter of 1.2 mm were purchased from Sellery Tools, and Sn-Pb (40/60) solder wires with a diameter of 1.2 mm were purchased from RS Components. Both of them were cut into small pieces with a length of about 5 mm and purified by washing with acetone to remove the rosin core.

**TABLE I**  
Injection Molding Conditions of Sn-Pb/PP Composites

|                          |     |
|--------------------------|-----|
| Melt temperature (°C)    | 250 |
| Mold temperature (°C)    | 70  |
| Injection pressure (MPa) | 850 |
| Injection duration (s)   | 10  |
| Post pressure (MPa)      | 300 |
| Post duration (s)        | 10  |

### Preparation of Sn-Pb/PP composites

It is well known that temperature strongly affects melt viscosity of a given Sn-Pb alloy, whereas viscosity of a Sn-Pb alloy at a given temperature is dependent on its composition. As two kinds of Sn-Pb alloys have different values of viscosity at a given temperature, two Sn-Pb/PP composites cannot be prepared at the same temperature, which has been known from our preliminary experiments on melt mixing (the results are not included in this article). For example, Sn-Pb (20/80) is unable to flow even through it is partly melted at 190°C. Thus, we chose 220°C to prepare the Sn-Pb (20/80)/PP composites. On the other hand, the viscosity of Sn-Pb (40/60) is too low at 220°C to be mixed well with PP, so that we chose 190°C to mix Sn-Pb (40/60) with PP. In summary, the Sn-Pb (20/80)/PP composites were prepared by melt mixing at 220°C in a HAAKE MiniLab (Thermo Scientific) at a screw speed of 80 rpm. The Sn-Pb (40/60)/PP composites were prepared at 190°C at the same screw speed.

Injection molding was performed on a HAAKE mini-Jet (Thermo Scientific), and the injection molding conditions are shown in Table I. The recipes of Sn-Pb/PP composites are shown in Table II, where the ratio of final Sn-Pb/PP composites was calculated from their density after injection molding. Furthermore, to study the effect of molding temperature on electrical conductivity of PP40-3, three different molding temperatures (namely, 190, 210, and 250°C) were used. The rest of the injection molding conditions were the same for all samples.

### Characterization

The densities of PP, alloys, and composites were measured on an electronic balance (Precisa Balances, Precisa 180A) using the buoyancy method with ethanol as the vehicle at 25°C. The volume electrical conductivity was acquired using a digital multimeter (Fluke, Fluke 110). The sizes of rectangular samples were 35.0 mm × 5.0 mm × 1.7 mm with both ends coated with the silver conducting adhesive. The size of dumbbell-shaped specimens (a) was designed according to the ASTM D 638 test method, and the rectangular specimen for flexural test (b) had a size of 35.0 mm × 5.0 mm × 1.7 mm. Mechanical tests

**TABLE II**  
**Formulation and Physical Properties of Sn-Pb/PP Composites Molded at 250°C**

| Samples    | Feeding ratio<br>(PP/Sn-Pb:V/V) | PP/Sn-Pb     |              | Density<br>(g·cm <sup>-3</sup> ) | Electrical<br>conductivity (S·cm <sup>-1</sup> ) |
|------------|---------------------------------|--------------|--------------|----------------------------------|--|
|            |                                 | Weight ratio | Volume ratio |                                  |  |
| PP         | —                               | —            | —            | 0.9                              | (10 <sup>-17</sup> ) <sup>34</sup>               |
| Sn-Pb20/80 | —                               | —            | —            | 10.2                             | 1.0 × 10 <sup>5</sup>                            |
| PP20-1     | 92/8                            | 50/50        | 92/8         | 1.7                              | <7.5 × 10 <sup>-7</sup>                          |
| PP20-2     | 84/16                           | 31/69        | 84/16        | 2.3                              | (7.4 ± 1.1) × 10 <sup>-3</sup>                   |
| PP20-3     | 68/32                           | 16/84        | 68/32        | 3.8                              | 53 ± 5   |
| Sn-Pb40/60 | —                               | —            | —            | 9.3                              | 1.0 × 10 <sup>5</sup>                            |
| PP40-1     | 92/8                            | 53/47        | 92/8         | 1.5                              | <7.5 × 10 <sup>-7</sup>                          |
| PP40-2     | 84/16                           | 36/64        | 85/15        | 2.2                              | <7.5 × 10 <sup>-7</sup>                          |
| PP40-3     | 68/32                           | 19/81        | 70/30        | 3.3                              | 4.2 ± 0.9  |

were carried out on an Instron universal testing machine (INSTRON 5569) at room temperature. The test speeds were 50 and 1 mm/min for tensile and flexural tests (three-point flexure fixture with a support span of 32 mm), respectively. The fractured surfaces of the rectangular specimen were coated with a thin layer of gold and observed by scanning electron microscopy (SEM, JEOL, JSM-5600LV).

## RESULTS AND DISCUSSION

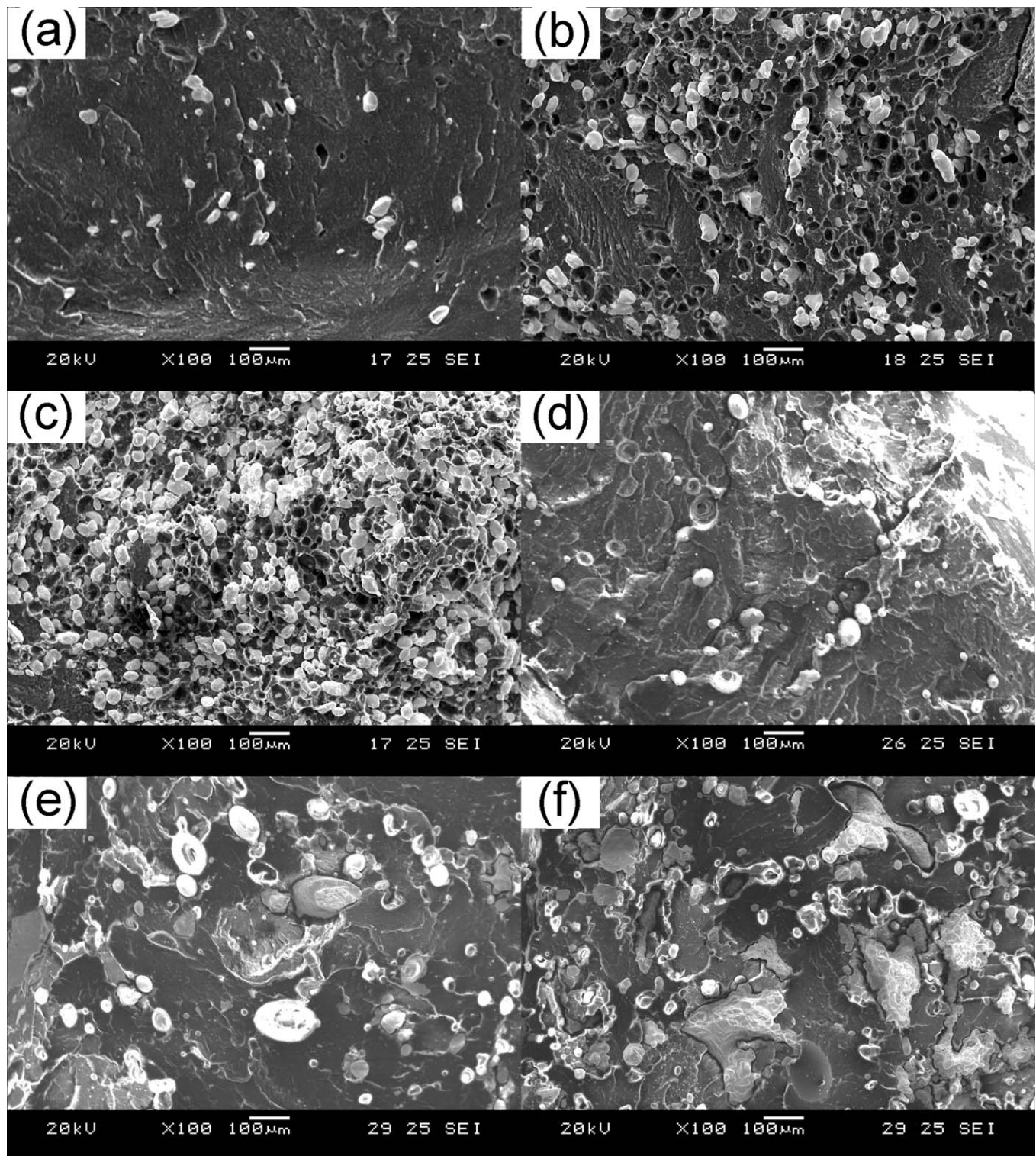
### Electrical conductivity of Sn-Pb/PP composites

The electrical conductivity of Sn-Pb/PP composites molded at 250°C is summarized in Table II. The conductivity of neat PP was around 10<sup>-17</sup> S·cm<sup>-1</sup> (Ref. 34), and the conductivity of PP20-1 was lower than the measurable range of our ohmmeter (7.5 × 10<sup>-7</sup> S·cm<sup>-1</sup>). With increasing the loading of Sn-Pb (20/80), the conductivity increased dramatically. For PP20-2, the conductivity was 7.4 × 10<sup>-3</sup> S·cm<sup>-1</sup>. At 32 vol % Sn-Pb (20/80), the conductivity exceeded 10 S·cm<sup>-1</sup> and reached 53 S·cm<sup>-1</sup>, which was an increase by 18 orders from that of neat PP. The similar dramatic improvement was also observed for Sn-Pb (40/60)/PP composites. The conductivity of PP40-3 achieved 4.2 S·cm<sup>-1</sup>. The conducting mechanism for composites involves the mutual contact of conductive fillers in matrix and the formation of long-range conducting channels. Figure 1 shows phase structures of Sn-Pb/PP composites with various loadings of Sn-Pb. The bright phase in SEM images is the Sn-Pb particles. From Figure 1(a–c), it can be seen that the average size of Sn-Pb particles was around 50 μm, and the density of Sn-Pb particles increased with increasing the loading of Sn-Pb (20/80). Apparently, at the high loading of Sn-Pb, Sn-Pb particles contacted closely with each other and formed a conducting network, which resulted in the dramatic increase in electrical conductivity. For Sn-Pb (40/60)/PP composites, the relation between phase structure and Sn-Pb loading was different from that for Sn-Pb (20/80)/PP composites.

As shown in Figure 1 (d–f), increasing the loading of Sn-Pb (40/60) does not result in increase of the number of Sn-Pb particles, but increase of the average particle size. Because there was no high enough density of Sn-Pb particles to form conducting networks, the electrical conductivity of PP40-3 molded at 250°C was much lower than that of PP20-3.

### Effect of molding temperature on electrical conductivity

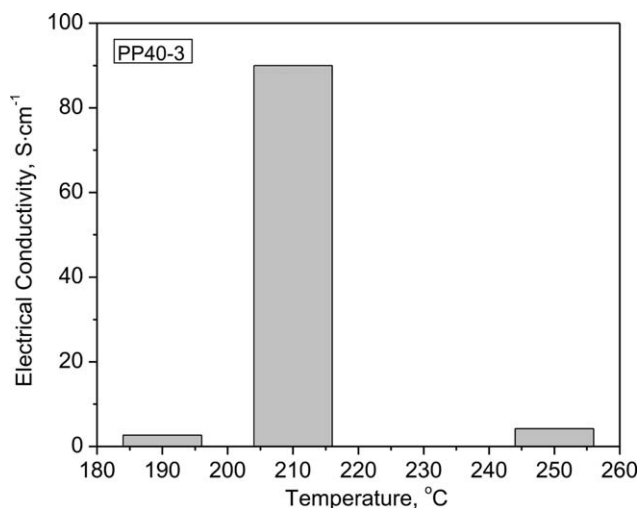
Figure 2 shows the electrical conductivity of PP40-3 molded at three different temperatures: 190, 210, and 250°C. It can be seen that PP40-3 molded at 210°C had the highest conductivity of 90 S·cm<sup>-1</sup> among those three samples, which was even higher than 53 S·cm<sup>-1</sup> of PP20-3 molded at 250°C. It is well known that the formation of long-range conducting paths is the determinant of HEC polymeric composites. From SEM images of PP40-3 as melting mixed and PP40-3 molded at three different temperatures (Fig. 3), it can be observed that there were differences in phase structures between before and after injection molding. Sn-Pb particles of PP40-3 molded at 190 and 250°C remained discretely dispersed in matrix, and there was no much formation of long-range conducting paths. For PP40-3 molded at 210°C, the particles of Sn-Pb formed a continuous network, which contributed to the higher electrical conductivity. This result may indicate that during injection molding, the alloy particles coalesced because of phase separation. If there is a gradient in cooling rate between the surface and the core of a specimen, the particle coalescence by phase separation can be different from the surface to the core, resulting in a difference in electrical conductivity between them. In our study, however, we did not observe a significant difference in morphology between the surface and the core for specimens, because of the small size of injection-molded specimens, which was unable to lead to a considerable difference in cooling rate between the surface and the core.



**Figure 1** SEM images of Sn-Pb/PP composites molded at 250°C: (a) PP20-1, (b) PP20-2, (c) PP20-3, (d) PP40-1, (e) PP40-2, and (f) PP40-3.

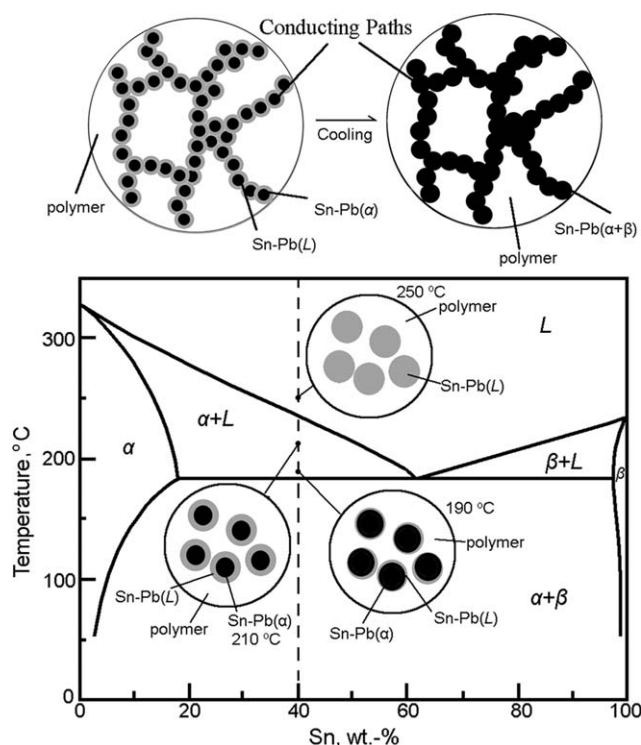
This indicated that the molding temperature has a significant effect on the phase structure. A schematic mechanism is proposed in Figure 4 to explain the formation of different phase structures induced by temperature, where the phase diagram of Sn-Pb alloy is shown for comparison.

From the phase diagram of Sn-Pb alloy, it can be known that the fraction of liquid phase for Sn-Pb (40/60) increased from 50 to 65.5% with increasing temperature from 190 to 210°C, and the alloy became completely liquid at 250°C. The viscosity of Sn-Pb particles decreased with increasing the



**Figure 2** Electrical conductivity of PP40-3 obtained at three molding temperatures.

fraction of liquid phase, and this process was a gradual change from solid to liquid in a temperature window, which was the melting range of Sn-Pb particles. Two particles would remain separated or be stuck together when they collided. The shape of the resultant particles depended on the viscosity of each particle. With increasing temperature, they would be discrete particles [as illustrated in Fig. 4(b)], long-range conducting paths formed from stuck particles soldered by the liquid phase [as illustrated in Fig. 4(c)], or even big discrete particles formed by small droplets' merging [as illustrated in Fig. 4(d)]. This mechanism explains why high electrical conductivity could hardly be achieved by adding conductive solid powders (an example of extremely high viscosity) even with a high loading as reported in previous literature.<sup>27,28,35,36</sup> Therefore, to prepare polymeric composites with high electrical conductivity, the conducting filler must be able to partially melt to

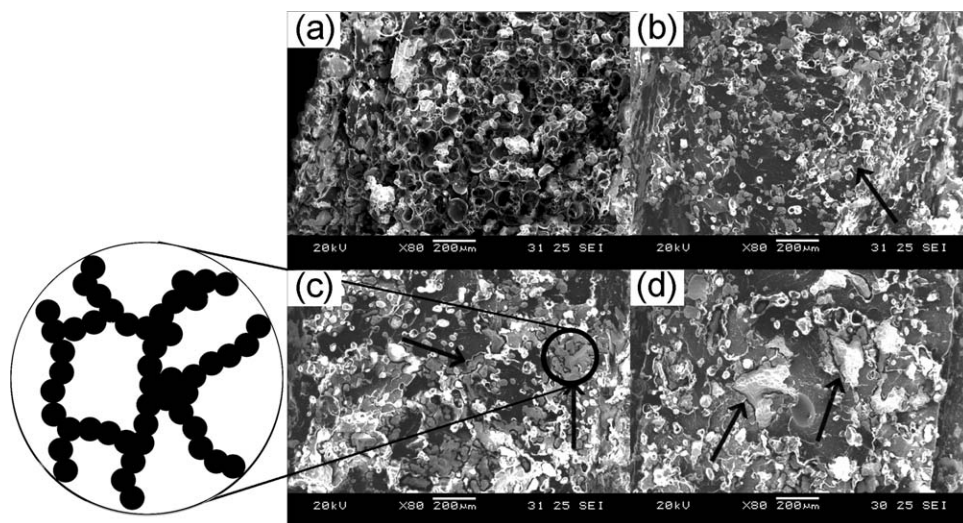


**Figure 4** Formation of a conducting network of Sn-Pb particles soldered by the liquid phase.

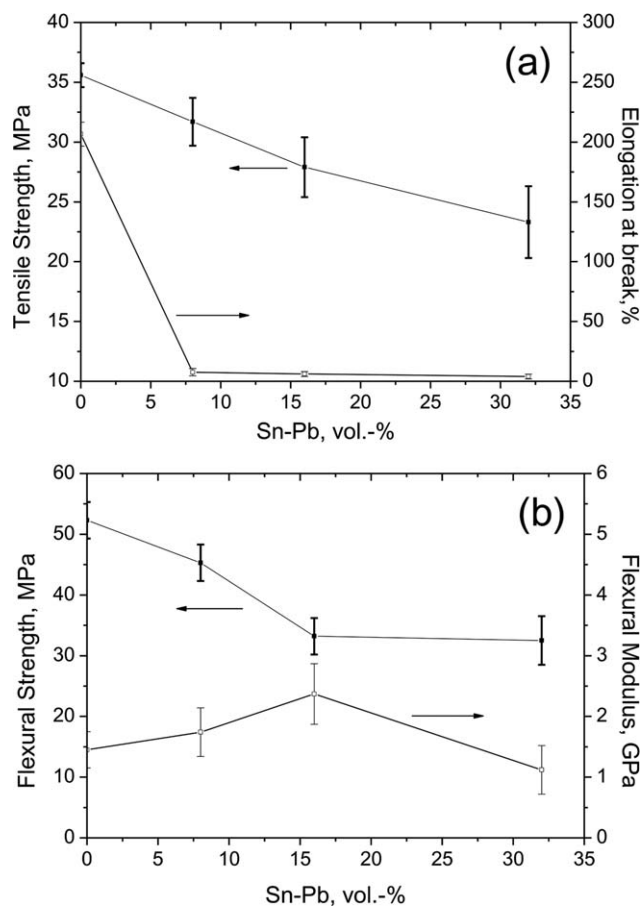
form a stable solid-liquid mixture when mixed with polymers.

**Mechanical properties of Sn-Pb/PP composites**

The influence of Sn-Pb loading on mechanical properties of Sn-Pb(20/80)/PP and Sn-Pb(40/60)/PP is shown in Figures 5 and 6, respectively. It can be seen from Figure 5(a) that the tensile strength and elongation at break of neat PP were 36 MPa and 220%, respectively. With increasing the loading of



**Figure 3** SEM images of PP40-3 as melting mixed (a) and PP40-3 molded at 190°C (b), 210°C (c), and 250°C (d).



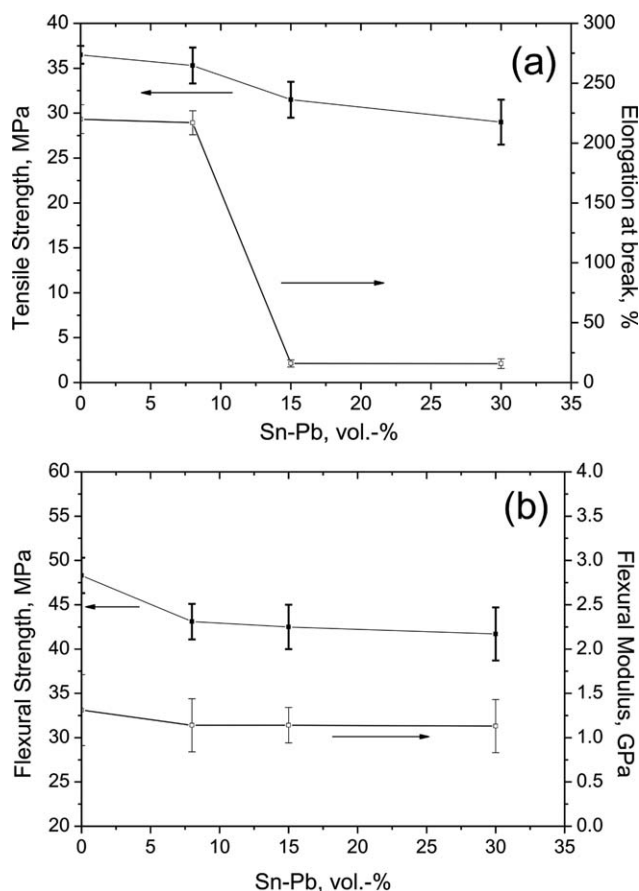
**Figure 5** Mechanical properties of Sn-Pb(20/80)/PP composites as functions of the Sn-Pb content: (a) tensile strength and elongation at break; (b) flexural strength and flexural modulus.

Sn-Pb (20/80), the elongation at break dropped sharply. The tensile strength decreased gradually and reached 23 MPa at 32 vol % of Sn-Pb, dropping by 34.5%. As shown in Figure 5(b), with increasing the loading of Sn-Pb, the flexural strength decreased gradually, dropping 37.9% at 32 vol % of Sn-Pb compared with that of neat PP. The flexural modulus increased and then decreased. For Sn-Pb (40/60)/PP composites, as shown in Figure 6, at the loading of 30 vol %, tensile and flexural strengths dropped by 20.5 and 13.7%, respectively, in comparison with those of neat PP. The decrease in mechanical properties was due to the poor compatibility between PP and Sn-Pb alloys. From Figure 1, it can be observed that there was almost no adherence between two phases, which impaired the mechanical properties of the composites.

## CONCLUSION

An injection moldable metallic alloy/polymer composite with high electrical conductivity was successfully prepared using PP and Sn-Pb alloys by melt

mixing. Two Sn-Pb alloys, Sn-Pb (20/80) and Sn-Pb (40/60), were chosen for comparison. The effects of Sn-Pb loading and molding temperature on electrical conductivity and mechanical properties of composites were studied. With increasing the loading of Sn-Pb, the electrical conductivity increased dramatically. It was confirmed that the molding temperature had a significant effect on electrical conductivity of products, because the viscosity of Sn-Pb was sensitive to the change of temperature in its melting range, and it thus affected the resultant phase structures in composites. The electrical conductivity was  $53 \text{ S}\cdot\text{cm}^{-1}$  for the Sn-Pb/PP composite containing 32 vol % of Sn-Pb (20/80) molded at  $250^\circ\text{C}$ , whereas that was  $90 \text{ S}\cdot\text{cm}^{-1}$  for the Sn-Pb/PP composite with 30 vol % of Sn-Pb (40/60) molded at  $210^\circ\text{C}$ . It was proved that a liquid phase in an appropriate amount could act as a solder to connect neighboring Sn-Pb particles together to form a long-range conducting network. Therefore, to prepare polymeric composites with high electrical conductivity, the conductive fillers must have a melting range and be able to form a stable solid-liquid mixture when mixed with polymers. Owing to the good flow property of Sn-Pb/PP composites, they



**Figure 6** Mechanical properties of Sn-Pb(40/60)/PP composites as functions of the Sn-Pb content: (a) tensile strength and elongation at break; (b) flexural strength and flexural modulus.

could be easily molded by injection molding. With increasing the loading of Sn-Pb, mechanical properties of Sn-Pb/PP composites became worse because of the poor compatibility between PP and Sn-Pb.

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