

Effect of Nano-fillers on Conductivity of Polyethylene/Low Melting Point Metal Alloy Composites

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Abstract A novel method for preparing conductive polyethylene (PE) composites has been developed. In the method, the powder of low melting point metal alloy (LMPA) is filled into the PE matrix by using twin screw extruder at a temperature below the melting point of the LMPA, and followed by a die drawing process at a temperature around the melting point of the metal alloy. It has been found that die drawing process, repeating the die drawing process and adding nano-fillers, such as montmorillonite (MMT) and multi-wall carbon nanotubes (MWCNTs), all help reduce the metal particle size in the PE matrix, thus improve the conductivity of the composite. The conductivity improvement is attributed to an increased number of the smaller metal particles. Therefore, conductive composites of polymer/metal alloy/nano-filler with high conductivity are possible to be prepared by using the new method.

Keywords: Conductive composites; Nano-filler; Metal alloy.

INTRODUCTION

Conductive polymer composites can be applied to many fields, such as heating elements, antistatic layers, electronic equipment^[1], electromagnetic interference (EMI) shielding^[2, 3], and sensing components^[4–6] because of their distinct properties, such as light weight, easy manufacturing and better chemical resistance; therefore, conductive polymer composites have attracted increasing interest over the last few decades. However polymers are usually very poor electrical conductors, with a resistivity of around 10^{15} Ω -cm. Consequently, conductive ingredients such as carbon blacks, carbon nanotubes, carbon fibers, metal particles or conductive polymers, are required as conductive fillers to improve the polymer's conductivity^[7–11]. Low melting point metal alloy (LMPA) powder is one of the best conductive fillers for achieving conductive polymer composites^[12–15]. However, it is difficult to add more than 2 vol% metal alloy into the polymer matrix because the melted metal alloy tends to coalesce during blending with the polymer^[16]. A possible approach to make polymer/metal alloy composites with high conductivity at low metal content is to reduce LMPA particle size. We have developed a die drawing processing method to reduce the metal particle size, by which ultra-fine metal particles or fibers are prepared^[17]. However, the obtained metal particle size was still not small enough for preparing polymer composites with high conductivity.

In this paper, a novel method for preparing conductive polymer composites through a modified die drawing process is introduced. Coates has described die drawing process in detail^[18]. The modified die drawing process can reduce the LMPA particle size in the polymer matrix effectively, and thus PE composites with better conductivity can be prepared accordingly.

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EXPERIMENTAL

Materials

Linear low density polyethylene (LLDPE) (7042) (melting point 121 °C, $\rho = 0.92 \text{ g/cm}^3$) was provided by SINOPEC Maoming PetroChem., China; Sn-Pb-Ag alloy powder (62.8 mass% Tin, 36.8 mass% lead and 0.4 mass% silver, melting point = 180 °C, $\rho = 8.8 \text{ g/cm}^3$) with a diameter of 24–45 μm was purchased from Beijing Sanhedingxin Gaoxinjishu Co., Ltd.; Multi-wall carbon nanotubes (MWCNTs, FloTubeTM 9000, $\rho = 1.75 \text{ g/cm}^3$) was purchased from CNano Technology Ltd.; and montmorillonite (MMT, Nanomer® I.44PSS, $\rho = 1.7 \text{ g/mL}$) was purchased from Nanocor Inc.

Sample Preparation

Figure 1 shows schematically the equipment and process used in this study. A HAAKE PolyLab co-rotating twin-screw extruder was used as the blending equipment, and a device composed of an electric motor and a roller was made by ourselves for die drawing process. The Sn-Pb-Ag alloy powder, LLDPE and nano-filler (MMT or MWCNTs) were melt blended by the twin-screw extruder and followed by die drawing process. The barrel temperature of the extruder was set at $T_1 = 150 \text{ °C}$, $T_2 = 160 \text{ °C}$, $T_3 = 170 \text{ °C}$, $T_4 = 175 \text{ °C}$, $T_5 = 175 \text{ °C}$, which were below the melting point of the metal alloy, and the die temperature was set at 180 °C, which was around the melting point of the metal alloy. It is important that the metal alloy particles remain in solid state in the barrel and begin to melt in the die, where the melted composite was drawn into filament at a speed of 160 m/min. The metal alloy particles deformed and broke into smaller particles while the composite was drawn in the die. Then the filaments were cut into pieces and the polyethylene composite samples were prepared by melt-compressing under 5 MPa for 5 min at 150 °C followed by cold-compressing under 5 MPa for 5 min at 20 °C. After measurement, the PE composite sample was further cut into pieces and extruded again, followed by the die drawing process under the same condition mentioned above. The die drawing process was repeated, up to seven times in this study. The volume fraction of LMPA, MWCNTs and MMT was 2.5 vol%, 0.05 vol% and 0.52 vol% respectively.

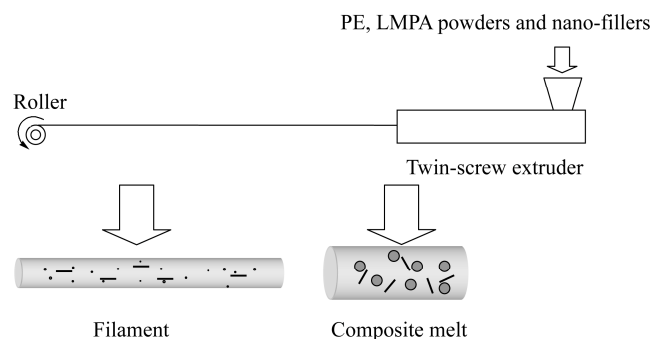


Fig. 1 Schematic illustration of the fabrication process of the composite filaments

Testing and Characterization

The scanning electron microscope (SEM) images of the composites were obtained on a SEI SL-30 scanning electron microscope with field emission gun, and the samples were imaged with a 5 kV accelerating voltage in high vacuum mode. The transmission electron microscope (TEM) image of PE/LMPA/MMT composites was obtained by using a Philips TECNAI 20 transmission electron microscope. Volume resistivity of the composites was measured by using a PC68 Digital Teraohmmeter (Shanghai Precision & Scientific Instrument Co., Ltd) according to the ASTM D257-2007.

RESULTS AND DISCUSSION

Figure 2 demonstrates die drawing, repetition of die drawing, addition of nano-filler and type of the filler all help reduce the volume resistivity, thus improve the conductivity of the composite. The improvement is caused by the

more and finer metal particles resulting from the above mentioned factors, as shown in Figs. 3, 4, and 5, which makes the distance among metal particles much smaller for better conductivity.

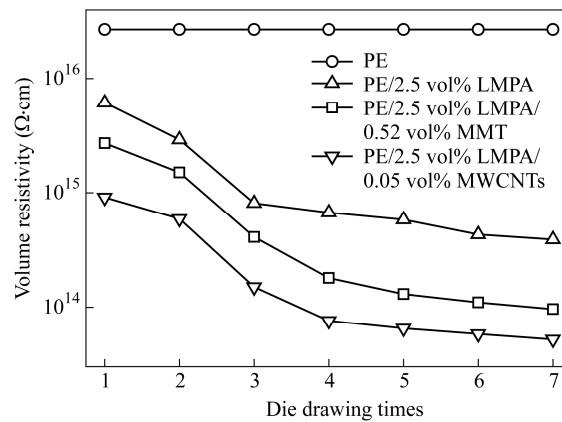


Fig. 2 The relationships of volume resistivity of PE composites with corresponding die drawing times

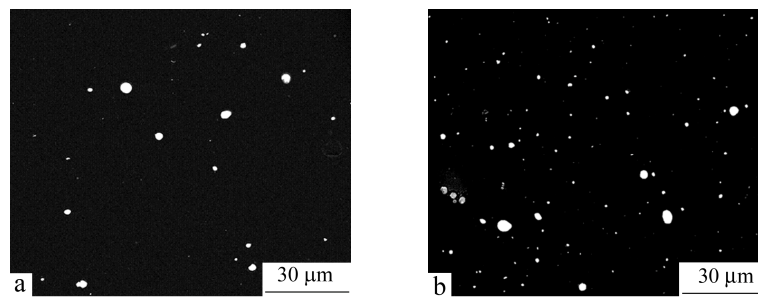


Fig. 3 SEM images of LLDPE/LMPA composites after die drawing process once (a) and 7 times (b)

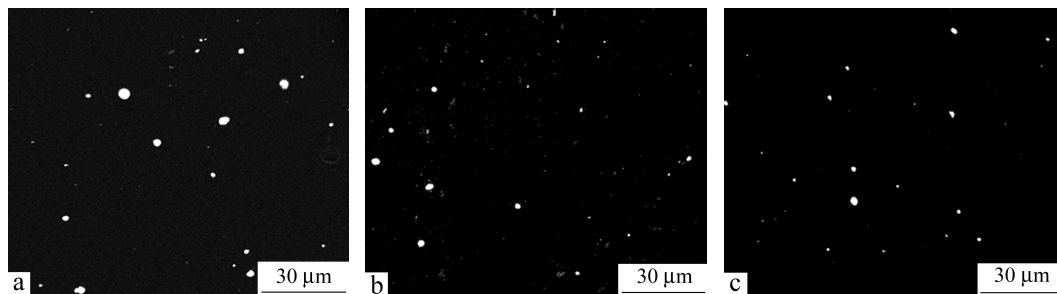


Fig. 4 SEM images of PE composites obtained by die drawing process once: (a) PE/LMPA composite, (b) PE/LMPA/MMT composite and (c) PE/LMPA/MWCNTs composite

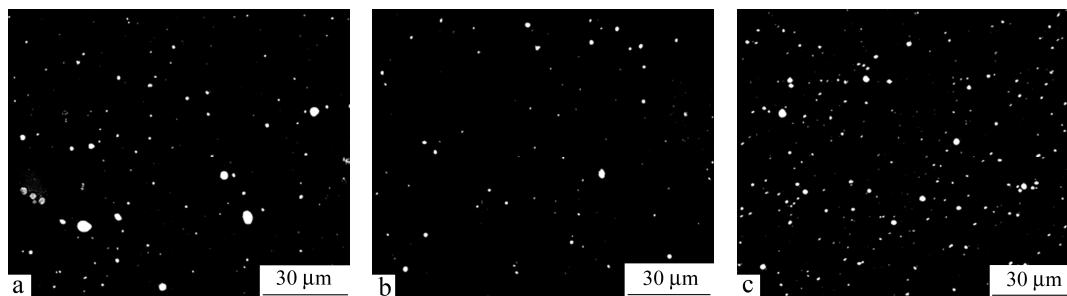


Fig. 5 SEM images of PE composites obtained by die drawing process 7 times: (a) PE/LMPA composite, (b) PE/LMPA/MMT composite and (c) PE/LMPA/MWCNTs composite

Die Drawing and Die Drawing Times

It can be seen from Fig. 3 that the metal particle size is reduced from 24–45 μm to several micrometers after die drawing once, and reduced further after die drawing 7 times. It can also be seen that much more ultra-fine metal particles are produced in the PE matrix after the die drawing process was performed 7 times, when compared with only one die drawing. Figure 2 confirms that the conductivity of the composite improves with the number of die drawing times, but the improvement gets inconspicuous after 4 times of repetition.

Addition of Nano-fillers

Figures 4 and 5 show that adding a small amount of nano-filler can reduce the metal particle size further during the die drawing process. Also, much more small fine metal particles are produced in the PE matrix after die drawing 7 times. Apparently, metal alloy particles break up during the die drawing process and the nano-filler, MMT or MWCNT, has assisted the breakup of the metal alloy particles during the process. As a result, the conductivity of the composite is improved by the nano-filler, either the conductive MWCNT or the non-conductive MMT, as shown in Fig. 2.

It is interesting that a small amount of nano-filler can help break up the metal alloy particles during the die drawing process. A possible reason is that the nano-filler, MWCNT or MMT, has much better affinity to the metal particles than the nonpolar, inert PE macromolecules. The metal particles are more likely to couple with MMT or MWCNT lamella, which increase the specific area of the metal particles. Such complex structure can also hinder the coalescence of the melted metal particles during the die drawing process. The TEM image of PE/LMPA/MMT composite in Fig. 6 well support this hypothesis. It is found from the TEM picture that some of MMT nano sheets are adsorbed onto the metal particles, which separate the particles from each other and makes the metal particle coalescence difficult during the die drawing process.

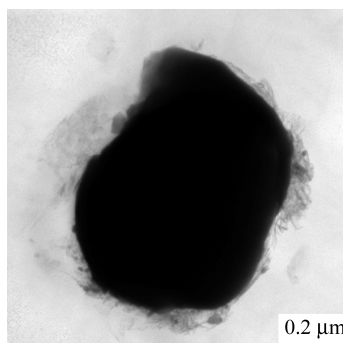


Fig. 6 TEM image of PE/LMPA/MMT composite

Type of Nano-filler

Although adding a small amount of nano-filler, either MWCNT or MMT, improves the conductivity of the composite, however, 0.05 vol% MWCNT is more efficient than 0.52 vol% MMT, as shown in Fig. 2. According to Fig. 2, MWCNT, which is conductive, can not only help break up the metal particles during the die drawing process, but also bridge the metal particles to form better conductive paths.

CONCLUSIONS

PE/LMPA/Nano-filler composites with higher conductivity compared with PE/LMPA composites can be prepared by the modified die drawing process. The higher conductivity of the composite attributes to the increased number of smaller metal particles in PE matrix achieved by the repetition of the die drawing process and the addition of a small amount of nano-filler. While the die drawing breaks the metal particles, the nano-filler helps the breakup, and a conductive nano-filler such as MWCNT additionally improves the conductivity by bridging the metal particles to form better conductive paths.

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