Polym. Bull. (2011) 67:1105–1110
DOI 10.1007/s00289-011-0538-4

ORIGINAL PAPER

# Enhancing the electrical and thermal stability of metallic fiber-filled polymer composites by adding tin–lead alloy

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Received: 11 April 2011 / Accepted: 30 May 2011 / Published online: 5 June 2011


**Abstract** This article presents a novel way of greatly enhancing the electrical and thermal stability of copper fiber (CuF)-filled acrylonitrile–butadiene–styrene (ABS) composites via the incorporation of small amount of tin–lead (Sn–Pb) alloy. It was observed that many fibers are soldered together by Sn–Pb, and a continuous CuF/Sn–Pb network is formed throughout the ABS matrix. As a result, the percolation concentration of ABS/CuF composite containing 1 vol% Sn–Pb is lower than for ABS/CuF composite, and the addition of Sn–Pb to the ABS composites containing 5 vol% CuF leads to a further decrease of electrical resistivity compared to ABS/CuF composites with corresponding filler contents. Furthermore, the electrical resistivity of ABS/CuF/Sn–Pb composite shows no temperature dependence, and remains constant during the thermal post-treatment.

**Keywords** Copper fiber · Electrical properties · Networks · Polymeric composites

## Introduction

With the rapid development of electrical industry, electromagnetic interference (EMI) has become a serious problem in modern society [1]. Considerable attention has been paid in recent years to the development of effective EMI shielding materials for their potential applications. In particular, polymer composites containing conductive fillers have been extensively investigated for use as EMI shielding owing to their unique combination of electrical conduction and polymeric flexibility [2–4]. Actually, the EMI shielding effectiveness is closely related to

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conductivity of the materials [5], and the addition of fibrous fillers generally provides a desired property at a low loading due to their high aspect ratio [6]. However, the electrical conductivity of those products is relatively low due to the separation of the conductive particles by thin interlayers [7, 8]. The contact resistance, $R_c$, which is determined either by the resistance of direct contact or by the properties of interparticle interlayer (which may be a polymer or an oxide film), is several orders of magnitude larger than for the pure fillers resistance [9].

In our previous study, we have already reported [10, 11] a self-assembled carbon nanofiber (CNF)/polyethylene (PE) network throughout the poly(methyl methacrylate) (PMMA) matrix where the PE domains are preferentially absorbed at the ends of the CNF filaments. With addition of 5 wt% PE, the percolation concentration of CNF/PMMA composites was reduced remarkably from 8.0 to 1.5 phr due to the architecture of the conductive scaffold. Interestingly, a further enhancement of electrical property can be expected if the solder (i.e., PE) is electrical conductive.

This study aimed to clarify influence of the incorporation of the second filler (tin–lead alloy, Sn–Pb) on the electrical property of copper fiber (CuF)-filled acrylonitrile–butadiene–styrene (ABS) composites. Due to the good solderability of copper, the fibers were soldered together by Sn–Pb and a continuous CuF/Sn–Pb network was formed throughout the ABS matrix. The preferential absorption of Sn–Pb indeed eliminated the contact resistance in those junction points and increased the uninterrupted length of the conductive paths, which led to a further increase of the electrical conductivity and EMI shielding effectiveness of the final products. The thermal stability and temperature dependence of electrical property of ABS/CuF/Sn–Pb composites were also studied.

## Experimental part

### Sample preparation

The ABS (HI-140, LG Yongxing Chemical Co.) was dried at 80 °C for 24 h under vacuum oven before using. CuF (average length 5 mm, diameter 30 μm, Chuntian Metal Wire-mesh Co.) and Sn–Pb alloy powders (63 wt% Sn, 37 wt% Pb, diameter 25–45 μm, $T_m = 183$ °C, Beijing Compo Advanced Technology Co.) were used as received. ABS was first mixed in a two-roll mill at 185 °C for 2 min, followed by addition of the CuF and mixed for 3 min, and then Sn–Pb was added and mixed for 5 min. The procedure of binary ABS/CuF or ABS/Sn–Pb composites was similar by increasing the mixing time of ABS. The mixtures were compression molded at 220 °C for 10 min under the pressure of 10 MPa.

### Characterization

Due to the extremely high electrical conductivity of the composites in this study, electrical resistivity was measured using a four-terminal technique. At least three specimens for each composition were tested.

A scanning electron microscope (SEM) (JSM-6360, JEOL) was used to observe the morphology of the CuF/Sn–Pb network at an accelerating voltage of 15 kV. The molded composite was etched with tetrahydrofuran (THF) to dissolve the ABS phase.

The melting behavior of Sn–Pb and CuF/Sn–Pb network (ABS matrix was extracted) were studied using differential scanning calorimetry (DSC) (PC200, Netzsch). The samples were heated from 20 to 220 °C at a rate of 10 °C $min^{-1}$.

The EMI shielding effectiveness of the composites was measured according to the ASTM D4935 standard for planar materials. For each composites studied, a minimum of two specimens were tested over a frequency range of 0.1–1.5 GHz.

## Results and discussion

Figure 1a shows SEM image of ABS-extracted ABS/CuF/Sn–Pb (90/5/5 in volume fraction) composite. It can be seen that CuF is encapsulated by a thin Sn–Pb layer, and is soldered together at the junction points. As the extraction leaves the sample compact, a continuous CuF/Sn–Pb network is formed throughout the ABS matrix during the compounding and/or compression-molding. From Fig. 1b, one can find that the possible formation of intermetallic compound has no appreciable influence on the melting behavior of Sn–Pb. Therefore, the percentage of Sn–Pb encapsulating on CuF can be determined by the ratio of $\Delta H_f$ to the product of the heat of fusion of pure Sn–Pb and the weight fraction of Sn–Pb to total filler loading. However, the value is low (31%), suggesting that a large amount of Sn–Pb is dispersed in ABS matrix.

Figure 2a shows the dependence of electrical resistivity on the filler content for the ABS/CuF, ABS/Sn–Pb, and ABS/CuF composites containing 1 vol% Sn–Pb. The percolation concentration of ABS/CuF composite (4 vol%) is much lower than for ABS/Sn–Pb composite (18 vol%) due to its high aspect ratio. When two or more conducting fillers (with different aspect ratio, no strong interaction with each other)

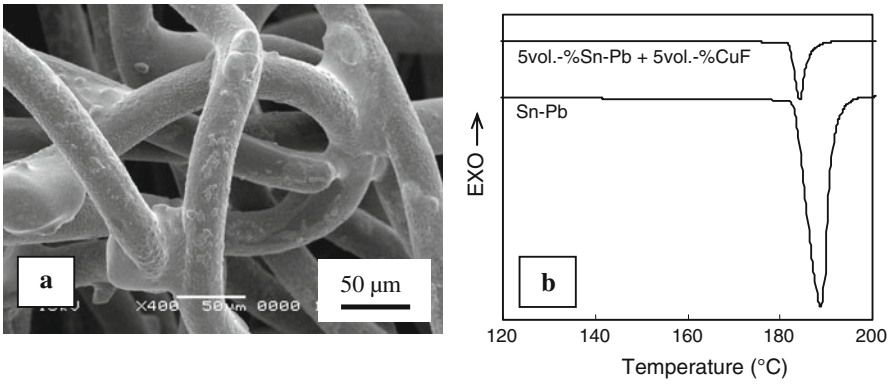


**Fig. 1** SEM image (**a**) and DSC curve (**b**) of ABS-extracted ABS/CuF/Sn–Pb composite contain 5 vol% CuF and 5 vol% Sn–Pb, DSC curve of Sn–Pb is also given for comparison

are incorporated with polymer, the electrical properties of the composites are closely related to the content of the filler with high aspect ratio, a high content of high aspect ratio filler will generally lead to a low electrical resistivity and percolation concentration [12]. However, the percolation concentration of ABS/CuF composites containing 1 vol% Sn–Pb (3 vol%) is lower than for ABS/CuF composites. Furthermore, the addition of Sn–Pb to the ABS composites containing 5 vol% CuF results in a further decrease of electrical resistivity compared to ABS/CuF composites with corresponding filler content as shown in Fig. 2b. This should be ascribed to the formation of the CuF/Sn–Pb network, which can eliminate the contact resistance in those junction points and increase the uninterrupted length of the conductive paths. As a result, the electrical resistivity of ABS/CuF/Sn–Pb (90/5/5 in volume ratio) composite is $2.56 \times 10^{-3}$ Ω cm, which is about one order of magnitude lower than for ABS/CuF composites. It is known that electrical resistivity and EMI shielding effectiveness are related properties, i.e., EMI shielding effectiveness increases with decrease in electrical resistivity. Therefore, a very high EMI shielding effectiveness (56.7 dB is the average shielding value of 2 mm thick plate composite in the 0.1–1.5 GHz frequency range) is achieved for ABS/CuF/Sn–Pb (90/5/5 in volume ratio) composite.

The temperature dependence of electrical resistivity for ABS/CuF (91/9 in volume ratio) and ABS/CuF/Sn–Pb (90/5/5 in volume ratio) composite are shown in Fig. 3a. A positive temperature coefficient (PTC) effect is observed for ABS/CuF composite. However, the electrical resistivity of ABS/CuF/Sn–Pb composite has no significant dependence on temperature. With the increasing temperature, the large difference of coefficient of linear thermal expansion between polymer matrix and filler leads to the increasing of gap thickness (i.e., contact resistance), while the formation of continuous CuF/Sn–Pb network throughout the ABS matrix can retain the conductive paths even when the temperature is above the $T_m$ of Sn–Pb.

Copper powder and fiber are usually used as filler in EMI shielding materials due to the high electrical conductivity and low-cost. However, the serious oxidation on the copper surface inevitably increases the contact resistance, and results in a

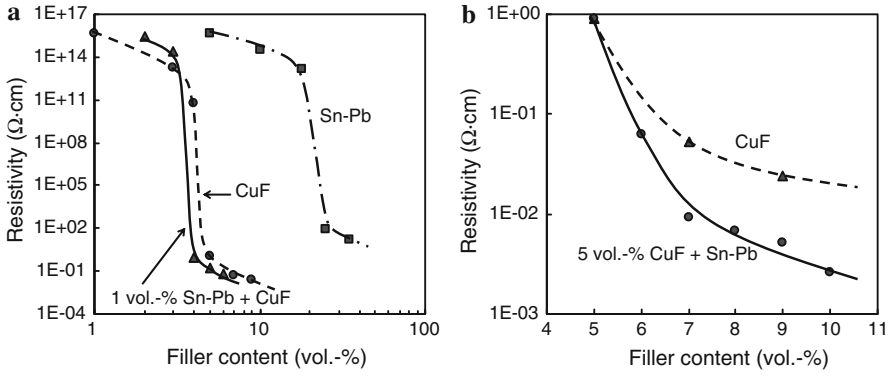


**Fig. 2** Resistivity versus filler loadings for **a** the ABS/CuF, ABS/Sn–Pb, ABS/CuF composites containing 1 vol% Sn–Pb and **b** ABS/CuF, ABS/Sn–Pb composites containing 5 vol% CuF

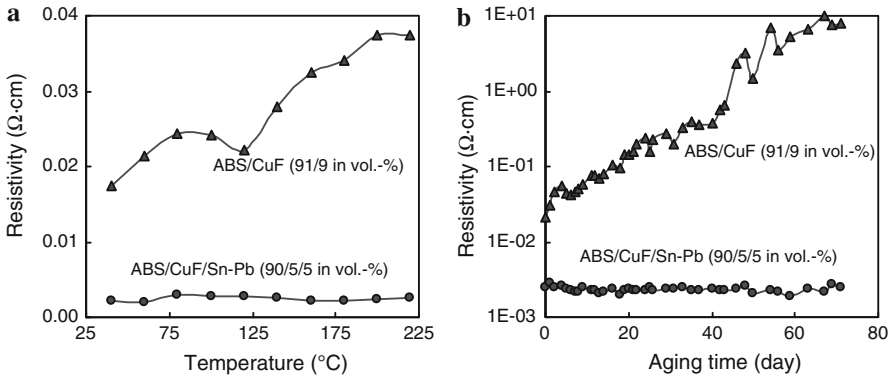


**Fig. 3** Temperature dependence (**a**) and thermal stability (**b**) of electrical resistivity for ABS/CuF (91/9 in volume ratio) composite and ABS/CuF/Sn–Pb (90/5/5 in volume ratio) composite. Samples are kept in air in an oven at 110 °C for aging tests

gradual decrease of EMI shielding effectiveness with time [13]. As shown in Fig. 3b, the electrical resistivity of ABS/CuF (91/9 in volume ratio) composite increases with the prolonging of aging time, and reaches 10 Ω cm after thermal post-treatment for 70 days, which is almost three orders of magnitude larger than the initial one. However, a constant electrical resistivity is observed during the thermal post-treatment for ABS/CuF/Sn–Pb (90/5/5 in volume ratio) composite, suggesting that the contact resistance changes little. This should be ascribed to the formation of the self-welded CuF/Sn–Pb network, preventing the CuF surface from oxidation at the junction points.

## Conclusions

The ABS composites containing various amounts of CuF and/or Sn–Pb were prepared by melt compounding. Morphology observation indicated that CuF is soldered together by Sn–Pb, and a continuous CuF/Sn–Pb network is formed throughout the ABS matrix due to the good solderability between CuF and Sn–Pb. As a result, the percolation concentration of ABS/CuF composites decreases from 4 to 3 vol% by the addition of 1 vol% Sn–Pb, and the addition of Sn–Pb to the ABS composites containing 5 vol% CuF leads to a further decrease of electrical resistivity, which is one order of magnitude lower than for ABS/CuF composites with corresponding filler contents. Therefore, a high EMI shielding effectiveness was achieved for ABS/CuF/Sn–Pb (90/5/5 in volume ratio) composite. Different form the traditional conductive polymer composites, the electrical resistivity of ABS/CuF/Sn–Pb composite showed no temperature dependence. Furthermore, the thermal stability of electrical resistivity for ABS/CuF composite is greatly enhanced by the incorporation of Sn–Pb, which constructs the self-welded CuF/Sn–Pb network and thereby prevents the CuF surface from oxidation at the junction points.

**Acknowledgments** This research was supported by grants from the National Natural Science Foundation of China (50873033, 20974033).

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