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Electrically conductive adhesives based on thermoplastic polyurethane filled with silver flakes and carbon nanotubes

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ABSTRACT

Flexible conductive adhesive could be used in flexible device electronic packaging. In this study, carbon nanotubes (CNTs) were used as one-dimensional conductive scaffolds to construct effective electrical networks among the silver flakes in electrically conductive adhesives (ECAs) for saving noble metal fillers and reducing the cost because CNTs used as conductivity fillers could bridge the neighboring silver flakes to accelerate the electron transport. The electrical, mechanical, and thermal properties have been enhanced after adding CNTs. The electrical conductivity increased 85.6% after 4.5 wt% CNT added into the 50 wt% Ag TPU adhesives. In addition, after the Ag flakes modified by succinic acid (SA), the electrical conductivity has also been improved. The development of highly conductive, flexible, and low cost ECAs will allow them to be widely used in flexible electronic devices packaging in the future.

1. Introduction

The interconnect technology in electronics has been dominated by tin/lead based solders since the very beginning [1–3]. However, as the environmental awareness increased, the tradition tin/lead based solders will be inhibited in electronic packaging gradually by law because they are toxic [4]. ECA as a substitution of tin/lead based solder, consisting of a polymeric resin (epoxy, silicone, or polyimide etc.) and conductivity fillers, has attracted more and more attentions in electronics industry [5]. Compared with solders, ECAs are more environmentally friendly, are easier to process, have lower processing temperatures, and allow for higher resolution printing. However, the high cost of metal fillers is one of the main impediments to the wide use of ECAs in microelectronics. This impeded ECAs as a substitution of Pb-containing solder. Therefore, it is highly desirable to reduce the cost of ECAs while maintaining the electrical conductivity.

Carbon nanotubes (CNTs) [6] have the potential to become the next generation of highly conductive electrical wires [7], with additional benefits of low weight, high mechanical performance [8], high thermal conductivity and low cost. With their unique electrical and physical properties, CNTs are able to lower percolation thresholds in matrix and intrinsic electrical resistivity [9–12]. Moreover, CNTs have very high aspect ratio, which would be optimal materials for connecting metal flakes in ECAs for constructing conductive networks and reducing the cost of ECA by the reduction of metal content. Therefore, CNTs could be one of the most promising fillers for low cost ECAs.

In this study, we used CNTs and Ag flakes as the co-fillers to build conductive networks. Thermoplastic polyurethane (TPU) was applied as matrix due to its superior flexible, processibility, low viscosity and good impact property [13,14]. Before use, Ag flakes were functionalized with SA for partially removing the long chain fatty acid lubrication on the metal flakes [15]. The results show that surface modification of Ag flakes by 0.5 wt% SA solution, the electrical conductivity was increased from 1.3×10^5 S/m to 2.7×10^5 S/m for 50 wt% Ag based ECAs. By using CNTs and Ag flakes as the co-fillers, the electrical conductivity achieved 6.6×10^6 S/m. In addition, by introducing CNTs, Ag filler loading was reduced at least ~5 wt% to achieve 10^5 S/m level conductivity. Moreover, the maximum tensile strength could reach to 13.5 MPa. The development of highly conductive, flexible, and low cost ECAs will allow them to be widely used in flexible electronic devices in the future.

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2. Experimental section

2.1. Materials

TPU granules were supplied by Suzhou Lan Huo Yan Plastics Co., Ltd. Ag flakes (4–6 μm) were donated by Shenzhen Lihongjin Technology Co., Ltd are 1600 dollars per kilogram. *N*,*N*-Dimethylformamide (DMF), SA and Polyvinyl Pyrrolidone (PVP) were purchased from Sinopharm Chemical Reagent Co., Ltd and the molecule weight was ~40,000. All chemicals were analytical grade and used as received without further treatment. Multi-walled CNTs (MWCNTs) were gained from Chengdu Organic Chemical Co. Ltd are 190 dollars per kilogram.

2.2. Fabrication of ECAs

0.5 g SA was dissolved in 95.5 g DMF solution by mechanical stirring for 1 h. Then, Ag flakes were put into SA DMF solution for surface modification then mixing and stirring treatment for 3 h. TPU particles were melted in DMF solution with mechanical stirring for 3 h and then kept overnight to remove air bubbles. CNTs (10 wt %) were dispersed with PVP DMF solution and then sonicated at 200 W for 30 min.

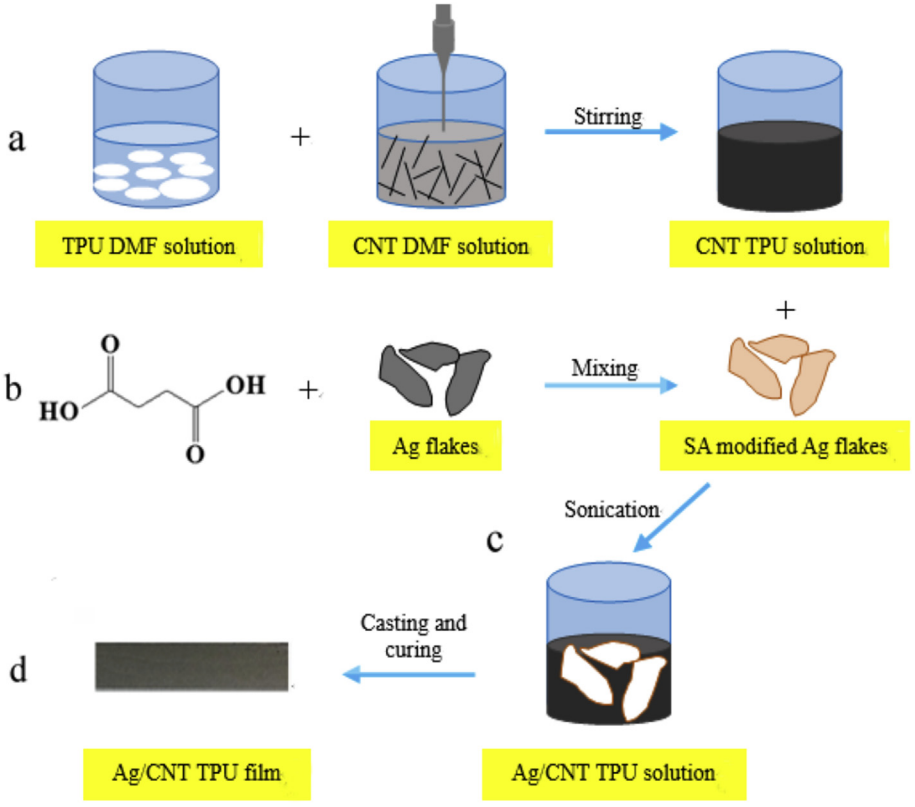
Scheme 1 shows the preparation process of ECAs in this study. Firstly, CNT DMF and TPU DMF solutions were mixed together with a certain ratio. Secondly, Ag flakes modified with SA solution by means of the mixing and stirring method. Thirdly, SA modified Ag flakes were added into the above CNT TPU solution. Finally, the formulated pastes were manually printed on the pre-cleaned glass slides by a small scraper to form stripe of 30 mm × 10 mm and then thermally cured at temperature of 120 °C for 1 h in vacuum oven for preparing CNT/Ag TPU film. The weight ratio of CNT in the pristine CNT DMF and TPU DMF solutions were varied from 0 wt% to 10 wt% (i.e. 0, 1, 3, 6.5, 8, and 10 wt%). The weight ratio of Ag in the composites were varied from 10 wt% to 80 wt% (i.e. 10, 20, 30, 40, 50, 60, 70, and 80 wt%).

2.3. Characterizations

Structure of the CNTs was characterized by transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN). Raman spectra were obtained by using a LabRAM ARAMIS Raman confocal microscope (HORIBA Jobin Yvon) equipped with a 532 nm diode pumped solid state (DPSS) laser. Glass slide was used as a substrate for Raman measurements. Morphologies of the composites and Ag flakes were studied by field emission scanning electron microcopy (SEM, JSM-6390). Electrical conductivity of as-made ECAs was calculated from the bulk resistance of the specimen with specific dimensions. The electrical conductivity ρ was calculated using following equation:

$$\rho = l/(R \cdot S) = l/(R \cdot t \cdot w),$$

Where S, *l*, *w*, and *t* are the cross sectional area, length, width, and thickness of the samples, respectively. After curing, the resistance (*R*) of polymer composite strips were measured by a U-NITUT39A multimeter (0–200 MΩ). The widths and lengths of the specimens were kept constant at 10 mm and 30 mm, respectively. The thickness of the specimen was measured by Heidenhain (thickness measuring equipment, ND 281B, Germany). The change of R/R_0 of as-made composites with the tensile-recycle test was recorded by



Scheme 1. Schematics for the preparation of Ag/CNT based adhesives. (a) CNTs were sonicated in DMF solvent and blended with TPU DMF solution for preparing CNT TPU solution. (b) Ag flakes modified with SA by means of the mixing and stirring method in 0.5 wt% SA DMF solution. (c) Ag/CNT TPU solution were prepared by sonicating SA modified silver flakes in Ag/CNT TPU solution (200 W for 10 min). (d) Hybrid Ag/CNT TPU film was finally obtained by drop casting and curing on the pre-cleaned glass.