Highly thermal conductive and electrically insulating polymer composites based on polydopamine-coated copper nanowire

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ABSTRACT

Thermally conductive but electrically insulating polymer composites are highly desired for thermal management applications because of their ease of processing, light weight, and low cost. Copper nanowires (CuNWs), due to their inherent thermal conductivity and high aspect ratio, hold great potential in thermal management applications. However, CuNW-based polymer composites usually suffer from the deterioration of electrical insulating property. Therefore, it is critically required to reduce significantly the electrical conductivity of CuNW-based composites. In this study, highly thermally conductive but electrically insulating epoxy nanocomposites were prepared by incorporating polydopamine-coated CuNWs. At the volume fraction of 3.1% of CuNW, the thermal conductivity of the nanocomposites reached $2.87 \, \mathrm{W \, m^{-1} \, K^{-1}}$, 14 times higher than pristine epoxy, while the electric resistivity remained to be greater than $10^{14} \, \Omega \, \mathrm{cm}$. These highly thermal conductive and electrically insulating nanocomposites are promising for applications in thermal management.

1. Introduction

With rapid development of electronic integration technologies and the increased power densities in modern electronics, heat dissipation performance of electronic devices has become a critical factor that affects their service life and ensures their normal operation with high reliability [1–4]. In order to remove heat rapidly, thermal interface materials (TIMs) with high thermal conductivity are generally applied between the two mating surfaces to provide good heat conduction path [5,6]. Thermally conductive polymeric composites, due to their ease of processing, light weight, and low cost, hold great potential as thermal management materials [7,8]. In many cases, the insulating property of thermal management materials is also critically important because they play a role of electrical insulators [9,10]. A typical example is light-emitting diodes (LED) where electrical insulation is required.

In fact, many works have been done to develop novel composites with high thermal conductivity and improved electrical insulation. For example, Zha et el [11]. constructed double-percolated thermal conductive networks to reduce the concentration of nanoparticles and fabricated the BNNSs/SEBS/PP nanocomposites with high thermal conductivity and excellent electrical insulation. Tian et el [12]. fixed

NH$_2$-functionalized graphene (NfG) sheets on the surface of h-BN via π-π interaction to prevent the directly contacting of NfG with each other to form the electric conductive pathway in the polymer matrix. Guo et el [13]. chose graphite (Gt) as the main filler and added silicon carbide as the electrically insulating filler into the system to reconnect separated Gt and further improve the thermal conductivity while keeping the electrical resistivity of the composite at a high level. As a result, thermally conductive and electrically insulating materials have attracted more attention for efficient heat transformation in thermal management.

Normally, thermally conductive polymeric composites are usually compounded with polymer matrix and thermally conductive fillers. Various low-cost fillers including Al$_2$O$_3$ [14,15], SiC [16,17], BN [18–20], AlN [21] and so on, were used to enhance the thermal conductivity of polymers because of their thermal conductivity and electrical insulating nature. Unfortunately, high-volume fractions of thermally conductive particles are required to achieve thermal conductivity of the composite in the range of $\sim$1–5 $\mathrm{W \, m^{-1} \, K^{-1}}$ at room temperature [7,18,22]. Meanwhile the increase of thermal conductivity is usually at the cost of significant deterioration of mechanical properties. Recently, carbon nanotubes [23,24] and graphene [25] have also been

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investigated because of their high intrinsic thermal conductivity. However, the high cost and electrical conductivity of these carbon materials can change the intrinsic insulating properties of the polymer composites. Morishita et al. [26] fabricated a novel MWCNT/PA6/PPS composite with a controlled morphology comprising a PA6 matrix and MWCNT-localized PPS domains surrounded by shell-layers formed from EGMA. These composites had improved thermal conductivity without decreasing the volume resistivity, despite using electrically conductive MWCNTs. However, the thermal conductivity of these composites still needs improvement for more applications.

Apart from the thermal conductivity, the morphology of the filler also plays an important role in the performance of composites. Nanowires, due to their inherent continuity and the high aspect ratio, are much more suitable to improve thermal conductivity as well as to reduce the percolation threshold compared with other nanostructures [27,28]. Recently, silver nanowires (AgNWs) have been extensively studied as filling materials to fabricate AgNW-based composites with superior thermal conducting performance [29]. However, because of the high cost, the industrial application of AgNW is limited. Compared with silver, copper is abundant and much less expensive. Most importantly, copper also has a high thermal conductivity of 400 W m^{-1} K^{-1}. Therefore, copper nanowire (CuNW) has great potential to be used as filler in thermally conductive polymer composites. Wang et el [30]. prepared CuNW-polyacrylate composites and obtained thermal conductivity of 2.46 W m^{-1} K^{-1} at 0.9 vol % of CuNW. And also, the composites were no more electrical insulating with the electrical conductivity of 0.04 S cm^{-1}. An ideal thermal conductive and electrically insulating polymer composites should possess a high thermal conductivity and a poor electrical conductivity. However, the strong interdependence of the two parameters (i.e., increasing thermal conductivity is usually accompanied by an increased electrical conductivity) imposes restrictions on practical applications. The thermal conductivity is composed of a lattice contribution and an electronic contribution, whereas the electrical conductivity can be limited by electronic defects, thus focus is placed on reducing electrical conductivity by decreasing electronic transport at the junctions [31–34]. What's more, CuNW can be easily oxidized without any protection even in composites, which will seriously affect the long-term good thermal performance of the CuNW-based composites during service. Therefore, in order to effectively use CuNWs as a TIM, it is critically required to take actions to prevent CuNWs from being oxidized and reduce the electrical conductivity of CuNW-based composites. Kim et al. [35] protected CuNWs with SiO$_2$ and fabricated CuNWs-SiO$_2$/EDTS composites with thermal conductivity of 1.1 W m^{-1} K^{-1} at 2 vol % of CuNW. Actually, relatively complicated syntheses process is big challenge for CuNWs-SiO$_2$ in real application.

Dopamine (DA), a well-known hormone and neurotransmitter which contains both the amine and catechol functional groups, and has been chosen as a specialized molecule mimic for adhesive proteins [36]. At a weak alkaline pH (8.5), DA can self-polymerize into a highly cross-linked polydopamine layer that has demonstrated superb adhesion toward various substrates including metals [37,38]. Polydopamine, similar to its monomer, is prone to diffusion on substrates through noncovalent binding interaction such as metal coordination or chelating. Metal or metal oxide surfaces are usually hydroxylated or hydrated under ambient conditions. As a result, coordination bonding and chelating bonding interactions play central roles in the adhesion of polydopamine on metal or metal oxide surfaces. In our previous work, we coated graphene oxide with polydopamine to fabricate a nacre-like layered material and achieved great improvement in mechanical and thermal properties [39]. Herein, we first coated the surface of CuNW with polydopamine (PDA) to enhance its electric insulation properties and improve the miscibility and affinity with organic polymers, and successfully obtained epoxy composites that are highly thermally conductive and electrically insulating at low filler loadings. This novel method is easy to operate and achieve the goal of low filler loading with

high thermal conductivity as well as electric insulation.

2. Materials and methods

2.1. Materials

Sodium hydroxide (NaOH), Hydrazine hydrate (N$_2$H$_4$·H$_2$O 85%), Copper nitrate trihydrate[Cu(NO$_3$)$_2$·3H$_2$O], 2,4,6-Tris(dimethylamino-methy)phenol, ethylenediamine (EDA), Tris(hydroxymethyl)amino-methane were provided by Sinopharm Chemical Reagent Co., Ltd. Dopamine (DA, 98%) and the curing agent Methylcyclohexene-1,2-di-carboxylic Anhydride were purchased from Aladdin. The epoxy resin (E-44) was purchased from Formosa Plastics Corporation.

2.2. Synthesis of copper nanowires

Synthesis of copper nanowires was based on the methods developed by Chang et al. [32]. In each synthesis, 20 mL of NaOH (15 M) and 1 mL of Cu(NO$_3$)$_2$ (0.1 M) aqueous solution were added to a glass reactor, 0.15 mL of ethylenediamine (EDA) and 25 μL of hydrazine (35 wt %) were also added continuously, followed by a vigorous mixing. The mixture was then heated to 60 °C for 1 h without stirring. Copper products were washed and filtered with deionized water and stored in a water-hydrazine solution to prevent oxidation.

2.3. Surface treatment of copper nanowires with polydopamine

Copper nanowire (0.1 g) was dispersed in deionized water (60 mL) with ultrasonicating into the dispersion and dopamine (0.05 g) was added into the above dispersion. Then, the pH of the reaction system was adjusted to 8.5 b y adding the Tris solution. The mixing solution was stirred gently at 30 °C for 3–24 h. After the solution starting to become black, the polydopamine coated copper nanowires were filtered with a 0.2 μm membrane filter and washed with deionized several times.

2.4. Preparation of the epoxy/PDA-coated-CuNWs composites

First, epoxy resin was dissolved in acetone solution and PDA-coated-CuNWs were dispersed in the above solution with ultrasonicating into the homogeneous suspension. Then, put the mixture into an oven at 60 °C to remove acetone. After that, the mixture, curing agent (Methylcyclohexene-1,2-dicarboxylic Anhydride) and accelerator (2,4,6-Tris(dimethylaminomethy)phenol) were uniformly mixed at room temperature. The weight ratio of the epoxy resin, curing agent, and accelerator was controlled in about 100:80:0.4. After mixing, the mixtures were transferred into a vacuum oven at 60 °C until air bubbles stopped appearing on the surface of the mixture. Finally, the composites were cured at 80 °C for 3 h and 120 °C for 3 h. A series of composites was prepared with PDA-coated-CuNWs loading between 0 and 3.1 vol %. The ratio is on the basic of the weight of CuNW, where PDA is considered as extra components, and their weights are not involved into the calculation. For comparison, epoxy composites filled with CuNWs were prepared via the same procedure.

2.5. Characterization

The morphologies of the CuNW and fracture surfaces of epoxy composites were characterized by scanning electron microscopy (SEM Hitachi S-4800). Composites were frozen by liquid nitrogen to break into small pieces for SEM analysis. The XRD patterns of samples were recorded on a Bruker-D8 X-ray diffractometer (Cu Kα radiation, Germany). Atomic force microscope (AFM MuLtimode 8, Bruker Nano, U.S.A.) was used to observe the microstructure of the CuNW. AFM samples were prepared by dropping a few drops of the CuNWs aqueous solutions onto a clean and smooth silicon substrate and drying.