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A facile approach to constructing efficiently segregated conductive networks in poly(lactic acid)/silver nanocomposites via silver plating on microfibers for electromagnetic interference shielding

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ABSTRACT

Here, a facile approach to constructing efficiently segregated conductive networks in the poly(lactic acid)/silver (PLA/Ag) nanocomposites were developed by coating Ag particles on PLA microfibers and then compression molding. The electrical conductivity and electromagnetic interference shielding effectiveness (EMI SE) of the nanocomposites were obviously enhanced by these efficiently conductive networks because of the well Ag coating layers on PLA microfibers. Furthermore, the electrical conductivity and the EMI SE of the nanocomposites increased with increasing the coating amount of Ag particles, which can be easily tuned by controlling the coating time. It was found that the chain-structured PLA/Ag nanocomposites with coating time of 7 min with 5.89 vol% Ag particles possessed the remarkable electrical conductivity of 254 S/m and outstanding EMI SE of 50 dB at 8.2–12.4 Hz when the testing samples with the thickness of 1.5 mm, which far surpassed the targeted value of 20 dB for commercial applications. The excellent EMI shielding properties of the nanocomposites were ascribed to the unique segregated chain-structures, which provide enormous interfaces to reflect, scatter and adsorb the electromagnetic waves many times. The PLA/Ag nanocomposites with segregated networks were also found to be an absorption dominated EMI shielding mechanism.

1. Introduction

The widespread development of electronic and wireless device applications has generated a great deal of interests in recent years to make our life easier. However, the electromagnetic radiation emitted by these electronic devices not only interfere with other electronic equipment but also harm human health. Accordingly, the materials with high-performance electromagnetic interference (EMI) shielding have been largely pursued to suppress the electromagnetic pollution in both academic and industrial fields [1–3]. Conventional electromagnetic shielding materials prepared from conductive metals or metal alloys have limited applications in special fields such as aerospace, weapon equipment, and microelectronics where the materials with properties of lightweight, superior chemical resistance, excellent flexibility and good processability, are required [4–6].

Recently, conductive polymer composites (CPCs) have been widely adopted for EMI shielding applications with above requirements [7–10]. Various carbon and metal fillers, such as carbon black, carbon nanotubes, graphene, silver and copper have been employed to prepare CPCs for EMI shielding applications [11–13]. The EMI shielding effectiveness (SE) of the final CPCs is significant dependent on the intrinsic conductivity, dielectric constant, aspect ratio and distribution of the fillers in polymer matrix [14–16]. However, the satisfactory EMI SE can usually be achieved by adding large amount of conductive fillers because of the poor distribution of conductive fillers in CPCs [17–20]. The introduction of high concentration of fillers not only increases the production cost, but also leads to poor processability of CPCs. Furthermore, the obtained CPCs usually hold deteriorated mechanical properties due to severe aggregation of fillers [21,22]. Therefore, it has been highly necessary to prepare CPCs with low filler loadings but superior EMI SE.

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The key to fabricating CPCs with high conductivity and EMI SE is to constructing well-connected conductive networks in the CPCs [23–25]. The three-dimensional structured architectures, such as graphene foam and carbon nanotube foam, have been used as filler skeleton through infiltration with epoxy resin or poly(dimethyl siloxane) for preparing high-performance CPCs [26–29]. However, the methods such as freeze-drying and template-directed chemical vapor deposition (CVD) used to graphene foam and carbon nanotube foam are always complex and expensive, which limit their large-scale application [30,31].

In recent years, the formation of segregated conductive network has also been proven its superiority in enhancing electrical conductivity, and improving EMI SE [32–36]. In segregated architectures, the conductive fillers are primarily located at the interfaces among the polymeric matrix particles, where they contact with each other and tend to form denser conductive paths around polymer regions instead of random dispersion in entire matrix, leading to high electrical conductivity, low percolation threshold, and highly efficient EMI shielding at low filler loadings [37–43]. However, the electrical conductivity and EMI SE performance of CPCs with segregated structure are much dependent on the segregated particle size and the coating degree of conductive layers [39–41]. Furthermore, the coating layers at surfaces are easily peeled away from polymer particles because of the weak interfacial interaction between polymer and fillers, which deteriorates the electrical performance of CPCs [44]. Therefore, to fabricate the segregated particles with well coated conductive layers is a main factor to obtain the segregated CPCs with high electrical conductivity and efficient EMI shielding. Fortunately, the filler dip-coating and metal-plating techniques have been reported as facile methods to construct well coating layers on the surface of polymer surfaces [45–50]. Besides, most of the present polymer-based EMI shielding materials are focus on the non-biodegradable petrochemical-derived polymer matrix, which will suffer from the depletion of nonrenewable petroleum and lead to the anabatic environmental concerns and feedstock crisis. Therefore, it is necessary to develop sustainable polymer matrix, such as poly(lactic acid) (PLA), for EMI shielding materials from renewable resources [51–54].

In this study, a biodegradable high-performance conductive PLA/silver (Ag) composite was fabricated with efficiently segregated structure of conductive Ag chain-like network interpenetrating the entire PLA matrix by sequential Ag plating of PLA microfibers and compression molding. The PLA microfibers were found to be well coated with Ag layers by the facile wet electroless deposition processing. Simultaneously, the continuous Ag layers could be tightly embedded in PLA matrix to form efficiently segregated structure, which endowed the PLA/Ag composites with excellently thermal stability, electrical conductivity and EMI SE.

2. Experimental

2.1. Materials

$AgNO_3$(≥99.8%) was purchased from Tianjin Ruijinte Chemicals Co., Ltd., China. $SnCl_2.2H_2O$ (98.0–103.0%) was received from Sigma-Aldrich Co., LLC, St. Louis, U.S.A. Potassium sodium tartrate tetrahydrate (analytical grade), NH_3OH (25.0–28.0%), HCl (36.0–38.0%) and ethanol (≥99.7%) were all supplied by Chongqing Chuandong Chemicals Co., Ltd., China. α-D-(+)-glucose (≥99%, [α]20 D+ 52.5–53.0°) and NaOH(≥99.5%) were brought from Chengdu Kelong Chemicals Co., Ltd., China. Poly(lactic acid) short fiber (trade name Hisun Revode 190) with 20–30 μm in diameter, a melt index of ~12 g/10 min at 190 °C and under 2.16 kg, and a density of 1.25 g/cm^3 was kindly provided by Zhejiang Hisun Biomaterials Co. Ltd., China. It has been reported that the better size of segregated phase was in micrometer scale for the high conductivity of the segregated composites [39,40]. Therefore, the PLA fibers with 20–30 μm in diameter are suitable to fabricate the PLA/Ag segregated composites with high electrical conductivity and EMI SE.

2.2. Preparation of the Ag plated PLA microfibers

A series of Ag plated PLA microfibers with different Ag coating amount were prepared in a way of wet electroless deposition processing via controlling the deposition time. The procedure of the Ag plated PLA microfibers can divide into two steps. First, the neat PLA microfibers (3.0 g) were immersed in acidic $SnCl_2$ solution which was prepared by dissolving 1.0 g $SnCl_2.2H_2O$ in 200 mL dilute HCl solution (1.0 wt%) with the assistance of ultrasonication for 10 min, allowing the deposition of nuclei on the PLA microfiber surfaces. Then the roughened microfibers were removed from the solution and rinsed with distilled water. Second, the roughened PLA microfibers were exposed to a mixture solution of Tollen's reagent, which was prepared by dissolving 2.0 g $AgNO_3$ in 100 mL distilled water and stirred by adding excessive NH_3OH until the solution turned from turbid to clear, and reducing solution, which was obtained from a mixture containing 5.0 g potassium sodium tartrate, 0.5 g NaOH, 0.7 g glucose and 50 mL distilled water, at room temperature. The Ag coating amount of the plated microfibers was easily controlled by deposition time. The Ag plated PLA microfibers were labeled as F-*x*, where *x* denotes the minutes of Ag deposition time. After Ag coating, the colour of PLA microfibers was changed from white, to yellow, and brawn by 1.5 and 5.5 min coating, respectively, as shown in Fig. 1.

2.3. Preparation of the PLA/Ag nanocomposites with segregated structure

Fig. 1 shows the procedure for the preparation of the PLA/Ag nanocomposites with segregated structure. All the dried neat PLA microfibers and Ag plated microfibers were compression molded into a circular sheet with the diameter of 25 mm and the thickness of 1.5 mm on a hot-press at 180 °C and 12 MPa, and then cooled down on a cold-press at room temperature (23 °C) and 12 MPa for 4 min. The PLA/Ag nanocomposites were named as S-*x*, where *x* also represents the minutes of Ag deposition time. The Ag contents for the S-1, S-2.5, S-3.5, S-5.5 and S-7 nanocomposites which were obtained by a thermogravimetric analyzer (TGA) were 6.80, 11.79, 16.75, 29.45 and 34.44 wt% (0.86, 1.57, 2.34, 4.73 and 5.89 vol%), respectively. The TGA results also showed that the thermal stability of the PLA/Ag nanocomposites was remarkably enhanced by the interconnected Ag layers when compared with neat PLA, as shown in Fig. S1.

2.4. Characterizations

The microstructure of the Ag plated PLA microfibers and segregated structure in the PLA/Ag nanocomposites were investigated by a field-emission scanning electron microscope (FE-SEM) (JEOL-7800F) at an accelerating voltage of 5 kV.

The electrical conductivity of the PLA/Ag nanocomposites with Ag deposition below and above 2.5 min were measured by a digital high resistance machine (PC68, Shanghai Precision Instrument Manufacture, China) and four-point probe instrument (RTS-8, Guangzhou Four-Point Probe Technology Co., Ltd., China) at room temperature (23 °C), respectively. At least five specimens were tested and average data was evaluated.

The rheological behaviors of neat PLA and PLA/Ag nanocomposites were evaluated by a rotational rheometer (TA AR200ex) with two parallel plates. The dynamic sweeping mode was