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Electrical, mechanical and thermal properties of aligned silver nanowire/polylactide nanocomposite films

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ABSTRACT

In this work, electrically conductive silver nanowire (Ag NW) filled polylactide (PLA) nanocomposites were fabricated and characterized. Ag NWs/PLA nanocomposite films were fabricated using simple solution mixing method and casted onto glass substrates via doctor blading. Following the obtainment of free standing nanocomposites through peeling off, electrical conductivity of the fabricated nanocomposites, interfacial interactions between Ag NWs and PLA as well as nanocomposite morphology, degree of alignment of Ag NWs, transition temperature and crystallinity among with mechanical performance were investigated. NWs showed good dispersion within the PLA matrix. Due to their high aspect ratio (≈150), a percolation threshold of 0.13 vol% was measured for the nanocomposites. Conductivity of the nanocomposites at the maximum loading (1.74 vol%) was measured as 27 S/m. It was also found that the transition temperatures of PLA matrix remain the same following the formation of nanocomposites. The results obtained herein revealed the potential of these nanocomposite films for electrostatic packaging and electromagnetic shielding applications.

1. Introduction

Electrically conductive polymer composites stand out with their application areas like antistatic packaging, transistors and heaters [1–3]. Besides these wide range of application areas, easy processability is another advantage of the conducting polymer composites. There is a critical filler content where a three dimensional (3D) network starts to form in a polymer matrix creating a conductive path for electrical conduction, known as the percolation threshold [4]. In literature, several additives such as carbon black, metallic nanoparticles, carbon nanotubes, metallic NWs and graphene were investigated for the production of conductive polymer composites [5–13]. A minimum filler content of 5 and 14 vol % for silver nanoparticles and carbon black particles were reported, respectively, for percolation [5,6]. 3D networks require a higher filler content for additives like nanoparticles. However, high filler content deteriorates the mechanical properties of the matrix materials, in addition to increasing the viscosity of the mixture, which would in turn reduce the processability. One dimensional (1D) nanostructures, on the other hand, were reported to provide higher conductivity at lower filler fractions as opposed to nanoparticles [7]. For instance, carbon nanotube (CNT) reinforced polymer matrix composites have been extensively studied with different matrix materials. The lowest percolation threshold was reported as 0.0025 wt % for CNT/epoxy composites; however, the maximum obtained conductivity was 10^{-1} S/m, which may not be enough for many electronic applications [8]. Therefore, fillers with higher intrinsic conductivity compared to CNTs are required to increase the obtained maximum conductivity from the nanocomposites. At this point, metallic NWs appear as promising candidates. In fact, copper (Cu), nickel (Ni) and Ag NWs have already been used as additives for different polymer matrices [9–11]. However, due to oxide layer formation on Cu and Ni NWs, maximum conductivity of the nanocomposites could not exceed 10^{-1} S/m [9,10]. In contrast, higher conductivity values were reported from the nanocomposites fabricated with Ag NWs [12,13].

Polymers synthesized from renewable sources received considerable attention due to their environmentally friendly character [14]. In addition, scarcity of petroleum resources increased demands for alternative renewable raw materials [15]. In this context, biodegradable poly (lactic acid) (PLA) seems to be one of the best alternatives among all biopolymers with its promising thermal and mechanical properties as well as low cost [16]. Due to these advantages, PLA has been used in a wide range of applications

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from food packaging to tissue engineering [16,17]. However, these properties still need to be improved for various other applications. For this purpose, different types of additives have been extensively studied. For instance, water vapor permeation and tensile properties of the PLA matrix nanocomposites have been improved through nanoclay addition [18]. In another case, metal nanoparticle/PLA composites were fabricated and their optical, antibacterial and catalytic properties were investigated [19]. Electrically conductive fillers like CNTs and graphene have been also studied within the PLA matrix [20,21]. Moreover, PLA is the most widely used polymeric ink for 3D printers [22]. With that respect, 3D printed PLA scaffolds were produced and used for tissue regeneration [23]. In terms of the 3D printing of PLA nanocomposites, carbon black was used as a conductive filler for the fabrication of electronic sensors [24]. Graphene was also used as a conductive additive for the fabrication of 3D printed graphene/PLA nanocomposites and turned into a commercial product [25,26].

In this study, a relatively less explored filler, Ag NWs are used for the first time as conductive fillers within the PLA matrix. Ag NW/PLA nanocomposites were produced through simple doctor blading technique. Effect of Ag NW content on the percolation threshold, electrical conductivity and mechanical properties of the nanocomposites were investigated. Important transition temperatures of the PLA matrix, interfacial interactions between the PLA and Ag NWs, and degree of alignment of Ag NWs within the matrix were also examined.

2. Experimental section

2.1. Materials

PLA granules used in our study were provided by Nature Plast (PLI 003). According to technical data sheet density of this PLA is 1.25 g/cm^3. Its molecular weight was measured as 980000 in our previous study [27]. Polyvinylpyrrolidone (PVP) (Mw = 55000), ethylene glycol (EG), silver nitrite ($AgNO_3$), sodium chloride (NaCl, 99.5%) were used for the Ag NW synthesis. These chemicals except PLA were purchased from Sigma-Aldrich. Chloroform was purchased from Merck. It was utilized for the dispersion of Ag NWs and for the dissolution of PLA. All materials were used without further purification.

2.2. Ag NW synthesis

Ag NWs were synthesized according to a previously reported procedure [28]. In brief, a 10 ml of 0.45 M EG/PVP solution was prepared and 7 mg of NaCl was added into the solution. This solution was placed into a silicon oil bath heated to 170 °C and stirred at 1000 rpm with a magnetic stirrer throughout the synthesis process. Meanwhile, a 5 ml of 0.12 M $AgNO_3$/EG solution was added dropwise into the PVP solution at a rate of 5 ml per hour by an injection pump (Top-5300 model syringe pump). At the end of the injection process, the solution was kept at the same temperature for another 30 min. Following synthesis, for purification, Ag NW solution was diluted with acetone and centrifuged at 7000 rpm for 20 min. Afterward, Ag NWs were again dispersed in acetone and another centrifuge process was applied with the same parameters. Later, Ag NWs were dispersed in chloroform for further processing.

2.3. Preparation of the nanocomposite films

PLA powders were dried at 80 °C for 12 h under vacuum. After that, 1 gr of PLA powder was dissolved in 10 ml of chloroform, through stirring (at 1000 rpm) at room temperature. Desired amount of Ag NWs (dispersed in chloroform) were then added to this PLA solution. Solution was mixed continuously at room temperature until it becomes a viscous liquid. Finally, the solution was doctor-bladed onto glass substrates in the form of a 20 μm thick composite film. To remove the solvent and entrapped bubbles from the nanocomposites, films were dried at 60 °C for 24 h under vacuum [29]. Finally, free standing nanocomposite films were peeled off from the glass substrates and used for the characterization.

2.4. Transmittance measurements

Ocean Optics Maya 2000 model spectrometer was used to measure the direct transmittance of the nanocomposite films within the visible range (400–700 nm).

2.5. Scanning electron microscopy (SEM) analysis

Morphology of the nanocomposites, NWs and orientation of Ag NWs within the nanocomposites was carried out by scanning electron microscopy (FEI Nova Nano SEM 430). SEM was operated under an accelerating voltage of 5 kV following a thin gold layer (5–10 nm) deposition onto the samples. Since electrical conductivity measurements were made along the thickness of the nanocomposites, fracture surface of the film samples were also examined via SEM. For the fracture surface analysis, nanocomposite films were immersed in liquid nitrogen (for 5 min) and then broken into pieces.

2.6. Thermogravimetric analysis (TGA)

To precisely determine the Ag NW content of each nanocomposite and to investigate the thermal degradation processes of the nanocomposites, TGA analysis was performed. An Exstar SII TG/DTA 7300 system operated under nitrogen atmosphere was utilized for this purpose. Samples were analyzed in between 30 and 550 °C with a heating rate of 10 °C/min. 10 mg of neat PLA sample was also analyzed to calculate the amount of ash.

2.7. Differential scanning calorimeter (DSC)

To investigate crystallinity and important transition temperatures of the nanocomposites, DSC analysis was performed. An Exstar SII X-DSC 700 system was utilized and operated under nitrogen atmosphere. Firstly, to erase the thermal history, 10 mg of the samples first heated with a heating profile from −80 to 220 °C at a heating rate of 5 °C/min. Then the sample was cooled to −80 °C with a cooling rate of 5 °C/min. Then second heating scan was performed with the same heating profile and rate. Crystallinity percent (X_c) of the neat PLA and the matrix of the nanocomposite films were calculated using the following equation,

$$X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0 \times w_{PLA}} \times 100,$$

where ΔH_m is the enthalpy of melting, ΔH_c is the enthalpy of cold crystallization, and w_{PLA} is the weight fraction of PLA, ΔH_m^0 is the enthalpy of melting of 100% crystalline polymer, which is equal to 93.0 J/g [30].

2.8. Fourier transform-infrared (FTIR) spectroscopy

To investigate the possible interfacial interactions between Ag NWs and PLA, attenuated total reflectance (ATR) unit of FTIR spectrometer (Bruker ALPHA) with a resolution of 4 cm^{-1} was used within a wavenumber range of 400–4000 cm^{-1}.