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The effect of nanofiller geometry and compounding method on polylactic acid nanocomposite films

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ABSTRACT

The effect of the compounding method and of the nanofiller geometry on the thermo-mechanical properties and electrical behavior of polylactic acid (PLA) nanocomposite films was investigated. The films were fabricated using two methods: (i) melt compounding followed by melt fiber spinning or (ii) solution compounding followed by electrospinning. Both the melt and electrospun fibers were then compression molded. In the case of melt compounding, both exfoliated graphite nanoplatelets (GNP) and carbon nanotubes (CNT) were used as reinforcement, whereas only CNT were used in the case of solution compounding. The microstructure was examined using scanning electron microscopy and the crystallization behavior, thermo-mechanical behavior, and electrical response of the PLA composite films were investigated as a function of nanofiller content, geometry, and compounding method. It was concluded that the GNP/PLA films had the highest percolation at greater than 3 wt% of GNP, while the CNT/PLA films had the lowest at less than 1 wt% of CNT. In addition, the solution method and electrospun fibers resulted in a higher conductance compared to the CNT/PLA films of the same CNT content made by melt compounding due to a more heterogeneous distribution and dispersion of CNT throughout the matrix that facilitated the formation of interconnected conductive networks.

1. Introduction

Electrically conductive polymer nanocomposite films have many applications such as for static charge dissipation in electronics packaging [1,2]. Microstructure has a strong impact on the electrical response of the nanocomposite. Previous studies have shown that the electrical response is strongly influenced by nanofiller distribution and dispersion [3,4], inherent material properties of the matrix and filler [5,6], as well as composite processing [7–10]. Better understanding of these factors is crucial to enhanced engineering design of conductive polymer nanocomposite films.

Polylactic acid (PLA) is a fully biorenewable and biodegradable thermoplastic polyester derived from cornstarch or sugarcane [11]. PLA is a good renewable alternative to petroleum based thermoplastics with comparable properties, such as

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polyethylene terephalate (PET) or polystyrene (PS) [11,12]. However, PLA is electrically insulating which hinders its potential for use in electromagnetic or electrostatic dissipation applications. Hence, there is much interest in the incorporation of electrically conductive nanofillers, such as exfoliated graphite nanoplatelets (GNP) and carbon nanotubes (CNT). Both GNP and CNT are electrically conductive with reported conductivities of greater than 10^4 S/m [13,14]. The use of these nanofillers in PLA would decrease the electrical resistivity of the resulting nanocomposite and enhance its potential for use in electrostatic dissipation applications.

Fabrication of CNT/PLA nanocomposites using mainly direct melt mixing [15,16] and other techniques such as polymer dissolution [17] and in situ polymerization has been reported. Due to the low solubility of CNT in organic solvents and/or PLA, surface modification of CNT or use of compatibilizers is often required [18–20], which results in better dispersion and thus properties of the CNT/PLA composites but makes the processing longer, costly, more complex and often non scalable. Similar processing techniques to those used for CNT/PLA nanocomposites have also been used for fabrication of graphite/PLA nanocomposites [21].

Natural or synthetic graphite, which consists of a planar arrangement of fused benzene rings, can be further intercalated and exfoliated to produce GNP. CNT are a tube-like configuration of graphite sheets with a high aspect ratio that allows for minimal electron scattering along the tube direction [22]. Both GNP and CNT have attracted much attention for their low density, high elastic modulus and tensile strength, as well as their superior electrical properties [14,23].

This study focuses on understanding the effect of compounding method and nanofiller type on the nanofiller distribution and dispersion, crystallization behavior, thermo-mechanical behavior, and electrical response of PLA nanocomposite films. Two different compounding methods, (i) melt mixing, followed by melt fiber spinning and compression molding (MC–CM), and (ii) solution mixing, followed by electrospinning and compression molding (E–CM) were employed. For the MC–CM case, both GNP and CNT were used to determine the effect of nanofiller geometry on the film properties. When comparing the compounding method, MC–CM versus E–CM, CNT was chosen as the nanofiller.

2. Experimental

2.1. Materials

Semicrystalline PLA (PLA 3051D) pellets were purchased from Nature Works LLC and used as the matrix material. The PLA has a flow index of 10–30 g/10 min, ASTM D1238, a specific gravity of 1.24, and an average molecular weight, $M_{w,}$ of 160 kg/mol. The ratio of the D-lactic acid (residual) content to the L-lactic acid is between 24:1 and 31/1. GNP (xGnP® Grade C) purchased from XG Sciences Inc. with an average diameter of 1–2 μm, thickness of 10–20 nm, and specific surface area of ~750 m^2/g were used as reinforcement along with CNT (multi-walled, >95 wt% purity) purchased from Cheap Tubes Inc. with an average length of 10–20 μm and an average outer diameter between 30 and 50 nm. Chloroform and dimethylformamide (DMF) were used as the solvents for electrospinning.

2.2. Processing and fabrication of films

Nanocomposite films were fabricated using two different compounding methods: (i) melt compounding followed by melt fiber spinning and compression molding and (ii) solution compounding followed by electrospinning and compression molding. For the melt compounded/compression molded (MC–CM) films, CNT and GNP were incorporated into the matrix by melt blending using a DSM 15 cc Compounder (a vertical co-rotating twin screw microextruder) at an operating temperature of 190 °C and a screw speed of 150 RPM for approximately 3 min. The nanofiller/PLA mixture was then extruded out of a 0.8 mm orifice at a 15 RPM pull-out rate and melt spun into fibers of ~100 μm diameter (draw ratio of ~8). By melt spinning fibers prior to compression molding, the nanofiller agglomeration size can be better controlled and minimized and partial control of the nanofiller orientation/distribution is achieved. Melt spun composite fibers with nanofiller content ranging from 0 to 3 wt% were then compression molded into films ~110 μm thick using a manual four-column 12 ton Carver hydraulic press (model 4122). The fibers were first softened for ~5 min at 180 °C before a load of ~1 MPa was applied for ~5 min. To minimize thermal residual stresses and plastic deformation, the samples were allowed to cool to below the glass transition temperature (~50 °C) via ambient air cooling prior to removal from the mold.

The electrospun/compression molded (E–CM) films utilized solution compounding. First, a 10 wt% solution of PLA in chloroform was prepared by stirring under low heat until the PLA pellets dissolved. The appropriate amount of CNT to produce a 1 wt% CNT/PLA composite fiber was added to DMF and sonicated for 3 h to homogenize. The PLA/chloroform solution and CNT/DMF suspension were combined and stirred for 1 h. The electrospinning was performed under ambient conditions using a rotating collector and applied voltage of 16 kV and a feeding rate of 100 μL/h. The distance between the syringe tip and the collector was 15 cm. The resultant CNT/PLA electrospun composite fibers were compression molded under identical conditions to the melt spun fibers, as described above. The CNT content was limited to 1 wt% in the E–CM films due to the relatively high viscosity of the CNT/PLA/chloroform/DMF solution.

It is noted that both melt-spun and electrospun fibers were randomly placed in the mold and thus no in-plane anisotropy is expected. The main difference between the two types of fibers is not their alignment or orientation within the resulted film but the dispersion/distribution of the CNT within the polymer due to the significant differences in the fiber diameter and the compounding method used.