Incorporation of supramolecular polymer-functionalized graphene: Towards the development of bio-based high electrically conductive polymeric nanocomposites

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ABSTRACT

Supramolecular polymer-functionalized graphene (SPFG), a combination of exfoliated graphite nano-platelets and a low-molecular-weight supramolecular polymer, can be incorporated into poly(*L*-lactic acid) (PLLA) matrices for efficient production of SPFG/PLLA composites; SPFG behaves as a highly efficient reinforcing material and substantially improves the overall physical properties compared to commercial PLLA. The SPFG content of the PLLA composites can be readily adjusted to obtain the desired composite products with specific crystallization and mechanical characteristics. At the optimized blending ratio of 10 wt% SPFG and 90 wt% PLLA, the resulting film exhibited a 65.2% lower oxygen permeation rate and two-fold higher ultimate tensile strength (47.8 MPa) than pristine PLLA. More excitingly, this newly-developed composite possessed superior electrical conductivity of up to 9.58×10^{-3} S/cm at a SPFG loading of 10.0 wt%, which was nearly four orders of magnitude higher than control graphite/PLLA composites at the same nanofiller content. Thus, SPFG provides a potential route towards the development of high performance graphene-based PLLA nanocomposites for a broad range of electronic and biomedical applications.

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1. Introduction

Growing global environmental awareness in recent years has led many governments to establish more stringent environmental standards and incentivized researchers to develop new eco-friendly biodegradable polymers for a wide range of practical applications, including the medical, automotive and packaging industries [1,2]. Poly(*L*-lactic acid) (PLLA) is one of the most widely used commercial bio-based biopolymers due to its unique biocompatibility, predictable spontaneous degradation kinetics, ease of production and regulatory approval by the United States Food and Drug Administration for materials used in biomedical applications; hence PLLA represents a potentially promising alternative to traditional synthetic polymers for high-performance biodegradable materials [3–8]. However, its inherent brittleness and poor crystalline characteristics limit the ability of PLLA to undergo extensive plastic deformation below its glass transition temperature (T_g; approximately 60 °C), resulting in insufficient

mechanical performance and restricting its use in further practical applications. Another major drawback of PLLA that limits its application is its inherently high permeability to various gases such as oxygen, nitrogen and carbon dioxide. Therefore, the mechanical and gas barrier properties of PLLA urgently need to be improved in order to promote PLLA as a more competitive alternative to synthetic polymers [4,5,9]. Over the last decade, a number of studies have attempted to improve the physical properties of PLLA, with chemical modification, physical blending and incorporation of nano-sized materials as reinforcing nanofillers in the PLLA matrix as representative approaches [6,10–19]. Nanofillers such as clays, silica nanoparticles, carbon materials and polyhedral oligomeric silsesquioxanes can be incorporated into the PLLA matrix to easily fabricate high-performance nanocomposites as a result of the large specific surface area of the nanofillers [11,12,16,18,19]. However, serious concern exists that nano-sized nanofillers tend to aggregate into individual domains and induce a microphase-separated morphology within the PLLA matrix, leading to a reduction in long-term physical performance [20–22]. This dilemma inspired us to develop a new nanofiller dispersion technology that integrates efficient manufacturing of nanofiller-reinforced PLLA composites

with stable morphological characteristics and superior physical performance.

A non-covalent functionalization approach is highly preferable for dispersion of various dimensional carbon materials in certain solvent media. Carbon materials enable the attachment of large number of target-specific molecules via van der Waals forces and π−π stacking interactions, allowing the unique properties of carbon materials to be manipulated at the nanoscale in order to develop new materials with potential applications in engineering, optoelectronics and biomedical fields [23—27]. Recently, this approach has been applied to oligomers to construct various novel supramolecular polymeric structures that exhibit interesting dynamic properties and which form reversible bonds between supramolecular units [28—30]. Using these supramolecular polymers, well-dispersed carbon nanotubes and graphene can be easily obtained in aqueous or organic solvent solutions, and the resulting solutions greatly enhanced the effectiveness of these unique carbon nanotubes/graphene dispersion processes via a low temperature spin-coating method [31—34]. Therefore, we reasonably speculated that incorporation of a small amount of a functionalized supramolecular polymer/carbon material complex into the PLLA matrix may profoundly alter miscibility behavior and enable the formation of a well-defined heterogeneous morphology to obtain high-performance PLLA nanocomposites in the bulk and thin film states. Fabrication of bio-based nanocomposites by employing non-covalent functionalization of a supramolecular polymer/carbon material within the PLLA matrix has not yet been reported. Thus, exploitation of dynamic supramolecular PLLA nanocomposites may provide a significant breakthrough in the development of next-generation environmentally friendly biopolymers with improved physical performance and controllability.

Recently, we successfully developed a simple, low-cost and high-yield synthesis approach for the mass production of ureido-cytosine (UrCy) end-capped polypropylene glycol (UrCy-PPG; molecular weight of ca. 1100 g/mol) to efficiently construct quadruple hydrogen-bonded supramolecular polymers [35,36]. We discovered that the UrCy-PPG self-assembly process is essential for manipulation of graphite nanoplatelet exfoliation, enabling direct exfoliation of natural graphite into high concentrations of uniform graphene as a result of the specific interaction between graphene and UrCy-PPG [37]. In addition, the number of graphene layers can be precisely controlled by tuning the UrCy-PPG content, and the resulting graphene nanosheets also exhibit excellent electrical properties and resistive switching behavior. Based on the findings described above, this study extended the application of graphite/UrCy-PPG composites to reinforce commercial PLLA polymers by proposing a simple solvent-blending method (Fig. 1). We demonstrate that incorporation of graphite/UrCy-PPG into the PLLA matrix substantially improved phase miscibility, crystallization behavior and mechanical properties, but also effectively reduced oxygen transmissibility. In addition, the resulting PLLA nanocomposite exhibits a high electrical conductivity of up to 9.58×10^{-3} S/cm at a 1/1 graphite/UrCy-PPG loading of 10.0 wt%, which was nearly four orders of magnitude higher than that of control graphite/PLLA composites at the same graphite content (5.0 wt%). To the best of our knowledge, this is the first reported application of supramolecular functionalized graphene to manipulate the structure and properties of bio-based polymer nanocomposites. Thus, this finding represents a novel, highly efficient approach for the fabrication of high-performance PLLA nanocomposites; this could represent a new class of reinforcement concepts to further develop existing biodegradable polymers for use in a wide variety of potential applications in various fields of engineering.

2. Experimental section

2.1. Materials

All chemicals and reagents were of analytical grade and purchased from Sigma-Aldrich (St. Louis, MO, USA). All solvents used for sample preparation and chromatography were high performance liquid chromatographic grade from TEDIA (Fairfield, OH, USA). Supramolecular polymer-functionalized graphene (graphite/UrCy-PPG) was prepared from a blend of UrCy-PPG and graphite as described previously [37]. PLLA was purchased from Wei Mon Industry Co. (Taipei City, Taiwan). PLLA has a melting point of 158—174 °C and glass transition temperature of around 60 °C. Gel permeation chromatography (GPC) analysis indicated PLLA has an average molecular weight (M_w) of approximately 172,000 g/mol and polydispersity index (PDI) of 1.58. PLLA has a glass transition temperature (T_g) of 60—65 °C and melting temperature (T_m) of around 170 °C.

2.2. Measurements

Ultraviolet−visible (UV−Vis) spectroscopy. UV−Vis spectroscopy was performed using a Hewlett-Packard 8453 diode array spectrophotometer (HP, Waldbronn, Germany) at 1 nm resolution. All UV−Vis experiments were carried out at 25 °C. The optical transmittance of each film was assessed at 550 nm. *Wide-angle X-ray diffraction (WAXD).* The WAXD patterns of the films were recorded at 25 °C using a Rigaku D/MAX 2500 diffractometer with a Cu Kα radiation ($\lambda = 1.5416$ Å) source operated at 40 kV and 200 mA. The diffraction data were collected in the 2θ range of 5—60° at a scan rate of 1° min^{-1}. *Differential scanning calorimetry (DSC).* DSC experiments were performed using a PerkinElmer DSC 4000 instrument (Beaconsfield, Buckinghamshire, UK) operated at a scan rate of 10 °C/min over the temperature range from −20 to 200 °C. DSC results of the second heating scan for all samples are presented in Fig. 3. *Polarized optical microscopy (POM).* A Nikon Optiphot-2 microscope (Nippon Kogakukk, Tokyo, Japan) fitted with polarizing filters and a Linkam THMS 600 heating/cooling stage was used for POM observations. Prior to POM, all samples were fully crystallized at 120 °C for 6 h after annealing at 200 °C, then cooled to room temperature. *Scanning electron microscopy (SEM).* SEM measurements were conducted using a field-emission scanning electron microscope (Hitachi S-4700, Tokyo, Japan) at an accelerating voltage of 10 kV. The films were cryo-fractured under liquid nitrogen and the fracture surfaces were sputter-coated with gold before SEM analysis. *Tensile tests.* Tensile tests were carried out using a universal testing machine (EZ-L; Shimadzu Corp, Kyoto, Japan) under a constant crosshead speed of 10.0 mm/min at ambient conditions (25 °C, 55% relative humidity). Tensile specimens have a width of 20 mm, wall thickness of 3 mm, and gage length of 50 mm. For all tests, at least three specimens were analyzed to ensure reproducibility. *Dynamic mechanical analysis (DMA).* DMA measurements were performed using a DMA 800 analyzer (TA Instruments Inc., New Castle, PA, USA) under the following conditions: frequency, 1 Hz; tensile preload, 0.01 N; and strain amplitude, 30 μm. Each specimen was heated from 0 °C to 120 °C at a rate of 3.0 °C/min in a nitrogen gas atmosphere. *Conductivity measurements.* The electrical conductivity values of the composites were measured using a Pico Ammeter (Keithley model 617, Cleveland, OH, USA). For conductivity measurements, each specimen was placed in a conductivity cell between two gold electrodes at 25 °C and relative humidity of 50%. *Oxygen permeability* (OP). OP tests were performed in oxygen at 25 °C using an OX-TRAN 2/21 unit (Mocon Inc., Minneapolis, MN, USA). The experimental procedures were carried out in accordance with