



Preparation and enhanced mechanical properties of non-covalently-functionalized graphene oxide/cellulose acetate nanocomposites



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ABSTRACT

Sulfonated poly (ether-ether-ketone) (SPEEK) was selected as a surface modifying agent to prepare non-covalently functionalized reduced graphene oxide (NFrGO) followed by the development of NFrGO/cellulose acetate (CA) nanocomposite (NFrGO-CANC) through solution mixing. The formation of the nanocomposite was governed via the hydrogen bonding interactions among the $-SO_3H$ group of NFrGO and $-OH/-C=O$ groups of CA. NFrGO-CANC was characterized by field emission scanning electron microscopy, FT-IR, X-ray diffraction, thermogravimetric analysis, and differential scanning calorimetry analysis. The tensile strength of the NFrGO-CANC increased significantly with increasing NFrGO loading. The tensile strength and modulus of the NFrGO-CANC with 1.5 wt.% NFrGO were improved by ~102 and 143%, respectively, compared to those of pure CA. The onset degradation temperature and oxygen gas barrier properties of the NFrGO-CANC also were enhanced with increasing NFrGO loading up to 1.5 wt.% compared to those of pure CA film.

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1. Introduction

Replacement of petroleum-derived traditional polymers by biodegradable polymeric materials has attracted considerable interest in the field of packaging applications [1,2]. Several types of biopolymers have been explored to develop eco-friendly packaging materials. However, the uses of biopolymers as packaging materials are limited due to their poor mechanical and barrier properties [3–7]. Interestingly, impermeable nanofiller distribution in a polymer matrix has been demonstrated to have enhanced barrier and mechanical properties. Hence, the fabrication of bioplastic nanocomposites with impermeable fillers is a successful way to overcome this problem. The incorporated nanofillers induce permeating molecules to undergo an extensive diffusion path that is referred to as a tortuous pathway in high barrier systems [8–10]. For this purpose, various types of fillers, such as cellulose

nanocrystals, silicate clay minerals, expanded graphite, and graphene, have been extensively used [11–14]. Among these materials, graphene, a monolayer of carbon atoms arranged in honeycomb networks, is a potential material due to its high aspect ratio, intriguing mechanical and barrier properties [15–18]. In order to utilize these properties, successful incorporation of graphene sheets into the polymer matrix with homogeneous distribution is necessary. However, the use of pristine graphene for nanocomposite application is challenging due to the existence of strong cohesive forces among the graphene sheets, leading to a strong tendency of graphene sheet agglomeration in the polymer matrix due to poor interfacial interaction between graphene and the polymer matrix [19–26]. Functionalization of graphene has become a widely accepted technique to improve the dispersibility of graphene in polymer matrix and to fabricate high-performance graphene-based polymer nanocomposites. Covalent and non-covalent techniques are currently used for chemical functionalization of graphene [27,28]. Non-covalent functionalization of graphene is associated with H-bonding [29] and $\pi \rightarrow \pi$ interactions [30,31] between graphene and surface modifying agents without

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altering the chemical structure of pristine graphene. Alternatively, covalent functionalization involves the formation of a direct bond between surface modifying agents and graphene, which may damage the π -conjugated network of the graphene ring through defect formation that decreases the superior properties of graphene.

In our previous study, SPEEK functionalized graphene/polyvinylidene fluoride nanocomposites were demonstrated to have enhanced mechanical and oxygen barrier properties [32]. Herein, CA has been selected as a biopolymer due to its biodegradability and natural availability. Cellulose is obtained from trees and its esterification produces CA. Thus, CA can act as a substitute for petroleum-derived plastic if the mechanical and gas barrier properties can be improved. SPEEK functionalized reduced graphene oxide has been used as a reinforcing filler to develop NFrGO-CANC through solution mixing. The $-\text{SO}_3\text{H}$ groups of NFrGO can interact with the $-\text{OH}$ (hydroxyl) and $-\text{C}=\text{O}$ (carbonyl groups) of CA through H-bonding interactions that may help to form the NFrGO-CANC.

2. Experimental

2.1. Materials

Natural flake graphite was purchased from Sigma Aldrich, Germany for the preparation of graphene oxide (GO). Sulfuric acid (Samchun Pure Chemical Co. Ltd., Korea) and potassium permanganate (TCI, Japan) were used as oxidizing agents. Hydrochloric acid and hydrogen peroxide were used as received from Samchun Pure Chemical Co. Ltd. (Korea). Poly-ether-ether-ketone (PEEK) (Victrex 450G, number average molecular weight $M_w \sim 115,000$) was purchased from Victrex Plc., UK. The reducing agent hydrazine monohydrate (TCI, Japan) was used as received. The CA used in this study was purchased from Sigma–Aldrich, Germany.

2.2. Synthesis of GO

GO was synthesized using the modified Hummers method [33]. Briefly, approximately 2 g of natural graphite flakes was dispersed in ~ 46 mL of concentrated sulfuric acid in a round bottom flask with vigorous stirring to form a homogeneous suspension in an ice bath (~ 0 – 5 °C). Then, 6 g of potassium permanganate was added slowly to the flask and stirred for 2 h. The flask was then transferred to a preheated oil bath at 35 ± 2 °C under constant stirring for 6 h to produce a thick paste. After that, ~ 92 mL of de-ionized (DI) water was carefully added to the reaction mixture and stirred for another 1 h. Then, ~ 280 mL of DI water was added to the deep brown reaction mixture followed by the addition of 35% hydrogen peroxide until the color changed to bright yellow. Finally, a dilute hydrochloric acid solution (5% by volume) was added to remove the manganese ions from graphite oxide. The synthesized brownish GO was washed with DI water several times until the pH of the solution was neutral. In order to obtain GO, the desired amount of GO was dispersed in DI water (1 mg mL^{-1}), sonicated for approximately 30 min followed by centrifugation to remove the un-exfoliated part. The resultant stable dispersion contained GO was collected through freeze drying.

2.3. Synthesis of NFrGO

SPEEK was synthesized by treating PEEK in concentrated H_2SO_4 . Briefly, PEEK pellets (5 g) were slowly added to 100 mL of concentrated H_2SO_4 (95–98% purity) under vigorous stirring at room temperature. After complete dissolution of PEEK in sulfuric acid, the solution was heated at 55 °C with vigorous stirring for 4 h.

The solution was then cooled to room temperature and slowly added to ice cold water for precipitation. The resulting precipitate was then washed with DI water several times until the pH of the filtrate became neutral. The product was dried at 60 °C in a vacuum oven to obtain SPEEK. The NFrGO was prepared by treating the aqueous solution mixture of GO and SPEEK with hydrazine [34]. The details of the procedure can be described as follows: 100 mg of GO was homogeneously dispersed in 100 mL of water in a conical flask via ultrasonication for 30 min. Approximately 100 mg of SPEEK was dissolved in 100 mL of DI water at 60 °C in another flask. Then, the SPEEK solution was added to the GO dispersion with constant stirring and allowed to sonicate for 1 h to achieve a homogeneous solution. After that, the solution was treated with a measured amount of hydrazine monohydrate (0.1 mL) and refluxed for ~ 6 h at 100 °C. The final product was filtered and washed through a CA membrane (0.2- μm pore size) to remove excess SPEEK. The obtained product was collected by drying at 60 °C in a vacuum for 72 h.

2.4. Preparation of NFrGOs-CANC

NFrGOs-CANC films with various amounts of NFrGO content were prepared using polyethylene glycol as a plasticizer by a conventional solution casting technique. In a typical procedure, the weighted amount of NFrGO was dispersed in 10 mL of DMF by ultra-sonication and the desired amount of CA and a polyethylene glycol mixture was separately dissolved in 10 mL of DMF. NFrGO dispersion was then poured into the polyethylene glycol mixture with constant stirring and allowed to sonicate for another 30 min to obtain the homogeneous solution. The resultant mixtures were poured into Petri dishes and the solution was allowed to evaporate at 60 °C to obtain the NFrGO-CANC films. A pure CA film was prepared in a similar procedure (evaporating only the CA-PEG solution mixture) without using any NFrGO. 0.5, 1.0, 1.5 and 2.0 wt.% NFrGO-CANC films were prepared and designated as NFrGO0.5-CANC, NFrGO1.0-CANC, NFrGO1.5-CANC and NFrGO2.0-CANC, respectively. The preparation of the NFrGOs-CANC nanocomposites is depicted in Scheme 1.

2.5. Characterization techniques

The dispersion characteristics of GO, RGO and NFrGO in DMF were measured by UV–visible (UV–vis) spectroscopy using a UVS-2100 SCINCO spectrophotometer. Fourier transform infrared (FT-IR) spectroscopy of GO, RGO and the nanocomposites films was performed with a Nicolet 6700 spectrometer (Thermo Scientific, USA) over a wide range of 4000 – 400 cm^{-1} . Transmission electron microscopy (TEM) (JEOL JEM-2200 FS, Japan) in Jeonju Center of KBSI was used to study the morphology of NFrGO. The X-ray diffraction (XRD) of pure CA and nanocomposites were conducted at room temperature on a D/Max 2500 V/PC (Rigaku Corporation, Japan) ($\text{Cu K}\alpha \sim 0.1541 \text{ nm}$) at a scan rate of $2^\circ (2\theta) \text{ min}^{-1}$. Field emission scanning electron microscopy (FE-SEM) was performed to investigate the morphology of pure CA and the nanocomposite films by free fracturing in liquid nitrogen and sputtering with osmium prior to imaging. Thermogravimetric analysis (TGA) was performed on a Q50 TGA (TA instruments, USA) from a wide range of 40 – 800 °C at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere. Differential scanning calorimetry (DSC, TA Instruments, USA) studies were conducted under a nitrogen atmosphere with a heating rate of 10 °C min^{-1} . The tensile testing of the resultant nanocomposite films were performed using a universal test machine (LR5 K, Lloyd Co., England) under a crosshead speed 1 mm min^{-1} at room temperature. The specimens were prepared and then at least six samples were tested for tensile behavior and statistically average

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