



The composites based on plasticized starch and graphene oxide/reduced graphene oxide

Tiantian Ma^a, Peter R. Chang^b, Pengwu Zheng^c, Xiaofei Ma^{a,*}

^a Chemistry Department, School of Science, Tianjin University, Tianjin 300072, China

^b Bioproducts and Bioprocesses National Science Program, Agriculture and Agri-Food Canada, 107 Science Place, Saskatoon, SK S7N 0X2, Canada

^c School of Pharmacy, Jiangxi Science and Technology Normal University, Nanchang, Jiangxi 330013, China

ARTICLE INFO

Article history:

Received 28 September 2012

Received in revised form 4 January 2013

Accepted 6 January 2013

Available online 11 January 2013

Keywords:

Polymer–matrix composites (PMCs)

Thermal analysis

Casting

Graphene oxide

ABSTRACT

The graphite was oxidized to prepare graphene oxide (GO), and GO was reduced by glucose to obtain reduced graphene oxide (RGO) sheet. There were abundant and residual oxygen-containing groups on GO and RGO, respectively. Compared to graphite, the GO and RGO sheets appeared flat and transparent, and the aqueous suspensions followed the Lambert–Beer's law well. The composites were also fabricated by using GO and RGO as the filler in plasticized-starch (PS) matrix. Because of more oxygen-containing groups, GO could form the stronger interaction with PS matrix than RGO. And GO/PS composites exhibited better tensile strength, elongation at break and moisture barrier than RGO/PS composites, but lower thermal stability. GO/PS composites could protect against UV light, while the conductivities of RGO/PS composites could reach 1.07×10^{-4} , 6.92×10^{-4} and 0.01 S/cm, respectively stored at RH50, 75 and 100%.

Crown Copyright © 2013 Published by Elsevier Ltd. All rights reserved.

1. Introduction

Nanocomposites based on natural polymers and nanometer-scale fillers are of scientific and industrial interest for use as alternatives to traditional plastic materials such as polyolefins. Due to excessive consumption and poor degradation of plastics, a massive accumulation of plastic waste has been disposed in the environment (Rodríguez, Galotto, Guarda, & Bruna, 2012). As a natural polysaccharide from a great variety of crops, starch has been investigated widely for the potential manufacture of degradable products, including water-soluble pouches for detergents and insecticides, flushable liners and bags, and medical delivery systems and devices (Fishman, Coffin, Konstance, & Onwulata, 2000). The nanometer-scale fillers are often introduced into a plasticized-starch (PS) matrix to improve the tensile strength and water barrier properties, and to add to the functional properties (Sreekumar, Gopalakrishnan, Leblanc, & Saiter, 2010). Recently, carbon materials have also been used as filler in the preparation of PS-based composites. Carbon nanotube (CNT) has been incorporated into PS matrix resulting in enhanced mechanical strength and electrical conductivity (Famá, Pettarin, Goyanes, & Bernal, 2011; Liu, Chang, et al., 2011; Liu, Zhao, Chen, & Yu, 2011; Ma, Yu, & Wang,

2008). Carbon black was also added into PS matrix to obtain electrically conductive composites, prepared by both melt extrusion and microwave radiation (Ma, Chang, Yu, & Lu, 2008). The composites prepared using microwave radiation exhibited better properties, including reinforcing effect, conductivity and water vapor barrier, than those from melt extrusion.

Graphene is a two-dimensional sheet of sp^2 -hybridized carbon arranged in a hexagonal lattice with a high surface area, excellent mechanical properties, and electrical conductivity. Recently, much work has focused on mechanically or electrically enhanced polymers using nanosheets of graphene oxide (GO) or reduced graphene oxide (RGO) as nanofillers (Feng, Zhang, Shen, Yoshino, & Feng, 2012; Potts, Dreyer, Bielawski, & Ruoff, 2011). It is well known that good interaction between the filler and matrix is necessary to obtain the best characteristics in composites. The hydrophilic GO can form strong hydrogen bonding interactions with multiple hydroxyl groups in starch due to the various oxygen functional groups of GO, including hydroxyls, epoxides, carbonyls and carboxyls (Li, Liu, & Ma, 2011). After the reduction process, the carbon arranged in the hexagonal lattice was mostly removed, and the RGO exhibited conductivity. The residual oxygen-containing groups on RGO can still form interactions with starch as well. In this study, graphite was oxidized to prepare GO using a modified Hummer's method and reduced by glucose to obtain RGO sheets. The GO and RGO sheets were explored for use as fillers in the preparation of GO/PS and RGO/PS composites with improved mechanical

* Corresponding author. Tel.: +86 22 27406144; fax: +86 22 27403475.

E-mail address: maxiaofei@tju.edu.cn (X. Ma).

and moisture barrier properties of the PS matrix, and may find their niche in applications such as ultraviolet–visible absorbance or electrical conductivity.

2. Experimental

2.1. Materials

Potato starch was supplied by Manitoba Starch Products (Manitoba, Canada). Natural graphite flakes were provided by Qingdao Tianhe Graphite Co., Ltd., China. The reagents (37.5% HCl, 98% H₂SO₄, 30% H₂O₂, 30% NH₃) and the analytical grade reagents (NaNO₃, KMnO₄, glucose, glycerol) were purchased from Tianjin Jiangtian Chemical Reagent Co., Ltd., China.

2.2. Preparation of GO and RGO

The GO was prepared by oxidizing graphite using a modified Hummer's method (Hummers & Offeman, 1958). Concentrated H₂SO₄ (46 mL) and NaNO₃ (1 g) were added into a flask and cooled to below 5 °C, followed by the addition of graphite (2 g). Solid KMnO₄ (6 g) was gradually added under stirring and stirred for 1 h at below 20 °C. The temperature was then increased and kept at 35 °C for 2 h. 92 mL distilled water was then added, and the temperature was increased to 98 °C for another 15 min. Excess distilled water (150 mL) was added to the mixture followed by 30% H₂O₂ (5 mL). The mixture was immediately centrifuged and the resulting GO sheets were washed three times with 5% aqueous HCl to remove metal ions, and then washed with distilled water to remove the acid. The GO sheets were air dried and dispersed in water.

The GO was reduced by glucose to obtain RGO sheets using the modified method of Wang et al. (2011). Typically, 2 g glucose was added into 250 mL of homogeneous GO dispersion (0.5 mg/mL), followed by stirring for 30 min. Then, 1 mL ammonia solution (30%, w/w) was added and stirred for 10 min. The RGO reaction was then kept at 95 °C for 60 min. The resulting black dispersion was filtered and washed with water several times.

2.3. Preparation of GO/PS and RGO/PS composites

GO and RGO were, respectively, dispersed into solutions of distilled water (100 mL) using ultrasonication for 10 min. The GO loading levels (0, 0.5, 1, 2, 3 and 4 wt%) and RGO loading levels (0, 2, 4, 6 and 8 wt%) were based on starch. Glycerol (1.5 g) and starch (5 g) were added to the obtained GO or RGO suspensions. The mixture was then heated at 90 °C for 0.5 h with constant stirring to plasticize the starch. The mixture was cast into a film and dried in an air-circulating oven at 50 °C. The GO/PS and RGO/PS composite films were preconditioned in a climate chamber at 25 °C and 50% RH for at least 48 h prior to testing.

2.4. Fourier transform infrared spectroscopy (FTIR)

FTIR analysis of graphite, GO, and RGO was performed on a BIO-RAD FTS3000 IR Spectrum Scanner. The sample powders were evenly dispersed in KBr and pressed into transparent sheets for testing.

2.5. Thermogravimetric (TG) analysis

Thermal properties of raw graphite, GO, RGO and the composites were measured with a ZTY-ZP type thermal analyzer. The sample weights were about 15 mg and they were heated from room temperature to 500 °C at a heating rate of 15 °C/min in a nitrogen atmosphere.

2.6. Scanning electron microscopy (SEM)

The graphite and the fracture surfaces of GO/PS composites were viewed by a NanoSEM 430 scanning electron microscope, while GO, RGO, and the fracture surfaces of RGO/PS composites were tested using an S-4800 scanning electron microscope. The graphite, GO, and RGO were, respectively, dispersed into water using ultrasonication for 5 min. The suspension drops were drawn on a glass flake, dried to remove water, and then vacuum coated with gold for SEM testing. The GO/PS and RGO/PS composites were cooled in liquid nitrogen and then broken. The fracture faces were vacuum coated with gold for SEM testing.

2.7. UV–visible (UV–vis) spectra

The UV–visible spectra of the aqueous solutions with different concentrations of graphite, GO, and RGO and the GO/PS composites were recorded from 200 to 800 nm using a UV–vis spectrophotometer model U-1800, Hitachi Company. The UV–visible spectrums of GO/PS composites were recorded using a blank glass plate as reference.

2.8. Dispersion in aqueous solutions

The graphite, GO, and RGO were, respectively, added to H₂O and the mixtures were dispersed by ultrasonication for 10 min. And water was added to obtain the solution with low concentration. Photos of the graphite, GO, and RGO dispersions were taken with a digital camera.

2.9. Mechanical testing

The Testometric AX M350-10KN Materials Testing Machine was operated at a crosshead speed of 50 mm/min for tensile testing (ISO 1184-1983 standard). The data was averaged over 6–8 specimens.

2.10. Water vapor permeability (WVP)

WVP tests were carried out by ASTM method E96 (1996) with some modifications (Guilherme, Mattoso, Gontard, Guilbert, & Gastaldi, 2010). The films were cut into circles, sealed over with melted paraffin, and stored in a desiccator at 25 °C. RH (relative humidity) 0% was maintained using anhydrous calcium chloride in the cell. Each cell was placed in a desiccator containing saturated sodium chloride to provide a constant RH 75%. Water vapor transport was determined by the weight gain of the permeation cell. Changes in the weight of the cell were recorded as a function of time. Slopes were calculated by linear regression (weight change vs. time) and correlation coefficients for all reported data were >0.99. The water vapor transmission rate (WVTR) was defined as the slope (g/s) divided by the transfer area (m²). After the permeation tests, film thickness was measured and WVP (g Pa⁻¹ s⁻¹ m⁻¹) was calculated as

$$WVP = \frac{WVTR}{P(R_1 - R_2)} \cdot x \quad (1)$$

where P is the saturation vapor pressure of water (Pa) at the test temperature (25 °C); R_1 is the RH in the desiccator; R_2 , the RH in the permeation cell; and x is the film thickness (m). Under these conditions, the driving force [$P(R_1 - R_2)$] is 1753.55 Pa.

2.11. Electrical conductivity

The RGO/PS composite films were stored in closed chambers over various materials at 20 °C for several days. The materials used were substantive 35.64% CaCl₂ solution, saturated NaCl solution,

Download English Version:

<https://daneshyari.com/en/article/10601551>

Download Persian Version:

<https://daneshyari.com/article/10601551>

[Daneshyari.com](https://daneshyari.com)