Mechanical, thermal, structural and barrier properties of crab shell chitosan/graphene oxide composite films

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ABSTRACT

To enhance the thermo-mechanical properties of food packaging materials, chitosan-based nano-composite films were prepared by blending crab shell chitosan (CS) and graphene oxide (GO) nanosheets in solution at selected concentrations (0.5, 1 and 2% w/w). The addition of GO did not influence the mechanical rigidity of the CS/GO blend in solution although the dielectric properties were influenced. Mechanical, thermal, structural, and barrier properties of blended films were compared with the neat film. By introducing GO, a more compact CS/GO network structure was formed with improved tensile properties and glass transition temperature (T_g) for the composite films. The addition of GO to the CS significantly lowered the lightness (L^*) value and UV light transmittance. GO was effective in enhancing the tortuosity of the diffusive path for the oxygen and water vapours to diffuse through the CS nano-composite film. Fourier transform infrared spectroscopy (FTIR) indicated an intermolecular hydrogen bond formation between CS and GO. The presence of GO clusters in the composite films and the change in the topography of CS/GO films were visualized through SEM and AFM measurements.

1. Introduction

Biodegradable packaging materials have created interest among consumers and researchers because of their biodegradability and compostability, and additionally, they are obtained either from natural sources or from biological waste materials. Among bio-polymers, chitin is the second most abundant polysaccharide found in nature (Muzzarelli, Greco, Busilacchi, Sollazzo, & Gigante, 2012). Chitosan (CS), a derivative of chitin, has been considered as a fu-turistic biopolymer because of its wide potential in the area of biomedical engineering, wound dressing, cosmetics and food packaging. CS has the potential to form a good film with antimi-crobial/antifungal activity, non-toxicity, and selective permeability to gases (Leceta, Guerrero, Ibarburu, Due nas, & de la Caba, 2013; Szymańska & Winnicka, 2015). Chitosan from crab shell (CS) has the advantages of excellent functional properties and great biocompatibility (Pradhan, Shukla, & Dorris, 2005). However, CS has many limitations as a film-forming material such as poor thermal stability (Paulino, Simionato, Garcia, & Nozaki, 2006) high water vapor permeability (Butler, Vergano, Testin, Bunn, & Wiles,

1996) and ultraviolet (UV) degradation (Yeh et al., 2006) which restrict its application in food packaging.

Various approaches have been made to improve the mechanical and thermal properties of the chitosan films by reinforcing nano-particles (NPs) including the incorporation of clay (Casariego et al., 2009), silver NPs (Yoksan & Chirachanchai, 2010), colloidal copper NPs (Cárdenas, Meléndrez, & Cancino, 2009), and multiwalled carbon nanotube (Hernández-Vargas et al., 2013). Recently, gra-phene oxide (GO) nanosheets, a novel two-dimensional nano-material prepared from natural graphite has attracted significant attention owing to its novel structure, greater chemical stability, superior mechanical property, biocompatibility and most impor-tantly its hydrophilic character so that an aqueous colloidal sus-pension of GO can easily be obtained by the complete exfoliation of bulk GO via simple sonication in water (Acik et al., 2010; Dikin et al., 2007). GO has been doped with various matrices including CS, starch, cellulose, polylactide and gelatin to produce functional biopolymer based nanocomposites with improved thermal, me-chanical and electrical properties (Han, Yan, Chen, & Li, 2011; Khan et al., 2016; Kumar & Koh, 2014; Layek, Kundu, & Nandi, 2013; Shen et al., 2012; Wan, Frydrych, & Chen, 2011). Nonetheless, it has been reported that the excess loading of GO has a negative effect on the microstructure of the composite, and even forms an aggregate

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because of the inadequate compatibility between the GO and polymer chains. Therefore, it is important to elucidate the compatibility and miscibility of GO into the polymer matrix which again depends upon molecular weight, pH and solution rheology. The objective of this study was to understand the compatibility between CS and GO for film formation, and thereafter, to characterize the developed films in terms of thermomechanical, optical, barrier, structural, and morphological properties.

2. Materials and methods

2.1. Materials

Highly viscous crab shell CS powder (deacetylation degree approximately 80%) and GO nanosheets (Product # 796034) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Glacial acetic acid and glycerol were procured from VWR (France) and SD Fine Chemicals Limited (Mumbai, India), respectively.

2.2. Chitosan film preparation

CS-based nanocomposite films were prepared by the solution casting as described by Han et al. (2011) with some modifications. A desired amount of GO powder (0.5, 1 and 2 g) was dispersed into 50 ml of distilled water and was sonicated for 30 min in a 250 mL beaker for the homogenization of NPs. About 2 g CS flakes were dissolved in 50 ml 2% acetic acid in a beaker separately (3 sets) using magnetic stirrer for 4 h at 30 °C. Finally, both solutions were mixed together to obtain desirable concentrations of GO in the final blend solution (0.5, 1 and 2% w/w). The film-forming suspension was cast on a rimmed silicone resin plate (5 × 5 cm^2) and dried under ambient conditions. For easy peeling, solidified films were kept in a constant temperature oven at 60 ± 0.2 °C for 4 h at a relative humidity of 0%. The resulting nanocomposite films were kept in desiccator for further analysis.

2.3. Measurement of film forming solution rheology

To understand the dispersion behavior among constituents in solution, oscillatory rheology was performed. The rheological measurements of the solutions (CS and CS/GO) were performed in a Discovery Hybrid Rheometer HR-3 (TA Instruments, New Castle, DE, USA) at 20 °C. A cone-plate geometry with a diameter of 40 mm and a cone angle of 2° was employed with a gap of 57 μm. Oscillatory measurements were carried out in the frequency range of 0.1–10 Hz within the linear viscoelastic range. All measurements were performed in duplicates.

2.4. Measurement of film forming solution dielectric properties

A network analyzer (Model: N5234A PNA-L, Keysight Technologies, Santa Rosa, CA) with an open-ended coaxial cable connected to a dielectric probe (N1501A, Keysight Technologies, Santa Rosa, CA) was employed to measure the dielectric properties of CS and CS/GO solutions. The built-in S-parameter test set provided a complete range of magnitude and phase measurements in both the forward and the reverse directions. The instrument was warmed up for at least 1 h and then calibrated with air, short-circuit block, and water at 20 °C. The sample of approximately 40 ml was placed in a 50 ml glass beaker and the open coaxial probe was set into the tube. The dielectric properties were measured in the frequency range of 750–3500 MHz. The dielectric spectra of the samples (dielectric constant ε' and dielectric loss factor ε'') were automatically computed and recorded with the manufacturer supplied computer software. All of the measurements were carried out in triplicate and

were reproducible to ±5%.

The penetration depth (D_p) of the sample was calculated according to von Hippel (1954). Details are available elsewhere (Ahmed & Luciano, 2009):

$$Dp = \frac{\lambda_o}{2\pi\sqrt{2\varepsilon'\left(\sqrt{1 + \left(\frac{\varepsilon''}{\varepsilon'}\right)^2} - 1\right)}} \tag{1}$$

where λ_0 values are 0.328 m and 0.122 m at 915 MHz and 2450 MHz, respectively.

2.5. Determination of film properties and characterization

2.5.1. Moisture content, thickness and color

The moisture content of the CS and CS/GO films were measured using a hot air oven at 100 ± 2 °C to a constant weight (Leceta et al., 2013). Film thickness was measured by a digital micrometer (MCD-1″PXF, Mituyoto Corp., Kawasaki-shi, Japan) with sensitivity of 0.001 mm, at ten random locations of each film.

The color of the films was determined using a CIE colorimeter (Hunter associates laboratory, Inc., Reston, VA, USA) in terms of lightness (L^*), redness/greenness (a^*), and yellowness/blueness (b^*) values. The total color difference (ΔE^*) was calculated using the following equation (2):

$$\Delta E^* = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{0.5} \tag{2}$$

where, ΔL^*, Δa^* and Δb^* are the differences between the corresponding color parameter of the samples and that of white standard ($L^* = 93.76$, $a^* = -1.39$, and $b^* = 0.25$). For each film five readings were taken and the average values were determined.

2.5.2. Mechanical properties

Tensile strength (TS) and elongation at break (EAB) of films were measured using a Texture Analyzer TA.XT plus (Stable Micro Systems, UK) with a 50 N load cell equipped with tensile grips (A/TG model) (D882, ASTM, 2002). Grip separation was set at 30 mm and cross-head speed was 50 mm/min. TS and EAB were evaluated in ten samples from each type of film.

2.5.3. Thermal property measurement

Thermal analysis was carried out using a TA Q2000 differential scanning calorimeter (DSC) (TA Instruments, New Castle, DE) with indium under an ultrahigh purity nitrogen atmosphere (flow rate, 50 ml/min). Briefly, 8–10 mg samples were run at a 20 °C/min heating/cooling ramp in two heating-cooling cycles. In the 1st cycle, film samples were equilibrated at 100 °C and isothermed for 1 min; heated to 300 °C at 20 °C/min and isothermed for 1 min. In the 2nd cycle, film samples were equilibrated at 300 °C and isothermed for 1 min; cooled to 100 °C at 10 °C/min and isothermed for 1 min. Thermal scans for each sample were carried out in triplicate and the average values were reported. The glass transition temperature (T_g) was analyzed from the 2nd heating/cooling cycle.

2.5.4. UV-barrier, light transmittance and transparency values

CS and CS/GO films were cut into 2.0 cm × 2.0 cm pieces. The percent transmittance (%T) of the films was measured at the UV (200, 280, and 350 nm) and visible (400, 500, 600, 700 and 800 nm) wavelengths using a spectrophotometer (Shimadzu UV-1800, Kyoto, Japan). The transparency value (TV) of films was calculated following equation (3):