Properties and structural characterization of chitosan/poly(vinyl alcohol)/graphene oxide nano composites

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Abstract: Chitosan (CS)/poly(vinyl alcohol) (PVA)/graphene oxide (GO) nanocomposites in the form of films are prepared in a casting and solvent evaporation method. Fourier-transform infrared spectroscopy (FTIR), X-ray diffractions (XRD), atomic force microscopy (AFM), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), tensile testing and moisture uptake were used to study the structure and properties of these chitosan/poly(vinyl alcohol) /graphene oxide (PCS/GO-n) nanocomposites. The result from tensile testing indicated that the nanocomposite containing 2 wt% GO exhibits high tensile strength (71.21 MPa) with a large elongation at break (51.8%). The high mechanical properties of the nanocomposite films are mainly due to uniform dispersion of GO sheets in the polymer matrix and strong interfacial interactions among components.

Keywords: Graphene oxide, Nanocomposites, Interaction, Properties

Introduction

Chitsan (CS), a (1-4)-linked 2-amino-2-deoxy- β -D-glucopyranose, is derived from chitin, a (1-4)-linked 2-acetamido-2-deoxy- β -D-glucopyranose [1]. As one of the most abundant natural polysaccharides, CS is well known for its good biocompatibility, biodegradability, antibacterial properties and multiple functional groups, CS has been widely investigated for several decades in applications such as biosensors, tissue engineering, separation membranes, food packaging films, artificial skin and water engineering [2, 3]. However, films made only from chitosan exhibit poor mechanical properties, low thermal stability and poor water resistance, which restrict them from more wide-ranging applications. A convenient and effective method to overcome these drawbacks is blending with synthetic or natural polymers [4]. In fact, chitosan (CS)/poly(vinyl alcohol) (PVA) blend film has been investigated as a potential polymer in several studies; however, because PVA is only partially compatible with CS, the tensile strength and elongation at break of the CS/PVA composites were not significantly improved. On the other hand, nanocomposite technology using nano-fillers such as carbon nanotubes, clay and silica has already proved to be another effective way to improve the mechanical, electrical and thermal properties of polymers [5-8]. Recently, a new application of graphene oxide (GO) as a nano-filler in polymer matrices to prepare polymer nanocomposites has also been explored and reported [9-11]. GO, an oxygen-rich carbonaceous layered material, is produced by the controlled oxidation of graphite [12-14]. Each layer of GO is an oxidized graphene sheet commonly referred to as graphene oxide [15]. According to recent studies [16-21], GO consists of covalently attached oxygen groups such as hydroxyl, epoxy,

carbonyl and carboxyl groups [22, 23]. Hence, GO is hydrophilic and readily swell and disperse in water [24, 25]. The facts that GO has so much oxygen-containing functional groups and can disperse well in water, which are able to interact by hydrogen bonding with -NH_2 groups of CS and -OH groups of PVA in the aqueous system. The use of GO represents a cross-linking agent to obtain interacting polymers which can promote the miscibility between CS and PVA molecules, and then produce a compatible blend with enhanced properties.

Herein, we report an investigation into the aqueous solution processing of GO nanosheets into the CS/PVA blend matrix. The effect of graphene oxide loadings on the structures and properties of chitosan (CS)/poly(vinyl alcohol) (PVA)/graphene oxide (GO) (PCS/GO-n) nanocomposite is investigated. The structure, thermal and mechanical properties of the nanocomposite films are studied by Fourier transform infrared (FT-IR) spectroscopy, wide-angle X-ray diffraction (XRD), atomic force microscopy (AFM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and tensile testing.

Results and discussion

Structural analysis

To reveal the interactions between GO nanosheets and CS/PVA matrix, FTIR spectra of PCS/GO-0 film and PCS/GO-4 hybridized film are acquired and shown in Figure 1(b).

Fig. 1(a). FT-IR spectra of GO.

Additionally, the FTIR spectrum of GO is also shown in Figure 1(a). The FTIR spectrum of the GO shows a broad absorption band at 3435 cm^{-1} , which is related to the OH groups, and absorption bands at 1636 cm^{-1} and 1390 cm^{-1} , which are typical of carbonyl and carboxyl groups [26]. For the chitosan/poly(vinyl alcohol) film (PCS/GO-0), the broad band at 2950-3200 cm^{-1} was the OH stretching vibrations,

which overlapped the N–H stretching vibrations in the same region. The peaks near 2880 cm^{-1} were typical C–H stretching vibrations [27]. A small peak near 1641 cm^{-1} was due to the C=O stretching vibrations (amide I). The band at 1545 cm^{-1} was the N–H bending vibrations (amide II) and the bands at 1022 cm^{-1} corresponded to C–O bond stretching [28, 29]. Compared with PCS/GO-0 film, PCS/GO-4 showed that the amide I ($\nu_{\text{C=O}} \sim 1641\text{ cm}^{-1}$) and amide II ($\delta_{\text{-NH}_2} \sim 1545\text{ cm}^{-1}$) shifted to higher frequency ($\nu_{\text{C=O}} \sim 1645\text{ cm}^{-1}$, $\delta_{\text{-NH}_2} \sim 1553\text{ cm}^{-1}$). Meanwhile, the –OH group band at 3216 cm^{-1} in matrix shifted toward high frequency. Changes in characteristic spectra peaks may reflect how components are mixed or interacted, physically or chemically [30, 31]. This result indicated that an enhanced hydrogen-bonding interaction generated between the chitosan, poly(vinyl alcohol) and GO nanosheets.

Fig. 1(b). FT-IR spectra of PCS/GO-0 film and PCS/GO-4 nanocomposite films.

The XRD patterns of the original materials and resulting nanocomposites are shown in Figure 2. In Figure 2(b), the characteristic XRD diffraction peak of GO sheets appeared at $2\theta = 11.5^\circ$. The interlayer distance was estimated from Bragg's law, $2d\sin\theta = \lambda$, corresponding to a d-spacing of 0.77 nm [32]. Chitosan (CS) film shows two main diffraction peaks around $2\theta = 13.0^\circ$ and 19.2° and two broad peaks around $2\theta = 9.2^\circ$ and 25° with low intensity. PVA showed an obvious diffraction peak at $2\theta = 19.28^\circ$ [33]. This peak may be attributed to the strong intermolecular interaction between PVA chains through the intermolecular hydrogen bond [34].

The XRD patterns of PCS/GO-*n* nanocomposites are shown in Figure 2(a). The PCS/GO-*n* nanocomposites show XRD patterns similar to that of the PCS/GO-0 blend film. It is hard to find the characteristic peaks of GO in the composites, which indicated that GO was uniformly dispersed in CS/PVA blend matrix and the

crystalline structure of CS/PVA was slightly affected by the incorporation of GO component.

Fig. 2. XRD patterns of PCS/GO-n nanocomposite films (a) and CS, PVA and GO (b).

Morphological image analysis

Fig. 3a and b shows high resolution and low magnification transmission electron microscopy (TEM) images of graphene oxide nanosheets. The central parts of the GO appear on TEM images as homogeneous and featureless region, whereas the edges of GO tend to scroll (Fig. 3b). In general, graphene oxide nanosheets tend to congregate together to form multilayer agglomerates [26]. For monolayer graphene oxide, a fold exhibits only one dark line. Scrolls and multiple folds can give rise to many number of dark lines even for monolayer graphene oxide, as indeed observed experimentally [35].

Fig. 3. TEM micrographs of GO.

In order to observe the morphology of the surfaces of the films, the atomic force microscopy (AFM) micrographs of the PCS/GO-0, PCS/GO-2, PCS/GO-4 and PCS/GO-6 composites are shown in Fig. 4. Surfaces of films were compared in terms of some of the roughness parameters, such as the mean roughness (R_a) and the root mean square of the Z data (R_q) [36]. The mean roughness is the mean value of surface relative to the center plane, the plane for which the volume enclosed by the image above and below this plane are equal, and is calculated as [37].

$$R_a = \frac{1}{L_x L_y} \int_0^{L_x} \int_0^{L_y} |f(x, y)| \, dx dy \quad (2)$$

Where $f(x, y)$ is the surface relative to the center plane and L_x and L_y are the dimensions of the surface.

The root mean square of the Z values (R_q) is the standard deviation of the Z values within the given area and is calculated as

$$R_q = \sqrt{\frac{\sum (Z_i - Z_{avg})^2}{N}} \quad (3)$$

Where Z_{avg} is the average of the Z values within the given area; Z_i , the current Z value; and N , the number of points within a given area. As shown in Fig. 4, the surface morphologies of PCS/GO-2, PCS/GO-4 and PCS/GO-6 composites were very different from PCS/GO-0 film. The surface roughness parameters of PCS/GO-2, PCS/GO-4 and PCS/GO-6 films calculated by Nanoscope Multimode processing software, such as the mean roughness (R_a) and the root mean square of the Z data (R_q) listed in Table 1 were lower than that of PCS/GO-0 film ($R_a = 9.783 \text{ nm}$, $R_q = 13.648 \text{ nm}$), especially for the PCS/GO-4 film with the lowest surface roughness parameters ($R_a = 1.298 \text{ nm}$, $R_q = 1.800 \text{ nm}$). The results indicated that the incorporation of GO enhanced the compatibility between CS and PVA and the GO fillers were dispersed uniformly in the matrix. This could be attributed to plenty of oxygen functional groups on the surface of GO, which were of benefit to form strong hydrogen bonding with both CS and PVA molecules. However, when GO loading was 3.0 wt%, the depressions could be observed on the surface of the PCS/GO-6

film, resulting in a higher roughness ($R_a = 1.681$ nm, $R_q = 2.302$ nm). The difference of microstructure was presumably due to the poor dispersion and aggregations of GO at high loading levels.

Fig. 4. AFM micrographs of PCS/GO-0, PCS/GO-2, PCS/GO-4 and PCS/GO-6 nanocomposite films.

Tab. 1. Codes of the samples, thermal analyses of PCS/GO-n nanocomposite films measured from the TGA and DSC curves; roughness parameters for surfaces measured from AFM and B .

Code	PCS/ GO-0	PCS/ GO-1	PCS/ GO-2	PCS/ GO-3	PCS/ GO-4	PCS/ GO-5	PCS/ GO-6
CS (g)	2.00	2.00	2.00	2.00	2.00	2.00	2.00
PVA (g)	0.50	0.50	0.50	0.50	0.50	0.50	0.50
GO (wt %)	0.00	0.50	1.00	1.50	2.00	2.50	3.00
T_{max} (°C)	285.57	—	285.60	—	285.58	—	285.66
T_m (°C)	174.40	—	188.40	—	188.90	—	191.40
R_a (nm)	9.78	—	4.74	—	1.29	—	1.68
R_q (nm)	13.65	—	6.00	—	1.80	—	2.30
B	—	0.33	0.71	0.74	1.26	0.41	0.01

T_{max} , temperature of the maximum rate of weight loss;

T_m , melting temperature;

R_a , mean roughness;

R_q , root mean square (RMS) of Z values;

B , interface interaction parameter.

Thermal analysis

The thermal stability of the PCS/GO-0, PCS/GO-2, PCS/GO-4 and PCS/GO-6 nanocomposites films was studied by thermogravimetric analysis (TGA) shown in Fig. 5(a). The initial weight loss of all samples, at 50-100 °C, was due to evaporation of water and solvent, whereas the weight loss in the second range (250-350 °C) corresponded to a complex process including the dehydration of the saccharide rings and depolymerization [38]. The temperatures of maximum loss ratio ($T_{\max}$) for PCS/GO-0, PCS/GO-2, PCS/GO-4 and PCS/GO-6 nanocomposites films are listed in Table 1. It can be seen that the $T_{\max}$ values of PCS/GO-2, PCS/GO-4 and PCS/GO-6 nanocomposite films are similar to that of PCS/GO-0. This could be explained that the loading levels of the GO were low so that it can hardly affect the decomposition temperature of the nanocomposite films.

Fig. 5(a). TGA curves of PCS/GO-0, PCS/GO-2, PCS/GO-4 and PCS/GO-6 nanocomposite films.

DSC traces of PCS/GO-0, PCS/GO-2, PCS/GO-4 and PCS/GO-6 nanocomposites films are shown in Fig. 5(b). Two endothermic peaks were detected for most of the films. The first endothermic peak that occurs over the temperature range of 94-100 °C was attributed to solvent evaporation [39-41], while the peaks in another endotherm at high temperature, corresponding to the crystalline melting point (T_m) were found in the DSC. Compared with the T_m of PCS/GO-0 matrix (174.4 °C), the melting temperatures of PCS/GO-2, PCS/GO-4 and PCS/GO-6 composites obviously increase. This is because hydrogen bonding generated among GO, CS and PVA and GO nanosheets plays the role of physical cross-linking points and restricts the

movement of molecular chains to decrease the entropy of blend. Hence, this results in an improved melting temperature of the films. The obtained results are presented in Table 1.

Fig. 5(b). DSC curves of PCS/GO-0, PCS/GO-2, PCS/GO-4 and PCS/GO-6 nanocomposite films.

Mechanical Properties

To illustrate the effect of the GO on the mechanical properties of PCS/GO-*n*, corresponding data for PCS/GO-0 were used as controls. The mechanical properties of the blends (PCS/GO-*n*) are shown in Figure 6(a). In the PCS/GO-*n* nanocomposite films, when the GO loading was 2.0 wt%, σ_b and ε_b simultaneously reached a maximum of 71.74 MPa and 51.8%, respectively. The obvious improvement in σ_b and ε_b for such extremely low GO loading levels may be attributed to the following factors: First, permeation required for the small-size effect. Second, GO consists of a two-dimensional (2D) sheet of covalently bonded carbon atoms bearing various oxygen functional group (e.g. hydroxyl, epoxy, and carbonyl groups) on their basal planes and edges. Therefore, there are plenty of intermolecular hydrogen bonding formed between GO and CS/PVA, which increased the miscibility and greatly improved the mechanical properties of the films. Meanwhile, the reinforcement effect can be quantitatively evaluated by measuring the increasing rates of Young's modulus ($\frac{dY_c}{d\phi_f}$) at low GO volume fractions (ϕ_f) for PCS/GO-*n* composites [33]. As

shown in Figure 6(b), Y_c increased with ϕ_f , and $\frac{dY_c}{d\phi_f}$ is fitted to be 2.4 GPa for

PCS/GO-4 containing 2.0 wt% GO. However, with higher GO loading (≥ 2 wt%), both the tensile strength, elongation at break and Young's modulus sharply reduced. The reason for this may be aggregation of the nano-sized sheets. Moreover, interfacial interaction between the filler and matrix was an important factor affecting the mechanical properties of the composites [42-44]. The Pukanszky model, using the parameter B , described the effects of composition and the interfacial interaction on tensile yield stress [43]. The parameter B was an interaction parameter that was related to the macroscopic characteristics of the filler–matrix interface and the higher the B values indicated the better interaction [44]. B values of the Pukanszky model for the PCS/GO- n composites are reported in Table 1. As seen in Table 1, PCS/GO-4 had the highest B value with the strongest strength of interaction compared to the others. The trend of B values obtained from the Pukanszky model was consistent with the trend of the mechanical properties.

Fig. 6. (a) The mechanical properties of PCS/GO- n nanocomposite films with different percent contents GO and (b) Young's modulus (Y_c) of the PCS/GO- n composite films as a function of volume fraction of GO (ϕ_f) (the densities of GO is 1.6 g cm^{-3}).

Moisture Uptake of the Films

Moisture absorption is an important factor when dealing with hydrophilic thermoplastics because high water uptake worsens the mechanical properties of the material. To study this point, samples were exposed to high humidity and the Mu was determined gravimetrically. The results of this experiment are summarized in Figure 7, which shows the variation in Mu with increasing GO loading levels. Compared with the PCS/GO-0 film, the PCS/GO- n (≥ 0.5 wt%) nanocomposites had lower moisture absorption, indicating that GO had an interactive effect with the polymer matrix forming hydrogen bonding and diminishing the number of $-OH$ groups available for interaction with migrating water molecules. However, when the GO loading levels was greater than 2 wt%, the Mu increased as GO loading increased but did not surpass the PCS/GO-0 level. The reason for this may be the aggregation of GO sheets. This tendency suggested that the presence of GO decreased the Mu and improved water resistance of the nanocomposites.

Fig. 7. Moisture uptake (MU) at equilibrium of the PCS/GO- n nanocomposite films.

Conclusions

A series of nanocomposite films that consisted of CS, PVA and GO were prepared by a solution casting method. The results from XRD and AFM indicated that the GO improved miscibility between CS and PVA, which results from hydrogen bonding interaction between GO and CS/PVA matrix, and the GO does play the role of physical cross-linking points. Compared to the tensile strength of the PCS/GO-0 matrix, it can be seen that the tensile strength and the elongation at break of the composite films increased by 20.0% and 183.5% with 2.0 wt% GO loading levels, respectively. The results from tensile testing and thermal analyses indicated that the incorporation of GO favored the polymer mechanical properties and the thermal stability of the nanocomposite films.

Experimental part

Materials and methods

Chitosan (CS) was purchased at Nantong Xincheng Biological Industrial Limited Company (Nantong, China) with a weight-average molecular weight (M_w) of more

than 300,000 g mol⁻¹ and >90% degree of deacetylation (DA). Poly(vinyl) alcohol (PVA) and acetic acid (36%) were obtained from Maoye Chemical Company (Chongqing, Chian). Graphite powder was purchased from Shanghai Huayi Huayuan Chemical Limited Company. Other reagents were of analytical grade and used without further purification.

Synthesis of PCS/GO-n nanocomposites

GO was synthesized from graphite power by the modified Hummers method [13]. The procedures for preparing PCS/GO-n nanocomposite films are described as follows. GO was dissolved in 10 mL of water and treated with ultrasound for 45 min to make a homogeneous brown dispersion (1 mg mL⁻¹). The CS/PVA solution was prepared by dissolving 2 g CS and 0.5 g PVA in a 2% (vv⁻¹) aq HAc at a concentration of 2 wt%. The GO was then added to the chitosan solution, followed by stirring at 60 °C for 6 h. After degassing under vacuum, the mixture was cast onto a glass plate and then dried at 55 °C for 12 h to obtain the final film. The dried film was peeled from the glass plate and kept in desiccators at 43% relative humidity at room temperature. By adjusting GO loading levels to 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 wt%, respectively. A series of nanocomposite films with thickness around 0.1 mm were prepared and coded as PCS/GO-n (where n coded as 0, 1, 2, 3, 4, 5, and 6). To serve as experimental controls, the PCS/GO composite film without GO was obtained through the same fabrication process, which was coded as PCS/GO-0. The codes of samples are listed in Table 1.

Characterization

-Fourier Transform Infrared (FT-IR) spectroscopy

Fourier Transform Infrared (FT-IR) spectra of the nanocomposites were recorded with a Nicolet (Madison, WI, USA) 170SX Fourier transform infrared spectrometer in the wavelength range of 4000-600 cm⁻¹, in the attenuated total reflection mode.

-X-Ray Diffraction (XRD)

X-ray diffraction (XRD) patterns of the samples were carried out with a XRD-3D, PuXi (Beijing, China) X-ray diffractometer under the following conditions: Nickel filtered CuK α radiation ($\lambda=0.15406\text{nm}$) at a voltage of 36 kV and current of 20 mA. The scanning rate was 4 °/min in the angular range of 3-50° (2 θ).

-Transmission electron microscopy (TEM)

TEM micrographs were obtained with a transmission electron microscope (JEM-100CXII, Japan) at an accelerating voltage of 80 kV.

-Atomic force microscopy (AFM)

The surface morphologies and roughness of the prepared composites were observed by atomic force microscopy (AFM) (Veeco Instruments, Inc. New York) in the tapping mode. The films surfaces were imaged in a scan size of 1 μm $\times$ 1 μm .

-Thermal Analyses

Thermogravimetric (TGA) and differential thermogravimetry (DTG) analyses of the PCS/GO-n nanocomposite films were carried out on a TA-STDQ600 (TA Instruments

Inc., New Castle, DE, USA). The thermograms were acquired between 30 and 500 °C at a heating rate of 10 °C/min. Nitrogen was used as the purge gas at a flow rate of 20 mL/min. An empty pan Al₂O₃ was used as a reference.

Differential Scanning Calorimetry (DSC) analysis of the PCS/GO-n nanocomposite films was carried on a NETZSCH DSC 200 F3 (Netzsch Co, Selb/Bavaria, Germany). Nitrogen at a rate of 20 mL min⁻¹ was used as the purge gas. Aluminum pans containing 2 to 3 mg of film were sealed with pierced lid using the DSC sample press. All samples were preheated with a scan rate of 20 °C/min over a temperature range of 25–110 °C and maintained at 100 °C for 10 min to remove the residual water, cooled to 30 °C, and heated up to 250 °C.

-Mechanical Properties

The tensile strength and elongation at break of the films were determined using a Micro-electronics Universal Testing Instrument Model Sans 6500 (Shenzhen Sans Testing Machine Co. Ltd., Shenzhen, China) according to the Chinese standard method (GB 13022-91). The films were cut into 10 mm wide and 100 mm long strips and mounted between cardboard grips (150 × 300 mm) using adhesive so that the final area exposed was 10 × 50 mm. Before testing, the samples were kept at 43% RH for more than one week at room temperature to ensure equilibration of the moisture uptake in the films. The cross-head speed was 10 mm/min. All measurements were performed on three specimens and averaged.

The moisture uptake of the nanocomposite films was determined. The samples used were thin rectangular strips with dimensions of 50 mm × 10 mm × 0.1 mm. They were dried overnight at 80 °C. After the samples were weighed, they were conditioned at 92% RH (CuSO₄ saturated solution) for two weeks to ensure equilibrium of the moisture before testing. The moisture uptake (*Mu*) of the samples was calculated as follows:

$$Mu = (W_1 - W_0) / W_0 \times 100\% \quad (1)$$

where *W*₀ and *W*₁ were the weight of the sample before exposure to 92% RH and after equilibrium, respectively. An average value of three replicates for each sample was taken.

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