Synergistic effects of Na⁺-montmorillonite and multi-walled carbon nanotubes on mechanical properties of chitosan film

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Received 15 February 2009; accepted in revised form 12 March 2009

Abstract. Chitosan/Na⁺-montmorillonite/multi-walled carbon nanotubes (CTS/MMT/MWCNTs) nanocomposite films were prepared by a simple solution-evaporation method. The effects of MMT and MWCNTs on mechanical properties of the nanocomposite films were investigated. The results indicate that the simultaneously introduced MMT and MWCNTs into CTS film could greatly improve the mechanical properties. The Young's modulus of the CTS film is increased about 50% as 1.0 wt% MMT and 1.0 wt% MWCNTs are introduced. The MMT could compensate the negative effect of MWCNTs on elongation at break of the CTS film. The highest elongation at break is obtained when the contents of MMT and MWCNTs are 0.5 and 0.5 wt%, respectively. Formation of the MMT...CTS...MWCNTs subassembly may be responsible for the observed synergistic effect of MMT and MWCNTs on mechanical properties of the CTS film.

Keywords: nanocomposites, chitosan, films, mechanical properties, multi-walled carbon nanotubes

1. Introduction

Chitosan (CTS), a high molecular weight polysaccharide from chitin, is the most abundant biomass in the world. Because of unique structure (active –NH₂ and –OH) and properties (bioactive, biocompatibility, biodegradability, antibacterial activities, etc.), CTS is still intensively investigated now and has been widely applied in various fields including controlled drug delivery, food packaging film, artificial skin, water treatment, biosensor, and so on [1–3]. CTS is frequently used in the form of film because of its good film-forming character, high hydrophilicity and low density. Recently, various composite films based on CTS and nanoparticles have been explored focused on improving the low mechanical property and brittleness of the neat CTS films. The introduced functional nanoparticles (such as silica [4], montmorillonite [5] and organic

rectorite [6]) could endow the neat CTS film with novel properties including electronic conductivity and sterilization [5, 7].

Carbon nanotubes (CNTs) have been widely focused in nanoscience since their discovery in 1991 [8]. The preparation of nanocomposites based on CNTs is one of the hot topics in the CNTs field [9, 10] because of their unique properties such as high modulus, high intrinsic electrical conductivity, small size and high thermal conductivity [11, 12]. CNTs have been proved to be advanced multi-functional fillers in polymer-based nanocomposites [13, 14]. IR photoresponse of CNTs is dramatically enhanced by embedding CNTs into the polycarbonate matrix [15]. However, the strong cohesive nature and low stability of CNTs in solution discourage greatly their manipulation and widespread applications in many fields [16, 17]. Considerable

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investigations have been done to overcome these problems by introducing appropriate solubilization groups (such as $-\text{COO}^-$, $-\text{SO}_3^-$ and $-\text{NH}_3^+$) either to the end or to the side wall of CNTs through a covalent or noncovalent way [18–20]. Various polymers, including peptides, amylase, DNA, poly(acrylic acid), CTS, etc., have been used to disperse CNTs through a noncovalent way and to keep the unique properties of CNTs [3]. Among them, the CTS/CNTs system is especially interesting because the introduced CTS endows CNTs with biocompatibility. Consequently, the CTS/CNTs system acquires electronic and optical properties and biocompatibility, which make the biological and medicinal applications of CNTs possible. The CTS/CNTs system has been used for the preparation of biosensors of cholesterol, glucose, DNA, etc. [21, 22]. Mechanical properties (including the tensile modulus and strength) of CTS film could be greatly improved by introducing only 0.8 wt% of CNTs [2]. However, the elongation at break of the neat CTS film decreased with the introduction of CNTs.

Polymer/layered silicate nanocomposites frequently exhibit remarkably improved mechanical and materials properties (such as a higher modulus, increased strength, decreased gas permeability and increased biodegradability of biodegradable polymers), and are attracting considerable interest in the polymeric materials field [23]. Na^+ -montmorillonite (MMT) is one of the most important layered silicates used for the preparation of these organic-inorganic nanocomposites. MMT is composed of an aluminate sheet sandwiched between two silicate sheets stacked together by weak ionic and van der Waals forces which make MMT easily to be intercalated and/or exfoliated [24]. Swelling ratio and mechanical behavior of the poly(*N*-isopropylacrylamide) hydrogel were improved by the introduction of MMT [25]. The $-\text{NH}_2$ groups of CTS are protonated in acidic aqueous solution and could intercalate into layers of MMT to form the CTS/MMT nanocomposites [5]. The CTS/MMT nanocomposite film was seldom investigated until now although the CTS/MMT systems have been applied in many fields.

Considering the high performance and unique properties of CTS, CNTs and MMT, the combination of them may generate a novel material which holds great potential for pharmaceutical and bio-

logical applications. In the present work, the CTS/MMT/multi-walled carbon nanotubes (CTS/MMT/MWCNTs) nanocomposite films are prepared by introducing MMT and MWCNTs into neat CTS film through a simple solution-evaporation method, and the synergistic effects on the mechanical properties of nanocomposite films are investigated.

2. Experimental

2.1. Materials

CTS (the deacetylation degree is 0.85, average molecular weight is $90 \cdot 10^4$) was supplied by Zhejiang Yuhuan Ocean Biology Co. (Zhejiang, China). MMT with a cation-exchange capacity of 102.8 mmol/100 g was supplied by Longfeng Montmorillonite Co. (Shandong, China) and was milled through a 320-mesh screen before use. MWCNTs (purity > 95%, diameter = 20~40 nm) prepared using the chemical vapor deposition method were purchased from Shenzhen Nanotech Port Co., Ltd. (China). The catalyst in the MWCNTs was removed by concentrated nitric acid, and then filtered and washed with double-distilled water until $\text{pH} > 5$. All solutions were prepared with double-distilled water.

2.2. Preparation of the CTS/MMT/MWCNTs nanocomposite films

The CTS/MMT/MWCNTs nanocomposite films were prepared according to the following procedure. 7.0 g of CTS was dissolved in 273 ml of the aqueous solution of acetic acid (2% v/v) to form the aqueous solution of CTS (2.5 wt%). Appropriate amount of MMT and MWCNTs were suspended in 8.0 ml double-distilled water with sonication for 20 min at 25°C, 40 kHz and 100 W. Subsequently, 48.75 g of the above aqueous solution of CTS was charged into the MMT/MWCNTs mixture and mechanically stirred at 1000 rpm for 1h followed by 20 min at 12 000 rpm, and then sonicated for 20 min to facilitate the intercalation of MMT and the dispersion of MWCNTs. After that, the CTS/MMT/MWCNTs mixture was poured into a glass dish (7 cm×13 cm) and the water was evaporated at 50°C. The uniform nanocomposite films with an average thickness of 40 μm were then obtained and no further treatment was employed. The weight

ratio of MMT and MWCNTs ($m_{\text{MMT}}:m_{\text{MWCNTs}} = 1:1$) to the total solid is kept at 0, 0.2, 0.5, 1.0, 2.0 and 5.0 wt%. The CTS/MMT and CTS/MWCNTs nanocomposite films were prepared according to the same procedure. The weight ratio of MMT or MWCNTs to the total solid is kept at 0, 0.2, 0.5, 1.0, 2.0 and 5.0 wt%.

2.3. Tensile test

The tensile tests were carried out using a New SANS universal material testing system (CMT 4304) at room temperature with gauge length of 10 mm and crosshead speed of 2 mm/min. Measurements were carried out in sextuple and the averaged results were shown.

2.4. Characterization

X-ray diffraction (XRD) analyses of the specimens were performed using an X-ray diffractometer with Cu anode (PAN alytical Co. X'pert PRO), running at 40 kV and 30 mA, scanning from 1 to 10° with a step size of 0.0167°. The micrographs of samples were taken using field emission scanning electron microscopy (FE-SEM, JSM-6701F, JEOL, Ltd). Before FE-SEM observation, all samples were fractured with liquid nitrogen, and then fixed on copper stubs and coated with gold.

3. Results and discussion

3.1. XRD analysis

XRD patterns of CTS, MMT and MWCNTs are shown in Figure 1a. As can be seen, the typical diffraction peak of MMT is observed at $2\theta = 6.94^\circ$ corresponding to a basal spacing of 1.274 nm, whereas, CTS and MWCNTs show no diffraction peak in the 2θ range investigated. The typical diffraction peak of MMT at $2\theta = 6.94^\circ$ disappears after incorporated into CTS (CTS/MMT) or simultaneously incorporated into CTS with MWCNTs (CTS/MMT/MWCNTs) as shown in Figure 1b, which indicates that MMT is exfoliated by CTS and the exfoliated nanostructure is formed. The $-\text{NH}_2$ groups of CTS convert to positively charged $-\text{NH}_3^+$ groups under acidic medium. A part of $-\text{NH}_3^+$ groups could exchange with Na^+ ions between layers of MMT through a cation exchange process and intercalate into layers of MMT [26].

Figure 1. a) XRD patterns of CTS, MMT and MWCNTs and b) XRD patterns of the CTS/MMT (2.0 wt% MMT), CTS/MWCNTs (2.0 wt% MWCNTs) and CTS/MMT/MWCNTs (1.0 wt% MMT, 1.0 wt% MWCNTs) nanocomposite films

The $-\text{NH}_3^+$ groups of CTS could bind tightly to the negative sites of MMT [5]. In addition, the hydrogen bonding between $-\text{NH}_2$ and $-\text{OH}$ groups of CTS and the layers of MMT also facilitates the intercalation of CTS chains. It also can be seen from Figure 1b that the introduced MWCNTs does not show obvious influence on the XRD patterns of CTS/MWCNTs and CTS/MMT/MWCNTs. This result indicates that the interaction between CTS and MWCNTs does not form any new crystalline structure or influence the intercalation of CTS into layers of MMT. Similar effect of MWCNTs on the XRD pattern of CTS has also been observed by Wang *et al.* [2]. It should be noted that factors like line broadening and MMT dilution may also contribute to the observed disappearance of diffraction peak of MMT according to Eckel *et al.* [27].

3.2. Morphology analysis

Figure 2 shows FE-SEM images of the fracture surfaces of the neat CTS film and the CTS/MMT/MWCNTs nanocomposite film. As shown in Figure 2a, the neat CTS film shows a smooth and tight fracture surface. An almost homogeneous dispersion of MMT (indicated with circles) and MWCNTs (indicated with rectangles) is observed throughout the CTS matrix as shown in Figure 2b except for some small aggregates of MMT on the top of the graph. Consequently, an effective three-dimensional network is constructed and the CTS/MMT/MWCNTs nanocomposite film is formed with MMT and MWCNTs as inorganic crosslinkers. It also can be seen from Figure 2b that there are some bubbles around the homogeneously dispersed MMT and MWCNTs, which may be attributed to their strong interfacial interaction with the CTS matrix. CTS has good film-forming character, however, the formed neat CTS film is mechanically

Figure 2. FE-SEM images of the fracture surfaces of
a) CTS film and b) CTS/MMT/MWCNTs
(1.0 wt% MMT, 1.0 wt% MWCNTs) nanocomposite film

weak and brittle. CTS chains could intercalate into layers of MMT and disperse MMT and MWCNTs uniformly according to Figures 1 and 2 and the previously reported literatures [2, 5, 20, 26]. The homogeneously dispersed MMT and MWCNTs act as bones of the CTS film, which may improve mechanical properties of the neat CTS film.

3.3. Mechanical properties

Figure 3a shows the effect of the content of incorporated MMT, MWCNTs, MMT and MWCNTs on Young's modulus of the nanocomposite films. As can be seen, the introduced functional additives impact Young's modulus of the CTS film markedly and differently. The Young's modulus increases gradually from 3378 to 4798 MPa with increasing MMT content from 0 to 5.0 wt%. The variation of Young's modulus with MWCNTs content exhibits an obviously different tendency. The Young's modulus firstly increases with increasing MWCNTs content from 0 to 2.0 wt%, and then decreases evidently with further increasing MWCNTs content to 5.0 wt%. For the CTS/MMT/MWCNTs nanocomposite film, the Young's modulus firstly increases greatly with increasing MMT and MWCNTs content, and then decreases slightly with further increasing their content. The highest Young's modulus of 5081 MPa is obtained when the contents of MMT and MWCNTs are 0.5 and 0.5 wt%, respectively. It can be concluded from Figure 3a that the incorporation of appropriate amount of MMT or MWCNTs could improve Young's modulus of the CTS film evidently. In addition, a synergistic effect of MMT and MWCNTs on Young's modulus of the CTS film is observed when the total content of MMT and MWCNTs is less than 2.0 wt%, which indicates that the introduction of two functional additives with different properties and structure (such as MMT and MWCNTs) may open a new approach for further improving mechanical properties of materials. The slight decrease of Young's modulus for the CTS/MMT/MWCNTs nanocomposite film with further increasing MMT and MWCNTs content is attributed to the negative effect of the further increased MWCNTs. The variation of tensile strength of the CTS/MMT, CTS/MWCNTs and CTS/MMT/MWCNTs nanocomposite films is similar to that of Young's modulus as shown in Figure 3b.

Figure 3. Variation of a) Young's modulus and b) elongation at break for the CTS/MMT, CTS/MWCNTs and CTS/MMT/MWCNTs nanocomposite films with content of MMT, MWCNTs, MMT and MWCNTs, respectively

Variation of elongation at break for the CTS/MMT, CTS/MWCNTs and CTS/MMT/MWCNTs nanocomposite films with content of MMT, MWCNTs, MMT and MWCNTs is shown in Figure 3c. The elongation at break of the CTS/MMT nanocomposite film increases from 5.78 to 12.91% with increasing MMT content from 0 to 0.5 wt%, and then decreases to 5.37% with further increasing

MMT content to 5.0 wt%. The introduction of MMT is often detrimental to the ductility of polymer materials. However, modified MMT could improve ductility of polymers as have been reported previously [28]. The key difference is the modification of MMT could enhance the interfacial interaction between MMT and the polymers. In this study, CTS acts as not only a polymer matrix, but also a modifier of MMT, which could intercalate into layers of MMT and enhance the interfacial interaction between CTS and MMT. Consequently, the elongation at break is improved. Unlike the positive effect of MWCNTs on Young's modulus and tensile strength of the CTS/MWCNTs nanocomposite film, the elongation at break of CTS/MWCNTs decreases gradually with increasing MWCNTs content. Similar phenomenon had also been observed by Wang *et al.* in the chitosan/carbon nanotube composites [2]. The introduction of MMT into the CTS/MWCNTs nanocomposite film could remedy the negative effect of MWCNTs on the elongation at break. The highest elongation at break is obtained when the contents of MMT and MWCNTs are 0.5 and 0.5 wt%, respectively.

3.4. Mechanism for the synergistic effect of MMT and MWCNTs

According to the results of Figure 3, the introduction of MMT and MWCNTs simultaneously could evidently improve mechanical properties of the neat CTS film owing to the synergistic effect of MMT and MWCNTs. Figure 4 schematically shows the synergistic effect of MMT and MWCNTs. The positively charged polymeric chains of CTS could intercalate into layers of MMT through a cation exchange process and cause the exfoliation of the weakly linked MMT sheets. The positively charged polymeric chains of CTS could adsorb onto the surface of MWCNTs and act as polymeric cationic surfactants in acidic medium. The positively charged polymeric chains of CTS repulse one another and are extended in acidic solution owing to the protonated $-NH_2$ groups, and then the homogeneous dispersion of MWCNTs is formed. Thus, there are two subassemblies in the acidic aqueous solution of CTS/MMT/MWCNTs: (1) exfoliated and homogeneously dispersed negative charged MMT sheets by positively charged polymeric chains of CTS; (2) homogeneously dispersed

Figure 4. Schematic structure of the CTS/MMT/MWCNTs nanocomposite film

MWCNTs wrapped by positively charged polymeric chains of CTS. The -NH_3^+ groups on the chains of CTS adsorbed on the surface of MWCNTs could also interact with the negative charged MMT sheets and form the third MMT...CTS...MWCNTs subassembly which may be responsible for the synergistic effect of MMT and MWCNTs on mechanical properties of the neat CTS film.

4. Conclusions

The novel CTS/MMT/MWCNTs nanocomposite films were successfully prepared by the simple solution-evaporation method. The synergistic effect of MMT and MWCNTs on mechanical properties of the nanocomposite film is obviously observed. The Young's modulus of the neat CTS film is greatly improved by the introduction of MMT and MWCNTs simultaneously. The introduction of MMT into the CTS/MWCNTs nanocomposite film could remedy the negative effect of

MWCNTs on the elongation at break. The -NH_3^+ groups of CTS wrapped on the surface of MWCNTs could interact with the negative charged MMT sheets and form the MMT...CTS...MWCNTs subassembly which may be responsible for the synergistic effect of MMT and MWCNTs on mechanical properties of the neat CTS film. The introduction of two functional additives with different properties and structure for the improvement of material's properties may be applicable to other materials.

Acknowledgements

We thank the Western Action Project of CAS (No. KGX2-YW-501) for financial support of this research.

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