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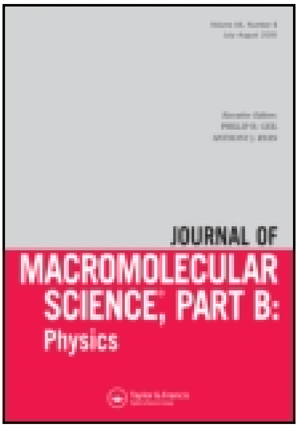

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Preparation and Characterization of Chitosan-Blended Multiwalled Carbon Nanotubes

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Preparation and Characterization of Chitosan-Blended Multiwalled Carbon Nanotubes

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Composites comprised of chitosan (CS) and multiwalled carbon nanotubes (MWCNTs) were fabricated by milling and ultrasonication dispersion methods. Scanning electron microscopy images showed homogeneous dispersion of MWCNTs throughout the CS matrix for samples prepared by either ultrasonication or milling methods. Further, the crystallinity of the CS component was found to decrease with the addition of MWCNTs, although the decomposition temperature and the storage modulus (E') of the samples were improved. The decomposition temperature for the composite prepared by milling was 7°C higher than that by the ultrasonication. Meanwhile, the E' decreased relatively slowly with temperature in the dynamic mechanical analysis measurements. In addition, IR analysis implied an interaction between CS and MWCNTs, which likely originated from hydrogen bonds between the amino, hydroxyl, and carboxyl groups of the two components. Compared with the ultrasonication, milling was more effective to promote the formation of the hydrogen bonds between CS and the MWCNTs and thus enhance the thermal stability of CS.

Keywords chitosan, composite, interface, multiwalled carbon nanotube

Introduction

Chitosan [CS, β-(1, 4)-2-amino-2-deoxy-D-glucopyranose] is a natural polymer derived by deacetylation of chitin, which is the second most abundant biopolymer in nature next to cellulose.[1] Compared with other polysaccharides, CS has several important advantages, including biocompatibility, biodegradability, no toxicity, good film-forming ability, and excellent chemical-resistant properties. Because of these merits, it has been widely studied for use in clinics, drug delivery systems, solid polyelectrolytes, surfactants and membranes for ultrafiltration, and reverse osmosis.[2–6]

Owing to its functional properties, CS has been widely investigated for the last two decades for industrial and biomedical applications. Due to its poor solubility in most organic solvents and its intrinsic brittleness, however, it is expected that it would have to be

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incorporated in composite materials to be useful for structural purposes. In this regard, many efforts have been preformed using different protocols.[7–18] For example, block-copolymers consisting of CS and polyethylene glycol (PEG),[11–14] and of CS and poly(vinyl alcohol) (PVA)[16–18] have shown improved solubility and decreased brittleness. In particular, the resultant CS-based materials usually acquire a sufficient mechanical strength once prepared as films and fibers. On the other hand, introducing inorganic fillers into CS matrix have often been considered to be an effective approach for improving its properties, such as mechanical strength and thermal stability, by the interaction between the components. Silica,[19–23] carbon nanotubes (CNT)[24–25] hydroxyapatite,[26] calcium phosphate cements,[27] and clay[28] are inorganic fillers that are frequently used to reinforce the CS matrix. Due to their nanometer size, high aspect ratios, and more importantly, extraordinary mechanical strength and high electrical and thermal conductivity, CNTs have been considered as ideal reinforcing fillers for polymer matrixes to achieve high performance and multifunctions.[29–32] However, it is difficult to achieve homogenous dispersion of CNTs within a polymeric matrix because the as-prepared CNTs usually aggregate into bundles and/or entangle together. Numerous studies report that high-energy sonication of the CNTs over prolonged periods of time is usually necessary to produce uniformly dispersed CNTs suspensions.[24,33–36] By homogenizing MWCNTs via an ultrasonic bath, Wang et al. prepared CS-MWCNTs and investigated the morphology and mechanical property of the composites.[24] As another example, Xia et al. reported that the CNTs were successfully dispersed into a polyol by mechanochemical milling with the aid of dispersing agent and consequently solved the dispersion problem of CNTs in highly viscous polyol liquid media.[36] Since chitosan also contains numerous hydroxy group (–OH), a similar process might be useful.

The object of this comparative study was to prepare CS-blended MWCNTs films by milling and ultrasonication methods, investigate the effect of MWCNTs on the crystallization, thermal stability and mechanical properties of the composites, and further probe the differences of these properties dictated by the varying dispersion procedures.

Experimental

Materials and Samples

Chitosan (deacetylation degree DDA >92%) was purchased from Shanghai Huashuo Fine Chemicals Co., Ltd. The MWCNTs were purchased from Shenzhen Nanotech Port Co., Ltd.; they were ca. 10–20 nm in diameter and 5–15 μm in length. The MWCNTs were refluxed for 6 h in concentrated nitric acid at 70°C, and then, the CNT powder was filtered and washed with deionized water until the pH value of the filtered solution was around 7. The resulting MWCNTs were then centrifuged, rinsed with absolute ethanol, and dried in a vacuum oven.

Ultrasonic dispersion of MWCNTs: MWCNTs (12 mg) were first swollen in 100 mL of acetic acid solution. The suspensions were homogenized in an ultrasonic bath for 1 h. After that CS (1.2 g) was added to the suspension (the concentration of the chitosan in the solution was ca.1 wt%, i.e., MWCNTs/CS = 1 wt%), and then, the mixture was stirred for 1 h to dissolve the CS. Finally, the CS/MWCNTs solutions were poured into a plastic dish (8 cm × 12 cm) and heated for 20 h at 50°C to allow the solvents to evaporate. For comparison, pure CS membranes were prepared via the same procedure.

Milling dispersion of MWCNTs: the mixture of MWCNTs and chitosan (MWCNTs/CS = 1 wt%) was blended homogeneously by hand milling in an agate mortar. Then 1 mL of acetic acid was added to the mixture and milling continued to dissolve the CS. After that the viscous mixture was poured into a beaker with additional of acetic acid and stirred (the concentration of the CS in the solution was 1 wt%). Finally, solutions were poured into a plastic dish (8 cm × 12 cm) and heated at 50°C to allow the solvents to evaporate. The dried and free-standing thin films were easily removed from the substrates and no particular treatment was performed.

Characterization

An X-ray diffractometer (XRD, D8 Bruker Corp) was used to obtain the diffractograms of the blend membranes. The X-ray source was Ni-filtered Cu K_α radiation, operated at 40 kV and 30 mA. The dry membranes were mounted on aluminum frames and scanned in transmission at a speed of 0.5°/min from 5° to 40° (2θ). A field emission scanning electron microscope (SEM, JEOL JSM 5600F) was used to observe the dispersion of the MWCNTs on the free surfaces of the composites, after coating the samples with a 5-nm layer of Au. IR spectra were collected on a TENSOR 27 FTIR spectrometer (Bruker Corp.) in absorption mode with 32 scans at a resolution of 2 cm^{-1} intervals. Thermogravimetry (TG) measurements were carried out on TG STA209PC (Netzsch Instruments). TG curves were obtained by heating samples from room temperature to 700°C at a heating rate of 10°C/min in nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were carried out on DSC Q100 (TA Instruments). DSC curves were collected by heating samples from 40°C to 350°C at a heating rate of 10°C/min under the nitrogen atmosphere. Prior to DSC runs, the temperature and enthalpy of transition of the device were calibrated with indium and sapphire standards, respectively. The samples subjected to DSC scans were further characterized by FTIR to investigate the thermal stability. Dynamic mechanical analysis (DMA) measurements were conducted to obtain the information of the storage modulus (E') and mechanical damping tangent ($\tan\delta$), which were recorded on a dynamic mechanical analyzer (DMA Q800, TA Instruments) from 35°C to 250°C at a frequency of 1 Hz and a heating rate of 3°C/min. All films used for the measurement were cut into strips of approximately 30 mm × 5 mm × 0.15 mm using a razor blade.

Results and Discussion

The fracture surfaces of CS/1% MWCNTs composites with ultrasonication and milling protocols are shown in Fig. 1. The well-dispersed bright dots and lines are the ends of the broken MWCNTs. For both samples prepared by ultrasonication or milling, the SEM images clearly indicate that a homogeneous dispersion of MWCNTs was achieved throughout the CS matrix. It is worth noting that most of the MWCNTs were broken upon failure rather than just pulled out of the matrix. This phenomenon indicates a strong interfacial adhesion between the MWCNTs and the CS matrix.[24]

It should be mentioned that the crystallinity and polymorphism of CS are affected by CS origin, molecular weight, presence of water, inorganic or organic acids, and annealing, etc.[37,38] So far, at least seven polymophs have been proposed for CS, including "tendon-CS," "annealed," "I-2," "L-2," "form I," "form II," and "noncrystalline." Ogawa et al. have proposed three forms: noncrystalline, hydrated ("tendon") crystalline, and anhydrous ("annealed") crystalline.[37] The hydrated crystalline structure gives a reflection at $2\theta = 10°$ (or peaks at around 8° and 12°), and the anhydrous crystalline structure gives one at $2\theta = 15°$. The diffraction patterns of the resultant membranes including the pure CS are shown in Fig. 2. In this case, pure CS included three characteristic crystalline peaks located at ca.

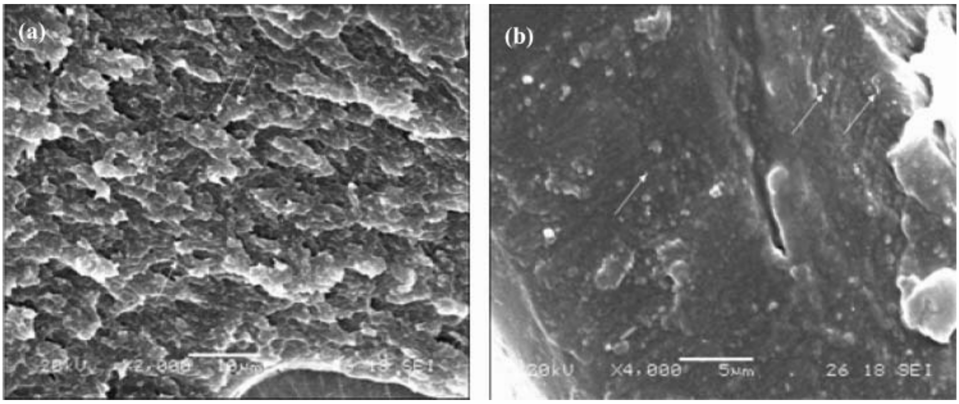

Figure 1. SEM images showing an overall morphology of a failure surface for chitosan/1% MWCNTs composites prepared by (a) ultrasonication and (b) milling.

8.6°, 11.8°, and 18.6° (2θ). This pattern is very similar to that described by Wang et al. for their "neat" chitosan and for a, presumably, hydrated sample.[24] The peaks at 8.6° and 11.8° (2θ) were attributed to the hydrated (tendon) crystal form in both references but neither described the origin of the 18.6° peak; we assume it also corresponds to the hydrated form. After adding MWCNTs, the three crystalline peaks still appeared, although their intensities were significantly weaker compared to that of the pure CS membrane. Besides these three peaks, which appeared for the samples prepared by both the ultrasonication and milling methods, a relatively broad peak at ca. 23° appeared, attributed to amorphous chitosan.[24] The sharp peaks in Fig. 2, curve (c), attribute to impurities or noise. All these results reveal that once the CS was effectively blended with MWCNTs, incorporation of MWCNTs did not significantly affect the crystalline structure of CS, although the crystallinity of CS decreases markedly. By comparison, the influence on the composites crystallinity by milling was stronger than that by ultrasonication. It should be mentioned that MWCNTs exhibit only one characteristic peak, around 26°, in the 2θ range between 5° and 40°.[39] However, the corresponding peak in the composites decreases in intensity or even disappears. The precise reason for this phenomenon remains unknown,[40,41] but is very likely due to the low content of CNT (1% loading, in this case).

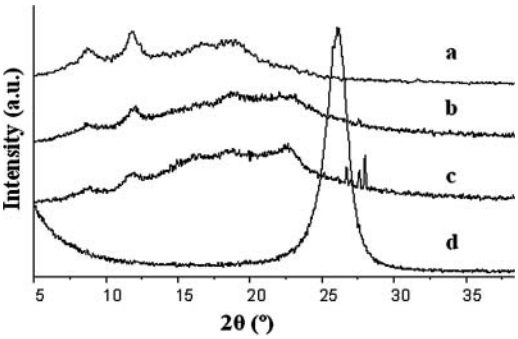

Figure 2. X-ray diffraction patterns of (a) pure chitosan, (b) chitosan/1% MWCNTs composite by ultrasonic method, (c) chitosan/1% MWCNTs composite by milling, and (d) MWCNTs.

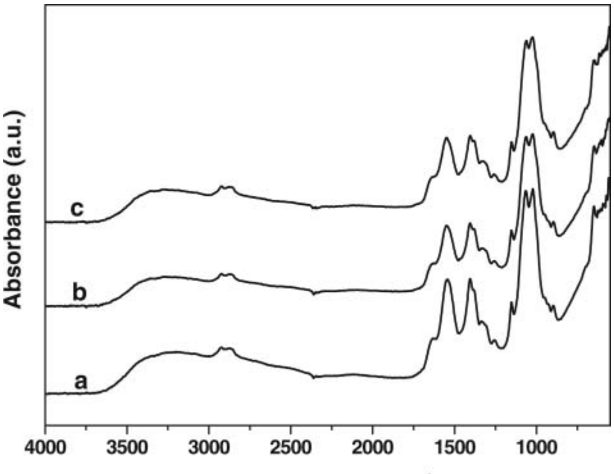

Figure 3. FTIR spectra of (a) pure chitosan, (b) chitosan/1% MWCNTs composite by ultrasonication, and (c) chitosan/1% MWCNTs composite by milling.

The pure CS and composites were characterized by FTIR to investigate the interaction being generated by the addition of MWCNTs and the results are depicted in Fig. 3. Pure CS displays distinct amide I, amide II, and amide III bands at 1638, 1547, and 1334 cm^{-1}. Meanwhile, the vibrations related with N–H stretching and O–H stretching can be characterized by the broad peak in the region of 3000–3500 cm^{-1}.[42] All these typical absorption peaks of functional groups present in CS can also be observed in the IR spectra of the composites. Although there was no obvious effect on O–H stretching present in the broad region between 3000 and 3500 cm^{-1}, which is due mainly to the severe overlapping with the N–H stretching; the amide I and amide II bands from CS, however, shifted slightly to lower wavenumber upon addition of MWCNTs. For the composite prepared by ultrasonication, the amide I band slightly shifted from 1638 to 1635 cm^{-1}, while the amide III band shifted from 1334 to 1328 cm^{-1}. However, for the composite prepared by milling, the above two bands, amide I (1638 cm^{-1}) and amide III (1334 cm^{-1}) shifted to lower wavenumber by 5 and 10 cm^{-1}, respectively. The hydrophilic biopolymer CS has amino groups and hydroxyl groups on its backbone, while carboxylic and hydroxyl groups are also normally generated on the surface of acid-treated MWCNTs (see Experimental). Accordingly, a thorough blending process will eventually allow hydrogen bonds to be formed between CS and the MWCNTs, which results in the amide I and amide III bands of CS shifting to lower wavenumber.[24] In comparison with the ultrasonication, the samples from milling show a greater shift toward lower wavenumber in the IR spectra, which directly implies that milling was more effective to promote the formation of the hydrogen bonds between CS and MWCNTs and thus the interaction between the components was stronger.

To investigate the thermal stability of the samples, pure CS and composites after heating at 350°C were further characterized by FTIR. The IR spectra of the samples subjected to DSC heating scan from 40 to 350°C in a nitrogen atmosphere are given in Fig. 4. Compared with the FTIR spectra of the samples without this treatment, the disappearance of characteristic bands of pure CS implies the complete decomposition of CS upon being heated to 350°C. Similar results can be found for the composite prepared by ultrasonication.

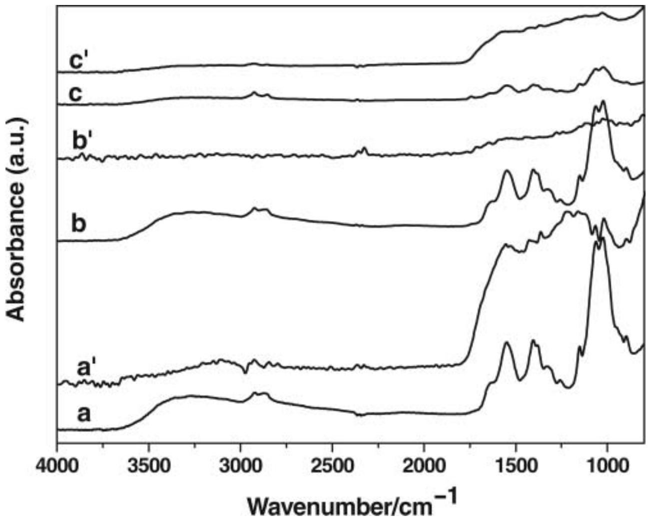

Figure 4. FTIR spectra of (a) and (a′) pure chitosan before and after heating to 350°C, (b) and (b′) composite prepared by ultrasonication before and after heating to 350°C, and (c) and (c′) composite prepared by milling before and after heating to 350°C.

However, for the milling counterpart, the two bands (located between 3000 and 2800 cm^{-1}), which are attributed to methyl and methylene groups, were still discernable after heating to 350°C, revealing that the composites decomposed incompletely. Hence, it can be concluded that the thermal stability of the composite prepared by milling was better than that prepared by ultrasonication.

To get more insights on the thermal behavior of the films, TG and DSC measurements were performed. Figure 5 exhibits the TG curves for pure CS and composites. All curves look similar in shape; however, with the addition of MWCNTs, there is a slight increase in the decomposition temperature. Upon close checking of the inserted part of Fig. 5, showing the differential TG curves, the shift toward higher temperature for the *fastest weight-loss temperature* (FWLT) for pure CS and the composites prepared by ultrasonication and milling were at ~266°C, ~269°C, and ~272°C, respectively. This phenomenon suggests

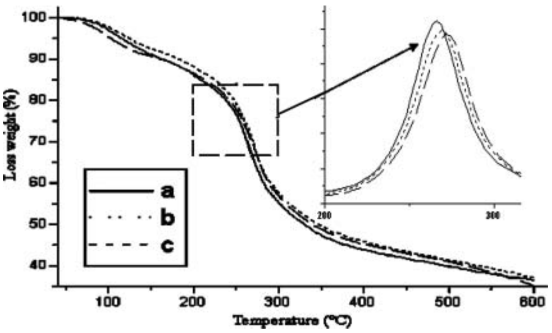

Figure 5. TG-DTA curves of (a) pure chitosan, (b) chitosan/1% MWCNTs composite prepared by ultrasonication, and (c) chitosan/1% MWCNTs composite prepared by milling.

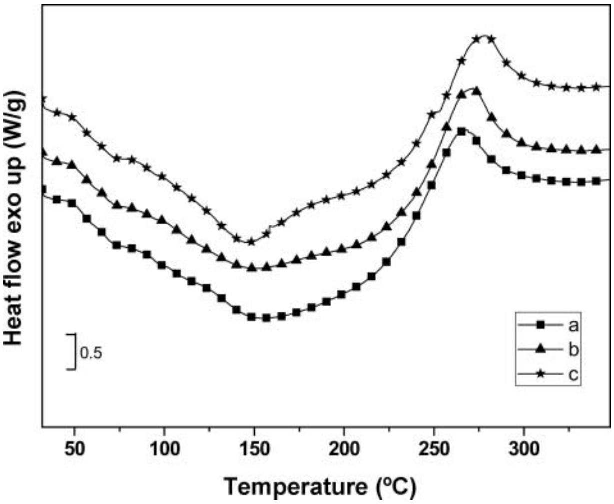

Figure 6. DSC curves of (a) pure chitosan, (b) chitosan/1% MWCNTs composite prepared by ultrasonication, and (c) chitosan/1% MWCNTs composite prepared by milling.

that the incorporation of MWCNTs can slightly increase the thermal stability of the CS owing to the reinforcement effect from the finely dispersed MWCNTs throughout the polymer matrix, i.e., the compatibility and the hydrogen bonds involved in the interaction between the MWCNTs fillers and the CS matrix enhanced the dispersion as well as the interfacial adhesion, and these effects increased the thermal stability and the E′ value (to be shown in the following DMA results section) of the composites. Furthermore, one could suppose that through milling stronger H-bonds formed between CS and MWCNTs and, consequently, the thermal stability of the composite prepared by milling was better than that of the composite prepared by ultrasonication.

In the DSC curves, a wide endothermic peak at ~150°C appears for pure CS and the composites (Fig. 6), which is probably attributable to evaporation of the solvents in CS since the membranes contained acetic acid, residual water, bound moisture, etc.[43] The other main event of these calorimetric curves is an exothermic peak at approximately 270°C, present in all the analyzed samples, which is due to the degradation of the main chain of CS. Although no significant changes were observed with adding the MWCNTs, the exothermic peak for the composites was shifted to higher temperatures. In comparison, the peak for the composite prepared by milling was at higher temperature than that for ultrasonication (for pure CS, and the composites prepared by ultrasonication and milling, they were recorded at ~268°C, ~272°C, and ~279°C, respectively). This observation is in good agreement with the TG results; namely, the MWCNTs increased the thermal stability of the CS membrane, and the effect of milling was stronger than that by ultrasonication.

One more distinction between ultrasonication and milling could be found in the DMA measurements, as shown in Fig. 7, which displays E′ and tan δ as a function of temperature for CS and the composites. The E′ of the composites was always higher than that of pure CS and, especially within the temperature range of 35°C~100°C, the composites display a E′ value, which was almost twice higher than that for pure CS. This implies that the stiffness of CS was improved significantly with the addition of MWCNTs. In comparison with the film prepared by milling, the film prepared by the ultrasonic method had a higher storage modulus in the lower temperature range, but the value become lower once the temperature

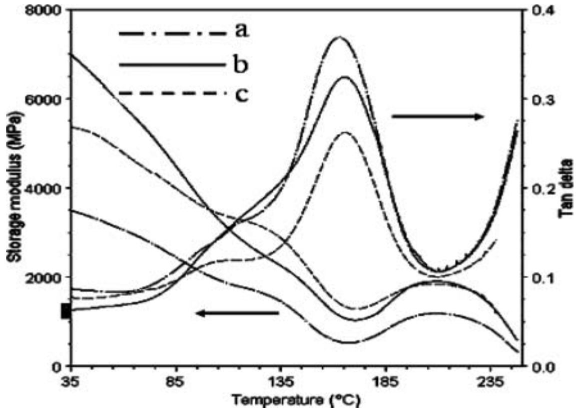

Figure 7. Storage modulus (E′) and tan δ curves of (a) pure chitosan, (b) chitosan/1% MWCNTs composite prepared by ultrasonication, and (c) chitosan/1% MWCNTs composite prepared by milling.

was beyond ∼100°C as the E′ dropped precipitously. It should be noted that the upturn in the E′ for all samples when the temperature was beyond about 180°C is due to the onset of degradation.

No significant differences in the peak of the tan δ curves, an alternative measurement of the glass transition temperature, T_g, were observed. For the pure CS, the peak recorded at about 162°C should be ascribed to the α-relaxation of CS (corresponding to its T_g[44]). With the addition of MWCNTs, the glass transition temperatures T_g were shifted slightly to higher temperature, by ∼4°C, for both preparation methods.

Conclusions

Neat CS and CS-blended MWCNTs films were fabricated by the methods of milling and ultrasonication. Subsequently, the crystallization, morphology, thermal stability, and dynamic mechanical properties of the corresponding samples were comparatively characterized by a series of measurements, including FTIR, DSC, and XRD. The results show that when MWCNTs were added to the CS, the decomposition temperature (slightly) and the storage modulus of the composites were enhanced. By comparison, milling resulted in a stronger influence on the composites according to the above measurements. In addition, FTIR analysis implied stronger interactions that probably result from more hydrogen bonds between CS and MWCNTs when prepared by milling than by ultrasonication. Further, DMA results show that the greater interaction by the milling was more helpful to enhance the stiffness of CS than ultrasonication.

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