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CHITOSAN AND MULTI-WALLED CARBON NANOTUBE COMPOSITE RODS*

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Abstract Multi-walled carbon nanotubes (MWNTs) and chitosan (CS) composite rods with layer-by-layer structure were prepared *via in situ* precipitation method. On the one hand, some MWNTs fragments with open tips played the role of nuclear agent to improve the crystallinity of CS. On the other hand, MWNTs embedded in CS matrix to absorb energy when the composite rods were destroying. Nanotubes pulled out from CS matrix, and lots of holes remained, so MWNTs could endure external stress effectively. The bending strength and bending modulus of CS/MWNTs rods (100/0.5, *W*/*W*) arrived at 130.7 MPa and 4.4 GPa respectively, increased by 34.3% and 7.3% compared with those of pure CS rods. Consequently, CS/MWNTs composite rods with excellent mechanical properties could be a novel device used for bone fracture internal fixation.

Keywords: Chitosan; Multi-walled carbon nanotube; Nanocomposites; Biomaterials.

INTRODUCTION

There are already available data suggesting that materials containing carbon nanotubes may be optimal for tissue engineering applications. This is not only due to their ability to simulate dimensions of proteins that comprise native tissue, but also due to their high reactivity for interactions involved in the cell attachment mechanism[1]. Meanwhile, carbon nanotubes can be used as reinforcement nanofillers in polymeric materials due to their excellent mechanical properties[2]. A small fraction of carbon nanotubes dispersed in the polymer matrix significantly improved the mechanical strength of the composites[3].

Chitosan (CS), as a kind of natural polymer, has been widely used for biomedical applications due to its excellent biocompatibility, biodegradable properties and inherent wound healing characteristics[4–7]. CS could be chosen for dispersion of carbon nanotubes, based on its ability to efficiently solubilize carbon nanotubes to form a stable dispersion[8]. Young's modulus and tensile strength of CS/carbon nanotubes nanocomposite films are doubled compared with those of pure CS films[3]. The mechanical strength of CS/carbon nanotubes semi-IPN hydrogels was remarkably improved compared with that of neat CS hydrogels[9]. So carbon nanotubes could be used for the improvement of the mechanical properties of CS based materials effectively. Novel 3-dimensional CS rod with layer-by-layer structure and its composite rod with multifunctional properties have been constructed *via in situ* precipitation method by our group[10–14]. Pure CS rods with layer-by-layer structure showed high

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mechanical properties with their bending strength and bending modulus of 92.4 MPa and 4.1 GPa, respectively. In order to meet the demand for the clinic application, CS rods should be reinforced. In this research, multi-walled carbon nanotubes (MWNTs) were used for the enhancement of mechanical properties of CS rods. The relationship between mechanical properties and microstructure was explored in the following sections.

EXPERIMENTAL

Materials

CS (Biomedical Grade, $M_\eta = 5.63 \times 10^5$, D.D = 91%, Qingdao Haihui Bioengineering Co., Ltd), acetic acid (CP, Yixing Niujia Chemical Reagent Plant), sodium hydroxide (NaOH, AR, Hangzhou Xiaoshan Chemical Reagent Corporation), MWNTs (40–50 nm in diameter, 5–15 μm in length, Shenzhen Nanotech Port Co., Ltd).

Preparation of CS/MWNTs Nanocomposite Rods

MWNTs (0.05 g, 0.1 g, 0.3 g and 0.5 g respectively) were added into 400 mL acetic acid aqueous solution (2%, *V*/*V*) and stirred for 2 h. Then 5 g CS powder was added and stirred for 2 h with ultrasonic dispersion. Another 15 g CS powder was added into the above solution and stirred for another 2 h with ultrasonic dispersion. The resulting solution was held for 24 h to remove air bubbles trapped in the viscous liquid. A little CS solution was spread on the internal surface of a cylindrical tube, and then put the tube into sodium hydroxide aqueous solution (50 g/L), soaked for 15 min to form CS membrane. The mold filled with the mixture solution was immerged into sodium hydroxide aqueous solution (50 g/L) for 6 h to get CS/MWNTs gel rods (Diameter: 16.5 mm). The gel rods were washed with deionized water, and then air-dried in oven at 60°C.

FTIR Analysis

All of the samples were pressed into KBr pallets. FTIR analysis was carried out on a Vector-22 FTIR spectrophotometer instrument (Bruker Company, Germany).

TEM and SEM Observations

Size and dispersion of MWNTs in the CS matrix were evaluated by TEM (JEOL, Japan, JEM-1200EX). HITACHI S-4800 SEM produced by Japan was used to observe the microstructure of the samples which were coated by gold before observation.

X-ray Diffraction Analysis

Crystallinity of the samples was studied with X-ray Diffraction (Rigaku D/max 2550PC) using a monochromatic Cu Kα radiation generated at 40 kV, 300 mA. The samples were scanned from 5° to 60° at 10 (°)/min.

Thermal Analysis

The TGA of the samples was studied on a Pyris-6 Thermo Analyses (TA) apparatus produced by Perkin Elmer, and measurements were recorded from 50°C to 600°C at a heating rate of 20 K/min in N_2 flow atmosphere (40 mL/min).

Testing of Mechanical Properties

All of the samples were air-dried in oven at 60°C for 2 h to remove the moisture before testing. Bending strength and bending modulus were determined by three-point bending tests, which were performed on a universal materials testing machine made by Shenzhen Reger Company (Shenzhen, China). The span length was 40 mm and the loading rate was 2 mm/min.

RESULTS AND DISCUSSION

Interactions between CS and MWNTs

XRD patterns of pure CS rod, CS/MWNTs (100/0.5, *W*/*W*) rod and CS/MWNTs (100/2.5, *W*/*W*) rod are shown in Fig. 1. The peaks at *ca*. 10° and *ca.* 20° are characteristic diffraction peaks of CS. Intensity of the peaks at *ca*. 10° and *ca*. 20° became augmented (Fig. 1b) compared with that of pure CS rod (Fig. 1a), indicating that crystallinity of CS has been increased after adding small amount of MWNTs into CS matrix, because some

fragments of MWNTs formed by ultrasonic dispersion played a role of nuclear agent[15]. But when more MWNTs were added, the crystallinity of CS decreased (Fig. 1c), because the free motion of CS molecules was hindered by rigid MWNTs, so crystallization growth of CS was restricted. Thus, small amount of MWNTs could improve the crystallinity of CS, and will be beneficial for the improvement of mechanical properties of the composite rods.

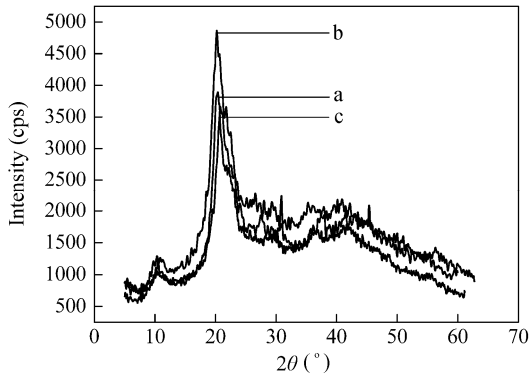

Fig. 1 XRD patterns for (a) CS rod, (b) CS/MWNTs (100/0.5, *W*/*W*) rod, (c) CS/MWNTs (100/2.5, *W*/*W*) rod

FTIR spectra of MWNTs, CS rod and CS/MWNTs (100/0.5, *W*/*W*) rod could be seen in Fig. 2. The peak at 1647 cm^{-1} (Fig. 2a) is assigned to C=C stretching vibration, which is the characteristic absorption of MWNTs. The peaks at 669 cm^{-1} and 3731 cm^{-1} are corresponding to the bending vibration and stretching vibration of —OH respectively, while the peak at 1742 cm^{-1} is belonged to C=O stretching vibration, indicating there are —COOH groups in the molecular chain of MWNTs. Meanwhile the peak at 2921 cm^{-1} is assigned to C—H stretching vibration of methyl groups, indicating that some defects may appear during the preparation process of MWNTs[16]. But the peaks at 1070 cm^{-1} and 1376 cm^{-1} belonged to C—O stretching vibration and C—H bending vibration became weak slightly in CS/MWNTs composite compared with that in pure CS rod, due to the rigidity of MWNTs and improvement of CS crystallinity.

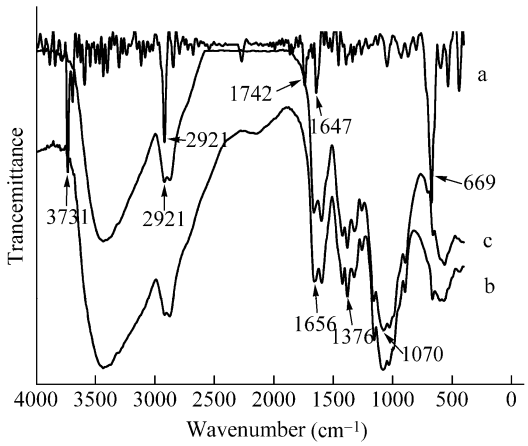

Fig. 2 FTIR spectra of (a) MWNTs, (b) CS rod, (c) CS/MWNTs (100/0.5, *W*/*W*) rod

Morphology of CS/MWNTs Nanocomposite Rods

Figure 3 shows SEM micrographs of the samples which were coated by gold before observation. Layer-by-layer structure could be seen clearly on the cross section of pure CS rod (Fig. 3a), CS/MWNTs (100/0.5, *W*/*W*) rod (Fig. 3b), CS/MWNTs (100/1.5, *W*/*W*) rod (Fig. 3d), and CS/MWNTs (100/2.5, *W*/*W*) rod (Fig. 3e). But layer-by-layer structure became irregular along with the increasing of the content of MWNTs, perhaps due to the

obstruct effect of MWNTs. Nanotubes pulled out from CS matrix (Fig. 3c) and lots of holes can be seen (Fig. 3f) from the vertical section of CS rods. MWNTs embedded in CS matrix could absorb energy when composite rods were destroying, so MWNTs could endure external stress effectively.

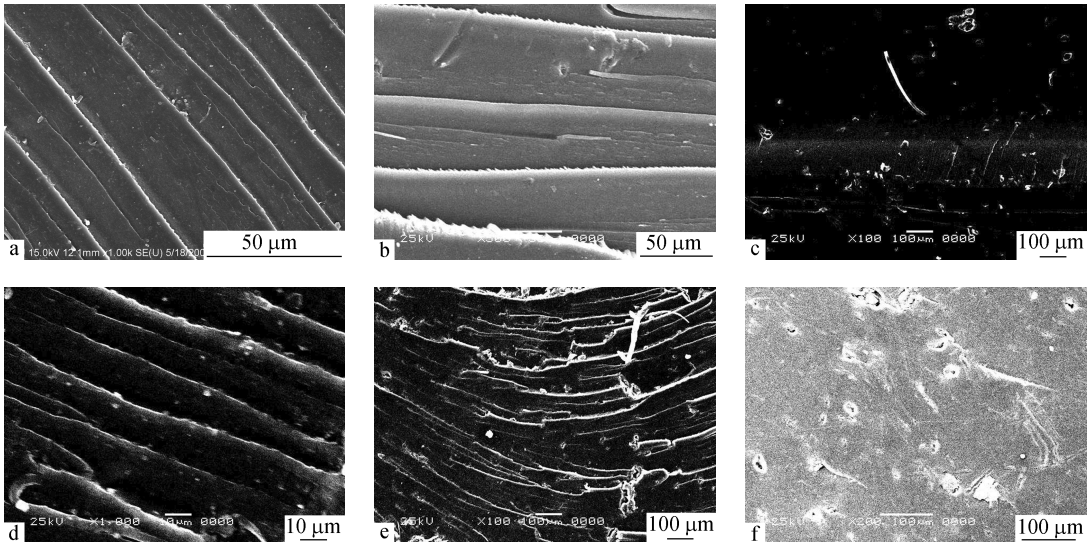

Fig. 3 SEM photographs of rods after bending tests: (a) CS rod, (b) CS/MWNTs (100/0.5, *W*/*W*) rod, (c) CS/MWNTs (100/0.5, *W*/*W*) rod, (d) CS/MWNTs (100/1.5, *W*/*W*) rod, (e) CS/MWNTs (100/2.5, *W*/*W*) rod, (f) CS/MWNTs (100/2.5, *W*/*W*) rod

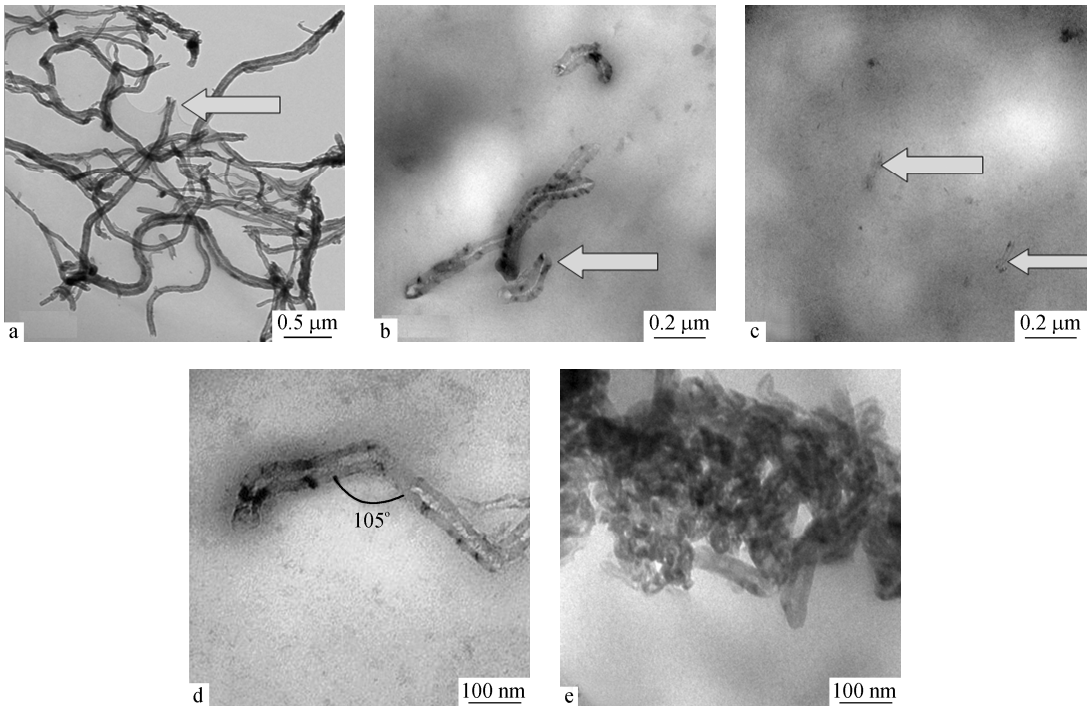

Fig. 4 TEM micrographs of (a) MWNTs, (b) CS/MWNTs (100/0.5, *W*/*W*) rod, (c) CS/MWNTs (100/0.5, *W*/*W*) rod, (d) CS/MWNTs (100/0.5, *W*/*W*) rod, (e) CS/MWNTs (100/2.5, *W*/*W*) rod

Figure 4 shows TEM micrographs of the samples. MWNTs with diameters of 40–50 nm were enlaced together with each other (Fig. 4a), and open tips of MWNTs could be seen in Fig. 4(a) and Fig. 4(b). MWNTs were random dispersed in CS matrix (Fig. 4b and Fig. 4e). Increasing the content of MWNTs, the nanotubes congregated obviously (Fig. 4e). The bending angle of MWNT could reach 110° in theory due to its rigidity[17]. Meanwhile, the bending angle of MWNT in CS matrix arrived at 105°, which could be seen in Fig. 4(d), due to the shrinkage of CS/MWNTs gel rod as dried in oven. Some fragments of MWNTs, formed due to ultrasonic dispersion, could be seen in Fig. 4(c) which played the role of nuclear agent and improved the crystallinity of CS.

Thermal Stability of Samples

Addition of MWNTs into PLLA and PLA matrix showed higher activation energy of thermal degradation, which confirmed the positive effect of the MWNTs on the thermal stability enhancement of polymer matrix[18, 19]. The thermal gravimetric (TG) curves of CS rod, CS/MWNTs (100/0.5, *W*/*W*) rod, CS/MWNTs (100/2.5, *W*/*W*) rod and MWNTs are shown in Fig. 5, which were tested in the temperature range of 50–600°C under N_2 atmosphere, and confirmed the thermal stability of MWNTs/CS composites was better than that of pure CS rods. The mass loss percentage of MWNTs arrived at 0.5% and 8.7%, respectively at the temperatures of 100°C and 600°C. Mass of MWNTs decreased due to the evaporation of small amount of water when the temperature is lower than 100°C. But, between the temperatures of 100°C and 600 °C, mass of MWNTs decreased because C—H groups and C—O groups degraded. The mass residual percentage of CS rod, CS/MWNTs (100/0.5, *W*/*W*) rod and MWNTs are 32.8%, 34.8% and 91.3% respectively at the temperature of 600°C. The mass percentage of MWNTs in CS matrix is 0.5%, but the mass residual percentage of CS/MWNTs (100/0.5, *W*/*W*) rod at 600°C was increased by 2% compared with that of pure CS rod, indicating that addition of MWNTs was beneficial for the thermal stability of composite rods.

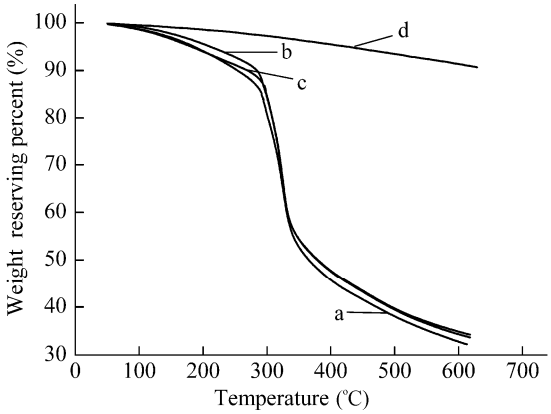

Fig. 5 TG curves for (a) CS rod, (b) CS/MWNTs (100/0.5, *W*/*W*) rod, (c) CS/MWNTs (100/2.5, *W*/*W*) rod, (d) MWNTs, at the temperature of 50–600°C under N_2 atmosphere

Mechanical Properties of CS/MWNTs Composite Rods

MWNTs blended with CS showed significant improvement in mechanical properties compared with pure CS. The tensile modulus and tensile strength of the CS/MWNTs films are greatly improved by 93% and 99%, respectively, with incorporation of only 0.8% MWNTs into CS matrix[20], and a small amount may counterbalance their non-degradable nature[3]. The mechanical properties of CS/MWNTs composite rods are shown in Fig. 6. The bending strength of CS/MWNTs composite rods was first increased and then reduced along with the increasing of the content of MWNTs. When 0.5% MWNTs added into CS matrix, the crystallinity of CS increased, and could endure outside stress effectively, so the mechanical properties of CS/MWNTs composite rods improved. But when much more MWNTs added, the crystallinity of CS decreased and MWNTs congregated obviously, so the mechanical properties of CS/MWNTs composite rods decreased. Bending strength and bending modulus of pure CS rods are 92.4 MPa and 4.1 GPa, respectively. However, the

bending strength and bending modulus of CS/MWNTs (100/0.5, *W*/*W*) rods arrived at 130.7 MPa and 4.4 GPa, respectively, increased by 34.3% and 7.3% compared with pure CS rods.

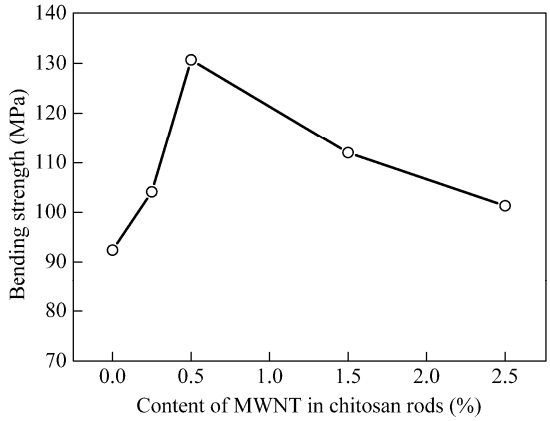

Fig. 6 Bending strength of CS/MWNTs composite rods influenced by the content of MWNTs

CONCLUSIONS

CS/MWNTs composite rods were prepared *via in situ* precipitation method, and the bending strength and bending modulus of CS/MWNTs (100/0.5, *W*/*W*) rods arrived at 130.7 MPa and 4.4 GPa, respectively, increased by 34.3% and 7.3% compared with pure CS rods. Some fragments of MWNTs with open tips played a role of nuclear agent and improved the crystallinity of CS. The TG curves indicated that the addition of MWNTs is beneficial for the thermal stability of composite rods. MWNTs embedded in the CS matrix may absorb energy when the composite rods were destroying. Nanotubes pulled out from CS matrix and lots of holes formed, so MWNTs could endure external stress effectively. Consequently, CS/MWNTs nanocomposite rods with excellent mechanical properties could be a novel device used for bone fracture internal fixation.

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