Study of poly(methacrylic acid-co-methyl methacrylate) /poly(N-vinyl-2-pyrrolidone) /multi-walled carbon nanotubes nanocomposites

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Introduction

Polymer nanocomposites are an important and widely studied class of materials [1÷3]. Among them, polymers/carbon nanotubes (CNTs) [4÷6]. CNTs can be present as single-walled nanotubes (SWNTs) or multi-walled nanotubes (MWNTs). Although SWNTs have much lower loading versus MWNTs to achieve the same electrical properties, enhancing mechanical properties even further [7], the difficult in dispersing SWNTs uniformly is still a big challenge for the use of SWNT in real application. In addition, the high cost and difficulty in purification also limits the large-scale production of SWNTs. In contrast MWNTs, production cost is much lower [8]. Therefore, MWNTs have been widely used as reinforcing fillers over the past few years [9].

Poly(N-vinyl-2-pyrrolidone) (PVP) is among the most common materials employed in medicine and in other applications interfacing with biological systems because of its excellent biocompatibility with living tissues and extremely low cytotoxicity [10, 11].

In the present study, P(MAA-co-MMA)/PVP/MWNTs nanocomposites were prepared via ultrasonic assisted emulsifier bulk free radical polymerization technique, which can be designed as potential biomaterials for use in wound dressing. The addition of MWNTs to P(MAA-co-MMA)/PVP blends may improve the mechanical and thermal properties. The effect MWNTs on the morphological, mechanical, and thermal properties of P(MAA-co-MMA)/PVP/MWNTs nanocomposite have been investigated.

Experimental

Materials

MWNTs were purchased from Shenzhen Nano-Technologies Port Co. Ltd., China, with a purity of above 96%, average length of microns, and surface area of 4.26 m2/g. Methacrylic acid (MAA), methyl methacrylate (MMA), 2,2'-azobis(isobutyronitrile) (AIBN) and N,N'-methylenebis(acrylamide) (MBAA) were analytical grade from Chengdu Reagent Factory. Poly(N-vinyl-2-pyrrolidone) (PVP) with the Mw=58000 (Aldrich) were used as received, which also played a role of an organic dispersant. MAA and MMA were distilled under reduced pressure before use. AIBN, used as a radical initiator, was recrystallized from ethanol solution. MBAA was used as a cross-linker without further purification.

Preparation

MWNTs with dimethyl sulfoxide were sonicated in a two-necked flask for 20 min. Then, MAA and MMA monomer, and PVP were added into the flask and stirred for 10 min, which were further sonicated for 10 min. AIBN (0.01 mol/l) and MBAA (0.02 mol/l) were added and nitrogen gas was purged into the flask to remove oxygen. The mixtures were sonicated using a bath sonicator for 1 hour. Polymerization was carried out with constant stirring at 60°C for 10 min. Then, the reaction mixture injected into the space between two glass plates separated by polyethylene spacers (3mm thick) or into a cylindrical glass tube with a diameter 7 mm and continued to polymerize at 55°C for 24 hours. The concentration of MAA and MMA were optimized by weight percent conversion of polymerization and MAA (1.0 mol/l), MMA (1.0 mol/l), and PVP (25wt% of the entire monomers) were kept constant for variation of MWNTs. The prepared P(MAA-co-MMA)/PVP/MWNTs nanocomposites were quenched and then dried under vacuum at room temperature for 10 days to remove unreacted monomers.

Measurements

Morphology

SEM observation was carried out with a JSM-5900LV scanning electron microscopy.

Thermal analysis

Thermogravimetric analysis (TGA) measurement was performed using TGA-7 (Perkin-Elmer). The dynamic mechanical analyses (DMA) were carried out with a Du Pont 983 DMA at a fixed oscillation amplitude of 0.1 mm and under nitrogen gas purging. The frequency of 1 Hz was chosen for all the samples examined.

Water absorption test

Swelling characteristics of samples in double distilled water were measured by weighing their water content rise. Approximately 1g of completely dried and extracted samples were weighed and then immersed into 500 ml of double distilled water. Swelling was performed at 27°C in thermostatically controlled water bath till reaching to an equilibrium state. Then the swelled samples were withdrawn from double distilled water and weighed after gentle surface wiping using absorbent paper. The equilibrium degree of swelling (ES) and equilibrium water content (EC) were calculated respectively, as follows:

$$ES = (W_s - W_d)/W_d \times 100 \tag{1}$$

$$EC = (W_s - W_d)/W_s \times 100 \tag{2}$$

Where Ws is the swollen weight of the sample at equilibrium state and Wd is the final dry weight of the extracted sample.

Results and discussion

The efficiency of nanofillers in reinforcing the polymer matrix is primarily determined by the degree of its dispersion in the matrix, which influences many properties of polymers/CNTs nanocomposites, including improving the mechanical, electrical, and thermal performances of the polymer matrix. Therefore, morphological characterization is very important for the evaluation of the dispersion state of carbon nanotubes in the polymer matrix. In this study, SEM observations were performed for cryo-fractured surfaces of P(MAA-co-MMA)/PVP/MWNTs nanocomposites, as shown in Figures 1 a÷d. A fibrous fractured surface is observed due to the elongation at break of P(MAA-co-MMA)/PVP/MWNTs nanocomposites; the random dispersed bright dots because of MWNTs high conductivity are the

ends of the broken carbon nanotubes [12]. In addition, it is found that some MWNTs are broken apart, and, as a result of poor interfacial adhesion, some MWNTs are pulled out of the matrix before the breakage, forming caves on the fractured surface; moreover, other MWNTs are observed with their one end still strongly embedded in the P(MAA-co-MMA)/PVP blends as an inset. Such interesting and typical breakage phenomenon of the MWNTs indicates that a strong interfacial adhesion exists between MWNTs and P(MAA-co-MMA)/PVP blends and that the load transfer takes place efficiently from the matrix to the nanotubes. The strong interfacial adhesion is usually responsible for the significant enhancement of the mechanical properties [13].

At low concentration of MWNTs, from Figures 1a, 1b, and 1c, it can be seen that the bright dots (i.e., MWNTs) embedded in P(MAA-co-MMA)/PVP blends and the caves (i.e., MWNTs) pulled out from P(MAA-co-MMA)/PVP blends are well dispersed; however, with an increase in MWNTs concentration, from Figure 1d, a nonuniform dispersion of MWNTs is observed in the nanocomposites, and a large aggregate of MWNTs having a diameter of over 500nm is presented. Those indicate that MWNTs were dispersed as nanotubes aggregates due to the imperfect dispersion of MWNTs.
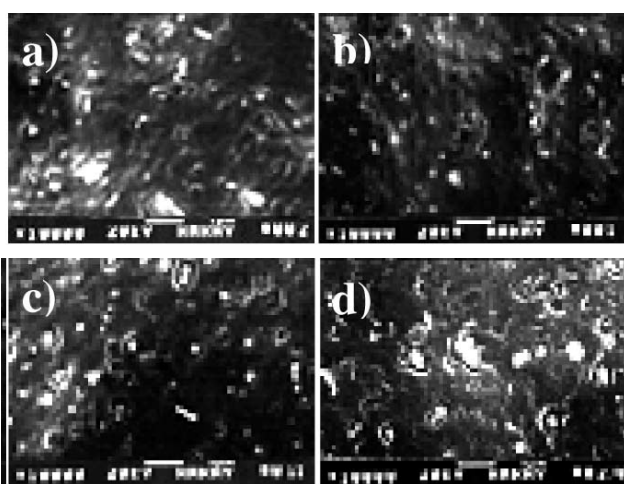

Fig. 1. SEM images of P(MAA-co-MMA)/PVP/MWNTs nanocomposites. a) P(MAA-co-MMA)/PVP/0.5wt% MWNTs, b) P(MAA-co-MMA)/PVP/1wt% MWNTs, c) P(MAA-co-MMA)/PVP/2wt% MWNTs, d) P(MAA-co-MMA)/PVP/3.0wt% MWNTs.

When the content of MWNTs is no more than 2.0wt%, owing to producing carboxylic or hydroxylic groups on the surface of the MWNTs by HNO3 treatment [14], which ensures the high dispersion quality of the MWNTs and prevents the severe aggregation of MWNTs [15, 16], reasonably uniform distribution of the MWNTs is observed in Figures 1a, 1b, and 1c. On the other hand, at compositions containing greater amounts of MWNTs, a small amount of aggregates is shown in Figure 1d). These results are in good agreement with the results of Wu et al. and Bikiaris et al. who reported that increasing the content of SiO_2 leads to larger agglomerates [17]; this is also the case in P(MAA-co-MMA)/PVP/MWNTs nanocomposites. In fact, there are more or less agglomerates of MWNTs formed in Figure 1. It is worth nothing, due to the strong interaction among the nanoparticles, the limited shear force provided by the mixing device might be impossible to pursue an efficient nanoscale dispersion of MWNTs.

Even at low volume fractions, the vast interfacial area created by well-dispersed nanoparticles can affect the behaviour of the surrounding polymer matrix, creating a co-continuous network of dramatically altered polymer chains, and fundamentally changing the mechanical and thermal properties of the matrix [18, 19]. The temperature-dependence plots of the storage modulus (E') of P(MAA-co-MMA)/PVP blends and P(MAA-co-MMA)/PVP/MWNTs nanocomposites, as measured from 18°C to 142°C, are shown in Figure 2, where each value is an average of 5 experimental results. As shown in Figure 2,

the glassy-state storage modulus E' (at 18°C) of P(MAA-co-MMA)/PVP/MWNTs nanocomposites at 0.5, 1, 2, and 3wt% MWNTs loading increases by 22, 41, 64, and 112% beyond that of P(MAA-co-MMA)/PVP blends, respectively. It is clear that the average glassy–state modulus increases with increasing filler weight fraction. The enhanced results for MWNTs are attributed to the superior interfacial bonding and persistently good dispersion: as the number of MWNTs increases, they impact the modulus both by their own inherent stiffness as well as by the enhanced stiffness of the increased "inter-phase" and P(MAA-co-MMA)/PVP blends molecular movements are restricted by the geometric confinement of MWNTs [20].
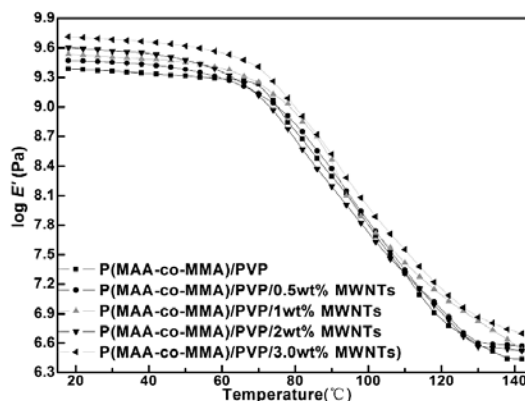

Fig. 2. Temperature dependence of tensile storage modulus E' for P(MAA-co-MMA)/PVP and various P(MAA-co-MMA)/PVP/MWNTs nanocomposites
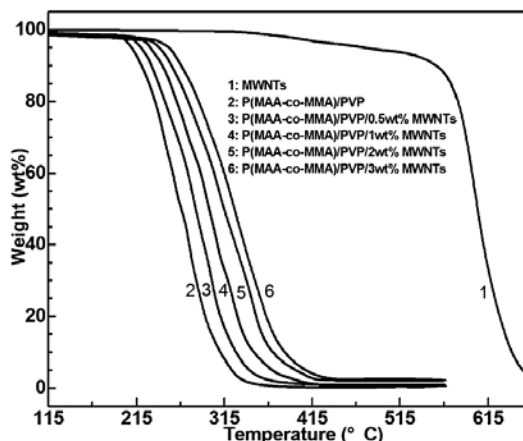

Fig. 3. TGA curves of MWNTs, P(MAA-co-MMA)/PVP blends and P(MAA-co-MMA)/PVP/MWNTs nanocomposites

Figure 3 shows TGA thermograms of P(MAA-co-MMA)/PVP blends, MWNTs and P(MAA-co-MMA)/PVP/MWNTs nanocomposites. The decomposition temperature (onset of inflection) for P(MAA-co-MMA)/PVP blends is lower than those of its nanocomposites, indicating that the thermal stability of nanocomposites has been improved because of addition of MWNTs. Besides that, the residual weight of P(MAA-co-MMA)/PVP/MWNTs nanocomposites left increases steadily with the increase of MWNTs loading. As shown in Figure 3, the weight loss at 300°C for P(MAA-co-MMA)/PVP blends is about 85%, whereas (MAA-co-MMA)/PVP/MWNTs nanocomposites are only around 30–70%. This also indicates that the thermal stability of P(MAA-co-MMA)/PVP blends is significantly improved on incorporation of MWNTs.

P(MAA-co-MMA)/PVP/MWNTs nanocomposites have three-dimensional polymer networks, i.e., crosslinked P(MAA-co-MMA) gels, which may be used for potential biomaterials, such as wound dressing. In this work, the equilibrium degree of swelling (ES) and equilibrium water content (EC), as important swelling characteristics of P(MAA-co-MMA)/PVP/MWNTs nanocomposite gels, were

measured. These characteristics indicated the ability of P(MAA-co-MMA)/PVP/MWNTs nanocomposite gels in absorption of fluids. Figures 4 and 5 demonstrate *ES* and *EC* of P(MAA-co-MMA)/PVP/MWNTs nanocomposite gels as a function of the amount of MWNTs. Both parameters show nearly similar decreasing trends by increasing the quantity of MWNTs. Although the swelling characteristics of P(MAA-co-MMA)/PVP/MWNTs nanocomposite gels decrease due to presence of MWNTs in comparison with P(MAA-co-MMA)/PVP hydrogel, but it seems that they have high enough swelling capacity. This effect may be caused due to incorporation MWNTs into P(MAA-co-MMA)/PVP hydrogel, dispersing in hydrogel and decreasing the polymer free volume, thus reducing the swelling of (MAA-co-MMA)/PVP/MWNTs nanocomposite gels.
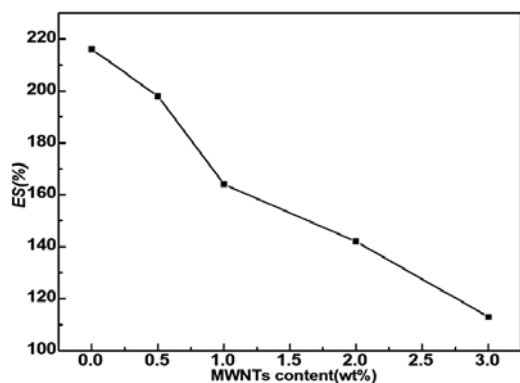

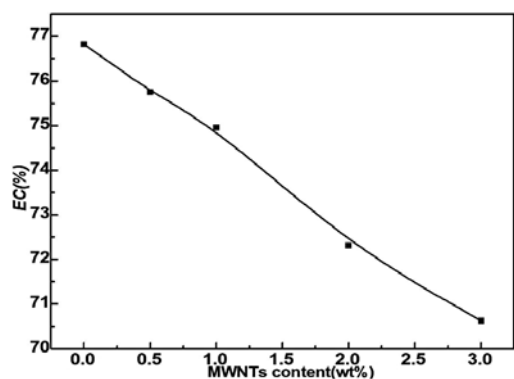**Fig. 4. Equilibrium degree of swelling of P(MAA-co-MMA)/PVP/MWNTs nanocomposite gels**

Fig. 5. Equilibrium water content of P(MAA-co-MMA)/PVP/MWNTs nanocomposite gels

Conclusion

MWNTs were dispersed into P(MAA-co-MMA)/PVP blends through ultrasonic assisted emulsifier solution free radical polymerization technique with 0.5%; 1%; 2% and 3% (wt/wt) of MWNTs loadings.

SEM analysis shows that, at low concentration of MWNTs, it is well dispersed; however, with an increase in MWNTs concentration, it is a nonuniform dispersion, and a large aggregate of MWNTs having a diameter of over 500nm is formed. DMA tests showed that the E' of P(MAA-co-MMA)/PVP/MWNTs nanocomposites increased with the increasing MWNTs content. The analysis of thermal degradation in airflow showed a clear improvement of thermal stability for P(MAA-co-MMA)/PVP/MWNTs nanocomposites, proportionally to MWNTs content. P(MAA-co-MMA)/PVP/MWNTs nanocomposites can be designed as potential biomaterials for use in wound dressing.

Literature

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