

Enhanced Compatibilization and Orientation of Polyvinyl Alcohol/Gelatin Composite Fibers Using Carbon Nanotubes

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ABSTRACT: Polyvinyl alcohol (PVA)/gelatin composite fibers containing carbon nanotubes (CNTs) had been prepared by wet-spinning method. A remarkable increase of tensile strength of the PVA/gelatin fibers was achieved by adding small amount of CNT. The mechanism of reinforcement has been studied using a combination of differential scanning calorimetry (DSC), 2D wide-angle X-ray diffraction (2D-WAXD) and scanning electron microscopy (SEM). SEM showed a decreased gelatin domain size by adding CNTs, suggesting a possible compatibilization effect

between PVA and gelatin. On the other hand, an increased crystallinity and degree of orientation of PVA/gelatin fibers has been observed by adding CNTs. Thus, the increased compatibilization, crystallinity and degree of orientation in PVA/gelatin/CNTs composite fibers should be the reasons for the observed increase of mechanical properties. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 4070–4075, 2008

Key words: PVA; gelatin; CNTs; compatibilization

INTRODUCTION

Recently, polymer/carbon nanotubes (CNTs) nanocomposites have gained intensive interest because of their unique and valuable in mechanical,^{1–3} thermal,^{4,5} and electronic^{6,7} properties compared with the pristine polymers. The CNTs can be used as nano-fibers, because of their inherent properties, such as unusual mechanical, thermal, and electronic properties. One of the advantages of CNTs as a reinforcement filler is their large surface area that can induce a better adhesion with the polymeric matrix, which is an important factor for an effective enhancement of the composite properties.⁸ However, CNT are strongly affected by van der Waals attraction just due to their small size and large surface area. These forces give rise to the formation of aggregation, which in turn, make dispersion of CNTs in polymers difficult, resulting in rather poor mechanical and electro-conductive properties. Therefore the key point to fully explore CNTs reinforcing potential

or enhancing the properties of a matrix is a uniform dispersion, exfoliation, and orientation,^{9,10} and improving the interaction between CNTs and matrix is also important.

Some unique structures and properties have been found by incorporating CNTs with polymers due to their special structure and assembling property. Bin et al. obtained highly oriented polyethylene filled with aligned CNT from solutions.¹¹ Kwangsok et al. found that CNTs in the MWNTs/polystyrene/poly(methyl methacrylate) blend thin film were dispersed on the silicon substrate without any aggregation and formed two-dimensional nano-wire arrays.¹² Pötschke et al. studied the morphology,¹³ electrical,¹⁴ and rheological¹⁵ properties of polycarbonate (PC)/MWNTs composites and obtained a notable reduction in volume resistivity for a polycarbonate/polyethylene blend by addition of 0.41 vol % MWNTs. A “pseudo-solid” behavior standing for a network structure has been reported by McNally et al.¹⁶ Du et al. investigated the network in the CNTs/poly(methyl methacrylate) nanocomposites by the linear viscoelastic behavior and electrical conductivity.¹⁷ In poly(ethylene terephthalate)/poly(vinylidene fluoride) blends, a triple-continuous structure in the CNT-filled polymer blend were formed where CNT segregates in the continuous PET phase, forming a continuous conductive path, resulting in a material with an electrical short circuit.¹⁸ A similar phenomenon was also being found in the CNTs/PA6/ABS

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blends.¹⁹ For CNTs/PPS/PA66 blends, CNTs were found to be selectively dispersed in the PA66 phase, and their assembling determines the final morphology of PPS/PA66 blends.²⁰ A largely improved tensile properties of polyvinyl alcohol (PVA)/CNTs composites were reported through functionalization of CNTs with denatured collagen.²¹ The similar result was reported in PMMA/MWNTs using amine-terminated PEO as a compatibilizer. In this article, we reported a novel compatibilization and reinforcement in PVA/Gelatin (GE) blends using MWNTs. By adding a small amount of acid treated MWNTs into PVA/GE blends, a dramatically decreased GE dispersed droplets were observed. After wet-spinning, an increased crystallinity and degree of orientation of PVA/GE composite fibers have been achieved, resulting in a great increase of tensile strength and modulus.

The choice of PVA/GE blends and wet-spinning process has been motivated by two considerations. First, PVA is a widely used synthetic biomaterial that is a nontoxic, water soluble, biocompatible, biodegradable polymer with excellent mechanical properties. While gelatin is a kind of biomaterials, cheap and easily available. The blending of PVA and gelatin combines the synthetic polymer and naturally derived materials together, and wider applications of this blends are expected. Second, by spinning, the alignment and orientation of CNTs in the matrix can be maximized, which favors to improve the efficiency of CNTs as reinforcing agent for polymer composites.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA) was 99% hydrolyzed with an average polymerization degree 1700 (Sichuan velon factory). The raw multi-wall CNT (MWNTs) provided by Nanotech Port, (Shenzhen, China). The main range of diameter of is about 10–30 nm, and their length is about 5–15 μm , the purity is larger than 95%. The MWNTs were then treated using the mixture of concentrated H_2SO_4 and HNO_3 ,²² for better dispersion in water. Gelatin (GE) is of industrial grade, purchased in Sitong (Sichuan).

Spinning solution preparation

In a typical procedure, appropriate amount PVA was first dissolved into water at 100°C, and agitated continuously for 4 h. Gelatin was suspended in water at 70°C and then centrifuged to remove impurity. Acid treated MWNTs were dispersed in basic aqueous solution (pH \approx 11), sonicated for 10 min with high-power sonic tip. For composites prepara-

TABLE I
Composition and Ratio of PVA/GE-Based Composite Fibers

Sample	Concentration (wt %)	PVA (g)	GE (g)	MWNTs (mg)
PVA/GE	11	20	2	0
PVA/GE/ 0.25 wt % MWNTs	11	20	2	50
PVA/GE/ 0.5 wt % MWNTs	11	20	2	100
PVA/GE/ 0.75 wt % MWNTs	11	20	2	150
PVA/GE/ 1.0 wt % MWNTs	11	20	2	200

tion, MWNTs suspension was added to PVA solution and stirred for 30 min, then gelatin solution was added. Meanwhile, the pH value of the mixture was adjusted to around 10, and the temperature was dropped to 40°C. A range of mass fractions could be obtained by blending these solutions in the required concentration. Detailed mixing proportions were listed in Table I.

SEM experiment was carried out to examine the phase morphology. The samples were fractured in liquid nitrogen. The fractured surfaces were then gold coated and investigated in an SEM instrument, JEOL JSM-5900LV SEM (Tokyo, Japan) with an acceleration voltage of 20 KV.

Fiber spinning and posttreatment

Fibers were spun using traditional wet-spinning technology. Saturated Na_2SO_4 solution (pH = 4) was adopted as coagulation bath. As-spun fibers were continuously collected on a fiber take-up unit at the rate of 24 m/min. In posttreatment procedure, the heat-draw temperature was 220°C, all the fibers were drawn to critical folds. After water-washing and drying at 40°C for 12 h, the fibers, being called composite fibers henceforth, were taken for the following measurements.

Characterization

Fiber tensile tests were carried out on a YGO01 tensile tester. The gauge length and crosshead speed were 20 mm and 20 mm/min, respectively. For tensile tests, 10 filaments were tested in each case. The 2D wide-angle X-ray diffraction (2D-WAXD) patterns were obtained on multifilament bundles on a SEIFERT (DX-Mo8*0.4s) diffractometer equipped a 2D Mar345 CCD X-ray detector. The wavelength of the monochromatic X-ray from Mo radiation was 0.71 nm and the sample-to-detector distance was 400 mm. The samples were placed with the fiber axis perpendicular to the beams. All the 2D WAXD

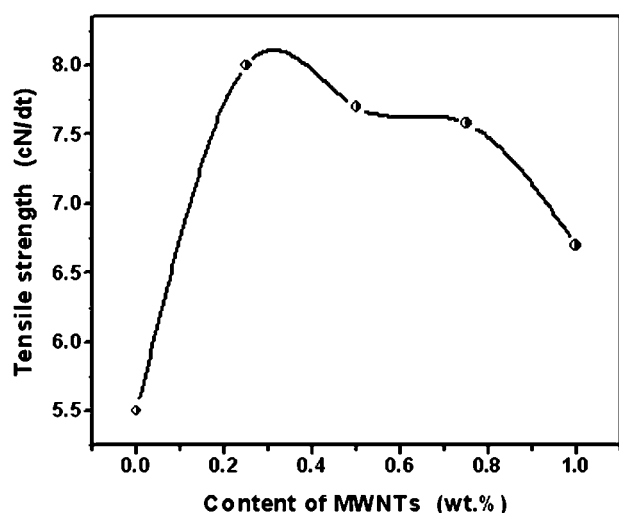


Figure 1 The tensile strength of PVA/GE based composite fibers as a function of MWNTs content.

patterns given in this article have extracted the background thus allows a qualitative comparison between various samples. The thermal analysis of the fibers was conducted using a Perkin–Elmer DSC Pyris-1. Typical sample weight used in these experiments was 5 mg. The samples were heated to desired temperature (260°C) at a rate of 10°C/min and held for 2.5 min, under the nitrogen flow. Then, they were cooled down at 10°C/min to room temperature. The temperature scale was routinely calibrated using indium standards.

RESULTS AND DISCUSSIONS

Figure 1 shows the plot of the tensile strength (cN/dt) as a function of MWNTs content in the composite fibers, at fixed ratio of PVA/GE = 100/10. The tensile strength of PVA/GE fiber is very much improved from about 5.5 to 8.0 cN/dt by adding only 0.25 wt % MWNTs. As increasing of MWNTs content, the tensile strength is not much changed. Even a decreased tensile strength is observed as MWNTs content is reached to 1.0 wt %. This is probably due to the aggregation of MWNTs at higher content. A similar trend is also found for the modu-

lus with decreased elongation (Table II). A dramatic enhancement of the Young's modulus (260%) and tensile strength (300%) of PVA has been reported through functionalization of SWNTs with denatured collagen.²¹ Here, in return, we observe an enhancement of PVA/GE (the hydrolysate of collagen at high temperature) blends by using MWNTs.

For the observed enhancement of tensile property, one logically considers the effect of MWNTs on crystallinity and orientation of the PVA/GE composite fibers. Figure 2 shows 2D-WAXD patterns for the composite fibers with different MWNTs contents. From inner to outward, the reflection arcs on the equator are originated from (101) and (200) planes of PVA, respectively. It is seen that the diffraction spots of both (101) and (200) planes of PVA crystallites in Figure 2(b,c) become stronger in comparison with PVA/gelatin fibers, as shown in Figure 2(a). This indicates that the orientation degree of PVA chains becomes more pronounced by adding MWNTs. A quantitative estimation of the orientation can be determined from (101) and (200) diffraction planes using Wilchinsky's equation.²³ It is calculated that the PVA orientation factor is 0.40, for PVA/GE composite fibers and 0.80 for the fibers with MWNTs. This also can be proved by sonic velocity method, and the result is shown in Table III. The observation of large increase of fiber orientation by adding MWNTs is unusual. This result suggests that MWNTs could serve as templates and promote the orientation of PVA. A similar increase of orientation of PVA fiber was reported by adding SWNTs.²⁴

The crystallinity of the spun fibers can be also determined by DSC melting experiment, by taking 138.6 J/g as melting enthalpy for perfect crystallization PVA,²⁵ the calculated crystallinity of the fibers by DSC as function of MWNTs is shown in Figure 3. The weight fraction of PVA was obtained by reducing gelatin content of the composite, for gelatin is kind of noncrystalline material. The crystallinity of PVA/GE fiber is remarkably increased by about 11% (from 46% to about 57%) by adding MWNTs compared with PVA/gelatin binary blends, disregarding the amount of MWNTs used. That is: MWNTs could serve as nucleating agents and promote polymer crystallization, as widely reported in literature.²⁶

TABLE II
Mechanical Properties of PVA/GE-Based Composite Fibers

Sample	Fineness (dtex)	Break elongation (%)	Tensile strength (cN/dt)	Modulus (cN/dt)
PVA/GE	2.1	21.5	5.5	97
PVA/GE/0.25 wt % MWNTs	1.1	15.9	8.0	110
PVA/GE/0.5 wt % MWNTs	1.9	15.4	7.7	131
PVA/GE/0.75 wt % MWNTs	1.7	14.0	7.6	116
PVA/GE/1.0 wt % MWNTs	1.7	11.3	6.7	119

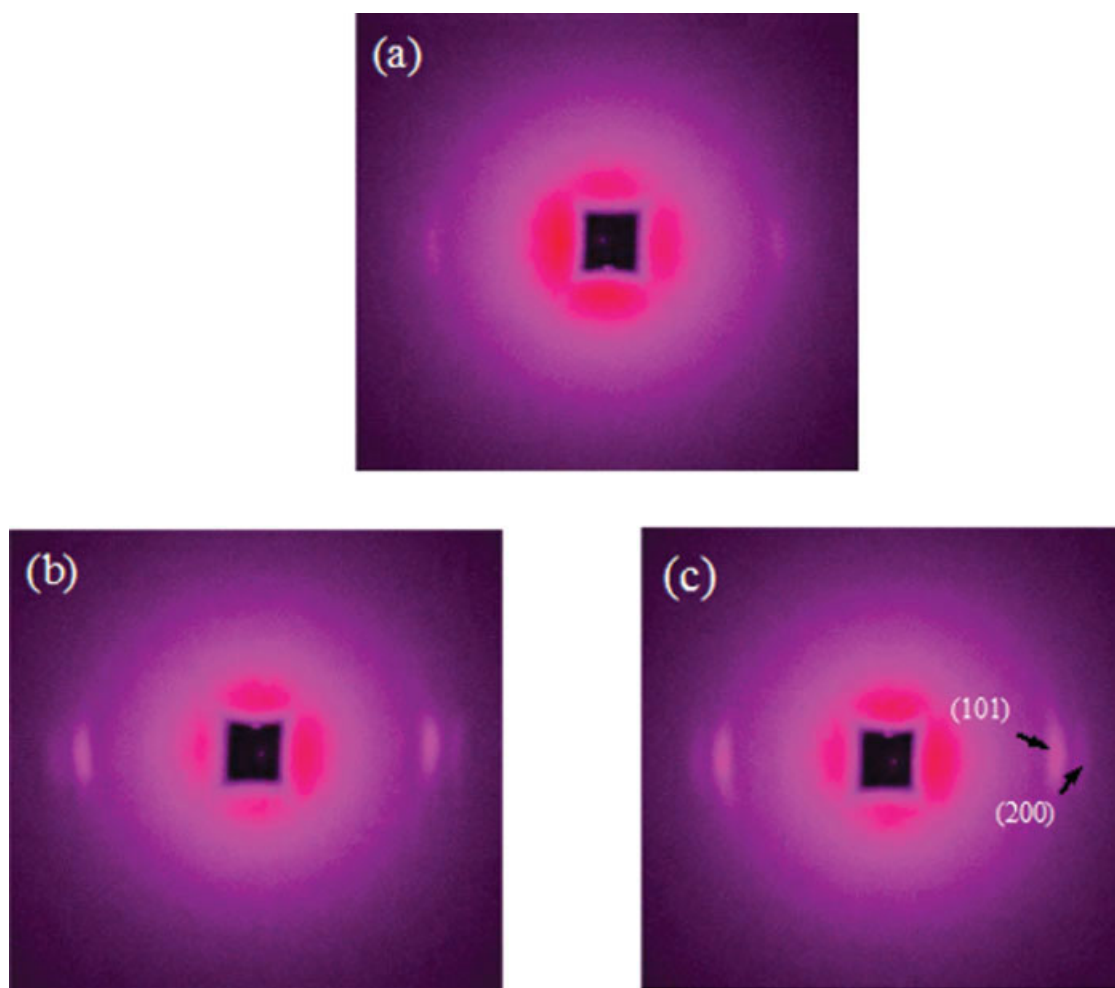


Figure 2 The 2D-WAXD patterns of PVA/GE based composite fiber yarns with vertical axis. (a) PVA/GE yarns, (b) PVA/GE/0.5 wt % MWNTs yarns, and (c) PVA/GE/1.0 wt % MWNTs yarns. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

It seems reasonable to explain the observed increased tensile property by considering the increased degree of crystallinity and orientation of PVA/GE fibers by adding MWNTs. However, as dealing with two-component polymer blends, one must consider the phase behavior and its change by adding MWNTs. PVA and GE are thermodynamically immiscible,²⁷ thus two phase morphology is usually observed. Figure 4 shows the morphology change of PVA/GE blends film prepared by spinning solution, at fixed ratio of 100/10, by adding MWNTs. One observes the typical sea-island morphology for PVA/GE blends. The boundary between PVA and GE is very sharp and the interfacial interaction is

weak. The size of GE droplets is in a range of 5–10 μm [Fig. 4(a)]. However, by adding MWNTs, the size of GE droplets is dramatically decreased for blends with different MWNTs content, Figure 4(b,c). For example, by adding 0.25 wt % of MWNTs, the size of GE droplets is down to 1–2 μm . At 1.0 wt % of MWNTs, GE droplets do not change much. It is also interesting to see that the MWNTs in this case are located in the interface or in GE phase. On the other hand, an increased aggregation of MWNTs is observed with increasing of MWNTs amount. Our result indicates a possible compatibilization of PVA and GE by using MWNTs. Thus the increased compatibilization between PVA and GE should be also

TABLE III
The Orientation Degrees of PVA/GE-Based Composite Fibers Tested by Sonic Velocity Method

Sample	PVA/GE	PVA/GE/ 0.25 wt % MWNTs	PVA/GE/ 0.5 wt % MWNTs	PVA/GE/ 0.75 wt % MWNTs	PVA/GE/ 1.0 wt % MWNTs
Degree of orientation (%)	33 \pm 5.0	87 \pm 1.5	84 \pm 2.4	80 \pm 2.5	88 \pm 4.9

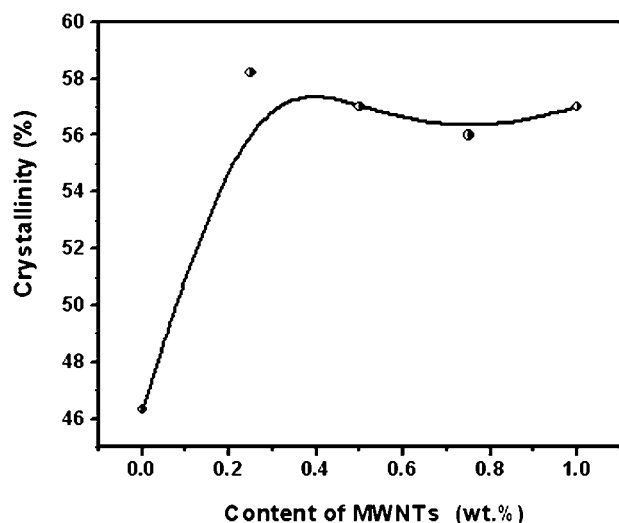


Figure 3 The crystallinity of the PVA/GE based composite fibers as a function of MWNTs content.

considered to explain, at least partially, the increased tensile property. In recent years, there has been intense interest in the application of inorganic nano-

particles as compatibilizers of immiscible polymer blends. Ray et al.²⁸ investigated the role of organically modified layered silicate as a compatibilizer for PS/PP immiscible composites. XRD and TEM observations showed that silicate layers were located at the interface between the two polymers, and it resulted in a decrease in interfacial tension and particle size and in a remarkable increase of mechanical properties. Then Ray and Bousmina²⁹ studied the compatibilization of organically modified montmorillonite for PC/PMMA composites and indicated that the key factor for compatibilization efficiency of the organoclay was the initial interlayer spacing. Río et al.³⁰ reported a partial compatibilization in PVDF/PA composites after adding carbon black, and they concluded it as a consequence of an improvement in component adhesion. Though some unique structures and properties have been found for polymer blends by incorporating MWNTs, the compatibilization effect of MWNTs is seldom reported. Our result is new and future work is needed to understand the possible mechanism for the compatibilization. For example, FTIR could be carried out to determine the

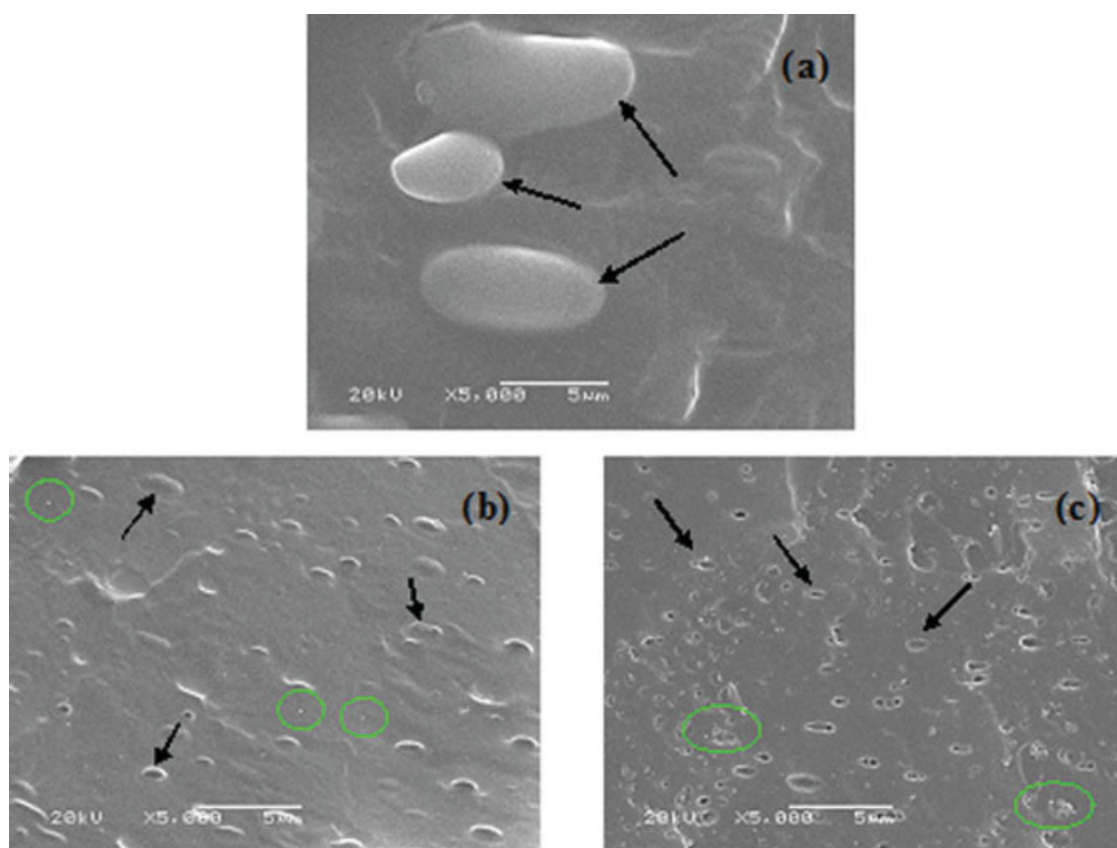


Figure 4 SEM pictures of PVA/GE based nanocomposite films prepared by spinning solution. (a) PVA/GE film (b), PVA/GE/0.25 wt % MWNTs film, and (c) PVA/GE/1.0 wt % MWNTs film. In the pictures, the droplets pointed out by black arrows are GE phase, and the white pots in the circles are MWNTs heads. One can see easily when MWNTs content reaches to 1.0 wt %, the MWNTs come to aggregate and in this case are located in the interface or in GE phase. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

possible hydrogen bonding between MWNTs and gelatin or PVA, since acid treated MWNTs contain lots of —COOH group.

CONCLUSION

In summary, PVE/GE composite fibers can be successfully obtained via wet-spinning method, and an increased tensile property of the fibers has been achieved by adding small amount of MWNTs. A preliminary investigation showed that the enhanced compatibilization, crystallinity and orientation by adding MWNTs could contribute to the observed change of tensile property. The observation of compatibilization by using MWNTs for the two immiscible polymers in the blends is somewhat new and worth to be further investigated.

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