The Journal of The Textile Institute
2011, 1–5, iFirst Article

Nanoscale three-point bending of single polymer/inorganic composite nanofiber

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(*Received 16 August 2010; final version received 19 January 2011*)

The pure polyvinyl acetate (PVAc) nanofiber and PVAc/titanium dioxide (TiO_2) composite nanofiber were prepared by sol–gel process with electrospinning. The effect of increasing TiO_2 contents on diameter distribution, surface morphology, and elastic modulus of nanofibers was characterized using a scanning electron microscope (SEM) and an atomic force microscope (AFM) equipped with picoforce. SEM images showed that the average diameter of composite nanofiber decreased with the increase in TiO_2. The three-point bending test indicated that the elastic modulus of PVAc/TiO_2 nanofiber significantly increased as TiO_2 increased.

Keywords: electrospinning; three-point bending test; nanofiber; elastic modulus

Introduction

For decades, polymer nanofibers have been known for their remarkable properties such as very small diameters, very high surface area per unit mass, small pore size, and high porosity. Due to these excellent properties, polymer nanofibers have been used for a wide range of applications such as tissue engineering, filter media, protective clothing, and sensors (Bhattarai, Yi, Hwang, Chad, & Kim, 2004; Li, Li, Ying, & Yang, 2009; Veleirinho & Lopes-da-Silva, 2009; Zhao, Gou, Bietto, Ibeh, & Hui, 2009). Electrospinning has been recognized as a simple and versatile technique for preparing nanofibers from a variety of materials. However, polymer nanofibers are not strong enough for some special applications. It has been demonstrated that polymer/inorganic nanofiber can be readily synthesized using a combination of sol–gel process electrospinning methods. Since the introduction of inorganic nanoparticles, polymer nanofibers carry the advantage of inorganic materials, such as high strength, thermal, and chemical stability (Chronakis, 2005). In order to investigate the effect of inorganic components on the mechanical properties of polymer nanofibers, several test methods were developed by researchers (Agic & Mijovic, 2005; Hasan, Zhou, & Jeelani, 2007; Rohatgi et al., 2008). However, the mechanical characterization of single nanofiber is still in an exploration stage.

In the present work, polyvinyl acetate (PVAc)/titanium dioxide (TiO_2) composite material with nanofibrous structure was prepared by electrospinning. The fibrous structure and diameter distribution of PVAc/TiO_2 nanofibers were indicated by a scanning electron microscope (SEM). The surface morphology and the elastic modulus of single PVAc/TiO_2 nanofiber were investigated by using an atomic force microscope (AFM) equipped with picoforce.

Materials and methods

Synthesis of PVAc/TiO_2 composite nanofibers

PVAc with a molecular weight of about 50,000 was obtained from Sinopharm Chemical Reagent Co. Ltd., China. Tetrabutyl titanate ($Ti(OC_4H_9)_4$) solution was used as a molecular precursor of TiO_2. Ethanol and acetone used were of analytical grade. Diethanolamine in chemically pure grade was used as the inhibiting agent for the hydrolysis process of TBT. Diethanolamine of 0.5 ml and 0.003 mol $Ti(OC_4H_9)_4$ were added to 14.0 ml ethanol with constant stirring (Solution A), while 1.0 ml distilled water was added to another 14.0 ml ethanol (Solution B). Then, Solution B was added dropwise into Solution A with vigorous stirring for 5 h at room temperature. After uniform mixing, the TiO_2 sol was obtained. PVAc solution with a concentration of 13 wt% was prepared by dissolving the PVAc particles in acetone. A controlled amount of prepared TiO_2 sol was added into the acetone PVAc solution, then reacted at room temperature for 24 h. Thus, three

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ISSN 0040-5000 print/ISSN 1754-2340 online

DOI: 10.1080/00405000.2011.557187
http://www.informaworld.com

transparent PVAc/TiO_2 composite solution samples with different TiO_2 sol content (0, 0.5, and 1 wt%) were obtained. In the electrospinning process, a high voltage power (20 kV) was applied to the solution contained in a syringe via an alligator clip attached to the syringe needle. The solution was delivered to the blunt needle tip via a microinfusion pump (WZ-50C2, Zhejiang, China) to control the solution flow rate in 0.5 ml/h. The electrospun fibers were collected on aluminum foils and grating. For convenience, the samples were labeled as $P/T_{0.5\%}$ for PVAc/TiO_2 with 0.5 wt% TiO_2 contents and $P/T_{1.0\%}$ for PVAc/TiO_2 with 1.0 wt% TiO_2 contents.

Characterization

The fibrous structures of the nanofibers were observed using the SEM (HITACHI S-4800, Japan) after a gold coating. The average fiber diameter of the electrospun nanofibers was measured by Photoshop CS3 Software. The AFM scanning was performed on a CSPM4000 AFM (Benyuan Co. Ltd., China) equipped with pico-force. The scanning frequency was set at 1.0 Hz. The surface morphology of single nanofiber was analyzed based on the AFM observations.

Three-point bending test

The nanoscale three-point bending test was performed by using the AFM cantilever tip to apply a load over the mid-span of a single-strand nanofiber suspended over a micro-sized grating groove. A cantilever tip with a spring constant of 0.35 N/m was applied. By measuring the small deflection of the nanofiber and the applied force, and using beam-bending theory, the mechanical properties of a single nanofiber can be obtained. The diameters of selected specimens are approximately in multiples of 50 nm for contrast. Because of the random distribution of nanofiber diameters, the average elastic modulus calculated in a certain diameter is the average value of 10 nearby specimens, e.g. the elastic modulus of PVAc nanofiber in 400 nm is the average value of the 10 specimens in the range of 400 ± 10 nm.

Results and discussion

The fibrous structure and diameter distribution of PVAc/TiO_2 nanofibers were investigated using SEM and mapping software, as illustrated in Figure 1. It is observed from the figure how fibrous structures are formed and the nanofibers are randomly distributed on the collector. The images in Figure 1 also indicate that the average diameter of the electrospun PVAc/TiO_2 nanofibers significantly decreases as the amount of TiO_2 increases, from 585 to 287 nm. It appears that the diameter distribution of the composite nanofibers in Figure 1(b) (100–700 nm) and Figure 1(c) (100–500 nm) becomes more uniform than that of the PVAc nanofibers in Figure 1(a) (200–1000 nm).

Figure 2 reveals the surface morphology of single PVAc/TiO_2 nanofiber with different TiO_2 contents. The particle-like structures surrounding the nanofiber in Figure 2 are the surface morphology of aluminum foils. As illustrated in Figure 2, the composition of TiO_2 sol significantly alters the surface characteristics

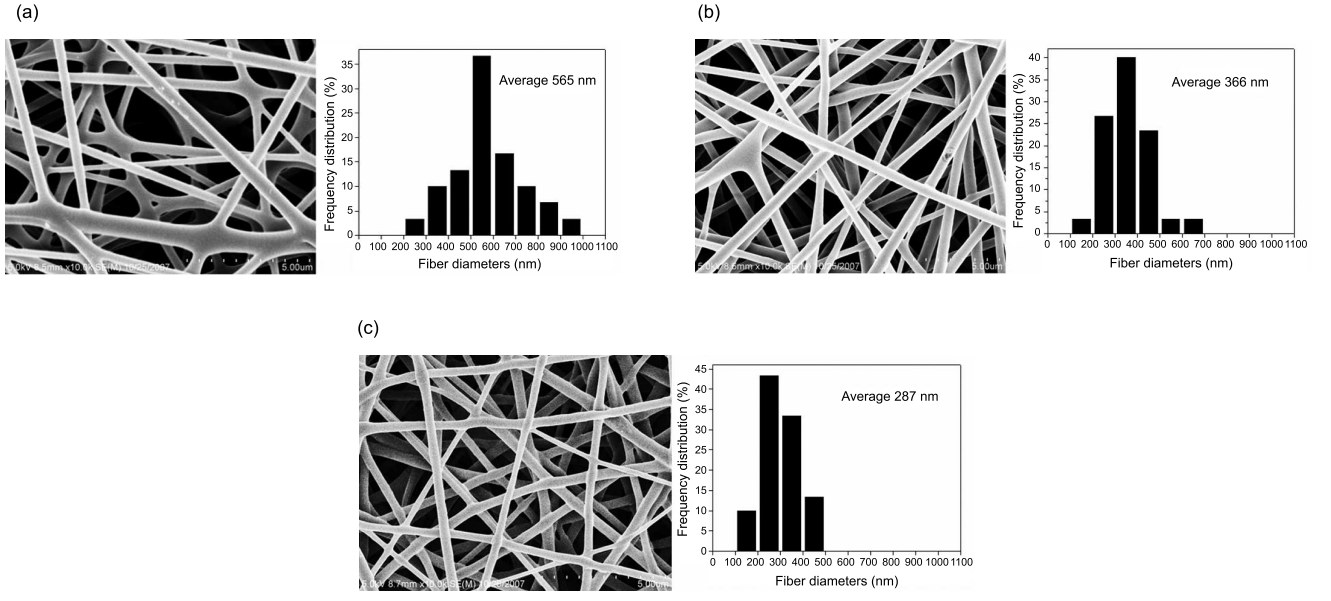

Figure 1. SEM images and diameter distribution histograms of (a) PVAc, (b) $P/T_{0.5\%}$, and (c) $P/T_{1.0\%}$ nanofibers.

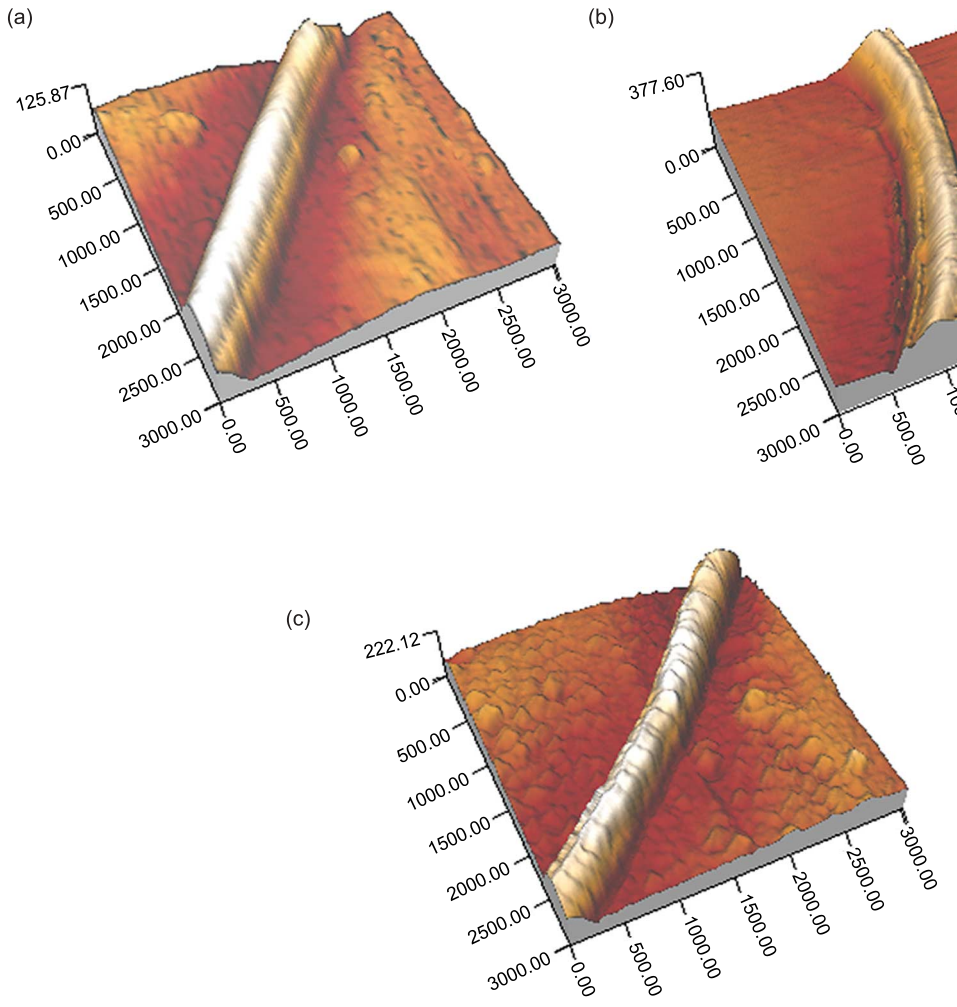

Figure 2. Surface morphology of single nanofiber: (a) PVAc, (b) $P/T_{0.5\%}$, and (c) $P/T_{1.0\%}$.

of the PVAc nanofiber. The AFM image in Figure 2a shows that the PVAc nanofiber has a relatively smooth and uniform surface. The composite nanofiber in Figure 2(b) reveals an uneven wrinkle surface structure. As the contents of TiO_2 increased to 1 wt%, the composite nanofiber (in Figure 2(c)) presented a rough surface with particle-like structures along the fiber axis. From SEM and AFM analysis, it can be concluded that the increase in TiO_2 contents not only influences the fineness and distribution of diameters, but also obviously alters the surface morphology of PVAc nanofibers.

The mechanical properties of electrospun PVAc/TiO_2 nanofibers were measured using an AFM based on the three-point bending test. A schematic of the three-point bending method is shown in Figure 3(a). In this technique, a fiber is suspended across the gap of a grating. The AFM tip impinges on the fiber, causing the deformation. The modulus measured in this manner is an entire property of a whole fiber, and can be obtained from the force–distance curve of the AFM probe. Figure 3(b) presents a typical force–distance curve by AFM, in which is included the sufficient information about surface forces. The curve is composed of six stages: (1) from A to B, the scanner extends and the tip approaches the sample surface, no interaction and no cantilever deflection, (2) from B to C, the tip being pulled down, deflection drops due to long- and short-range tip–sample attractions, (3) from C to D, as the tip contacts the surface, a force acts on the fiber and the cantilever bends upward, (4) from D to E, the scanner retracts from the sample, when reach the E point, the upward force equal to the tip–sample attraction, (5) from E to F, cantilever performs a sudden rebound as the scanner retracts continues, and (6) from F to A, at a certain distance the tip is detached from the sample and the cantilever comes back to its non-deflected state. All the followed parameters are

tested in the extension process. Knowing the vertical displacement of the AFM piezo, $Z–Z_0$, and the cantilever deflection, ΔZ_c, the vertical deformation of the fiber, δ, can be calculated (Equation (1)) Tombler et al., 2000):

$$\delta = (Z - Z_0) - \Delta Z_c. \quad (1)$$

The elastic modulus of nanofibers was calculated from beam-bending theory given by Equation (2), where F is the force applied, L is the suspended length, I is the second moment of area of the beam (where $I = \pi D^4/64$), and D is the fiber diameter.

$$E = \frac{FL^3}{192\delta I}. \quad (2)$$

As shown in Figure 4, the y-axis reflects the deflection of the cantilever, and the applied force can be calculated from the deflection using Hooke's law ($F = k\Delta Z_c$, where k is the spring constant of cantilever).

The effect of TiO_2 contents on the elastic modulus of PVAc/TiO_2 nanofiber was calculated and summarized in Figure 4. As can be seen from Figure 4, the elastic modulus of PVAc, P/$T_{0.5\%}$, and P/$T_{1.0\%}$ nanofibers decreases as the diameters increases. It is suggested that the decline of the elastic modulus can be ascribed to the fact that shear deformations become an important factor at relatively low length-to-diameter (L/D) ratios (Tan & Lim, 2004). It can also be seen in Figure 4 (inset) that all the three kinds of nanofibers in the range of 350–500 nm have been obtained from data points. The magnified image reveals that the elastic modulus increases with the increase of TiO_2 contents, which demonstrated that without regard to the difference of diameters, the introducing of TiO_2 improved the bending strength of PVAc nanofiber. Equations (3)–(5) illustrate the three-step $Ti(OC_4H_9)_4$ hydrolysis reaction process for TiO_2 sol preparation (R is *tert*-butoxycarbonyl group):

$$n\mathrm{Ti(OR)_4} + n\mathrm{H_2O} \rightarrow n\mathrm{HOTi(OR)_3} + n\mathrm{CH_3CH_2CH_2CH_2OH} \quad (3)$$

$$n\mathrm{HOTi(OR)_3} + n\mathrm{H_2O} \rightarrow n\mathrm{(OH)_2\,Ti(OR)_2} + n\mathrm{CH_3CH_2CH_2CH_2OH} \quad (4)$$

$$n\mathrm{(HO)_2\,Ti(OR)_2} + n\mathrm{H_2O} \rightarrow n\mathrm{(OH)_3Ti(OR)} + n\mathrm{CH_3CH_2CH_2CH_2OH.} \quad (5)$$

As seen from Equations (3)–(5), a large amount of –OH is generated in the hydrolysis process. When TiO_2 sol was mixed with PVAc solution, some secondary bonds or interaction forces would be formed between the TiO_2 sol molecular (–OH) and PVAc molecular (C=O) during the process of polymer/inorganic network formation, which resulted in the reinforcement of nanofibers.

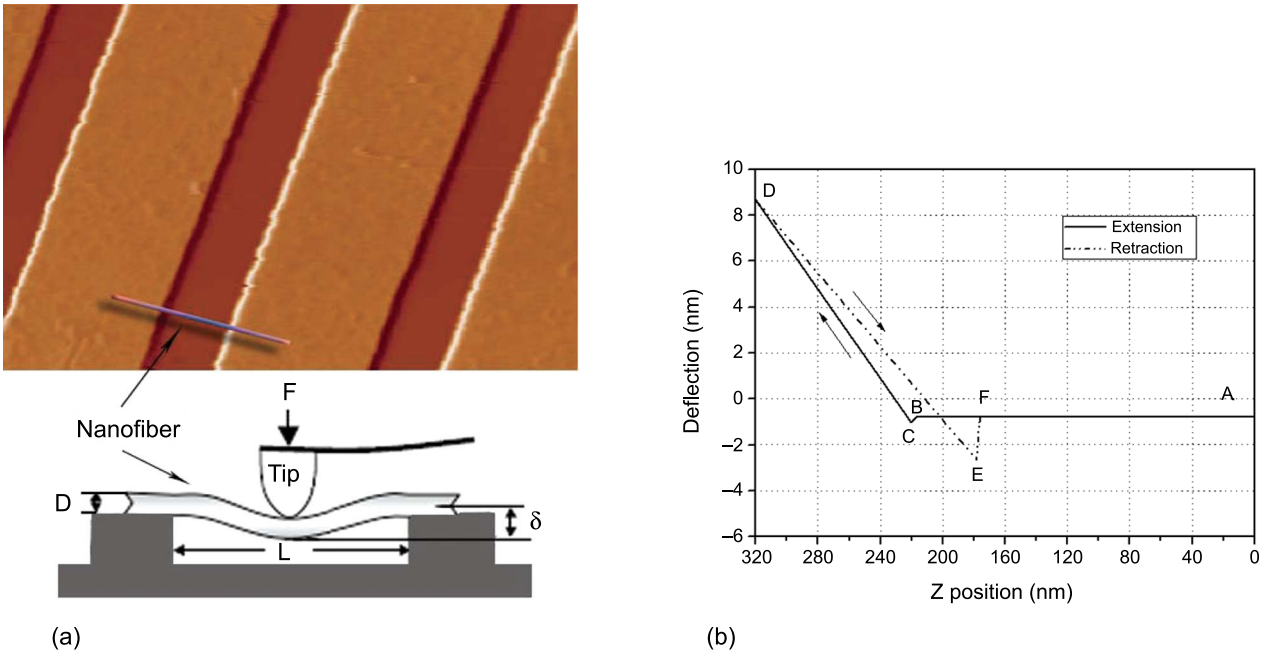

Figure 3. Schematic of the three-point bending method (a) and force–distance curve method (b).

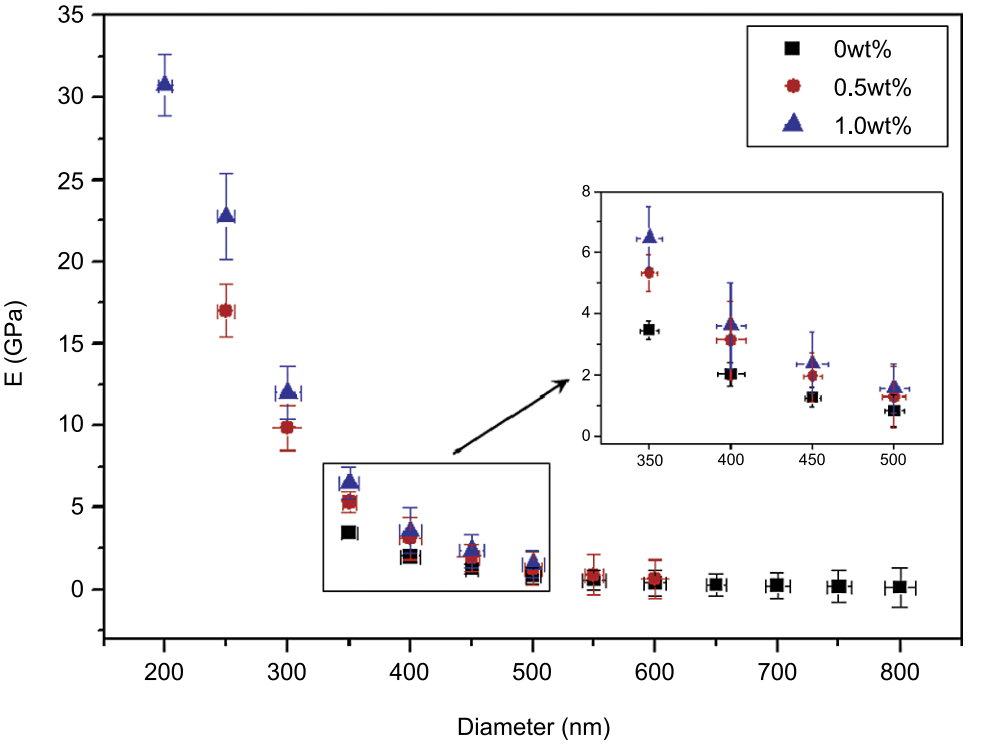

Figure 4. Effect of TiO_2 contents (0 wt%, 0.5 wt%, and 1.0 wt%) on the elastic modulus (E) of PVAc/TiO_2 nanofiber.

Conclusion

This study investigated the effect of organic/inorganic composite on the elastic modulus of nanofibers. The PVAc and the PVAc/TiO_2 nanofibers were fabricated by using sol–gel process and electrospinning method. SEM examination revealed that the average diameter of nanofibers decreased as TiO_2 increased. It was found from AFM images that the increasing TiO_2 led to the formation of rough surface of nanofibers. The results of bending property analysis indicated that the elastic modulus of both PVAc and PVAc/TiO_2 nanofibers decreased with the increase in diameters, as smaller diameters have larger decrease extent. The addition of TiO_2 sol to PVAc matrix significantly enhanced the elastic modulus of nanofibers.

Acknowledgements

The research work was supported by the Program of Tianjin Technology (No. 08JCZDJC24400) and the Program for New Century Excellent Talents in University (NCET-06-0485).

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