

Characterization of PVAc/TiO₂ Hybrid Nanofibers: From Fibrous Morphologies to Molecular Structures

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ABSTRACT: Polyvinyl acetate (PVAc)/titanium dioxide (TiO₂) hybrid nanofibers were fabricated by combining sol-gel process with electrospinning technology, which consisted of PVAc as organic segment and TiO₂ as inorganic part. The surface structures of the PVAc/TiO₂ hybrid nanofibrous mats were examined using scanning electron microscopy (SEM). The surface morphology and bulk structures of single nanofiber were investigated by atomic force microscopy (AFM) and transmission electron microscopy (TEM). Fourier transform infrared spectroscopy (FTIR) was employed to analyze the chemical structures of

the PVAc/TiO₂ hybrid nanofibers. SEM scanning revealed that the fibrous structure was formed. AFM observations presented a significant difference in the morphology of the nanofibers before and after hybridization. It was observed from TEM images that some black streaks with various lengths distributed in a nanofiber. The FTIR analysis indicated the newly formed associated hydrogen bond because of the hybrid effect between PVAc and TiO₂ sol. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1481–1485, 2009

Key words: fibers; FTIR; morphology; surfaces; AFM

INTRODUCTION

Organic–inorganic hybrid nanocomposite materials have attracted a great deal of attention in the last few decades. In these materials, organic and inorganic phases can be integrated with each other, and the domain size of one of the two phases is in nanoscale. The resulting materials are more homogenous than conventional composite materials. They can carry both the advantages of organic materials like flexibility, light weight, and the advantages of inorganic materials such as high strength, thermal, and chemical stability.¹

Besides the hybrid materials, another interesting topic in materials science is nanomaterials. When the size of materials is reduced to the nanometer scale, some new characteristics can often be found. For example, as the diameters of fibrous materials reduce from micrometers to nanometers, some appealing characteristics may arise, such as extremely large surface area, various surface functionalities, excellent mechanical strength, etc.²

Electrospinning has been recognized as a simple and versatile technique for preparing nanofibers from a variety of materials including polymers, ceramics, and composites.^{3–6} In a typical electrospinning process, the surface of a polymer droplet, suspended at the tip of a needle, is charged by the application of an electric field. As mutual charge repulsion on the drop surface overcomes surface tension, a charged polymer jet is elongated and accelerated by the electric field, undergoing a variety of instabilities, dries, and deposited on a substrate as a random nanofiber web.^{7,8}

In this work, the preparation of polyvinyl acetate (PVAc)/titanium dioxide (TiO₂) hybrid material with nanofibrous structure was achieved by the electrospinning of nanocomposite PVAc/TiO₂ hybrid materials. The effects of PVAc/TiO₂ hybrid processing conditions on the surface morphology and inner structures were investigated by scanning electron microscope (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR).

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EXPERIMENTAL

Materials

PVAc (Sinopharm Chemical Reagent, Shenyang, China) with a molecular weight of 30,000–50,000 was used. Tetrabutyl titanate (TBT) of chemically pure reagent grade was used for preparing TiO₂ sol. Both ethanol and acetone of analytical grade were used as

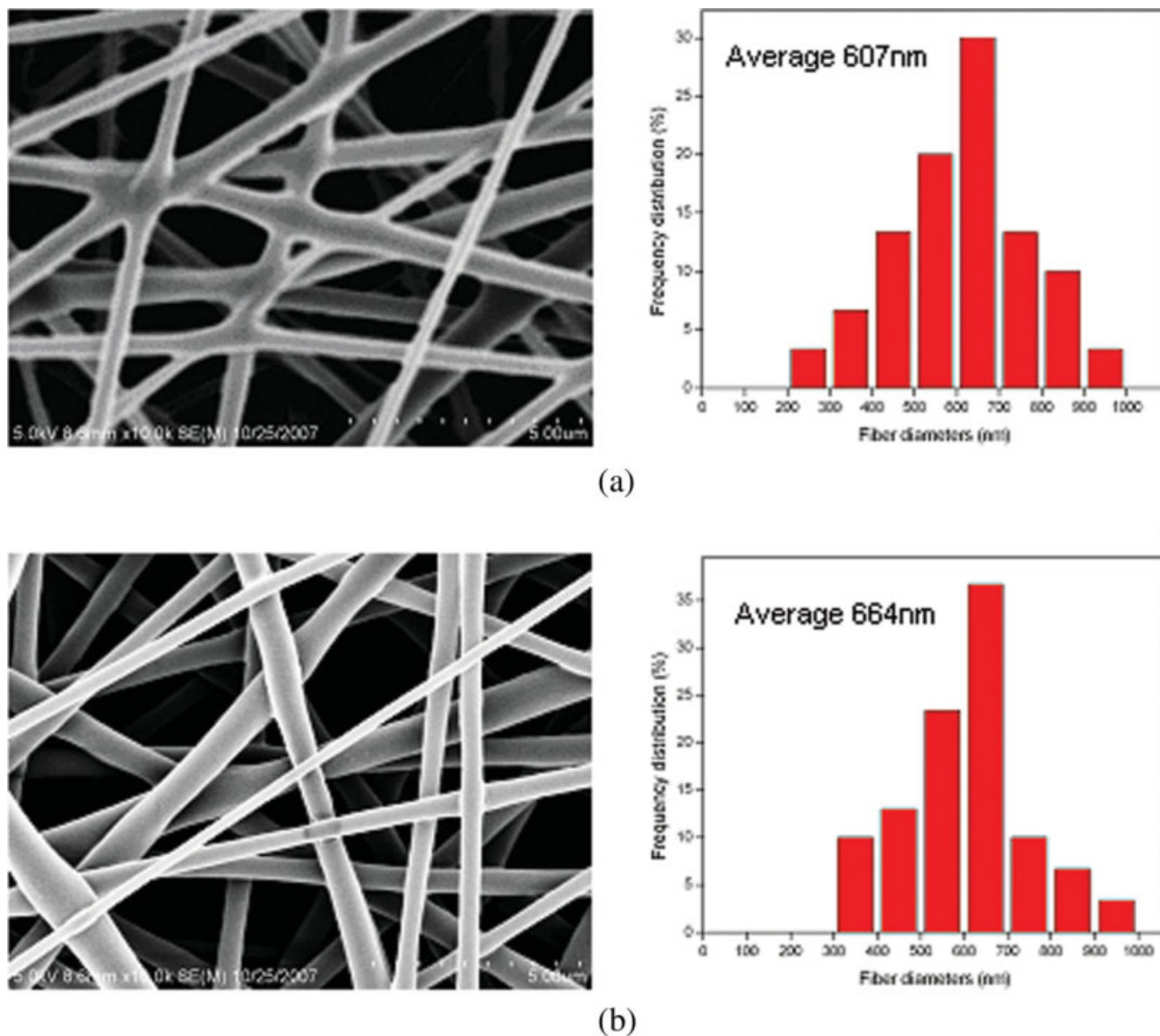


Figure 1 SEM images of (a) PVAc and (b) PVAc/TiO₂ nanofibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the solvents. Diethanolamine was used as the inhibiting agent for the hydrolysis process of TBT.

The preparation of PVAc/TiO₂ hybrid sol

Diethanolamine (0.5 mL) and TBT (1.0 mL) were added to 10.0 mL ethanol with stirring (Solution A). Deionized water (1.0 mL) was added to another 10.0 mL ethanol (Solution B). Then, Solution B was added dropwise into Solution A with vigorous stirring for 2 h at room temperature. After mixing uniformly, stable, transparent, and white TiO₂ sol was obtained. PVAc solution with a concentration of 13.0 wt % was also prepared by dissolving the PVAc particles in acetone. A certain amount of the prepared TiO₂ sol was added into the PVAc solution and stirring for 6 h, and then the PVAc/TiO₂ hybrid sol

was obtained. The obtained hybrid sol was used for viscosity test, FTIR analysis, and electrospinning.

Viscosity

The viscosities of the solutions were determined by using a rotating viscometer NDJ-79 (Shanghai, China). All the tests were made at 25°C.

Electrospinning

A voltage of 12 kV with a working distance of 10 cm (the distance between the needle tip and the collection plate) 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 (the nozzle diameter is about 0.7 mm) tip via a

TABLE I
The Viscosity of TiO₂ Sol, PVAc Solution, and PVAc/TiO₂ Solution

Solutions	TiO ₂ sol	PVAc	PVAc/TiO ₂
Viscosity (mPa s)	2.05	33.52	35.46

microinfusion pump (WZ-50C2, Zhejiang, China) to control the solution flow rate at 1.0 mL/h. The electrospun fibers were collected on different substrates for SEM, AFM, and TEM observations.

Characterization

SEM

The nanofibrous mats were collected on an aluminum foil with a dense web for SEM observation. The fibrous structures of the nanofibers were observed with SEM (HITACHI S-4800) after a thin layer of

gold coating by sputtering. The average fiber diameter of the electrospun nanofibers was measured using Photoshop 7.0 software.

TEM

The electrospun nanofibers for TEM observation were collected on a 300-mesh copper grid during the electrospinning. The TEM images of the hybrid nanofibers were obtained by using a TecnaiG220 microscope with an accelerating voltage of 200 kV.

AFM

The electrospun nanofibers were collected on the aluminum foil collector, which were used for AFM scanning. The AFM scanning was performed on a CSPM4000 AFM (Benyuan, China). Scanning was carried out in tapping mode because of the soft surface of the electrospun fibers. The scanning

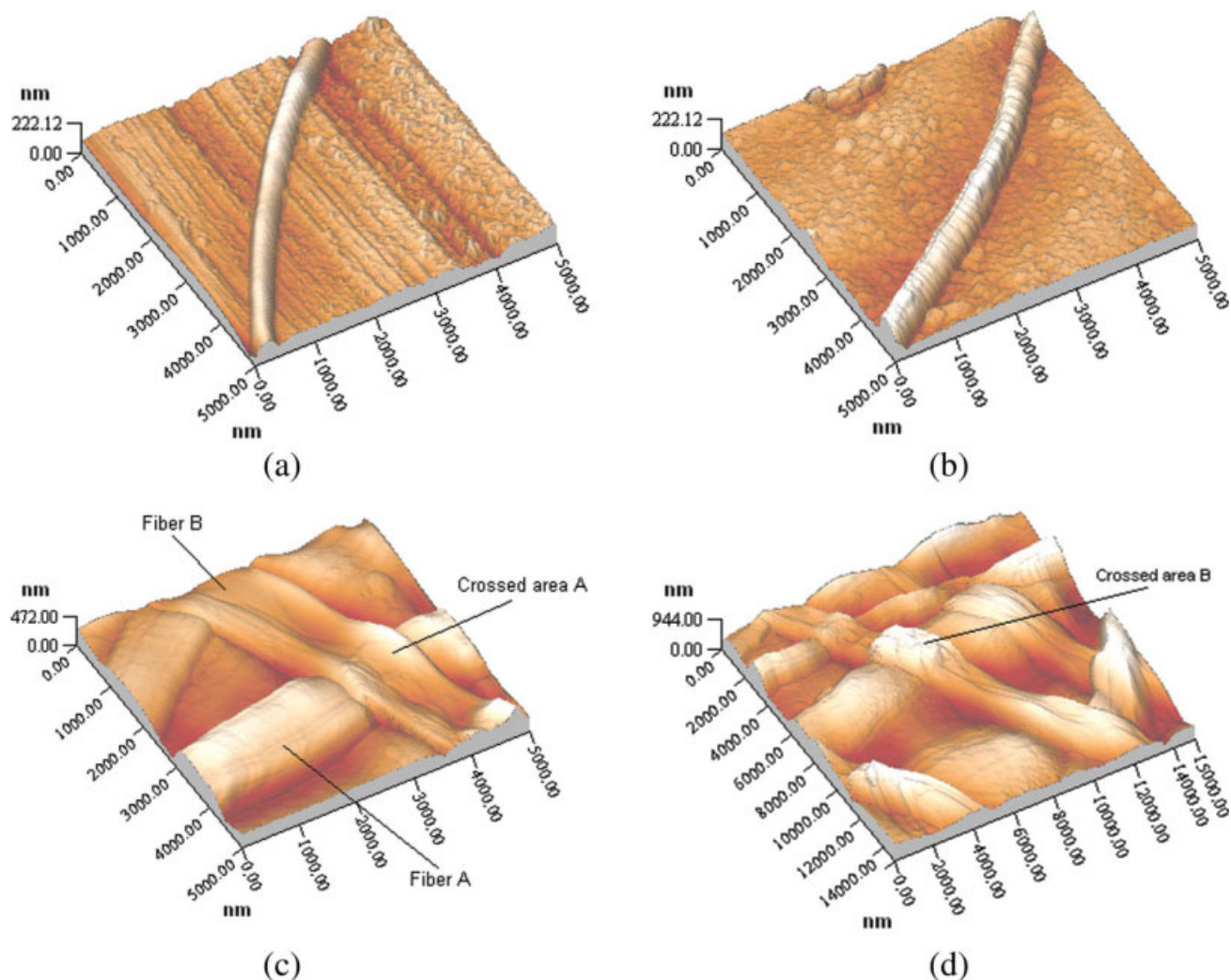


Figure 2 Surface morphology of the nanofibers on the aluminum foils: (a) single PVAc nanofiber; (b) single PVAc/TiO₂ nanofiber; (c) crossed PVAc nanofibers; (d) crossed PVAc/TiO₂ nanofiber. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

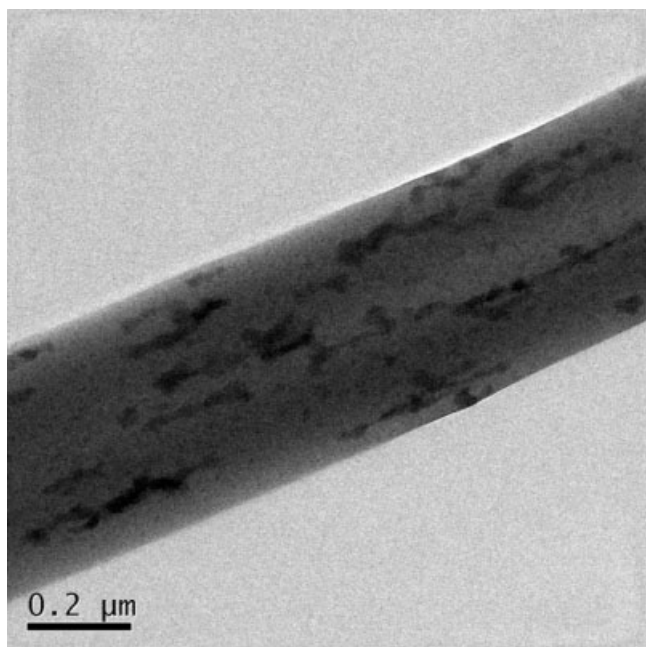


Figure 3 TEM image of PVAc/TiO₂ nanofiber.

frequency was set at 1.0 Hz. The surface morphology of single nanofiber was analyzed based on the AFM observations.

FTIR

FTIR spectra were obtained from Nicolet Nexus ATR-FTIR, in which samples were coated on the KBr slices. The scanning rate was 64 s⁻¹ and the resolution was 4 cm⁻¹, using simple point reflect.

RESULTS AND DISCUSSION

Fibrous structures of the hybrid nanofibers

The fibrous structures and diameter distribution of the PVAc and PVAc/TiO₂ electrospun nanofibers were examined using SEM. It can be seen that the nanofibers electrospun from PVAc and PVAc/TiO₂ solutions form fibrous webs and the nanofibers are randomly distributed in the webs, as presented in Figure 1. Figure 1 indicates that the average diameter of the electrospun PVAc nanofiber is increased from 607 to 664 nm as the TiO₂ sol is added, and the diameter distribution becomes narrower, indicating the improved uniformity of the fibers. In general, the increase in viscosity leads to the increased fiber diameter. Table I indicates that the viscosity of TiO₂ sol is far less than that of PVAc solution. However, as the TiO₂ sol is added, the viscosity of PVAc/TiO₂ hybrid sol is increased. The increase in viscosity is attributed to the increased molecular entanglement between the TiO₂ sol and PVAc solution during the process of mixture.⁹ SEM images present the fibrous

structures of the electrospun nanofibers, but the SEM images obtained fail to show distinguishable TiO₂ domain in the PVAc/TiO₂ hybrid nanofibers. The AFM and TEM observations were also used in this work to obtain more details on the surface morphology and bulk structures of the hybrid nanofibers.

Surface morphology of hybrid nanofibers

The surface morphologies of the PVAc and PVAc/TiO₂ nanofibers are presented in Figure 2. The AFM image in Figure 2(a) shows that the PVAc nanofiber has a relatively smooth and uniform surface. The particle-like structures surrounding the nanofiber revealed in Figure 2 are aluminum foils. Compared with Figure 2(a), the hybrid nanofiber in Figure 2(b) shows a rough surface with particle-like structures along the fiber axis. The coarse nanofibers and crossed nanofibers also show some different characteristics of the surface morphology before and after hybridization, as presented in Figure 2(c,d). It is observed that the fiber A has a columned shape and the fiber B looks like a flat belt, which is formed by the instability during electrospinning process. The shape of hybrid nanofiber in Figure 2(d) does not show any obvious difference from PVAc nanofibers in Figure 2(c). However, the crossed area A shows a flat and smooth surface, whereas the crossed area B shows a significant particle-like structure on the surface morphology of hybrid nanofibers. The particle-like structure in area B may be attributed to the inorganic components agglomerated in the nanofiber.

Bulk structures of hybrid nanofibers

The distribution of inorganic hydrolysis products in hybrid nanofibers was examined in TEM. The result is presented in Figure 3. From Figure 3 it can be found that some black streaks with various lengths distributed in the nanofibers, which are the mixture

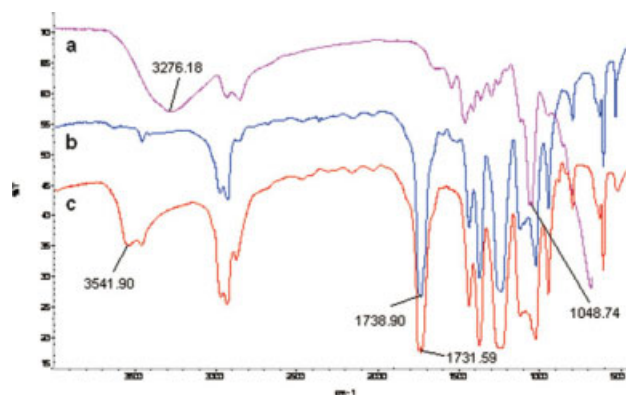


Figure 4 FTIR spectra of (a) TiO₂ sols, (b) PVAc, and (c) PVAc/TiO₂. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

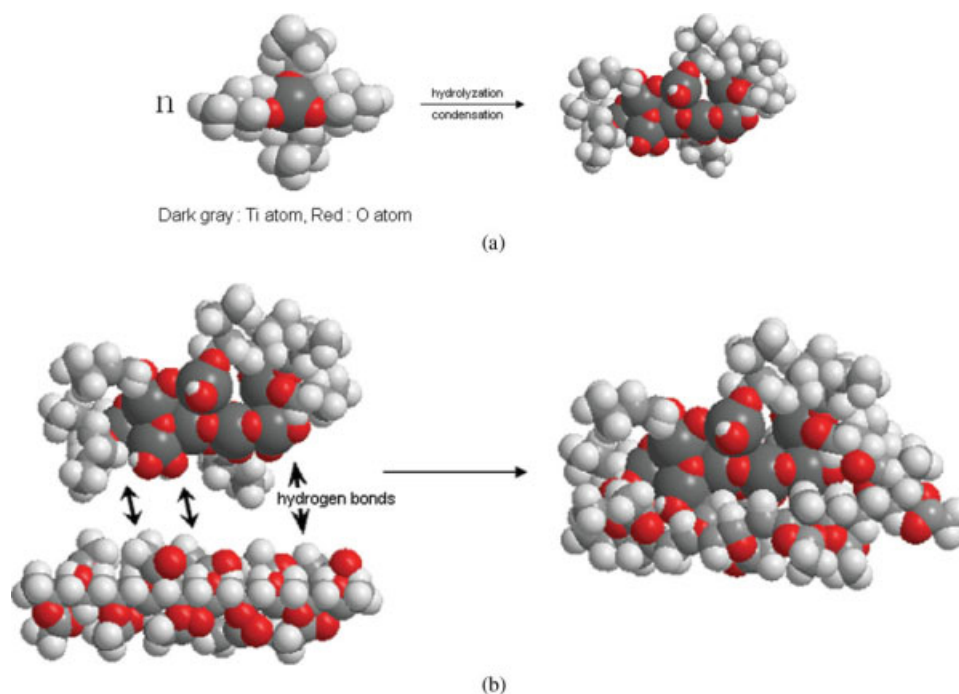


Figure 5 The formation of the hybrid: (a) TiO₂ inorganic network formation; (b) PVAc/TiO₂ network formation process. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of TiO₂ and other TBT hydrolysis products. From AFM and TEM analysis, it can be concluded that the particle-like structures on hybrid nanofiber surface are attributed to the inorganic hydrolysis products dispersed in nanofibers and on nanofiber surface.

Molecular structures of hybrid nanofibers

Figure 4 presents the FTIR spectra of the TiO₂ sols (Spectrum a), the PVAc (Spectrum b), and the PVAc/TiO₂ (Spectrum c) membranes in the wave number ranging from 4000 to 400 cm⁻¹. The Ti—OH wide absorption peak appears at 3276.18 cm⁻¹. The strong absorption peak at 1048.74 cm⁻¹ indicates the presence of Ti—O—C group in the TiO₂ sols. It can be found that the characteristic peaks of O···H group at 3541.90 cm⁻¹ appeared in Spectrum c, which is regarded as associated hydrogen bonds among molecules. From viscosity measurement and FTIR analysis, it could be regarded that some hydrogen bonds were formed between the TiO₂ sols and PVAc molecular chains during the process of organic/inorganic network formation. The hydrogen bonds also seems to bring the —C=O frequency shift from 1738.90 cm⁻¹ in Spectrum b to 1731.59 cm⁻¹ in Spectrum c.

The FTIR spectral analysis reveals the formation of the hybrid system, which is demonstrated in Figure 5. The formation of PVAc/TiO₂ hybrid system can be considered in two steps, including the formation of TiO₂ inorganic network and PVAc/TiO₂ hybrid network.

CONCLUSION

This study explored the fibrous structure, surface morphologies, and molecular structure of the PVAc/TiO₂ hybrid nanofibers. The SEM images indicated that the average diameter of the electrospun PVAc/TiO₂ nanofibers was increased after hybridization. From the AFM and TEM analysis, it could be concluded that the inorganic hydrolysis products led to the formation of the particle-like surface morphology of hybrid nanofibers. It was also found from the viscosity measurement and FTIR analysis that newly associated hydrogen bonds were formed between the organic and inorganic components in hybrid nanofiber. The analyses by SEM, AFM, TEM, and FTIR analysis provided new insight into the structures of hybrid nanofibers.

References

1. Chronakis, I. S. *J Mater Process Technol* 2005, 167, 283.
2. Huang, Z. M.; Zhang, Y. Z.; Kotaki, M.; Ramakrishna, S. *Compos Sci Technol* 2003, 63, 2223.
3. Son, W. K.; Youk, J. H.; Lee, T. S.; Park, W. H. *Polymer* 2004, 45, 2959.
4. Lu, J. W.; Zhu, Y. L.; Guo, Z. X.; Hu, P.; Yu, J. *Polymer* 2006, 47, 8026.
5. Yan, E. Y.; Huang, Z. H.; Xin, Y.; Zhao, Q.; Zhang, W. *Mater Lett* 2006, 60, 2969.
6. Deng, X. L.; Sui, G.; Zhao, M. L.; Chen, G. Q.; Yang, X. P. *J Biomater Sci Polym Ed* 2007, 18, 117.
7. Dzenis, Y. *Science* 2004, 304, 1917.
8. Shao, C.; Kim, H. Y.; Gong, J.; Ding, B.; Lee, D. R.; Park, S. J. *Mater Lett* 2003, 57, 1579.
9. Wongsasulak, S.; Kit, K. M.; McClements, D. J.; Yoovidhya, T.; Weiss, J. *Polymer* 2007, 48, 448.