

Ning Wu,
Xin Xia,
Qufu Wei,
Fenglin Huang

Preparation and Properties of Organic/Inorganic Hybrid Nanofibres

Key Laboratory of Eco-textiles,
Ministry of Education,
Jiangnan University,
Wuxi 214122, P. R. China
E-mail: qfwei@jiangnan.edu.cn

Abstract

Considerable attention has been paid to hybrid organic-inorganic nanocomposites in recent years. Organic-inorganic hybrids have both the advantages of organic materials, such as a light weight, flexibility and good moldability, and inorganic materials, such as high strength, heat stability and chemical resistance. In this work, a polyvinyl acetate (PVAc)/titanium dioxide (TiO_2) organic-inorganic hybrid was prepared by the sol-gel technique. Electrospinning was used to fabricate PVAc/ TiO_2 hybrid nanofibres. Scanning Electron Microscopy (SEM) was employed to study the morphology of the hybrid nanofibres. The mechanical and thermal properties were examined by an electronic tensile instrument and thermo gravimetric analyser (TGA), respectively. The results indicated that the mechanical and thermal properties were improved with TiO_2 included in the hybrids.

Key words: electrospinning, characterisation, PVAc/ TiO_2 , hybrid nanofibres.

reactions starting from Tetrabutyl titanate (TBT) as a precursor for inorganic domain formation. The use of a suitable coupling agent allows to obtain a strictly interconnected network preventing macroscopic phase separation [11].

The novelty of this work lies in the fact that a TiO_2 nanophase was grown in situ within the PVAc matrix, and nanofibres of a PVAc/ TiO_2 hybrid were prepared for probably the first time. The present paper describes a comparison of the morphological, thermal and mechanical properties of the hybrid nanofibres and hybrid films.

Experimental

Materials

Polyvinyl acetate (PVAc) with a molecular weight of 2000-4000, supplied by Sinopharm Chemical Reagent Co, Ltd, China, was used. Tetrabutyl titanate (TBT) of chemically pure reagent grade, supplied by Sinopharm Chemical Reagent Co, Ltd, China, was used as a precursor for inorganic domain formation. The ethanol and acetone used were of analytical grade. Chemical ethanol-ammonia solution was used as a catalyst for the hydrolysis of TBT, prepared in a laboratory.

Preparation of PVAc/ TiO_2 sols

PVAc solution with a concentration of 15 wt% was prepared by dissolving PVAc particles in acetone. TiO_2 sol of different content (0, 3.4, 4.6, and 5.6 wt%) was added to the acetone PVAc solution in drops and then left at room temperature for 24 h. Thus, a milk white and transparent sol of PVAc/ TiO_2 hybrid composites was obtained.

Preparation of nanofibre mats

Nanofibre mats were prepared by electrospinning. The PVAc/ TiO_2 sol was contained in a plastic syringe. The pinhead, which had an inside diameter of 0.7 mm, was connected to an anode, and aluminum foil served as a counter electrode. The distance between the pinhead and the surface of the aluminum foil was adjusted to 10 cm, and the ejection rate was set at 0.2 ml/h. A voltage of 15 kV was applied to the solution, and a dense web of fibres was collected on the aluminum foil. The nanofibre mats obtained were dried and then conditioned at $65 \pm 5\%$ relative humidity, 20 ± 2 °C for the following experiments.

Characterisation of the hybrid nanofibres

The PVAc and PVAc/ TiO_2 nanofibres were observed with a JSM-5610 scanning electron microscope (SEM), which was used to examine the structures of the nanofibres. An SEM Quanta 200 equipped with energy dispersive X-ray spectroscopy (EDX) was used to investigate the content of Ti elements in the hybrid nanofibres. An accelerating voltage of 20 kV with an accounting time of 100 s was applied. Thermo gravimetric analyser (TGA) measurements were carried out using a Mettler TGA/SDTA 851e thermal analyser. The experiment was performed by heating the sample from 200 to 500 °C using a heating rate of 10 °C/min. The measurements were made in a nitrogen atmosphere. The tensile properties were tested using an electronic tensile instrument (YG001, China) at 20 °C and 65% relative humidity. The measuring length of the sample was 20 mm, the width 1 mm, and the cross head speed was 20 mm/min.

Introduction

The research and development of the electrospinning method has rapidly increased during the past few years. For example, a charged jet can now be created from a polymer solution or melt when the electrical force overcomes the surface tension. The jet typically develops bending instability and then solidifies to form fibres [1 - 3].

Recently, quite a lot of attention has been given to organic-inorganic hybrid materials [4 - 7]. Organic-inorganic hybrids can combine the basic properties of organic and inorganic materials as well as offer specific advantages that enhance both thermal and mechanical properties [8].

A commonly used technique for obtaining these hybrid nanocomposites is the sol-gel process, which allows to incorporate inorganic domains, such as TiO_2 , into the polymer network [9, 10]. It involves a series of hydrolysis and condensation

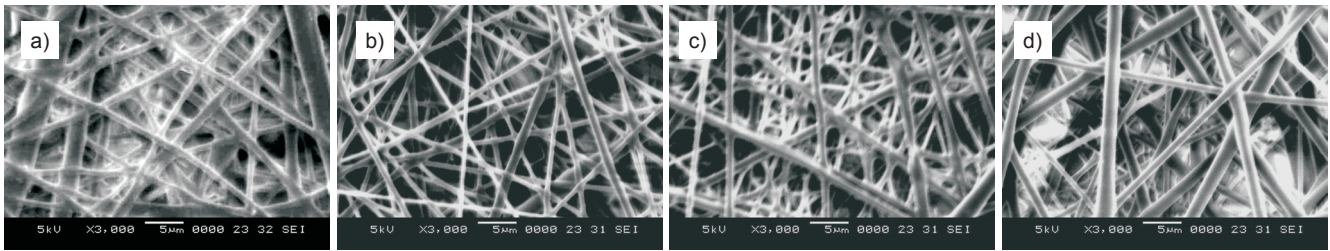


Figure 1. SEM images of PVAc/TiO₂ nanofibres of different TiO₂ concentration: a) 0 wt%, b) 3.4 wt%, c) 4.6 wt%, and d) 5.6 wt%.

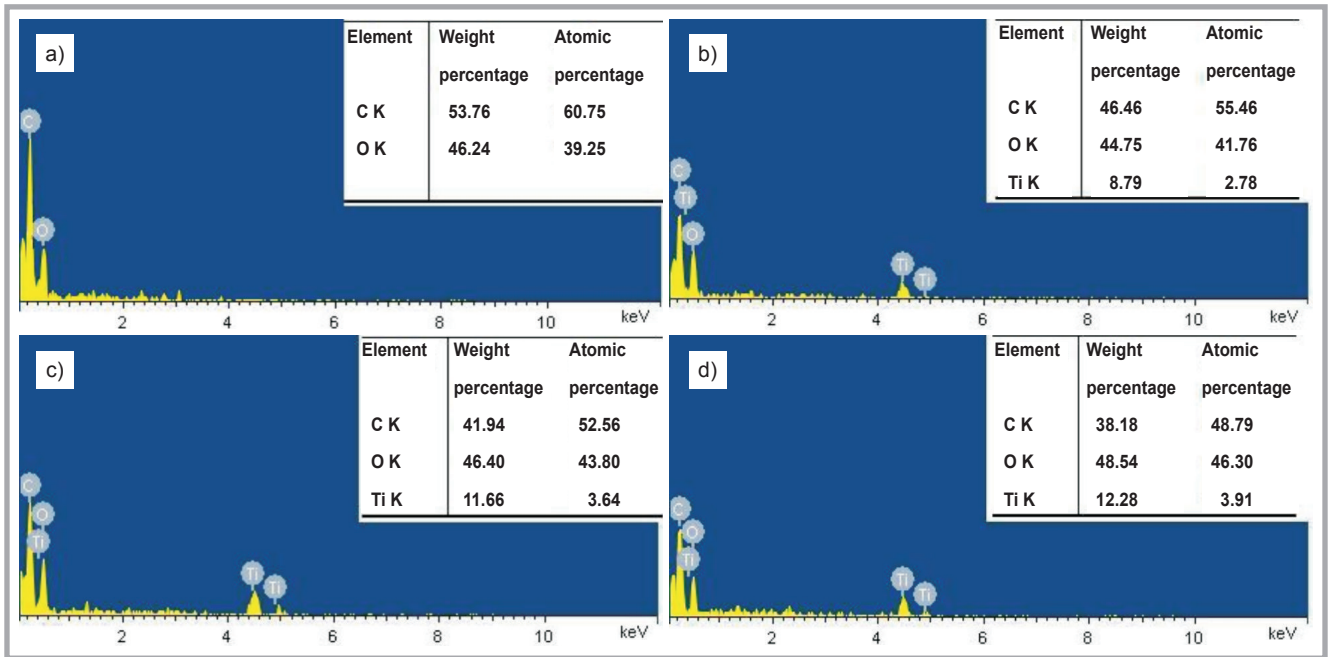


Figure 2. EDX spectra of various PVAc/TiO₂ fibres of different TiO₂ content: a) 0 wt% (pure PVAc), b) 3.4 wt%, c) 4.6wt%, d) 5.6wt%.

Results and discussion

Morphology

Figure 1 shows a series of SEM images of pure PVAc and the hybrid nanofibres. In these four cases, thin and rod-like fibres were obtained. The fibres were randomly distributed and oriented on the collector. The structures of the hybrid nanofibres were clearly different from that of the pure PVAc sample, as indicated in Figure 1.a.

It was also observed that the pure PVAc nanofibres looked softer than the hybrid nanofibres and tended to stick together at their intersections, but an increase in the content of TiO₂ reduced the stickiness at fibre intersections, as shown in Figure 1. It can also be found from the SEM images that the diameter distribution of the pure PVAc nanofibres was mostly located within the range of 400 nm and 1000 nm, some larger fibres having diameters over 3000 nm. The diameter distribution of the hybrid nanofibres was more uniform than that of pure PVAc. Among the hybrid nanofibres the average diameter increased

as the TiO₂ content increased. The smallest average fibre diameter could be obtained at 3.4 wt% TiO₂ (about 660 nm). At a concentration of 4.6 wt%, the average diameter of fibres increased to about 780 nm. The largest average diameter was observed (970 nm) at a concentration of 5.6 wt% TiO₂.

EDX analysis

Figure 2 gives the EDX spectra for various fibres samples. As is shown in Figure 2.a, the pure PVAc was mainly composed of C and O elements, and the atomic percentage was 60.75% and 39.25%, respectively. The H element was too light to be detected in the EDX analysis. As can be seen from Figure 2 (2.b, 2.c, 2.d), each spectrum shows three characteristic peaks of the Ti elements: 0.4 keV, 4.5 keV and 4.9 keV, respectively. These differences occurred because the x-ray aroused various energy levels in the Ti atoms. The spectra in Figures 2.b, 2.c and 2.d reveal the presence of Ti and O elements. It was also observed that the atomic percentages of the O and Ti elements rose with an increase in TiO₂ con-

centration (Ti: from 2.78 to 3.91, O: from 41.76 to 46.30), while the atomic percentage of the C element decreased with an increase in TiO₂ content (from 55.46 to 49.79).

Thermal properties

The thermal stability of the hybrid systems was detected using a thermo gravimetric analyser (TGA). The TGA curves of the pure PVAc and hybrid materials with different amounts of TiO₂ are shown in Figure 3, which clearly indicates that the thermal stability of the pure PVAc network was enhanced after hybridisation. The thermal stability improved with an increase in TiO₂ content. The only exception was curve d, which could have been caused by experimental error. As can be seen from curves a, b and c, the decomposition temperature initialised increased with an increase in TiO₂ content (from 311 °C to 324 °C). It was believed that the interaction of the hydrogen bond or other coordinate bonds between the TiO₂ inorganic network formed after the sol-gel process and polymeric chains restricted the thermal action of macromolecules, increasing the rigidity of the

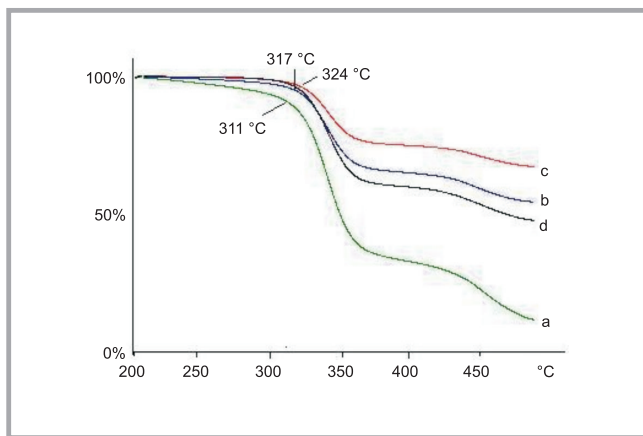


Figure 4. TGA thermograms of PVAc/TiO₂ hybrid nanofibres versus TiO₂ content: a) 0 wt%, b) 3.4 wt%, c) 4.6 wt%, d) 5.6 wt%;

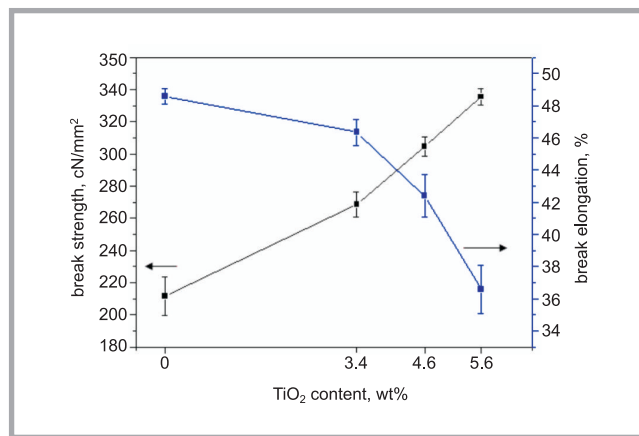


Figure 4. Tensile properties of PVAc/TiO₂ nanofibres of different TiO₂ content: a) 0 wt% (pure PVAc), b) 3.4 wt%, c) 4.6 wt%, d) 5.6 wt%.

macromolecular chain and enhancing the energy needed for polymeric chain movement and breakage [12].

Tensile properties

The effects of TiO₂ content (3.4 wt%, 4.6 wt%, 5.6 wt%) on the breaking strength and breaking elongation of PVAc/TiO₂ hybrid nanofibre mats are shown in **Figure 4**. It can be seen from **Figure 4** that the PVAc/TiO₂ nanofibres exhibited much better tensile strength as the TiO₂ content was increased, whereas the elongation at break dropped.

From the results of TGA and tensile analyses, it was believed that the interaction of the hydrogen bond or other coordinate bonds might be formed in the nanofibres between the TiO₂ inorganic network and polymeric chains after the sol-gel process [13, 14]. The enhancement of thermal stability and tensile strength were attributed to the presence of bonds, which increased the rigidity of the macromolecular chain and enhanced the energy needed for polymeric chain movement and breakage. On the other hand, an increase in the TiO₂ network restricted the movement of polymer molecules, which weakened the flexibility of the nanofibre. Therefore, the elongation at break decreased with an increase in TiO₂ content.

Conclusion

A PVAc/TiO₂ organic-inorganic hybrid was prepared by the sol-gel process. PVAc/TiO₂ hybrid nanofibres were fabricated by electrospinning. The SEM examination revealed that the diameters of these hybrid fibres became more uniform after hybridisation. The content of Ti and O was significantly increased in the hybrid nanofibres examined by EDX

analysis. The TGA scans indicated that the thermal stability of the hybrid nanofibres was improved, which proved the formation of new secondary bonds. The rigidity of the hybrid nanofibres was enhanced and the elongation decreased, as revealed in the tensile testing.

Acknowledgment

This work was supported by the Innovation Project of Jiangsu Graduate Education (NO. CX09B-172Z), the Specialised Research Fund for the Doctoral Program of Higher Education (NO. 20090093110004) and the Self-determined Research Program of Jiangnan University (No. JUSRP20903).

References

1. Kosuke O., Chenhua Z., Mitsuhiro K., 2003. "Preparation of non-woven nanofibres of Bombyx mori silk, Samia cynthia ricini silk and recombinant hybrid silk with electrospinning method", *Polymer*, vol. 44, pp. 841-846.
2. Funda C., Izabella K., 2009. "Comparative Analysis of Various Electrospinning Methods of Nanofibre Formation", *FIBRES & TEXTILES in Eastern Europe*, Vol. 17, pp. 13-19.
3. Liu Y., He J., 2007. Preparation and Morphology of Poly (butylene succinate) Nanofibres via Electrospinning *FIBRES & TEXTILES in Eastern Europe*, Vol. 15, pp. 30-33.
4. Choi S., Youngchu B., Sunhwang D., Goolee S., Hopark W., Kyoopark J., 2005. "Preparation and characterization of polyaniline nanofibre webs by template reaction with electrospun silica nanofibres" *Thin Solid Films*. vol 477, pp. 233-239.
5. Yamamoto K., Otsuka H., Wada S., Sohn D., Takahara A., 2005. "Preparation and properties of [poly(methyl methacrylate)/ imogolite] hybrid via surface modification using phosphoric acid ester" *Polymer* vol. 46, pp. 12386-12392.

6. Yua Q., Shia M., Deng M., Wang M., Chen H., 2008. "Morphology and conductivity of polyaniline sub-micron fibres prepared by electrospinning" *Materials Science and Engineering B*, vol. 150, pp. 70-76.
7. Viswanathamurthi P., Bhattarai N., Kim C. K., Kim H. Y., Lee D. R., 2004. "Ruthenium doped TiO₂ fibres by electrospinning" *Inorganic Chemistry Communications*. vol 7, pp. 679-682.
8. Tarek A., Hajime T., Tsutomu T., 2004. "Novel organic-inorganic hybrids prepared from polybenzoxazine and titania using sol-gel process" *Polymer*, vol. 45, pp. 7903-7910.
9. Guizard C., Bac A., Barboiu M., Hovnanian N., 2001. "Hybrid organic-inorganic membranes with specific transport properties Applications in separation and sensors technologies" *Separation and Purification Technology*. vol. 25, pp. 167-180.
10. Rajatendu S., Abhijit B., Sunil S., Tapan K., Chakia, Anil K., Bhowmicka, 2005. "Polyamide-6,6/in situ silica hybrid nanocomposites by sol-gel technique: synthesis, characterization and properties" *Polymer*. vol. 46, pp. 3343-3354.
11. Chiang P., Whang W., Tsai M., Wu S., 2004. "Physical and mechanical properties of polyimide/titania hybrid films" *Thin Solid Films*. vol. 447/448, pp. 359-364.
12. Yang Y., Wang P., 2006. Preparation and characterizations of a new PS/TiO₂ hybrid membranes by sol-gel process. *Polymer*. vol. 47, pp. 2683-2688.
13. Shin Y. M., Hohman M. M., Brenner M. P., Rutledge G. C., 2001. "Experimental characterization of electrospinning: the electrically forced jet and instabilities" *Polymer*, vol. 42, pp. 9955-9967.
14. Cao X., Ma J., Shi X., Ren Z., 2006. "Effect of TiO₂ nanoparticle size on the performance of PVDF membrane" *Applied Surface Science*, vol. 253, pp. 2003-2010.

Received 02.03.2009 Reviewed 06.11.2009