

# Preparation and Characterization of Organic/Inorganic Hybrid Nanofibers

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A new class of nanocomposites based on organic and inorganic species integrated at a nanoscale has obtained more attention these years. Organic-inorganic hybrids have both the advantages of organic materials, such as light weight, flexibility and good moldability, and inorganic materials, such as high strength, heat stability and chemical resistance. In this work, PVAc/TiO<sub>2</sub> organic-inorganic hybrid was prepared by sol-gel process. Electrospinning technique was used to fabricate PVAc/TiO<sub>2</sub> hybrid nanofibers. The structures and properties of the hybrid nanofibers were characterized by Scanning Electron Microscopy (SEM), Atomic Force Microscope (AFM), Differential Scanning Calorimeter (DSC) and Fourier-transform infrared (FTIR) spectra. SEM and AFM were employed to study the topography of the hybrid nanofibers. The chemical structure of the hybrid nanofibers were examined by FTIR. The DSC scans revealed the second order transition temperature of the hybrid materials were higher than PVAc.

Keywords: hybrid nanofibers, PVAc/TiO<sub>2</sub>, characterization.

## Introduction

During the last few years new materials having nanophasic morphology where an organic phase is strictly integrated with an inorganic one<sup>[1]</sup>. These new materials are called hybrid nanocomposites. They are used to combine the organic materials, such as light weight, flexibility and good moldability, and inorganic materials, such as high strength, heat stability and chemical resistance<sup>[2]</sup>.

A commonly used method for obtaining these hybrid nanocomposites is in situ sol-gel process, which allows to obtain inorganic domains, such as titanium oxide into the polymer network<sup>[3]</sup>. It involves a series of hydrolysis and condensation reactions starting from a Tetrabutyl titanate (TBT) as precursor for the inorganic domain formation. The use of suitable coupling agent permits to obtain a strictly interconnected network preventing macroscopic phase separation<sup>[4]</sup>.

Some PVAc/TiO<sub>2</sub> nanocomposites have been reported.

However, among them, only the gels or films properties of these were investigated. To our knowledge, there is no report on the preparation of the nanofibers of PVAc/TiO<sub>2</sub> hybrid nanocomposite. In this study, PVAc/TiO<sub>2</sub> organic-inorganic hybrid was prepared by sol-gel process<sup>[5,6]</sup>. Electrospinning technique was used to fabricate PVAc/TiO<sub>2</sub> hybrid nanofibers. Various methods were used to characterize the structure and topography of the hybrid nanofibers.

## Experimental

### 1 Materials

PVAc with a molecular weight 2 000 - 4 000, supplied by chemical reagent company, was used. The chemically pure of TBT was used as precursor for the inorganic domain formation. The ethanol and acetone were analytical grade. Pure chemical ethanol-ammonia solution was used as the catalyst for the hydrolysis of TBT, prepared in the laboratory.

### 2 Preparation of PVAc/TiO<sub>2</sub> sols

A titanium dioxide sol was prepared by hydrolysis and condensation by dropwise addition of ethanol-ammonia solution to TBT with strong stirring at room temperature. After the above mixture reacted for 5 h, the titanium dioxide sol was prepared. PVAc solution with a concentration of 15 wt % was prepared by dissolving the PVAc particles in acetone. A certain amount of titanium dioxide sol was dropwisely added into the acetone PVAc solution, then reacted at room temperature for another 24 h. Thus, a milkwhite and transparent sols of PVAc/TiO<sub>2</sub> hybrid composites was obtained.

### 3 Preparation of fiber mats

The solution of PVAc/TiO<sub>2</sub> composites was contained in a plastic syringe. The pinhead was connected to anode and the aluminium foil served as counter electrode. A voltage of 12 kV was applied to the solution and a dense web of fibers was collected on the aluminium foil<sup>[7]</sup>. The obtained fiber mats were then dried for the characterization.

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## 4 Characterization of the hybrid nanofibers

### 4.1 SEM

The PVAc and PVAc/ TiO<sub>2</sub> nanofibers were observed with a JSM - 5610 scanning electron microscope (SEM), which was used to examine the morphology of the nanofibers.

### 4.2 AFM

AFM observations were made on the PVAc and PVAc/ TiO<sub>2</sub> films cast on a metal substrate. Benyuan CSPM 4 000 Atomic Force Microscope (AFM) was employed to image the morphology of the film surfaces. Scanning was carried out in contact mode AFM with a silicon cantilever. All images were obtained at ambient conditions.

### 4.3 DSC

Differential scanning calorimeter (DSC) measurements were carried out using a NETZSH DSC 200 F 3 thermal analyzer. The experiment began by heating the sample from - 5 to 200 °C, using a heating rate of 10 K/ min. The measurements were made in the nitrogen atmosphere.

### 4.4 FTIR

Fourier-transform infrared (FTIR) spectra were obtained from Nicolet Nexus ATR - FT - IR, in which samples were palletized with KBr powder. The scanning rate was 64 and the resolution was 4 cm<sup>-1</sup>, using simple point reflect.

## Results and Discussions

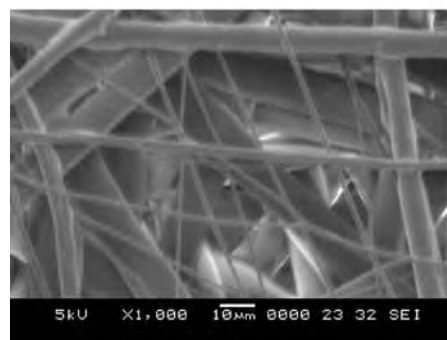
### 1 Morphology

The SEM images in Fig. 1 show the fibrous web collected on the nonwoven substrate. The examination reveals that the diameters of these fibers are in the nanoscales. The fibers are randomly distributed and oriented on the collector.

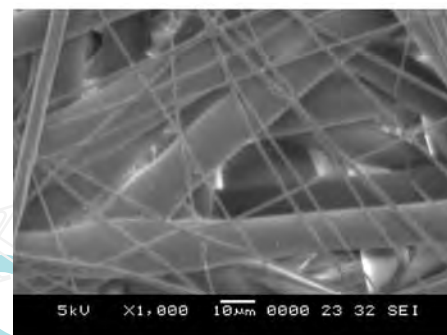
Surface morphology of the hybrid material has also been studied by SEM and AFM, respectively. The pure PVAc nanofibers and PVAc/ TiO<sub>2</sub> hybrid nanofibers are shown in Fig. 1. It can be seen that both PVAc nanofibers and the hybrid nanofibers surfaces are quite smooth and uniform. It is observed that the diameters of the hybrid nanofibers are between 500 and 1 000 nm, the extent of PVAc nanofibers are 700 - 1 200 nm. So the former is thinner than the later on the whole. This may be attributed to the decrease in surface energy.

AFM observations clearly reveal the change in surface morphology before and after hybridization. The AFM image in Fig. 2(a) shows the relatively smooth film surface with air holes. The diameter of air hole from 20 to 200 nm, no obvious rule. The PVAc/ TiO<sub>2</sub> hybrid film in Fig. 2(b) shows the rough and densified surface with clearly recognized nanoparticles structures<sup>[8]</sup>. The average

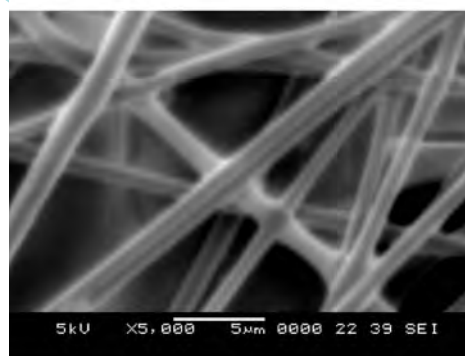
particle diameter of these nanoparticles are about 40 nm.



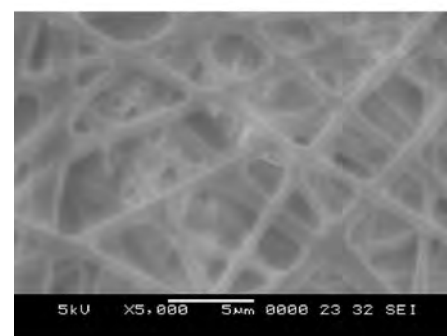
(a)



(b)



(c)



(d)

Fig. 1 The SEM images of (a), (c) pure PVAc nanofibers 700 - 1 200 and (b), (d) PVAc/ TiO<sub>2</sub> hybrid nanofibers

### 2 FTIR analysis

The FT-IR spectra obtained are shown in Fig. 3. The peak at 2 925.33 is attributed to C —O vibration. The peak

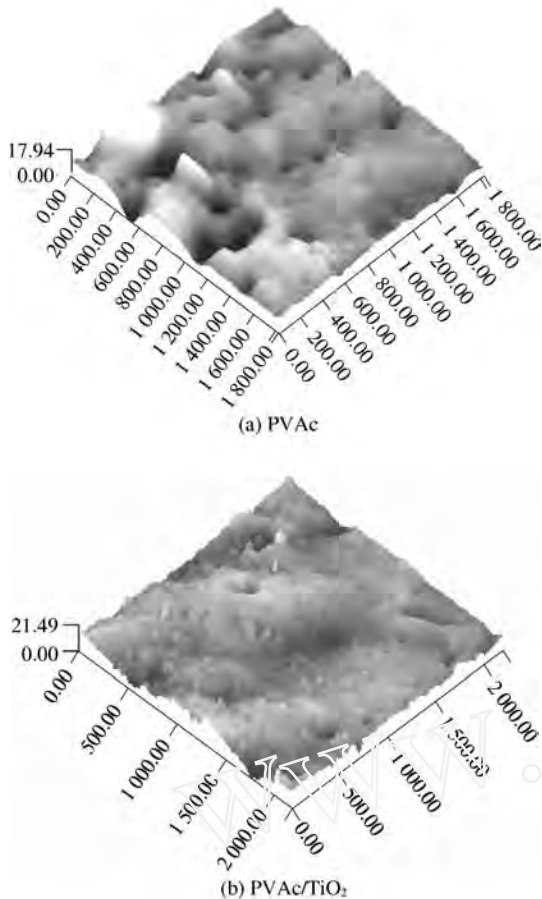


Fig. 2. Surface morphology of the pure PVAc and PVAc/ TiO<sub>2</sub> hybrid film in AFM

at 1 021.10 and 1 121.60 corresponds to the C—H vibration. The peak at 683.23 is the vibration of Ti—O. Both the hybrid composite and PVAc show a characteristic ester absorption band at 1 733.40 cm<sup>-1</sup> (characteristic of —CO—O—), but the hybrid composite peak is lower than the pure PVAc. It could be the formation of C—O—Ti induce the reduce of —CO—O—. The strong absorption peak at 1 234.11 cm<sup>-1</sup> indicates that there is a significant number of C—O groups due to the new condensation reaction.

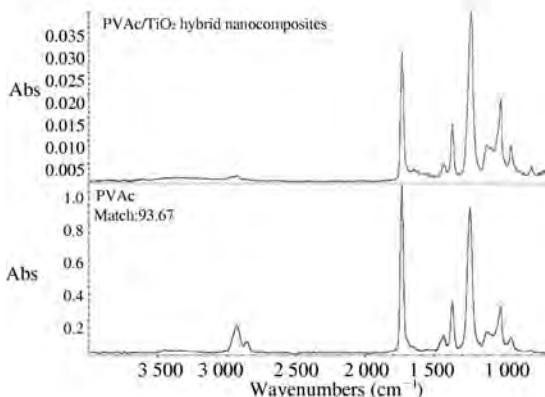


Fig. 3 FT-IR spectra of PVAc/ TiO<sub>2</sub> nanocomposites and pure PVAc

### 3 DSC analysis

The DSC thermograms of the pure PVAc and PVAc/ TiO<sub>2</sub> nanofibers samples are presented in Fig. 4. It reveals

that  $T_g$  of the starting point of PVAc is 36.7 °C, and the hybrid fibers are 39.0 °C.  $T_g$  is enhanced of 2.3 °C compared with pure PVAc. It can be deduced that interaction of hydrogen bond or other coordinate bonds between TiO<sub>2</sub> inorganic network and polymeric organic network have formed after sol-gel process, restricting the thermal action of macromolecules, increasing the rigidity of macromolecular chain and then enhancing the energy needed by polymeric chain movement and breakage<sup>[9,10]</sup>.

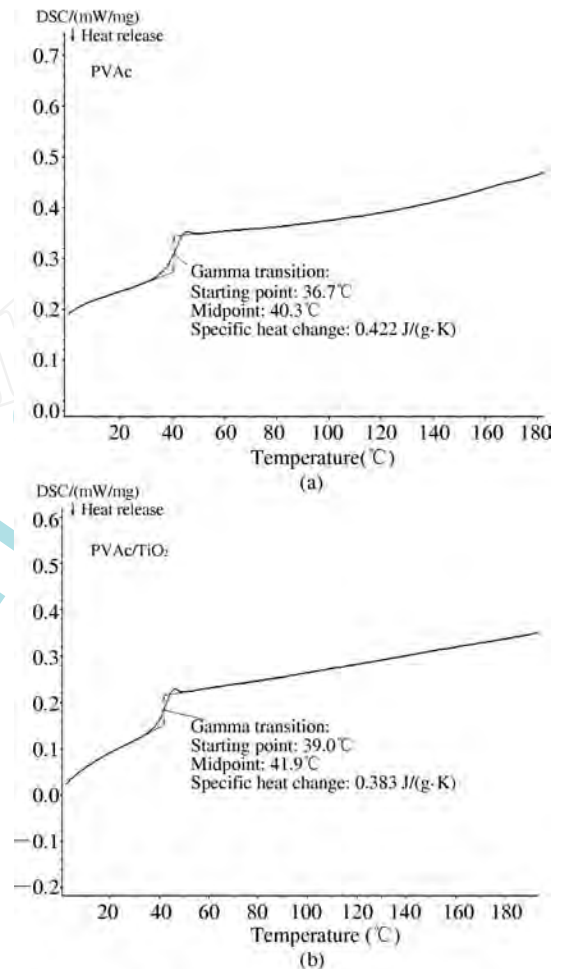


Fig. 4 The DSC graphs of pure PVAc and PVAc/ TiO<sub>2</sub>

### Conclusion

PVAc/ TiO<sub>2</sub> organic-inorganic hybrid was prepared by sol-gel process. PVAc/ TiO<sub>2</sub> hybrid nanofibers were fabricated by electrospinning. PVAc/ TiO<sub>2</sub> hybrid solutions were made in solvent mixtures of ethanol/acetone. The SEM examination reveals that the diameters of these hybrid fibers are in the nanoscales. The AFM observations indicate that the hybrid nanocomposite has rough and density structure. The FTIR analysis detects the strong absorption peak at 1 234.11, which indicates the addition of C—O, and it is likely to form C—O—Ti. The DSC scans reveal that the second order transition temperature of

the hybrid material is higher than PVAc, which indicate the formation of new substance.

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