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LETTER

Thermal property of TiO_2–fluoropolymer fiber nanocomposites

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Introduction

The semiconductor–polymer nanocomposites were widely used in the high-tech field, such as membrane separation, photoelectric, and catalytic materials [1]. The fluoropolymer nanofiber is a kind of suitable carrier for catalyzing because of its high surface areas, weatherability, thermal, and radiate resistance for the protection of C–F bond around the main chain [2]. Thermal property of semiconductor–fluoropolymer nanocomposites is one of the most important parameters for its application as photoelectric or catalytic materials [3]. However, most studies focus on the preparation and functional performance of semiconductor–fluoropolymer nanocomposites [4], but few reports on its thermal property, especially the thermal property of semiconductor–fluoropolymer fiber nanocomposites which was prepared by loading methods in the past decades.

In this communication we investigated the thermal property of TiO_2–fluoropolymer fiber nanocomposites prepared by the blending and loading method. This work conform both the influencing factors of thermal stability and melting peak temperature of TiO_2–fluoropolymer fiber nanocomposites in the preparation method and composites structure.

Experimental method

The synthesis of MAA–TFA (methacrylic acid and trifluoroethyl acrylate) random copolymers was carried out by using an automated reactor system [5]. The TiO_2 nanoparticles were prepared by hydrothermal synthesis [6]. The TiO_2–fluoropolymer fiber nanocomposites were prepared in two ways. One is the blending method, the mixed solution of TiO_2 particles, Poly(MAA-*co*-TFA) and Poly(vinylidene difluoride) (PVDF) was achieved in *N*,*N*-dimethylformamide by ultrasonic dispersion, then TiO_2–fluoropolymer fiber composites were prepared by mixed solution electrospinning. The other is the loading method, the TiO_2 particles were loaded on the surface of poly (MAA-*co*-TFA)/PVDF electrospun fiber through the hydrothermal synthesis of titanium oxo-sulfate [7].

Differential scanning calorimetry (DSC) analysis was carried out by using a TA instrument 2920 Modulated DSC. The materials were heated from 30 to 300 °C at a rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) was employed to observe the thermal stability of composites on a TA instrument Netzsch TG-209-F3 at a scan rate of 10 °C min^{-1} from room temperature to 700 °C. JSM-6700F scanning electron microscopy (SEM) was utilized to study the surface morphologies of the products. Transmission electron microscope (TEM) image and the selected area electron diffraction (SAED) pattern were taken on JEOL 2010 using an acceleration voltage of 200 kV.

Results and discussion

The poly(MAA-*co*-TFA)/PVDF electrospun fiber mats were made of random nonwoven mesh of fibers with about

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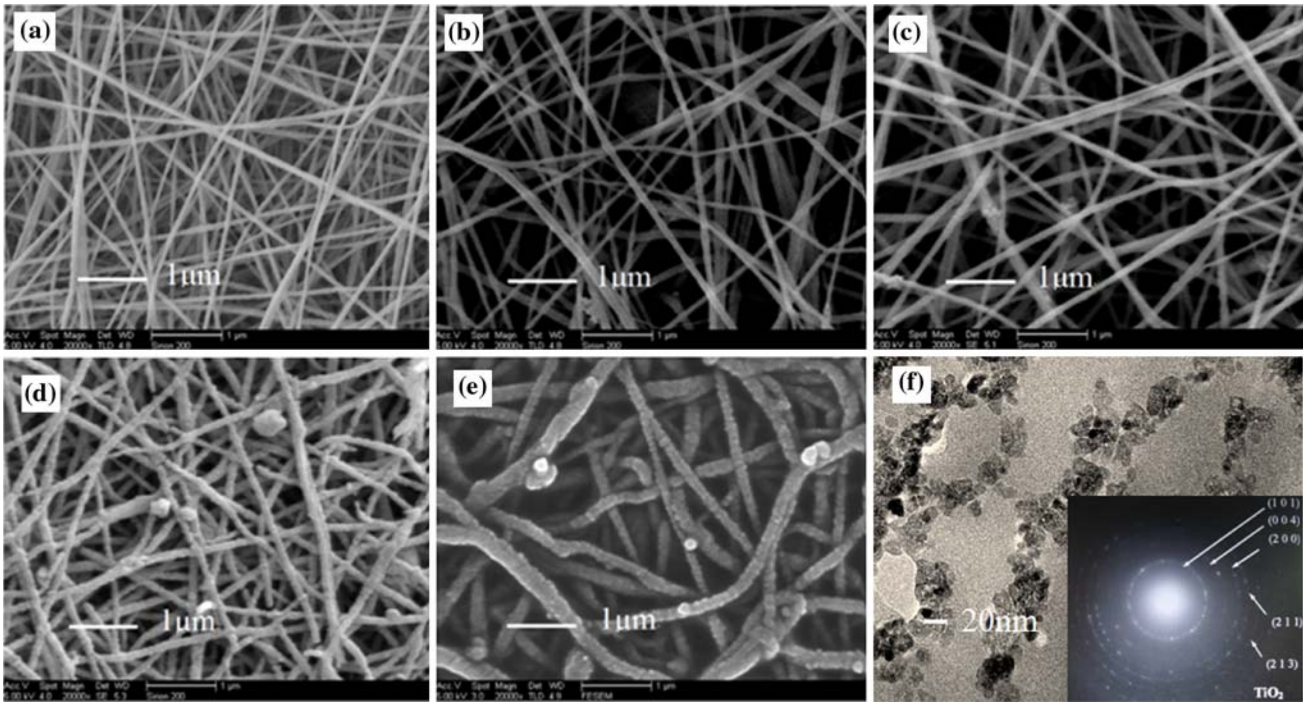

Fig. 1 SEM images of (**a**) poly(MAA-*co*-TFA)/PVDF electrospun fiber mats, TiO_2–fluoropolymer fiber composites prepared by blending method (**b**) TiO_2 content is 8.43 wt%, (**c**) TiO_2 content is 11.58 wt%, loading method (**d**) TiO_2 content is 17.76 wt%, (**e**) TiO_2 content is 22.61 wt%. (**f**) TEM and SEAD images for (**e**)

100 nm diameters, and an interconnected open porous structure, as shown in Fig. 1a. The SEM images of TiO_2–fluoropolymer fiber nanocomposites prepared by the blending method with different TiO_2 contents show that most TiO_2 nanocrystals were included in the fluoropolymer fiber, and few TiO_2 nanocrystals were exposed on the surface of fluoropolymer fiber, as shown in Fig. 1b and c. The corresponding TiO_2 content was 8.43 and 11.58 wt% that was calculated from the weight loss obtained from TGA, as shown in Fig. 2b and c. The TiO_2–fluoropolymer fiber nanocomposites prepared by hydrothermal methods at 150 °C for different time were compared in Fig. 1d and e. The TiO_2 nanocrystals were immobilized tightly on the surface of poly(MAA-*co*-TFA)/PVDF electrospun fibers, and the size of TiO_2 particles increased from 10 to 20 nm with reaction time prolonged. The corresponding TiO_2 content is 17.76 and 22.61 wt% that calculated from the weight loss obtained from TGA, as shown in Fig. 2d and e. The TEM image of TiO_2–fluoropolymer fiber composites prepared by the loading method shows the slight agglomeration of TiO_2 particles, which are inclusive of nanocrystallites with indistinct polygonal shape of about 20 nm in size, and the selected area electron diffraction (SAED) patterns of anatase are shown in Fig. 1f.

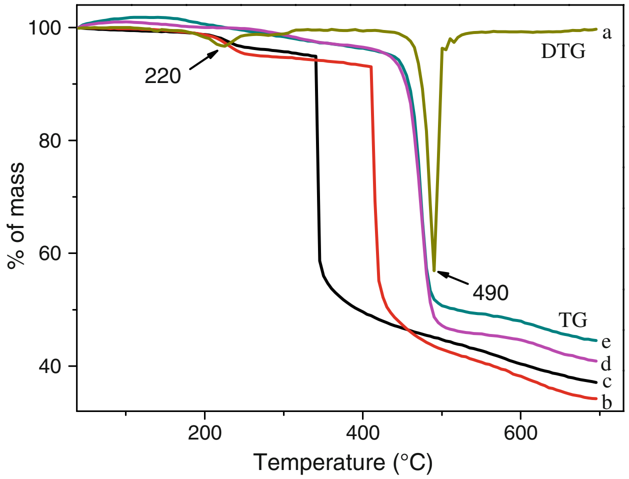

Fig. 2 Thermal gravity analytical of (*a*) poly(MAA-*co*-TFA)/PVDF electrospun fiber mats, TiO_2–fluoropolymer fiber composites prepared by blending method (*b*) TiO_2 content is 8.43 wt%, (*c*) TiO_2 content is 11.58 wt%, loading method (*d*) TiO_2 content is 17.76 wt%, (*e*) TiO_2 content is 22.61 wt%

According to the TGA, the fluoropolymer electrospun fibers contain four decomposition stages, and the corresponding DTG cure was shown in Fig. 2a, the decomposition temperature of poly(MAA-*co*-TFA) and PVDF was about 220 and 490 °C, respectively. The decomposition temperature of poly(MAA-*co*-TFA) in TiO_2–fluoropolymer fiber composites has took no obvious changes, but PVDF in TiO_2–fluoropolymer fiber composites was lower than that in the pristine fluoropolymer fiber matrix, as shown in Fig. 2. This experimental result was different from the report of Ouafa Tahiri Alaoui [8]. The phenomenon explains that the TiO_2 nanoparticles have some catalysis under high temperature, and lead to the decrease of decomposition temperature of TiO_2–fluoropolymer fiber composites. The decomposition temperature of TiO_2–fluoropolymer fiber composites prepared by the blending methods was far lower than that of the pristine fluoropolymer fiber matrix, and the decomposition temperature decreased sharply from 417 to 342 °C with the TiO_2 nanocrystallites content improved in composites, as shown in Fig. 2b and c. The reason resulted from the well dispersion of TiO_2 nanocrystallites into the fluoropolymer matrix, which improved the catalytic efficiency. The TG curves in Fig. 2b and c change abruptly at about 400 degree were attributed to the catalysis of TiO_2 nanocrystallites in composites [9]. However, the decomposition temperature of TiO_2–fluoropolymer fiber composites prepared by the loading methods was 475 °C, and did not decreased remarkably compare with that of the pristine fluoropolymer fiber matrix, as shown in Fig. 2a, d, and e. That is because the fluoropolymer fibers were coated by TiO_2 particles, and shell structure of TiO_2 formed only on the surface of fluoropolymer fiber, as shown in Fig. 1d and e. The catalysis of TiO_2 particles was determined only by the limited interface between TiO_2 particles and fluoropolymer fiber, so the decrease of decomposition temperature for the composites prepared by the loading method was far less than that for the composites prepared by the blending method. The decomposition temperature of composites prepared by loading method did not decrease with the TiO_2 content improved which also demonstrated the inference above, as shown in Fig. 2d and e.

According to the DSC analysis, the melting peak temperature of the pristine fluoropolymer fiber was about 172 °C, and the melting peak temperature of the TiO_2–fluoropolymer fiber composites was slightly higher than that of the pristine fluoropolymer fiber, as shown in Fig. 3. The good dispersion or coating of TiO_2 particles with the fluoropolymer matrix was able to improve the crystallization by hindering the extending and moving of fluoropolymer macromolecular chain at low temperature [10], so accordingly the melting peak temperature of composites was improved. The nucleation of TiO_2 nanocrystallites has different effect on the poly(MAA-*co*-TFA) and PVDF [3], so the DSC curve has two overlapping melt peaks when the addition of TiO_2 particles in fluoropolymer, as shown in Fig. 3b–e. However, this nucleation effect was so weak for the improvement of melting peak temperature of composites that the melting peak temperature of TiO_2–fluoropolymer fiber composites was only slightly increased compared with that of the pristine fluoropolymer fiber.

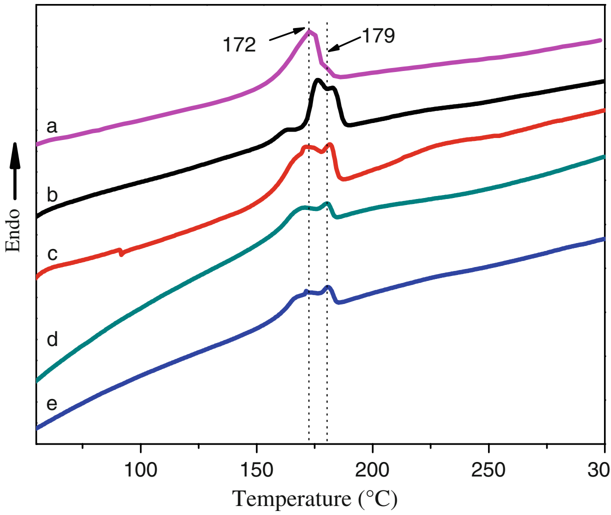

Fig. 3 Differential scanning calorimetry analysis of (*a*) poly(MAA-*co*-TFA)/PVDF electrospun fiber mats, TiO_2–fluoropolymer fiber composites prepared by blending method (*b*) TiO_2 content is 8.43 wt%, (*c*) TiO_2 content is 11.58 wt%, loading method (*d*) TiO_2 content is 17.76 wt%, (*e*) TiO_2 content is 22.61 wt%

Conclusions

The decomposition temperature of TiO_2–fluoropolymer fiber composites was determined by the catalysis of semiconductor particles under high temperature, so the high interphase area between TiO_2 nanocrystallites and fluoropolymer resulted into the decrease of decomposition temperature of composites. The melting peak temperature of the TiO_2–fluoropolymer fiber composites was improved slightly because of the nucleation of semiconductor particles in the fluoropolymer matrix.

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