Enhanced thermal conductivity and mechanical property through boron nitride hot string in polyvinylidene fluoride fibers by electrospinning

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ABSTRACT

The electrospun polyvinylidene fluoride (PVDF) based modified boron nitride (m-BN) composite with high thermal conductivity and flexible mechanical property was successfully fabricated by electrospinning method. The uniform dispersion and ordered orientation of m-BN in the m-BN/PVDF composites form a hot string, denoted as a series of thermal conduction fillers, in the direction of the fiber. Hence, the thermal conductivity of the m-BN/PVDF film could reach to 7.29 W m^{-1}K^{-1} with the addition of 30 wt% m-BN. Besides, the obtained composites also show improved mechanical properties with the tensile strength of 24.06 MPa, low dielectric permittivity of 2.45 and dielectric loss of 0.0242 @ 10^3 Hz. Therefore, this work provides a new route to prepare the high thermal conductivity films with potential application as flexible power devices.

1. Introduction

Polymer composites with high thermal conductivity and mechanical property are of great significance as their widely used in the portable displays and medical instruments [1–4]. Polymer materials such as polyethylene terephthalate (PET), poly(-dimethylsiloxane) (PDMS), and polyimide (PI) play a key role in the flexible electronics industry as substrates due to their excellent mechanical and electrical properties [5–9]. However, conventional polymer materials have low thermal conductivity, typically in the range of 0.1–0.5 W m^{-1}K^{-1} at room temperature, which could not meet the special demand of flexible electronics industry [10,11]. To overcome this problem, different strategies including cast blending, chemical vapor deposition, stretching, induction by magnetic field, and electrospinning were applied to improve their thermal properties [12–17]. Among these methods, electrospinning technology has attracted a growing interest in the field of preparation of aligned fiber arrays due to its easy operation and large scale production [18].

Until now, many works have been done to develop novel electrospinning composites with excellent performance for flexible power devices [19,20]. Wong et al. has demonstrated that the thermal conductivity can reach values as high as 0.8 W m^{-1}K^{-1}, which is about three times higher than that of casted epoxy substrate fabricated by spin-coating [21]. In addition, the thermal conductivity can be tuned by varying the diameter of fibers. Nevertheless, since there were no fillers added to the polymer, the thermal conductivity did not improve significantly. Guan et al. successfully manufactured electrospun polyamide (PA) 66 nanofiber bundles with high conductivity, improved strength, and robust flexibility through simply adsorbing multiwall carbon nanotubes (MWNTs) on the surface of electrospun PA66 nanofibers. It proves that the adsorption of thermally conductive particles on the surface of electrospun fiber can effectively improve the properties of electrospinning film [22]. Thus, it is expected to realize a high thermal conductivity through electrospinning technology.

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Besides the orientation of the anisotropic fillers, the reduction of interface thermal resistance is an important factor in achieving high thermal conductivity. Surface modification is an effective way to increase compatibility and reduce surface resistance [23–25]. Dopamine chemistry as a convenient and eco-friendly strategy was applied to modified the functional fillers [26].

To prepare the composite material with high thermal conductivity and excellent mechanical properties, another basis which could not be ignored is the choice of matrix and fillers. Poly(vinylidene fluoride) (PVDF) with four different crystalline phases has aroused much attention for its valuable properties such as high energy storage, high flexibility [27–30]. Hexagonal boron nitride (BN), a similar hexagonal structure to graphite, has been extensively studied for various applications in the recent decade, based on its lower density, excellent mechanical strength, and extremely electrical insulating. In addition, due to the extraordinary thermal conductivity, BN has been considered as ideal fillers to fabricate thermal conductivity polymer-matrix composites for flexible electronics applications [31–33].

In this work, we report a novel and simple approach to prepare oriented fibers and fillers along the axial direction by facile electrospinning technology. The well-aligned PVDF ultrafine fibers with the m-BN have been fabricated. The string of m-BN in PVDF fiber would provide much more thermal conductivity channels in plane. The morphology, structure, thermal conductivity and mechanical properties of the as-prepared hybrid film were comprehensively examined. The mechanism of thermal conductivity was further studied.

2. Experimental

2.1. Materials

Acetone and N,N-dimethylacetamide (DMF) were obtained from Beijing Chemical Works. Nitric acid was purchased from Sinopharm Chemical Reagent Co. Ltd, China. PVDF (FR904) was purchased from Inner Mongolia 3F-Wanhao Fluorine Chemical Co. Ltd, China. The h-BN powder (1–2 μm, purity >99.5%) were obtained from Aladdin Industrial, Inc. (China). All these chemicals were of analytical-reagent grade and were used without further purification.

2.2. Preparation of m-BN

The modified BN powder, named as m-BN, was prepared by a solution method. Firstly, the BN powder was fully dissolved in the mixed solution of 150 mL of tris-buffer solution (10 mM, pH 8.5) and 50 mL of ethanol. Then the mixed solution was ultrasonically for 4 h to make BN evenly dispersed. After that, 400 mg of dopamine hydrochloride was added and the mixture was stirred for 8 h at 60 °C. Dopamine molecules were easily oxidized to self-polymerize into polydopamine (PDA) coating on the surface of BN platelets.

2.3. Preparation of the PVDF fibrous film

Prior to use, the PVDF was dried at 80 °C for 24 h in a vacuum oven. A mixture of DMF and acetone (10:1 by weight) was prepared as the solvent. Subsequently, PVDF was dissolved in this solvent and stirred at a concentration of 10 wt% for 5 h at 60 °C before electrospinning. Then electrospinning was carried out at an applied voltage of 15–20 kV at room temperature. The distance between the metallic needle and the steel drum was 15 cm and the aluminum foil (20 cm × 31.5 cm) covered onto a steel drum was applied to collected the fibers. Then, the electrospun PVDF fibrous films were dried at 60 °C for 12 h to evaporate the residual solvent.

2.4. Preparation of PVDF films anchored with m-BN and BN

The modified BN were dissolved into DMF and acetone (10:1 by weight) and then the mixtures were dispersed by an ultrasonic processor for half an hour. 2 g dried PVDF was added in the above solution to make a final solution with m-BN mass ratios of 10%, 20%, 30% and 40%, respectively. The electrospinning process was similar with the preparation of pure PVDF membranes. Finally, the prepared PVDF films with m-BN were put in a vacuum oven at 80 °C for 24 h until all of the solvent was removed by evaporation. For comparison, the electrospun PVDF films filled with unmodified BN were prepared by the same procedure. In addition, the casting PVDF films filled with m-BN was prepared by simple casting method.

2.5. Characterization

The morphology of the electrospun film was tested by Hitachi, S-4800 scanning electron microscopy (SEM). It was performed at an acceleration voltage of 10 kV. Prior to SEM examination, the surfaces of samples were sprayed with Au. Transmission electron microscope (TEM) studies were tested on a JEM-2100F (JEOL, Japan) at an accelerating voltage of 200 kV.

Crystalline and thermal properties were analyzed using a differential scanning calorimetry (DSC) Q2000 (TA company, USA). The measurements were carried out at 10 °C min^{-1} heating rate in nitrogen atmosphere, from 20 °C to 200 °C and holding at 200 °C for 2 min to erase thermal history, and then cooled to 20 °C, and then heated to 200 °C, and the second heat curve was analyzed. The PVDF crystallinity (Xc) was calculated according to equation (1) [34].

$$X_c = \frac{\Delta H}{\Delta H_{100} \times \phi} \times 100\% \tag{1}$$

where ΔH is the melting enthalpy of the sample. ΔH_{100} is the crystalline melting enthalpy of PVDF. This experiment adopts the $\Delta H_{100} = 104.7$ J/g.

Dielectric properties were tested using an impedance analyzer (Agilent 4294A) in the frequency range from 10^3 Hz to 10^6 Hz at the temperature of 25 °C. Prior to measurement, the surface of the film was plated with copper electrodes to ensure good electrical contact.

The tensile strength at breaking points of the composite samples were determined using an electronic tensile strength meter (5965, Instron, UK) equipped with a 500 N load cell, according to the ASTM D882-02 method, with a cross head speed of 200 mm/min and a gauge length of 20 mm at room temperature. The tests were repeated at least five samples to obtain average values.

The thermal conductivities of samples were measured using a LFA467 light flash system (NETZSCH, Germany) at 25 °C. The specimens were 25 mm in diameter and around 40 μm in thickness, spraying coated with a thin layer of fine graphite powder at both sides. The in-plane thermal conductivity is calculated from equation (2) [35].

$$\lambda(T) = \alpha(T)\, \rho(T)\, c(T) \tag{2}$$

where $\alpha(T)$ is the thermal diffusivity of the composite, $\rho(T)$ is the density of the composite and $c(T)$ is the specific heat capacity which is obtained by DSC.

3. Results and discussion

FT-IR spectra and TEM of both BN and m-BN were carefully examed. As shown in Fig. 1a, BN showed two distinct peaks for B-N