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Enhanced thermal and mechanical properties of polyvinlydene fluoride composites with magnetic oriented carbon nanotube

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A B S T R A C T

Carbon nanotube (CNT) is an attractive material to many scientists worldwide due to its outstanding thermal and mechanical properties. In this paper, magnetic carbon nanotube (mCNT) with excellent magnetic response was successfully synthesized by coating iron oxide particles. In order to improve the thermal conductivity and mechanical strength of polyvinylidene fluoride (PVDF) composite, mCNT was supplemented and aligned under the external magnetic field during the composite fabrication. Subsequently, orientation effects of mCNT, including the in-plane, through-plane and random patterns, on the overall thermal performance of mCNT-PVDF composite were evaluated by the X-ray diffraction, scanning electron microscope, transmission electron microscope and thermal conductivity meter, and further simulated by Effective Medium Approximation model. The results indicate that the thermal conductivity of mCNT-PVDF composites is related to the anisotropy and the thermal resistance of mCNT, and could be improved by controlling the orientation of the mCNT. The thermal conductivity of vertically-aligned mCNT-PVDF composite is 62% higher than that of unaligned one. In addition, the aligned mCNT-PVDF composite exhibits excellent mechanical strength and heat exchange ability, which makes it a potential material for use in the heat exchange industry.

1. Introduction

Heat exchangers are widely used in number of fields for various purposes including generation of electricity, chemical processing and petroleum refining [1–5]. Corrosion is currently an unavoidable problem during the operation of traditional metal heat exchangers, which causes severe environmental issues and substantial economic losses [6–8]. It is of great significance to design and fabricate a thermal conductive material characterized by the high conductivity, excellent corrosion resistance and good mechanical property to replace the metallic materials currently used for manufacturing heat exchangers. Polymers are considered to be a favorable substitute in view of the good anti-corrosion ability and physical property. Polyvinylidene fluoride (PVDF) possesses great chemical stability, mechanical properties and easy-processing ability, which makes it an outstanding thermoplastic polymer and a potential material for use in the heat exchanger industry. However, further application of PVDF in the field of heat exchange has been substantially limited due to its low thermal conductivity, which was determined to be 0.2 $W \cdot m \cdot K^{-1}$ [9–11]. Therefore, the thermal conductivity enhancement is critical to explore the adaptability of PVDF for the heat exchange industry.

In the past few years, several effective processing techniques have been developed to improve the thermal conductivity of polymer. Crystallinity improvement and crystallite alignment of the polymer have been proposed to be feasible, but further applications are greatly hindered due to the difficulty and high-cost of the fabrication process [12,13]. Thereafter, high-thermal conductive fillers have attracted great attention, mainly due to the simplicity of operation. Researches indicated that many fillers, including metals [14], metallic oxides [15,16], ceramics [17,18] and polymers [19],

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could remarkably enhance the thermal conductivity of polymer-based composites after being introduced during the fabrication process.

Characterized by the high thermal and electrical conductivity, negligible thermal expansion coefficient and outstanding mechanical properties [6,20–23], carbon nanotube (CNT) is considered to be an ideal one-dimensional anisotropic nanofiller for the polymer-based composites. Specifically, CNT exhibits a distinctly anisotropic thermal property due to its highlighted aspect ratio, i.e. the thermal conductivity in the longitudinal direction (parallel to the nanotube axis) is much higher than that in the transverse direction (perpendicular to the nanotube axis) [24]. Recently, a large number of CNT materials have been involved in the fabrication of high performance thermal conductive polymer-based composites [25,26]. But due to some limitations, the reported thermal conductivity value is still far below the prediction. The orientation effect is a major reason for the unsatisfied thermal conductivity of the composites. Due to forces of gravity and thermal motion, the carbon nanotube can't be arranged along the thermal conductive direction within the polymer-based composites, which impedes the heat conduction and extremely lowers the thermal conductivity [27]. Hence several preparation methods have been proposed to induce the CNT oriented in the well through-plane direction. Polymer infiltration and in-situ polymerization are both the practical approaches but they are yet too complicated to implement efficiently [28,29]. In addition, external electric and magnetic field have been investigated to be feasible to align the CNT in the polymer matrix, but due to high energy consumption those technologies are inapplicable in the ordinary laboratories. It has been reported that the through-plane oriented CNT-polymer composites could be obtained exclusively under the direct-current electric field of 1250 V/cm or magnetic field of 1200 Gauss [30,31]. Consequently, it's imperative to explore a more effective method to align CNT in the polymer matrix in the direction of thermal conduction.

In recent years, magnetic nanofillers have been successfully prepared and aligned in the polymer matrix [27]. In general, nanofillers are diamagnetic and exhibit no response to low magnetic field. However, magnetic performance of the nanofillers could be greatly enhanced by coating with superparamagnetic iron oxide nanoparticles [32,33]. Then the thermal conductivity of composites could be substantially improved through regulating the orientation of magnetic nanofillers towards the through-plane direction under low magnetic field. Certain two-dimensional nanofillers, including graphene and hexagonal boron nitrite have been successfully applied to improve the thermal conduction of the polymer-based composites through the magnetic modification method [34–37]. Compared to two dimensional nanofillers, one dimensional fillers such as CNT are more likely to form thermal conductive network due to the high aspect ratio. Although a few achievements about thermal conductive composite with magnetic CNT alignment were reported recently, there are still many questions that should be addressed [38,39].

In the work herein, CNT coated with superparamagnetic iron oxide particles was successfully obtained by electrostatic interactions, which was further applied to fabricate polymer composite with enhanced thermal conductivity through controlling magnetic orientation. X-ray diffractometer (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM) were utilized to examine the attachment of iron oxide on the CNT, and characterize the orientation of the magnetic nanofillers. Thermal measurements were conducted to determine the thermal performance of the polymer-based composite with different orientations. A theoretical model, effective medium approximation (EMA), was applied to further illustrate the experimental results and investigate the potential mechanism. In addition, tensile tests were conducted to examine the mechanical stability of the polymer-based composite. Finally, heat exchange experiment was carried out to examine the composite potential in industrial practice.

2. Experimental section

2.1. Materials

Ferric trichloride hexahydeate ($FeCl_3 \cdot 6H_2O$), ferrous sulfate heptahydeate ($FeSO_4 \cdot 7H_2O$), sodium chloride (NaCl) and calcium chloride ($CaCl_2$) were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Hydrochloric acid (HCl), ammonium hydroxide ($NH_4 \cdot OH$) and tetramethylammonium hydroxide were purchased from Tianjin Jiangtian Chemical Technology Co. Ltds (Tianjin, China). Multiwall carbon nanotube (TNM5) with a diameter of 30–100 nm and length of 5–30 μm was obtained from Chengdu Organic Chemicals Co. Ltd (Chengdu, China). The PVDF with a purity of 98% was purchased from Beijing HWRK Chem Co. Ltd (Beijing, China). Polyelectrolytes, including the poly(sodium 4-styrene sulfonate) (PSS) and poly(dimethyldiallylammonium chloride) (PDADMAC), were purchased from Tianjin Heowns Biochemical Technology Co. Ltd (Tianjin, China). Other chemicals were of reagent grade and used without further purification.

2.2. Preparation of magnetic iron oxide nanoparticles

The magnetic iron oxide nanoparticles were prepared by the coprecipitation method. A mixture of 20 mL $FeCl_3 \cdot 6H_2O$ (aq; 1 M) and 5 mL $FeSO_4 \cdot 7H_2O$ (aq; 2 M) HCl (0.12 M) solution was dropwise added into 250 mL $NH_4 \cdot OH$ (0.7 M) under rapid stirring (400 rpm, the same as following). The formed black deposits were collected and transferred into 200 mL tetramethylammonium hydroxide (0.1 M) solution. Subsequently, 5 mL PDADMAC (aq; 20 wt%) was supplemented under rapid stirring to prepare the stable solution containing magnetic iron oxide particles. The concentration of iron oxide in solution is 0.05 mol/L.

2.3. Preparation of mCNT

The mCNT was prepared as per the procedure reported by Correaduarte et al. with minor modifications [38]. Specifically, 2 g CNT was suspended in 150 mL PSS (aq; 1 wt%) and then 5 mL magnetic iron oxide nanoparticle solution (0.05 mol/L) was dropwise added under ultrasonic-assisted rapid stirring at 40 °C for 2 h. The black deposits containing mCNT was precipitated with time. After collection, the black deposits were washed with deionized water and then centrifuged at 11000 rpm for 1 h. The aforementioned washing-centrifugation cycle was performed for three times. Thereafter the precipitate as re-separated mCNT was dried at 60 °C for 12 h in an oven. The CNT coated with PSS was electronegative while the iron oxide particles with PDADMAC were electropositive. Hence the mCNT stability could be greatly enhanced by the electrostatic attraction between the CNT and iron oxide particles. The iron oxide content of mCNT was calculated to be 24 wt% according to thermogravimetry (Fig. S1). Based on the characterization of magnetic analysis, the magnetic response increases with the iron oxide content and almost reaches saturation at 24 wt% (Fig. S2).

2.4. Fabrication of PVDF composites with different-oriented mCNT

The mCNT-PVDF composites were prepared by the solvent transfer method. Previous study in our laboratory found that the