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Thermal conductivity of graphene/poly(vinylidene fluoride) nanocomposite membrane

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ABSTRACT

Compared to metallic materials for the use of heat exchanger, polymeric materials have been enjoyed superior advantages such as corrosion resistance, low density, fouling resistance, facile processing and low cost. Poly(vinylidene fluoride) (PVDF) is semi-crystalline thermoplastic polymer with excellent corrosion resistance, thermal and electrochemical stability. In order to improve its thermal conductivity, graphene/PVDF composites were prepared and studied in this paper. The graphene was doped in PVDF matrix for preparing graphene/PVDF composite membranes. In addition, electric field was applied for graphene alignment during membrane formation. The morphology, structure, thermal conductivity and tensile strength of the composite membranes before and after alignment were characterized and analyzed. The tensile strength and thermal conductivity of composite membranes were significant improved with the addition of graphene. This tendency was further enhanced by the application of electric field. When graphene content was 20 wt%, the thermal conductivity of the composite membrane was increased by 212% than that of pure PVDF and it was further enhanced to 226% after applying electric field. The maximum tensile strength was obtained when graphene content was 3 wt%. This study may be beneficial to further development of thermal conductive polymeric materials.

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1. Introduction

Currently, most of heat transfer apparatus is prepared with metal materials, for the good heat resistance, excellent mechanical properties and high heat transfer efficiency. However, there are still many deficiencies, such as high cost, scaling surface and poor corrosion resistance (leading to reduced heat transfer performance and rising energy consumption, as well as environmental pollution from chemical descaling). For these deficiencies, researchers in science, technology and engineering fields have been making their efforts on seeking for alternative polymer materials with high thermal conductivity [1–3]. As we all know, most polymeric materials enjoy superior advantages such as corrosion resistance, low density, fouling resistance, facile processing and low cost. The defects of metal materials in heat transfer apparatus can be supplemented by polymers, with great potential in the application of heat exchanger.

Poly(vinylidene) fluoride (PVDF) is an excellent thermoplastic polymer, with good chemical stability, heat resistance and stain resistance. In recent years, PVDF has been widely applied in many fields such as chemistry engineering, electronics and food industry with outstanding

mechanical properties, wide processing temperature range and easiness in the fabrication of films [4]. PVDF can be dissolved in various solvents including *N*-methylpyrrolidone (NMP), *N,N*-dimethylformamide (DMF), dimethylacetamide (DMAC) and dimethylsulfoxide (DMSO). However, the application of PVDF in the field of heat exchanger is limited for its poor thermal conductivity. Therefore, increased heat transfer performance of PVDF will enable more applications in fields of heat transfer.

For improving the thermal conductivity of polymers, various thermal conductive fillers were added to the matrix for preparing thermal conductive composites [5–7]. The PVDF composites were prepared via nano-carbon fillers including zero-dimensional superfullerene (SF), one-dimensional carbon nanotube (CNT) and two-dimensional graphene sheets (GS) by compression molding method. The thermal conductivity of PVDF composites with 20 wt% two-dimensional GS reaches a maximum (2.06 W/mK) [5]. Xu has investigated the thermal conductivity of epoxy and PVDF composites filled with AlN powder and whisker. When the particles and whiskers of AlN were mixed in a volume ratio of 25.7:1, and the total volume of AlN reached 60%, the highest thermal conductivity of 11.5 W/(m·K) was attained. When the total volume of AlN was relatively low at 25%, with the particles and whiskers of AlN in a 1:1 volume ratio, the thermal conductivity of PVDF-matrix composite was 1.73 W/(m·K). However, with the addition of AlN, the tensile strength, modulus and toughness of the composites

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would be attenuated [8]. Graphite nanoplatelets (GNPs) were added to the epoxy for preparing thermal interface material. When the volume fraction of GNPs was approximately 25%, the thermal conductivity of composite was increased by 6.44 W/(m·K) [9]. Comparing with PVDF matrix composite, epoxy resin matrix composite needs curing agent to be added and the curing cycle is shorter and there may be not enough time for the fillers to agglomerate. This may be one reason why the thermal conductivity of epoxy resin matrix composites is more outstanding. However, the thermal and electrochemical stability, mechanical properties and toughness of PVDF is much better than that of epoxy resin. For our research, we chose PVDF as the composite matrix and the thermal conductivity of the composite materials was studied under the low-weight loading of fillers.

At present, graphene, as the representative of the new carbonaceous material, has attracted wide attentions. Graphene is a single layer of carbon atoms arranged as two-dimensional honeycomb crystal. In 2004, Andre Geim and Konstantin Novoselov in the University of Manchester successfully prepared the stable graphene for the first time [10]. Since then, graphene has become a research hotspot in the field of materials. There are many excellent properties in graphene, such as high electron mobility at room temperature [11], high thermal conductivity [12] and good mechanical properties [13]. Thus, it has broad application prospects in the fields of electronic device, biological and chemical sensors, energy storage devices and composite materials [14–16]. The two-dimensional plane structure of graphene enables very high thermal conductivity, thus, it has become one of the most ideal materials for improving thermal conductivity of polymers.

So far, researchers have developed several preparation methods for graphene, including mechanical exfoliation, chemical vapor deposition and oxidation–reduction method [17]. The oxidation–reduction method is the most common method for graphene preparation because of its low cost, high yield and batch production. Many reductants can be applied for reducing graphene oxide and the most common reductants are hydrazine hydrate [18] and sodium borohydride [19]. Hydrazine hydrate is high in reducibility and does not react with water. Thus, it is one of the most desirable reductants for reducing graphene oxide [20]. For the reduction of aqueous solution of graphene oxide, the efficiency of sodium borohydride is higher than hydrazine hydrate, while it can slowly react with water. Other reductants such as hydroquinone [21] and strong alkaline solution [22] may also be applied for reducing graphene oxide.

The conductivity and mechanical properties of the polymer composites can be adjusted by aligning the fillers in the matrix with mechanical stretching, electric field, magnetic field and so on [23–27]. In a recent study, multi-walled carbon nanotubes (MWCNTs) reinforced PVDF composite film was fabricated by solution casting technique. MWCNTs were well aligned with the application of voltage and pulsed current. Both the electrical conductivity and tensile strength were improved after alignment compared to corresponding controls.

In this study, graphene was added to PVDF matrix for improving the thermal conductive performance of composite membranes. First, graphite oxide (GO) was synthesized with Hummers method and dispersed to be graphene oxide. The graphene was prepared by reducing graphene oxide with hydrazine hydrate. Then, the graphene/PVDF composite membranes were prepared with solvent casting method. Third, the electric field was applied for aligning the graphene in PVDF matrix during formation of the membranes. Their morphology, tensile strength and thermal conductivity were investigated with different contents of graphene in the composite membranes.

2. Experiments

2.1. Materials

The natural flake graphite was 325 meshes, with carbon content of 99.95% (Beijing HWRK, China). Concentrated sulfuric acid (mass

fraction of 98%) and Hydrochloric acid (mass fraction of 36%) were purchased from JiangTian Chemical Technology (Tianjing, China), potassium permanganate (YuanLi Chemical, Tianjing, China) and sodium nitrate (Guangfu Fine Chemical Research Institute, Tianjin, China) were grade AR. Hydrogen peroxide (30 wt%), hydrazine hydrate (98 wt%), *N*-methylpyrrolidone (NMP, 98% purity) were purchased from Aladdin (Shanghai, China). PVDF 904 was supplied by Oflourine Chemical Technology Co., Ltd. (Shanghai, China), with the density of 1.75–1.77 g/mL, melt flow index of 0.5–2.0 g/10 min and melt point of 156–165 °C.

2.2. Preparation of graphene

Hummers method [28] was applied to prepare the GO. 0.5 g of natural flake graphite and 0.25 g of sodium nitrite were added to 12.5 mL of concentrated sulfuric acid. The mixture was well mixed and cooled to 0 °C. 1.5 g of potassium permanganate was slowly added to above mixture and the reaction temperature was controlled below 20 °C in ice bath. The mixture was stirred for a certain time, then the ice bath was removed. The reaction was maintained for 2 h below 35 °C. 23 mL of deionized water was slowly added. Then, appropriate amount of hydrogen peroxide was added to the mixture to reduce the residual potassium permanganate and manganese dioxide. The mixture was filtered and washed with 10% of hydrochloric acid and deionized water for three times. The obtained graphite oxide was dialyzed against deionized water. The obtained solids were intensively dried in a vacuum oven at 60 °C.

A certain amount of GO was dispersed in an aqueous solution, to give a tan suspension. Then, the solution was dispersed with ultrasonic cleaner for 2 h. A stable dispersion solution of graphene oxide could be obtained. The solution was heated to 90 °C after centrifuge and 2 mL of hydrazine hydrate was added. After reacting for 24 h, the obtained product was filtered and washed with ethanol and deionized water for several times. The product was thoroughly dried at 60 °C in vacuum oven and the graphene powder was saved at room temperature for further use.

2.3. Preparation of graphene/PVDF composite membrane

5 g of PVDF was dissolved in hot NMP. An appropriate amount of graphene was dispersed in additional NMP by high-shear mixing for 30 min followed by bath sonicated for 2 h (sonic power 270 W) to obtain the dispersion of graphene. Graphene dispersion was added dropwise to the dissolved PVDF in NMP and constantly stirred. The mixture was mechanically stirred for 6 h at 50 °C to form a homogeneous casting solution. The casting solution was filtered with a 300 mesh sieve to remove possible impurities in solution. The solution was then evacuated and ultrasonic degassing for 2 h and allowed to stand for 1 h. The casting solution was poured in a clean and horizontal self-made mold, then drying overnight at 60 °C in oven. Then heating to 100 °C until the solvent was evaporated completely. Graphene/PVDF composite membranes were finally obtained and peeled off from the mold for further characterization. The pure PVDF membrane without graphene was prepared with similar conditions.

2.4. Alignment of graphene/PVDF composite membrane

Electric field was applied to the composite membranes for the alignment. After the prepared solution of graphene/PVDF mixture in different ratios was transferred into the mold, an electric field of 1100 V was applied with a DC power supply (HVA-502NP5, Tianjing Shenghuo tech. Co., Ltd.) perpendicular to the surface of mold. At this point, both the casting mold and electrode plate of electric field device were setup in the oven (Schematic 1). The mold was heated overnight at 60 °C in oven. Then heating to 100 °C until the solvent was evaporated completely. Aligned graphene/PVDF composite membranes were finally

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