



## Macromolecular Nanotechnology

## Multifunctional poly(vinylidene fluoride) nanocomposites via incorporation of ionic liquid coated carbon nanotubes

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## ABSTRACT

In this work, simultaneously enhanced thermal conductivity, heat dissipation and dielectric constant of poly(vinylidene fluoride) (PVDF) were prepared by adding ionic liquid (IL)-coated carbon nanotubes (IL@CNTs). IL@CNTs and common CNTs were melt-compounded with PVDF to prepare the composites, respectively. The results clearly demonstrated that IL@CNTs exhibited better dispersion and higher ability to form the percolated network structure. Studying on crystallization behaviors showed that IL@CNTs not only exhibited better nucleation effect on PVDF crystallization but also induced a large number of the polar  $\beta/\gamma$ -form crystallites formation in the composites. Thermal properties measurements showed that IL@CNTs exhibited more apparent role in enhancing the thermal conductivity of the composites. Specifically, IL@CNT endowed the composite sample with higher heat dissipation ability compared with the common CNTs during the cooling process. In addition, the largely enhanced dielectric constant was also achieved for the PVDF/IL@CNT composites. The mechanisms were analyzed and suggested to be mainly related to the improved dispersion and denser percolated network structure of IL@CNTs in the composites, the improved interfacial interaction between fillers and matrix, and the varied crystalline structure of the PVDF matrix. The prepared composites have great potential application as the heat management material of the flexible electronic devices.

## 1. Introduction

As one of the semicrystalline polymers, poly(vinylidene fluoride) (PVDF) exhibits great potential applications in microelectronic devices due to its good processing ability, tailorable crystalline structures, excellent chemical resistance, intriguing properties such as piezoelectric and ferroelectric properties originated from the polar  $\beta/\gamma$ -form crystals, etc. [1]. Recently, much attention of researchers has been focused on designing and developing novel PVDF-based composites with promising functional properties. Various nanofillers have been introduced into PVDF to prepare the composites. For example, to enhance the electrical conductivity of the PVDF materials, various carbon-based fillers have been incorporated into PVDF [2,3]. To enhance the dielectric properties of PVDF composites, barium titanate ( $\text{BaTiO}_3$ ),  $\alpha$ -silicon carbide ( $\alpha$ -SiC), nano-potassium tantalate-niobate loaded by Ag (nano KTN@Ag) particles, and polyaniline nanorods, etc. have been used [4–8]. Incorporating graphene oxide (GO) into PVDF matrix not only induces the variation of crystal form but also benefits the enhancement of dielectric properties [9].

Generally speaking, properties of the polymeric composites are

mainly dependent upon the dispersion of fillers and the interfacial interaction between polymer matrix and the fillers. Actually, the good interfacial interaction also benefits the good dispersion of fillers in the polymeric composites. To date, many strategies have been developed to improve the interfacial interaction between fillers and polymer matrix through surface functionalization of fillers, such as covalent functionalization and noncovalent functionalization methods [10]. Although the modification efficiency is relatively low, the noncovalent functionalization method does not apparently affect the intrinsic features of fillers. Besides, the method is easily to be controlled and applied and therefore, it is widely adopted in industrial applications. Surface-modified fillers usually exhibit nucleation effect on the crystallization of the semicrystalline polymers, which may induce the increase of crystallinity and/or the variation of crystal form [11]. For PVDF-based materials, this aspect is very important because the modified fillers provide more probability to tailor the crystalline structures of the PVDF matrix. It is well known that PVDF usually crystallizes in  $\alpha$ -form, and the polar  $\beta/\gamma$ -form can be only obtained under certain crystallization conditions, such as the presence of special nucleating agent, with the aid of shear stress and/or in the temperature gradient condition, or crystallization

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from solution, etc. [12,13]. Recently, many researches have already demonstrated that the presence of some functional groups on the surface of the fillers benefit the crystallization of the polar  $\beta$ -form PVDF [14].

Among those noncovalent modifiers, ionic liquid (IL) recently attracts attention of researchers and it has been demonstrated an efficient dispersing agent to improve the dispersion of fillers in the polymer matrix through enhancing the interfacial interaction between polymer matrix and fillers [15–17]. Specifically, it has been reported in literature that either in the PVDF samples containing only IL [18] or in the PVDF composites containing IL-modified fillers [15,19], the polar  $\beta/\gamma$ -form PVDF can be easily obtained. Consequently, the materials exhibit excellent piezoelectric properties.

With the miniaturization or intelligentization of electron devices, heat generating and controlling or enhancing energy storage ability attracts increasing concerns of researchers. PVDF has been thought as a good dielectric material compared with other polymers and many researches have also been done to further enhance the dielectric properties of the PVDF-based materials [20]. However, the thermal conductivity of PVDF is only 0.19 W/m K, which is smaller than most of other polymers [21]. Therefore, it is urgent to simultaneously enhance the thermal conductivity of the PVDF materials when the materials are applied to microelectronic devices. To date, some methods have been developed to prepare the thermal conductive PVDF-based materials and these methods are mainly related to the incorporation of fillers with high thermal conductivity, such as carbon nanotubes (CNTs) [22–24], boron nitride (BN) [25], graphite [26], graphene [27], etc. It is suggested that improving the interfacial interaction to reduce the interface thermal resistance and constructing the network structure of fillers to form the highly efficient conductive path in the composites are the most important aspects to insure the achievement of high thermal conductivity.

In this work, our attention is focused on investigating the effects of IL on dispersion and network structure formation of CNTs in the PVDF-based composites and the resultant microstructure-performance relationship of the composites. Specifically, IL induces the crystalline structure changes of the PVDF matrix and in this condition, the mechanisms relating to the enhancement of thermal conductivity of the composites can be better understood. It is interesting to observe that compared with the common CNTs, the IL-coated CNTs (IL@CNTs) exhibit more apparent role in simultaneously improving the thermal conductivity and dielectric constant of the PVDF composites.

## 2. Experimental part

### 2.1. Materials

PVDF (Kynar 720) was purchased from Arkema (France). The density is 1.78 g/cm<sup>3</sup> and the melt flow rate is 22.8 g/10 min (230 °C/3.8 kg). CNTs were obtained from Chengdu Institute of Organic Chemistry, Chinese Academy of Science (Chengdu, China). The content of oxygen-containing groups is about 0.51 wt%. The average diameter and length of a single CNT are 50 nm and 10–30  $\mu$ m, respectively. Ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate, BMIM<sup>+</sup>PF<sub>6</sub><sup>-</sup>, CAS number of 174501-64-5) was purchased from Chengjie Chemical Co. Ltd (Shanghai, China). The molecular weight is 284.18 g/mol and the purity is above 99%.

### 2.2. Sample preparation

Before sample preparation, PVDF and CNTs were dried in an oven which was set at 60 °C for 6 h to eliminate the effect of water. CNTs and IL in a weight ratio of 1:1 were firstly mixed and grinded for 40 min to obtain the IL-coated CNTs (IL@CNTs). After that, the IL@CNTs were melt-compounded with PVDF using a mini-extruder. The melt-compounding was carried out at a melt temperature of 200 °C and the compounding duration was 6 min. In this work, the content of IL@CNTs

was varied from 1 to 5 wt%. For comparison, the materials containing only IL or CNTs were also prepared through the same processing conditions. Correspondingly, the sample notations were defined as PVDF/IL@CNT-*x*, PVDF/CNT-*y* and PVDF/IL-*z*, where *x*, *y*, and *z* represent the contents of IL@CNTs, CNTs and IL in the materials, respectively. After being granulated, the droplets were compression-molded to obtain the sample disk for microstructural characterization and physical properties measurements. The compression-molding processing was carried out at a melt temperature of 200 °C, a pressure of 10 MPa and a dwell time of 8 min.

### 2.3. Transmission electron microscopy (TEM)

A transmission electron microscope (TEM) JEM-2100F (JEOL, Japan) was used to characterize the morphology of the IL@CNTs. The characterization was carried out at an operating voltage of 200 kV.

### 2.4. Optical microscopy (OM)

Optical microscope (OM) (LEICA DM 2700P, Germany) was employed to characterize the dispersion states of CNTs and IL@CNTs in the PVDF matrix.

### 2.5. Scanning electron microscopy (SEM)

The dispersion states of CNTs and IL@CNTs in the PVDF composites were further characterized using a scanning electron microscope (SEM) Fei Inspect (FEI, the Netherlands), which was operated at an accelerating voltage of 20 kV. Before SEM characterization, sample was cryogenically fractured in liquid nitrogen and then the fractured surface was coated with a thin layer of gold.

### 2.6. Rheological measurements

Rheological measurements were conducted on a stress-controlled rheometer DHR-1 (TA Instrument, USA). The sample disk, which was prepared through the above compression-molding processing, had a diameter of 20 mm and a thickness of about 1 mm. The measurements were carried out at a melt temperature of 190 °C and a frequency range of 0.01–100 Hz.

### 2.7. Fourier transform infrared (FTIR)

A Fourier transform infrared (FTIR) AVATAR360 (Thermo Nicolet, USA) was used to characterize the crystalline structure of the PVDF matrix. The measurements were carried out at a resolution of 4 cm<sup>-1</sup> through an attenuated total reflection (ATR) mode, and the wave-number range was set at 400–4000 cm<sup>-1</sup>.

### 2.8. Wide angle X-ray diffraction (WAXD)

The crystal transformation of PVDF and its composites was characterized using a wide angle X-ray diffraction (WAXD, Panalytical Empyrean) operated at 40 kV and 40 mA. The continuous scanning angle range was from 5° to 50°.

### 2.9. Differential scanning calorimetry (DSC)

The melting and crystallization behaviors of samples were detected using a differential scanning calorimeter STA449C Jupiter (Netzsch, Germany). Sample of about 8 mg was heated from 20 to 210 °C at a heating rate of 10 °C/min, maintained at 210 °C for 3 min to erase any thermal history, and then the sample was cooled to 20 °C at a cooling rate of 5 °C/min. All the measurements were carried out in nitrogen atmosphere.

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