



Preparation of poly(vinylidene fluoride) films with excellent electric property, improved dielectric property and dominant polar crystalline forms by adding a quaternary phosphorus salt functionalized graphene



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ABSTRACT

In our work, a novel modifier, quaternary phosphorus salt, (1-hexadecyl) triphenylphosphonium bromide (HTPB), was introduced for the noncovalent functionalization of graphene for the first time. With it, an excellent dispersion of graphene in organic solvent and later in poly(vinylidene fluoride) (PVDF) matrix has been achieved, e.g., transmission electron microscopy (TEM) shows a single-layer dispersion and multi-layer structure of graphene sheets in PVDF matrix. As a result, the films exhibit outstanding electric property with a very low percolation threshold of 0.662 wt% being observed. Their dielectric property is also improved, the dielectric constant of PVDF/graphene composites at 1000 Hz with a loading lower than 0.86 wt% shows an obvious increase (more than 3 times of that of PVDF at most), while the dielectric loss remain quite low (all lower than 0.07). Even more intriguingly, the quaternary phosphorus salt also induces dominant polar β and γ crystalline forms in the prepared composite films. These PVDF/graphene films with good electric and dielectric property as well as dominant polar β and γ forms promise a wide range of potential applications in electronic devices.

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1. Introduction

In recent years, graphene has attracted great attention of scientific researchers. It is a two-dimensional monolayer graphite with excellent electronic [1], mechanical [2], and thermal properties [3] as well as high specific surface area [4]. With these remarkable characteristics, it is expected to endow polymers with outstanding performances in a variety of areas, such as increasing the bulk conductivity by several orders of magnitude [5–13] and improving the dielectric property [14–19] of polymers. So far, there have been several methods to prepare graphene, including chemical vapor deposition [20], epitaxial growth [21], raw graphite exfoliation [22,23] and graphite oxide (GO) reduction [24], among which chemical reduction of GO is considered to be the most efficient way. However, direct reduction of GO will result in inevitable aggregation of graphene sheets due to the strong Van der Waals' force. It is well known that the excellent properties of graphene are tightly associated with its individual sheets. Therefore, dispersion of single-layer graphene in polymer matrix is a key factor for preparing high performance polymer/graphene composites. Up to now, covalent [25–28] and noncovalent [14,29–33] functionalization, mainly aimed at single layer dispersion in polymer matrix,

have been developed to prevent the aggregation of graphene sheets during reduction. Unfortunately, covalent functionalization inevitably induces defects onto the parallel plane of graphene, which impairs the properties of graphene, and that of the polymer composites as a result. While effectively avoiding defects, noncovalent functionalization is still possible to bring decline to properties of graphene. For example, we have tried using polyvinyl pyrrolidone (PVP) to noncovalently functionalize graphene. Although an excellent dispersion of graphene sheets was achieved, the conductivity was rather poor due to the nonconductive PVP coating on the surface of graphene [34]. Hence, it is very important to explore suitable modifier to achieve an excellent dispersion of graphene in polymer matrix while maintaining its intrinsic properties. Some aromatic molecules captured scientists' attention, since the π – π interactions between their aromatic rings and graphene sheets [14,31,35], are able to facilitate not only the satisfying dispersion but also the electron conduction of graphene.

Poly(vinylidene fluoride) (PVDF) is an interesting polymer with many excellent properties, such as good mechanical property, chemical and weathering resistance, and more remarkably, the unique piezoelectric and ferroelectric properties which are closely associated with its polar crystalline forms. There are mainly five crystalline forms of PVDF: α , β , γ , δ and ϵ . Among them, polar β and γ , especially the β form, make great contributions to the piezoelectric and ferroelectric properties of PVDF [36,37]. However,

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PVDF are usually dominated by α form since the conformation of α form is more stable than those of β and γ forms [38]. Therefore, many methods have been employed to induce polar β and γ forms in PVDF matrix, for instance, drawing under certain temperature [39], electrospinning [40], application of high electric field [41] and Langmuir–Blodgett (LB) deposition [42]. Recently, we found that some quaternary ammonium salts and quaternary phosphorus salts could also induce the formation of polar forms in PVDF [43]. Luckily, some of them with aromatic rings are also ideal modifiers to prevent the aggregation of graphene sheets during or after reduction through π – π interactions. In this way, both the excellent dispersion of PVDF/graphene composites and the polar forms in PVDF is expected to be accomplished simultaneously through one simple agent.

In this work, graphene was noncovalently functionalized with one kind of quaternary phosphorus salts, called (1-hexadecyl) triphenylphosphonium bromide (HTPB), which is indeed capable of preventing the aggregation of graphene sheets after reduction. The functionalized graphene was added into PVDF, and an excellent dispersion (single layer dispersion) and layered structure of graphene sheets within PVDF matrix were observed. The composite films showed excellent electric property and improved dielectric property, as well as dominant polar β and γ forms.

2. Experimental details

2.1. Materials

PVDF powders (Solef 6010, density 1.78 g cm^{-3}) were purchased from Shanghai Alliedneon Co., Ltd., China. Graphite powders were provided by Qingdao Black Dragon graphite Co., Ltd., China. Potassium permanganate (KMnO_4), sulfuric acid (H_2SO_4 98%), hydrogen peroxide (H_2O_2), sodium nitrate (NaNO_3), sodium hydroxide (NaOH), Dimethylacetamide (DMAC) and hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) were purchased from Kermel Chemical reagent plant (Tianjin, China). (1-hexadecyl) triphenylphosphonium bromide (HTPB) was purchased from Alfa Aesar. They were used as received.

2.2. Methods

2.2.1. Preparation of graphite oxide (GO)

GO was prepared by a modified Hummers method [34]. In a typical procedure, graphite (2 g) was mixed with NaNO_3 (1 g) and H_2SO_4 (50 mL) at 0°C , then KMnO_4 (6 g) was slowly added into the system, followed by stirring at room temperature for 30 min after being kept at 0°C for 2 h. After that, distilled water (100 mL) was slowly added into the system, and the temperature was kept well below 98°C for 3 h. The mixture was further treated with 5% H_2O_2 (50 mL), stirred for one night at room temperature. At last, it was filtered and washed by centrifugation with deionized water for several times until neutral to acquire purified GO suspensions which were stored for future use. The concentration of the GO suspension was determined by calculating the solid content of the suspension (suspension was dried under 50°C).

2.2.2. Preparation of HTPB noncovalent functionalized reduced graphite oxide (HTPB-rGO)

First, GO aqueous solution (0.5 mg mL^{-1}) was ultrasonicated for 10 min, meanwhile, HTPB was dissolved in deionized water by stirring in another beaker (8 mg mL^{-1}). After that, the HTPB solution was slowly added into the stirred GO solution (the mass of HTPB was excessive, approximately 5 times of that of GO), precipitates were formed immediately due to the electrostatic self-assembly (GO is electric negative while HTPB is electric positive in aqueous

solution). Then, the precipitates were filtered and added with DMAC to obtained a solution (100 mg GO in 200 mL DMAC), followed by rotary evaporation in order to remove the residual water. Subsequently, the solution was ultrasonicated for 30 min and then reduced with hydrazine hydrate (4 times of GO in weight) at 95°C for 3 h [44], to give homogenous black suspensions of HTPB-rGO. Reduced graphite oxide (rGO) was prepared in the same way but in the absence of HTPB.

2.2.3. Preparation of PVDF/HTPB-rGO composites films

First, the desired amount of HTPB-rGO suspensions was added into a beaker and sonicated for several minutes. Then, PVDF (1 wt% to the whole solution) was added and stirred for 2 h at 60°C . After that, composite films were prepared by casting the homogenous solution and evaporating it at 90°C for 12 h. For dielectric property test, dozens of the obtained films were stacked layer-by-layer and hot-pressed into a wafer (10 mm in diameter and 1 mm in thickness) at 210°C for 5 min under a pressure of 10 MPa. For comparison study, pure PVDF and PVDF with different contents of HTPB were prepared in the same way.

2.3. Characterizations

The morphologies of graphene and PVDF/HTPB-rGO were observed with scanning electron microscope (SEM, JEOL JSM-5900LV) at an accelerating voltage of 20 kV, atomic force microscope (AFM, nanoscope multimode, explore veeco instruments) operated in tapping mode and transmission electron microscopy (TEM, FEI-Tecnaï G2 F20 S-TWIN type) operated at 200 kV. The microstructure of HTPB-rGO was investigated by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos Co., UK) and thermal gravimetric analysis (TGA Q500, TA Instruments). The direct-current (DC) electrical conductivities of PVDF/HTPB-rGO films were measured with a Keithley 6487 electrometer, two-point method was used. Silver paint was coated on both two sides of the sample, in order to make the contact resistance negligible compared with sample resistance. The dielectric property was carried out with Agilent HP4294A; samples are wafers with a diameter of 10 mm and thickness of 1 mm. The polymorphs of PVDF/HTPB-rGO films were investigated by Fourier transform infrared spectroscopy (FTIR, Nicolet 6700) with a transmission mode.

3. Results and discussion

3.1. Morphology and microstructure of HTPB-rGO and PVDF/HTPB-rGO

It is well known that the direct reduction of GO will result in inevitable aggregations, thus noncovalent functionalization with HTPB (the chemical structure is shown in Fig. 1) through π – π interactions [31,35] was adopted to achieve an excellent dispersion of graphene. Fig. 2 shows the schematic of the preparation of HTPB-rGO and rGO, it is obvious that the noncovalent functionalization of graphene with HTPB results in a homogenous dispersion of HTPB-rGO in DMAC, while rGO without functionalization could not disperse in DMAC. Fig. 3 shows the FTIR spectra of HTPB, HTPB-rGO and rGO. Compared with rGO, HTPB-rGO shows obvious different peaks at 1587 cm^{-1} , 1437 cm^{-1} , 722 cm^{-1} , 691 cm^{-1} , 533 cm^{-1} , 509 cm^{-1} and 444 cm^{-1} , which are characteristic peaks of HTPB. It indicates that HTPB has been successfully noncovalent functionalized on graphene sheets, which is due to the π – π interactions between the aromatic rings of HTPB and graphene sheets. The mass fraction of HTPB is determined from TGA test in Fig. 4, it indicates that HTPB-rGO consists of 29 wt% graphene sheets and 71 wt% HTPB. From the SEM images (Fig. 5(a)), rGO sheets

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