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Material Properties

Thermal, mechanical, and dielectric properties of graphite reinforced poly(vinylidene fluoride) composites

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ABSTRACT

Poly(vinylidene fluoride) (PVDF)/graphite composites were prepared by a solution precipitation method for the first time. The mechanical, thermal and dielectric properties of these composites were studied by dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and an impedance analyzer, respectively. The results indicated that graphite content has a significant effect on the crystallization behavior of the PVDF. The storage modulus and the dielectric constant of the composites increased linearly with graphite concentration. When the graphite loading amount was 10 wt%, the storage modulus at 20 °C and the dielectric constant at 10^4 Hz were approximately 83% and 93% higher than those of pure PVDF, respectively.

1. Introduction

Poly(vinylidene fluoride) (PVDF) is an important engineering plastic and has been widely investigated because of its good mechanical properties, resistance to chemicals, high dielectric permittivity and unique pyroelectric and piezoelectric properties [1,2]. It is also well known that PVDF is a semicrystalline polymer exhibiting five crystalline phases (α, β, γ, δ and ϵ) and complicated crystalline structure [3]. Incorporation of organic polymer or inorganic fillers into PVDF matrix to produce composites has been extensively studied with the objective to further improve its properties, such as mechanical performance, thermal stability and dielectric properties. For example, Nandi and co-workers [4] employed an *in-situ* reducing method to prepare PVDF/Ag composites. In their system, it was observed that the storage modulus of the PVDF/Ag composites increased significantly. Pramoda et al. [5] prepared PVDF/caly nanocomposites by a melt compounding method. It was found that storage modulus improved greatly over a temperature range of 20–150 °C, and the coefficient of thermal expansion decreased with increasing clay loading. Recently, Goh and co-workers [2] reported that the storage modulus of PVDF is increased by nearly 150% at 20 °C upon the incorporation of 1.93 wt% PMMA-grafted MWNTs. For the PVDF-PP (polypropylene)/carbon black composite [6], the addition of 1 vol% carbon black can improve its dielectric constant by about 38% at 10^4 Hz.

As one of the most important inorganic fillers, graphite, which possesses good electrical conductivity and high modulus [7], has been widely used. In addition, graphite is naturally abundant with a low cost. Although there has been much work in the field of PVDF-based composites, little work on PVDF/graphite composites has been carried out so far [8–10]. In the present work, we for the first time prepared poly(vinylidene fluoride) (PVDF)/graphite composites by a solution precipitation method and characterized their crystallization behavior, thermomechanical properties, and dielectric permittivity.

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2. Experimental

2.1. Materials and sample preparation

PVDF (Solef 6008) was supplied by Solvay (Shanghai) Co., Ltd. Graphite particle was generously provided by Qingdao Dingding graphite products factory. *N*,*N*-dimethylformamide (DMF) were purchased from Guangzhou Chemical Reagent Company and used directly without any further treatment.

The PVDF/graphite composites were prepared by mixing the desired amount of graphite particles and PVDF in 100 ml of DMF solution at 80 °C under stirring for 2 h, and then treated with ultrasonication for another 2 h. The mixture was poured into 200 mL of deionized water for rapid precipitation (precipitation method), and the product was kept in a vacuum oven at 70 °C for 3 days. The precipitation samples with graphite concentration of 1, 5, and 10 wt% were designated as PG1, PG5, and PG10, respectively. For comparison, the composites were also obtained by the solution casting method: solution mixture of PVDF and graphite was poured onto the surface of a glass glide and dried at 70 °C for 3 days to remove DMF solvent. The solution cast samples with graphite concentration of 5 and 10 wt% were designated as PG-S-5 and PG-S-10, respectively.

2.2. Characterization

Crystallization behavior was tested with a Perkin Elmer DSC-7 differential scanning calorimeter under a nitrogen atmosphere. Samples were initially heated to 200 °C at a rate of 10 °C/min and held for 5 min at this temperature to eliminate previous thermal history before cooling to 30 °C at a rate of 10 °C/min. To analyze the non-isothermal crystallization process, samples PVDF and PG10 were melted at 200 °C for 5 min and then cooled at cooling rates of 5, 10, 15, and 20 °C/min, respectively. The exothermal curves of heat flow as a function of temperature were recorded for crystallization kinetic analysis.

DMA experiments were carried out using a Perkin Elmer diamond DMA lab system in tension mode at a frequency of 1 Hz. The samples were tested over a temperature range from −80 to 80 °C.

For the dielectric measurements, aluminum electrodes with a diameter of 3 mm were coated on both sides of the films by thermal evaporation. Dielectric properties of the samples were measured using an Agilent 4294 A impedance analyzer in the frequency range of 10^2–10^7 Hz.

3. Results and discussion

3.1. Non-isothermal crystallization analysis

The non-isothermal crystallization curves of PVDF and its composites recorded at a cooling rate of 10 °C/min are illustrated in Fig. 1. It can be seen that composites obtained from the solution casting method show double crystallization peaks, which are different from those prepared by rapid precipitation. It is believed that the formation of the double crystallization peaks can be ascribed to the poor dispersion of graphite particles in the PVDF matrix. Generally speaking, for polymer/inorganic filler system, polymer chains can crystallize by themselves (self-nucleation effect) or crystallize with inorganic filler as nucleation agent (heterogeneous nucleation effect). When inorganic fillers are well dispersed in the polymer matrix, the heterogeneous nucleation effect dominates the crystallization process and only one crystallization peak can be observed. It has been reported that inorganic fillers can aggregate again in the conventional solution casting method when the solvent evaporates slowly [11]. Consequently, double crystallization peaks of solution cast composites occur, resulting from the co-existence of self-nucleation and heterogeneous nucleation effects. Because the homogenous dispersion of filler in the polymer matrix is a critical factor to obtain a high performance composite, and homogeneous dispersion of inorganic fillers can be achieved by the solution precipitation method [11], all the composites samples investigated thereafter were prepared by rapid precipitation.

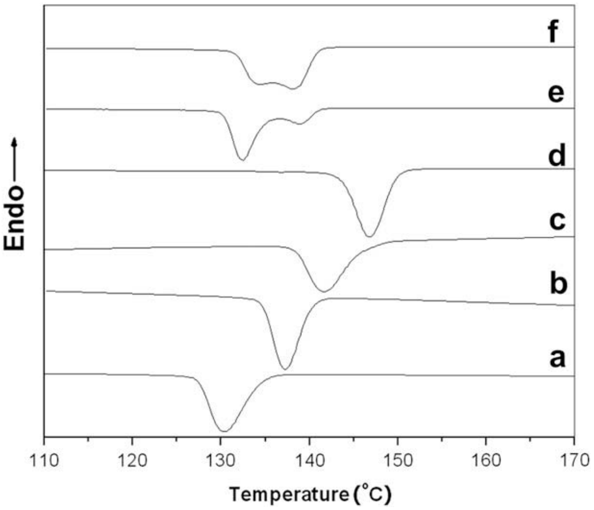

Fig. 1. The non-isothermal crystallization curves recorded at a cooling rate of 10 °C/min for (a) pure PVDF, (b) PG1, (c) PG5, (d) PG10, (e) PG-S-5 and (f) PG-S-10.

According to the DSC curves shown in Fig. 1, the peak crystallization temperature (T_p), the heat evolved during crystallization (ΔH_c) and the degree of crystallinity (X_c) at a cooling rate of 10 °C/min for PVDF and its composites can be obtained, which are listed in Table 1. The degree of crystallinity (X_c) can be calculated by

$$X_c(\%) = \frac{\Delta H_c}{\left(1 - \Phi\right)\Delta H_c^0} \times 100 \qquad (1)$$

Table 1
Values of T_p, ΔH_c and X_c for PVDF and its composites

Sample	T_p (°C)	ΔH_c (J/g)	X_c (%)
PVDF	130.3	45.74	43.73
PG1	137.3	46.05	44.02
PG5	141.6	46.52	44.47
PG10	146.8	48.46	46.33