Material Properties

Evaluation of rheological and thermal properties of polyvinylidene fluoride (PVDF)/graphene nanoplatelets (GNP) composites

Bin Yang[a,*], You Shi[a], Ji-Bin Miao[a], Ru Xia[a], Li-Feng Su[a], Jia-Sheng Qian[a], Peng Chen[a], Qian-Lei Zhang[b], Jing-Wang Liu[c]

[a] School of Chemistry & Chemical Engineering, Key Laboratory of Environment-Friendly Polymeric Materials of Anhui Province, Key Laboratory of High-Performance Rubber & Products of Anhui Province, Anhui University, Hefei, 230601, Anhui, PR China
[b] University of Science and Technology of China, Hefei, 230026, Anhui, PR China
[c] State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu, 610065, Sichuan, PR China

ARTICLE INFO

ABSTRACT

Polyvinylidene Fluoride (PVDF)/graphene nanoplatelets (GNP) composites were prepared by solution blending with various loadings of graphene nanoplatelets (GNP). Rheological behavior and thermal properties of the composites were investigated, and the results showed that the composites displayed rheological complexity with the increase of the GNP. Thermal conductivity of the PVDF composites was considerably improved with increasing GNP content. Results of in-situ temperature measurement were consistent with the variation of the thermal conductivity as a function of GNP content. Interestingly, thermal stability of the composites was hardly affected by the filler content. The present study will be practically significant to further extend the application field of PVDF composites.

1. Introduction

Polyvinylidene Fluoride (PVDF), a semi-crystalline thermoplastic polymer, has good overall performance, such as, excellent weather resistance, thermal and chemical stability, and can easily be processed via general resin processing methods [1,2] (e.g., extrusion, injection, blow molding, and so on [3,4]). So far, PVDF resin has been widely applied in packaging materials [5], electromagnetic interference shielding [6], adsorbent [7–10], sensing [11], energy [12] and many other fields.

During the processing operation, the polymer molding process was heavily related to the viscoelastic and rheological properties of the polymer melt, which were dictated by the material's microstructure, composition as well as the external conditions (such as, temperature, pressure, filler content, etc) [13,14]. Two of the widely used conductive fillers currently on the market are carbon nanotube (CNT) and graphene nanoplatelet (GNP), and GNP is not only of high thermal conductivity but also easier to form a network structure in polymer matrix [15–19]. There existed lots of research regarding the graphene nanoplatelets (GNP) filled PVDF composites [20–23]. *Xiao* et al. [24] investigated PVDF/carbon nanotube (CNT)/graphene nanoplatelets (GNP) composites, and they reported that as compared with the PVDF/GNP composites which exhibited percolated network structure of filler at extremely high filler content (20 wt%), the addition of CNT greatly

promoted the formation of 3D hybrid network structure in the composites, as illustrated in Cole-Cole plot. Besides, all the ternary PVDF/CNT/GNP composites displayed an apparent deviation from linear relationship between storage modulus (G′) and loss modulus (G″), which further demonstrated the formation of the percolated network structures of fillers in the composites. *Achaby* et al. [25] prepared the PVDF/GNP composites by melt blending. It was found that with increasing GNP content, the *Newtonian* behavior disappeared in low frequency zone, suggesting a viscoelastic transition from liquid-like to solid-like behavior. *Mohamadi* et al. [26] prepared PMMA/GNP masterbatch via in-situ polymerization, and then mixed the masterbatch with PVDF to prepare the composite films. GNP was found to show lubrication effect to a great extent from the rheological behavior of the composites in the low frequency region. *Dong* et al. [27] studied the PVDF/MWCNT nanocomposites, when MWCNT% ranged from 1% to 3%, significant changes in melt-state viscoelastic properties were observed, e.g., a great increase in G′, little dependence of loss factor (tan δ) on frequency, etc. As the MWCNT content increased, the heterogeneity of the polymeric systems increased, for instance, the curves of 3 wt% and 5 wt% MWCNT loadings deviated obviously from the master curve in the Cole-Cole plot. Similar results were also reported by *Chen* et al. [28] *Martins* et al. [29] also prepared the PVDF/MWCNT nanocomposite by melt blending, and the electrical percolation threshold of the nanocomposite

---

* Corresponding author.
  E-mail address: yangbin@ahu.edu.cn (B. Yang).

at room temperature occurred at *ca.* 1.2 wt% MWCNT. Interestingly, the rheological percolation threshold fitted from viscosity curves was about 1.0 wt%, which was quite close to each other.

Sharma et al. [30] added ionic liquid modified MWCNTs into PVDF to prepare the composites. Their results showed that the MWCNTs modified by ionic liquid dispersed more uniformly in the PVDF matrix through SEM observation, which could be further documented by a significant improvement in the conductivity of the composites. *Ke* et al. [31] studied the crystallization, rheological and dynamic mechanical properties of two molecular weight PVDFs/MWCNT composites, the high molecular-weight PVDF composites was found to show higher peak crystallization temperature, shorter crystallization half-time and higher *Avrami* index than the low molecular-weight PVDF counterparts. *Wu* et al. [32] prepared the CNT/PVDF nanocomposites by melt mixing, and found that in comparison to neat PVDF, the nanocomposites showed an enhanced pseudoplastic behavior (e.g., the reduced non-*Newtonian* index, the increased flow activation energy during steady shear sweep). The formation of the percolated CNT network was temperature-dependent, and the percolation threshold values decreased with increasing temperature.

For the thermal properties of PVDF composites, the thermal conductivity of PVDF composites was improved mainly by adding carbon fillers [33–38]. For example, *Yu* et al. [39] prepared PVDF/hybrid functionalized graphene sheets (FGS)/nanodiamonds (NDs) composites by solution blending method. The thermal conductivity of the prepared composite containing 45 wt% hybrid FGS/NDs filler was up to 0.66 W/m·K, and the PVDF composites consisting 20 wt% hybrid filler showed the best thermal stability. *Cao* et al. [40] prepared PVDF thermally conductive composites by adding superfullerene, CNT and graphene sheets, respectively, among which the thermal conductivity of the composites containing graphene sheets reached a maximum of 2.06 W/m·K. *Xiao* et al. [24] prepared the ternary composites of PVDF/CNT/GNP by changing the order of adding fillers, and they found that the addition of CNT into PVDF/GNP composites could more greatly promote the formation of the network structure of the filler, and showed higher thermal conductivity and higher synergistic efficiency than the addition of GNP into PVDF/CNT, with a maximum thermal conductivity of 1.92 W/m·K. *Guo* et al. [41] prepared the graphene/PVDF composite films under electric fields, and the graphene was arranged vertically along the interfacial interaction direction, which significantly improved the thermal conductivity and tensile strength of the composite film. Their maximum thermal conductivity was 0.562 W/m·K at a graphene content of 20%. *Zhang* et al. [42] studied the addition of small amounts of GO to CNT/PVDF composites. They argued that the thermal conductivity was greatly improved because of the formation of γ-type crystal in the PVDF matrix, and the presence of GO was favorable to a better dispersion of CNT as well as the formation of denser CNT/GO network structure.

On the basis of previous studies, the aim of this work was to study the thermorheological behavior of PVDF/GNP composites, with an attempt to disclose the effect of filler content on the rheological properties of the composites. Complex rheological behavior was observed with the addition of GNP in an attempt to understand the internal structure of the PVDF/GNP composites. The thermal conductivity and thermal stability of the composites were also investigated. The present study will be of practical significance to further investigation on the "structure-property" relationship of PVDF composite as well as wide extension of its application fields.

2. Experimental

2.1. Materials

Polyvinylidene fluoride (PVDF), model: JD-10, with a density of 1.76 g/cm³ and a melt index (MI) of 1.25 g/10min, was bought from Juhua (Zhejiang) Co., China. N,N-Dimethylformamide (DMF),

Table 1
Composition of PVDF/GNP samples in this study.

Samples	PVDF	GNP
S1	100	0
S2	100	2
S3	100	4
S4	100	6
S5	100	8

analytical reagent, was supplied by Qiangsheng (Jiangsu) Functional Chemical Co., China. Graphene nanoplatelets (GNPs), with average thickness of 4–20 nm and average diameter of 5–10 μm, was bought from Yueda (Jiangsu) New Material Technology Co., China.

2.2. Sample preparation procedure

According to the experimental ratio, firstly GNPs was scattered for 4 h in an ultrasonic disperser (Model: KQ3200DB, product of Kunshan Ultrasound Instrument Co., China). 100 g PVDF was put into the DMF solvent in water bath for 1 h at 60 °C. After the PVDF was completely dissolved, GNP was added with various GNP loadings (cf. Table 1, for clarity, S1-S5 were denoted corresponding to GNP content) and the magnetic stirring was carried out for 30 min. After the dispersion was uniform, the mixed solution was poured into the tray, and the composites were eluted by coprecipitation. Subsequently, the samples were molded using a vulcanizing machine (Model: XLB-1, Shanghai First Rubber Machinery Factory, China) into disc shapes with various dimensions in accordance with subsequent measurements at 190 °C under 10 MPa.

2.3. Dynamic rheological measurement

Dynamic rheological properties were characterized using a strain-controlled rheometer (model: Bohlin Gemini-200, *Malvern Instruments Ltd., U.K.*), run in the dynamic mode with a 25.0-mm-diameter parallel-plates geometry. Disc samples with different compositions were measured at 200, 220, 240 and 260 °C, respectively. The frequency range applied was from 0.01 to 10 Hz. Linear viscoelastic behavior was measured by performing a dynamic frequency sweep at a constant strain of 1.0%.

2.4. Thermal conductivity measurement

Disc samples with diameter of 25 mm and thickness of 1 mm were placed on the test platform of a thermometer (model: TCI, *C-THERM Co., Ltd., Canada*). Water was used as the test media, and all tests were carried out at the room temperature. The principle of instrument testing was a transient method.

2.5. Thermogravimetry analysis (TGA)

Thermal stability of the materials was examined by a Thermal Gravimetric Analyzer (model: Pyris-1, Perkin-Elmer Co., Ltd., U.S.A.) at a heating rate of 20 °C/min within a nitrogen atmosphere. The range of temperature was from the ambient temperature to 800 °C. The samples weighted about 3–6 mg.

2.6. The in-situ temperature measurement

The sample (ca. 3 g) was put at the bottom of a specially-designed metallic cubic container with a side length of 5.0 cm. The wall thickness of the metallic container was only 1 mm so as to ensure the good thermal conduction. There existed a cross-shaped clamp on top of the container with an armored copper-constantan micro-thermocouple