Composites Science and Technology 129 (2016) 183–190

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Facile green fabrication of well dispersed poly(vinylidene fluoride)/graphene oxide nanocomposites with improved properties

Jun Tong, Han-Xiong Huang*, Min Wu

Lab for Micro Molding and Polymer Rheology, The Key Laboratory of Polymer Processing Engineering of the Ministry of Education, South China University of Technology, Guangzhou 510640, China

ARTICLE INFO

Article history:
Received 29 December 2015
Received in revised form
17 April 2016
Accepted 23 April 2016
Available online 25 April 2016

Keywords:
Nano composites
Polymer-matrix composites (PMCs)
Interface
Mechanical properties
Extrusion

ABSTRACT

Poly(vinylidene fluoride)/graphene oxide (PVDF/GO) nanocomposites are fabricated for the first time by one-step water-assisted mixing extrusion (WAME) via injecting GO suspension into PVDF melt. Introduced GO layers increase the crystallinities especially the β-phase fractions of the PVDF due to the special interaction between carbonyl groups at the GO surface and fluorine groups in the PVDF. The GO layers are found to reinforce the PVDF matrix, as evidenced by the increased Young's moduli and tensile strengths. Predicted aspect ratio of the GO layers using the Halpin–Tsai equation is much larger than that in the PGOs samples, which may be attributed strong interaction between the PVDF chains and GO layers. TEM micrographs demonstrate that the GO layers are well exfoliated and dispersed in the PVDF matrix, the mechanism of which is analyzed from interactions among the PVDF chains, GO layers, and water molecules during the WAME. The WAME can be an excellent method for facile, continuous and mass fabrication of polymer/graphene nanocomposites.

1. Introduction

Graphene, a two-dimensional carbon material, is well known for its high mechanical properties, thermal conductivity, electron mobility, and large surface area [1–3]. Since Geim and Novoselov successfully stripped off a single layer of graphene from a graphite flake in 2004 [4], researchers have paid intensive attention to investigating the applications of graphene in many fields. Graphene oxide (GO), a derivative of graphene, is actively investigated for its potential applications in engineering [5–8] and biomedical fields [9,10].

For polymer/graphene nanocomposites, good dispersion and distribution of graphene in polymer matrix is a critical factor to improve their properties. Polymer/graphene nanocomposites were mainly prepared via solution mixing and melt mixing methods. Layek et al. [6] used solution mixing method to prepare poly(vinylidene fluoride) (PVDF)/poly(methyl methacrylate)-functionalized graphene (MG) nanocomposites with enhanced β-phase PVDF formation. The MG was prepared from GO using atom transfer radical polymerization and then reduction. Achaby et al. [7] prepared PVDF/GO nanocomposites using solution mixing method and investigated the crystallization behaviors. The results demonstrated that well dispersed GO layers induce the formation of piezoelectric β-phase. However, solution mixing method has some disadvantages, such as inefficiency and environmental pollution. Maio et al. [8] prepared master batches with a higher GO content by wet phase inversion. The master batches were then ground into powder and used as fillers for the preparation of polyamide 6/GO and poly(ethylene-*co*-vinyl acetate)/GO nanocomposites by melt mixing method. Achaby et al. [11] prepared PVDF/chemically reduced graphene nanocomposites by melt mixing using a laboratory scale twin-screw mixer to improve thermal stability and tensile and flexural properties of PVDF. Extra steps, such as grinding polymer matrix into fine powder [11], preparing master batch [8], and functionalizing the graphene [5,12], are required to improve the dispersion of graphene in polymer matrix, which results in a complex and/or non eco-friendly process for the melt mixing method.

Water-assisted mixing extrusion (WAME) was previously proposed to prepare nanocomposites from polar polymers and pristine clays [13–17]. A rather good dispersion of nanoclay is achieved upon extrusion with water injection. GO surface is decorated with hydroxyl, epoxy and carboxyl groups, which facilitates its exfoliation into single- or few-layer GO in water and polar organic solvents

---

* Corresponding author.
E-mail address: mmhuang@scut.edu.cn (H.-X. Huang).

http://dx.doi.org/10.1016/j.compscitech.2016.04.027

via sonication or stirring [18]. Moreover, PVDF is well known for its outstanding piezo-, pyro- and ferro-electric properties [19] and as well as biocompatibility [20]. Therefore, WAME is used to prepare PVDF/GO nanocomposites in this work, aiming at improving the dispersion and distribution of the GO in the PVDF matrix in an efficient way. To the best of our knowledge, this work presents the first report concerning the use of WAME for preparing polymer/graphene nanocomposites.

2. Experimental

2.1. Setup and materials

A WAME setup, which mainly consists of a co-rotating twin-screw extruder with a screw diameter of 22 mm and a length-to-diameter ratio of 42:1, a metering pump with an injection pressure of upto 20 MPa and flow rate of upto 2 L/h, and a vacuum pump, was recently constructed in this laboratory. Fig. 1 schematically illustrates the WAME setup. The extruder screw configuration is specially designed with three geometrical sections via using different screw elements. The first section consists of conveying and kneading elements for fully melting the polymer. The second section is the most important one, where the water/suspension is injected into the molten polymer. Several reversed screw elements and kneading elements are arranged in this section to maintain the water in liquid state in the extruder and to mix the polymer and nanofiller, respectively. Water vapor is removed from a vacuum vent port in the third section.

PVDF resin (grade FR 906, Shanghai 3F New Materials Co., Ltd., China) with a melt flow index of 18.0 g/10 min (at 230 °C and 5 kg) and a density of 1.79 g/cm^3 was used as received. Graphite oxide (Xianfeng Nanomaterials Technology Co., Ltd., China) was suspended in deionized water (10 mg/ml) under ultrasonication for 2 h to obtain GO suspension. Then the obtained GO suspension was diluted to different concentrations of suspension for preparing PVDF/GO nanocomposites.

2.2. Preparation of PVDF/GO nanocomposites

The PVDF/GO nanocomposites were prepared by WAME. The PVDF pellets were added into the extruder with a feeding rate of 3 kg/h. The extruder barrel temperatures were 175, 220, 240, 235, 225, 220, and 185 °C from hopper to die, and the screw speed was 100 rpm. When the melt pressure in the second screw section of the extruder was high enough to keep water in the liquid state at such high temperatures, the GO suspension was injected into the PVDF melt at a rate of 2 L/h. At the vent port, water vapor was removed from the mixture by vacuum degassing. The as-prepared PVDF/GO nanocomposites were denoted as PGO*m*, where *m* represented the weight percentage of the GO (0.1, 0.3, 0.5 and 0.6 wt%) in the nanocomposites. For comparison, neat PVDF was also extruded at the same temperatures and screw speed with water injection at a rate of 2 L/h. After drying in a vacuum oven at 80 °C for 12 h, both PVDF and PGOs pellets were compression molded into samples with a thickness of 2 mm at a temperature of 200 °C. Specimens used for characterization were taken from the molded samples as illustrated in Fig. 2.

It is worth emphasizing that no extra step mentioned in Section “1. Introduction” was introduced and no compatibilizer was added in the preparation of the PVDF/GO nanocomposites.

2.3. Characterization

Atomic force microscopy (AFM; Bruker Multimode 8, Germany) in tapping mode was used to characterize both lateral dimension and thickness of the GO layers in the aforementioned GO suspension prepared under ultrasonication. The sample used for AFM imaging was prepared by placing two or three drops of the GO suspension onto a freshly peeled mica surface, followed by drying at room temperature.

Wide-angle X-ray diffraction (WAXD) measurements of the specimens were conducted on a D8 Advance X-ray diffractometer (Bruker, Germany; Cu Kα, $\lambda = 0.154$ nm, 40 kV, 40 mA). The measurements were performed at 2θ angle of 5–40°, a scanning rate of 2°/min, and a scanning step of 0.02°.

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Vertex 70 spectrometer (Bruker, Germany) in transmission mode to investigate the structural information of the PVDF and PGOs samples and also the GO layers. Powder (about 1 mg) scraped from the samples was finely ground in an agate mortar with dried KBr at a mass ratio of approximately 1:200 (powder to KBr) and then pressed into a disk for FTIR testing. The scanning range was from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

The melting and crystallization behaviors of both PVDF and PGOs samples were investigated using a differential scanning calorimeter (DSC; Netzsch 204F1, Germany). Specimens (about 4 mg) cut from the samples were heated from room temperature to 200 °C and kept at this temperature for 5 min to erase any thermal history before initiating the test. Then cooling and heating were performed at a rate of 10 °C/min. The melting and crystallization temperatures are taken as their respective peak temperatures, and the crystallinities (X_cs) of the PVDF and PGOs samples are calculated using the following equation:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0 \times \omega} \times 100\% \qquad (1)$$

where ΔH_m is the melting enthalpy measured in the process of heating, ΔH_m^0 is the melting enthalpy of 100% crystalline sample of

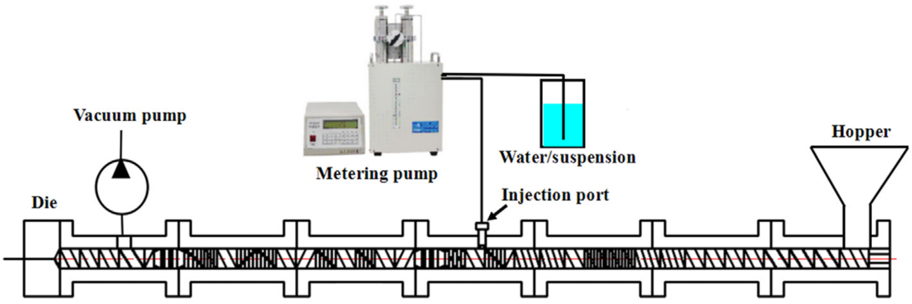

Fig. 1. Schematics of water-assisted mixing extrusion setup used in this work.