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Material Properties

Poly(vinylidene fluoride)/polycarbonate blend-based nanocomposites with enhanced rigidity — Selective localization of carbon nanofillers and organoclay

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ABSTRACT

Carbon nanotube (CNT), graphene nanoplatelet (GnP) and organo-montmorillonite (15 A) individually and simultaneously served as reinforcing fillers to prepare poly (vinylidene fluoride) (PVDF)/polycarbonate (PC) blend-based multicomponent nanocomposites. Scanning electron microscopy and transmission electron microscopy results confirmed the selective localization of individual and hybrid fillers within the PC domains. Some 15 A was located at the interface of PVDF/PC phases to modify the blend morphology. Addition of CNT led to the development of a quasi co-continuous PVDF-PC morphology. Differential scanning calorimetry results showed that 15 A, not CNT/GnP, facilitated PVDF crystallization in the composites. Among the fillers, 15 A alone induced β-form PVDF crystals, as revealed by the X-ray diffraction results, and consequently caused the complex crystallization and melting of PVDF. The rigidity (Young's and flexural moduli) of the PVDF/PC blend increased after the formation of various blend-based nanocomposites. The hybrid filler of CNT/15 A increased the Young's modulus by approximately 90% compared with that of the blend. Rheological property measurements confirmed the formation of a pseudo-network structure in the composites. Adding CNT increased the complex viscosity of the samples to a higher extent than did adding GnP, and the viscosity further increased with the co-existence of carbon nanofiller(s) and 15 A.

1. Introduction

Polymer blends and composites continue to receive interest from academia and industry because of the feasibility of achieving tailor-made properties. Commercial polymer blends/composites are designed to improve the parent polymer components significantly. The evolved phase morphology and/or dispersion status of added fillers play important roles in determining the resultant properties. Compared with conventional blends/composites, polymer nanocomposites have attracted more attention in the past two decades. Various combinations of polymers and nanofillers have been fabricated to examine their potential to improve the thermal resistance, flame retardancy, barrier properties and rigidity of parent polymers with minimal addition of nanofillers (ca. <3 wt%) [1–5]. Organically modified montmorillonite (O-MMT), one of the nanofillers that has been tested, is suitable for preparing high-performance nanocomposites. Subsequently, carbon nanomaterials with superior properties have been utilized to fabricate polymer nanocomposites. Carbon nanotubes (CNTs) and graphene nanoplatelets (GnPs) demonstrate the potential to produce polymer nanocomposites possessing high rigidity and improved thermal/electrical conductivity [6–8].

Poly (vinylidene fluoride) (PVDF), an engineering plastic, possesses high mechanical strength, good dielectric properties, remarkable thermal/chemical stability and other advantageous properties [9]. PVDF has five distinct polymorphs (α, β, γ, δ, and ε). The polar form induced piezo- and pyro-electric characteristics allow for advanced PVDF applications in sensors and actuators [10,11]. Priya and Jog [12] were among the first to study PVDF nanocomposites. In their study, melt-intercalated samples showed improved storage modulus after the addition of different O-MMTs. Yang et al. [13] simultaneously applied shear force and added O-MMT to the PVDF matrix; they obtained a high content of polar β-

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form crystals and a highly aligned structure. Good piezoelectric property and enhanced ductility were also achieved in the nanocomposites. Chiu [14] compared the differences in the physical properties of PVDF/O-MMT and PVDF/CNT nanocomposites. O-MMT addition induced β-form PVDF crystal formation, but CNT hardly affected the α-form crystal development. Both nanofillers facilitated the nucleation of PVDF, but CNT exhibited better nucleation efficiency than O-MMT.

Bisphenol A-type polycarbonate (PC) is an important engineering plastic that possesses good physical/chemical properties, such as transparency, high mechanical strength and flame retardancy. It has been utilized in the car industry, medicine, electronics and other fields. Hsieh et al. [15] prepared intercalated PC/O-MMT nanocomposites with reduced ductility. When the O-MMT loading reached 3.5 wt%, the relaxation of the composite changed from liquid-like to pseudo-solid-like behavior. Potschke et al. [16] used a master batch of PC-CNT (15 wt%) composite to prepare PC/CNT nanocomposites with various CNT loadings. CNT was uniformly dispersed within the PC matrix, and the electrical percolation was between 1 and 1.5 wt%. Lai et al. [17] prepared PC/CNT nanocomposites that exhibited a rheological percolation threshold at 2 wt% CNT loading. The composites showed superior thermal stability and enhanced storage modulus compared with neat PC.

Polymer/nanofiller binary nanocomposites have been extensively investigated. However, polymer blend-based multicomponent nanocomposites have rarely been studied. Multicomponent systems are expected to exhibit increased versatility and potential in advanced applications [18–25]. Hejazi et al. [19] reported the improved mechanical properties of polypropylene (PP)/ethylene–propylene–diene–monomer blend-based nanocomposites with O-MMT as the nanofiller. Chiu et al. [20,21] used different maleated polyolefins as compatibilizers to prepare PP/high-density polyethylene/O-MMT ternary nanocomposites. The morphology, depending on the type of added maleated compatibilizers, played a significant role in governing the mechanical/thermal behavior of the composites. Chiu et al. [22,23] also characterized miscible PVDF/poly (methyl methacrylate) blend-based nanocomposites with O-MMT and CNT as nanofillers. The dispersibility of nanofillers and the crystallization/melting behavior of PVDF in the nanocomposites were evaluated. Li et al. [24] studied PVDF/polycaprolactone (PCL)/CNT nanocomposites and found that CNT was selectively localized in the PCL phase. A double-percolation morphology developed and led to increased electrical conductivity. Cao et al. [25] prepared PVDF/polystyrene blend-based nanocomposites with the incorporation of hybrid fillers (CNT and silicon carbide). The selective localization of both fillers in PVDF domains was confirmed, and the developed morphology led to increased thermal conductivity of the nanocomposites.

Polymer blend-based nanocomposites produced with hybrid nanofillers have rarely been studied. From academic and industrial viewpoints, the influences of simultaneous incorporation of different nanofillers into polymer blends (multicomponent nanocomposites) merit a systematic investigation. PVDF and PC are both important engineering plastics. However, a PVDF/PC blend-based nanocomposite has never been studied. The current study aims to examine the individual or simultaneous incorporation of CNT and/or GnP into the fabrication and physical properties of PVDF/PC blend-based nanocomposites. Further incorporation of O-MMT into the composites was also investigated. The dispersion (localization) status of nanofillers within the blend matrix and the thermal/mechanical/rheological properties of the different blend-based nanocomposites were evaluated and compared. The efficiency of different filler combinations in improving the rigidity of the PVDF/PC blend was highlighted.

2. Experimental

2.1. Materials and sample preparation

PVDF (Kynar 7, Arkema) with a weight average molecular weight of 1.8×10^5 g/mol was used in this study. Amorphous bisphenol A-type PC (Tarflon IR 1700) purchased from Taiwan Chemical Fiber Co. with a melt flow rate of 30 g/10 min was used as a counterpart for the PVDF blend. Commercially available CNT (Golden Innovation Co., Taiwan) and GnP (XG Sciences, USA) were used as carbon nanofillers for the preparation of the composites. The CNT (multi-walled) had a carbon purity of >99%, an average outer diameter of 60 nm, and an average length of 10 μm. The GnP (xGnP M-15 grade) had high purity (>99.5%) and a thickness of about 6–8 nm. A commercial O-MMT (Cloisite 15 A, denoted as 15 A) was used as the other nanofiller for composite preparation. 15 A was purchased from Southern Clay Products Inc., USA, and was modified with dimethyl dihydrogenated tallow quaternary ammonium ion.

A Haake PolyDrive mixer (R600) with a pair of Banbury-type rotors was used to prepare the blend and composites. The polymer and nanofiller components were dried in an oven at 70 °C for 24 h before they were fed to the Haake mixer at prescribed ratios. The weight ratio of PVDF-PC in the blend and composites was fixed at 7:3. Each blend and composite was mixed for 13 min at 240 °C under a rotor speed of 60 rpm. For the composite preparation, the PVDF/PC blend was mixed for 5 min; afterwards, the nanofiller(s) was added to the blend for another 8 min of mixing. The sample designation of FC represents the PVDF/PC blend, and FC-A#, FC-T#, FC-P#, FC-T#A#, FC-P#A#, and FC-T#P#A# represent the # wt.% of the different nanofillers included in the composites. T, P, and A represent CNT, GnP, and 15 A, respectively. For instance, FC-T2 is the blend-based composite with 2 wt% CNT inclusion, and FC-T1P1A1 is the composite with 1 wt% of each CNT, GnP, and 15 A inclusion. Neat components of PVDF and PC were also treated under the same mixing condition for comparison.

2.2. Characterization

Scanning electron microscopy (SEM) combined with energy-dispersive spectroscopy (EDS) was conducted to examine the phase morphology and nanofiller dispersibility of the prepared samples. The experiments were performed on cryo-fractured (in liquid nitrogen) surfaces of the samples with a Hitachi S-3000N system. Transmission electron microscopy (TEM, Jeol JEM-1230) was utilized to determine the dispersion status of 15 A within the blend matrix. The TEM experiments were performed on ultrathin sections of cryo-microtomed composite films (approximately 100 nm thick). X-ray diffraction (XRD) was used to examine the polymorph of PVDF in different samples. A D2 Phaser Bruker X-ray unit with CuK$_\alpha$ radiation ($\lambda = 1.54$ Å) operating at 30 kV and 10 mA was employed for the XRD experiments.

The crystallization and melting behavior of PVDF in the neat state and in the blend/composites were measured with a TA DSC Q10 analyzer equipped with an intercooler. The samples were melted at 240 °C for 4 min then cooled to 20 °C at different rates for crystallization experiments. The crystallized samples were subsequently heated to 240 °C at 20 °C/min to assess the melting behavior of PVDF. The thermal stability of the samples was assessed with a thermogravimetric analyzer (TGA, TA Q50). The samples were scanned from room temperature to 700 °C at 20 °C/min under air. The tensile (Young's) modulus (YM) and elongation at break (EB) of the compression-molded specimens (according to ISO 527) were measured at a crosshead speed of 4 mm/min with a Gotech Al-3000 system. The flexural modulus (FM) of the specimens was measured at a crosshead speed of 1 mm/min with the same Gotech