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Melt rheological properties of ethylene-vinyl acetate/multi-walled carbon nanotube composites

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ABSTRACT

In this study, the rheological properties of Ethylene-Vinyl Acetate (EVA) filled with various contents (0.1–5 wt.%) of multi-walled carbon nanotubes (MWCNTs) were investigated using a capillary rheometer at temperatures and shear rates relevant to the injection molding process. The shear viscosity was calculated after the Bagley and Weissenberg-Rabinowitsch corrections, and the master curves were constructed applying the Time-Temperature Superposition (TTS) principle and the Cross model.

The results show that, under shear flow, the EVA/MWCNT composites exhibit some of the key rheological behaviors. At low shear rates (lower than 100 s^{-1}), the EVA/MWCNT composite behaves as Newtonian fluid for loading up to 0.5 wt.%, while at higher loading, the non-Newtonian behavior is more prominent. At shear rates higher than 100 s^{-1}, all composites exhibit shear thinning behavior ($n < 0.4$), indicating that the EVA/MWCNT composites are viable for the injection molding process. The dependence of shear viscosity on temperature is consistent with the Arrhenius equation and, for the investigated temperatures and shear rates, the viscosity increases linearly with increasing MWCNTs wt.%.

1. Introduction

In the last years, the incorporation of carbon nanotubes (CNTs) into polymers has become an effective approach for developing polymer/CNT composites with improved mechanical, electrical and thermal properties [1–7]. The main advantage of using carbon nanotubes is related to the fact that these composites can reach electrical, thermal and/or rheological percolation at a very low CNT content. However, the final properties of polymer/CNT composites are highly dependent on a number of direct and indirect factors, including filler (aspect ratio, dispersion, distribution and orientation), polymer type, interface (surface treatment, functionalization, surface energy, etc.), and compounding and manufacturing methods, as documented in several reviews and research articles [1–7].

Among several manufacturing methods, the injection molding process has received considerable interest due to its industrial importance and ability to disperse the nanotubes into the polymer matrix [8–10]. However, the fabrication of high-quality products by injection molding depends to a great extent on the processing conditions (e.g. melt temperature, mold temperature, shear flow rate, etc.).

Generally, melt processing of polymer/CNT composites requires flow through complex molds, thus rheology is an essential part of product design and manufacturing. Understanding the rheology of polymer/CNT composites is necessary for an accurate design of the mold cavity and for an efficient selection of processing parameters which in turn affect the end properties of the products. If viscosity is not suitable under the processing conditions, short shots, flashing and flow instability (melt fracture, sharkskin, extrudate distortion or/and swell, surface undulation and ripples) may occur during the injection molding process [11,12].

In particular, during the injection molding of polymer/CNT composites, due to high shear rates, the melt is subjected to a combination of shear and elongation flows, and CNTs experience gradually alignment in the shear flow direction leading to inhomogeneous structure [8–10]. Moreover, as a result of the large temperature gradient between the mold and melt and extensional flows along the melt direction [13], the injection molded parts generally exhibit a so-called skin-core structure. In the case of polymer/CNT composites, carbon nanotubes freeze in the orientation direction and, thus, the skin is expected to have more aligned carbon nanotubes or/and agglomerates and different mechanical properties as compared with the core [14]. Due to the temperature

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gradient, the inner layer cools slowly with respect to the skin layer, the solidification process being favorable for residual stress, which is one of the factors that can cause shrinkage in the final products.

On the other hand, it was shown that particle–particle interactions, particle–polymer interactions, and the orientation of dispersed particles can be reflected by the rheological properties [15,16]. Through rheological characterization, indications on the internal structure of polymer/CNT composites, which depends on the dispersion state, shape, loading, and surface condition of fillers, can be obtained. Consequently, several authors have adopted rheology as a main analysis tool [17–19].

Based on rheological experimental measurements, the material parameters in the constitutive models required by the flow simulation software can be determined. However, the generation of reliable rheological properties (material property database), that can be used for the flow simulation during the manufacturing processes involving polymer/CNT composites, is very costly as it requires special facilities, experts and very long durations. A survey of the most important commercial simulation softwares (e.g. Moldflow, Moldex3D, etc.) shows that details of the rheological properties of polymer/CNT composites are rarely available.

Although the capillary flow properties are valuable both for the optimization of processing parameters and for the understanding of the fundamental properties of polymer/CNT composites, only limited data are available on the rheology of polymer/CNT composites [20–28].

In recent years, Ethylene-Vinyl Acetate (EVA) filled with carbon nanotubes has attracted a great deal of attention especially for developing flexible, electrically and thermally conductive components with reduced weight but improved mechanical performances [29–34]. The effect of carbon nanotubes on the properties of EVA/CNT composites, including mechanical properties, thermal conductivities, and electrical conductivities, has been presented in a number of research papers [29–34], but more investigations on the rheological behavior of EVA/CNT composites under different shear conditions are required especially from a manufacturing point of view.

For this reason, in this work, the rheological behavior of EVA filled with different multi-walled carbon nanotube (MWCNT) loadings (0.1, 0.3, 0.5, 1, 3, and 5 wt.%) is investigated using a capillary rheometer for melt temperatures and shear rates relevant to extrusion and injection molding process. The shear viscosity is calculated from the true wall shear stress and true shear rate after the Bagley and Rabinowich corrections, and the master curves are obtained by the Time-Temperature Superposition (TTS) principle through the Cross-WLF model.

The final goal of this research is to provide the rheological properties of polymer/CNT composites that can be imported in commercial softwares to be tested virtually under realistic processing conditions and thus reduce the time span from product design to manufacture.

2. Materials and methods

2.1. Materials

The composite used in this investigation is a commercial Ethylene-Vinyl Acetate (EVA) copolymer (EVATANE 20-20, Arkema), containing 20 wt.% of VA filled with industrial multi-walled carbon nanotubes NC7000 (Nanocyl S.A., Belgium), produced by the catalytic decomposition method [35].

The EVA/MWCNT composite (pellets) filled with nanotubes in weight percentages (wt.%) of 0.1, 0.3, 0.5, 1, 3, and 5, supplied by Nanocyl S.A. (Belgium), were prepared by dilution of masterbatch PLASTICYL™ EVA2001 containing 20 wt.% of MWCNTs in a co-rotating twin screw extruder at a barrel temperature of 170 °C.

2.2. Capillary rheometry

Rheological measurements were carried out using a high pressure capillary rheometer (Rheograph RG75, Goettfert Inc., Germany) equipped with three different round-hole capillary dies with a length-to-diameter ratio (L/D) of 10:1, 20:1, and 30:1. The instrument is equipped with a pressure transducer able to detect pressure up to 2000 bar. The capillary experiments were performed at four different temperatures (120, 140, 160, and 180 °C) above the melting temperature. The shear rate examined in this study (50–5000 s^{-1}) covers the shear experienced during most polymer processing methods, including extrusion and injection molding.

The initial melting time was set to 3 min for all tests regardless of the carbon nanotube wt.%. Before testing, the EVA/MWCNT pellets were vacuum dried at 60 °C for 4 h in a vacuum dry oven (Raypa, Spain) to stabilize the moisture content. It should be noted that the measurements were carried out by randomly setting the shear rate values. The melt viscosity values for each experiment correspond to the average of at least 3 trials.

2.3. Rheological analysis

The apparent shear viscosity is calculated by Ref. [36].

$$\eta_a = \frac{\tau_a}{\dot{\gamma}_a} \ (\mathrm{Pa \cdot s}) \tag{1}$$

in which the apparent shear stress at the capillary wall is

$$\tau_a = \Delta P \frac{R}{2L} \ (\mathrm{Pa}) \tag{2}$$

and the apparent shear rate is given by

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3} \left(\mathrm{s}^{-1}\right) \tag{3}$$

where Q is the volumetric flow of the polymer melt, R is the capillary die radius, ΔP is the pressure drop across the capillary length of L.

With regard to the flow in a capillary rheometer, initially the polymer melt flows in the barrel of the capillary, where the extensional and shear flows are mixed, as shown in Fig. 1. In the core region of the barrel, the flow is largely extensional with the highest rate occurring at the centerline, and becomes shear close to the wall [11,37–40]. The shear effects are more dominant closer to the wall, where the shear rate and residence time are higher [37,38,40]. The extensional flow in the barrel orients the molecules and nanotubes and possibly creates a significant amount of precursors and small crystals [11]. In the capillary die, the polymer chains close to the wall exhibit large shear rates and thus form oriented structures close to the wall in the form of layers parallel to the flow direction [11].

In general, the capillary rheological data are subjected to Mooney, Bagley (capillary entry pressure loss) and Weissenberg-Rabinowitsch corrections to determine the true (corrected) shear stress τ_w and the true shear rate $\dot{\gamma}_w$ [28,36,39]. The Bagley correction takes into account the pressure losses at the entrance and end of the capillary. This correction requires repeating the measuring test with capillary dies of different lengths. The Bagley correction allows the determination of the true wall shear stress [28,36,39].