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Influence of reduced graphene oxide on the rheological response and chain orientation on shear deformation of high density polyethylene

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ABSTRACT

The rheological response of high density polyethylene/reduced graphene oxide nanoplatelets (HDPE/rGON) composites, and the influence of rGON on chain orientation and crystallization behavior after shear flow are investigated. Melt rheology reveals the presence of strong interaction between polymer chains and the filler. Above 4.0 wt % of the filler concentration, the terminal region of frequency sweep shows changes in the linear viscoelastic properties of the composites. In particular, at these high concentrations the cross-over frequency at which the transition from predominantly elastic to viscous behavior occurs significantly shifts to lower values, indicating the formation of a solid-like percolated network. A drop in G' at high frequency (100 rad/s) is observed in the presence of the filler, and the storage modulus shows minima at filler concentration between 2.0 and 4.0 wt %. The influence of chain–filler interaction on chain orientation, and subsequent crystallization behavior after application of shear is followed by time resolved WAXD/SAXS. The orientation of the crystalline domains was quantified by the Herman's orientation factor that supports the presence of strong chain–filler interaction. The Deborah number of reptation and retraction suggests that during the applied non-linear shear, polymer chains in the composites experience mild stretch that is not significant enough to induce crystallization at the high temperature (136 °C). However, restriction imposed by the filler on the chain mobility is pronounced enough to preserve oriented state that causes anisotropy in crystallization on cooling. The enhanced orientation with increasing filler content is conclusively attributed to the strong chain–filler interaction.

1. Introduction

Polymer nanocomposites with improved mechanical, electrical or thermal properties have been investigated intensively, and they have become one of the important classes of materials [1,2]. The change in their properties is intimately related to the aspect ratio, microscopic arrangement of the disperse phase, chain–filler interaction, as well as the formation of filler–filler networks. For example, the presence of filler could significantly influence the polymer chain dynamics, consequently influencing crystallization during shear flow and ultimately mechanical properties of the polymer [3,4]. Melt rheological studies have revealed that the presence of nanoparticles in polymers perturbs the microscopic inter-chain arrangement of the polymer network, influencing the linear rheological properties [5]. Understanding the influence of nanofillers on polymer dynamics is crucial for the design and process of nanocomposites with desired properties, for example decrease in entanglement density and ease in processability by incorporating nanofillers [6–10]. It has also been reported that a strong shear flow, with $De\ (\tau_{\mathrm{retraction}} \times \dot{\gamma}) > 1$, plays a crucial role in the polymer chain stretching and orientation, resulting in the formation of highly anisotropic, oriented structures upon crystallization [11,12]. For example, shish-kebabs composed of two distinctive

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morphologies have been observed under flow condition: the shish structure having large crystal thickness and kebab by relatively thinner folded chain crystals [11]. It is reported in early research on formation of shish-kebab structure during crystallization that the long chain component plays a catalytic role that recruits adjacent chains into the formation of the shish [13]. Important to notice is that in the presence of nanoparticles, the shish-kebab structure that arises from the significant chain stretch and orientation can be enhanced [11]. However, the influence of the filler and filler–chain interaction on the formation of anisotropic structure induced by shear flow remains unclear.

Recently, graphene has attracted considerable attention due to its remarkable electrical, thermal and mechanical properties and its potential in developing high performance nanocomposites [14–17]. Due to its very high aspect ratio [18] and theoretical specific surface area −2630 m^2/g [19], graphene is capable of modifying the material properties at very low loadings. For example, 0.028 vol % of graphene in UHMWPE is reported to produce a composite having electrical conductivity [20]. To obtain graphene or reduced graphene oxide, one of the most commonly used method is thermal reduction of graphene oxide nanoplatelets (GON). It is reported in early research that at temperature as low as 150 °C, GON can be reduced to rGON, as indicated by XPS [21]. In addition, low graphene concentrations could hinder polyethylene chain dynamics causing a drop in complex viscosity [6]. To recall, Liu et al. reported that with increasing graphene content up to 0.8 wt %, the complex viscosity of UHMWPE drops to a minimum value [6]. It is of interest to investigate the influence of molar mass, in the presence of graphene, on the rheological response. The drop in viscosity in the presence of filler is of commercial as well as fundamental interest. The reduction in viscosity facilitates the ease in processing of polymers, and demonstrates the significance of chain–filler interaction on morphology development in quiescent as well as flow conditions.

Prior to the reported studies on graphene, the influence of rigid and layered nanoclay particles [22–25] and high aspect ratio carbon nanotubes (CNTs) [11,26] on the shear induced orientation of polymer composites or composites solutions has been extensively investigated. The orientation of clay/polymer nanocomposites induced by shear has been mainly attributed to the orientation of clays that formed regular structure during shear [21]. CNTs filler is found to be responsible for the chain orientation, that results into the orientated structure of the composites after shear and crystallization [11]. It has also been reported that CNTs could act as shish in the formation of hybrid shish-kebab structure due to its considerably high relaxation time and nucleation efficiency [25].

In this publication, following a two-step preparation method, the HDPE/rGON composites are prepared [6]. To recall, combination of the stability of GON dispersion in water and the ease in reduction of GON by heat treatment allows the homogeneous dispersion of nanosheets in the polymer matrix. The influence of rGON on chain orientation during shear deformation and subsequent crystallization is investigated by time-resolved WAXD/SAXS studies. These findings are linked with linear rheological response of the composites. A comparison with our earlier studies shows the relevance of molar mass on the drop in storage modulus at high frequency.

2. Experimental

2.1. Materials

Graphene oxide nanosheets (GON) were prepared using a modified Hummers method [6,27]. Materials for the synthesis of GON were purchased from Sigma–Aldrich. HDPE (in the form of fine powder) was purchased from Dow Chemicals. All the reagents were used as received. The estimation of molar mass (M_w) and molecular weight distribution (MWD) of HDPE was carried out by melt rheology using an Advanced Rheometrics Expansion System (ARES) rheometer. The molar mass parameters were calculated using an Orchestrator software based on Refs. [28,29] and the results are shown in Fig. 1.

2.2. Preparation of HDPE/rGON nanocomposites

HDPE/rGON nanocomposites were obtained by a two-step preparation method: In Step 1 the required amount of GON was weighed and re-dispersed in 40 ml of water followed by 15 min ultrasonication, while the required amount of HDPE powder was suspended in acetone and kept under magnetic stirring. The ultrasonicated GON water suspension was added to the acetone-suspended HDPE. The mixture was kept under magnetic stirring in a fume cupboard until most of the solvent evaporated and the resultant solid was further dried in a vacuum oven at 40 °C for at least 12 h. Due to the hydrophilic character of GON, the use of GON in this step allowed for a better dispersion of the nanoparticles in water. In Step 2, powders prepared in the Step 1 were compression-molded at 160 °C with pressure reaching 1660 bars in a hydraulic press on a round mold having diameter of 5.0 cm. The heat treatment of the polymer composite allowed the simultaneous reduction of GON to rGON, as described previously in Ref. [6]. The hydrophobic character of reduced GON over the hydrophilic GON is preferred to ensure a good interaction with the hydrophobic polymer matrix. The compressed reduced composite samples were used for rheological analysis or X-ray characterization. 1.0 wt % of anti-oxidant (Irganox 1010, Ciba) was added to avoid any possible oxidation or thermal degradation during compression molding. Composites having varying amount of rGON, ranging from 0.0 wt % to 6.0 wt %, were prepared using the method described above.

2.3. Characterization of filler and composites

A JEOL-2000FX Transmission Electron Microscope (TEM) was used to observe the exfoliation state of GON in water with an applied voltage of 200 kV. A bench top D2 X-ray Diffraction (XRD) with a radiation wavelength of CuK$_\alpha$, 0.154 nm, was used to characterize the oxidation state of GON. X-ray photoelectron spectroscopy (XPS), using Al K$_\alpha$ micro-focused monochromator as X-ray source, was used to characterize the elemental composition of GON and rGON, respectively. The XPS spectra were fitted using Thermo

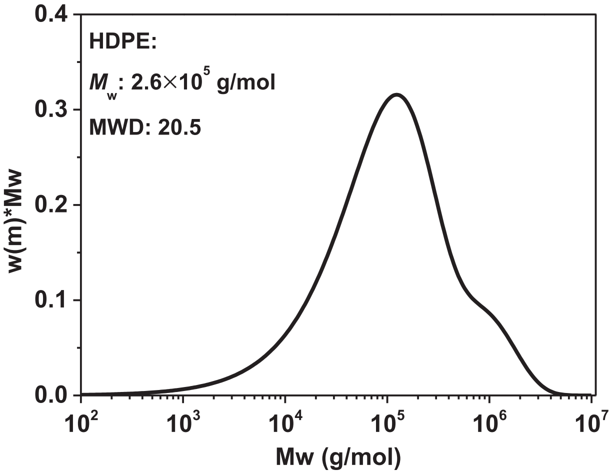

Fig. 1. Estimation of M_w and MWD of HDPE by melt rheology.