Composites: Part B 52 (2013) 164–171

Contents lists available at SciVerse ScienceDirect

Composites: Part B

journal homepage: www.elsevier.com/locate/compositesb

Effects of modified and non-modified clay on the rheological behavior of high density polyethylene

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ARTICLE INFO

Article history:
Received 3 April 2012
Received in revised form 31 January 2013
Accepted 7 April 2013
Available online 17 April 2013

Keywords:
A. Nano-structures
B. Interface/interphase
E. Extrusion

ABSTRACT

HDPE nanocomposites containing 2.5, 5 and 10 wt.% of non-modified and modified clays (NMC and MC) were prepared by melt extrusion in a twin screw extruder. Compression molded samples were prepared. Transmission electron microscopy (TEM) indicated a partial intercalation of the modified clay nanofiller within the HDPE matrix comparing to that of non-modified clay. The moduli of nanocomposites increased with increase in nanofiller concentration; but this increase was greater in the low frequency region. The non-modified clay had a greater increase in the elastic behavior, while the modified clay increased viscose behavior because of more interactions with the matrix and partial intercalation. The rheological behaviors of both HDPE/NMC and HDPE/MC nanocomposites are more sensitive to nanoparticles' concentration at low frequencies. The HDPE/MC nanocomposites showed semi-circle shapes comparing to HDPE/NMC nanocomposites. While the Cole–Cole plot of HDPE/NMC nanocomposite had more departure of semi-circle shape. The agglomerated particles could concentrate the imposed stress so the yield stress reached at lower shear rates comparing to pure HDPE and HDPE filled 2.5 wt.% NMC nanocomposite. Study of suspension models showed that the Eilers-Van Dijck and Einsten models fitted to almost experimental data satisfactorily.

1. Introduction

Nanocomposites have attracted attention in recent years because their mechanical, physical, optical, and rheological properties can often be modified with a minimal increase in density as a result of low inorganic loading [1–4]. Interest in polyolefin nanocomposites has emerged due to their improved performance in packaging and engineering applications. Because of the light weight, good process ability, low cost, etc. polyethylene is the most common polymers which, used as a matrix [3–6]. Recently, three ways are used to prepare PE/clay nanocomposites: the solution method, in situ polymerization and melt intercalation method. Of these methods, melt intercalation method is the easiest method to prepare nanocomposites [5–8].

The incorporation of nanometer scale reinforcement (e.g., layered silicates of clay and nanofiber) may dramatically improve selected properties of the related polymer. From an application point of view, melt rheological properties are vitally important for processing of polymer-based nanocomposites. Meanwhile, rheometry is a powerful tool for inspecting the internal microstructure of polymer nanocomposites containing nanoparticles [9–19]. A direct consequence of the incorporation of nanofillers in a molten polymer is a significant change in the viscoelastic properties. Consequently, linear rheology is a way generally used to assess the state of dispersion of nanocomposites directly in the molten state. Dynamic melt rheometry is a powerful means to inspect the effect of inorganic filler on the motion and relaxation of polymer chains [9]. Rheological investigations give important information about the structure formation during the synthesis and could be used for optimizing the formulation and processing of nanocomposites. There have been a few former studies on the rheology of polymer-layered silicate nanocomposites [20–22]. Authors reported, that polymer-layered silicate nanocomposites exhibit similar rheological behavior in shear flow to other intrinsically anisotropic materials such as block copolymers and liquid crystalline polymers, as well as end-tethering of the polymer molecules to the organically modified silicate surfaces alters the relaxation dynamics of macromolecules. Structural effects, such as aggregation, flocculation (edge–edge clay layers interaction), and flow-induced flocculation–deflocculation of the layered silicates in the organic matrix are reported. On the other hand, the study on the relationship between the non-linear properties of polymers during elongation and the structure is very important from the research and technological aspects. Experimental studies on the elongation flow of polymer composites show that, if hard macroscopic filler particles are incor-

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http://dx.doi.org/10.1016/j.compositesb.2013.04.010

porated in polymer, the strain-hardening properties become weaker, as well as strain softening appears when glass fibers are used as filler [23].

In the proposed study, the effect of clay on rheology of HDPE in oscillatory shear and rotation flow are analyzed in order to consider the effects of the basic variables (modification and composition) on rheological behavior. The study aims to improve the knowledge about the relation between rheological behavior and the structure of polymer/clay nanocomposites using several proposed models for rheology of suspensions [24–29].

1.1. Rheology of suspensions

The flow behavior of suspensions of rigid particles in liquids is important in filled systems because many fabrication techniques for composites involve the flow of suspensions of liquids or molten polymers and most of the theories of the moduli of composites have their origin in the theory of the viscosity of suspensions.

The Einsten's equation for the viscosity of a suspension of rigid spherical particles is [25].

$$\eta = \eta_m(1 + K_E\phi_f) \tag{1}$$

The coefficient of volume fraction of the filler (K_E) has the value 2.50. An equation that describes the viscosity of many kinds of suspensions over the entire concentration range is the Mooney equation [26]

$$\ln\frac{\eta_c}{\eta_m} = \frac{K_E\phi_f}{1 - \frac{\phi_f}{\phi_{\max}}} \tag{2}$$

The constant K_E is again Einsten coefficient and has the value of 2.5 for dispersed spheres if there is no slippage at the interface. The value drops to 1.0 if there is slippage at the interface. $\phi_{\max}$ is the maximum volume fraction that the filler can have. $\phi_{\max}$ for random close packing is 0.632 theoretically [27]. Another equation that fits many experimental data on viscosity of all kinds of suspensions is the modified Roscope equation [28].

$$\frac{\eta_c}{\eta_m} = \left(1 - \frac{\phi_f}{\phi_{\max}}\right)^{-2.5} \tag{3}$$

An equation of wide utility is Eilers-van Dijck equation [29].

$$\frac{\eta_c}{\eta_m} = \left(1 + \frac{1.25\phi_f}{1 - (\phi_f/\phi_{\max})}\right)^2 \tag{4}$$

If the suspensions are partially aggregated, Eq. (4) must be modified to

$$\frac{\eta_c}{\eta_m} = \left(1 + \frac{1.25(\phi_f/\phi_{\max})}{1 - (\phi_f/\phi_{\max})}\right)^2 \tag{5}$$

$\phi_{\max}$ is 0.37 for aggregated systems and also for nonagglomerating particles packed randomly [27].

2. Experimental

2.1. Materials

High density polyethylene was provided by Arak Petrochemical Company (Iran) under a trade name of EX3 (GM5010T2N), the density was 0.944 g/cm^3, melt flow index according to ASTM 1238 (200 °C and 5 kg) was 0.5 g/10 min. Two used clay were: (1) Cloisite Na$^+$ was a natural montmorillonite. It had a density of 2.86 g/cm^3. (2) Cloisite 20A was a natural montmorillonite modified with a quaternary ammonium salt. It had a density of 1.77 g/cm^3. They supplied by Southern Clay products Inc., USA.

2.2. Material processing

For each type of nanocomposite, as well as for the neat polymer, the same processing procedure was applied so that the thermomechanical history of the nanocomposites and that of neat polymers remain similar. The pellets were dry blended and fed in a ZSK (ZSK 18 Megalab, Germany) co-rotating twin-screw extruder. The mixing was carried out at a temperature distribution of 140–200 °C, and speed of 100 rpm. The extruded nanocomposites were pelletized at the die exit, dried and then compression molded at 180 °C for 1 min, to obtain circular disks for the rheological measurements. The samples were quenched in the cold press of the compression molding machine. Nanocomposites containing 2.5, 5 and 10 wt.% of both clay nanoparticles (Cloisite Na$^+$ and Cloisite 20A) were prepared. Hereafter we will denote HDPE, Cloisite Na$^+$ (non-modified clay) and Cloisite 20A (modified clay) with the H, NMC and MC symbols respectively.

2.3. Transmission electron microscopy (TEM)

A piece of the compression molded thin film samples containing 5 and 10 wt.% of nanoparticles were cut for TEM studies. The dispersion quality of the nanoparticles within the matrix, and the nanostructures of the nanocomposites were investigated using a transmittance electron microscope (TEM). It was performed on a Philips EM208 microscope and operated at 100 kV.

2.4. Melt dynamic rheometry

All rheological measurements were performed on a controlled strain rheometer (MCR 300 Rheometer, Anton Paar Physica, Otriš) with a torque transducer range of 1–15,000 μNm using 25 mm diameter parallel plates at 180 °C. Testing sample disks with a thickness of 0.7 mm and a diameter of 25 mm were used. Oscillatory shear measurements were conducted within a 5% strain and frequency range of 0.03–600 rad/s.

Rotation mode measurements were conducted within a shear rate range of 0.01–100 s^{-1}. For ensuring the reliability of rheological data all measurements were conducted under nitrogen atmosphere to minimize oxidative degradation of the polymer and nanocomposites.

3. Results and discussion

3.1. Dispersion of nanoparticles in the matrix

The microstructure of HDPE nanocomposites was evaluated by TEM to observe the distribution of nanoparticles within the extruded nanocomposites. Fig. 1 shows micrographs of thin film of H/NMC and H/MC nanocomposites. Comparing the non-modified clay nanocomposite (Fig. 1a) and modified clay nanocomposite (Fig. 1b) showed a partial intercalation for nanocomposite containing modified clay. As can be seen, partial coalescence was unavoidable at high concentration for H/NMC 10 (Fig. 1c). Many particles have undergone coalescence especially at higher clay contents. A good dispersion of nanofillers within the matrix could improve the rheological properties of the nanocomposites even at lower nanofiller loadings owing to enhanced filler–matrix interaction.

3.2. Melt dynamic rheometry

Rheometry was used as a powerful tool for study the internal microstructure of polymer nanocomposites containing nanoparticles. The silicate platelets form different levels of 3D physical network in the polymer matrix depending on their structure