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A simple method to interpret the rheological behaviour of intercalated polymer nanocomposites

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A B S T R A C T

Nanocomposites are a new class of polymer composites that exhibit an interesting combination of chemical, physical, thermal and mechanical properties. Only small amounts of nanofiller are sufficient to generate great variations of many properties.

This work focuses on the rheological behaviour of the intercalated polymer nanocomposites in shear flow. The increase of the viscosity and the more pronounced non-Newtonian behaviour is interpreted simply considering the increase of volume of the inert phase caused by the intercalation of the macromolecules. Indeed, the volume of the intercalated tactoids increases with increasing the interlayer distance. On the other hand, the interlayer distance can be correlated with the increase of the viscosity or with the more pronounced non-Newtonian behaviour. This simple method cannot be applied to exfoliated nanocomposites or when interactions between the matrix and the nanoclay occur, thus leading to a modification of the polymer chains, e.g., degradation of the matrix due to the interaction with the organo-modifier of the clay.

1. Introduction

Polymer-layered silicate nanocomposites exhibit remarkable improvement in material properties when compared with virgin polymer or conventional microcomposites [1,2]. In particular, the presence of filler incorporation at nano-level induces significant improvement of some mechanical and thermomechanical properties (i.e. elastic modulus, HDT, etc) [3–5].

Two different morphologies can be obtained after compounding, i.e. intercalation and exfoliation, or a hybrid morphology where intercalation and exfoliation coexist. The first term indicates a morphology where the macromolecules go inside the galleries of the silicate increasing the interlayer distance between the platelets; the exfoliation occurs when the layers becomes independent one each other. The intercalation and the exfoliation depend on several factors such as the compatibility between matrix and nanoparticles, the thermomechanical stress transmitted from the melt to the inert filler as well as the residence time. A good adhesion between matrix and particles is then a necessary condition for intercalation or exfoliation.

Generally, three main behaviours have been observed for the flow curves of polymer nanocomposite systems depending on the achieved morphology, i.e. intercalated and/or exfoliated, namely an increase of the values of the viscosity in presence of the nanofiller with presence of a Newtonian viscosity [6–18], a similar behaviour but with an upturn of the flow curve at low values of the shear rate (or of the frequency) [19–24], a decrease of the viscosity [25–27]. This latter behaviour is difficult to interpret and it has been explained with a possible lubricant effect of the single, flexible platelets when the clay particles are completely exfoliated [27] but a low compatibility between polymer matrix and clay could be the cause of this behaviour. In many cases, the increase of the flow curve, with an upturn at low values of the shear rate (or of the frequency) and a more pronounced non-Newtonian behaviour have been correlated with the increase of the exfoliation level [28]. As for the intercalated nanocomposites, the features of the rheological behaviour well assessed are: the increase of the viscosity with or without the presence of the Newtonian viscosity, the more pronounced non-Newtonian behaviour and the increase of the dynamic storage modulus at low frequency (solid-like behaviour) [6,10–12,29].

In a previous work [9] the changes of the rheological properties in shear and elongational flow of intercalated EVA nanocomposites

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have been interpreted in terms of increase of the interlayer distance. Indeed, with increasing the interlayer distance an increase of Newtonian viscosity and a more pronounced non-Newtonian behaviour has been measured. An increase of the contact area between platelets and macromolecules has been considered as the responsible for this behaviour. In elongational flow the increase of the interlayer distance gives rise to a more pronounced strain hardening behaviour. However, Gupta et al. [30] found a reduced strain hardening in EVA nanocomposites samples at large values of the Hencky strain. The authors hypothesized that the change of the interlayer distance, that can occur along the test because of the contraction perpendicular to the stretching direction was responsible for this behaviour, as reported also in other papers [31,32].The interlayer distance change with both the amount of nanoparticles and with the processing conditions but also during the rheological test itself.

Eslami et al. developed models for the prediction of the rheological properties of polymer/layered silicate nanocomposites and used them to relate the rheological behaviour to the physics taking place in the nanocomposites on a mesoscopic level [33–36].

Aim of this work is to propose a simple method to interpret the rheological behaviour of intercalated nanocomposites correlating it with the change of the interlayer distance of clay tactoids, i.e. the increase of the tactoid volume due to the intercalation of the polymer chains. On the other hand, this correlation could be used to evaluate the interlayer distance from the flow curves of the polymer nanocomposite.

In this work, the proposed method was applied to different nanocomposite systems, i.e. HDPE and LDPE based nanocomposites prepared purposely for this work and other nanocomposite systems (EVA, PET and PA6/HDPE based nanocomposites) reported in our previous works [19–21].

2. Correlation between rheological behaviour and interlayer distance

It is well known that the viscosity of the filled polymers increases with the volumetric content of the filler and, at the same concentration, with increasing the surface/volume ratio. Moreover, it is well known that the viscosity of polymer based clay nanocomposites generally increases with the clay content, although in some case a decrease of the viscosity can occur. Moreover, the viscosity can be affected also by processing conditions [20],. However, the viscosity of nanocomposites is generally higher with respect to the microcomposites at the same filler content and this has been interpreted in terms of very high contact surface between matrix and nanoparticles.

In particular, in our previous work [9] it has been put in evidence that the viscosity increases with increasing the interlayer distance and, moreover, also the non-Newtonian behaviour becomes more pronounced increasing the interlayer distance. In the same paper [9], this behaviour has been correlated with the increase of the contact area between inert filler and polymer matrix because of the increase of the interlayer distance.

In this work, we reconsider this idea and present a simple method to interpret the rheological behaviour of intercalated clay nanocomposite samples as a function of the interlayer distance or, on the other hand, to correlate the interlayer distance with the rheological properties. Indeed, in intercalated nanocomposite samples, the macromolecules penetrate during the flow inside the galleries of the tactoids giving rise to an increase of the interlayer distance between the platelets, (see Fig. 1).

Really, the surface contact area does not change because the contact area between macromolecules and platelets is that of the external platelets with the macromolecules. Rather, there is a change of the apparent volume of the tactoid, because of the increase of the interlayer distance (see Fig. 1), but not of the surface contact area that remains constant, whatever is the level of the intercalation. The volume of the tactoid, on the contrary, increases with increasing the interlayer distance according to the following equation:

$$V_{c(int)} = V_i \cdot \frac{ID_f}{ID_i} \tag{1}$$

where $V_{c(int)}$ is the volume of the clay tactoid after intercalation, V_i is the initial volume of the virgin tactoid, ID_f is the interlayer distance of the intercalated clay and ID_i, the interlayer distance of the virgin clay.

The change of the volume of the single tactoid because of the intercalation, changes, of course, the total volume concentration of the clay nanofiller in the same way. It is worth to mention that the viscosity, like other properties depend on the volume content of the filler and not on the weight concentration.

The clay volume fraction $\phi_{V,c}$ and the clay weight fraction w_c are related according to

$$\Phi_{V,c} = \frac{V_c}{V_c + V_m} = \frac{\frac{w_c}{\rho_c}}{\frac{w_c}{\rho_c} + \frac{w_m}{\rho_m}} \tag{2}$$

where V_c, w_c and ρ_c are respectively the volume, the weight fraction and the density of the clay and V_m, w_m and ρ_m the weight fraction and the density of the polymeric matrix. Taking into account equation (1), i.e. the increase of the clay volume due to the increase of the interlayer distance, the final volume fraction ($\phi_{V,c(int)}$) of clay in intercalated nanocomposite is, then:

$$\Phi_{V,c(int)} = \frac{\frac{w_c}{\rho_c} \cdot \frac{ID_f}{ID_i}}{\frac{w_c}{\rho_c} \cdot \frac{ID_f}{ID_i} + \frac{w_m}{\rho_m}} \tag{3}$$

Of course, this does not mean that the increase of viscosity or of the more pronounced non-Newtonian behaviour is the same for all the matrix/clay nanocomposites and that depend only on the increase of the volume concentration. Indeed, the absolute value of the increase depends also on other factors and in particular on the adhesion between the two phases.

Moreover, no interactions must occur during processing between matrix and nanoclay, for example, degradation of the matrix due to the radicals formed, at high thermomechanical stress, because of the breaking of the organomodifier of the clay [19,21].

3. Experimental

3.1. Materials and preparation

The polymer used in the experimental part of this work are a moulding grade high density polyethylene sample, HDPE, (MP94 by Versalis) having a MFI value of about 7 g/10 min (190 °C, 2.16 kg) and a film grade low density polyethylene sample, LDPE, (FC 30 by Versalis) having a MFI value of about 0.3 g/10 min (190 °C, 2.16 kg).

The organoclay, supplied by Southern Clay Products, used as nanofiller, was a Cloisite 15A, a montmorillonite modified by 125 meq/100 g of dimethyl bis(hydrogenated tallow alkyl)ammonium cations. The density is about 1.8 g/cm^3. The interlayer distance is 3.15 nm.

The nanocomposites were prepared by melt compounding using a Brabender counter rotating twin screw compounder (D = 42 mm; L/D = 7) with a thermal profile of 110–130–160–180 °C for LDPE based nanocomposites and