



Research paper

Migration of clay and its role in droplet morphology establishment during melt mixing of clay polyethylene/polyamide nanocomposites

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ABSTRACT

The migration of clay particles during mixing of organically montmorillonite polyethylene/polyamide nanocomposites was investigated. Special attention was paid to the observation of PA droplet morphology establishment as well as clay localization and exfoliation at different mixing times. During the incorporation step in internal mixer, the simultaneous mixing of all components favors the presence of a great number of micrometric clay agglomerates within the matrix. The migration of clay particles from the polyethylene (PE) matrix towards the polyamide (PA) dispersed phase is a very short process that takes about 1 min. From the beginning of the dispersion step (~2 min), clay particles are exclusively localized at the PA droplet frontier. Then, they are sheared and redistributed, forming a nanometric interphase. The correlation between droplet morphology establishment and clay migration mechanisms until the formation of a developed interphase is discussed.

1. Introduction

Immiscible polymer blends filled with spherical, tubular or lamellar nanofillers have attracted great attention in the last decade, due to great potential interest in various industrial applications. The effect of nanofiller addition on the morphology, interfacial properties, and end-use performances of immiscible polymer blends is governed by the interactions of nanoparticles with polymer phases, which influence both their localization and dispersion state within the polymer blend (Scaffaro and Botta, 2014). Among all inorganic nanofillers of potential interest in applications, organically modified montmorillonite (Mt) nanolayers were shown to be good candidates for the improvement of mechanical (Mehrabzadeh and Kamal, 2002; Chen et al., 2005; Ray et al., 2006; Tiwari and Paul, 2011; Motamedi and Bagheri, 2016; Ebadi-Dehaghani et al., 2016; Huitric et al., 2017), barrier (Brulé and Flat, 2006) and thermal (Gelfer et al., 2003; Wang et al., 2003) properties of immiscible polymer blends. Indeed, Mt nanoparticles were shown to be able to influence the blend morphology (Yoo et al., 2005; Médéric et al., 2011; Salzano de Luna and Filippone, 2016), and also, in some cases, the miscibility and compatibility between thermoplastic phases (Ray et al., 2004; Hong et al., 2006).

It is now established that the localization and dispersion state of nanoclays within a thermoplastic polymer blend strongly depends on the thermodynamic affinity of clay towards polymers (Sumita et al., 1991; Beuguel et al., 2017), but also on the viscoelastic properties of

both thermoplastic phases (Labaume et al., 2013a). The impact of the localization of nanofillers within polymer blend on the final morphology of clay polymer nanocomposites was thoroughly studied (Salzano de Luna and Filippone, 2016), mostly when nanoclays present a selective affinity towards one of the two polymers. When Mt nanofillers are dispersed in the thermoplastic matrix, they lead to a reduction of the dispersed domain size (Khatua et al., 2004), due to matrix viscosity increase and coalescence suppression by a barrier effect mediated by nanolayers (Huitric et al., 2009; Hajibaba et al., 2016). When Mt nanoparticles are located in the dispersed phase, they limit its breaking-up because of clay-induced viscosity increase, which can eventually hinder the emulsification process (Labaume et al., 2013a; Xu et al., 2015). However, in most cases, Mt nanolayers are mainly located at the interface of the two polymers, forming an irregular interphase, composed of Mt nanoparticles intercalated by the thermoplastic chains which present the best affinity towards clay. The dispersed phase size reduction was attributed to i) coalescence inhibition, due to steric repulsions between dispersed phase droplets, mediated by the interphase (Huitric et al., 2009; Labaume et al., 2013b; Hajibaja et al., 2016) and ii) compatibilizing effect of nanoclay (Ray et al., 2004).

However, the migration processes and mechanisms of nanoparticles during melt mixing were not much studied in the literature, in spite of their major interest in explaining the final structural and mechanical properties. The transfer of carbon black (Zaikin et al., 2001), silica nanospheres (Elias et al., 2008), carbon nanotubes (Tao et al., 2011), or

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clay nanolayers (Xu et al., 2015), from a thermoplastic phase towards the interface, or towards the other thermoplastic phase, was observed and attributed to selective thermodynamic affinity, but also to mixing-induced kinetic effects (Zhang et al., 2004).

The migration mechanisms of silica spherical nanoparticles from a polypropylene matrix towards a poly(ethylene-co-vinyl acetate) dispersed phase, and vice versa, were thoroughly studied (Elias et al., 2008). The results show that the migration of nanoparticles from the matrix towards the dispersed phase is mainly driven by nanoparticle/droplet collisions, but also by the trapping and embedding of particles within the dispersed phase during droplet coalescence. On the other hand, the migration of nanoparticles from the dispersed phase towards the matrix is mainly driven by the shear field inside the dispersed phase, that moves particles to the interface and eventually to the matrix.

In the case of Mt, Xu et al. (2015) studied the effect of migration of clay nanolayers on the morphology of poly(ethylene terephthalate)/polyamide 6 (PET/PA6) blend, by imposing different melt compounding sequences (simultaneous mixing or use of a pre-mixing). The compounding sequence was shown to influence the migration of Mt nanolayers from the apolar PET matrix towards the PA6 polar dispersed phase. However, the migration process of Mt are somewhat complex because of clay intercalation or exfoliation mechanisms during melt mixing. For example, complete polymer intercalation, obtained after a few minutes mixing (Lertwimolnun and Vergnes, 2005), followed by exfoliation of clay nanoparticles, was shown to modify the clay aspect ratio and flexibility, which both influence the migration process (Médéric et al., 2011; Fu et al., 2011).

The present work aims at describing and discussing the successive steps of Mt nanoparticles migration within a polyethylene/polyamide (PE/PA) blend, taking into account the time evolution of clay structure during the mixing process. Several Mt PE/PA nanocomposites were prepared by simultaneous mixing in an internal mixer at different mixing times, ranging from 30 s to 12 min. For each mixing time, the morphology of PA dispersed phase was observed by confocal microscopy and scanning electron microscopy, the localization and structure of clay entities were characterized by transmission electron microscopy observations and XRD measurements.

2. Experimental part

2.1. Materials

Mt PE/PA nanocomposites were prepared from two commercial immiscible polymers: a linear low-density polyethylene (PE) copolymer and a polyamide 12 (PA), supplied by Enichem (Flexirene® FG 20F) and Arkema (Rilsan® AECHVO), respectively. The main characteristics of the two components are reported in Table 1: the number and weight average molar masses, M_n and M_w respectively, and the melting point, T_m . The Newtonian viscosity, η_0^* , was measured at 200 °C.

The layered silicate is an organically modified montmorillonite clay, supplied by Southern Clay Products, namely Cloisite® C30B. This organoclay is a methyl tallow bis-2-hydroxyethyl ammonium exchanged montmorillonite clay, with a modifier concentration of 90 milli-equivalent per 100 g. It has a good affinity towards PA (Aubry et al., 2005), but a very poor affinity towards PE (Médéric et al., 2005). The

Table 1
Main characteristics of thermoplastics.

Characteristics	PE	PA12
Density	0.92	1.01
M_n (g/mol)	37,000	20,000
M_w (g/mol)	140,000	37,000
T_m (°C)	121	183
η_0^* (Pa·s) at 200 °C	10,750	2000

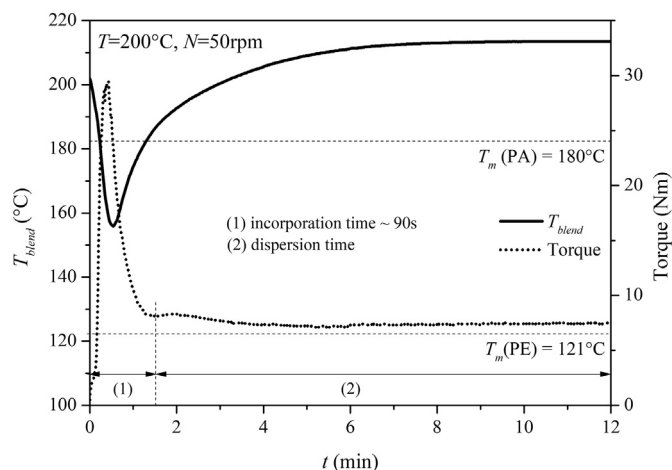


Fig. 1. Sample temperature and torque versus mixing time.

individual clay layers are ~ 0.7 nm thick and ~ 200 nm long (Paul and Robeson, 2008), corresponding to an average aspect ratio of ~ 350 . The specific gravity of this organophilic clay is close to 2.

2.2. Blending

All clay polymer nanocomposites have been prepared at a fixed PA mass fraction of 20%, with a clay volume fraction, $\phi = 2\%$, relative to PA. All components were simultaneously mixed in a Haake internal mixer (Rheomix 600). The temperature was imposed at 200 °C during mixing in order to minimize the degradation of polymer phases, but also the thermal degradation of the organic modifier of Mt (Xie et al., 2001). A moderate blade rotational speed of 32 rpm, corresponding to an estimated average shear rate of 32 s^{-1} (Bousmina et al., 1999), was used in order to limit the mechanically induced thermal degradation (Médéric et al., 2009). The time evolutions of clay polymer nanocomposite morphology, and structure during mixing were characterized at 30 s, 1 min, 2 min, 4 min, 6 min and 12 min. The sample temperature and the torque curves versus mixing time over 12 min are plotted in Fig. 1. The temperature of the mixing chamber decreases down to 160 °C after 1 min mixing and then increases up to about 200 °C because of viscous dissipation. In parallel, the torque increases up to a peak value of 30 N·m before a drastic decrease, in the incorporation step, followed by a stabilization at ~ 8 N·m after 90 s melt mixing, in the dispersion step. Therefore, Fig. 1 suggests that the whole amount of PA is molten after 2 min mixing.

After melt mixing, samples were then pelletized and prepared by compression molding into 2 mm thick plates; the temperature was fixed at 200 °C and the pressure was increased by steps, from 5 MPa to 25 MPa, in order to avoid the formation of air bubbles during the compression process. Because of the hygroscopic character of PA, all samples were dried for 4 h at 80 °C in a vacuum oven before experiments.

2.3. Morphological observations

Using the natural fluorescence of PA, confocal microscopy was performed with a Zeiss confocal microscope LSM 780, equipped with a laser diode of wavelength 405 nm, a 32 GaAsP PMT detector and a $\times 63$ oil lens, allowing a three-dimensional observation of the PA dispersed phase. For a more quantitative investigation of droplet morphology, Hitachi S-3200 N Scanning Electron Microscope (SEM), with an accelerating voltage of 15 kV, was used. SEM observations were made from cryofractured samples whose surface was vacuum-metallized. The number average diameter, D_n , was obtained from SEM micrographs (Fig. 2) by measuring at least 200 PA droplets with SigmaScan® PRO

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