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Influence of clay mineral structure and polyamide polarity on the structural and morphological properties of clay polypropylene/polyamide nanocomposites

Quentin Beuguel, Julien Ville, Jérôme Crepin-Leblond, Pascal Mederic, Thierry Aubry *

IRD L – FRE CNRS- 3744, Université de Bretagne Occidentale – UFR Sciences et Techniques, 6 avenue Victor le Gorgeu – CS 93 837, 29 238 Brest Cedex 3, France

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ABSTRACT

The influence of the clay mineral structure and of the polyamide dispersed phase polarity on the structure and morphology of polypropylene/polyamide blends filled with clay mineral nanoparticles was investigated. Two polyamides (PA) were used: a polar PA6 and a less polar PA12. The clay mineral nanofillers used were either organically modified montmorillonite (Mt) or synthetic talc (ST), having preferential affinity towards PA dispersed phase. For all clay polymer nanocomposites (CPN), a decrease of PA nodule size was observed. However, the mechanisms governing the morphology establishment were shown to depend mainly on the clay structure, and also on the polyamide polarity. Mt nanoparticles were shown to be mostly located at the interface, forming a nanocomposite interphase. The decrease of PA nodule size induced by Mt nanoparticles was attributed to coalescence inhibition by steric repulsions, mediated by the interphase, which is more developed in the case of PA6. Besides, the interphase was shown to play a key role in the change from a nodular to a non-nodular morphology, even at low Mt fractions. ST particles were shown to be exclusively dispersed within PA nodules. In this case, nodule size reduction was attributed to the presence of some larger ST particles, exhibiting numerous structural defects, which favor the nodule break-up, especially in the case of PA12.

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1. Introduction

Since a few decades, immiscible thermoplastic blends have attracted interest of scientific and industrial communities (Utracki, 1998). In this context, polypropylene (PP) and polyamide (PA) blends have been thoroughly investigated because they combine the thermomechanical properties of polyamide and the easy processing characteristics of polypropylene. Blend properties depend on the composition and on the morphology, either nodular, fibrillar, lamellar or co-continuous (Huitric et al., 1998), formed during melt mixing process. The shape and size of the dispersed phase result from a competition between break-up and coalescence during mixing (Serpe et al., 1990). The viscoelastic properties of the two components play a key role in the establishment of the morphology (Starita, 1972; Grace, 1982).

Addition of a compatibilizing agent is most often used in order to get a fine dispersion, to stabilize the blend morphology, and to improve interfacial adhesion. A macromolecular compatibilizer, either a block or a graft copolymer, is classically used, leading to a decrease of the interfacial tension (Moan et al., 2000) and an enhancement of interfacial adhesion (Xanthos and Dagli, 1991). More recently, a considerable scientific interest has focused on the influence of nanoparticles on the

morphology establishment of immiscible polymer blends as shown by the numerous references cited in the paper by Salzano de Luna and Filippone (2016). In this context, clay nanolayers, mainly from the family of organically modified montmorillonite (Mt), have been successfully chosen to play the role of compatibilizing agent (Ray et al., 2004; Hong et al., 2006). Indeed, when Mt nanoparticles are located at the matrix/nodule interface, they form a nanocomposite interphase, which leads to the refinement and stabilization of the morphology (Huitric et al., 2009). The interphase, which exhibits numerous defects (Ville et al., 2012; Labaume et al., 2013), inhibits coalescence by steric repulsion (Gahleitner et al., 2006; Ville et al., 2012; Labaume et al., 2013; Huang et al., 2014), but it destabilizes the nodular morphology of the polyethylene/polyamide blends at low clay fractions (Labaume et al., 2013). However, Mt nanoparticles are not systematically located at the interface in Mt/polymer nanocomposites (Yoo et al., 2005; Gahleitner et al., 2006; Labaume et al., 2013; Huang et al., 2014). Indeed, clay localization depends on the affinity of nanofillers towards the two polymers (Sumita et al., 1991), on the rheological behavior of both thermoplastic phases (Labaume et al., 2013), and on intrinsic properties of the particles, such as aspect ratio (Médéric et al., 2011) and flexibility (Fu et al., 2011). The presence of clay nanoparticles within dispersed phase or matrix is known to strongly influence the mechanisms of morphology establishment (Yoo et al., 2005). On the one hand, the dispersion of nanoclay within the matrix enhances nodule size reduction (i) by

* Corresponding author.

E-mail address: thierry.aubry@univ-brest.fr (T. Aubry).

increasing matrix viscosity, which favors the breaking-up of dispersed phase entities and (ii) by generating a barrier effect, which inhibits coalescence (Gelfer et al., 2003; Ray et al., 2006; Zou et al., 2006; Huitric et al., 2009; Babaei and Arefazar, 2016). On the other hand, the presence of clay within the dispersed phase is known to increase the nodule viscosity and elasticity, which impedes droplet deformation and limits the breaking-up (Gahleitner et al., 2006; Labaume et al., 2013; Huang et al., 2014).

The exfoliation degree and location of Mt were shown to influence the micrometric morphology of polymer blends filled with organically modified nanoclays (Médéric et al., 2011). Additionally, some studies, conducted on the barrier (Brulé and Flat, 2006), optical (Ray et al., 2006), thermal (Gelfer et al., 2003; Wang et al., 2003) or mechanical (Mehrabzadeh and Kamal, 2002; Ray et al., 2006; Motamedi and Bagheri, 2016) properties of blends filled with Mt nanoparticles, highlighted the role played by structural and morphological characteristics on the end-use properties. However, the lack of knowledge about the migration mechanisms of clay nanolayers during the mixing process, as well as the relative low degradation temperature of Mt modifier (Xie et al., 2001), limit the industrial use of such clay polymer nanocomposites (CPN).

Another type of clay mineral, a synthetic talc (ST), provided under the form of a hydrogel, and which presents the advantage to exhibit no degradation at melt processing temperature, has been recently used (Martin et al., 2008a, 2008b, 2008c; Le Roux et al., 2013). ST nanoparticles exhibit a higher aspect ratio than that of natural talc microparticles, and present numerous structural defects (Dumas et al., 2013). Moreover, they have a hydrophilic character, contrary to natural talc particles, which are hydrophobic (Dumas et al., 2013). Very recently, twin screw extruder was clearly shown to be more appropriate than internal mixer for the elaboration of nanocomposites, obtained from the mixing of a PA matrix and a ST nanoparticles hydrogel (Beuguel et al., 2015a). ST/PA nanocomposites were shown to be characterized by a multi-scale structure, mainly composed of individual layers or particles constituted of some layers whose dimensions are close to those of Mt nanoparticles (Beuguel et al., 2015b), making synthetic talc a good potential competing product (Yousfi et al., 2013; Beuguel et al., 2015b). Furthermore, the use of a PA6 matrix, which is more polar and more hydrophilic than PA12 matrix, was shown to be more efficient than PA12 to get a good ST dispersion state (Beuguel et al., 2015b). The morphological, thermal and mechanical properties of polymer blends filled with such ST nanoparticles are promising (Yousfi et al., 2013, 2014).

In this paper, PP/PA immiscible blends filled with either synthetic nanotalc or organically modified montmorillonite nanoparticles are compared, focusing on the effect of the clay mineral structure and polyamide polarity on the structural and morphological properties of the CPN.

2. Experimental part

2.1. Materials

Blends studied in this work were prepared from polypropylene (PP), supplied by Lyondellbasell (Moplen® HP500N), which was chosen as the matrix, and two commercial polyamides, polyamide 12 (PA12) and polyamide 6 (PA6), supplied by Arkema (Rilsan® AECHVO) and Rhodia (Technyl® S-27-BL), respectively. It is worth reminding that PA6 is more polar than PA12 because of a higher concentration of amine end groups (Cabrera Alvarez et al., 2012), and the water absorption of PA12 is weaker than that of PA6 (Elf, 1997).

The main characteristics of PP, PA12 and PA6 are reported in Table 1: the density, the number and weight average molar masses, M_n and M_w , the melting point, T_m , the radius of gyration, R_g , determined from the freely jointed chain model, and the Newtonian viscosity, η_0^* , measured at the mixing temperature, that is 220 °C for PA12 and 240 °C for PA6.

Table 1
Characteristics of PP, PA12 and PA6.

Characteristics	PP	PA12	PA6
Density	0.9	1.01	1.14
M_n (g/mol)	79,000	38,000	39,000
M_w (g/mol)	250,000	60,000	79,000
T_m (°C)	165	183	222
R_g (nm)	5	11	8
η_0^* (Pa.s)	580 at 220 °C 260 at 240 °C	450 at 220 °C	~300 at 240 °C

Number and weight average molar masses have been determined by gel permeation chromatography and correspond to a polydispersity index close to 3.3, 1.6 and 2 for PP, PA12 and PA6, respectively. Newtonian viscosities, reported in Table 1, are measured from oscillatory shear tests in the linear response regime. The viscosity ratio, defined as the ratio of the Newtonian viscosity of the dispersed phase to that of the matrix, is 0.8 for PP/PA12 blend and 1.1 for PP/PA6 blend. From steady-state measurements, performed on a RT 1000 Göttfert capillary rheometer, it was verified that viscosity ratios were not significantly changed at shear rates applied during melt mixing.

PP/PA blends were filled with either synthetic nanotalc or organically modified montmorillonite nanoparticles. The organically modified montmorillonite, supplied by Southern Clay Products, namely Cloisite® C30B, is a methyl tallow bis-2-hydroxyethyl ammonium (quaternary ammonium) exchanged montmorillonite, with a modifier concentration of 90 milliequivalent per 100 g. It has a good affinity towards polyamide (Aubry et al., 2005). This organophilic Mt is characterized by a significant specific surface area $\sim 700 \text{ m}^2 \text{ g}^{-1}$, together with a high anisometry. Indeed, the individual clay layers are $\sim 0.7 \text{ nm}$ thick and $\sim 200 \text{ nm}$ long (Paul and Robeson, 2008), corresponding to an average aspect ratio of ~ 350 . The interlayer distance, corresponding to basal distance (d001) as estimated from XRD measurements, using Bragg's equation, is close to 1.2 nm, and the specific gravity of Mt is close to 2.

The synthetic talc hydrogel was prepared at GET Laboratory (University of Paul Sabatier, France) according to a patented hydrothermal process (Le Roux et al., 2013). The specific surface area is about $150 \text{ m}^2 \text{ g}^{-1}$ and the interlayer distance is 0.3 nm (Dumas et al., 2013). The specific gravity of ST is 2.8. It has been shown that average length and thickness of ST particles were close to 150 nm (Dumas et al., 2013) and 8 nm (Beuguel et al., 2015b), respectively. As previously mentioned, ST particles exhibit a hydrophilic character and present numerous structural defects (Dumas et al., 2013), as illustrated in Fig. 1.

It is worth pointing out that the difference in the structure of ST and Mt entities (Fig. 1) leads to distinct separation mechanisms of Mt and ST particles: intercalation of PA into interlayer spaces and exfoliation in the case of Mt particles (Aubry et al., 2005); penetration of PA into defects and separation in the case of ST particles (Beuguel et al., 2015b).

2.2. Sample preparation

Because of their hygroscopic character, PA12 and PA6 were dried in vacuum at 80 °C during 4 h and 24 h, respectively. Then, all blends were prepared by simultaneous melt mixing of all components, using DSM Xplore lab twin screw extruder. The screw rotational speed was fixed at 50 rpm for 6 min. Because of their difference in melting temperature (Table 1), the barrel temperature was fixed at 220 °C and 240 °C in presence of PA12 and PA6, respectively. After mixing, all samples were pelletized and dried. Then, they were prepared by compression molding into 1.5 mm thick plates; pressure was increased by steps, from 5 MPa to 25 MPa, in order to avoid the formation of air bubbles during the compression process.

All CPN have been prepared at a fixed PA12 or PA6 dispersed phase mass fraction of 20%, which is expected to lead to nodular morphology (Huitric et al., 2009; Ville et al., 2012). The filler volume fraction ranges from 0.3% to 1% for Mt, and from 0.4% to 2.2% for ST, relative to PA. The

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