Structural and rheological properties of different polyamide/polyethylene blends filled with clay nanoparticles: A comparative study

Isabelle Labaume, Jacques Huitric, Pascal Médéric, Thierry Aubry*

LIMATB, Equipe Rhéologie, Université de Bretagne Occidentale, UFR Sciences etTechniques, 6, Avenue Victor Le Gorgeu, CS 93837, 29238 Brest Cedex 3, France

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ABSTRACT

This study mainly aims at showing that the compatibilizing effect of organically modified nanoclay particles in 80/20 polyethylene (PE)/polyamide (PA) immiscible blends with nodular morphology, is strongly influenced by the rheological behavior and molecular characteristics of both polymers. Four PE/PA blend couples, based on two polyethylenes and two polyamides with different molecular characteristics and properties, were filled at various clay fractions and investigated using SEM, TEM, XRD and rheometrical techniques. The results show that there is no compatibilizing effect of clay when a high viscosity polyamide and/or a low viscosity polyethylene are used. The role played by the molecular characteristics of both polyamide and polyethylene chains in the structure and properties of the interphase was discussed. At last, the viscoelastic properties of PE/PA blends were shown to be significantly influenced by clay addition and content, through various mechanisms which involve changes in dispersed phase interfacial area, in blend morphology, in clay localization and in interphase structure.

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1. Introduction

The scientific interest in stabilization of immiscible fluids by colloidal particles is not new: it goes back to the early twentieth century, when Pickering mentioned that fine solid particles could stabilize two low viscosity liquid immiscible phases [1]. The preparation and properties of emulsions of such low molecular weight liquids stabilized by interfacial colloids has been reviewed by Aveyard et al. [2]. Even though comparing low viscosity fluids emulsions with high viscosity polymer blends might seem questionable because of significant differences in time and length scales, there are many similarities between these biphasic systems, mainly regarding their rheological behavior, as reviewed by Derkach [3]. Therefore adding micro or nanoparticles to immiscible polymer blends was expected to have the same stabilizing effect as that observed with Pickering emulsions. The morphology development in polymer blends filled with various particles, mainly carbon black, silica and clay nanoparticles, was addressed in a more recent literature, as reviewed by Fenouillot et al. [4]. This review focused on the various physical mechanisms controlling the nanofiller localization, which seems to govern partly the blend morphology and its stability. From that point of view, the localization of nanoparticles at the interface seems to induce a finer morphology and a better stability by suppressing break-up and coalescence, as suggested by morphological and rheological studies performed with silica nanoparticles [5], or clay nanoparticles [6]. Moreover, even though the concept of interfacial tension is quite questionable when the interfacial region contains solid particles, some authors claim that nanofillers located at the interface tend to reduce that (apparent) tension [7,8]. Such results are reminiscent of effects induced by block copolymers often used as compatibilizers in immiscible polymer blends [9], which explains why nanoparticles are often referred to as particulate compatibilizers in the literature [10,11]. However, the so-called compatibilizing effect of nanofillers in immiscible polymer blends is contentious, and the potential mechanisms of compatibilization are not as well understood as in the case of diblock copolymer compatibilization. For example, a finer morphology can be observed even though nanofillers are not located at the interface [12], or coarse morphology can be observed even though particles are located at the interface [13].

The present study concerns investigation and discussion of the so-called compatibilizing effect of nanofillers, namely organically modified nanoclay particles, in polyethylene/polyamide immiscible blends with nodular morphology, focusing on the influence of the two polymers. More precisely, we studied four PE/PA blend couples, based on two polyethylene matrices and two polyamide dispersed

* Corresponding author. Tel.: +33 (0)2 98 01 66 86; fax: +33 (0)2 98 01 79 30.
E-mail address: thierry.aubry@univ-brest.fr (T. Aubry).

phases with different molecular characteristics and properties, filled with the same organically modified layered clay nanoparticles at different clay fractions. Both structural and rheological properties were investigated, aiming at highlighting and discussing the most prominent differences in those properties between the four different PE/PA couples.

2. Experimental

2.1. Materials

All polymer blends studied in this work are PE/PA blends. Two polyethylenes (PE) with different Newtonian viscosities were chosen for the matrix phase. Both are ethylene copolymers. The more viscous PE, named HVPE (which stands for High Viscosity PE) in the paper, was supplied by Enichem (referenced as Flexirene® PE FG20F), it has a Newtonian viscosity of about 10,750 Pa s at 200 °C. The less viscous PE, named LVPE (which stands for Low Viscosity PE) in the paper, was supplied by Dow Chemical Society (referenced as PE Elite™), it has a Newtonian viscosity of about 2300 Pa s at 200 °C, that is nearly 5 times lower than that of HVPE.

Two polyamides 12 (PA) with different Newtonian viscosities were chosen for the dispersed phase, which were supplied by Arkema. The more viscous PA, named HVPA (which stands for High Viscosity PA) is referenced as Rilsan® PTL40, it has a Newtonian viscosity of about 11,700 Pa s at 200 °C. The less viscous PA, named LVPA (which stands for Low Viscosity PA) is referenced as Rilsan® AECHVO, it has a Newtonian viscosity of about 2000 Pa s at 200 °C, that is nearly 6 times lower than that of HVPA. Table 1 gives the main characteristics of the four polymers used in this study: the number and weight average molecular weights, M_n and M_w respectively, and the melting point, T_m.

The layered silicate used as filler in this work is an organically modified montmorillonite clay (C), 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 milliequivalent per 100 g; it has a good affinity towards PA [14], but a very poor affinity towards PE [15]. The specific gravity of this organophilic clay is very close to 2. The individual nanoclay platelets are ∼0.7 nm thick and ∼500 nm long, corresponding to an average aspect ratio of ∼700.

2.2. Blending

All blends studied in this work were prepared using a Haake Rheomix 600 internal mixer. The components were simultaneously mixed at a blade rotational speed of 32 rmp during 6 min, and under a continuous purge of dry nitrogen. The temperature imposed during mixing was 200 °C, chosen in order to minimize the degradation of the blend components, and particularly that of the organic modifier of clay particles. Blends were prepared at a PA weight fraction of 20% and at clay volume fractions, ϕ_c, ranging from 0.5% to 2% relative to PA. The polymer blends studied in this work were referred to as M_1, M_2, M_3 and M_4 samples, as defined in Table 2.

$M_{i(i = 1, 2, 3 \text{ or } 4)}$ polymer blends filled with $x\%$ clay were referred to as $M_i/C^{x\%}$. For example, M_2 blend with 1% clay was named $M_2/C^{1\%}$.

Table 1
Main characteristics of the polymers used in the study.

	M_n (g mol^{-1})	M_w (g mol^{-1})	T_m (°C)
HVPE	37,000	140,000	121
LVPE	15,800	272,500	121
HVPA	25,500	48,000	170
LVPA	20,000	37,000	183

Table 2
Polymer blends studied.

Notation	Dispersed phase	Matrix	Newtonian viscosity ratio at 200 °C
M_1	LVPA	HVPE	0.19
M_2	LVPA	LVPE	0.87
M_3	HVPA	HVPE	1.09
M_4	HVPA	LVPE	5.09

2.3. Structural and morphological characterization

The blend morphology at a microscopic scale was observed by scanning electron microscopy (SEM) using a Hitachi S-3200N with an accelerating voltage of 15 kV. The samples were cryofractured and the surface was vacuum metallized with gold/palladium.

The localization and dispersion state of clay particles were determined by transmission electron microscopy (TEM). Ultrathin sections were cut at − 130 °C with ultracryomicrotome, using a diamond knife. Imaging was performed with a JEOL JEM 1400 transmission electron microscope at 80 kV.

Wide angle X-Ray scattering was used at ambient temperature to determine the structure of clay entities. It was performed using a Seifert XRD 300PTS with Cu Kα radiation of wavelength 0.154 nm.

2.4. Rheological measurements

Oscillatory shear tests were performed using a RDAII Rheometrics Scientific controlled strain rheometer, equipped with parallel plate geometry (25 mm diameter and 2 mm spacing). All viscoelastic measurements were performed in the linear regime at a temperature of 200 °C, under a continuous purge of dry nitrogen in order to avoid sample degradation. The thermal stability at 200 °C of all systems studied in this work was systematically investigated by performing time sweep experiments; no significant variation in the rheometrical data was observed over 1 h 30 min.

All rheometrical experiments were shown to be reproducible within ±5%.

3. Results and discussion

3.1. Structure

3.1.1. Structure of PE/Cloisite® and PA/Cloisite® composites

The two PE matrix composites, LVPE/C and HVPE/C, were prepared at a clay volume fraction of 2.5%. SEM micrographs of these composites are shown in Fig. 1a and Fig. 1b, which evidence the presence of micrometric clay aggregates with characteristic size greater than 0.3 μm. Thus, adding clay to PE leads to a microcomposite, because of the bad affinity of clay towards PE [15].

The two PA matrix composites, LVPA/C and HVPA/C, were prepared at a clay volume fraction of 2%. The structure of clay particles is evidenced in TEM micrographs for both systems (Fig. 2a and b). The degree of exfoliation of clay in the PA matrix can be estimated by measuring the specific particle density, which is the average number particle per μm^2 divided by the clay mass fraction [16]. The specific particle density is about 4 for LVPA/$C^{2\%}$ nanocomposite, whereas it is about 17 for HVPA/$C^{2\%}$ nanocomposite, suggesting a higher degree of clay exfoliation for the latter system.

Fig. 3 shows the diffraction patterns of the organically modified clay and of the two PA/clay composites. For the two nanocomposites, the basal reflection peak which appears at $2\theta = 5.7°$ is attributed to the crystalline properties of the PA phase [17]. The basal reflection peak of C30B clay appears at $2\theta = 4.5°$, corresponding to an interlayer gallery height of about 1 nm [14]. For