Solid-state morphology, structure, and tensile properties of polyethylene/polyamide/nanoclay blends: Effect of clay fraction

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ABSTRACT

The effect of nanoclay fraction on the linear and non-linear tensile properties of a polyethylene/polyamide 12 blend with droplet morphology was investigated. All ternary blends were prepared at a fixed polyamide (PA) weight fraction of 20%, and at clay volume fractions varying from 0.5 to 2.5% relative to PA. Scanning electron microscopy and transmission electron microscopy were used to characterize the morphology of the blends and the clay interphase structure. The nanoclay content was shown to strongly influence both linear and non-linear tensile properties. Young's modulus, elongation at yield, yield strength, tensile strength and elongation at break as a function of clay fraction were studied and discussed in terms of morphological changes and strain-induced structural reorganization of the clay interphase.

1. Introduction

It has long been known that blending polymers is an efficient strategy in order to design polymer-based materials with good and versatile end-use properties. Final properties depend on the type and characteristics of the blend morphology, which mainly results from a delicate balance between break-up and coalescence of droplets induced by the flow during processing [1]. Therefore, phase morphology must be controlled and stabilized in order to get the best end use mechanical properties. However, because of the incompatibility of most polymers, addition of a compatibilizer is generally needed. Classically, this surface active agent is a block or graft copolymer [2], but, more recently, solid nanoparticles were used as a compatibilizer to control and stabilize the morphology of immiscible polymer blends [3—8]. For example, ternary blends composed of two immiscible polymers and clay nanofillers have been shown to be attractive systems because of the presence of two different structural length scales: a micrometric structural length scale due to the minor phase inclusions within the matrix, and a nanometric structural length scale due to clay nanoparticles [9]. However, the control and stability of blend final morphology strongly depend on clay localization [10], which is affected by the selective affinity of nanofillers towards one of the two polymer phases [11], but also by the rheological behavior of both polymers [12], or by intrinsic properties of the clay nanoparticles, such as aspect ratio [13] and flexibility [14].

In the case of immiscible polyethylene (PE)/polyamide (PA) blends, addition of organically modified montmorillonite, namely Cloisite® C30B having a selective affinity towards PA, was shown to strongly influence the mechanisms of morphology establishment. First, the exclusive presence of clay nanoplatelets at the matrix/nodule interface was shown to lead to the formation of an intercalated-PA/clay interphase exhibiting numerous different structural defects [15,16]. Even if clay stacking and orientation defects at the interface have been shown, clay localization defects, characterized by the absence of clay nanoparticles in some regions of the interphase, play a prominent role in the morphology establishment. Indeed, the establishment of the final blend morphology was shown to depend on the relative clay interfacial coverage [15]. More precisely, it was shown that the formation of a PA12-intercalated clay interphase inhibits coalescence by steric repulsion, resulting in a drastic reduction of droplet size at low clay fractions [17,18], and stabilization of the droplet morphology over a limited clay fraction range [12]. To sum up, these results suggest that adding clay nanoparticles exclusively located at the interface leads to the formation of a more or less developed complex interphase which can act as an active interfacial agent by decreasing the interfacial tension [12], by inhibiting coalescence and by stabilizing the morphology [15]. However, in order to prove that clay nanoparticles do play the role of compatibilizer, an improvement of the

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adhesion between polymer phases is needed, which requires the investigation of the solid-state mechanical properties of these ternary blends.

To our knowledge, only very few authors have investigated the linear and non-linear mechanical properties of immiscible polymer blends filled with nanoclay in the solid state [18–21]. Moreover, most of those published studies focused on the effect of clay fraction on tensile properties, such as Young's modulus or elongation at break, when clay is dispersed within the matrix or in the dispersed phase, but not when clay is exclusively located at the interface. The present study aims at investigating the mechanical properties of the above-mentioned immiscible PE/PA/clay ternary blends with nodular morphology, where clay is exclusively located at the interface. Particular attention will be paid to the study of the relationships between the linear and non-linear tensile properties of these materials and the structural properties of the interphase before and after tensile test. The academic objective is to investigate whether clay can be considered as a compatibilizer, and the more applied objective is to study whether these materials can have good mechanical properties under both small and large deformations in terms of Young's modulus, elongation at yield, yield strength, tensile strength and elongation at break.

2. Experimental

2.1. Materials

The immiscible commercial polymer blends studied in this work were composed of a linear low density polyethylene (LLDPE) matrix and a polyamide 12 (PA12) dispersed phase. LLDPE, referenced as Flexirene® FG20F, was supplied by Enichem; PA12, referenced as Rilsan® AECHVO, was supplied by Arkema. The main characteristics of these two polymers are reported in Table 1. It should be noted that The Newtonian viscosity of LLDPE is about 10750 Pa.s at 200 °C, whereas that of PA12 is close to 2000 Pa.s at the same temperature, that is about 5 times lower than that of LLDPE.

In this study, LLDPE/PA12 blends were filled with an organically modified montmorillonite (OMMT), namely Cloisite® C30B (C30B), supplied by Southern Clay Products. 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 good affinity towards PA [22], but very poor affinity towards PE [23]. The individual C30B particles are nanoplatelets with ~0.7 nm thickness and ~500 nm length, corresponding to an average aspect ratio of 700 [15]. The specific gravity of C30B organoclay is about 2.

2.2. Blending

All blends have been prepared at a fixed PA12 weight fraction of 20% by simultaneous mixing of the three components in a Haake Rheomix 600 internal mixer. The volume fraction of added C30B, ϕ_c, varied from 0.5 to 2.5% relative to PA12. The mixing temperature was fixed at 200 °C, in order to minimize the degradation of the components, especially that of the organic modifier of the clay [24]. All blends were mixed under the following blending conditions:

blade rotational speed of 32 rpm and residence time of 6 min [16]. Then, samples were pelletized and dried at 85 °C for 4 h in a vacuum oven, before being processed by compression molding at 200 °C for 5 min under a pressure of 10 MPa, using a Daragon hydraulic press, to get standard tensile bars (ISO NF 527, type 1a). Owing to the hygroscopic nature of PA12, all blends were stored under vacuum before experiments. The same elaboration procedure was applied to all samples studied in this work, so that they experienced the same thermo-mechanical history.

2.3. Morphological and structural characterizations

On a microscopic scale, the blend morphology was observed by scanning electron microscopy (SEM), using a Hitachi S-3200N microscope with an accelerating voltage of 15 kV. SEM observations were made from cryo-fractured samples, whose surface was vacuum metallized with gold/palladium.

The localization and the dispersion state of nanoclay particles were determined by transmission electron microscopy (TEM), using a JEOL JEM 1400 microscope at 80 kV. Ultrathin sections of 40 nm thickness were cut from the central core region of bars, at −130 °C, with an ultracryomicrotome using a diamond knife, mounted onto glow-discharge carbon coated film 200-mesh copper grid and dried on filter paper. Imaging was performed before and after mechanical tests.

2.4. Mechanical characterization

Static tensile tests were performed using a C43 MTS Criterion machine (Material Test System), equipped with a 500N load cell according to ISO 527-2, with type 1a dumb-bell shaped specimens. The rate of cross-head motion was fixed at 1 mm/min, and tests were all performed at a room temperature of 20 ± 2 °C. For all samples, five tensile tests were systematically performed, and the data reported in all Figures are averages over the five tests. Elongation was not measured with an extensometer, but by means of an optical device: four black ink dot-shaped markers were printed on the front sample surface, as shown in Fig. 1, and the position of the center of gravity of these dots was acquired using a high-speed video camera during the whole tensile test. In order to determine the axial strain, the two dots aligned on the tensile axis were used, whereas the two dots on the transversal axis were used in order to estimate the reduction of the cross sectional area needed for the
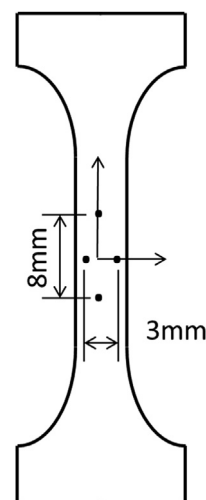

Fig. 1. 1a dumb-bell shaped specimen with four black ink dot-shaped markers.

Table 1
Main characteristics of LLDPE and PA12 : weight average molar weight M_w; number average molar weight M_n; zero-shear Newtonian viscosity at 200°C, η^*_0; melting temperature T_m.

Material	M_w (g/mol)	M_n (g/mol)	η^*_0 (Pa.s)	T_m (°C)
LLDPE	140000	37000	10750	121
PA12	37000	20000	2000	183