# Tailoring of Co-Continuous Polymer Blend Morphology: Joint Action of Nanoclays and Compatibilizers

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The effect of both organoclay (Cloisite® 30B) and compatibilizers (EVA copolymer or MAgPE) on the morphology and mechanical properties is investigated with a special focus on co-continuous structures. For that purpose, LDPE and PBAT are selected as an inert/reactive polymer pair model. The influence of the nature of the nanoclay/compatibilizer pair on the morphology of the nanocomposite is studied by means of SEM and TEM. Depending on the compatibilizer, it comes out that the organoclay can be selectively located in either the polyolefinic or polyester phase while the interface is invariably stabilized by clay platelets. Interestingly enough, it appears that such a combination (organoclay plus compatibilizer) allows for tailoring the final properties of polymer blends.
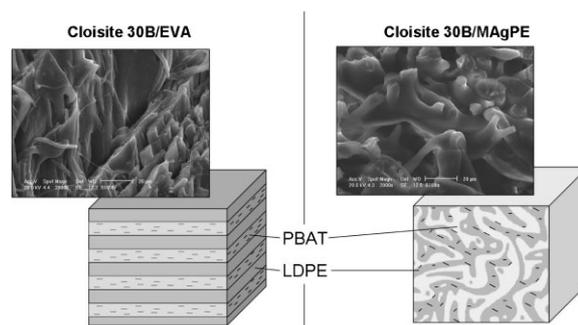
Introduction

The increasingly demanding applications require improved or new combinations of properties for which the existing polymers failed. Thus, both industrial and scientific communities show interest in modifying and mixing together the existing polymers in order to achieve specific or uneven properties. Polymer blending has gained much interest as a suitable way to tailor the properties of polymeric materials without investing in new chemistry.[1–3] In general, polymer blend morphologies can be divided into three classes, i.e., dispersed, stratified, and co-continuous morphologies.[4] However, poor interface

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between the different polymeric phases of the blend usually leads to a significant loss of properties and more specifically a decrease of mechanical performances is observed. To face this problem, traditionally, an organic compatibilizing agent is used to strengthen the interface.[5,6] Among the different morphologies, compatibilized co-continuous polymer blends exhibit the best performance improvements because both components, in all directions, can fully contribute to the properties of the blend.[4]

Another way to enhance polymer properties is the filling with inorganic particles or nanoparticles such as organo-modified clays leading to nanocomposite materials when properly dispersed. In fact, clays have been used to improve thermal and mechanical, ablative, electro-rheologically sensitive, stable electro-optical, corrosion protective, or conducting properties of nanocomposites.[7–9] Recently, organoclays were found to act as compatibilizers for immiscible polymer blends and they also appeared to promote the establishment of co-continuous structure.[10–32] More particularly, attention has been paid to the possible

use of nanoclay as an alternative to organic compatibilizer. Nanoclays influence on the morphology, melt viscosity, and solid properties of nanocomposites based on polymer blends have been mostly investigated. However, the literature focused on the combined roles of both nanoclays and organic compatibilizers on the blend nanostructure is still lacking.[32]

This contribution aims at studying the ability of the combination of both organically modified clays and compatibilizers to tailor the morphology and properties of polymer blends with a special emphasis on the formation of co-continuous structures. For that purpose, low-density polyethylene (LDPE) has been selected as an inert and nonpolar component and poly(butylene adipate/terephthalate) (PBAT) as a polar and reactive partner.

In order to study the effect of the combination clay/compatibilizer on polymer blends morphology, two types of compatibilizers have been considered: inert or reactive polymeric agents. For this purpose, the ethylene/vinyl acetate copolymer (EVA) as nonreactive compatibilizing agent and maleic-anhydride-grafted polyethylene (MAgPE) as reactive compatibilizing agent have been selected. Cloisite® 30B (C30B) has been chosen as organomodified clay because its ammonium-based organomodifier bears two hydroxyethyl groups able to react with the pending maleic anhydride moieties forming covalent bonds with MAgPE. Then, the tuning of the morphology has been related to the resulting mechanical properties of the blends.

Experimental Part

Materials

The LDPE used for this work was a sample of TOTAL FE8000 [with a melt flow index (MFI) of $0.7 \, \text{g} \cdot (10 \, \text{min})^{-1}$ at 190 °C/2.6 kg] kindly supplied by TOTAL Petrochemicals. PBAT [$\overline{M}_n = 48\,000$, polydispersity index (PDI) = 2.45 relative to polystyrene standards, as determined by size-exclusion chromatography (SEC)] was supplied by BASF and commercialized under the trade name ECOFLEX®. MAgPE was supplied by Dupont and the grade used for the study was Fusabound MB528. EVA copolymer studied was Escorene UL00328 and it was supplied by Exxon Mobil. It contains 27 wt.-% of vinyl acetate. Organoclay selected for the study was C30B and C20A (Cloisite® 20A) from Southern Clay products. C20A is organically modified with dimethyl dihydrogenated tallow quaternary ammonium (38 wt.-%), while C30B is organically modified with methyl tallow bis-2-hydroxyethyl quaternary ammonium cations (30 wt.-%). Prior to melt blending, both PBAT and organoclays were overnight dried at 80 and 105 °C, respectively.

Processing and Specimen Preparation

40/60 wt.-% (ca. 50/50 v/v) LDPE/PBAT blends were produced using a Brabender® internal kneader. To highlight the effect of the nature

of both the organic compatibilizer and the nanoclay on the morphology of the blends, two types of procedures were followed.

First, direct compounding was conducted at 150 °C for 10 min at 150 rpm. Second, a two-step process was followed: in a first step, the organoclay/compatibilizer pair was first compounded with one of the two polymers and then, in a second step the resulting nanocomposite was compounded with the second polymer. The compounding was performed at 150 °C for 10 min at 150 rpm. In all cases, 3 mm thick plates were prepared by compression molding at 150 °C.

Characterization

The blends morphology has been studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM analysis was performed using a JEOL JSM 6100 apparatus at 10 kV. In order to evidence the formation of co-continuous structure, cryo-fractured surfaces were analyzed after PBAT etching using chloroform. All the specimens were covered by an aluminum thin layer in order to make them conductive. TEM analysis was realized using FEI Tecnai 12 microscope at 120 kV and equipped with a SIS Megaview II camera. The specimens were previously prepared by ultra-cryo-microtome cutting (Leica Ultracut). Mechanical characterization was carried out on specimens obtained by compression molding (3 mm thick plates) and cut according to ASTM D638 standard required dimensions using a Hess 5 MP milling equipment. Tensile tests were realized using a LLOYD tensile test machine following ASTM D638 standard.

Results and Discussion

Morphology Study

Initial Morphologies

Mainly depending on the amount of each polymer, LDPE/PBAT blends can exhibit different types of morphology (dispersed, stratified, and co-continuous). The present work is focusing on LDPE/PBAT blends containing 40 wt.-% of LDPE and 60 wt.-% of PBAT. Such a composition of LDPE/PBAT 40/60 wt.-% corresponds approximately to 50/50 vol.-% and the morphology obtained is clearly co-continuous.

Prior to the observation of combined influence of compatibilizer/organoclay pair on polymer blends, the effect of polymeric compatibilizers alone on one hand and organoclay alone on the other hand has been investigated by SEM after etching of the PBAT phase using chloroform as selective solvent.

First, the morphology of the uncompatibilized LDPE/PBAT 40/60 w/w blend has been compared to that of blends compatibilized by either EVA or MAgPE (Figure 1). Interestingly enough, both compatibilized compositions presented surfaces composed of long LDPE cylinders similar to the unmodified blend (Figure 1b and c). It is worth noting
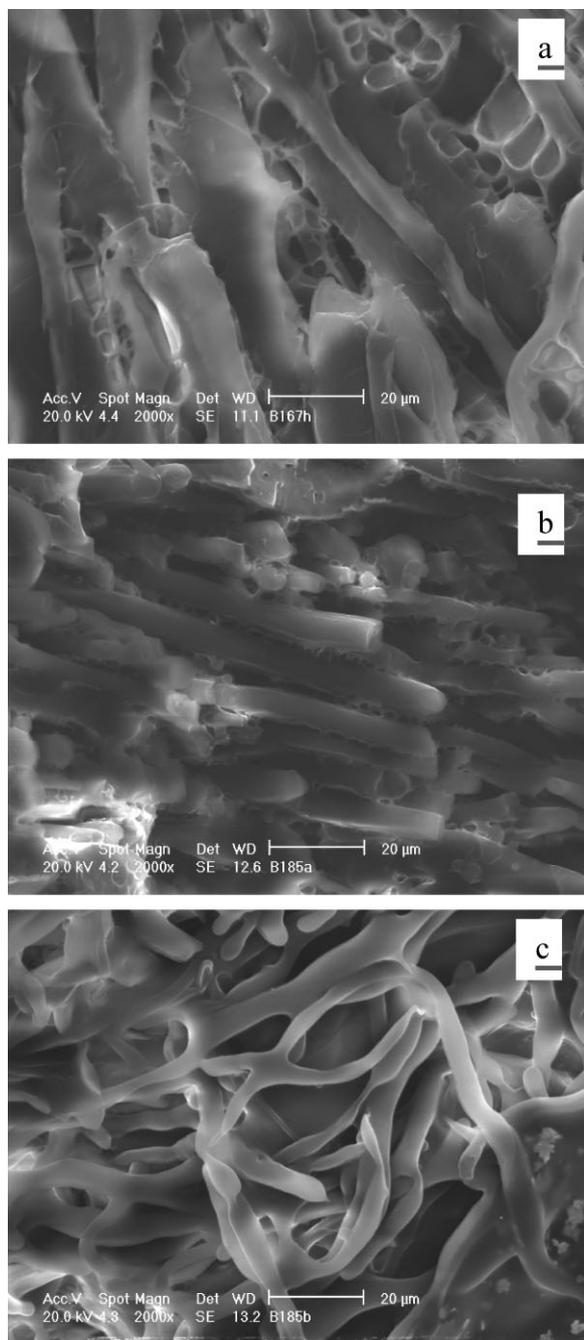
Figure 1. SEM microphotographs of cryo-fractured surfaces of LDPE/PBAT 40/60 w/w blend: (a) uncompatibilized, (b) EVA 4 wt.-%, and (c) MAgPE 4 wt.-%.

Figure 2. SEM microphotographs of cryo-fractured surfaces of LDPE/PBAT 40/60 wt.-% nanocomposites: (a) EVA 4 wt.-%, C30B 3 wt.-%; (b) MAgPE 4 wt.-%, C30B 3 wt.-%; and (c) uncompatibilized, C30B 3 wt.-%.

that LDPE filaments tended to joint together in the presence of MAgPE (Figure 1c).

Second, the examination of the cryo-fractured surface of the nanoclay-modified and compatibilizer-free nanocomposite shows a morphology similar to that of the uncompatibilized polymer blend (Figure 1a and 2c).
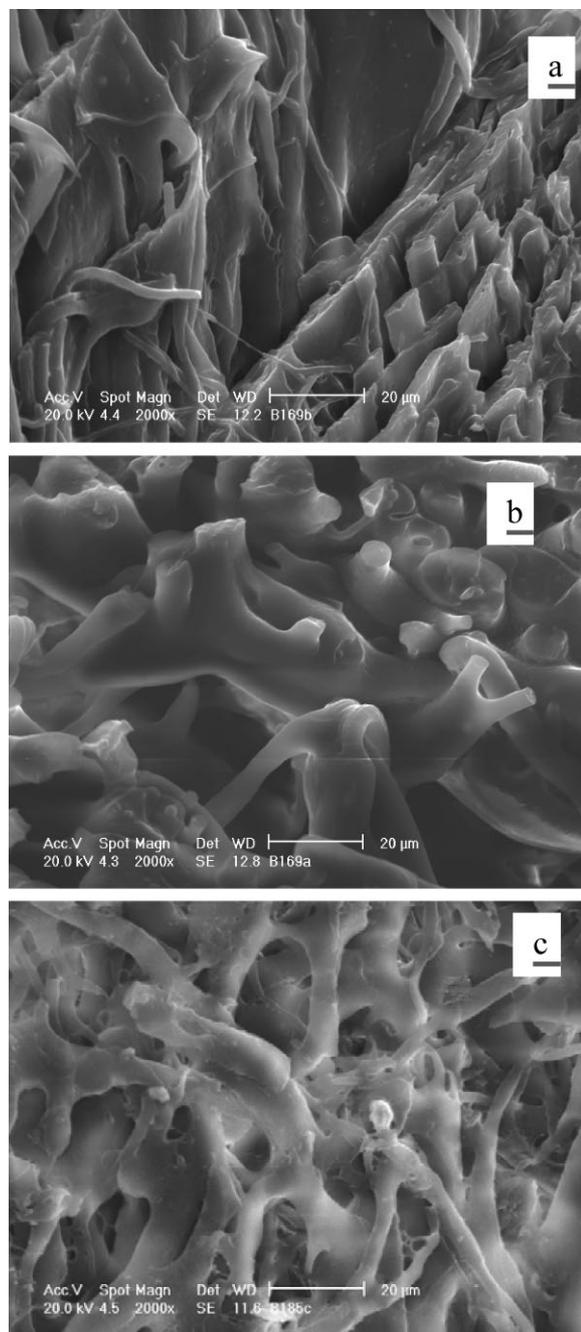
Direct Compounding

It is only when organoclays are introduced in the LDPE/ PBAT 40/60 w/w blend simultaneously with the organic modifier that its morphology is drastically modified. Indeed, by comparison with the morphology of the

uncompatibilized composition (Figure 2c), a stratified structure was obtained for the blend compatibilized by the C30B/EVA pair (Figure 2a) while substituting MAgPE for EVA led to a typical co-continuous morphology (Figure 2b). This structural modification allows considering that the hydroxyl functions of C30B organoclay react with the maleic anhydride groups of MAgPE.

In order to understand this morphology modification, the distribution of clay nanoplatelets has been investigated by TEM. In presence of EVA, the so-obtained microphotographs evidenced that clay nanoplatelets were both located in the PBAT phase and at polymer interface (Figure 3a). Remarkably, a reverse situation was observed if MAgPE is used as compatibilizer instead of EVA (Figure 3b). Indeed, MAgPE led to exclude nanoclays from the PBAT phase and promoted their exclusive dispersion within the polyolefinic matrix. Such an observation attests for the ability of MAgPE to react with the C30B organomodifier. Indeed, only a grafting of MAgPE chains on the C30B platelets (via the hydroxyl functions attached to the alkylammonium cations) was able to drastically modify their affinity for LPDE and allows their dispersion in such an nonpolar polymer. At this stage, both SEM and TEM analyses demonstrated that only the joint

action of organically modified clay and compatibilizers was responsible for the tailoring of blend structuring.

Further investigation on the role of clay/compatibilizer pair has been carried out by varying the EVA/MAgPE ratio in C30B-filled blends. For that purpose, compatibilized LDPE/PBAT 40/60 wt.-% nanocomposites containing both EVA and MAgPE in various proportions were prepared. The morphology of the so-obtained compositions has been characterized by SEM and TEM. First, SEM microphotographs (after PBAT etching by selective solubilization in chloroform) showed the appearance of a finer and organized LDPE phase when MAgPE content is increased (Figure 4). It seems that MAgPE plays a key role on the establishment of the co-continuous morphology relying upon interconnected polymer cylinders. As clearly evidenced by TEM microphotographs, the clay platelets migration from one polymer phase to the other appears to be responsible for the rocking motion from the stratified to the co-continuous structure (Figure 5). Indeed, as far as EVA/MAgPE 75/25 composition is concerned, clay nanoplatelets remain located in the PBAT phase (Figure 5a). At EVA/MAgPE 50/50 composition, inorganic nanoplatelets are observed to be dispersed and delaminated in both PBAT
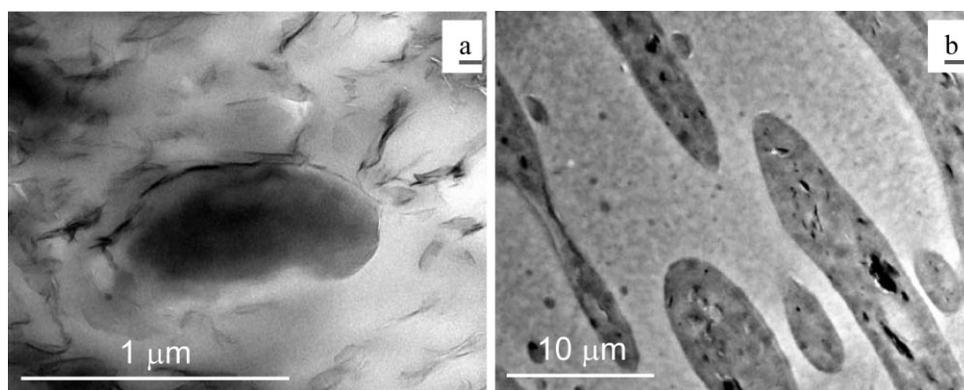

Figure 3. TEM microphotographs of cryo-fractured surfaces of LDPE/PBAT 40/60 wt.-% nanocomposites: (a) EVA 4 wt.-%, C30 3 wt.-% and (b) MAgPE 4 wt.-%, C30 3 wt.-%.
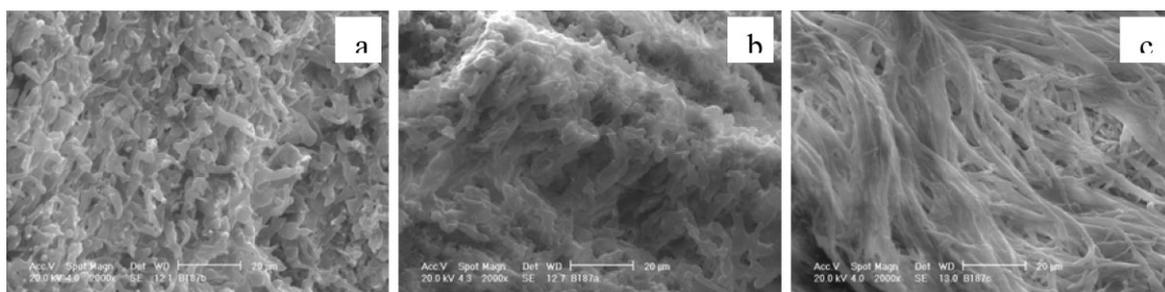

Figure 4. SEM microphotographs of cryo-fractured surfaces of LDPE/PBAT 40/60 wt.-% nanocomposites: (a) EVA/MAgPE 75/25 4 wt.-%, C30 3 wt.-%; (b) EVA/MAgPE 50/50 4 wt.-%, C30 3 wt.-%; and (c) EVA/MAgPE 25/75 4 wt.-%, C30 3 wt.-%.
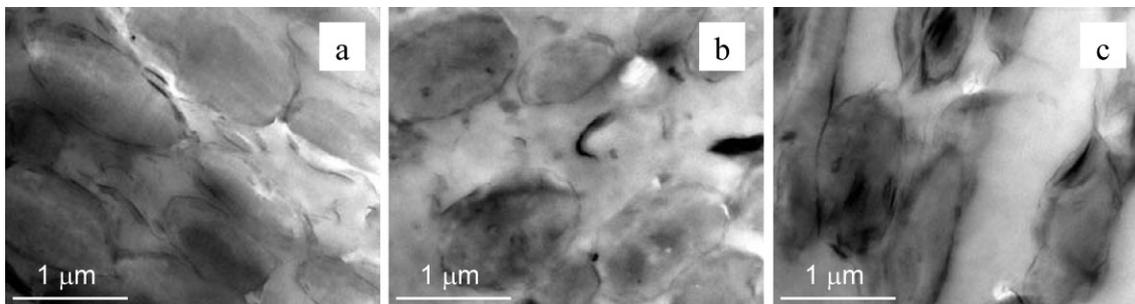
Figure 5. TEM microphotographs of cryo-fractured surfaces of LDPE/PBAT 40/60 wt.-% nanocomposites: (a) EVA/MAgPE 75/25 4 wt.-%, C30 3 wt.-%; (b) EVA/MAgPE 50/50 4 wt.-%, C30 3 wt.-%; and (c) EVA/MAgPE 25/75 4 wt.-%, C30 3 wt.-%.

and LDPE phases (Figure 5b). At higher MAgPE content, e.g., at EVA/MAgPE 25/75 ratio, clays are observed at the interface and within the LDPE phase (Figure 5c). Such a clay migration and morphology transition clearly highlighted the synergy between organoclay and polymeric compatibilizer and its impact on blend morphology.

Sequential Compounded Blends

In the previously discussed blends, the clay nanoparticles were blended simultaneously within both polymers. To investigate the kinetics of inorganic nanoplatelets diffusion within the blend, a series of experiments were performed where C30B nanoclay was first compounded with one of the two polymers and then the resulting nanocomposite was compounded with the second polymer. Depending on the nature of the compatibilizer used, C30B interacts more favorably with LDPE phase in presence of MAgPE while it migrates more within the PBAT phase when EVA is added as compatibilizer. Thus, in a composition in which C30B is blended with PBAT/MAgPE first and then with LDPE in a second consecutive step, it is expected that

clay platelets will migrate to the interface and/or in the LDPE matrix. TEM analyses have been performed to assess such evolution of the clay migration (Figure 6a). As observed, clay platelets were located only at the interface. Therefore, no further diffusion throughout LDPE matrix was allowed within the kneading time. Remarkably, a same clay location was observed if C30B was blended with LDPE/EVA first and then with PBAT (Figure 6b). These observations again give credit for the key importance of the reactivity of MAgPE toward C30B allowing its dispersion in LDPE. As clearly observed, a non-reactive polyethylene-based compatibilizer such as EVA is definitely not efficient enough for improving the compatibility between C30B and apolar polyolefin while MAgPE grafting onto C30B allows for excluding this hydrophilic organoclay from the polar polyester matrix.

Schematic Representation

As a conclusion for the morphology study, a model depicting the various morphological structures made available by modifying the nature of the organoclay/
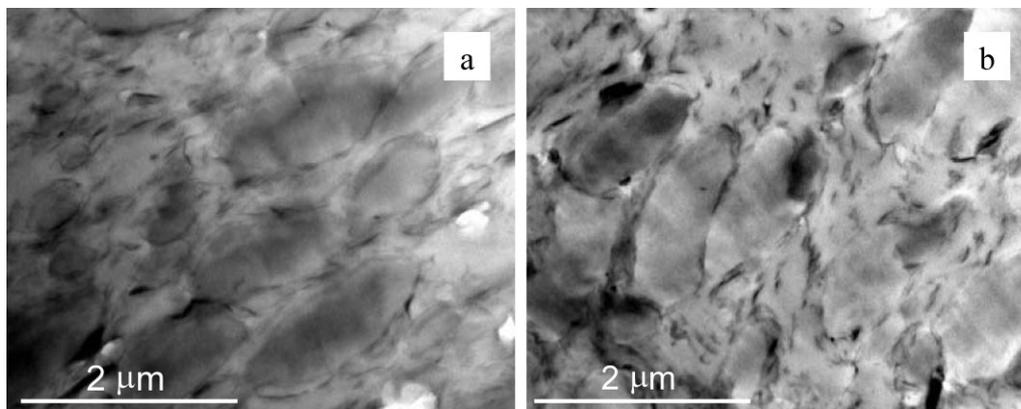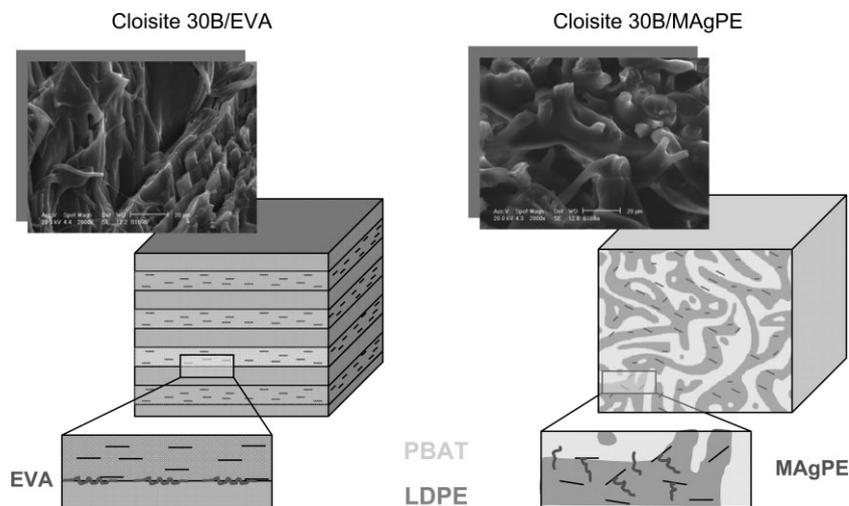

Figure 6. TEM microphotographs of cryo-fractured surfaces of LDPE/PBAT 40/60 wt.-% nanocomposites prepared by sequential compounding: (a) C30B was blended with PBAT/MAgPE first and then with LDPE; and (b) C30B was blended with LDPE/EVA first and then with PBAT.

■ *Scheme 1.* Representation of morphologies obtained for nanocomposites compatibilized with C30B/EVA and C30B/MAgPE.

compatibilizer pair is proposed (Scheme 1). Both stratified and co-continuous structures are outlined for nanocomposites compatibilized with C30B/EVA and C30B/MAgPE, respectively. Clay dispersion is shown in the PBAT phase for the EVA-based composition and in LPDE when MAgPE is used. As illustrated, this preferential location of C30B is a direct consequence of the compatibilizer action: EVA acts only as a surfactant while MAgPE can additionally react with the organomodifier of C30B (via the hydroxyl functions attached to the alkylammonium cations covering the inorganic nanoplatelet surface).

Mechanical Properties

To demonstrate the close and significant link existing between mechanical performances of the LDPE/PBAT-based nanocomposites and their microstructure, the mechanical properties of LDPE/PBAT 40/60 wt.-% systems have been evaluated by tensile testing and compared to data recorded for unfilled and uncompatibilized compositions (Table 1). In addition to C30B, another organoclay, i.e., C20A has also been considered. C20A is organomodified by non-reactive alkylammonium cations and therefore cannot react with MAgPE compatibilizer. As observed, highest tensile strength and elongation were obtained by using a C30B/MAgPE combination. Comparing the properties obtained for this combination with that obtained for C20A/MAgPE and C30B/EVA gave further evidence for the ability of MAgPE to react with the C30B organomodifier (Table 1). As previously shown by morphological analyses, the grafting of MAgPE chains onto the C30B nanoplatelets allows modifying the clay location with the polymer blend and promotes the formation of a co-continuous structure characterized by such high tensile properties.

■ *Table 1.* Effect of organoclays and compatibilizers nature on the mechanical properties of LDPE/PBAT 40/60 wt.-% nanocomposites.

Organoclay	Compatibilizer		Young modulus	Tensile strength	Strain at break
	Type	Content	MPa	MPa	%
		wt.-%			
	–	–	252 ± 7	11.2 ± 1.6	313 ± 61
	–	–	395 ± 6	12.5 ± 1.4	264 ± 62
C20A	EVA	4	355 ± 11	13.5 ± 3.6	339 ± 83
	MAgPE	4	288 ± 5	14.7 ± 0.9	380 ± 22
	–	–	355 ± 6	10.6 ± 2.9	430 ± 104
C30B	EVA	4	300 ± 29	7.7 ± 1.5	333 ± 93
	MAgPE	4	266 ± 4	20.4 ± 0.1	531 ± 6

Table 2. Effect of compatibilizers ratio on the mechanical properties of LDPE/PBAT 40/60 wt.-% nanocomposites.

Compatibilizer[a]	Young modulus	Tensile strength	Strain at break
	MPa	MPa	%
MAgPE 100%	350 ± 7	22.8 ± 0.6	531 ± 26
MAgPE/EVA 75/25	219 ± 7	7.5 ± 0.2	15 ± 1
MAgPE/EVA 50/50	261 ± 24	17.1 ± 2.2	459 ± 60
MAgPE/EVA 25/75	230 ± 7	7.3 ± 0.3	17 ± 1
EVA 100%	300 ± 29	7.7 ± 1.5	333 ± 93

[a]Total weight fraction: 4 wt.-%.

When nanocomposites prepared with both EVA and MAgPE in various proportions are considered, best results were obtained for the EVA/MAgPE 50/50 combination (Table 2). The use of 25 or 75% of EVA undoubtedly led to poor ultimate properties (Table 2, entries 2 and 4). The properties of these nanocomposites were in accordance with their inherent morphology. Indeed, only the EVA/MAgPE 50/50 combination allowed reaching good dispersion and delamination of the clay nanoplatelets throughout the blend (Figure 5b).

Conclusion

In the present study, the effect of a combination of organomodified clays and compatibilizers on the morphology and properties of LDPE/PBAT blends was investigated. The in-depth morphology study clearly evidenced that clay platelets can be selectively located in one of the two polymer phases depending on the ability of the compatibilizer to react with the clay organomodifier. This phase selection modifies the blend morphology, which rocks from a stratified to a co-continuous structure. The mechanical properties of the blends proved to be strongly dependent upon their morphology. Best results were achieved by using a compatibilizer able to react with the organoclay leading to the establishment of a co-continuous structure.

As demonstrated, an opportune choice of the clay/compatibilizer pair allows tailoring the final morphology and properties of polymer blends. This concept can be applied more generally to other polymers as a new compatibilization route for enhancing plastic performances such as mechanical and gas barrier properties.

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