Preparation, physical and mechanical characterization of montmorillonite/polyethylene nanocomposites

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Abstract. In this paper, we report the preparation of polyethylene composites with organically modified montmorillonite. Three different Na+-montmorillonites were modified in order to obtain organoclays and two grades of high-density polyethylene were used as composite matrices. All composites were prepared by melt blending, and their physical and mechanical properties were thoroughly characterized. The extent of clay platelet exfoliation in the composites was confirmed by X-ray diffraction (XRD). Mechanical properties under static and impact conditions were evaluated to assess the influence of the reinforcement on the properties of polyethylene.

Introduction

Recently, synthesis of polymer nanocomposites using organophilic clay has drawn the attention of many researchers since they often exhibit better properties, compared with their micro- and macrocomposite counterparts [1]. Polymer-layered silicate nanocomposites containing low levels of exfoliated clays such as montmorillonite and vermiculite have a structure consisting of platelets with at least one dimension in the nanometer range. The platelet aspect ratio exceeds 300, giving raise to a high degree of polymer-clay surface interaction which results in barrier and mechanical properties that are far superior to those of the base material [2].

Interest in polyolefin nanocomposites has emerged due to their promise of improved performance in packaging and engineering applications [2]. Polyethylene (PE) is one of the most widely used polyolefin polymers. Melt processing is the most appropriate technique for the industrial preparation of polymer layered silicate nanocomposites of thermoplastic polymers: it is environmentally sound since no solvents are required and it minimizes capital costs due to its compatibility with existing processes. The preparation of nanocomposites requires extensive delamination of the layered clay structure and complete dispersal of the resulting platelets throughout the polymer matrix. Nanocomposite preparation by conventional polymer processing operations therefore requires strong interfacial interaction between the polymer matrix and the clay in order to generate shear forces of sufficient strength. This is readily achieved with high surface energy polymers such as polyamides, where polarity and hydrogen-bonding capacity generates considerable adhesion between the polymer and the clay phases. However, low-energy materials such as polyethylene and polypropylene interact only weakly with mineral surfaces, making the preparation of polyolefin nanocomposites by melt compounding considerably more difficult.

Among the various layered aluminosilicates, generally used as fillers, montmorillonite (MMT), which is classified into 2:1 type dioctahedral smectites, has received a significantly large attention because of its good swelling properties and high exchange capacity. As pointed out above, due to

the large surface area of nanoparticles, the strong interparticular interactions make dispersion of the nanofiller particles very difficult. To overcome this problem literature recommends the modification of the PE-matrix, or the organic modification of the layered silicates to form the so-called 'organoclay', or both [3]. Organoclays are produced by replacing the cation originally present in the galleries with one organic cation containing at least one long n-alkyl chain such as ammonium. The aliphatic tail renders organophilic the normally hydrophilic silicate surface. A well-ordered organic/inorganic multilayer with a disordered liquid like arrangement of chains within the gallery is thus formed. While the natural clays are in general hydrophilic, the organically modified clays (organoclays) are hydrophobic or organophilic in nature [4].

The objective of this work was to prepare composites based on PE of different characteristics and organophilic MMT by melt compounding, and to characterize their mechanical and physical properties.

Experimental

Materials. Three different Na^+-montmorillonites were used as the starting material for organoclays: a Wyoming Bentonite B-3378 provided by Sigma (SW), a Brazilian clay from Campina Grande, Paraiba (B), and an Argentinean montmorillonite (A). As a quaternary alkyl ammonium salt, hexadecyl trimethyl ammonium chloride (HDTMA) CTAC-50-CT provided by GENAMIN was used. This salt is 94% C_{16}, 5% C_{14} and 1% C_{12}.

Two grades of high-density polyethylene were used: a pipe grade (PEp), BF-48100/P, MFI=11.1g/10min (21.6kg/190°C), d=0.948g/cm^3, gently provided by Rio Polímeros S. A., and a blow grade (PEb), 40055L MFI=10 g/10min (21.6kg/190°C), d=0.9530g/cm^3, gently provided by Repsol YPF.

Preparation of organoclays. Aqueous 4 wt% clay suspensions were prepared adding clay to distilled water with agitation, and then stirred for 20 minutes. Then aqueous solutions of HDTMA salts (25% wt) were added while mechanically stirred. Mixtures were then stirred vigorously with the turbulent flow for 20 min to prevent the coagulation of clay particles and after that were allowed to stand for 24 h at room temperature. The resulting organoclays (oSW, oB and oA) were then washed with distilled water to remove excess salts and filtered with Büchner funnel and 60-mmHg vacuum. Organoclays (oMMT) were finally dried at 60ºC ± 5ºC for 48 h and disaggregated with manual mortar.

Preparation of organoclay/polyethylene composites. Before blending, materials were dried in an oven for 16 hours at 60ºC. All composites were premixed in a tumbler and then prepared by melt blending in a TW 100 twin screw counter-rotating extruder, Rheocord 9000-Haake, at 60 rpm and a temperature profile of 190-195-205-210ºC. Materials obtained from the extruder were cut into pellets and reprocessed in order to improve homogeneity of the composites. Composites were prepared with 3%wt of organoclay. Prepared materials are listed in Table 1.

X-Ray diffraction. X-rays diffractometry has been used to evaluate the degree of interaction of the organoclay and polymer matrix. The extent of clay exfoliation in the composites was determined by X-ray diffraction (XRD) analysis using a Phillips X'PERT MPD diffractometer (CuKα radiation λ=1.5418 Å, generator voltage = 40 kV, current = 40 mA). Samples were pressed films approximately 100 μm thick and were scanned in 2θ ranges from 2 to 40º. Measurements were recorded at every 0.02º for 1 second each.

Mechanical characterization. Pellets of each material were compression-molded into 3 mm thick plaques at 190ºC. The plaques were then annealed for 1 h at 120ºC and slowly cooled to room temperature to release residual thermal stresses generated during molding. Machined dumbbell-shaped specimens (ASTM D 638 type I) were used for uniaxial tensile tests. Uniaxial tensile testing was performed at room temperature at a crosshead speed of 10 mm/min with an Instron 4467 testing machine. The yield stress (σ_y), elastic modulus (E), ultimate stress (σ_u) and elongation at break (ε_b) were determined.

Disk specimens 80 mm in diameter were machined from plaques for impact measurements. Dart impact testing was performed on these plaques using a Fractovis Ceast falling weight machine. The tests were carried out at room temperature with a hemispherical tup at an impact velocity of 3 m/s.

Table 1. Composition and properties of PE/oMMT composites

Material	Composition PE/oMMT (%wt)	Degree of exfoliation (XRD)	Steady-state Torque (Nm)	σ_y (MPa)	E (GPa)	σ_u (MPa)	ε_b (%)	Impact strength (J/mm)
PEp	100/0	-	141	30.00 ± 0.63	1.30 ±0.02	16.32 ± 0.27	6.2 ± 0.2	12.64 ±3.68
PEp/oSW	97/3	Int	**33**	31.04 ± 0.09	1.26 ±0.04	17.50 ± 0.13	7.5 ± 0.4	6.33 ±0.19
PEp/oB	97/3	Int	37	**31.07 ± 0.63**	**1.44 ±0.02**	**17.59 ± 0.27**	**8.4 ± 0.2**	**7.78 ±0.71**
PEb	100/0	-	138	28.71 ± 2.32	1.29 ±0.16	16.77 ± 0.27	13.3 ± 0.2	10.05 ±0.28
PEb/oSW	97/3	Int	36	31.18 ± 0.06	**1.57 ±0.01**	18.12 ± 0.07	7.2 ± 0.2	8.07 ±0.80
PEb/oB	97/3	**Exf**	**30**	30.74 ± 0.73	1.32 ±0.02	18.17 ± 0.16	9.1 ± 0.1	8.34 ±0.43
PEb/oA	97/3	Int	64	**32.88 ± 0.20**	1.34 ±0.11	**19.94 ± 0.27**	**14.9 ± 0.6**	**9.55 ±0.44**

Results and Discussion

Extent of exfoliation. XRD traces for pure PE, unmodified and modified MMTs, and their composites are shown in Fig 1. Three main types of composites may be obtained when layered clay is dispersed in a polymer. When the polymer is unable to intercalate between the silicate sheets, a phase-separated composite is obtained, whose properties stay in the same range as traditional microcomposites. Beyond this classical family of composites, two types of nanocomposites can be recovered. Intercalated structure in which a single (and sometimes more than one) extended polymer chain is intercalated between the silicate layers resulting in a well-ordered multilayer morphology built up with alternating polymeric and inorganic layers. When the silicate layers are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure is obtained [5].
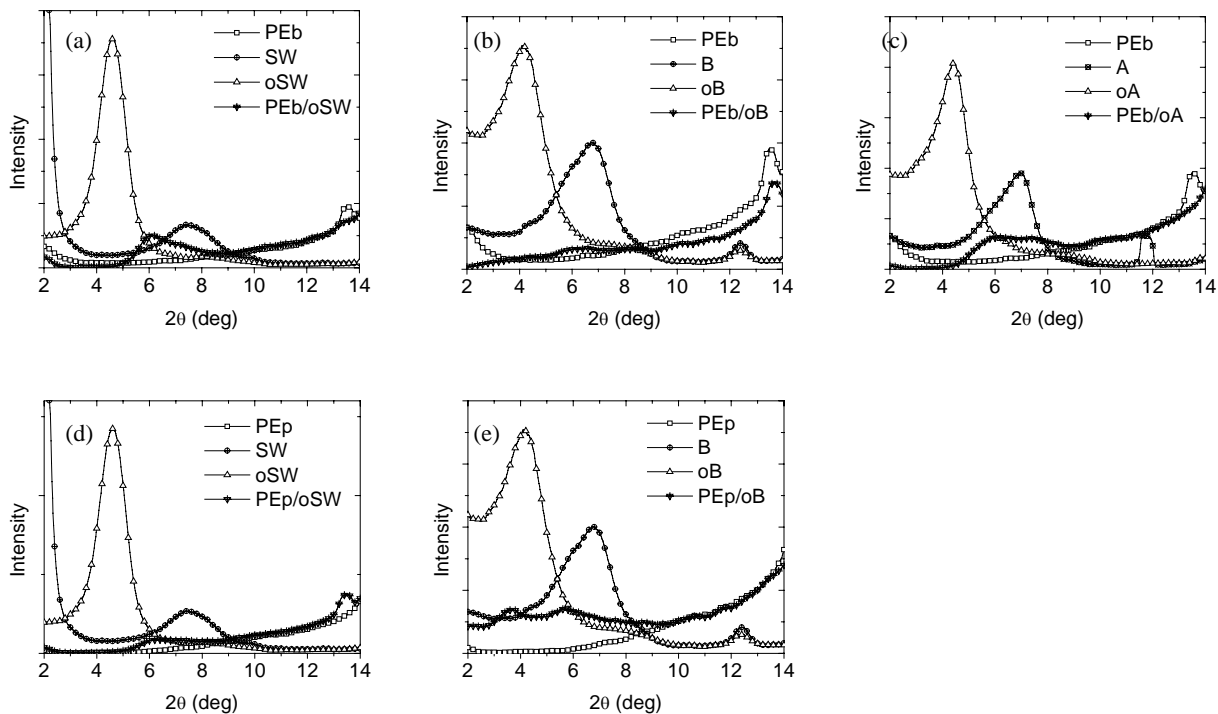

Fig. 1. X-ray diffraction profiles for the 001 reflection of pure materials and obtained composites.

For PEb/oB no basal peak is seen in XRD traces (Fig. 1b) while a weak and broad peak can be observed for the other prepared composites. The absence of basal peaks suggests that there is either an exfoliated system or at least a significant amount of disorder has occurred, while the weak and broad peaks signal the presence of a hybrid structure consisting of partially exfoliated and

intercalated clay. Many authors pointed out in literature that only when in situ polymerization is performed [5], or maleated PE is used [3] or EVA copolymer is added to the system [6] nanocomposite formation can be achieved. However, other authors stated that exfoliated or intercalated maleated-PE/clay composite can be obtained when the number of methylene units in alkylammonium chain is larger than 16 [3], and this is the number used in the present work. It is therefore quite possible that under conditions of great shear, as those obtained with the twin-screw extruder used in this work, one may be able to directly obtain an exfoliated polyethylene nanocomposite depending on the type of clay.

From XRD data it can also be seen that the replacement of inorganic exchange cations by organic onium ions on the gallery surfaces of montmorillonite not only serves to match the clay surface polarity with the polarity of the polymer, but it also expands the clay galleries. This facilitates the penetration of the polymer macromolecules into the gallery space (intercalation) [7]. Moreover, the hydrophobic organic modifier can facilitate the intercalation of a hydrophobic polymer into MMT by reducing the surface energy.

Processing behavior. The steady-state torque recorded during melt compounding was assessed and is reported in Table 1. Torques recorded during the second extrusion used to obtain the composites were lower than that measured for the pure polyethylenes. Paul and coworkers [8-9] observed that melt compounding nylon 6 nanocomposites showed lower steady-shear viscosities than those exhibited by pristine polymer in regions of high shear. They stated that the lower shear viscosities for nanocomposites, compared to their pristine matrices, may be attributed to higher degrees of exfoliation and smaller platelet sizes. Platelets on the nanometer scale can easily align during shear flow. In our work the lower steady state torque was achieved for PEb/oA composite, confirming the high degree of exfoliation suggested by XRD analysis.

Mechanical properties. Typical nominal stress-displacement curves obtained in tensile tests are shown in Fig. 2 and the derived mechanical properties are listed in Table 1. Regarding pure matrixes, stress-displacement curves are fairly similar, but elongation at break of PEb is higher than that of PEp. This is an expected result since the blow grade (PEb) has a wider molecular weight distribution including macromolecules of very high molecular weight, and a lower MFI than the pipe grade polyethylene (PEp). This factors are responsible of the higher permanent deformation.

It simply emerges that mechanical properties are enhanced by the presence of clay while the best performance was achieved by intercalated nanocomposites. Mechanical properties of composites are influenced by the kind of clay employed, in agreement with previously reported findings [10]
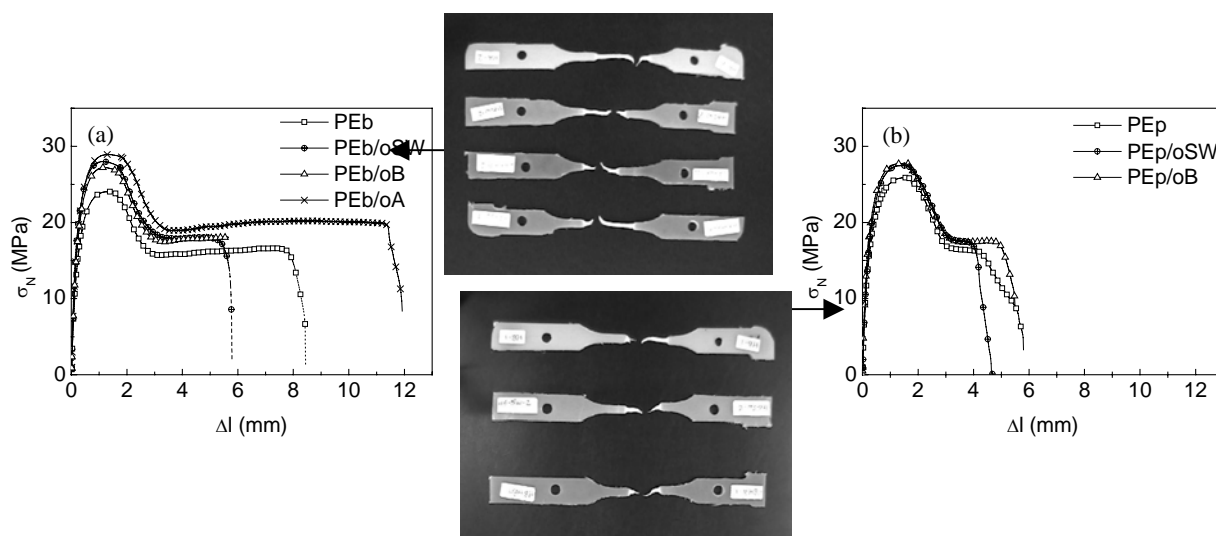

Fig. 2. Typical stress displacement curves for (a) PEb and (b) PEp based composites in tensile tests.

Some important characteristics of composites have to be considered. The quality of the polymer-filler interface in composites, i.e. the static adhesion strength as well as the interfacial stiffness,

usually plays a very important role in the materials' capability to transfer stresses and elastic deformation from the matrix to the fillers [11]. This is especially true for nanocomposites, because they impart a high portion of interface. If filler/matrix interaction is poor, the particles are unable to carry any part of the external load. In that case, the strength of the composite cannot be higher than that of the base polymer. If the bonding force between fillers and matrix is strong enough instead, the yield strength of a composite can be higher than that of the neat polymer [12]. In the same way a high composite modulus corresponds to a high interfacial stiffness. Hence, the increase in stiffness and tensile strength observed reveals that stresses are in some way efficiently transferred via the interface.

The strain at break of microparticle filled composites is known to be reduced with filler content [13], but the effect of nanocomposite formation on the elongation at break has not been widely investigated [5]. One has to recall that the composite is in part filler and in part matrix. Due to the rigid nature of the fillers, most of the deformation comes from the polymer. The actual deformation experienced only by the polymer matrix is much larger than the measured deformation of the sample, with the result that the polymer reaches the failure strain limit at a lower total deformation. However, it is surprisingly observed that for some of the prepared nanocomposites the strain-to-break behaves contrary to conventionally filled composites. This increment suggests that the nanoparticles are able to introduce additional deformation mechanisms and energy consumption without blocking matrix deformation.

In thermoplastic-based (intercalated or exfoliated) nanocomposites, the stresses at break vary strongly depending on the nature of the interactions between the matrix and the filler [5]. In our case, σ_u is enhanced for all composites.

Typical force-displacement traces obtained under impact conditions are shown in Fig. 3, and impact strength is reported in Table 1. On one hand, the formation of PEb nanocomposites does not markedly reduce the impact properties. This is in agreement with what has been reported in literature [5] that the decrease in the impact strength of various nanocomposites is not very pronounced over a relatively large range of filler content. On the other hand, impact strengths of PEp based composites are perceptible lower than that of pristine matrix. A more detailed characterization should be made in order to elucidate the causes of these findings.
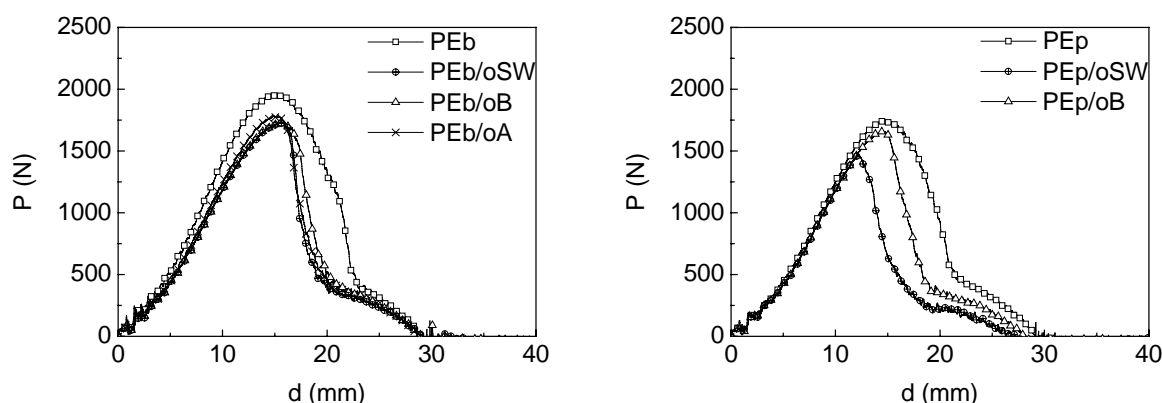

Fig. 3. Force-displacement curves for (a) PEb and (b) PEp based composites under impact conditions.

Conclusions

We have investigated the morphology and mechanical properties of several PE/oMMT nanocomposites by XRD, torque measurements, tensile tests and dart impact tests. The compounding in a twin-screw extruder of molten PE with hexadecylammonium modified clay

leads to the formation of intercalated and exfoliated nanocomposites depending on the raw materials used.

Young's modulus, tensile strength, and ultimate stress of prepared composites are enhanced by the presence of clay while the best performance was achieved by the PEb/oB composite.

The large array of improved mechanical properties attained at very low filler content together with the ease of production through a simple process such as melt intercalation, directly applicable by extrusion or injection molding make PE/oMMT nanocomposites a very promising material. The future work will aim to elucidate the micromechanism acting in the deformation, the swelling behavior, permeation and thermal properties of the composites.

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