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Polyethylene/(organo-montmorillonite) composites modified with ethylene/methacrylic acid copolymer: Morphology and mechanical properties

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ABSTRACT

Several composites based on high-density polyethylene (PE), organically modified montmorillonite (OMMT) and ethylene/methacrylic acid copolymer (EMAA) were prepared by melt compounding. Three Na⁺-montmorillonites (MMT) of different precedence were modified with hexadecyl trimethyl ammonium chloride in order to change their nature from hydrophilic to organophilic. The composites morphology was examined by XRD, SEM and TEM. Mechanical properties were evaluated under static conditions. A slight reinforcement was achieved only when OMMT was added to PE. When EMAA was added to the composites, it negatively interacted with OMMT, diminishing the interlayer distance of OMMT, changing the composite morphology, as if OMMT was not present in composites, and deteriorating their mechanical properties.

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1. Introduction

Inorganic fillers are commonly added to polymers to increase their strength, or enhance other properties such as electrical conductivity, barrier properties (e.g. oxygen and water vapor), thermal resistance, etc. [1]. In recent years, polymer-clay nanocomposites have attracted great academic and industrial interest because of the anticipated improvements in properties [2,3], such as stiffness, gas barrier, flammability, thermal resistance, etc. when the aluminosilicate platelets of clays like montmorillonite are well-exfoliated into polymers [4–7]. Polymer layered silicate nanocomposites are hybrids composed of layered silicates (also called phyllosilicates or clays) about 1 nm thick and an aspect ratio between 100 and 1000 dispersed in a polymer matrix. It has been argued that the interaction between polymer and clay at the nanoscale level should enhance properties [7].

Henceforth, during the last years the central scientific issue of many researchers has been focused on how to achieve high levels of exfoliation of the nanoclay platelets within the polymer matrix since this is necessary to reach a large filler aspect ratio. Experimental approaches for improving clay exfoliation include optimization of processing conditions, selection of appropriate organoclays (surfactant treatment), and chemical modification of the polymer matrix to improve matrix-organoclay affinity.

Polyethylene (PE) is one of the most widely used polyolefin polymers, and interest in polyolefin nanocomposites has emerged in an attempt to improve PE performance in packaging and engineering applications [3]. Melt compounding is the most attractive processing for thermoplastic based nanocomposites from an industrial point of view. It is environmentally sound since no solvents are required and it minimizes capital costs due to its compatibility with existing processes. The difficulty is that polyolefins seem incapable of exfoliating the clays by themselves, because they lack suitable interactions with the polar aluminosilicate surface of the clay.

Clays are in nature organophobic, but they can be turned into organophilic by replacing the Na⁺ or Ca²⁺ cation originally present in the galleries with one organic cation such as alkylammonium ions via an ion-exchange reaction [8]. A well-ordered organic/inorganic multilayer with a disordered liquid like arrangement of chains within the gallery is thus formed.

However, the organically modified clay does not disperse well in nonpolar polymers as PP or PE [9–11]. Therefore, addition of an appropriate compatibilizer [12] or chemical modification of the polymer matrix [13] is required. The most developed approach to overcome the aforementioned difficulty is to graft maleic anhydride to the polyolefin backbone for use as the matrix polymer or as a compatibilizer in polypropylene [14,15] and polyethylene [16–20]. Grafting of maleic anhydride on the polyolefin backbone is known to significantly improve the interactions between polyolefins and organoclays, and thus, improve exfoliation. However,

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maleated polyolefins are expensive (with a cost about seven times that of conventional packaging polymers).

Another novel and attractive proposal recently reported in the literature to improve exfoliation is to copolymerize the olefin monomer with polar monomers like methacrylic acid or acrylic acid [21–24]. It has been claimed that the random incorporation of ionic functionalities along the polymer backbone could heighten interactions between the charged mineral surface and the ionic functionality of the acid, and that the incorporation of as little as 1 mol% of ionic content was found to significantly affect the morphology and achieve considerable exfoliation of the nanocomposites. Ionomers, where some of the acid groups of such acid copolymers are neutralized to form sodium, zinc or magnesium salts, offer an extension of this option. In the last years, the preparation of ionomers of a variety of thermoplastics used as matrixes or compatibilizers to prepare nanocomposites has been reported [21–29].

The use of a commercially available thermoplastic like ethylene methacrylic acid copolymer (EMAA) in order to improve matrix clay interactions appears appealing and promising. Besides improving the toughness of the matrix, these thermoplastics are said to have excellent adhesion to polar substrates. EMAA contains both ethylene segments – that have a specific interaction with ethylene – and methacrylic acid segments – that may have specific interactions with organoclays – and so may be used as a compatibilizing agent. The miscibility of PE and EMAA in the amorphous phase has been proved in previous works. It has been demonstrated that no interaction exists between the crystalline components of PE/EMAA blends, but there is interpenetration between PE chains and PE segments of EMAA in the amorphous phase [30,31].

In this work, we explored the possibility of obtaining PE/organoclay/EMAA nanocomposites by direct melt compounding from commercial PE, EMAA, and organoclays of different precedence, maintaining the low cost and good mechanical properties of PE. The Na⁺-montmorillonites were modified with a quaternary ammonium salt in order to obtain the organoclays before blending. The morphology of the obtained composites was assessed by X-ray diffraction, scanning electron microscopy and transmission electron microscopy, while their mechanical behavior was evaluated by quasistatic tensile tests and heat distortion temperature determination. The derived properties were related to the obtained morphologies.

2. Experimental

2.1. Materials

Commercial high-density polyethylene blow grade 40055L MFI = 10 g/10 min (21.6 kg/190 °C), $d = 0.9530 \text{ g/cm}^3$, used as composite matrix was gently provided by PBB Polisor, Argentina (PE). A commercial ethylene/methacrylic acid copolymer (Nucrel 1202HC, $T_m = 99 \text{ °C}$, acid groups = 12%, MFI = 1.5 g/10 min (2.16 kg/190 °C) provided by DuPont was selected as modifier.

Three different Na⁺-montmorillonites (MMT) were used as the starting material for organoclays: a Wyoming Bentonite B-3378

Table 1
Characteristics of montmorillonites

MMT	Water content (%)	Ion exchange capacity (meq/100 g clay)	Specific area BET (m ² /g)	Accompanying minerals (Q = quartz, K = kaolin)	Particle size after organophilization (μm)
SW	11.4	124	40	Q	7.4
B	11.9	151	82	Q,K	7.4
A	11.7	110	70	Q,K	7.4

provided by Sigma (SW), a Brazilian clay from Campina Grande, Paraíba (B), and an Argentinean montmorillonite (A). Properties of clays are listed in Table 1. As a quaternary alkyl ammonium salt, hexadecyl trimethyl ammonium chloride (HDTMA) GENAMIN CTAC-50-CT was used as received. This salt is 94% C₁₆, 5% C₁₄ and 1% C₁₂.

2.2. Organic modification of clays

Aqueous 4 wt% clay suspensions were prepared adding clay to distilled water under stirring and then further stirred for more than 20 min. Aqueous solutions of HDTMA salts were prepared taking into account clays ion exchange capability, and were added to clay suspensions while mechanically stirred. Mixtures were then stirred vigorously with the turbulent flow for 20 min to prevent the coagulation of clay particles. After that, they were allowed to stand for 24 h at room temperature. The resulting organoclays (OMMT) were then washed with distilled water to remove the excess salts and vacuum filtered with Büchner funnel at 60 mmHg. The obtained organoclays (denoted here by OSW, OB and OA) were finally dried at 60 °C ± 5 °C for 48 h and disaggregated with a manual mortar.

2.3. Compounding of polyethylene/organoclay composites

Before blending, materials were dried in an oven for 16 h at 60 °C. All composites were premixed in a tumbler and then prepared by melt blending in a TW 100 twin screw counter-rotating extruder coupled to a Haake Rheocord 9000, at 60 rpm with temperature profile of 190–195–205–210 °C. After extruding, the materials were cut into pellets and reprocessed at the same processing conditions to improve homogeneity of the composites. During the second processing, steady state torque was measured. The prepared materials are listed in Table 2. The aim of this work was to improve PE properties maintaining its low cost and good mechanical properties. Therefore a low content of EMAA (1%) was selected. Addition of larger quantities of EMAA would result in higher costs, and noticeable decrease of modulus and yield stress due to the elastomeric nature of EMAA. The composition of each composite was calculated from the amount of clay, compatibilizer and polymer charged to the extruder.

2.4. Morphological characterization

The resulting morphologies were studied by combined techniques: X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electronic microscopy (TEM).

XRD analysis was performed on pressed films approximately 100 μm thick using a Phillips X'PERT MPD diffractometer (CuKα

Table 2
Composition, steady-state torque and XRD results of PE/MMT composites

Material	Composition (wt %) (PE/OMMT/EMAA)	Steady-state torque (Nm)	XRD results	
			2θ	d-Spacing (Å)
OSW			4.60	19.2
OB			4.10	21.6
OA			4.40	20.1
PE	100/0/0	138	–	–
PE/EMAA	100/0/1	82	–	–
PE/OSW	97/3/0	36	4.40	20.1
PE/OSW/EMAA	96/3/1	40	6.18	14.3
PE/OB	97/3/0	37	–	–
PE/OB/EMAA	96/3/1	38	–	–
PE/OA	97/3/0	64	4.26	20.7
PE/OA/EMAA	96/3/1	62	5.58	15.8

radiation $\lambda = 1.5418 \text{ \AA}$, generator voltage = 40 kV, current = 40 mA). Measurements were recorded every 0.02° for 1 s each varying 2θ from 2° to 40° . The interlayer distance of clay was calculated from the (001) peak by using Bragg equation, which is reported in Table 2.

It has been reported that XRD is not a fully reliable tool for analyzing the complex dispersion of clay layers in ternary nanocomposites like the ones prepared in this work [32]. Therefore TEM was combined with XRD to corroborate the microstructure of nanocomposites. Microphotographs were obtained from a TEM Jeol 100 CX microscope using an acceleration voltage of 200 kV. Samples were ultramicrotomed at room temperature with a diamond knife to a 70-nm thick section.

SEM was carried out on a JEOL JMS-5300 instrument with a voltage of 15 kV. Samples were etched for 15 min at 60°C with a 70 g l^{-1} solution of potassium permanganate in sulphuric acid [33] and were examined after coating them with a thin gold layer.

2.5. Mechanical characterization

To characterize the effect of the addition of organoclays and EMAA copolymer on the mechanical behavior of polyethylene, uniaxial tensile properties and heat distortion temperature were assessed.

To this aim, pellets of each material were compression-molded into 3 mm thick plaques at 190°C and then rapidly cooled to room temperature. During this kind of processing residual stresses that interfere in mechanical determinations are generated. Therefore, the plaques were annealed afterwards for 1 h at 120°C 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, which were performed at room temperature at a crosshead speed of 10 mm/min in an Instron 4467 testing machine. Values of yield stress (σ_y), elastic modulus (E), ultimate stress (σ_u) and elongation at break (ϵ_b) were obtained from experiments.

Heat distortion temperature (HDT), defined as the temperature at which a 0.25 mm deflection occurs under 0.46 MPa, was measured by thermal mechanical analysis using the method developed by Scobbo [34]. This method translates the standardized load and deformation into modulus assuming approximately linear stress-strain behavior for small loads and deformations typically specified in the standards. For the displacement of 0.25 mm and load of 0.46 MPa, this translates into $\log(\text{modulus in Pa units}) = 8.9$. Modulus was measured with a Perkin-Elmer dynamic mechanical analyzer (DMA-7) at a fixed frequency at 1 Hz in a three-point bending mode, while increasing the temperature from 10 to 130°C at a heating rate of 2°C min^{-1} .

3. Results

3.1. Processing behavior

Steady-state torques recorded during second extrusion are presented in Table 2. The recorded torques values of PE/OMMT composites were lower than that ones measured during the processing of pure PE. The addition of EMAA diminished PE steady-state torque but did not greatly influence the composites steady-state torques.

According to a study on polyethylene/clay nanocomposite reported in the literature [3], the steady-state torque recorded during melt compounding is an indirect indicator of the extent of clay exfoliation within polyethylene. These authors have found that torque was higher for the exfoliated composite than the one obtained for the neat polymer and the intercalated composite, i.e. indicating

increase in the viscosity for the nanocomposites, which may be correlated with the increase in the interaction level between clay platelets and polymer phase. On the other hand, it has been claimed that the time at which rheological measurements are made is the relevant information to define the rheological behavior of a material [35]: when very low shear rate is applied, clay particles take a longer time to attain complete planar alignment along the flow direction, but when higher shear rate is applied the measurement time is long enough to attain such alignment. Hence, the same composite may display different rheological behavior depending on the applied shear rate. Therefore, assuming that the rheological behavior of nanocomposites is close to the one of

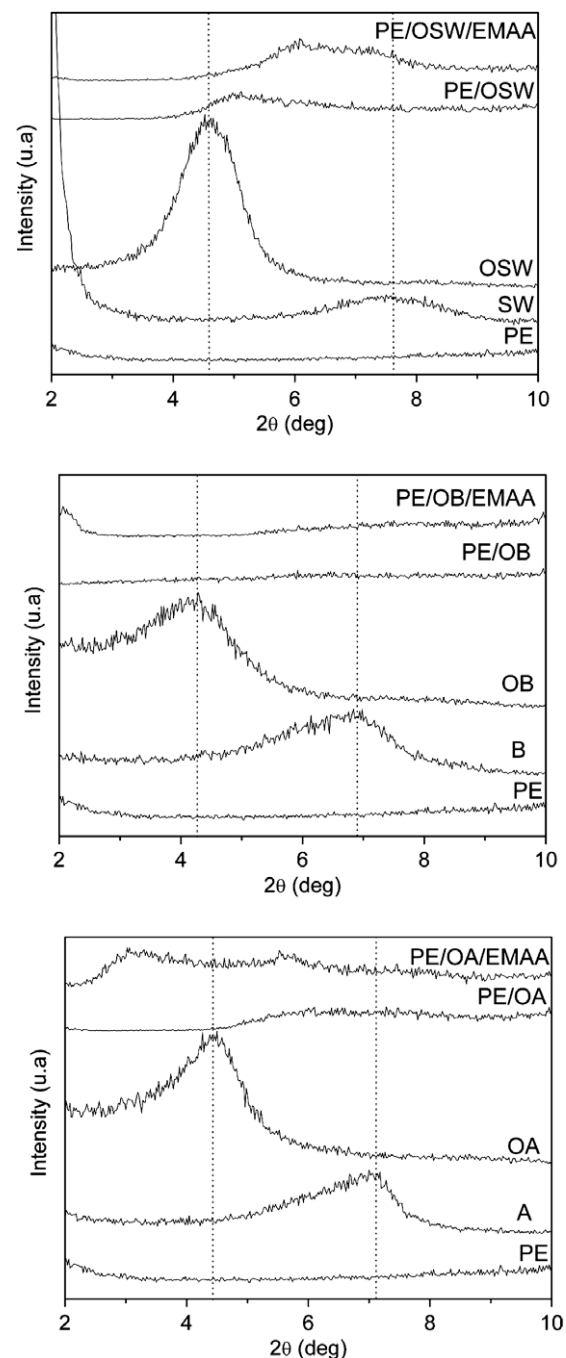


Fig. 1. X-ray diffraction profiles at low angle region for PE, as received MMT, organomodified MMT and composites.

very fine fillers composites [36] nothing can be said about the degree of exfoliation from torque measurements. Only a qualitative comparison can be made.

OA affected the steady-state torque in a different way when compared to OSW and OB, giving the impression that PE/OA interactions are different from those of the others PE/clays.

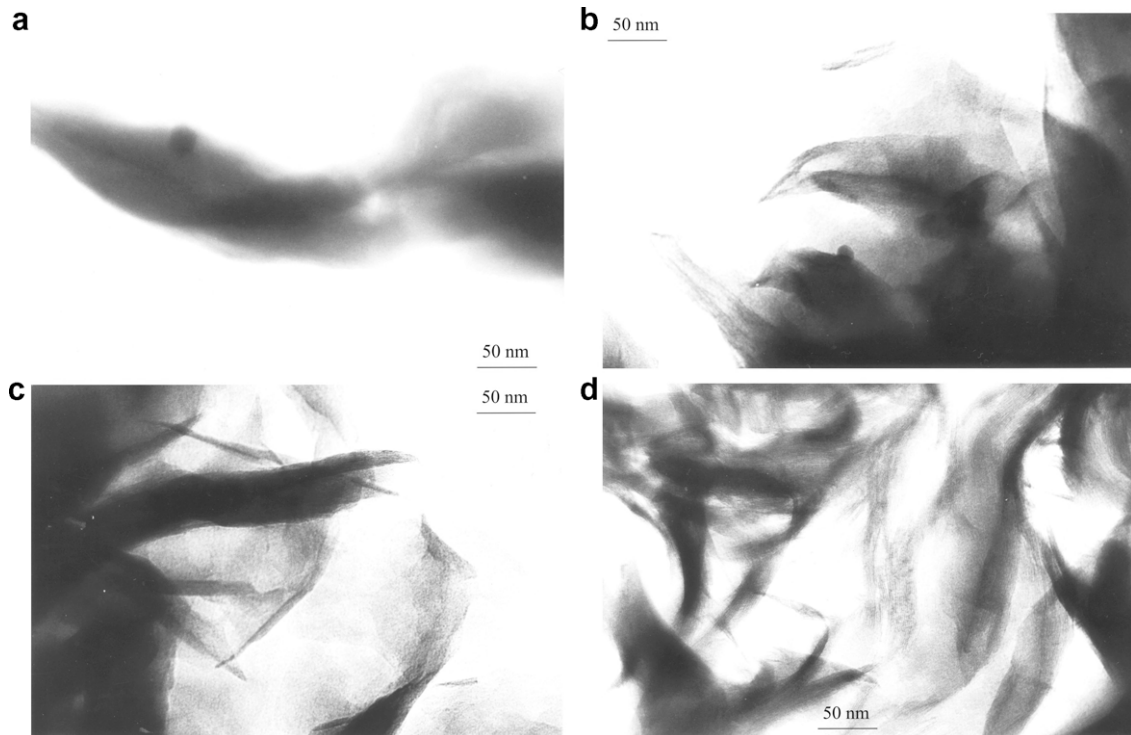


Fig. 2. TEM images of (a) PE/OB; (b) PE/OB/EMAA; (c) PE/OSW; (d) PE/OSW/EMAA.

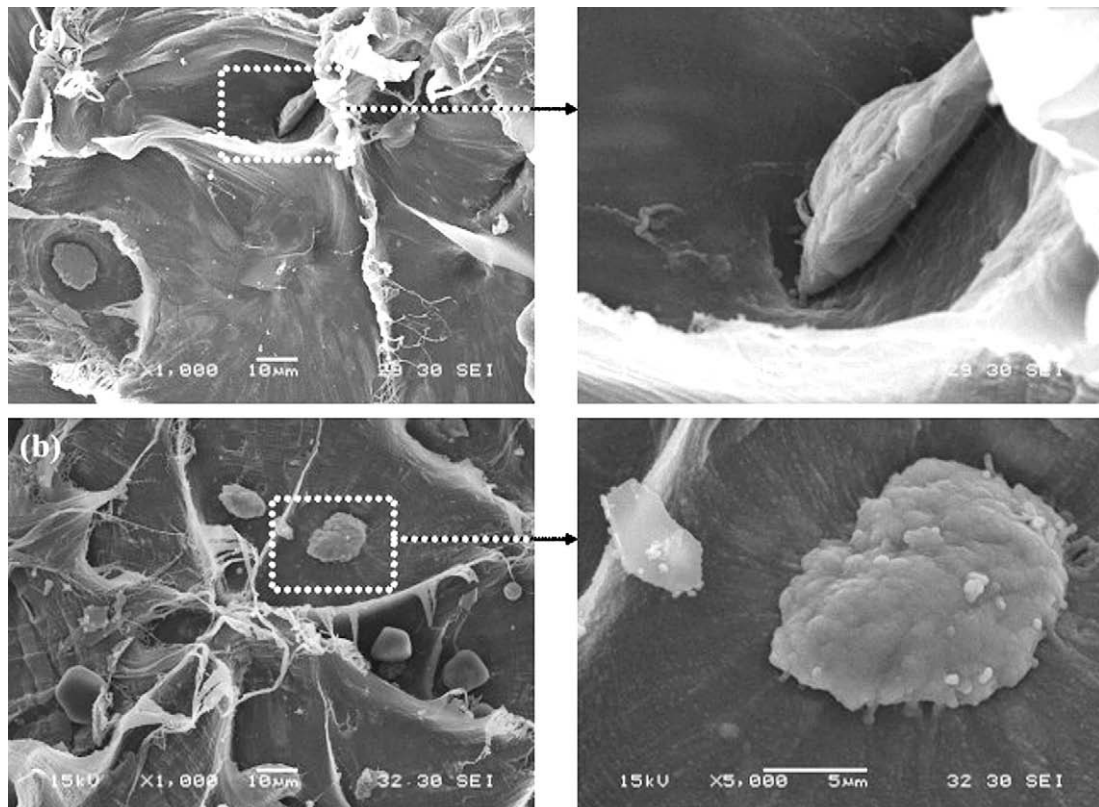


Fig. 3. SEM images of (a) PE/OA; (b) PE/OA/EMAA.

3.2. Morphology

XRD traces for pure PE, unmodified and modified MMTs, and their composites are shown in Fig. 1. Clays used in this work belong to the same class (Na^+ -montmorillonite), but they show different d -spacing. The B Na^+ clay showed originally higher d -spacing (13.1 Å) than the A Na^+ clay (12.6 Å) and the SW Na^+ clay (11.9 Å). These three MMT with different exchange capability and specific area were supposed to attain diverse change in interlayer distance when treated with HDTMA. After treatment with HDTMA, the organoclays OB, OA and OSW present d -spacing 21.6 Å, 20.1 Å and 19.2 Å, respectively, maintaining the original difference between them. The organophilization procedure increases layer distances approximately 8 Å. This is not surprising, since it depends on the chemical structure of the surfactant and its orientation, which are similar.

Regarding XRD patterns of composites, for composites based on OB with and without EMAA (PE/OB and PE/OB/EMAA) no characteristic basal diffraction peak of the organoclay appears in the range of $2\theta = 2 - 10^\circ$. It is possible to identify that for PE/OSW and PE/OA a small peak appeared with a maximum at low 2θ angle ($<4^\circ$). When EMAA is added to these two composites (PE/OA/EMAA and PE/OSW/EMAA), a weak and broad peak can be observed in XRD patterns (Fig. 1a and c). In these composites, addition of EMAA to the system shifts the diffraction peak of the organoclay to higher angles, indicating decreasing of d -spacing in comparison with OA and OSW. Nevertheless, the d -spacing is still higher than it is in the original Na^+ -montmorillonites.

The position of the scattering peak for nanocomposites is dependent on several phenomena that come out during melt processing. One of them is the reduction in d -spacing caused by the thermal degradation of the organoclay that occurs when nanocomposites are processed at temperatures between 180 and 200 °C [37]. The other factor is the intercalation of the polymer in the interplatelet region of the organoclay which results in an increase in its d -spacing. It appears that in PE/OMMT composites the intercalation effect dominates while in PE/OMMT/EMAA composites the degradation effect may dominate.

According to XRD results it could be claimed that in some of the prepared composites (PE/OB and PE/OB/EMAA), organoclays are exfoliated and dispersed in the PE matrix during melt compounding, or at least that a significant amount of disorder has occurred. Nevertheless, TEM reveals that either in composites where no characteristic basal diffraction peak of the organoclay appears in the range of $2\theta = 2 - 10^\circ$ in XRD traces, or in composites in which small peaks appear in the mentioned low 2θ range, most clay platelets are still stacked, i.e. clay platelets are, at the most, intercalated (Fig. 2). It clearly emerges from our results that XRD analysis alone is not enough to determine clay exfoliation, i.e. TEM is also needed.

Fig. 3 shows typical SEM images of PE/OMMT and PE/OMMT/EMAA composites. In PE/OMMT some small clay agglomerates with a high aspect ratio (approximately $15 \mu\text{m} \times 4 \mu\text{m}$, i.e. aspect ratio ~ 4) are seen between the deformed PE matrix. In PE/OMMT/EMAA samples more spherical agglomerates of approximately $15 \mu\text{m}$ in diameter are seen. The surface appearance of agglomerates is also different. These observations give evidence of some OMMT encapsulation by EMAA.

3.3. Mechanical characterization

Typical nominal stress–displacement curves obtained in tensile tests of the prepared composites are shown in Fig. 4. The mechanical properties, including Young's modulus E , tensile strength σ_y , ultimate stress σ_u and elongation at break ϵ_b of the composites together with the corresponding values of the virgin polymers have been evaluated and results are presented in Table 3. Tensile curves exhibit a simple sharp yield point after which the stress decreases to the draw stress. The neck is stable and the drawing of the whole gauge length occurs. Stress–displacement curve features are not modified by the presence of OMMT or EMAA.

The presence of clay in the PE/OMMT slightly enhances E , σ_y and σ_u and no perceptible differences in the mechanical properties of composites with the kind of clay employed are found. The increase in stiffness could not be attributed to an increase in crystallinity of the PE resulting in a nucleation effect of the particles (there were no differences in DSC measurements). It must then result either from a restriction of the molecular motion in the amorphous regions of the polymer or from simple mechanical reinforcement by the dispersed phase.

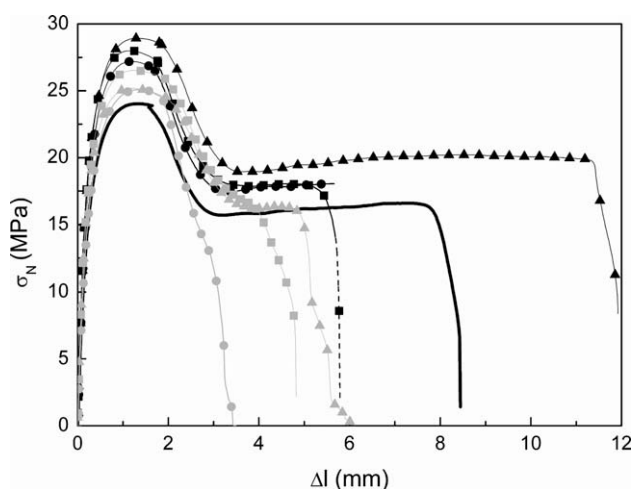


Fig. 4. Typical stress displacement curves for composites in tensile tests. Straight line PE, in black PE/OMMT composites, in grey PE/OMMT/EMAA composites: —■— PE/OSW, —●— PE/OB, —▲— PE/OA.

Table 3
Mechanical properties of PE and PE/OMMT composites

Material	Tensile properties				HDT at 0.46 MPa
	σ_y (MPa)	E (GPa)	σ_u (MPa)	ϵ_b (%)	
PE	28.7 ± 0.23	1.29 ± 0.16	16.8 ± 0.27	13.3 ± 0.25	95 °C
PE/EMAA	25.7 ± 0.42	1.23 ± 0.01	16.8 ± 0.12	>100	—
PE/OSW	31.2 ± 0.28	1.57 ± 0.02	18.1 ± 0.07	7.2 ± 1.58	107 °C
PE/OSW/EMAA	30.3 ± 0.73	1.29 ± 0.13	16.7 ± 0.14	5.8 ± 2.71	103 °C
PE/OB	30.7 ± 0.20	1.32 ± 0.02	18.2 ± 0.15	9.1 ± 1.47	102 °C
PE/OB/EMAA	30.1 ± 0.79	1.27 ± 0.03	17.4 ± 0.27	7.2 ± 3.17	97 °C
PE/OA	32.9 ± 0.21	1.34 ± 0.09	19.9 ± 0.27	14.9 ± 1.74	104 °C
PE/OA/EMAA	29.0 ± 0.79	1.30 ± 0.11	16.7 ± 0.58	9.9 ± 2.28	101 °C

Unfortunately, and contrary to expectations, the addition of EMAA copolymer deteriorates the mechanical properties of composites. Tensile properties of PE/OMMT/EMAA composites are lower than PE/OMMT properties, approaching the level of the virgin polymers, following the same tendency found in DSC measurements. Also, the scatter of results is larger for composites with EMAA than for composites without EMAA copolymer (see Table 3).

Table 3 also shows that the addition of OMMT improves the heat distortion temperature of composites. HDT increases between 5 and 12 °C with the addition of OMMT to PE without any marked difference among diverse organoclays. In the temperature range used in the analysis, the complex modulus is higher for composites when compared to the pristine matrix. Unfortunately, the incorporation of EMAA always decreases the composites modulus.

4. Final discussion

Based on previous works using ionomers [28,38], it was expected that the addition of small amount of EMAA to the composites would result in improvement of the level of exfoliation. However, our results showed that there is no positive effect on exfoliation when EMAA is added to the system. XRD patterns of PE/OMMT/EMAA exhibit a peak with lower *d*-spacing than OMMT. Uniaxial tensile tests and HDT follow the same tendency: as EMAA is added to the system, properties of composites are deteriorated approaching the level of the pristine matrix. Also, SEM micrographs give some evidence of OMMT encapsulation by EMAA.

At this point it would be interesting to estimate the level of exfoliation of organoclays in the obtained composites. Using a few simple assumptions, the extent of exfoliation can be estimated quantitatively from the analysis of nanocomposites yield stress values. Pukánszky et al. [39] have developed a simple model to describe the composition dependence of tensile yield stress and tensile strength for composites that could be used to evaluate the extent of exfoliation of clays in nanocomposites. The validity of the model has been demonstrated for various heterogeneous systems from particulate filled polymers to blends and short fiber reinforced composites, and recently in layered silicate nanocomposites [40]. The model has been applied first to about 40 PP-clay composites [41], and then to more than 80 thermoplastic-layered silicate composites, including PE based composites [42], concluding that it is suitable for the evaluation of the reinforcing effect of silicates in these composites. This model states that there is a linear correlation when the natural logarithm of reduced yield stress (σ_{yrel}) is plotted against filler content (volume fraction φ) [43]:

$$\ln \sigma_{yrel} = \ln \frac{\sigma_y}{\sigma_{y0}} \frac{1 + 2.5\varphi}{1 - \varphi} = B\varphi \quad (1)$$

where σ_y is the yield stress of the composite. Parameter *B* is related to the load carried by the dispersed component [44]. According to this model *B* depends linearly on the specific surface area of the filler (A_f):

$$B = (1 + A_f \rho_f l) \ln \frac{\sigma_{yi}}{\sigma_{y0}} \quad (2)$$

where *l* and σ_{yi} are the thickness and the yield stress of the inter-phase, and σ_{y0} is the yield stress of the matrix. However, *B* values do not give a direct estimate of the extent of reinforcement because changing matrix properties also influences the value of *B*. A linear correlation was proved to exist between *B* and the natural logarithm of matrix yield stress using CaCO₃ composites prepared with various matrices (shown by the broken line plotted in Fig. 5). The extent of reinforcement is indicated by the deviation from this line in the vertical direction. Usually *B* is determined from composition

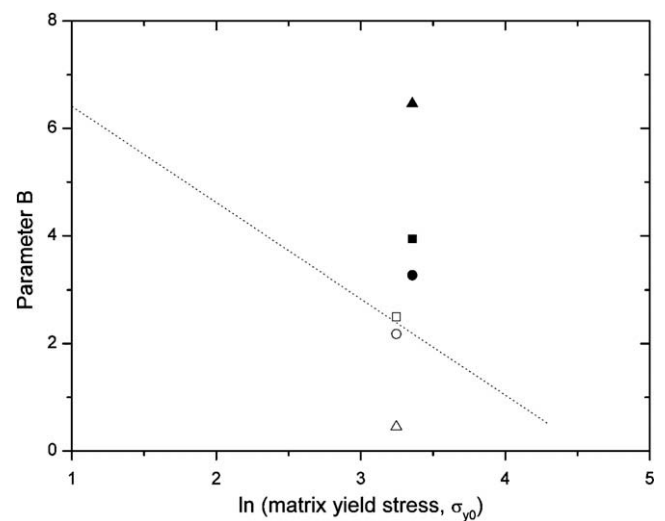


Fig. 5. Comparison of the reinforcing effect of obtained composites. Reinforcement is given by the distance of the broken reference line. Symbols: (●) PE/OB, (○) PE/OB/EMAA, (■) PE/OSW, (□) PE/OSW/EMAA, (▲) PE/OA, (△) PE/OA/EMAA.

dependence, but in order to get some insight into the achieved exfoliation level, we calculated *B* parameter from a single composition and the zero condition (for zero content of clay σ_{yrel} is equal to 1), keeping in mind that it is only an estimation of real *B* values. Fig. 5 shows that *B* values for PE/OMMT composites are above the dotted line suggesting a better reinforcement than regular fillers, while PE/OMMT/EMAA lie on the line or even below it, i.e. these last composites behave like regular filled ones or even worse.

We can then compare the estimated extent of theoretical reinforcement achieved at complete exfoliation to the values actually

Table 4
Extent of exfoliation estimated from yield stresses of composites

Material	Extent of exfoliation (%)
PE/OB	2.97
PE/OB/EMAA	2.44
PE/OSW	3.30
PE/OSW/EMAA	2.59
PE/OA	4.54
PE/OA/EMAA	1.58

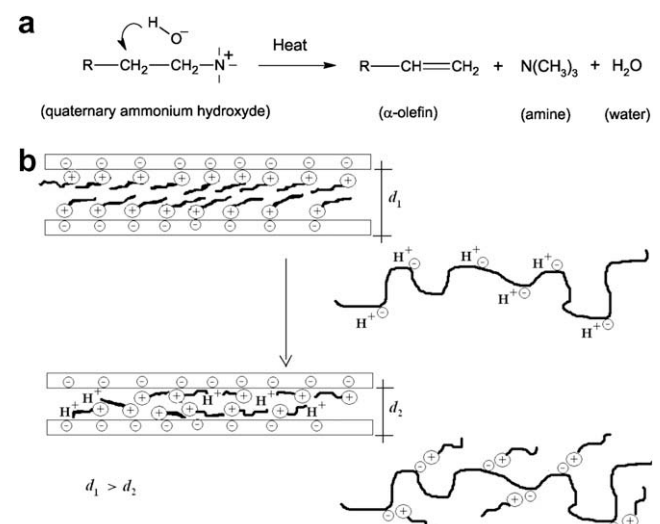


Fig. 6. Possible interaction between OMMT and EMAA.

reached (Table 4) using the calculated parameter B and the theoretical value of parameter $B = 195$ for complete exfoliation calculated from data published for the specific surface area of montmorillonite. The analysis indicated that the extent of exfoliation is very low in most composites; it reaches maximum 4.5%, and when EMAA is added the level of exfoliation is always worsen.

There are different possible explanations for this fact. The first one is that EMAA may favor organoclay degradation. It has been claimed in previous publications that the initial degradation of the organoclay follows a Hoffman elimination mechanism with the release of long chained α -olefins (Fig. 6a) [37]. The α -olefins should be readily soluble in PE, and so they are easily extracted from the clay galleries into the matrix polymer. This combined with possibly some effects of the mechanical forces generated during extrusion result in the collapsing of the clay galleries. The second explanation is that the acidic carboxyl groups ($-\text{COO}^- \text{H}^+$) of EMAA may interact with the ammonium cations inside the clay galleries removing part of them from the galleries [45]. The result is a partially protonated clay with a collapse of interlayer space (Fig. 6b), as observed in XRD. In concordance with this interaction between OMMT and EMAA, the decrease of HDT of the composites containing OMMT and EMAA with respect to those EMAA free could be explained considering the presence of α -olefins or alkyl ammonium in the matrix phase besides the presence of EMAA which has Vicat softening point (75 °C) lower than HDPE (126 °C). However, regardless which is the interaction between organoclays and EMAA, the final consequence is that the effect of EMAA is contrary to the expected one: it does not induce exfoliation but it diminishes OMMT interlayer distance in PE/OMMT/EMAA composites.

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