Preparation and Characterization of Polymer/Organosilicate Nanocomposites Based on Unmodified LDPE

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ABSTRACT: Low-density polyethylene (LDPE)/silicate nanocomposites were prepared by the melt compounding and solution blend methods using unmodified LDPE polymer and layered silicates with different aspect ratio. X-ray diffraction (XRD) analysis performed on composites obtained by dispersing the organosilicates in molten LDPE evidenced an exfoliated or partially exfoliated structure for the low aspect ratio silicate (laponite) in contrast to the high aspect ratio silicate (montmorillonite), which led to the formation of intercalated nanocomposites. With regard to the preparation method, the melt compounding method was more effective in forming exfoliated/highly intercalated LDPE nanocomposites compared with the solution blend method (using CCl_4 as a solvent). A gradual increase in crystallization temperatures (T_c) with increasing laponite content for LDPE-organolaponite nanocomposites was revealed by differential scanning calorimetry (DSC) measurements. Thermogravimetric analysis and tensile measurements results indicated that thermal stability and elastic modulus increment were more prevalent for nanocomposites prepared using organomontmorillonite as filler. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 83–89, 2009

Key words: PE; nanocomposites; organoclay; TGA; DSC

INTRODUCTION

Polymer-layered silicate nanocomposites have attracted great interest due to their improved thermal, mechanical, and gas barrier properties compared with conventional composites or neat polymers.[1,2] Because layered silicate nanoparticles are completely hydrophilic, interactions between them and hydrophobic polymers are not favorable. Thus, the first step in the direction of a successful nanocomposite synthesis is to convert the hydrophilic surface of layered silicates (being mainly smectite clays, such as montmorillonite, fluorohectorite, etc.) to organophilic by ion-exchange of the charge-balancing metal cations in the interlayer region with alkylammonium ions.[3] Despite the organic modification of the silicates they do not disperse well in nonpolar polymers, such as polypropylene or polyethylene, due to the very high hydrophobicity of these polymers.[4] Another approach for the synthesis of nanocomposites involves the use of modified polymers, in particular via grafting of pendant anhydride groups, to mediate the polarity between silicate surface and polymer, and to achieve miscibility between the two phases.[5,6]

Low-density polyethylene (LDPE) is widely used for packaging applications and the synthesis of LDPE/inorganic nanocomposites with improved properties, such as mechanical and barrier properties, is expected to further boost its use in that direction. However, the achievement of nanocomposite structures with highly dispersed inorganic nanoparticles is much more difficult than in HDPE because of the branched macromolecules (in LDPE), which hinder the penetration of the polymer chains into the clay galleries.[7] Nanocomposites based on LDPE using organoclays and maleic anhydride-grafted PE[8] or ethylene vinyl acetate[9,10] as compatibilizer were synthesized, obtaining intercalated or partially exfoliated structures. However, there are no reports in the open literature, at least to our knowledge, that have studied the preparation and characterization of unmodified LDPE-based nanocomposites.

The objective of this study was to synthesize LDPE-based nanocomposites, without any polymer modification and with two kinds of layered silicates (clays), one with low aspect ratio (i.e., synthetic laponite) and another with high aspect ratio (i.e., montmorillonite). The effects of synthesis parameters, such as melt or solvent mixing, and type of

layered silicate on the structure and properties of the resulting LDPE/silicate (nano)composites have been systematically investigated.

EXPERIMENTAL

The layered silicates (clays) used in this work were (i) laponite (Lp), a synthetic hectorite composed of two tetrahedral silica sheets and a central octahedral magnesia sheet obtained from Southern Clay Products, with cation exchange capacity (CEC) 50 meq/100g of clay (its surface modification is described later) and (ii) organomontmorillonite (OMt) NANOMER®-I.44P produced by Nanocor Company and supplied by Aldrich (Milwaukee, WI). NANOMER-I.44P is an onium ion modified clay containing ∼ 40 wt % dimethyl dialkyl (C14-18) ammonium surfactant. The surfactant was identified as Arquad® 2HT-75[11] di(hydrogenated tallow) dimethylammonium chloride produced by Akzo Nobel Company (Amsterdam, The Netherlands). The structure of this surfactant is $R_2N^+(CH_3)_2Cl^-$, and its alkyl chain distribution was reported[11] as C_{12}, 1%; C_{14}, 4%; C_{16}, 31%; and C_{18}, 64%.

Surface modification of the synthetic laponite carried out using the same surfactant as that used by Nanocor in NANOMER-I.44P organoclay, namely Arquad 2HT-75, produced by Akzo and supplied by Fluka (Buchs SG, Switzerland) (Fig. 1). A 1 wt % solution of surfactant in warm water was prepared and added dropwise to a 1 wt % laponite suspension in the same solvent. The obtained mixture was stirred vigorously for 24 h at 70°C. The amount of the surfactant added was equivalent to 0.8, 1.5, or 3.0 × the CEC of laponite. The resulting samples were washed four times with deinozed water and once with ethanol to remove the excess of surfactant and dried in a vacuum oven at 40°C.

Ion exchange of the interlayer alkali cations by alkylammonium ions increases the interlayer distance and modifies the interlayer space of silicates from organophobic to organophilic, capable to accommodate nonpolar polymeric chains. The idea to use various amounts of surfactant for the organic modification of laponite aimed at further increment of interlayer space and better interaction of clay surface with a nonpolar polymeric matrix as LDPE.

The laponite (Lp) had a low aspect ratio (20–30) and the montmorillonite had high aspect ratio (100–200).
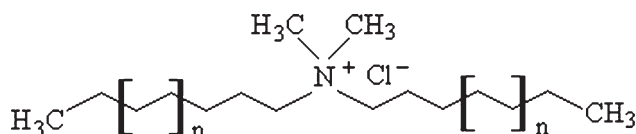

Figure 1 Structure of the surfactant di(hydrogenated tallow) dimethylammonium chloride.

The polyethylene used for the nanocomposites preparation was LDPE supplied by Aldrich, with Melt Index = 25 g/10 min (190°C/2.16 kg) and density 0.915 g cm^{-3}.

LDPE-organolaponites (OLp) composites with 2, 5, and 10 wt %, and LDPE-OMt composites with 2 and 10 wt % organosilicate loadings have been obtained via solution blend method[12] by diluting appropriate amounts of LDPE in CCl_4 at 85°C and mixing the solution, under vigorous stirring, with 1.5 × CEC-OLp or OMt suspensions, respectively, in the same solvent. The mixtures remained for 24 h under stirring at 85°C (to avoid solvent evaporation a vertical condenser was adapted on the reaction flask). The final composites were received after solvent evaporation. A second series of nanocomposites with the same OLp and OMt loadings were prepared by melting at 180°C in an oven, the as earlier received composites. For better homogenization periodical mechanical stirring (out of the oven) using a micromixer (IKA-WERKE model DI 25) with stirring speed 8000 rp/min was applied.

The organic phase content in the organomodified silicates and the thermal stability of the obtained LDPE nanocomposites were estimated by thermogravimetric analysis (TGA) using a NETZSCH STA 449C apparatus. Samples of about 10 mg were heated in air from 25 to 900 °C at a rate of 10°C min^{-1}. DSC measurements of LDPE nanocomposites were carried out at the same instrument. Samples of about 10 mg were heated from −15 to 170°C, melt annealed for 5 min, cooled down, and heated again at a rate of 5°C min^{-1} in N_2.

Samples of layered organosilicates for X-ray diffraction (XRD) analysis were prepared by spreading about 1 mL of their water suspension (10 mg/mL) on glass slides. The water was evaporated (at RT) before the X-ray measurements. The XRD measurements were performed on a D8 Advanced Bruker diffractometer with CuK$_\alpha$ radiation (λ = 1.5418 Å) and the basal spacing of the samples was estimated from the d-spacing of the 001 reflection. XRD analyses of polymer nanocomposites took place on films prepared using a hydraulic press with heated platens, in the same diffractometer.

Tensile tests were performed on an Instron Tensile Testing Machine model 3344 according to ASTM D638 using dogbone-shaped specimens with dimensions 22 × 5 × 0.22 mm at 50 mm/min crosshead speed. Three specimens from each sample were tested to establish reproducibility of the measurements.

RESULTS AND DISCUSSION

The XRD patterns of the parent laponite, the OLp with various surfactants' loadings and the OMt, are shown in Figure 2. An increase of the basal spacing
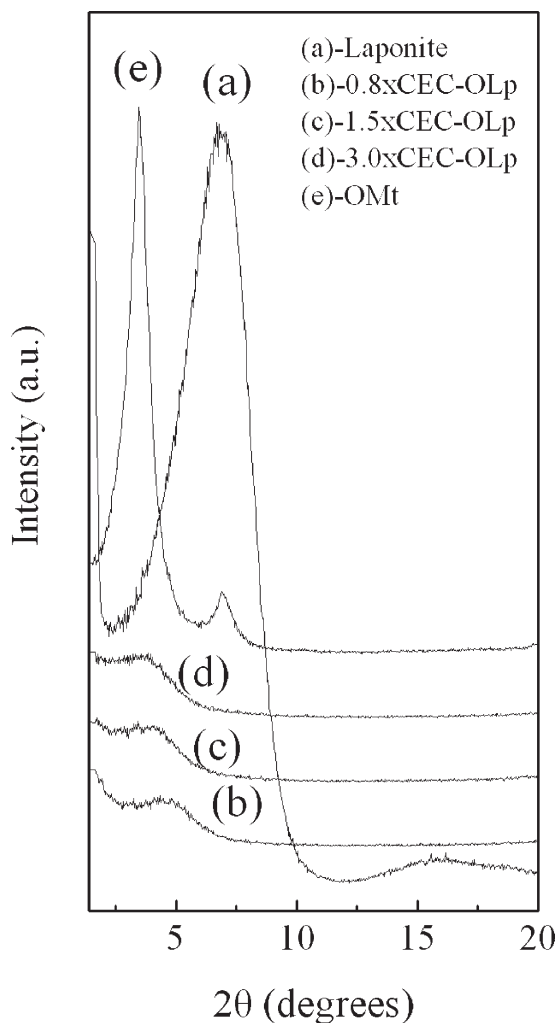
Figure 2 XRD patterns of the pristine laponite (a), the OLp at various organic phase loading: 0.8 × CEC (b), 1.5 × CEC (c), 3.0 × CEC (d), and the organomontomorillonite (e).

(d_{001}) of the laponite is observed after the insertion of the surfactant (di(hydrogenated tallow) dimethy-lammonium ions). More specifically, the pristine laponite (Lp) shows a d_{001}-spacing of 1.21 nm, which correspond to an interlayer space D = 1.21 − 0.95 = 0.26 nm, where 0.95 nm is the thickness of the individual clay sheet. In the case of the OLp, very broad diffraction peaks were obtained. This indicates a nonuniform interlayer opening. The maxima of the peaks correspond to basal spacing, d_{001} = 1.75 nm for 0.8 × CEC-OLp and 1.99 nm for both 1.5 × CEC-OLp and 3.0 × CEC-OLp, with corresponding interlayer space: D_1 = 0.8 nm, D_2 = D_3 = 1.04 nm. For the OMt, the basal spacing was measured to be d_{001} = 2.51 nm, which corresponds to an interlayer space of D_4 = 1.56 nm. In addition to the larger interlayer space of the OMt compared with those of the OLps, a more ordered layered structure has been also identified for the former layered organosilicate based on the intensity and the sharpness of the XRD

reflections. The relatively disordered structure of the OLps and on the basis of the size and shape of the alkylammonium ion (Fig. 1) an inclined monolayer configuration with random distribution between the silicate layers can be suggested for these organosilicates. On the other hand, the more ordered structure of OMt and the larger interlayer space could also imply a lateral bilayer structure of the surfactant, in addition to the inclined configuration described for the OLps.

The organic phase content of the organosilicates was estimated by thermogravimetric analysis assuming that the weight loss between 160 and 720°C is due to the loss of organic matter. The obtained TG curves of the pristine Lp and the organosilicates are shown in Figure 3. The corresponding weight losses (theoretical and experimental) are given in Table I.

The weight loss between 30 and 160°C for all the organosilicates is very low compared with that for the pristine/inorganic laponite sample (Table I), indicating the increased hydrophobicity of the organomodified samples. The weight losses which correspond to the organic matter for the samples 0.8 × CEC-OLp (25.1 wt %) and 1.5 × CEC-OLp (32.6 wt %) were very close to the theoretical amounts that were expected for complete adsorption/ion-exchange of the surfactant quantity added in the ion-exchange experiment. For the 3.0 × CEC-OLp the estimated organic content was 35.4 wt %, this value being by far lower compared with the surfactant quantity added. As discussed earlier, the interlayer distance for 1.5 × and 3.0 × CEC-OLp is identical. Because the organic content of the latter sample is by 2.8% higher, it can be suggested that more surfactant molecules have been adsorbed on the clay
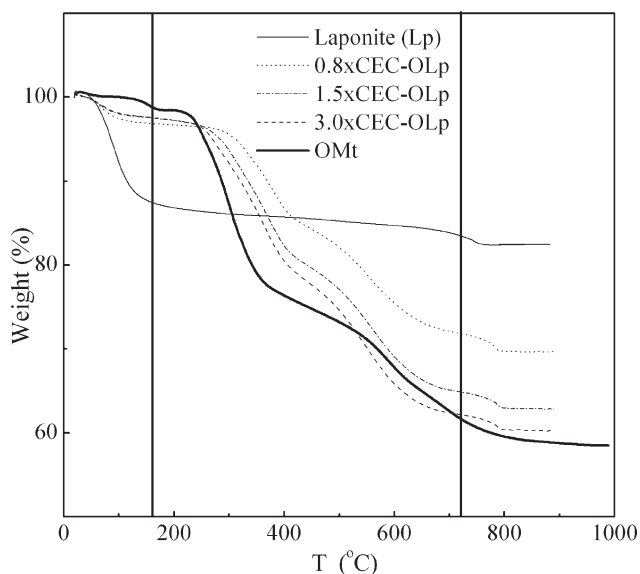

Figure 3 TGA curves of the pristine laponite, the OLps, and the OMt.

TABLE I
Water Content (% Weight Loss at the Temperature Range 30–160°C), % Weight Loss at the Temperature Range
160–720°C, Theoretical Organic Content (Based on the Amount of Organic Surfactant Used for Preparing
the Organoclays) and Basal Spacing Values of Pristine Laponite and Organosilicates

Material	Water content (% weight loss at 30–160 °C)	% Weight loss at 160–720 °C	Theoretical organic content (wt %)	Basal spacing (d_{001}) (nm)
Laponite (Lp)	12.5	4.0	–	1.21
0.8 × CEC-OLp	3.4	25.1	23.1	1.75
1.5 × CEC-OLp	2.4	32.6	35.9	1.99
3.0 × CEC-OLp	2.4	35.4	53.1	1.99
Organomontomorillonite (OMt)	1.1	37.2	35–45	2.51

surface of 3.0 × CEC-OLp and as a result the free lateral distance between the adsorbed molecules in the interlayer space becomes shorter compared with 1.5 × CEC-OLp. This indicates that there is an upper limit above which the laponite's sheets gallery cannot expand more by accommodating more alkylammonium ions. For the OMt, the estimated organic content was 37.2 wt %.

XRD patterns of the prepared composites are shown in Figure 4. Graphs in the left hand column of Figure 4 correspond to materials prepared using the solution blend method and in the middle column to materials received after melting process, both using the 1.5 × CEC-OLp sample as filler. XRD patterns of composites prepared either by solution blend or melt compound method, using the OMt sample as filler, are shown in the right hand column of Figure 4. In some cases, the characteristic reflections of the clay filler in the composites were clearly identifiable and the corresponding d-spacing values are presented in Table II.

The XRD patterns for the composites prepared via the solution blend method present: (i) a broad and low intensity peak at the same 2θ as for OLp, for composites prepared with organolaponite and (ii) a low intensity peak at the same 2θ as for OMt, for composites prepared with OMt. This means that in both cases the polymer chains were not incorporated effectively between the silicate layers. The presence of these XRD reflections that are due to clay tactoids with the same ordering as in the parent organocilicate sample indicates that a conventional, phase separated composite has been formed. Probably the strong affinity between the solvent molecules and the surface of organoclays did not favor the intercalation of polymer chains into the interlayer space of nanosilicate sheets. The absence of XRD reflections characteristics of the clay filler peaks, is indicative for probable formation of an exfoliated or partially exfoliated structure. Complete exfoliation of the clay layers, in which the individual clay layers lose their ordered stacking and are exfoliated and dispersed in the continuous polymer matrix is the desired goal of the formation process. However, this ideal morphol-

ogy is frequently not achieved and varying degrees of dispersion are more common. For completely exfoliated organosilicate, no X-ray peak is expected for the nanocomposite because there is no regular spacing of the platelets. However, the absence of such a peak is not conclusive evidence for a highly exfoliated structure.[14] In the case of the LDPE/OMt composites prepared by the melt process method, the XRD peaks that correspond to clay basal spacing are still present but are shifted to lower 2θ angles (i.e., higher d-spacing values). The basal spacing values of the clays for the LDPE composites with 2 and 10 wt % OMt loadings were estimated 3.49 and 3.39 nm, respectively, compared with the d-spacing of 2.51 nm of the OMt sample used as filler. This is indicative of an intercalated structure where the polymer chains are incorporated between the silicate layers, increasing their gallery height but maintaining their layered stacking with alternating polymer/silicate layers.

From the earlier results, it becomes obvious that the use of the melt process method for the preparation of unmodified LPDE/organosilicate nanocomposites is more effective than the solution blend method, when CCl$_4$ is used as a solvent. Furthermore, the use of laponite, a particularly low aspect ratio silicate (20–30), favors the formation of exfoliated or partially exfoliated nanocomposite structure whereas silicates with high aspect ratio (100–200) like montmorillonite prefer intercalated nanostructure formation.

Typical TGA curves of pure LDPE and LDPE composites with 10 wt % organosilicates are shown in Figure 5. The thermal stability of the LDPE polymer is not significantly affected by the presence of 10 wt % organosilicate, because both the neat polymer and the various composite samples start to lose weight due to decomposition and desorption of organic fragments at similar temperatures (ca. at about 220°C). However, for weight loss between ca. 1 and 10% the composites are more stable compared with neat polymer with the melt mixing process providing the best results for both OLp and OMt. For higher weight loss the composite prepared with
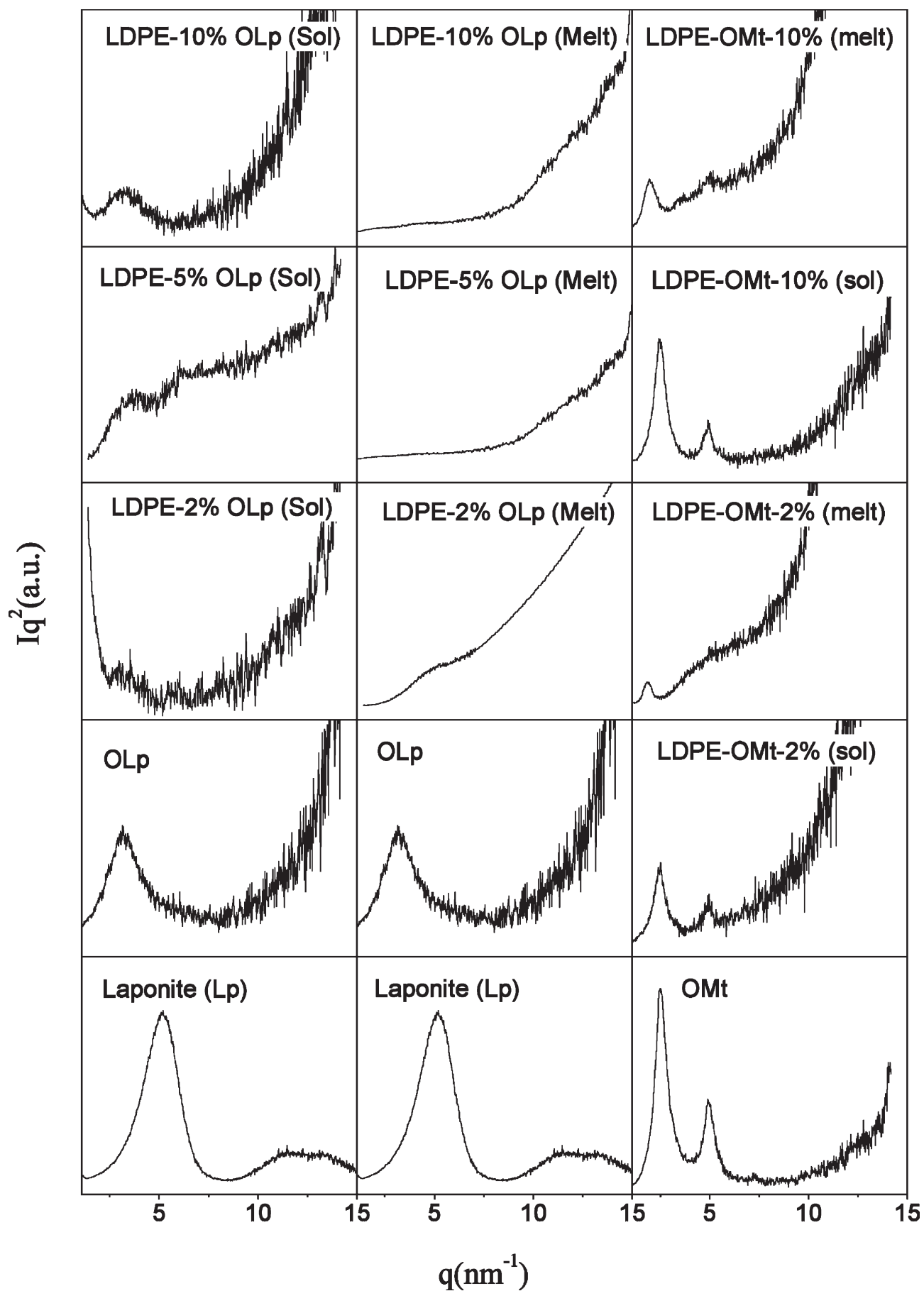
Figure 4 XRD patterns of various LDPE/organosilicate composites prepared by OLp and OMt in the form of $Iq^2 = f(q)$ where I is the intensity and $q = 4\pi \sin\theta/\lambda$.[13] The patterns of pristine laponite, OLp and OMt samples are also shown for direct comparison.

TABLE II
Basal Spacing (d$_{001}$) of Clays in the LDPE/Organosilicate Composites, Crystallization and Melting
Temperatures of Composites, % Residues at the End of Weight Loss, as Well as Elastic Modulus,
Tensile Stress at Break and Yield Strain Values for Neat Polymer and Composites

Material	d$_{001}$ (nm)	T_c (°C)	T_m (°C)	Residue at the end of weight loss (%)	Elastic modulus[b] (MPa)	Tensile stress at break[c] (MPa)	Yield strain[d] (%)
LDPE (neat)	–	100.2	115.2	0.2	288	6.0	10.2
LDPE-2% OLp (solution)	1.99	101.7	115.1	2.3	286	10.2	10.1
LDPE-5% OLp (solution)	1.99	102.1	114.7	4.1	295	12.2	8.8
LDPE-10% OLp (solution)	1.99	102.6	114.2	7.2	215	11.1	7.3
LDPE-2% OLp (melt)	NP[a]	102.1	114.5	4.3	269	12.7	9.4
LDPE-5% OLp (melt)	NP	102.4	114.5	4.5	305	14.4	9.9
LDPE-10% OLp (melt)	NP	102.6	114.7	7.9	345	11.6	10.8
LDPE-2% OMt (solution)	2.51	100.9	115.5	2.1	311	7.4	9.9
LDPE-10% OMt (solution)	2.51	100.9	115.4	7.0	350	19.6	8.9
LDPE-2% OMt (melt)	3.49	100.6	115.7	2.3	303	12.1	10.4
LDPE-10% OMt (melt)	3.39	100.9	115.5	8.9	423	17.5	9.9

[a] NP, no peak.
[b] Relative probable error 5%.
[c] Relative probable error 10%.
[d] Relative probable error 5%.

OMt and the solution blend method behaves similarly to that prepared with the same organosilicate and the melt process method. Furthermore, both these composites are more stable than the composites prepared with OLp using either method. The weight loss profile of these two latter composites becomes similar to that of the neat polymer. The better thermal stability (or the lower rate of weight loss with increasing temperature) of OMt nanocomposites compared with OLp nanocomposites could be attributed to increased barrier effects of the higher aspect ratio clay layers (in the case of montmorillonite) against oxygen diffusion through the polymer matrix.

The values of crystallization temperatures (T_c) and melting temperatures (T_m) during the second heating were obtained from the DSC melting endotherms and crystallization exotherms and are presented in Table II. For both the neat polymer and the LDPE composites, the melting started early and achieved a peak at about 114.2–115.7°C. Similar results have been published recently by Morawiec et al.[8] for the LDPE-OMt system.

With regard to the crystallization process, a gradual increase of T_c with increasing clay content from 100.2°C (for pristine LDPE) to 102.6°C (for LDPE-10 wt % OLp composites) was observed. Similar crystallization behaviour has been reported by Gopakumar et al.,[6] for PE or PE-g-MAn/organomontmorillonite composites. They observed that the crystallization peak temperature (T_c) of all composites was much higher ($\sim$ 5°C) than that of PE-g-MAn and PE. The observed increase of T_c with increasing clay content was attributed to the nucleation-controlled polymer crystallization, where the

presence of small silicate layers induces the formation of nuclei and crystals can start growing at higher temperature. The nucleating role of the low aspect ratio silicate which increases the crystallization temperature of PE-g-MA/organolaponite composites was underlined by Wang et al.[15] as well. In particular, crystallization temperature of composite was increased with silicate addition, but it was not changed further with silicate content increment.

In the case of the OMt-based composites, an increase in the crystallization temperature compared with that of the neat polymer was also observed (from
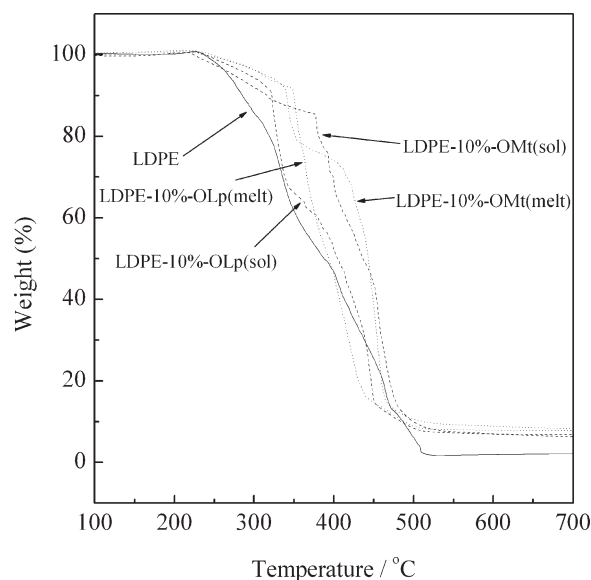

Figure 5 Characteristic TGA curves of neat LDPE polymer and LDPE composites with 10 wt % organolaponite (OLp) or OMt content.

100.2°C for the neat LDPE to 100.6–100.9°C for the LDPE- OMt composites), but it was marginal and not systematically affected by the clay loading (Table II). It seems that the montmorillonite clay platelets with relatively large aspect ratio do not induce the nucleation-controlled polymer crystallization because it was suggested for the "smaller" platelets of laponite.

Regarding the mechanical properties of the LDPE composites the average values of elastic modulus (E) as well as Yield strain and stress at the break values are given in Table II. Elastic modulus of the samples was determined from the slope of the initial elastic region in the stress-strain measurements. The value of E for the neat LDPE polymer was 288 MPa and similar values were estimated for the composites with 2 wt % organolaponite (1.5 × CEC-OLp) content irrespective of the preparation method, which means that the small addition of filler does not induce any reinforcing effects. As the OLp content increases the E values exhibit a significant differentiation depending on the preparation method. Particularly, in the case of 10 wt % OLp content, the value of E was increased by 30% for the exfoliated nanocomposite prepared by the melt process whereas for the conventional composite received by solution blending method the value of E decreased by 25%, when compared with the neat LDPE polymer. Interestingly, in the case of all OMt-based composites the value of E was higher than that for the neat polymer by ca. 5–8% for the composites with 2 wt % OMt and by ca. 20–45% for the composites with 10 wt % OMt. The highest increase (45%) was observed for the LDPE-10 wt % OMt, indicating that the intercalated or partially exfoliated structure with the relatively high aspect ratio montomorillonite clay platelets can induce superior mechanical properties to the LDPE polymer. Yield strain values indicate that with augmenting filler loading, the conventional LDPE/ OLp composites become less ductile in contrast to the probably exfoliated LDPE/OLp nanocomposites where a monotonous increase in yield strain was observed. Also in LDPE/OMt composites, the increment of the filler loading leads to decreased yield strain indicating loss in ductility. Stress at the break increment for both LDPE/OMt and LDPE/ OLp composites compared with neat LDPE suggests a decrease in brittleness. Especially for LDPE/OMt composites, the increment in filler loading from 2 to 10% makes them less brittle.

CONCLUSIONS

LDPE-based nanocomposites were prepared using unmodified LDPE polymer and two organomodified layered silicates (montmorillonite and synthetic laponite), using solution blend and melt compounding methods. XRD-patterns for the materials received using the melt process, revealed a nanocomposite structure, in contrast to that prepared by solution blending method, where mainly conventional composites were received. Using the melt process method in the case of laponite, we obtained probable exfoliated or partially exfoliated nanostructure, whereas in montmorillonite intercalated nanostructure was formed.

TG analysis results indicated that thermal stability increment was more prevalent for nanocomposites prepared using organomontmorillonite as filler, compared with those prepared with organolaponite. DSC measurements for LDPE/OLp nanocomposites revealed a gradual increase in crystallization temperatures (T_c) with increasing Laponite content, whereas for nanocomposites prepared using organomontmorillonite, T_c values remained constant and similar to that of neat LDPE, irrespectively the preparation method.

Tensile measurements evidenced an increase in elastic modulus of polymer with the addition of organosilicate. This increment was more prevalent for nanocomposites prepared by melt process using high aspect ratio silicate and high organosilicate content (i.e., 10 wt %), compared with conventional composites prepared by solution blend method.

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