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ORIGINAL CONTRIBUTIONS

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A brief survey on CLAYPEN and Nanocomposites based on unmodified PE and organo-pillared clays

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Abstract New clay fillers are mixed with linear low-density polyethylene at 160 °C for 10 min to obtain clay-PE nanocomposites (CLAYPEN) by melt intercalation. Raw montmorillonite (Mt) was pillared (PMt) with partially hydrolyzed Al and Fe salt solutions and further reacted with hexadecyl trimethylammonium bromide (OPMt). For comparison, the hexadecyl trimethylammonium-montmorillonite (OMt) was prepared as a reference material. PE is not intercalated by organoclay. In investigating the pillared clay-PE nanocomposites, XRD is not an appropriate indicator of intercalation of PE, which penetrates into the mesoporous OPMt as shown by TEM. All the nanocomposites have higher Young modulus values than the pristine PE. The best compromise between the other mechanical properties (tensile strength and elongation at break) is obtained with the OPMt-PE nanocomposite. Cone-calorimeter study shows that peak heat release rate value of PE decreases substantially (34%) on addition of 5 phr of this novel OPMt filler.

Keywords Organo-pillared clay · LLDPE · Nanocomposite · Mechanical properties · Cone calorimeter · Fire retardant properties

Importance of nanoclay fillers in clay-polymer nanocomposites

Understanding the clay-polymer interactions has been stressed for a long time [1]. Nevertheless, clays have been recognized only very recently as important nanoparticle fillers of different polymers leading to a new class of materials, called nanocomposites, which has many applications in high-tech industries [2–4]. Clay particles are often added to the polymer to improve the toughness and strength, to increase the thermal properties, and to enhance the conductivity of the material obtained. Also, some barrier properties can be expected, regarding the pristine polymer. Clay-polymer nanocomposites have received a great deal of attention, not only because of their potential industrial applications, but also from their fundamental point of view. However, the knowledge of the unmodified (and/or modified) clay mineral properties has to be taken more into consideration in future research on polymer behavior at the clay interface.

Composites, with immiscible phases leading to microcomposites, are generally defined as nanocomposites when the dispersed phase has at least one dimension in the nanometer range, and when specific or improved properties result from the mixture, compared to those of the starting components. Each phase (or both phases) can be amorphous, partially crystalline or crystalline. Komarneni [5] has described many categories of nanocomposites including the "intercalation-type bidimensional nanocomposites". This later category is related to intercalated organic or inorganic species in bidimensional materials such as clay minerals or graphite. Alexandre and Dubois [6] distinguish three types of nanocomposites according to the number of dimensions of the filler, which is at the nanometric scale. Consequently, a clay-polymer nanocomposite is characterized as 1-dimensional (as for smectites), and even the clay mineral is a well-known bidimensional material. According the importance of the clay fillers in nanocomposite preparation, however, it is less confusing for clay scientists to classify the nanocomposites according the dimensionality of the fillers. Then, a dispersed clay mineral which has a 2-D structure and at least one (like montmorillonite) or more (like laponite) dimension at the nanometric scale leads to a 2-D nanocomposite.

Introduction

State of the art on nanocomposites based on PE and nanoclay fillers

Polyethylene (PE) is one of the most commercially used polymer, ~44 million metric tons/year are consumed worldwide [7], in many industrial applications (mostly in the film market). This is due to its low specific weight and cost, high chemical resistance and mechanical flexibility. However, the synthesis of polyolefins-clay nanocomposite remains a scientific challenge. Since the first patents on clay-PE mixtures published more than 25 years ago [8, 9], the studies on clay-PE nanocomposites (CLAYPEN) have been very few, compared to the huge literature on nanocomposites obtained from clay minerals and other particularly polar polymers. In most of these papers published, high density polyethylene (HDPE) has been used, and very scarce experiments are carried out using the linear low density polyethylene (LLDPE). Sometimes, the variety of PE used is not at all reported.

Effectively, non-polar and uncharged polyolefins, as PE, are difficult to intercalate in the interlayer space of hydrophilic swelling clays without chemical modification of one of the two pristine components.

The first paper on clay-PE mixture has been published by Jeon et al. [10]. It is the only paper which uses direct addition of polymer in appropriate solvents. These authors add a solution of HDPE in xylene and benzonitrile used as co-solvents to 20 wt.% of Na^+ Mt initially exchanged with decyl ammonium ions. XRD and TEM results of the composite system show that the basal spacing increases by about 0.1 nm and that the organo clay mineral layers are stacked in thick aggregates. The authors claim that lamellar HDPE crystals are parallel to these clay stacks and they expected improving mechanical properties of this HDPE-organo modified clay. Bergman et al. [11] have published the first synthesis of CLAYPEN by in-situ polymerization of ethylene in the clay mineral. They first intercalate a synthetic organo-fluorohectorite by a cationic Pd complex as a catalyst. This intercalation increases the basal spacing of the tetradecyl ammonium fluorohectorite, enough to support the idea that this spacing accommodates the Pd complex, but the explanation of this mechanism remains unknown. Exposition of this Pd-loaded compound to ethylene gas (reaction followed in time by XRD) leads to a delaminated nanocomposite, confirmed by the complete absence of diffraction peak after 24 h. Heinemann et al. [12] have reported that in-situ polymerization of ethylene in organo-modified synthetic hectorite and purified bentonite with incorporated methylaluminoxane (MAO)-activated transition-metal catalyst leads to an exfoliated nanocomposite. These authors show that this in-situ method is more effective in nanocomposite formation than melt intercalation which leads to inhomogeneous dispersion of the clay, as shown by TEM. However, the mechanical properties presented in this paper do not support clearly the conclusion that composites are obtained by melt compounding of clay with PE, and nanocomposites are obtained by in-situ polymerization. Jin et al. [13] have also used an in-situ exfoliation method. Ethylene polymerization is performed on a Na^+ montmorillonite (Cloisite) and on the corresponding organo-montmorillonite both pretreated with a Ti based Ziegler-Natta catalyst. Exfoliated nanocomposite (absence of XRD peaks) is obtained with the organo-modified clay in the presence of the catalyst. The TEM image shows disordered, but well dispersed clay particles in the PE matrix. However, a further melting process of this nanocomposite in PE leads to stacking of thicker particles. The authors stress that although the technology of various thermoplastic and thermoset polymer systems is well known, the development of the clay-polyolefin systems is still at a very early stage. The in-situ ethylene polymerization in non-organo clays have been reported [14]. In the so-called ‘‘polymerization-filling technique’’, MAO is fixed to a montmorillonite (Swy 1) and to Laponite RD, both semi purified by decantation technique. A Ti-based catalyst is added in a reactor to the MAO pretreated filler under ethylene pressure flow. In some experiments, H_2 flow is added as transfer agent for ethylene polymerization. The mechanical properties are strongly dependant of the presence or absence of hydrogen gas, but also of the nature of the clay. Lower molecular weight PE is obtained by H_2 addition and the resulting Laponite-PE nanocomposite has a partial exfoliated structure with irregular distribution of interlayer spaces as confirmed by XRD (moderate slope of the curve in small angle area) and by TEM (where discrete domains of exfoliated clay mineral particles are scattered in PE matrix). More recently, in-situ polymerization of ethylene monomer has been reported in a one-pot synthesis [15]. The organo-montmorillonite, the monomer, the Zr based catalyst and the MAO co-catalyst are directly mixed together. In other cases, the organoclay is first mixed with the MAO co-catalyst and then with the catalyst. The mixture is then in situ blended with ethylene to initiate its polymerization. The authors [15] have investigated the crystallization behavior of the CLAYPEN obtained by DSC and NMR, in addition to the classical tools used as XRD and TEM. Small amounts of clay filler lead to a homogeneous and good dispersion of clay in PE. Increasing the clay amount results in a faster rate of PE crystallization; however, the rigidity of the nanocomposite tends to increase too, probably with the formation of a nematic phase.

This in-situ polymerization of ethylene is very useful at the laboratory scale, but it is less interesting at the industrial level, where the melt blending is the most convenient method. The preparation of CLAYPEN by melt intercalation method started after 2000 and is by far the most reported [6, 12, 16–26]. A recent review from preparation to processing on polymer/layered silicate nanocomposites with different polymers including PE has been published by Ray and Okamoto [27].

Depending on the method of preparation used, intercalated and/or exfoliated clay-PE structures are reported in the literature. However, organo-modified clay-PE nanocomposites obtained by melt extrusion frequently show a more complex structure, with the clay mineral partially exfoliated in individual layers and thick stacks of clay mineral layers dispersed in the PE matrix [16]. Ishida et al. [17], using different swelling agents in nanocomposites preparation, have noticed two possible reactions: (1) the clay mineral is exfoliated with PE in the presence of poly(dimethylsiloxane), and (2) the clay mineral is completely intercalated when different amounts of epoxy resin are added with PE while in the absence of epoxy resin PE does not intercalate in the clay mineral.

The clay mineral is generally modified with alkylammonium ions to facilitate interaction with PE, but this hydrophobic polyolefin can interact only if the clay mineral is treated by a long-chain surfactant such as octadecyl ammonium salts and when a certain level of grafting by maleic anhydride (MA) is performed on the polymer [18]. These authors have obtained at these conditions completely exfoliated CLAYPEN, but an intercalated nanocomposite has been prepared when nongrafted LLDPE is used with (C18) organo Mt. The exfoliated CLAYPEN has been studied by in-situ scattering upon deformation using synchrotron beams [19] to identify the mechanism responsible for the improvement of the mechanical properties. The rheological properties measured [20, 21] confirm the exfoliated state and show a strong interfacial adhesion during tensile deformation between PE and the exfoliated clay mineral. Wang et al. [22] have shown that it is possible to obtain purified Na^+ Mt-HDPE nanocomposites with reduced heat-release rate (by 32%) by adding the C16 surfactant as reactive compatibilizer. Su et al. [23] have noticed that the type of nanocomposites (intercalated or exfoliated) is not very important for some properties that are required like fire retardation. They have used two new organically modified clays (with oligomeric styrene and methacrylate), which are expected to have better thermal stability than the organoclays obtained by conventional ammonium salts. Zhang and Wilkie [24] have shown that both immiscible and intercalated structures occur for C18 organoclay-LDPE nanocomposites and that intercalation is improved in the presence of grafted MA on PE. A reduction in peak heat release rate of about 30–40% in all the cases (with or without MA) is observed. It is the first paper in which flammability properties of clay-LDPE nanocomposite are reported. Waché et al. [25] have studied the CLAYPEN preparation by melt extrusion, which is commonly used in oil drilling because of its barrier properties. The initial organoclay (Cloisite 15 A) shows three peaks corresponding, respectively, to 3.4, 2 and 1.24 nm. After melt intercalation of PE, there is a slight decrease of the first basal distance observed. This could be due to degradation of the organic agent, or the organic agent being desorbed from the interlamellar space, or its conformation changing with formation of kinks, as already observed in the literature, and the last hypothesis is that conditions of the process create osmotic pressure like it occurs in clay dispersion. However, increasing time of mixing seems to allow intercalation of PE. This result highlights the importance of the kinetic factor and that difficulty of intercalation is not due to thermodynamic factors. An original study on 3D hierarchical orientation of organoclay-grafted MA-PE has been carried out [26] and has shown two results: (1) the highly organised structures observed on a large scale are attributed to modified clay minerals, and (2) there is an orientational relationship between unmodified clay mineral and the polymer lamellae. Thus, orientation and dispersion are independent structural features, which must be simultaneously taken into consideration for the clay-PE nanocomposite structures. Shear forces during extrusion orient the LDPE lamellae at low volume fraction in the normal direction. This suggests that the nanocomposites obtained with clay-LDPE have some advantages over clay-HDPE nanocomposite.

Another method consists of a two-step preparation: a composite of clay and PE (with or without modification of each component) is first obtained as the masterbatch, and then this masterbatch, acting as a new nanofiller, is diluted by adding pure PE [28].

Smectites are the most used clay minerals in all these clay-PE nanocomposites. Three papers mention the use of other clay minerals, kaolinites [29, 30] and vermiculites [31], as fillers for PE.

Objective of this study

The study involves an attempt to obtain nanocomposites from clay-polymer mixtures prepared by melt intercalation of LLDPE and different modified clays. PE is chosen to develop a halogen-free fire retardant (HFFR) CLAY-PEN. These modified clays are a classical organo-clay and two novel types of modified clays, namely pillared clay and organo-pillared clay. The latter is used for the first time in nanocomposite preparation [32]. All modified clay samples are prepared from unpurified bentonite. The advantage of the pillaring process [33] is that the presence of inorganic pillars avoids the collapse of the clay mineral structure at the melting temperature and allows the melted PE to enter into the mesopores of the pillared clay.

Our objective is to improve the thermal and firing properties of the PE by adding small amounts of the modified clays. The aim is to use these nanocomposites in the field of low-voltage power cables.

Materials and methods

Starting materials

a. Polymer: a commercial (LLN 1004 YB) grade Polyethylene (PE) was supplied by Exxon Mobil. It is a linear low-density PE, with a density of 0.918 g/cm^3 and a melt flow index (MFI) of about 2.8 g/10 min. This polymer was used without further grafting.
b. Clay: a Wyoming (SPV) montmorillonite (Mt) purchased from Comptoir des Minéraux et des Matières Premières, France, was used as a starting clay mineral without any purification.
c. Modified clay fillers: three differently modified clays namely organo-montmorillonite (OMt), pillared montmorillonite (PMt) and organo-pillared montmorillonite (OPMt) were prepared as follows:
   - OMt: a 0.01 M solution of the hexadecyl trimethylammonium bromide (HDTMAB) is added dropwise to the 2% Mt dispersion, with vigorous stirring. The amount of the added surfactant was equivalent to the cation exchange capacity (CEC) of the clay. The clay product was then filtered and washed with de-ionized water till it was free from halide ions. The organoclay was then lyophilized (freeze-dried). The advantage of this freeze-drying technique is to obtain a material with aerated fine particle size.
   - PMt: a detailed method of preparation of PMt has already been described elsewhere [34]. To the 2% Mt dispersion previously prepared, oligomeric Al-Fe solutions with a molar ratio $Fe/Fe+Al=0.5$ were added simultaneously with vigorous stirring. The metal/clay ratio was 30 meq/g. The clay dispersion obtained was centrifuged and washed with de-ionized water till it was chloride free. The intercalated clay obtained powder was lyophilized. After lyophilization, the clay powder was heated at 300°C for 3 h to get the pillared material. Its CEC measured by $(EDA)_2Cu\ Cl_2$ [35] exchange was 49 meq/g of clay (calcined at 1,000 °C), which corresponds to about the half of the CEC of the starting raw clay (92 meq/g of calcined clay).
   - OPMt: a 0.01 M of HDTMAB solution was added with vigorous stirring to a dispersion of the PMt dispersed in de-ionized water. The amount of the added surfactant was half to that of the initial CEC of the clay. The clay was then washed and centrifuged till it was free from halide ions. The product thus obtained was also freeze-dried.

Nanocomposite preparation

Nanocomposites were prepared by melt intercalation as described by Vaia et al. [36]. It has been established as the most interesting method used for industrial purpose. It consists to mix 5 phr (parts per hundred resin) of solid modified clays and PE above the softening point of this polymer. In compounding applications, phr are commonly used for blend formulations, and give the addition of the second compound to 100 parts of resin (polymer matrix). To transform phr in w/w%, each weight part of the components is divided by the total amount (i.e. 5:105 and 100/105). This leads to the ratio of 4.8/95.2 w/wt%. The components were mixed for 10 min, at 160 °C. Experiments were also performed with 10 phr. A Brabender internal mixer with a chamber size of 300 cm^3 was used and the roller blades' speed was 30 rpm. The blend was then passed through a two-rolled mixer at the same temperature. In order to characterize the nanocomposites by the different techniques, the samples were prepared in platy shapes of various thicknesses using a hot press under 100 bar at 160 °C.

Characterization

XRD is the most commonly used technique to characterize nanocomposite structures. The XRD patterns of the clays and the nanocomposites were recorded on the Philips instrument (Generator Philips PW 1830, goniometer PW 3020) using Cu Kα radiation by reflection method. The clays were used in powder form and nanocomposites as 1 mm thick plates. This technique gives information on the long-range ordering within the particles. The intensity of the 001 reflection depends also on the degree of orientation of the particles in the sample. When all the unit layers are totally disoriented, the 001 reflection disappears.

TEM is also considered as a powerful technique to observe the clay mineral layers and particles forming the clay-PE nanocomposites. The preparation of the sample is delicate to perform. The major disadvantage of this technique is that it gives only a local observation not necessarily representative of the whole sample. TEM study of the clay and of the nanocomposites was performed on a Philips CM20 type electron microscope operating at 200 kV. For the nanocomposites, ultra-thin samples were obtained by cutting a 7-mm plastic plate under liquid nitrogen temperature, and the sample was deposited on a copper grid.

Mechanical properties (Tensile strength Ts, Elongation at break Eb and Young modulus YM) were studied on a Z01 Tensile machine from Zwick. Tests were performed at a speed of 100 mm/min on dumbbells H2, which are mainly used in cable industry to measure the mechanical properties as described in European Standard NF EN 60811-1-1 (April 1996).

The flame retardant properties were studied with a cone calorimeter. This technique provides important information on fire properties and formation of nanocomposites. The parameters measured were heat release rate (HRR) and smoke release under thermal conditions. Specimens (100×100×3 mm dimensions) were burned in ambient air conditions while being subjected to an external irradiance from a cone heater. Due to the low amount of nanoclays incorporated in the polymer matrix, the heat-flux irradiance was established at 30 kW/m^2. Measurements of oxygen concentration and exhaust flow rates were taken continuously. The cone data reported are the averages of two replicated experiments.

TGA was performed using a TA Instruments Q500. The TGA scans were recorded at a rate of 10 °C/min from room temperature to 600 °C, under air flow (75 ml/min). The weight loss was followed in order to evaluate the delay in degradation of the clay-PE nanocomposite compared to the pristine polymer matrix.

Results

OMt and OMt-PE nanocomposites

The XRD of the OMt having d_{001} at 1.8 nm (Fig. 1) is indicative of the formation of bilayers of the surfactant chains in the interlayer space, where two surfactant chains lie parallel to each other, according to the conventional models proposed [37]. The basal spacing is typical of the organoclay prepared from a surfactant having an alkyl chain with 16 carbon atoms and when the amount of the added surfactant is equivalent to the CEC of the clay mineral. The OMt is well organized, having clay particles composed of several layers, as shown by the narrow peak of Fig. 1. According to the Debye Scherrer formulae, about six layers are stacked per particle.

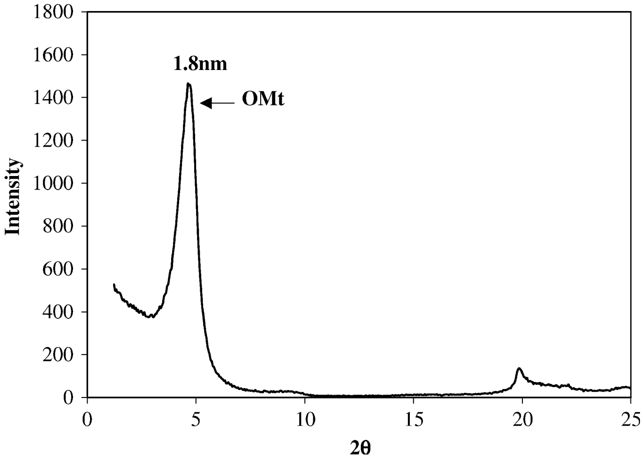


Fig. 1 XRD patterns of the lyophilized OMt powder

As noted in the introduction, the usual hydrophilic clay is not compatible with the unpolar PE, and the short hexadecyl chain of the surfactant is not long enough to allow intercalation of the polymer, even if the clay is made organophilic [24]. Intercalation of the polymer chains between these layers does not occur during nanocomposite preparation. This is confirmed by our results for the OMt sample where the peak at 1.8 nm remains unchanged for the OMt-PE nanocomposite, in agreement with the results of Wang et al. [18].

PMt and PMt-PE nanocomposites

The XRD pattern of the Al/Fe (initially 50%) PMt shows two reflections (Fig. 2), the first intense appears at

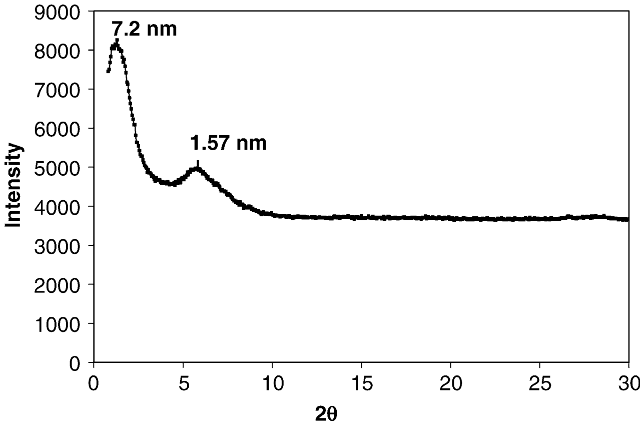


Fig. 2 XRD patterns of Al-Fe PMt (50%) oriented sample. The dispersion is deposited and dried on a glass slide, and the oriented film is heated (with its support) at 300 °C

a very low 2θ angle corresponding to a distance of 7.2 nm, while the second and less intense corresponds to the basal spacing of 1.57 nm of the pillared clay mineral [34, 38]. In comparing the XRD patterns (Fig. 2) and the TEM images (Fig. 3), we have already shown by image analysis of the TEM pictures [39] that the first reflection is not a diffraction peak but corresponds to a peak of correlation. The correlation length corresponds to 7 nm, which is the most probable dimension characteristic of both Fe oxide clusters generating mesopores of the same size (around 6–7 nm) and the particles (corresponding to a stack of a few pillared layers) alternating in the sample. These two different reflections appear only when an oriented sample is used (the uncalcined intercalated clay is deposited on a glass slide, air-dried and heated at 300 °C). While for the powder sample (the intercalated clay paste is dried by lyophilization and then heated at 300 °C), as the clay mineral layers attain a random orientation under this condition, the XRD powder pattern does not give any correlation or diffraction peaks (Fig. 4). Lyophilization already leads to a delaminated material where particles composed of very few layers are randomly oriented leading to the total absence of XRD reflections.

There is no change in the XRD spectra of the PMt-PE nanocomposites. The PE cannot enter the small space of 1.57 nm separating the layers in the PMt sample. Also, the XRD patterns do not change if the melted PE enters the mesopores because the distance between the particles (7 nm) is high enough.

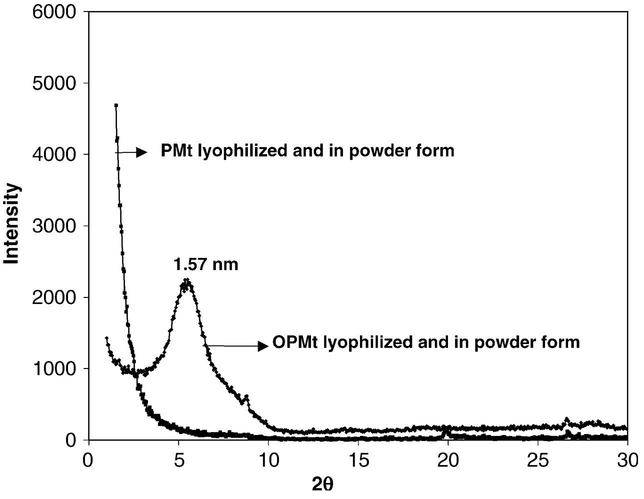


Fig. 4 XRD patterns of the lyophilized PMt and OPMt powder

OPMt and OPMt-PE nanocomposites

The XRD pattern of the lyophilized OPMt (in powder form) shows a basal spacing of 1.57 nm (Fig. 4), though the PMt has no peak under the same conditions. This basal spacing of the OPMt has the same value as the second peak obtained for the PMt on an oriented plate (Fig. 2). The appearance of this peak indicates that intercalation of the surfactant takes place in the OPMt and suggests that addition of the surfactant to the PMt orients again the pillared clay particles which are otherwise randomly oriented. However, the reflection (corresponding to correlation peak) at lower angle of 2θ does not appear furthermore, because the lyophilized pillared clay powder cannot be obtained as oriented film on a glass slide.

A comparison between OMt and OPMt XRD patterns shows that in the latter case, the distance (1.57 nm) is less than the distance obtained with OMt (1.8 nm) even though the same C16 surfactant is used for the two samples. This means that intercalation in OPMt do not lead to an intercalated bilayer by ionic exchange, but probably monolayers are intercalated in the pores between the lateral pillars. The TEM image of the OPMt (Fig. 5) shows an almost homogeneous distribution of

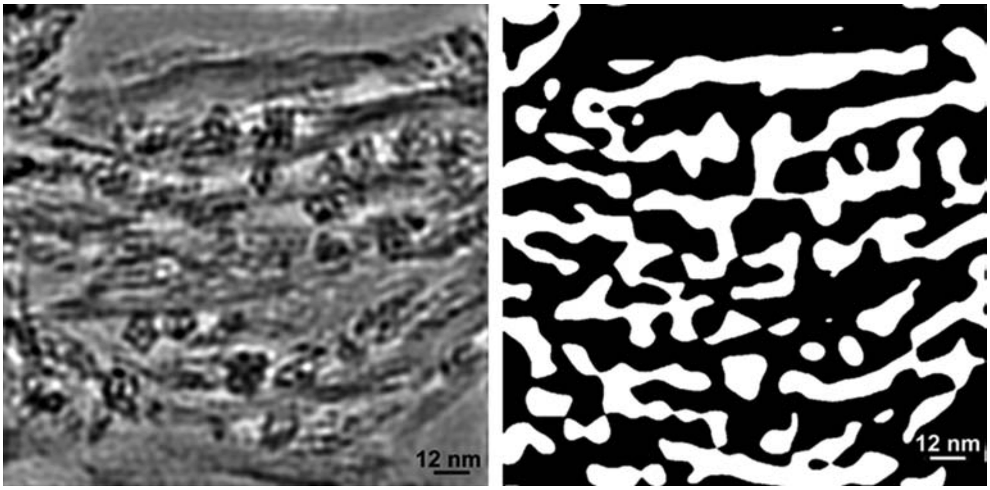


Fig. 3 HRTEM image analysis of the Al-Fe PMt (50%) (from [39])

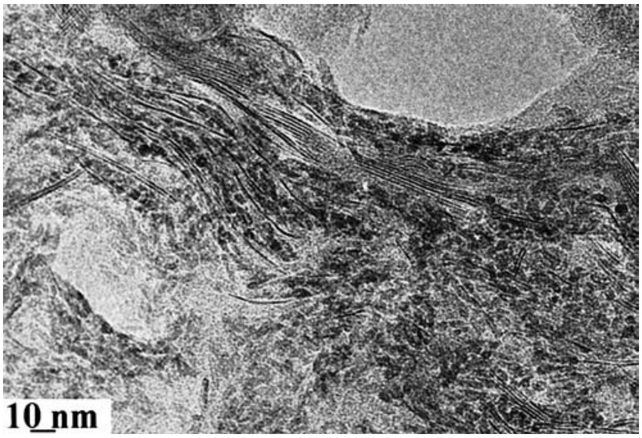


Fig. 5 TEM image of the OPMt at high magnification showing a homogeneous distribution of the Fe-oxide clusters within the clay matrix, and polydisperse clay particles

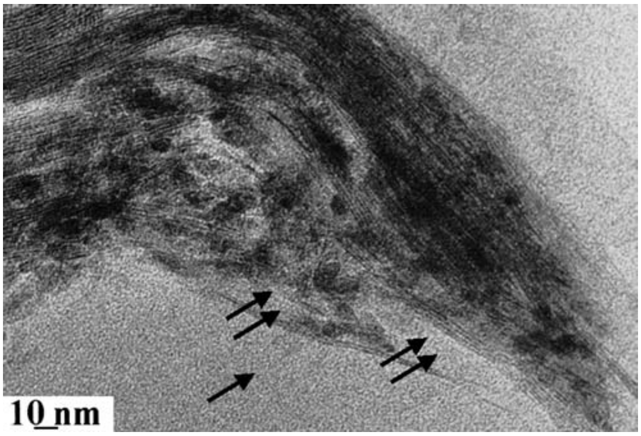


Fig. 7 TEM image of the OPMt-PE nanocomposite at high magnification showing the cohesion at the clay mineral/PE interface

the Fe oxide clusters within the clay matrix. The anisometric clay particles are rather oriented. However, a broad distribution of the number of layers per particle is observed, from individual layers to about ten layers. The distance observed between the layers confirms the distance (about 1.6 nm) already observed by XRD for PMt. This distance does not change, because the pillared clay has a rigid structure with no expandable layers, in contrast to what can occur with the organoclay.

In OPMt, the addition of surfactant at the interface of the mesopores promote entrance of the melted PE, and again without any effect on the XRD pattern.

TEM images of the OPMt-PE nanocomposite at low magnification (Fig. 6) confirm the homogeneous distribution of the clay in the polymer matrix, indicating that probably PE enters between the particles of the clay aggregates. The TEM image at high magnification (Fig. 7) clearly shows the interfacial contact between clay aggregate and PE to be continuous and showing good adhesion between the two constituents. There are no bubbles at the interface. PE appears in the image as a homogeneous grey texture (in the bulk, indicated by an arrow). The same grey color is shown in the mesopores between the particles within the aggregate (indicated by double arrows) and contrasts with the lighter grey color inside the interlamellar space where PE is absent.

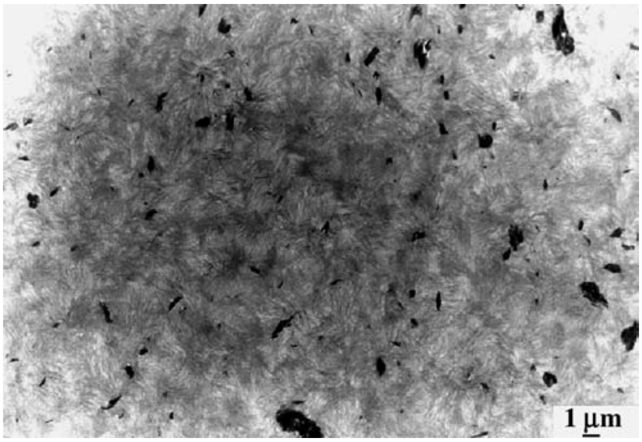


Fig. 6 TEM images of the OPMt-PE nanocomposite at low magnification

Mechanical properties of the nanocomposites

The tensile strength (TS), elongation at break (Eb) and Young modulus (YM) are presented in Table 1. Addition of the unmodified raw clay to the polymer decreases TS and Eb. Therefore, modification of the filler (or of the polymer) is necessary to obtain better mechanical properties of the nanocomposites.

Addition of all modified clays (with 5 and 10 phr) to the PE shows that the mechanical properties generally decrease compared to PE, except for the YM values which increase for all clay amounts, like it is expected, and as is usually shown in the literature. However, all mechanical properties of the nanocomposites with 5 phr

Table 1 Mechanical properties of PE and different clay-LLDPE nanocomposites

Composition	TS (Mpa)	Eb (%)	YM (Mpa)
PE	23.0 ± 1.0	866 ± 46	205 ± 29
PE + 10 phr OMt	15.4 ± 1.3	671 ± 40	236 ± 58
PE + 10 phr PMt	15.4 ± 0.5	687 ± 32	312 ± 104
PE + 10 phr OPMt	17.1 ± 1.5	703 ± 41	296 ± 65
PE + 5 phr OMt	20.9 ± 0.9	821 ± 94	259 ± 37
PE + 5 phr PMt	18.2 ± 0.7	699 ± 22	341 ± 65
PE + 5 phr OPMt	21.4 ± 1.2	796 ± 67	322 ± 33
PE + 5 phr Raw Mt	19.01 ± 1.48	704 ± 29	299 ± 44

TS tensile strength, *Eb* elongation at break, *YM* Young modulus of the clay are always higher than those with 10 phr of the filler. This indicates that a small amount of the modified clay leads probably to better dispersion within 10 min of mixing time. Comparing the results obtained with 5 phr of clay fillers shows that the mechanical properties (TS and Eb) of the nanocomposites obtained with the two organo-modified clays are less reduced compared to the pristine PE or to the nanocomposite obtained with 5 phr of unmodified raw clay as filler. The nanocomposite obtained with the pillared clay leads to lower TS and Eb values. The organotreatment of the fillers are responsible for these higher mechanical properties of the corresponding nanocomposites.

If we compare the mechanical properties of the nanocomposites obtained from the three modified fillers, for the same amount (5 phr) of modified clay, TS is the highest for the OPMt-PE nanocomposite, and Eb with standard deviation values, is similar for OPMt and OMt nanocomposites. YM is similar for OPMt and PMt nanocomposites. Thus, OPMt as filler shows the best compromise for the three mechanical properties of the corresponding nanocomposites that were measured.

Flame retardant and thermal properties of nanocomposites

The cone calorimeter is an instrument which measures the flame retardant properties, the heat release rate (HRR) and smoke release under thermal conditions. Only two papers have been published very recently on the flammability of clay-PE nanocomposites [22, 24]. The cone calorimeter results (Table 2, Fig. 8) show that incorporation of the modified clays in the polymer decreases the peak heat release rate (PHRR) considerably, especially with the two novel nanofillers. Nanocomposites with OMt and OPMt have high values of total smoke release as they contain large amounts of surfactant, which release smoke during burning. However, OPMt has less total smoke released than OMt. Both OMt and OPMt promote char formation during combustion. Some dripping has been noticed on PMt nanocomposites, which explains the highest weight loss and the lowest time of ignition obtained for this compound. No char formation has been observed, so polymer dripped on the frame and was not submitted to the fire.

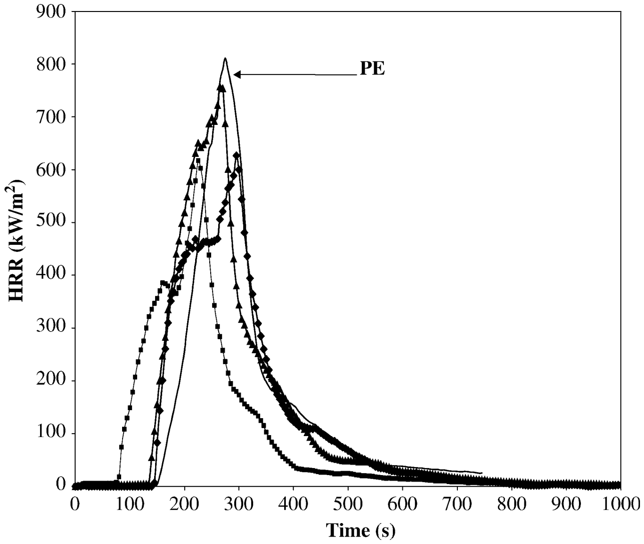


Fig. 8 Comparison of the HRR plots for pristine LLDPE and the clay-LLDPE nanocomposites: (*filled triangle*)OMt-PE; (*filled square*) PMt-PE and (*filled diamond*) OPMt-PE

Considering total heat release, no significant differences are observed between the different formulations although the OPMt has the smallest value. Adding 5 phr of the OPMt changes the kinetics of the burning of the polymer (Fig. 8). A decrease of 34% for OPMt-PE nanocomposite (compared to 20% obtained for OMt-PE) on PHRR shows significant changes of the kinetics of degradation with a lower rate of diffusion of the degradation products into the gas phase. This value is similar to the PHRR reduction obtained with a functionalised clay-LLDPE nanocomposite [24].

The OPMt-PE shows a weight loss (Fig. 9) with an initial delay of temperature of 35 °C compared to the pristine PE.

Discussion

Due to the big size of the clay aggregates formed by particles, the OMt is not dispersed homogeneously in the

Table 2 Cone calorimeter results of PE and different clay-LLDPE nanocomposites

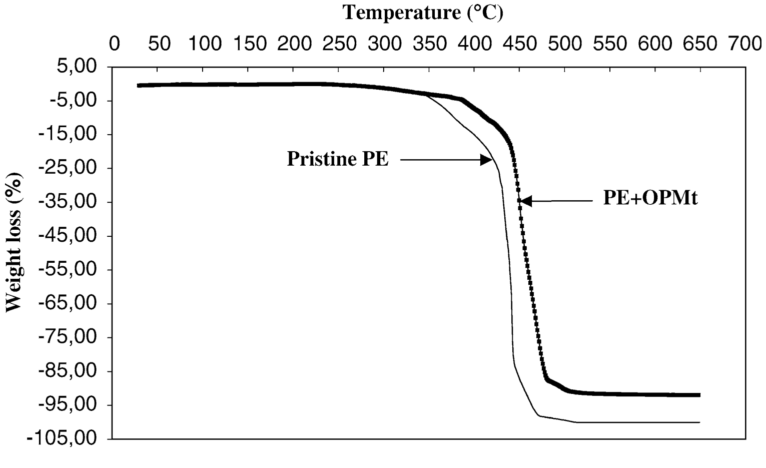
Composition nanocomposite	Weight loss (phr)	Time of ignition (s)	Total heat evolved (MJ/m^2)	Total smoke released	PHRR (kW/m^2)
PE	97.5	131	118.7	603	949.1
PE + 5 phr OMt	96.8	109	119.6	1,144.6[a]	763.2
PE + 5 phr PMt	92.0[b]	63	110.1	646.3	627.2
PE + 5 phr OPMt	93.7	120	109.6	1,009.7[a]	626.6

PHRR peak heat release rate

[a] Smoke released because of the presence of the organo compound

[b] Lowest value of weight loss because of dripping

Fig. 9 Weight loss of OPMt-PE nanocomposites compared to the weight loss of pristine PE



polymer matrix. The polymer chains cover the external surfaces of the clay aggregates. This poorly dispersed clay does not show any improved thermal properties but is without a significant loss of mechanical properties.

The PMt is composed of particles with a smaller number of layers (about 4) than in the case of OMt (about 6) and even less, in the case of the lyophilized sample. The small clay mineral particles separated by mesopores created by the iron oxide clusters are almost homogeneously distributed. The distance between the layers in the particles is smaller (1.57 nm) than for OMt (1.8 nm). Thus, the polymer cannot be intercalated between these layers which are not organophilic. The polymer again surrounds the aggregates and does not penetrate into the mesopores which are again lacking organophilicity. The nanocomposite prepared from PMt without organic treatment does not show improved thermal properties. For this material, except for the high YM value, the mechanical properties (TS and Eb) are the lowest, even less than the values obtained with the unmodified raw clay.

The OPMt filler has a partially re-ordered structure (as an XRD peak appears, Fig. 4), compared to the PMt filler, where organophilicity is generated by surfactant treatment. On nanocomposite preparation, these small particles disperse well in the polymer matrix. Some authors [40] have studied the structural change of LLDPE by SAXS during isothermal crystallization from the melt. Their data have shown that the polymer structure changes with time: immediately after cooling, the sample shows a correlation length around 7 nm as predicted by theory. This distance is in the same order of the correlation distance observed in the PMt samples (Fig. 2) used in the present study. The PE, attracted by the surfactant, can occupy the empty spaces offered by the organopillared clay. The previous authors show that the PE forms lamellar sheets of about 5 nm thickness. This distance again is smaller than the correlation distance observed in PMt (and probably in OPMt). This probably suggests facilitated diffusion of the PE in the mesopores created by pillaring, without changing the XRD pattern.

The OPMt-PE nanocomposite shows the best thermal properties compared to the nanocomposites prepared with the two other modified fillers. In the lyophilized OPMt sample, melted PE fills the empty mesopores created by the Fe-oxide clusters located between thin clay membranes as the interparticle distance is high enough (7 nm) and the surface of the mesopores are rendered organophilic due to the added surfactant. PE can enter these fixed confined spaces without any apparent changes of the XRD patterns. Unfortunately, it is very annoying that this generally used technique to follow the intercalation is not helpful in this case. Further experiments as neutron scattering using deuterated PE are needed to reveal the structure and location of the polymer in this nanocomposite. However, compared to the pristine PE, the improved thermal properties and less-degraded mechanical properties prove the formation of OPMt-PE nanocomposites.

Conclusion

Among the polyolefins, PE is the most interesting to study because, it is the cheaper halogen-free fire retardant polymer and because it is more workable than other polyolefins, polypropylene (PP) for example. The clay is used as filler without any purification as usually reported. This is easier to adapt to industrial processes with a potential cost reduction of materials.

As many authors have shown, organo treatment (up to C16 alkyl chains) of the clay is not enough to enable PE intercalation. However, the two-step treatment of the raw montmorillonite filler, i.e. pillaring followed by surfactant addition promotes intercalation of the PE in the permanent mesopores created between the organophilic nanoparticles (composed of about four layers).

This cannot be shown by XRD because the initial mesopore size of the filler is big enough to allow the entrance of the polymer chain without any apparent effect on the XRD patterns. However, in agreement with Su et al. [23], XRD and TEM alone are not enough to characterize the nanocomposite. Cone calorimeter offers an advantage since bulk material is tested rather than small pieces. The thermal properties of the melted LLDPE with OPMt-as filler are improved to evidence a nanocomposite formation.

In summary, the best result of thermal properties of clay-PE nanocomposites is obtained with OPMt as filler, according to the lowest values of PHRR (626.6 kW/m^2) and of total heat release (109.6 MJ/m^2). The delay in time of ignition (120 s) of PHRR is the less decreased. The char formation shows the barrier effect of this modified phyllosilicate in the release of volatile products.

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