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Effect of Ionic Liquid Modified Synthetic Layered Silicates on Thermal and Mechanical Properties of High Density Polyethylene Nanocomposites

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Abstract: In this work, synthetic layered silicates denoted Somasif ME-100 and Laponite® RD were modified with dialkyl imidazolium and alkyl phosphonium ionic liquids by cationic exchange reaction. In both cases, the phosphonium (P-ME, P-RD) or imidazolium ion (I-ME, I-RD)-treated micas and laponites display an excellent thermal stability compared to commonly used quaternary ammonium salts. To highlight the effect of these ionic liquids, the modified layered silicates were introduced in a high density polyethylene (HDPE). Thus, polyethylene nanocomposites filled with a low amount of nanoparticles (2 wt%) were prepared by twin screw extrusion. Then, transmission electronic microscopy (TEM) analysis has been used to investigate the effect of ILs on the different morphologies of these nanocomposites. In addition, the use or not of compatibilizer such as PEgMA (20% by weight) has been also studied on the mechanical behaviour of these polymer nanocomposites. Even though the thermal stability of polyethylene matrix remains unchanged, a good stiffness-thoughness compromise has been observed.

Keywords: cationic exchange; ionic liquid; mechanical properties; nanocomposite; polyethylene; synthetic layered silicates

Introduction

Although the clays are well known for a long time, academic and industrial research were recently focused on the use of organically modified clays as reinforcing agents in polymeric materials.[1–3] In fact, due to their nanometric dimensions, their high specific surface and their high aspect ratios, the addition of layered silicates in polymer matrices can lead to significant effects on the mechanical properties,[4,5] barrier performances[6,7] and flammability resistance.[8] Generally, montmorillonite or synthetic layered silicates (Somasif ME-100) are commonly used.[9,10] However, to obtain a good compatibility between polymer and clays during the preparation of nanocomposites, a surface treatment of pristine nanoclays is required.

For years, the alkyl ammonium salts are commonly used[11–13] but nevertheless, their low thermal stability results in a degradation of these salts at 180 °C due to the Hofmann elimination which limits their use in the nanocomposites processing at higher temperatures.[14,15] Thus, to increase the thermal stability of organically modified clays, the use of thermally stable ionic liquids (ILs) such as imidazolium and phosphonium cations can offer a new alternative to ammonium salts.[16–20] According to the literature, imidazolium and phosphonium ILs are known to have an excellent thermal stability thanks to aromatic ring and phosphore, respectively. However, few studies report the influence of the chemical nature of these surfactant agents on the final properties of the nanocomposites.

In this paper, the use of synthesized ionic liquids as intercalating agents of synthetic

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clays based on imidazolium and phosphonium cation has been studied in order to obtain thermally stable organically treated clays. Then, a high density polyethylene (HDPE) was selected to be blended with layered silicates treated with thermally stable ionic liquids. Finally, these modified clays with and without the presence of compatibilizing agent denoted PEgMA are incorporated to a HDPE matrix, and the final structure/properties relationships are also studied in detail.

Experimental Part

Materials

A synthetic fluorohectorite, denoted Somasif ME-100 was provided by CO-OP chemical Co., Japan. The Somasif ME-100 has a cation exchange capacity of 70 meq/100g and is described by the following formula $Na_{2x}Mg_{3.0\text{-}x}Si_4O_{10}(F_yOH_{1\text{-}y})_2$ (x = 0.15-0.5; y = 0.8-1.0). Then, a synthetic hectorite Laponite® RD with intercalated sodium was also selected. The Laponite® RD is a white powder and it's composed of platelets, with a thickness of 1 nm and a diameter of 25-30 nm. The Laponite® RD described by the following formula $Na_{0,65}[Al,Fe]_4Si_8O_{20}(OH)_4$ was purchased from Rockwood additives Ltd. In addition, its cation exchange capacity of 75 meq/100g is similar to Somasif ME-100 one. Triphenylphosphine (Aldrich, 95%), imidazole (Aldrich, 99.5%), iodooctadecyl (Aldrich, 95%), and all the solvents (toluene, sodium methanoate, pentane and acetonitrile) were supplied from Aldrich and used as received.

The polyethylene used in this study, called HDPE, is a high-density polyethylene from Basell, with the trade name Hostalen GF 4750 showing a melt flow index of 0.4. Polybond 3009 was chosen as maleic anhydride grafted HDPE from Chemtura, showing a melt flow index of 5 g/10 min.

Synthesis of Phosphonium and Imidazolium Salts

The synthesis of imidazolium and phosphonium ionic liquids was already reported in previous works.[20,21] The structure of salts was checked by ^1H NMR and ^{13}C NMR spectroscopy collected on a Bruker AC 250 (250 MHz) spectrometer.

Synthesis of Octadecyltriphenylphosphonium Salt

^{13}C NMR ($CDCl_3$): δ 14.00 ($\mathbf{C}H_3$); 22.67 ($\mathbf{C}H_2Me$); 23.2; 29.37-29.66; 30.24; 31.85 (P-$\mathbf{C}H_2$); 118.45; 130.43; 133.70; 135.15 (P-**C**).

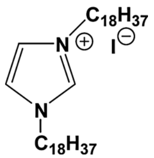
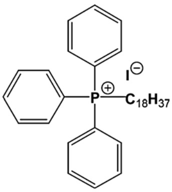
Synthesis of N-octadecyl-N′-Octadecylimidazolium Salt

^{13}C NMR ($CDCl_3$): δ 14.10 (2$\mathbf{C}H_3$); 22.67 (2$\mathbf{C}H_2Me$); 26.23; 28.97; 29.35-29.69; 30.24; 31.91 ($\mathbf{C}H_2$); 50.10; ($CH_2N{=}$); 50.32 ($\mathbf{C}H_2N{-}$); 121.69; 122.48 (=**C**N); 136.88 (N—**C**=N).

Organic Modification of Clays

The synthetic layered silicates (2 g, 1.9 meq) were dispersed in 400 mL of deionised water. The amount of surfactant added was about 2 CEC, based on the cation exchanged capacity (CEC = 75 meq/100 g) of the synthetic layered silicates used.[22] This dispersion was mixed and stirred vigorously at 80 °C for 6 h, followed by filtration and continuous washing at 80 °C with deionised water until no iodide ions were detected using an aqueous silver nitrate ($AgNO_3$) solution. The solvent was removed by evaporation *under vacuum*. The modified clays were then dried for 12 hours, at a suitable temperature (not greater than 80 °C). The chemical structure of imidazolium and phosphonium ions used for the exchange reactions are presented in Table 1. The following abbreviations were used to design the different synthetic layered silicates: A phosphonium-treated laponite denoted P-RD, a phosphonium-modified Somasif ME-100 denoted P-ME were obtained when octadecyltriphenylphosphonium iodide was used like surfactant. An imidazolium-modified laponite denoted I-RD, an imidazolium-treated Somasif ME-100 denoted I-ME were obtained when the N-octadecyl-N′-octadecylimidazolium iodide was used like intercalation agent.

Table 1.
Designation of synthesized ionic liquid modified synthetic layered silicates.

Designation	Intercalant
I-ME I-RD	
P-ME P-RD	

Processing and Characterization of the HDPE/Clay Nanocomposites

Nanocomposites were obtained by melt intercalation of modified montmorillonite into a high density polyethylene (2% by weight) by using a twin screw DSM micro-compounder. The mixture was sheared for about 3 min with a 100 rpm speed at 190 °C and injected in a 10 mL mould at 30 °C to obtain dumbbell-shaped specimens. Different nanocomposite samples were prepared by varying the surface treatment used to modify the lamellar silicates.

Thermogravimetric Analysis (TGA) of organically modified clay and composites were performed on a Q500 thermogravimetric analyser (TA instruments). The samples were heated from 30 to 800 °C at a rate of 20 K·min^{-1} under nitrogen flow.

Surface Energy of modified clays was determined with the sessile drop method on a GBX goniometer. From contact angles measurements performed with water and diiodomethane as test liquids on pressed modified clay discs, polar and dispersive components of surface energy by using Owens-Wendt theory were determined.[23]

Wide Angle X-ray Diffraction spectra *(WAXD)* were collected on a Bruker D8 Advance X-ray diffractometer at the diffractometry center H. Longchambon. A bent quartz monochromator was used to select the Cu Kα_1 radiation ($\lambda = 0.15406$ nm) and run under operating conditions of 45 mA and 33kV in Bragg-Brentano geometry. The angle range scanned is 1–10°2θ for the modified clays and 1–30°2θ for the nanocomposite materials.

Uniaxial Tensile measurements were carried out on a MTS 2/M electromechanical testing system at 22 ± 1 °C and 50 ± 5% relative humidity. Tensile tests were performed with a speed of 10 mm·min^{-1}.

The Transmission Electron Microscopy (TEM) was carried out at the Center of Microstructures (Université C. Bernard Lyon) on a Philips CM 120 field emission scanning electron microscope with an accelerating voltage of 80 kV. The samples were cut using an ultramicrotome equipped with a diamond knife, to obtain 60 nm thick ultrathin sections. Then, the sections were set on copper grids.

Results and Discussion

Characterization of Modified Clays

Thermal Stability of Modified Synthetic Layered Silicates

The characterization of imidazolium- and phosphonium-treated synthetic layered silicates was performed by ThermoGravimetric Analysis (TGA) in order to investigate the degradation mechanisms and the influence of the chemical nature of the organic cation on the thermal behaviour of these organically modified clays. Figure 1 represents the TGA and the derivative DTG of P-ME and I-ME while the imidazolium- and the phosphonium-treated laponite RD I-RD and P-RD are reported in Figure 2.

After cationic exchange with the imidazolium and phosphonium salts, the thermal degradation of modified lamellar silicates is similar as one observed for organically treated montmorillonites in a previous study.[24] In fact, two organic species populations have been identified: i) the physically adsorbed species onto the clay surface which are degraded between 300 °C and 400 °C and ii) the interlacted species which are situated in the clay galleries and where the degradation

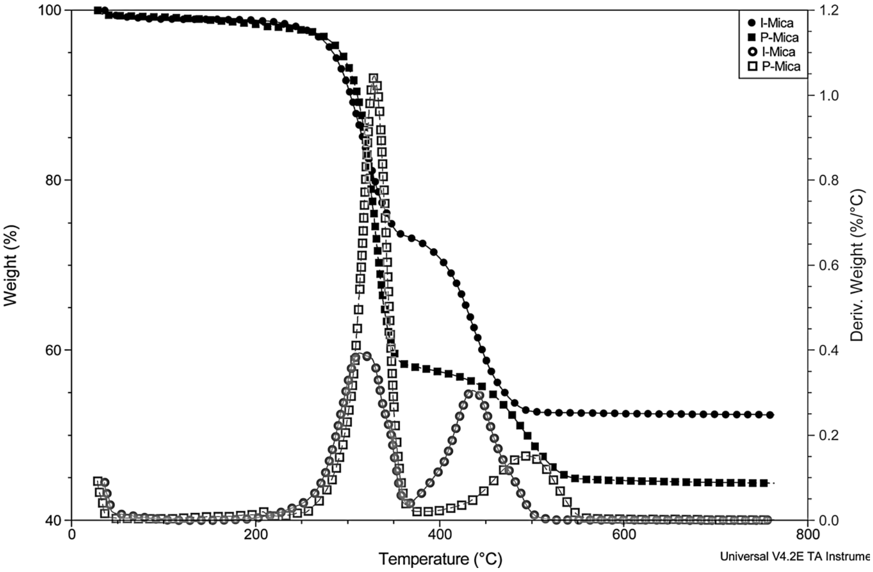


Figure 1.
Weight loss and weight loss derivative as a function of temperature (TGA, DTG) of the imidazolium- and phosphonium-treated mica (I-ME and P-ME) (heating rate: 20 K·min^{-1}, nitrogen atmosphere).

temperatures are between 400 °C and 500 °C. Whatever the chemical nature of surfactant agents (imidazolium or phosphonium), their decomposition temperature clearly exceeds 320°C. These results are in agreement with various studies reported in the literature and highlight the better thermal stability of these ionic liquids compared to commonly used

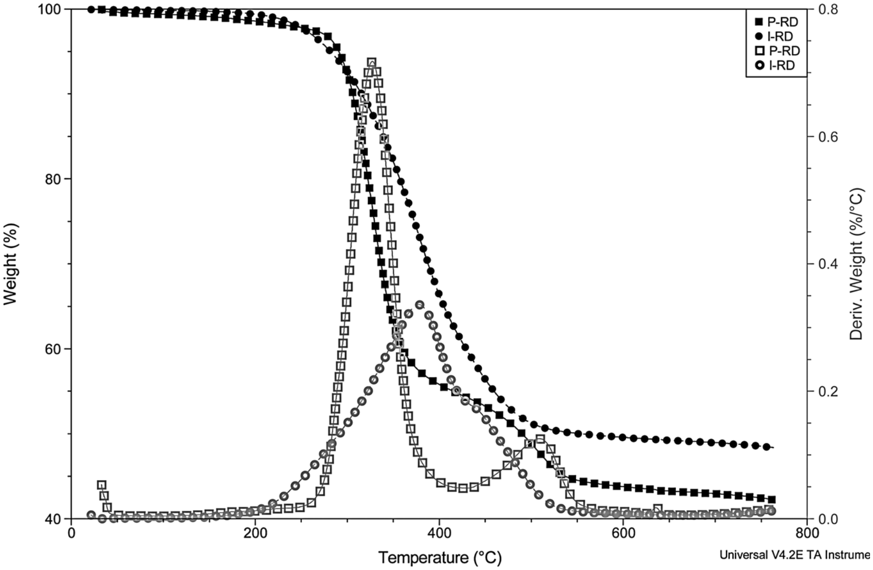


Figure 2.
Weight loss and weight loss derivative as a function of temperature (TGA, DTG) of the imidazolium- and phosphonium-treated laponite (I-RD and P-RD) (heating rate: 20 K·min^{-1}, nitrogen atmosphere).

ammonium salts.[24–25] Nevertheless, the phosphonium IL has a better thermal stability than the imidazolium IL. Indeed, concerning the well intercalated species between clay layers, the use of phosphonium salt causes a shift measured at 60 °C at higher temperatures (500 °C instead of 440 °C) of the degradation peak.

In the case of P-RD, no difference is observed (330 °C for physisorbed species and 510 °C for intercalated ones). Synthetic clays (Mica or Laponite® RD) are modified in the same way by the phosphonium salt. In the opposite, a difference is observed for the imidazolium-treated Laponite® RD. In Figure 2, a main and large peak is observed at 380 °C with the presence of a shoulder at 440 °C. This difference can be explained from the fact that clay has a different geometry and the negative charges are at the surface.

In conclusion, the organic treatment of synthetic clays is successful and is similar to the results obtained for ionic liquid modified montmorillonites in previous study.[20,24] In addition, these new synthesized nanoclays have excellent thermal stability which allows their use in the processing of the nanocomposites at high temperature.[26]

Structural Analysis by WAXD

The cationic exchange is clearly detectable by X-ray diffraction as shown in Figure 3.

Before surface treatment, the basal spacing of the sodic laponite is 1.4 nm, and 1.2 nm for the pristine mica ME-100 which corresponds to the d-spacing of these synthetic clays reported in literature.[27,28] After organic treatment in water by the phosphonium ionic liquid, the P-ME displays a (001) diffraction peak at 2.30°2θ,

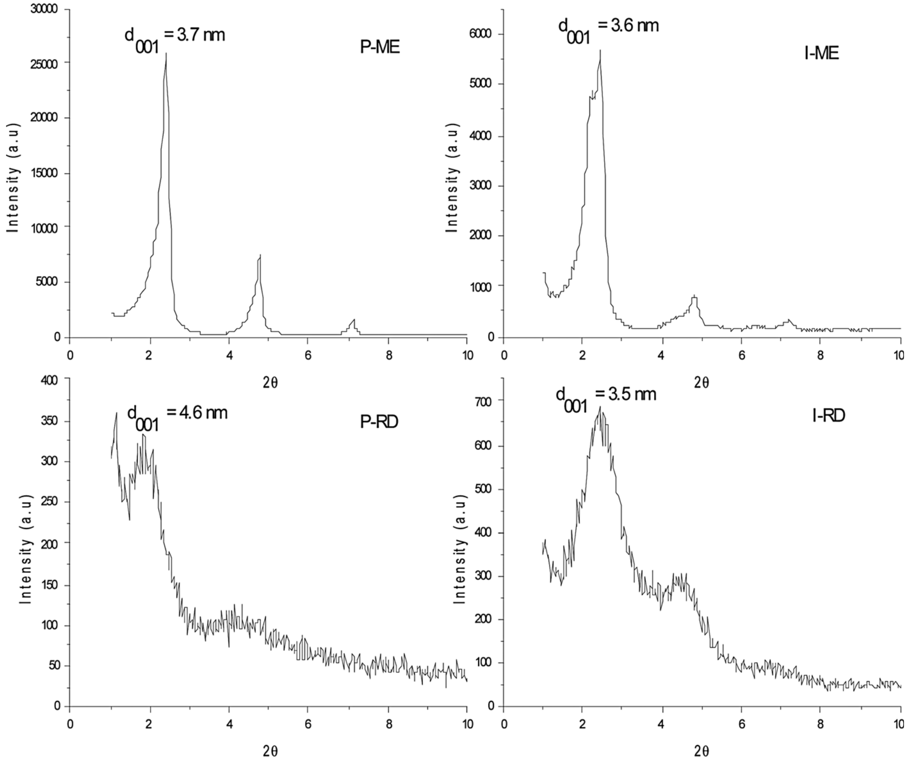


Figure 3.
X-Ray diffraction spectra of ionic liquid modified mica somasif ME-100 and laponite RD: (a) P-ME; (b) I-ME; (c) P-RD; (d) I-RD.

corresponding to an interlayer distance of 3.7 nm while for phosphonium-treated laponite (P-RD), an intercalation distance of 4.6 nm is obtained. These values could be explained by the swelling of layered silicates due to steric volume of the three benzyl rings and the long alkyl chain (C_{18}).

In the case of I-ME and I-RD, the diffraction peaks are situated at 2.35°2θ which corresponds to an interlayer distance of 3.6 nm. These values are characteristics of a paraffinic conformation with trans-trans positions of the alkyl chains. In both cases, the cationic exchange leads to an excellent intercalation of the ionic liquid between basal spacing combined with large interlayer distances (> 3.7 nm) which can allow the intercalation of polymer chains in the clay layers during the preparation of nanocomposites. Compared to ammonium-treated montmorillonites, such as MMT-DMBT (MMT modified with dimethyl benzyl tallow quaternary ammonium) or MMT-DMDT (MMT treated with dimethyl ditallow quaternary ammonium), the interlayer distance values obtained here are higher (3.0 nm for MMT-DMDT and 1.9 nm for MMT-DMBT).[24] Müller et al have also demonstrated that the use of ammonium salts such as hexadecylammonium (HDTA) or octadecylammonium salts in the cation exchange of laponite leads at basal spacings between 2.0 and 2.3 nm which corresponds to a pseudotrimolecular layer of surfactant.[29,30] The authors have also highlighted that high-charged laponite induces an interlayer distance of about 3.0 nm.[31]

Surface Energies of Modified Clays

To evaluate the possible interactions between the organically modified lamellar silicates and polyethylene matrix, the contact angles and surface energy determined by the sessile drop method on pressed powder discs are collected in Table 2.

In both cases, the use of ionic liquids based on phosphonium and imidazolium ions make the synthetic clays (Mica, Laponite) more hydrophobic with a surface energy similar to the surface energy of a polyolefin matrix.[32] In addition, the polar components are very low (0,9–4.6 $\mathrm{mN \cdot m^{-1}}$) which is an evidence that the hydroxyl groups are well covered by the organic chains. In fact, the steric hindrance of imidazolium and phosphonium cations functionalized by benzyl groups and long alkyl chains leads to an efficient screening of the hydrophilic surface of lamellar silicates. However, a slight difference is observed between the Laponite® and mica in terms of surface energy. Indeed, a stronger hydrophobic character is obtained for P-ME and I-ME which can be explained by a larger presence of hydroxyl groups onto the Laponite® surface.

In conclusion, the relevant choice of the surfactant agents *i.e* its chemical nature plays a key role on the good or poor affinity of modified clays with in the polymer matrix.

Characterization of HDPE/Treated Synthetic Clays Nanocomposites

Morphology of the PE/Clays Nanocomposites

The Figure 4 shows the X-ray spectra performed on the nanocomposites filled

Table 2.
Determination of polar and dispersive components of the surface energy on pristine and on exchanged lamellar silicates from contact angles with water and diiodomethane (determination on pressed clays powders).

Mica/Laponite RD	Θ_{water} (°)	Θ_{CH2I2} (°)	γ polar ($\mathrm{mN \cdot m^{-1}}$)	γ dispersive ($\mathrm{mN \cdot m^{-1}}$)	γ total ($\mathrm{mN \cdot m^{-1}}$)
RD	22.9 ± 0.9	33.6 ± 0.8	30.5	42.7	73.2
I-RD	79.2 ± 0.2	47.5 ± 0.7	4.6	35.7	40.3
P-RD	80.9 ± 0.2	44.1 ± 0.7	3.6	37.6	41.2
I-ME	90.1 ± 0.1	50.2 ± 0.6	3.3	34.1	37.4
P-ME	92.2 ± 0.1	46.2 ± 0.7	0.9	36.4	37.3

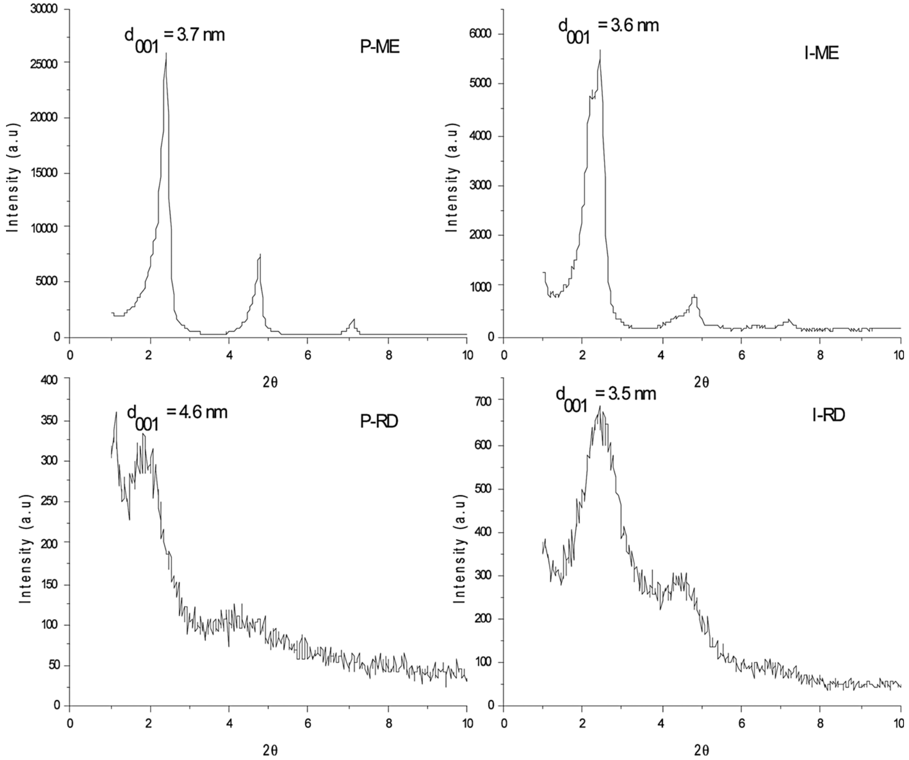


Figure 4.

X-Ray diffraction spectra of nanocomposites based on polyethylene matrix filled with 2 wt% of phosphonium and imidazolium modified mica somasif ME-100 (PE-(P-ME), PE-(I-ME)); phosphonium and imidazolium treated Laponite® RD (PE-(P-RD), PE-(I-RD)).

with the phosphonium and imidazolium modified clays (2 wt%).

The diffraction peaks corresponding to the interlayer distance are located at the same 2θ angle measured for the imidazolium and phosphonium modified synthetic clays (Figure 3). In fact, the nanocomposite based on phosphonium- and imidazolium-modified mica denoted PE-(P-ME) and PE-(I-ME) display a peak at 2.3–2.4°2θ, corresponding to interlayer distances of 3.7–3.8 nm. The same observations were made in the case of PE-(P-RD), PE-(I-RD) nanocomposites. In conclusion, based on the results of the X-Ray diffraction, it seems that the PE chains did not enter in the intergallery spacing when melt intercalation is used to process thermoplastic polymer (TP)-based nanocomposites.

Nevertheless, the distribution and dispersion of synthetic clays in polyethylene matrix were analyzed by transmission electronic microscopy on the nanocomposites processed with 2 wt% of only P-ME and P-RD. TEM micrographs are reported in Figure 5.

When PE/clays nanocomposites are prepared with phosphonium ionic liquids as intercalating agent of layered silicates (Mica), the morphology is more uniform than the modified laponite one and the TEM micrographs highlight a good level of dispersion of clay layers in the form of isolated layers, despite the presence of small tactoïds. Compared to a previous study,[24] the dispersion of mica in the high density polyethylene matrix is similar to the distribution of the phosphonium- and imidazolium-treated montmorillonites. In the opposite, the surface treatment of the laponite leads to an aggregation of the nanoclays. These results can be explained

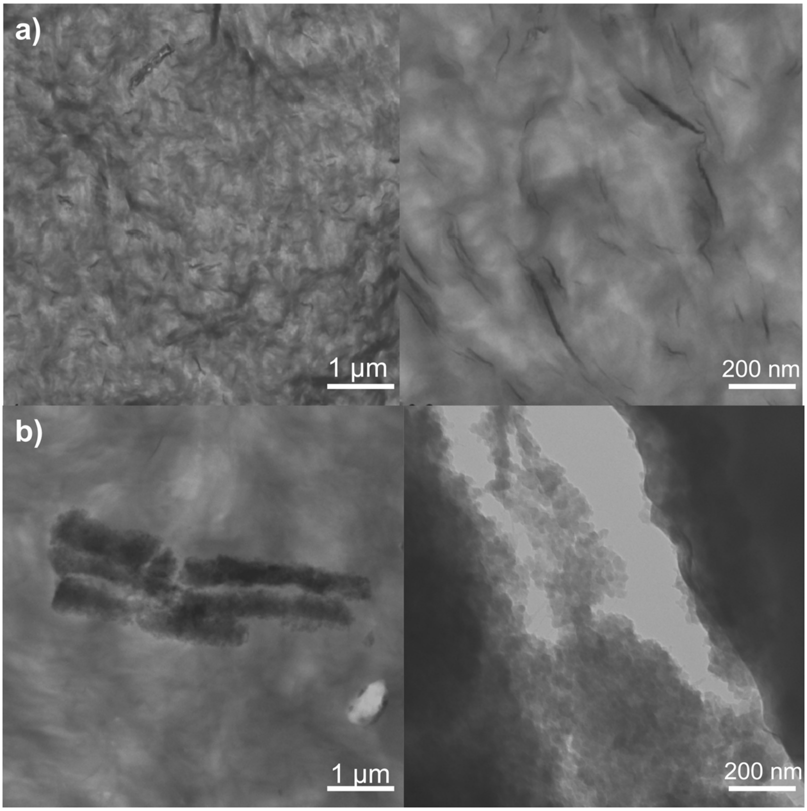


Figure 5.
TEM micrographs performed on 2%wt of (a) phosphonium-treated mica-polyethylene nanocomposites (PE-(P-ME)) and (b) phosphonium-modified Laponite® RD-polyethylene nanocomposites (PE-(P-RD)).

by the small diameter of the laponite (20 nm) and the use of excessive surfactant (2 CEC) which creates a strong attraction of the clay particles. In summary, a very good level of dispersion is obtained for phosphonium- and imidazolium-treated micas without the use of compatibilizing agents such as maleic anhydride-grafted polyethylene (20 wt%), commonly used with ammonium-modified montmorillonites to prepare thermoplastic nanocomposites.[33–35]

Mechanical Properties of the PE/Clays Nanocomposites

The uniaxial tensile properties were performed to highlight the effect of this very small amount of phosphonium- and imidazolium-modified synthetic clays on the mechanical properties of HDPE matrix. The moduli and fracture properties are summarized in Table 3.

When the polyethylene nanocomposites were processed with imidazolium- and phosphonium-treated micas (PE-(P-ME) and PE-(I-ME)), a significant increase in Young's Modulus is observed without reducing the fracture behaviour. In fact, an improvement of +50% for P-ME and +40% for I-ME are obtained. The effect of phosphonium- and imidazolium-treated micas on the mechanical behavior of these nanocomposites is similar to the influence of ionic liquid modified montmorillonites.[24] In the case of organically modified laponites, their poor dispersion in the polyethylene matrix generates a slight increase in stiffness of 20%. Then, in order to improve the mechanical properties of these nanocomposites, the use of the maleic

Table 3.
Effect of clay on tensile properties of the 2 CEC ionic liquid modified synthetic layered silicates-high density polyethylene nanocomposites (2 wt %) (crosshead speed: 10 mm·min^{-1}).

Sample	Tensile modulus (MPa)	Strain at break (%)	Stress at break (Mpa)
PE	740 ± 10	18 ± 2	84 ± 2
PE-ME	720 ± 25	19 ± 2	71 ± 3
PE-RD	720 ± 25	17 ± 2	62 ± 3
PE-ME-PEgMA	850 ± 15	17 ± 2	75 ± 2
PE-RD-PEgMA	731 ± 20	19 ± 2	78 ± 2
PE-(P-ME)-PEgMA	1033 ± 30	16 ± 2	96 ± 3
PE-(P-RD)-PEgMA	870 ± 10	18 ± 2	76 ± 4
PE-(P-ME)	1100 ± 15	17 ± 2	97 ± 2
PE-(I-ME)	1041 ± 20	17 ± 2	96 ± 4
PE-(P-RD)	887 ± 10	18 ± 2	88 ± 4
PE-(I-RD)	883 ± 15	19 ± 2	87 ± 4

anhydride grafted polyethylene (20 wt%) was investigated.[36] In both cases, when the compatibilizing agent and the ILs-treated synthetic clays are combined, no improvements in mechanical properties are observed. In fact, the addition of PEgMA has no effect on the moduli and on the strain to failure. These results can be explained by the fact that the physisorbed ionic liquids onto the surface of clays act as a compatibilizer and finally, the incorporation of PEgMA is not required. According to the literature, Livi et al have demonstrated that the washing of the excess of salts leads to poor distribution of the fillers in the polymer matrix as well as poor mechanical properties.[24] In conclusion, the ionic liquid has a dual function: it acts as a surfactant agent but also as a compatibilizer.[20,24]

Conclusion

In this work, new surfactants based on imidazolium and phosphonium ionic liquids have been used in order to prepare organically modified synthetic clays with an excellent thermal stability for the processing of nanocomposites at high temperature. In fact, the use of these thermostable ionic liquids as modifier agents leads to a greater increase in the degradation temperature compared to ammonium- and pyridinum-treated montmorillonites.[11,12] Moreover, large interlayer distance are obtained for P-ME, I-ME, P-RD and I-RD with ionic liquids functionalized by long alkyl chains (C_{18}). In particular, for the phosphonium-treated laponite where an interlayer distances of 4.6 nm is obtained. Compared to the literature, this increase is significantly higher than one induced by the commonly used ammonium-treated laponites.[30,31] Then, the use of ionic liquids-modified mica leads to significant increases in the mechanical properties of polyethylene combined with an excellent dispersion of the clay layers in the polymer matrix without resorting to the use of a compatibilizing agent.

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