



*Dedicated to Professor Bogdan C. Simionescu  
on the occasion of his 70th anniversary*

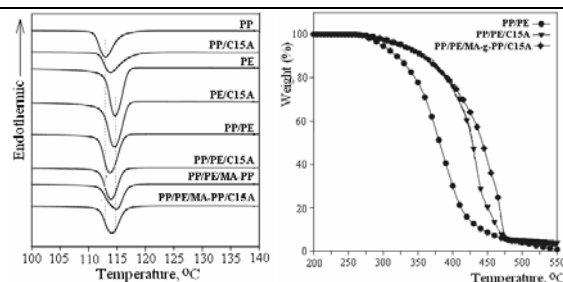
## CLAY REINFORCED COPMPATIBILIZED POLYOLEFIN BLENDS. EFFECT OF THE INTERACTIONS BETWEEN COMPATIBILIZER AND ORGANICALLY MODIFIED CLAY ON COMPOSITES PROPERTIES

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This paper reports on some recent results concerning polymer-clay nanocomposites (PCNs) based on isotactic polypropylene (PP) and high density polyethylene (HDPE), having complex compositions containing single polymer and polymer blend matrices (PP, PE and PP-PE), with or without a compatibilizing agent, namely maleic anhydride grafted polypropylene (MA-g-PP), and a commercially available organically modified clay (Cloisite® 15A). The study confirmed that the enhanced interfacial interactions between components have a notable beneficial influence on the basic thermal and mechanical properties of the composites.



### INTRODUCTION

Polymer-clay nanocomposites (PCNs) have been considered a new generation of composite materials due to their properties achieved after including small amounts (3-5 wt%) of inorganic platelets having a high aspect ratio, as a result of synergetic contributions of components.<sup>1,2</sup> Therefore, PCNs have constantly attracted considerable interest and numerous studies have investigated the properties, and levels of performance of various combinations of polymers and clays have been evaluated.<sup>3-7</sup>

Polyolefins, such as polypropylene (PP), polyethylene (PE), ethylene-propylene rubber (EPR), represent one of the most widely used groups of commodity thermoplastics. Among them, PP and PE have been employed up to a large extent in clay reinforced composites, due to their low cost, excellent performance, long life cycle; they are

readily processable on existing technology, and can be easily recycled and up-cycled without complex and expensive processes of separation.<sup>8-12</sup>

Different clays were used to obtain high performance PCNs, and among them montmorillonite (MMT) was acknowledged as suitable for hybrid materials. MMT refers to a very soft phyllosilicate class of minerals that belongs to the smectite group having a 2:1 sheet structure (one central sheet of octahedral alumina placed between two tetrahedral sheets of silica).<sup>13</sup> One of the requirements for obtaining PCNs with superior properties is to reach an excellent dispersion of the completely exfoliated clay platelets inside the polymer matrix. In practice, it is difficult to enable this feature, and very good properties were acquired even when the morphology of composites was preponderantly intercalated. These problems had arisen due to the severe disparity in the hydrophil/hydrophob

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balance between the polymer matrix and clay. Due to its hydrophilic nature, it is difficult to finely disperse MMT into hydrophobic polymer matrices, and, therefore, it is chemically modified with certain organic molecules, acting as surfactant agents, to improve its affinity to hydrophobic polymers. In some complex formulations, compatibilizers are used in addition to organically modified MMT to allow composites with superior properties granted by the improved interfacial interactions, as they can be considered to act as bridge between components.<sup>1,9,12</sup>

Compatibilizers with different structure and polar functional groups have been studied aiming at optimizing the dispersion of clay platelets and, subsequently, the composites properties. In the case of polyolefin-based composites, maleic anhydride grafted polypropylene (MA-g-PP) or polyethylene (MA-g-PE) are the most commonly used,<sup>12</sup> and their effects were investigated in correlation with their molecular weight, the type and the content of the functional groups (pendant or end groups, such as: maleic and poly(maleic anhydride), succinic anhydride),<sup>14,15</sup> processing parameters, etc.<sup>16-21</sup> Maleated PP and PE showed significantly increased polarity that strongly favour the exfoliation of the clay platelets in polypropylene<sup>22,23</sup> and polyethylene.<sup>24,25</sup>

This paper presents some of our recent results concerning PCNs based on isotactic polypropylene (PP) and high density polyethylene (HDPE). The study deals with a series of composites specially designed for a comparative assessment of properties in correlation with their formulation, as the interfacial interactions between components are known to notably influence the basic composites properties or even to add some new ones. Thus, simple to complex compositions comprising single polymer and polymer blend matrices (PP-PE) were prepared with or without a compatibilizing agent, namely maleic anhydride grafted polypropylene (MA-g-PP), and a commercially available organically modified clay, namely Cloisite<sup>®</sup> 15A. The expected promising

results are very useful in view of developing new studies on re-/up-cycling PP and PE waste.

## RESULTS AND DISCUSSION

All PCNs samples were prepared by melt-blending at temperatures above melting point of each polymeric component. The formulation and sample designation for the prepared blends and composites are listed in Table 1.

According to literature data for compatibilized PCNs based on polymers and/or polymer blends,<sup>1</sup> the driving force of the dispersion of clay tactoids and platelets inside the polymer matrix is the strong hydrogen bonding between the oxygen-containing maleic anhydride groups of the compatibilizer and the polar surface of the organically modified clay. It was suggested that the process evolves in two stages. First, during the melt blending, the modified polyolefins are intercalated between the clay platelets, which entails the increase of the interlayer spacing. As a consequence, in the second stage, as the interactions between platelets inside tactoids become weaker, the polymer chains can penetrate the clay layers, favoured by the shear force during processing, yielding in PCNs with exfoliated morphology.

### Melting behavior and crystallization dynamics

Differential scanning calorimetry (DSC) is generally used to investigate thermal behavior of polymers and polymer blends, including phase changes, crystallization and crystallites morphology, melting, glass transition, etc. Incorporation of nanofillers in such matrices is expected to affect these characteristics not only during heating, but on cooling as well.

Table 1

Specimen code and composition of studied samples

Specimen code	Composition, wt.%			
	PP	PE	MA-g-PP	C15A
PP	100	—	—	—
PP/C15A	97	—	—	3
PE	—	100	—	—
PE/C15A	—	97	—	3
PP/PE	50	50	—	—
PP/PE/C15A	48.5	48.5	—	3
PP/PE/MA-g-PP	42.5	42.5	15	—
PP/PE/MA-g-PP/C15A	41	41	15	3

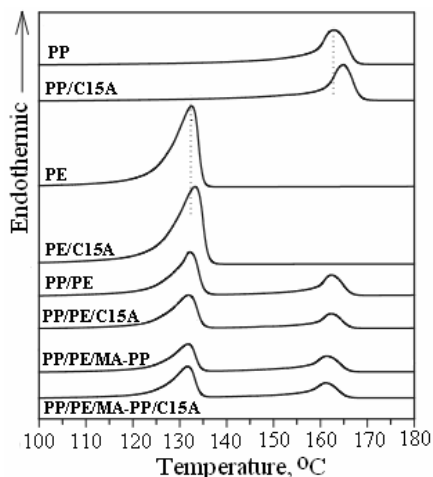


Fig. 1 – The DSC heating thermograms of samples.

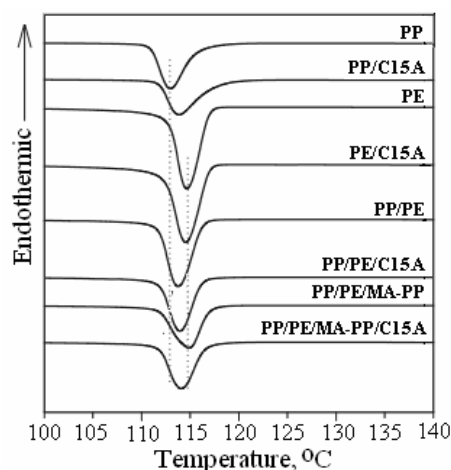


Fig. 2 – The DSC cooling thermograms of samples.

The crystallization behaviour of a polymer blend is more complex than that of a single polymer due to the existence of a second component, whether crystalline or not. An extensive DSC study on the crystallization of a PP-HDPE blend<sup>26</sup> evidenced three different types of behavior considering three temperature intervals. Thus, below 125°C, simultaneous crystallization of PP and HDPE was observed; in the range 125-127°C, two crystallization peaks were observed, when PP was the first to crystallize; above 127°C, HDPE did not crystallize, while PP crystallized from the PP-HDPE melted blend. The addition of the inorganic nanofiller that has higher thermal stability, such as clays and their organically modified correspondents, can increase the thermal stability by altering the crystallization dynamics of the polymer, as confirmed by literature.<sup>1,8,9,23,27-29</sup>

The DSC heating and cooling scans of PP, HDPE, their blends and corresponding nanocomposites are illustrated in Figs. 1 and 2.

Data registered for the DSC heating thermograms (Fig. 1) evidenced that the presence of the organically modified clay (C15A) caused increased melting temperatures in neat polymers, but a poor improvement in blend melting point. At the same time, the melting temperature ( $T_m$ ) of blends and nanocomposites slightly varied upon the addition of compatibilizer MA-g-PP, which confirmed the role of the clay in the improvement of the thermal stability of composites. Another feature observed was the decrease in the melting enthalpies of PP and HDPE in blends and nanocomposites, indicating that both polymers have achieved a lower crystallinity.

The crystallization behavior of the selected samples (Fig. 2) revealed the influence of each additive and the cooling regime. Thus, the

exothermic peak ( $T_{exo}$ ) of HDPE was slightly higher (114.7°C) than that of PP (113.0°C). Upon addition of C15A, the  $T_{exo}$  of PP/C15A shifted towards higher temperatures as compared with neat PP, while PE/C15A showed a decreased  $T_{exo}$ . The same trend was noticed for samples PP/PE and PP/PE/C15A. These data suggested that the clay had a greater influence on the crystallization dynamics of PP than that of HDPE, even in their blend, fact proved by the presence of one single exothermic peak in all samples. The stronger nucleation phenomenon caused by the addition of C15A to the considered samples entailed sharp endotherms, and wider crystallization peaks visible in the heating thermograms (as shown in Figs. 1 and 2). When MA-g-PP was added to the formulations, very small differences were recorded for  $T_{exo}$ , and the wider endothermic peak corresponding to the sample PP/PE/MA-g-PP/C15A also indicated a more pronounced nucleation process. This behavior can be explained considering the compatibilization promoted by MA-g-PP and the complex interaction between the compatibilizer and the organically modified clay, so that an improved dispersion of clay inside the matrix was reached, and this contributed to the overall process of crystallization. At the same time, the wide peak corresponding to the composite sample PP/PE/MA-g-PP/C15A implied that the crystallites had a wide dimensional distribution. These results are in good correlation with data already reported in the literature.<sup>9,27,30-32</sup>

### Thermal stability

Thermal stability of the selected samples was evaluated by TGA and the experimental data are

summarized in Table 2 and graphically represented in Fig. 3. The first information obtained evidenced that all samples decomposed in one single stage, at temperatures over 300°C, and most of the weight loss could be attributed to the degradation of polymers (PP, HDPE, MA-g-PP) and the organic modifier used for C15A, as well as to the residual humidity in samples.

Thermograms recorded for the selected polymer samples evidenced similar behavior for PP and MA-g-PP, and a higher thermal stability for HDPE. When PP/PE blends were compared with PP/PE/C15A and compatibilized nanocomposites, it was obvious that the presence of C15A enabled the formulations with the higher thermal stability, as expected, although the two samples showed a similar behavior up to 410°C. Sample PP/PE/MA-g-PP/C15A proved to be thermally stable up to 470°C. The most significant jumps in stability were evident when comparing the thermograms of the binary blend PP-PE (Fig. 3b) with the corresponding individual polymers (Fig. 3a), on the one hand, and the samples PP/PE/C15A and

PP/PE/MA-g-PP/C15A with PP-PE, on the other hand (Fig. 3b).

The explanation resides in the barrier effect of C15A: the better the dispersion of clay platelets inside the polymer matrix, the more intense the barrier effect was observed. Thus, the increased tortuosity achieved in clay nanocomposites with preponderantly exfoliated morphology is strongly limiting the heat and oxygen diffusion from outside toward interior, and, at the same time, the diffusion of volatiles (products of thermal degradation) in the opposite direction. Even more, the char resulted during the decomposition is localized around the clay platelets contributing to the overall barrier effect.<sup>33</sup>

### Mechanical properties

The mechanical properties of composites depend, generally, on the interphase morphology (if the case) and interface interactions between components.

Table 2

Thermal data of the selected samples by TGA

Sample code	Temperature, °C	
	T <sub>10</sub>	T <sub>50</sub>
PP	300.35	345.1
PE	377.2	414.8
PP/PE	321.7	383.4
PP/PE/C15A	361.6	430.2
PP/HDPE/MA-g-PP/C15A	358.4	441.5

T<sub>x</sub> – the temperature at which the sample weight loss is 10% and 50%, respectively, during thermal decomposition in air environment

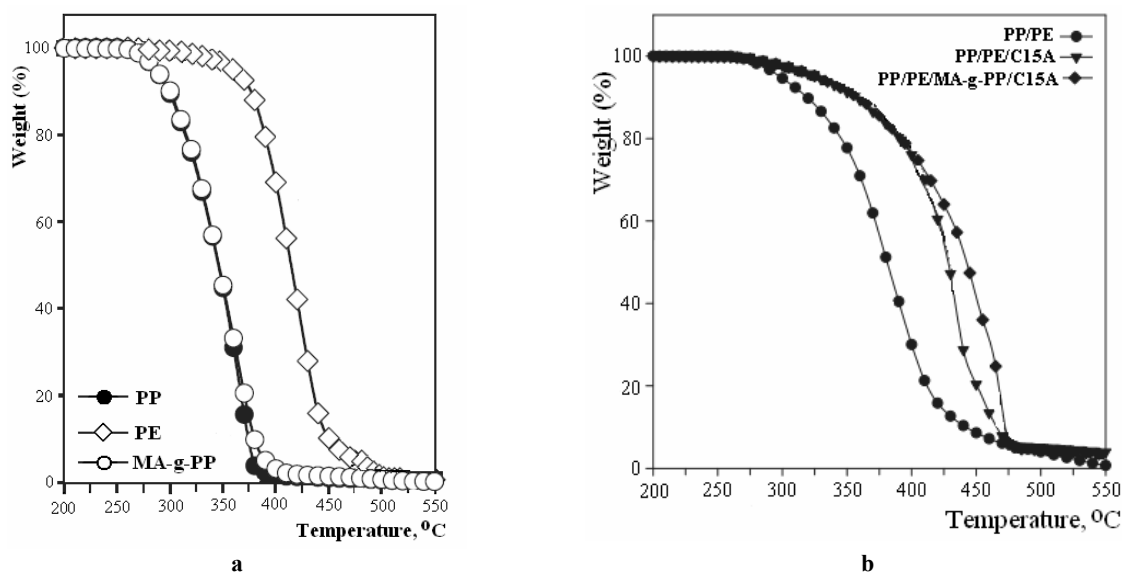


Fig. 3 – Thermograms for neat polymers and compatibilizer (a) and blends and composites (b).

Table 3

Mechanical properties of polymers and corresponding blends and nanocomposites

Sample code	Mechanical properties			
	Tensile strength, MPa	Flexural modulus, GPa	Flexural strength, MPa	Impact strength, J/m
PP	34.5	1.54	49.7	4.6
PE	24.1	0.71	23.6	18.7
PP/PE	28.8	1.19	39.8	3.9
PP/PE/C15A	29.5	1.35	40.4	4.4
PP/PE/MA-g-PP/C15A	29.2	1.36	41.3	2.3

The PCNs can exhibit superior mechanical properties as compared to the corresponding polymers when the nanoclay is preponderantly exfoliated inside the matrix, the reinforcing effect occurring either the morphology is co-continuous or not. This feature is achieved due to the presence of the organic modifier in the clay, which increases the intergallery distance and also changes the polarity, making the clay tactoids better wetted and more available to the non-polar polymers (PP, HDPE).<sup>34</sup> Hence, the intergallery attraction forces become weaker and the polymer chains penetrate more easily the clay structure, yielding in an extended clay delamination.<sup>9</sup>

On the other hand, clay particles contribute to the enhanced strength of the corresponding composites due to their properties, but also affect the crystallization process in the polymer matrix and, thus, its ultimate supramolecular structure.<sup>35</sup>

Taking into account all these considerations, enhanced mechanical properties are expected in our selected samples. Experimental data obtained during mechanical tests are presented in Table 3.

#### *Tensile strength*

The interactions in the PCNs, either compatibilized or not, are responsible for significant changes in mechanical properties. A strong interfacial adhesion leads to high tensile strength and low elongation, whereas a weak interfacial adhesion yields in low strength and relatively high elongation.<sup>36</sup>

Our selected samples showed a particular behavior: the polymer blend had a tensile strength value intermediate to those of the corresponding components; the addition of C15A entailed an increased tensile strength, confirming that the incorporation of clays into a polymer matrix improved the stiffness, but it slightly decreased after adding MA-g-PP to the formulation. This feature can be assigned to the incompatibility of PP and PE, as their ratio in the formulation has changed due to the addition of MA-g-PP in a significant amount (15%).

#### *Flexural properties*

The flexural modulus and strength of the samples showed a similar trend to the tensile strength, as it can be observed from Table 4, namely the values recorded for the PP/PE blend and the corresponding nanocomposites are intermediary between those of the neat polymers. Neither C15A, nor MA-g-PP, significantly improved the flexural properties of the samples, leading to the conclusion that a higher amount of clay is required in order to obtain nanocomposites with noteworthy improved stiffness.

#### *Impact strength*

The results revealed that the impact strength of blend and composites registered a severe decrease: both PP/PE and PP/PE/C15A samples had values close to the PP, while the value corresponding to sample PP/PE/MA-g-PP/C15A is about half of that of PP. This particular behavior might be explained considering the changes in the crystalline character of the nanocomposite. PP is more crystalline than HDPE and the crystallinity of the blend also increased along with the addition of MA-g-PP (15 wt.%), as well as C15A, findings that are consistent with thermal data obtained by TGA for blend and composites.

Another phenomenon must be considered as well: the cavitation of PP upon thermal and mechanical processing is negatively affecting the impact strength, although the addition of MA-g-PP reduced its influence to some extent.

The particles size is another factor that influences the impact strength, as it is known that large particles are stress concentrators and can be considered as crack initiation sites. Some studies reported that a mixed intercalated-exfoliated morphology yields in a better impact strength because particles with various dimensions combine different effects: small particles contribute to the load transfer as they are better wetted by the polymer matrix (the elastic component), while

medium size particles contribute to the dispersion of large particles (considered as stress concentrators) at long distances inside the matrix.<sup>37</sup> Still, for particles smaller than 10  $\mu\text{m}$ , the tendency to agglomerate is more pronounced, which results in aggregates of large dimensions.<sup>38</sup> In our case, the granulometric distribution is as follows: 50% of particles are of medium size (less than 6  $\mu\text{m}$ ), but large size particles (less than 13  $\mu\text{m}$ ) are in a relevant amount (40%) as well, while only 10% of particles are of low dimensions (less than 2  $\mu\text{m}$ ).

## EXPERIMENTAL

### Materials

Two polymers used as main components for matrix were commercial products: isotactic polypropylene (PP) and a high density polyethylene (HDPE).

Polypropylene (Malen P F401) was supplied by Basell Orlen Polyolefins (Plock, Poland) in the form of pellets. Main characteristics: density  $\rho = 0.905\text{--}0.910\text{g/cm}^3$  (23°C); melting temperature  $T_m = 163\text{--}164^\circ\text{C}$ ; melt flow index MFI = 2.4–3.2g/10 min (for 230°C, 2.16 kg); isotactic index is  $\approx 95\%$ . High density polyethylene (Lupolen 6021D) was supplied by BASF AG. Its main properties:  $M_w = 182\text{kg/mol}$ ,  $M_n = 25\text{kg/mol}$ ,  $M_w/M_n = 7.2$ , melt flow index MFI = 2.6g/10 min (for 190°C, 2.16 kg), density = 0.962g/cm<sup>3</sup>.

Modified montmorillonite Cloisite<sup>®</sup> 15A (denoted as C15A) was purchased from Southern Clay (Southern Clay Products Inc. Texas, USA). Cloisite<sup>®</sup> 15A is a natural montmorillonite modified with dimethyl dihydrogenated tallow-ammonium chloride salt (quaternary salt, 2M2HT). The modifier concentration is CEC = 125meq/100g. The organic surfactant 2M2HT residing at the surface of the Cloisite<sup>®</sup> 15A has no polar group. The following tallow composition is: 65% C18, 30% C16, and 5% C14. Average size of the powder particles was 2–13 microns. Main properties of nanoclay are given in Table 4.

The maleic anhydride-grafted PP (MA-g-PP), grade Fusabond M-613-05 of MFR = 49g/10 min (MFR method = 190°C/10min), and with ca. 0.55wt. % of MA was obtained from DuPont Canada, and was used as compatibilizer for the system of PP/PE, with or without organoclay.

### Composites manufacturing

Prior to the melt processing step, the components were dried in a vacuum oven at least for 24 h at 70°C, in order to eliminate the hydrolyzing effect of the absorbed water. The ingredients were weighed at a prescribed ratio before feeding into the mixer. The feeding amount is calculated by considering the volume of the cavity, density of the material and 85% of the capacity utilization.

All blends have been prepared by melt mixing in a counter-rotating twin rotor Haake Rheocord 9000 mixer (equipped with two internal roller mixers and a volumetric capacity of mixing chamber of 50 cm<sup>3</sup>). The content of clay in the polymer matrix and blends was 3wt.% and the compatibilizer content was loaded at 15wt.%.

The following operational conditions have been used for melt blending: temperature 220°C, mixing time 10 minutes, and the rotational speed 100 rpm.

Each sample was removed from the mixing chamber, cooled, and cut into smaller pieces, then milled to produce granules for standard specimens.

The pelletized and dried powder was placed in a 4 mm thick steel frame between two Teflon sheets. The whole system was inserted between plates of a hydraulic press heated to 220°C and kept without external pressure for 6 min, allowing a complete pre-melting. After this period, a pressure of 255 kPa was applied for 5 min.

Polymer matrices used for this study, either neat polymers or blends, were processed in the same manner in order to ensure similar thermal history to all specimens, so as to minimize any possible side effects that might occur during the subsequent tests due to processing discrepancies.

## Characterization of hybrid nanocomposites

### Dynamic scanning calorimetry

The crystallization and melting behavior of samples was studied by DSC using a TA instrument from Perkin-Elmer DSC-7 (USA), Pyris Diamond model. The DSC apparatus was calibrated with indium ( $T_m = 156.6^\circ\text{C}$  and  $\Delta H_m = 28.4\text{ Jg}^{-1}$ )<sup>39</sup> before experiments. For the crystallization experiments, the samples were first melted at 200°C for 4 min, and then cooled to 20°C at a rate of 10°C/min. The crystallized samples were subsequently heated to 200°C at 10°C/min for the evaluation of melting behavior. All measurements were performed under N<sub>2</sub> atmosphere. The degree of crystallinity of the PP samples was obtained by dividing the melting enthalpy of the sample by 209 J/g, which is the estimated melting enthalpy of a pure PP,<sup>40</sup> and for HDPE samples by dividing the melting enthalpy of samples by 293.6 J/g, which is enthalpy of a pure HDPE.<sup>41</sup>

### Thermogravimetric analysis (TGA)

TGA was used to investigate the thermal decomposition behaviour of samples and was carried out using a Jupiter STA 449F1 thermogravimetric analyzer (Netzsch, Germany).

Tests were performed under air atmosphere, with a gas flow rate of 20 mL/min, at a heating rate of 10°C/min. Samples of about 3–6mg were heated from room temperature to 600°C.

### Mechanical properties

The tensile properties of samples were determined according to ASTM D-638 using dumb shell shaped specimens having 1mm thickness, at a crosshead speed of 10 mm/min, on an Instron 5 kN test machine (Instron 3345, Instron Corp., Norwood, MA, USA). The gauge length was set to 40.0 mm. The thickness of the narrow portion was measured using a digital thickness gauge.

Flexural properties were measured by a three point loading system using Universal Testing Machine (UTM, Shimadzu AG-X) according to ASTM-D-790. The flexural properties were determined using rectangular shaped samples at a crosshead speed of 5 mm/min.

In order to measure the Izod impact strength, impact bars were obtained by cutting specimens in rectangular shapes. These rectangular specimens are of thickness 3 mm, width 12 mm and length 62 mm according to ASTM D 256. Tests were performed using a CEAST impact tester (Instron, USA). The test was carried out with impact energy of 5 J and a span length of 60 mm at room temperature. The average value of notched Izod impact energy was obtained from each group of five specimens. The mechanical properties and values reported were averaged from at least five specimens of the same sample.

Table 4  
Main characteristics of Cloisite® 15A

Typical properties	
Organic modifiers	2M2HT *
Modifiers concentrations (meq/100 g clay)	125
Moisture (%)	< 2
Density (g/cm <sup>3</sup> )	1.66
Typical dry particle sizes (microns, by volume)	10 % less than 2µm 50 % less than 6µm 40 % less than 13µm
d-spacing (nm)	d <sub>001</sub> = 3.15

\* Dimethyl, dehydrogenated tallow, quaternary ammonium

## CONCLUSION

Novel nanocomposites (PCNs) based on isotactic polypropylene (PP) and high density polyethylene (HDPE) were successfully prepared and characterized. The formulations comprised single polymer and polymer blend matrices (PP, PE and PP-PE), with or without a compatibilizing agent, namely maleic anhydride grafted polypropylene (MA-g-PP), and a commercially available organically modified clay (Cloisite® 15A).

The thermal investigations indicated that the presence of the C15A caused increased melting temperatures in neat polymers, but a poor improvement in blend melting point, just like the compatibilizer, confirming thus the significant role of the clay in the improvement of the thermal stability of composites. The decrease in the melting enthalpies of PP and HDPE in blends and nanocomposites suggested that both polymers have achieved a lower crystallinity. At the same time, data showed that the clay had a greater influence on the crystallization dynamics of PP than HDPE and the wide peak corresponding to the composite sample PP/PE/MA-g-PP/C15A implied that the crystallites have a wide dimensional distribution. As for the thermal stability of samples, it was shown that the improvement is due to the combined barrier effects of C15A and char, that are strongly limiting the diffusion of the heat, oxygen, and volatiles through the composite.

In terms of the mechanical properties, experimental data confirmed the reinforcing effect of clay, as the tensile strength, flexural modulus and strength of PP/PE blend increased upon addition of C15A. The presence of the compatibilizer altered the PP/PE and clay/polymer ratios, so as the clay reinforcing effect was weaker in the corresponding samples. Neither C15A, nor MA-g-PP, significantly improved the flexural properties of the samples with compatibilized

formulations, leading to the conclusion that a higher amount of clay is required in order to obtain nanocomposites with noteworthy improved stiffness. The cavitation of PP proven to occur upon processing is negatively affecting the impact strength, although the addition of MA-g-PP reduced its influence to some extent. The tendency to aggregate showed by particles smaller than 10µm is also contributing to this effect.

Therefore, it can be stated that, in polymer-clay nanocomposites with complex formulations, the clay strongly influences the thermal stability and crystallization dynamics, while the compatibilizing agent is affecting rather the mechanical properties as it modulates the interfacial interactions.

Since we have used in our research polymer blends where the ratio was PP/HDPE=50/50, it would be of interest to investigate the influence of the blending ratio on the properties of nanocomposites, taking into account the promising opportunities to re-/up-cycle polyolefins waste. Even more, a further comparative study using another maleated polyolefin as compatibilizer, namely the maleated polyethylene (MA-g-PE), would also be of interest in order to quantify and assess the level of performance of the corresponding clay composites, and to ascertain which one of the two compatibilizers (MA-g-PP and MA-g-PE) is more appropriate for PP/PE blends.

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