

# Reactive block copolymers as versatile compatibilizers for polymer-clay nanocomposites

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## ABSTRACT

Considering the limitations of the current technology used to prepare polyolefin/clay nanocomposites, this work deals with new approach involving the use of block copolymers to enhance the affinity between montmorillonite and low polarity polymeric matrices. In this approach sodium montmorillonite slurry is directly modified using an amphiphilic diblock copolymer which has a reactive block capable of reacting with montmorillonite and a low polarity block that has affinity towards low polarity polymeric matrices. X-Ray diffraction and thermogravimetric analyses show complete exfoliation and better thermal properties compared to commercially available organoclays.

**Keywords:** montmorillonite, intercalating agents, block copolymers, polypropylene.

## 1 POLYMER-CLAY NANOCOMPOSITES

Silicate-polymer nanocomposites offer a number of significant advantages over traditional silicate-polymer composites. Polymer nanocomposites can reach high tensile strength, improved heat deflection temperature and flame retardance, with typically 3-5 wt.% of the nanofiller (compared to 10-50%wt in the case of traditional fillers), producing materials with specific gravity close to that of the unfilled polymer, good surface appearance and better processability. Other properties of nanocomposites such as optical clarity and improved barrier properties cannot be duplicated by conventionally-filled resins at any loading [1]. The most common nanoclays used in polymer nanocomposites are montmorillonite and hectorite [2].

Dispersion of layered clays into a polymer matrix can lead to either a conventional composite or a nanocomposite depending on the nature of the components and processing conditions. Conventional composites are obtained if the polymer can not intercalate into the galleries of clay minerals. The properties of such composites are the similar to that of polymer composites reinforced by microparticles. On the other hand, if the polymer intercalates into the clay galleries two extreme nanostructures can result. One is an

intercalated nanocomposite, whose ordered layers are maintained with the polymer existing between the silicate layers, in addition to surrounding the clay particles. The other is an exfoliated or delaminated nanocomposite, in which the silicate layers are completely dispersed within a continuous polymer matrix, and thus the clay particles lose the ordered structure. In general, exfoliated nanocomposites exhibit greater improvements to the material properties than exfoliated nanocomposites, and therefore is typically the more desired scenario [3]. In order to obtain exfoliated clay nanocomposites, several processing strategies have been proposed, including: In situ polymerization, solution exfoliation and melt intercalation. Melt intercalation is a usual technique for polystyrene and polyolefins. Although in the case of polyolefins a compatibilizer is required. The main disadvantage of this technique is the slow penetration (transport) of polymer within the confined gallery. Comparing this strategy with the first two, it has an environmentally benign approach since no solvent is required and in this case nanocomposites can be processed with conventional plastic extrusion and molding technology.

In order to achieve separation of the stacked clay layers, many studies on nanocomposite formation have focused on the modification of clay by introducing organic molecules into the clay layers through a cation-exchange reaction either using organic cations. The objective of the modification of the clay is to provide hydrophobic characteristics to the hydrophilic surface of a clay layer, which may permit the entry of organic polymers; at the same time, the spacing of the clay is increased [4-7]. Organoclays are commercially available materials from producers such as: Southern Clay Products Inc. under the trade name of Cloisite®, Süd-Chemie Inc., under the trade name of Nanofil® and Nanocor, under the trade name of Nanomer®.

Among the disadvantages of commercially-available organoclays are: i) the limited amount of organic cations do not guarantee a good interaction between the polymer and the clay, and a good exfoliation is not easy to achieve; and ii) the low thermal stability caused by the thermal degradation of amines according to the Hofmann mechanism. To overcome these problems a number of strategies have been explored [8-10]. Whereas most of the patents related to clay modification are related to discrete

organic molecules bearing a positive charge, fewer examples describe the use of oligomeric or polymeric species to intercalate or exfoliate clays. The use of oligomeric or polymeric species tends to enhance the interaction between the polymer and the clay, since the tensoactive species is chosen to be compatible with or of similar composition as the polymeric matrix [11-13]. In most of the cases the strategies are very specific for a specific group of polymers, mainly those that can react with an amine.

In the case of polymers with very low polarity such as polyolefins, the panorama is more complicated, since organic clays are not intercalated at all when they are added directly to polymers like polyethylene or polypropylene [14]. To overcome this problem, compatibilizers such as maleic anhydride grafted polypropylene (PP-g-MA) have been used [15]. The amount of PP-g-MA in the final blend may vary but it's usually around 20-30%wt considering the amount of PP as 100%[16]. This large amount of PP-g-MA has some disadvantages [17]. First, since the molecular weight of PP-g-MA is usually low, it causes a detriment in the mechanical properties of the nanocomposites. Second, PP-g-MA has a higher cost than PP, which adds to the total cost of the nanocomposites.

Polypropylene's attractive combination of low cost, low weight, heat distortion temperature above 100°C, and extraordinary versatility in terms of properties, applications, and recycling have stimulated exceptional growth of polypropylene production. There is a considerable interest in obtaining PP/clay nanocomposites, and most of it is focused on a better processing methodology to exfoliate intercalated clays using a compatibilizer or finding a better compatibilizer.[16, 18-22] A great deal of work has been done in the field of producing clay or silicate and polymer composites. While significant improvements have been made over the years in improving the compatibilization of clays with polymers, there is still considerable room for improvement.

The present approach involves the direct modification of sodium montmorillonite slurry with amphiphilic block copolymers in order to improve the affinity between montmorillonite and low polarity polymeric matrices. The benefits of this approach include the elimination of maleated polyolefins as compatibilizers, with the consequent detriment of mechanical properties and the improvement in thermal properties, compared with commercially available organoclays.

## 2 EXPERIMENTAL

Reagents: Dibenzoyl peroxide (BPO) and 2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane (T101) were acquired from Akzo Nobel; p-tert-butyl styrene (TBS) and 2-(diethylamino)ethyl methacrylate (DEAEMA) were acquired from Sigma-Aldrich; 2-(dimethylamino)ethyl methacrylate (DMAEMA) was acquired from Degussa and

Dibenzyl trithiocarbonate (DBTTC) was acquired from Arkema. Reagents were used as received.

Molecular weight distributions relative to polystyrene were determined through GPC (ASTM D3536-91) using a Waters 410, RI detector, THF eluent, 1.0 mL/min, at 40°C; Styragel columns HR 4 and HR 3. Results are shown in Table 2.

X ray Diffraction (XRD): X-Ray diffractograms of powders from samples 3 and 4 were acquired using a SIEMENS D5000, and a radiation of Cu K $\alpha$  ( $\lambda=1.5406 \text{ \AA}$ ), using an interval from 1.5°<2 $\theta$ <15°. For examples 5 and 6, samples of blends were pressed at 200°C and a pressure of 3000 g/cm<sup>2</sup> obtaining films of 0.36 mm thickness. Circles of a diameter of 2.2 cm were cut from this film and placed in the glass support of the Diffractometer

The amount of adsorbed organic material (block copolymer) is determined by thermogravimetric analysis (TGA) using the following method: 1: Ramp 20.0°C/min to 120.0°C; 2: Isothermal for 10.0 min; 3: Equilibrate at 35.0°C; 4: Ramp 20.0°C/min to 1000.0°C.

**Preparation of block copolymers** (see Table 1 for the amount of reagents in each example). Reagents were placed in a double jacket glass reactor and oxygen was removed with nitrogen bubbling during 3min. Preheated oil (130°C) is circulated through the outside jacket and stirring is started (300rpm). After the desired conversion is reached (68% for example No.1 and 80% for example No.2), heating is suspended and additional TBS (750.62mmol for example No. 1 and 594.41 mmol for example No. 2) is added to the reactor with stirring. After 3 min. of stirring, the reaction was either continued in the glass reactor until 10-20% more conversion was reached or directly poured into a second reactor. Nitrogen is bubbled and the reactor is immersed in an oil bath previously heated to 120-125°C for 18h to reach the desired conversion. The remaining monomer is removed by devolatilization.

No.	FIRST BLOCK					
	TBS	DEAEMA	DMAEMA	DBTTC	BPO	T101
1	560.0	1680.0		20.5	2.6	
2	500.0		1500.0	15.8	2.0	1.2

Table 1. First block of block copolymers composition. All amounts are expressed in mmol.

No.	FIRST STEP		TOTAL	
	Mn	Mw	Mn	Mw
1	6869	8965	8118	11129
2	16235	24770	19339	37332

Table 2. Block copolymers molecular weight. Preparation of polyolefin nanocomposites using clays modified with block copolymers.

**Clay modification using block copolymers.** 63.05g of water and 1.95g of Cloisite Na<sup>+</sup> (acquired from Southern Clay Products Inc.) were mixed at 10,000 rpm and 60°C for 15 minutes. The block copolymer (Block copolymer from example 1 and 2, obtaining modified clays examples 3 and 4 respectively) previously dissolved in water (0.57g of selected block copolymer in 35g of hot water) was added to the mixture; the pH was adjusted to 1 and the mixture is stirred at 1200 rpm for 1 hour at 60°C. The block copolymer modified clay suspension was then filtered and the solid was dried at 50°C for 24 hours. The dry material was grinded to obtain a fine powder (5-10µm). The powder obtained was characterized using X-ray Diffraction and thermogravimetric analysis.

Example 5. 38.65g of injection grade polypropylene (for example Profax SL648M from Indelpro), 7.29g of maleated polyolefin (Polybond 3200 from Crompton) and 3.85g of Cloisite 20A were physically mixed by dry blending so as to produce 60g of the mixture. The mixture was then mixed using a Brabender Mixer at 80 rpm and 200°C for 15 minutes.

Example 6. 39.18g of injection grade polypropylene (for example Profax SL648M from Indelpro), 7.35g of maleated polyolefin (Polybond 3200 from Crompton) and 3.47g of Cloisite 30B were physically mixed by dry blending so as to produce 60g of the mixture. The mixture was then mixed using a Brabender Mixer at 80 rpm and 200°C for 15 minutes.

### 3 DISCUSSION

The XRD of examples 3 and 4 present a complete exfoliation (no peak is observed), as shown in figure 1, which is completely outstanding, considering that commercially available organic clays only show different degrees of intercalation but not a complete exfoliation. These examples show that the block copolymers of the present invention have the unusual property of exfoliating completely the clay, which is expected to facilitate its incorporation into a variety of polymeric matrices (depending on the composition of the blocks of the block copolymer) and improve the performance of the polymer/clay nanocomposite. As a reference, diffractograms of examples 5 and 6 show an interlayer distance of 26.7Å and 14.6Å, respectively.

The TGA (Figure 2) shows an outstanding performance of the block copolymer treated montmorillonite in comparison with commercially-available clays. The degradation temperature of the block copolymer modified clay is higher than the commercially-available clays and since less amount of organic material (block copolymer, in this case) is required to modify the clay, the amount of solid content is also increased considerably (80% vs 70 or 63%). Both the higher degradation temperature and the higher amount of solids are beneficial for the modification of different polymeric matrices. A higher temperature allows it to be used in a wider variety of polymers (with higher

melting point or glass transition temperature), including engineering thermoplastics. Higher solids content allows one to use less modified clay in the polymeric matrix. Considering also that the added block copolymer modified clay is already exfoliated, then it is expected that a polymeric nanocomposite containing a block copolymer modified clay would have a better performance than the same polymeric nanocomposite with the same percent of a commercially-available organic clay that is not completely exfoliated.

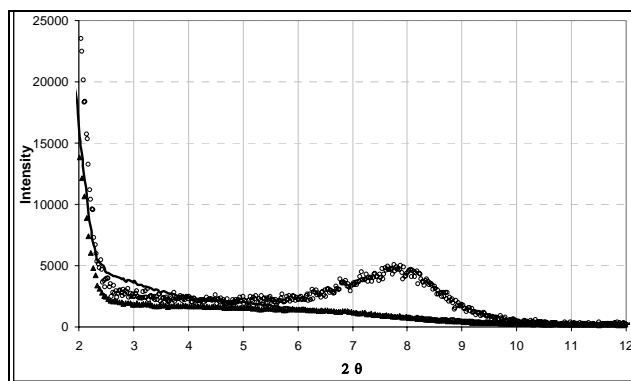


Figure 1. X-ray diffractogram for (○) Cloisite Na<sup>+</sup>, (▲) Example 3 and (-) Example 4.

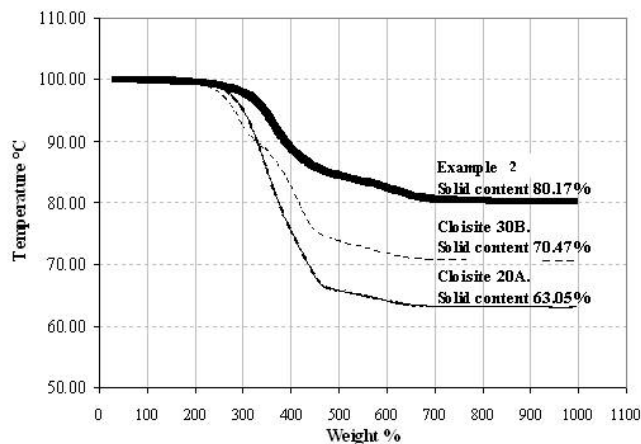


Figure 2. TGA of example 2, 5 and 6 (labeled Cloisite 20A® and 30B® respectively)

### 4 CONCLUSIONS

Montmorillonite modified with amphiphilic block copolymers is completely exfoliated and shows higher degradation temperatures compared with commercially available organoclays. This is a promising strategy for the preparation of polyolefin/clay nanocomposites, eliminating the use of maleated polypropylene and opening the possibility of using montmorillonite as nanofiller for engineering polymeric matrices.

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