Poly(propylene)/PET/Undecyl Ammonium Montmorillonite Nanocomposites. Synthesis and Characterization

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Summary: A natural bentonite rich in calcium montmorillonite (CaMMT) was initially purified and ion-exchanged to obtain sodium montmorillonite (NaMMT). Both clays were organophillised by cationic exchange reaction with undecyl-ammonium chloride, and characterized. Isotactic poly(propylene) (PP) was melt-compounded with both the unmodified and the organophilic montmorillonites. The hybrids produced have been characterized structurally, thermally and mechanically. Maleic anhydride-grafted PP (MAH-g-PP) was used as compatibilizer in some of the formulations. Homologous series of hybrids were also synthesized employing blends of PP/PET and compared with those of the pure PP to investigate possible beneficial effects due to the presence of small amounts of PET on the microstructure and properties of this kind of materials. The analysis of the results indicates some extension of both macromolecules intercalation and clay particles exfoliation in the hybrids prepared with the organophilic montmorillonite. The hybrids prepared with compatibilized PET/PP blends were found to have a better nanostructure.

Keywords: blends; clay; nanocomposites; PET; PP

Introduction

The method called polymer melt intercalation was proposed by Giannelis to fabricate polymer/clay nanocomposites[1]. Nowadays, polypropylene/clay nanocomposites show great research interest[2-8] since this thermoplastic is one of the most widely used because of its good ratio between properties and cost, as well as due to its high versatility. Kawasumi et al.[9] used maleic anhydride modified PP oligomers as compatibilizer to prepare PP nanocomposite by melt blending. They found that the dispersibility of the clay layers depends on the miscibility of the PP maleic anhydride oligomers with the matrix PP matrix. Hasegawa et al.[4] reported a novel approach to prepare PP/octadecylamine modified montmorillonite using maleic anhydride-graft-

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polypropylene as compatibilizer and they obtained that silicate layers were partially exfoliated and dispersed to monolayers. Gloaguen and Lefebvre[10] prepared by melt blending dispersion of organophilic clay in PP without compatibilizer and they found that polymer-clay interaction exists although no specific treatment was used to promote it. Nam et al.[11] prepared intercalated polypropylene/clay hybrid by using small amount of maleic anhydride groups as compatibilizer to achieve disordered structures. Recently, Liu and Wu[3] reported the synthesis of intercalated polypropylene/MMT nanocomposites by melt grafting.

In this work we have synthesized PP/clay hybrids using a natural bentonite, which was firstly purified to obtain sodium montmorillonite, and secondly treated with undecylammonium chloride. A blend of homopolymer PP with maleic anhydride-grafted PP was used as matrix to promote affinity with the organophilic montmorillonite. Moreover, taking in mind the affinity of some polar thermoplastics (i.e. polyesters, polyamides...) for high-polarity particle surfaces, homologous series of hybrids were synthesized using a blend of PP/PET as matrix, with the aim to investigate possible beneficial effects on the composite microstructure and properties due to the presence of PET.

Morphology and microstructure of the hybrids have been characterised by means of WAXS and TEM. Furthermore, thermal and mechanical properties as well as flame resistance of the nanocomposites have been evaluated.

Clay treatment

The bentonite (Minas de Gador, Spain) was treated physically in order to obtain a fine high-purity clay fraction (< 2 μm) before its chemical treatment. The procedure was performed in three steps: milling in a porcelain mortar, sieving, and centrifuging at 6000 rpm for 20 minutes. This fraction consists mainly of calcium montmorillonite.

Two types of cationic exchange reactions were performed on this clay. On one hand, sodium montmorillonite (NaMMT) was produced from CaMMT and, on the other hand, organophilic clays (CaOMMT and NaOMMT) were prepared by reaction of CaMMT and NaMMT respectively with undecyl ammonium chloride.

Each 30 g of CaMMT were first dispersed into 400 ml of 1 N solution of NaCl for two hours at room temperature. After centrifugation at 3000 rpm for 15 min the solid fraction was separated.

To assure complete ion exchange, that is, to obtain an homoionic NaMMT the same process was repeated five times. The product was washed several times with a mixture of deionised water and ethanol (1:1 by volume) until no chloride was detected by adding one drop of 0.1 N $AgNO_3$ solution. The purified clay was dried at 110°C and stored in a desiccator.

Organophilic clays were prepared using a similar method to that reported by Yano et al.[6]. In a 500 ml beaker 10 g of 11-aminoundecanoic acid, 5 ml of concentrated hydrochloric acid, and 100 ml of water were placed. The solution was heated at 80 °C. Moreover, 20 g of MMT was dispersed in 400 ml of water at 80 °C. The dispersion of MMT was added to the solution of undecyl ammonium chloride, and this mixture was stirred for 12 hours. A white precipitate was isolated by filtration, placed in a 500 ml beaker with 400 ml of hot water, and stirred for 1 hour. This process was repeated twice to remove the residue of ammonium salt. The final product was then filtered and dried at 110 °C, and stored in a desiccator.

Materials, compounding and specimens

A commercial grade (Repsol-IPF, Isplen PP050) of homopolymer PP was used as matrix to prepare the hybrids. A commercial compatibilizer (Eastman, Epolene G-3003) consisting of maleic anhydride-grafted PP copolymer (MA-g-PP) was added in some formulations. To investigate possible beneficial effects of the existence of poly(ethylene terephthalate) (PET) on the characteristics of these materials, analogous hybrids were synthesized using a blend of PP with PET (Catalana de Polímers, *Extrupet EW36*) and compared with those of pure PP.

Polypropylene/clay (PP/MMT) hybrids were prepared by a melt-compounding process performed in two stages. Firstly, highly filled PP/MMT and PP/OMMT compounds with nominal MMT concentration of 20 wt% were produced using a *Collin ZK-35* co-rotating twin-screw extruder (D = 25 mm; L/D = 36). Intensive dispersive mixing was assured by means of three kneading blocks inserted in the screw configuration. A barrel temperature profile was selected from 150 °C at the polymer feeding to 190°C at the die. Clay was fed in the extruder through a feeding port located at a distance of 12D from the polymer feeding. Vacuum devolatilization was applied at a distance of 24D and the screw speed was fixed at 300 rpm. Under these conditions, the melt temperature measured at the die was never higher than 200°C. A circular cross-section die of 3 mm diameter was employed. The extrudate was cooled in a water bath and pelletised. In a second extrusion

process, performed under the same conditions, the clay concentration was reduced to nominal percentage of 4 wt% by dilution with the neat PP. Four polymer/clay hybrids were prepared: two hybrids containing pure PP and both kinds of clay (CaMMT and CaOMMT) called respectively PPMMT and PPOMMT, and their analogous containing 2 wt% of MA-g-PP as compatibilizer, called PMMMT and PMOMMT respectively. Table 1 shows their nominal composition by weight. The clay percentage was 4 wt% in all cases.

Square plaques (150 x 150 x 0.8 mm^3) and discs (diameter 80 mm, thickness 3 mm) were compression-moulded using a hot-plate press. The moulding cycle was optimised for each plaque geometry and material. The temperature was never higher than 190 °C. For burning test, the square plaques specimens were machined to 120 x 10 x 0.8 mm^3 dimensions. Standard tensile specimens (type IV, ASTM D-638) were also cut off. Square specimens (20 x 20 x 3 mm^3) were machined from the discs to determine the Vicat softening temperature and for WAXS and TEM analysis.

Testing procedure

Clay density was measured using an He pycnometer model AccuPyc 1330. The cationic exchange capacity (CEC) of the clays was determined using the following procedure: on one hand, 100 mg of clay were stirred for 10 minutes in 50 ml of ammonium acetate (pH 7.0) in order to exchange ions. It was left to stand 24 hours and, afterwards, the solution was analysed by atomic absorption spectroscopy (AAE) and atomic emission spectroscopy (AES) to quantify respectively the residual Ca^{2+} and Mg^{2+}, and K^{+} and Na^{+} ions.

Table 1. Composition of both unmodified and organophilic MMT-containing hybrids.

Unmodified MMT series:	PP-MMT	PM-MMT	BP-MMT	BMP-MMT
Modified MMT series:	PP-OMMT	PM-OMMT	BP-OMMT	BMP-OMMT
PP (wt.%)	96	94	91	89
MA-g-PP (wt. %)		2		2
PET (wt. %)			5	5

On the other hand, the clay was washed thoroughly with isopropyl alcohol to remove any excess of NH_4^+ ions. This was checked using a Nessler reactive. The sample was then treated with 30 ml of a NaCl 1N solution slightly acidified with 0.005N HCl to extract the NH_4^+ ions from the clay. This procedure was monitored by flux injection analysis (FIA).

Thermogravimetric analysis (TGA) was carried out on a Setaram TG-DTA92 thermoanalyser. The sample was heat from 20 °C to 900 °C at 1°C/min under oxygen atmosphere.

Wide angle X-ray scattering (WAXS) was performed using a Siemens D-500 diffractometer with CuK_α radiation (wavelength λ=0.154 nm), operating at 40 KV and 30 mV. The step size was 0.05° and the measuring time 5 s/step. The clay samples were prepared using a technique for aggregates orientation, and the polymer hybrids specimens were machined from the circular plaques. The clay interlayer basal spacing (BS) was evaluated through the (001) reflection of montmorillonite.

The melt flow index (MFI) of the PP/clay hybrids was measured at 230 °C and 2160 g. The Vicat softening temperature was determined at a heating rate of 120 °C/h with a load of 50 N.

Differential scanning calorimetry (DSC) was carried out in a Perkin Elmer Pyris-1 calorimeter to analyse the polymer thermal characteristics in the hybrids (typically 10 mg taken from the circular plaque). After erasing the thermal history (4 min at 220°C) the sample was cooled at 10 °C/min to 40 °C to observe the PP crystallization. The temperature was next raised from 40 to 220°C at 10 °C/min to observe the polymer melting signal. All tests were conducted under nitrogen atmosphere.

The silicate layers in the hybrids were observed by transmission electron microscopy (TEM) on ultrathin microtomed sections taken from the compression-moulded discs.

The mechanical properties of the hybrids were evaluated by tensile tests carried out at 1 mm/min, according to ASTM D-638 standard.

To analyse eventual flame retardancy effects, vertical burn test (UL-94) was carried out. The time from the ignition to the occurrence of the first burning drops (TFBD) was measured.

Results and Discussion

The CEC values of the clays have been compiled in Table 2. On one hand, it can be seen that the value obtained (95,1 meq/100 g) for the original montmorillonite (CaMMT) is concordant with

values of usual MMT commercial grades employed in nanocomposites. On the other hand, the efficiency of the clay organophillisation process was high, as the low Na^+ and Ca^{2+} residues values (from AAS and AES) obtained for samples CaOMMT and NaOMMT reveal, which indicates that a high fraction of all metallic ions in the clay have been exchanged by organic ones. This result was confirmed by TGA. Besides the weight loss due to the adsorbed water and structural OH^-, a weight loss was observed in OMMT in the interval 180-300°C which should be related to the organic substance. This weight loss of 16 wt% was in accordance with a CEC value of 95 meq/100g.

Table 2. Some physicochemical characteristics of the clays.

	Density	Cationic Exchange Data		Basal Spacing
		AAS / AES	FIA	
	g/cm^3	meq/100 g	meq/100 g	Å
CaMMT	2.52	85.8	95.1	14.9
NaMMT	2.41	121.1	134.6	12.6
CaOMMT	2.18	11.2	93.3	16.6
NaOMMT	2.13	8.4	99.4	16.7

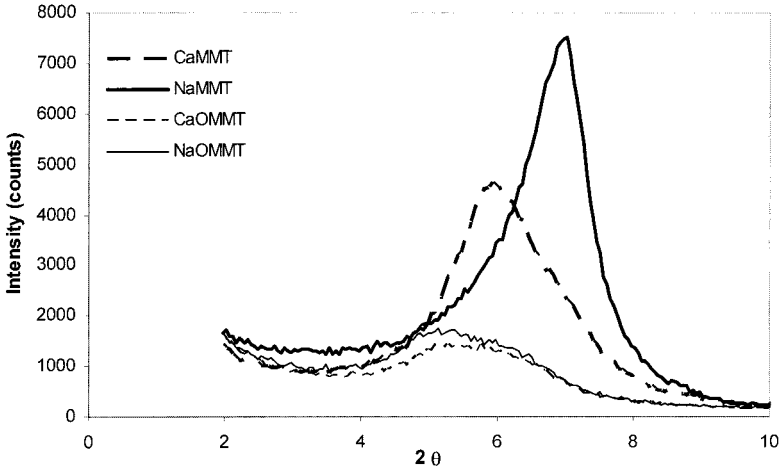


Figure 1. WAXS difractograms of the different clays.

The WAXS diffractograms of the original clay exhibited a peak at $2\theta = 5.93°$ corresponding to a basal spacing of 14.9 Å. Treatment with undecyl ammonium chloride produced a slight expansion to 16.6 Å (Fig. 1). The lower density values of the organophilic clays are explained due to this increase of the clay basal spacing. Owing to the fact that this value was similar for both organophilic clays, we decided to employ the original calcium-based clays (CaMMT and CaOMMT) to prepare the polymer/clay hybrids instead of NaMMT and NaOMMT.

A diffraction peak exists in the WAXS diffrcatograms of the hybrids. A better degree of delamination could be achieved in BMP-OMMT sample since its (001) intensity resulted very low (Fig. 2).

Poly(propylene) intercalation into the galleries of the organophilic clay seems to be evident after the TEM analysis (Fig. 3a). Furthermore, intercalation of PET molecules would be expected due to the presence of the undecanoic acid group into the organophilic clay galleries. It was observed that PET encapsulated clay platelets and particles due to its high polarity (Fig 3b).

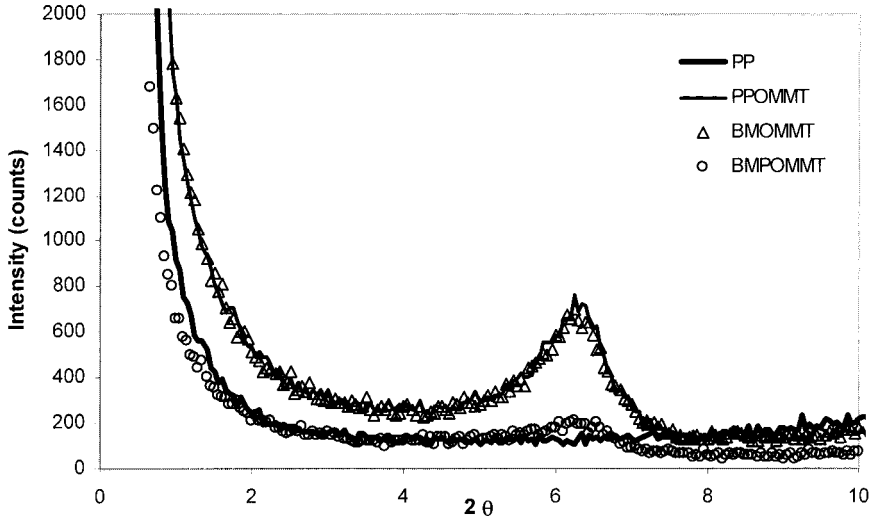


Figure 2. WAXS diffractograms of some selected hybrids.

The presence of organophilic clay promotes an increase in the PP Vicat softening temperature, which is especially relevant in the hybrid PPOMMT and in those containing PET (Table 3).

Moreover the hybrids PPOMMT and PMOMMT exhibits TFBD values notably higher than the rest of the samples, indicating a flame retardant effect of OMMT for poly(propylene).

Table 3. MFI, Vicat and TFBD values of all the samples.

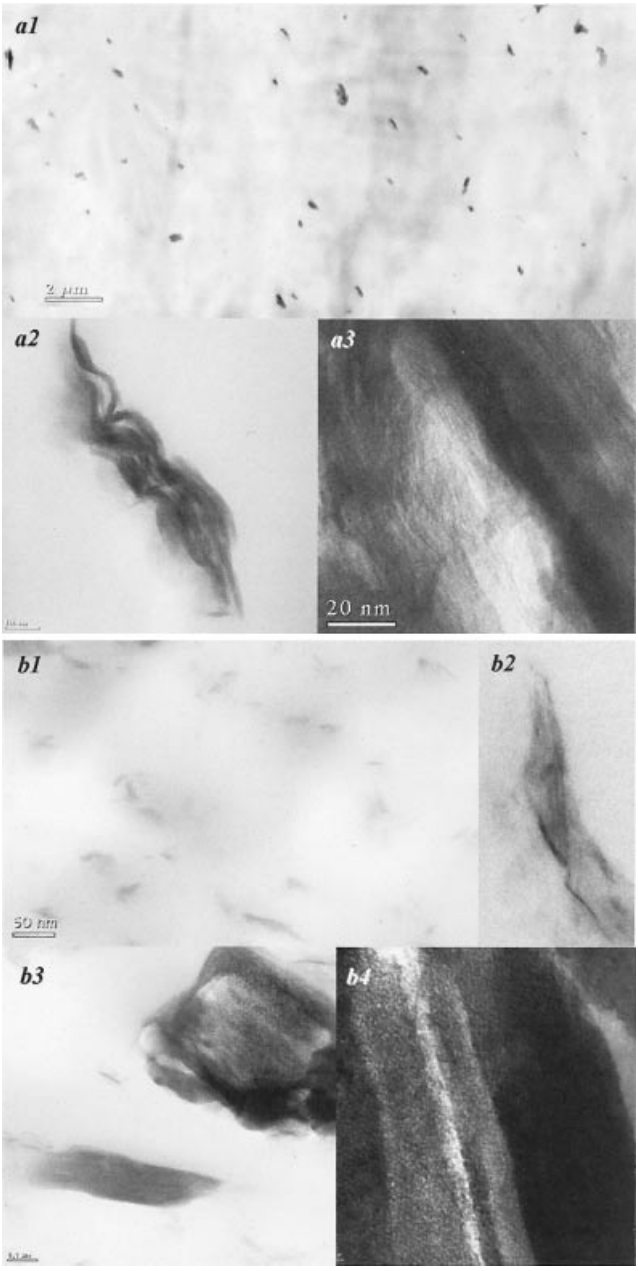
	Melt Flow Index	Vicat Softening Temperature	TFBD[a)]
	g/10 min	°C	sec
PP	5.8	97.3	2
PP-MMT	3.9	101.3	3
PM-MMT	4.3	101.9	4
PP-OMMT	5.9	108.6	7.5
PM-OMMT	5.8	101.4	7
BP-MMT	3.9	97.1	2.5
BMP-MMT	4.4	108.6	3
BP-OMMT	4.1	103.4	3.5
BMP-OMMT	4.8	109.0	2.5

a) Time from ignition to the first burning drop (test geometry UL-94).

Table 4. Thermal and mechanical characteristics.

	T_m [a)]	T_c [a)]	X_m [b)]	X_c [b)]	E [c)]	σ_{max} [d)]	$\varepsilon_{\sigma max}$ [e)]	ε_{break} [f)]
	°C	°C	%	%	MPa	MPa	%	%
PP	159.5	111.5	53.9	52.9	690	28.9	13.8	> 100
PP-MMT	161.4	117.1	56.5	55.8	820	31.1	12.5	> 100
PM-MMT	162.7	120.0	53.0	50.7	851	30.7	11.8	21
PP-OMMT	164.8	121.3	55.9	53.4	884	32.1	9.9	27
PM-OMMT	162.8	120.3	53.1	51.5	932	31.6	10.0	29
BP-MMT	165.1	123.1	53.8	52.4	876	26.8	6.4	6.4
BMP-MMT	164.0	123.7	54.8	52.3	869	30.2	8.0	11
BP-OMMT	165.3	126.6	49.1	49.2	879	29.8	8.5	80
BMP-OMMT	164.5	126.6	49.2	47.4	880	30.4	7.8	17

a) Melting and crystallization peaks temperatures. b) Crystallinity values from melting and crystallization signals. c) Young modulus. d) Tensile strength. e) Elongation at maximum stress. f) Elongation at break.



a1) Primary clay particles and agregates dispersed within PP matrix.

a2) Agregate of primary clay particles.

a3) Magnification of a primary clay particle.

b1) Exfoliated clay platelets and PET domains dispersed within PP matrix.

b2) Individual clay platelets surrounded by PET.

b3) Primary clay particles surrounded by PET.

b4) Magnification of a primary clay particle.

Figure 3. TEM analysis of a) PP/OMMT and b) PP/PET/OMMT hybrids.

However, it is remarkable that the TFBD values of the hybrids containing PET did not increase with respect to the pure PP. The low viscosity of PET, together with the encapsulation of the clay platelets by this polymer, could be the responsible for this apparent contradiction.

After thermal analysis by DSC (Table 4) the clay was found to be a nucleating agent for the PP crystallinity, as the increase in the crystallization peak temperature revealed. PP/MMT hybrids showed higher melting temperatures than pure PP, indicating higher ordered structure in the PP crystal. No differences in the crystallinity fraction were found in these hybrids. Hybrids containing PET displayed the highest crystallization and melting temperatures and the lowest crystallinity fraction, especially with organophilic clay and MA-g-PP compatibilization. PET was also found to be a nucleating agent for PP crystallinity. Its molecules could not only interact with OMMT clay, but also with PP, through the MA-g-PP functionality. These interactions could be the main cause of reduction of the PP crystallinity.

The hybrids exhibited higher stiffness and tensile strength but lower strain values than pure PP especially when OMMT was used. The higher Young's modulus exhibited by PMOMMT and the high strain at break of PPMMT were especially relevant. As shown in Table 4, the existence of PET did not improve the mechanical properties of the hybrids.

Conclusions

The modification of a natural bentonite, rich in calcium montmorillonite, by ionic exchange reaction with 11-undecyl-ammonium chloride has been shown to be successful. As a result, affinity between the clay and PP was achieved when the organophilic montmorillonite was employed in the synthesis of PP/MMT hybrids by melt compounding.

The improved morphology, as well as the mechanical (stiffness and tensile strength), thermal and flame retardant properties of the hybrids could be due to the polymer molecules intercalation into the montmorillonite galleries. The effect of adding MA-g-PP did not result in significant changes.

Hybrids prepared with a blend PP/PET as matrix resulted in improved morphology, which could be due to the higher affinity between PET molecules and the organophilic clay. Only thermal properties were improved with respect to PP/MMT hybrids.

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