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Effect of the amount and functionalization grade of PPgMA compatibilization agent in polypropylene/clay nanocomposites

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Summary

Polypropylene-organoclay nanocomposites were prepared by melt processing via twin-screw extrusion of three components: PP, maleic anhydride modified polypropylene oligomers (PPgMA) and clays modified by octadecylammonium for the purpose of evaluating the effect of the amount of the grafted compound of the PP on the mechanical properties. Two ways were used to compatibilize the PP and nanoclay. First, varying the PPgMA percentage on the nanocomposite, and secondly its degree of functionalization. The rheological and mechanical properties were studied in relationship to the microstructure of the nanocomposites varying both parameters. X-ray diffraction was used to detect the formation of nanocomposites and the transmission electron microscopy (TEM) was used to characterise the dispersion of the organoclay.

Introduction

Polymer-layered silicate nanocomposites are a new class of materials of great industrial as well as scientific interest attributed to their improved mechanical, barrier, flame retardant, high temperature durability properties over their pristine macrocomposite counterpart [1]. In order to obtain good interfacial adhesion and mechanical properties, the hydrophilic clay needs to be modified prior to its introduction in most polymer matrices, which are organophilic. This is an essential treatment in order to make the clay sufficiently organophilic to enable the polymer to insert between the clay layers. Modified organoclays can be formed when the hydrated exchangeable clay cations are replaced by long chain alkylammonium. Also, the gallery sizes between the silicate layers increase and interact optimally with the polymer matrix. However, the polarity of the polymer matrix is very important for the formation of the nanocomposites. Because the silicate layers of the clays have polar hydroxyl groups in their structure, non polar polymers like polyolefins need to be treated to favour the compatibility. Consequently the matrix modification with polar oligomers is necessary prior to the introduction of the modified clays in the polymer in order to achieve nanometric dispersion of the clays [2–7].

Among other thermoplastics, Polypropylene has the strongest growth in the world market materials due to its attractive combination of properties and low cost. Since PP does not include any polar group in its backbone, the formation of PP nanocomposites demands to be previously compatibilized. The general approach for improving the compatibility of PP with organically modified clays has been the addition of polar functional groups to the PP polymer.

During the last decade a large number of works has been reported on the preparation, characterization and properties of layered silicated nanocomposites of polypropylene. Some of them are focused on the study of the influence of the molecular weigth of the matrix [8] or the experimental conditions for the fabrication of the nanocomposites [9–12]. The compatibilization agent used to prepare the nanocomposites is also a well studied aspect [13–17], concluding that the PPgMA is the most convenient surfactant to be used.

In 1997 Kawasumi and col. from Toyota described a ratio of PPgMA/clay of 3/1 as the optimal proportion, independently of the degree of functionalization of the surfactant [18]. This ratio is actually the most used to prepare PP-nanocomposites [18,19]. However, in this paper we investigate the optimisation of this ratio varying the percentage of PPgMA for different degrees of functionalization. This study consists of the analysis of the influence of the MA groups percentage on the dispersion of the clays in the matrix and the properties of the nanocomposites. Two different studies were made, one of them varying the percentage of the PPgMA in the nanocomposite and the other one with two types of modified PP oligomers containing different amounts of maleic anhydride groups (degree of functionalization). The obtained results will allow to detect the optimum value for the percentage of PPgMA.

Layered silicates can assembly into tactoids which are relatively large aggregates and thus resemble a conventional composite. Intercalated structure indicates that a single polymer chain diffuses into the galleries between the layers resulting an alternated layer of polymers and inorganic mineral. In the ideal exfoliated structure, the silicate layers are completely opened up and dispersed disorderly and uniformly in a continuous polymer matrix.

Twin screw extrusion has proven to be most effective for the exfoliation and dispersion of silicate layers in the polymer matrix, leading to composites with properties near to those produced by in situ polymerization [20]. The pellets of the nanocomposite were finally melt injected due to its compatibility with existing processes and consequently minimising capital costs to the industry.

Experimental

Materials

The materials used for the preparation of the nanocomposites are commercial PP (Stamylan 17M10, DSM), two different coupling agents, a maleic anhydride (MA) grafted PP oligomer (Polybond 3200) with 1 wt % of MA (PPgMA-1) from Cromptom and a maleic anhydride (MA) grafted PP oligomer (Epolene E-43) with 4 wt % of MA (PPgMA-4) from Eastman Chemical. The clay used was a commercial organophillic montmorillonite (I30.TC) supplied by Nanocor.

The functionalized grade of the polymer is calculated by ATR-FTIR (MB155 BOMEM, FTIR Spectrophotometer) with a calibrated curve obtained with diethyl maleate and iso-heptane. A deeper description of the process can be found in the literature [21–24].

Preparation of PP-clay nanocomposites

Nanocomposites were obtained by previous preparation of a masterbatch by mixing the compatibilized PP with maleic anhydride and the clays in a ratio of 50/50. The effect of the percentage of MA in the nanocomposite properties was analysed using a PPgMA with a degree functionalization of 1 wt % (Polybond 3200). The percentage of PPgMA used in ranged from 5 up to 45 wt % with 3–4 wt % of clay and the composition of nanocomposites is detailed in Table 1.

This masterbatch is prepared in a Leistritz 27 GL intermeshing twin screw extruder operating at 190–210 ºC and 50 rpm in corrotating mode. The clays were added through a side feeder. Subsequently, to obtain the final nanocomposite the desired amount of pure polypropylene, masterbatch and grafted polypropylene if necessary, were mixed in the twin screw extruder at 190–210 °C and 250 rpm.

After being dried, pellets of the nanocomposites were injection molded into test pieces for mechanical tests by using an injection molder Margarite JSW110. The temperature of the cylinders was 190–200 ºC and that of the mold was 40 ºC.

The contents of the inorganic clay of the polypropylene nanocomposites were measured by burning the samples in a Thermogravimetry Analysis Mettler Toledo Model TGA851.

Microstructure

X-ray patterns diffraction of the nanocomposites were obtained to determine the mean interlayer spacing of the (001) plane (d_{001}) and was performed in a Philips X'Pert MPD using Cu Kα radiation. The injection molded sample was cut and microtomed at –70 ºC on a Reichert-Jung Ultracut E microtome to produce a section thickness of about 100 nm. Transmission electron micrographs (TEM) were taken by using a Jeol JEM 2000FX Electron Microscope with 200 kV accelerating voltage.

Mechanical properties

The mechanical behaviour of the nanocomposites was characterized via tensile test according to UNE-EN ISO 527-1 and 527-2 using an Instron Model 5500R60025. Modulus were measured at a crosshead speed of 1 mm/min and an dynamic extensometer was used to accurately determine Young´s modulus. Tensile property values reported here represent an average of eight samples with standard deviations tipical of 4 % for modulus. For Notched Izod impact strength a pendulum trademark Frank Model 53566 was used under UNE-EN ISO 180. An average values of ten samples was presented with standard deviations of 8 %.

Melt fluid Index was measured under UNE-EN ISO 1133 with a Ray-Man device model 3A, at 190ºC and a weigth of 2,16 kg.

Results and discussion

The first study was focused to analyse the effect of the amount of MA groups in the nanocomposite properties. The grafting compound (MA) in the polypropylene produces interactions between the matrix and the clays increasing the viscosity of the nanocomposites. Consequently MFI values which are related to the viscosity of the material will be influenced by the interactions between the matrix and the filler [25]. In Table 1 are presented PP nanocomposites with a percentage of 3–4 wt % of organoclays and different amount of compatibilizing agent (PPgMA with 1 wt % of MA), with different amounts of %wt of MA in the nanocomposite. The values of MFI versus the amount of PPgMA, are presented in Figure 1. The graft polymer without

Table 1. Characteristics of the PP nanocomposites

Sample	MA oligomer (%)	% weight MA	TGA (% clays)
PP	–	–	–
PP-PPgMA	PPgMA-1 (15)	0.20	–
PP-PPgMA-MMT-1	PPgMA-1 (5)	0.07	3.2
PP-PPgMA-MMT-2	PPgMA-1 (15)	0.14	3.0
PP-PPgMA-MMT-3	PPgMA-1 (25)	0.34	3.6
PP-PPgMA-MMT-4	PPgMA-1 (35)	0.48	3.1
PP-PPgMA-MMT-5	PPgMA-1 (45)	0.61	3.4

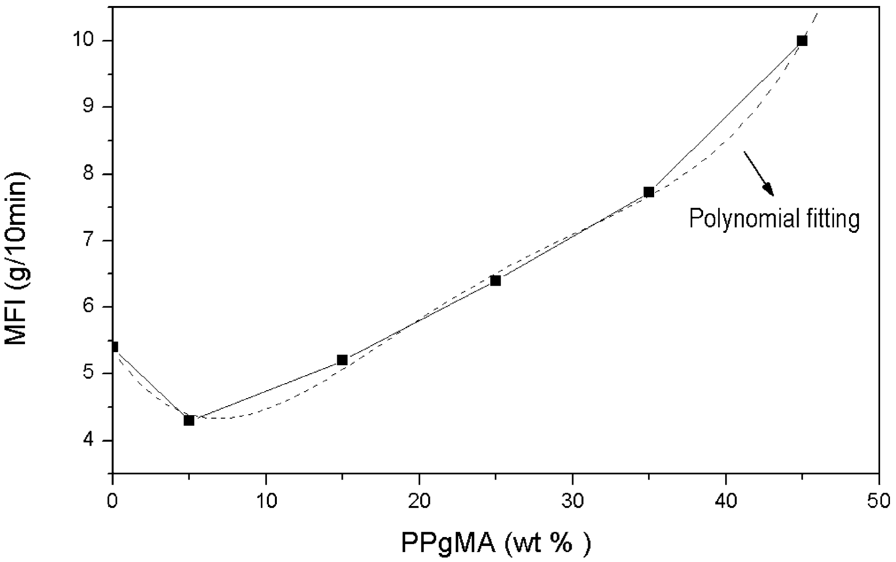

Figure 1. MFI versus maleic anhydride modified PP

nanoclays (PP-PPgMA) has been used as reference material. The fitting of this curve shows a minimum for the MFI value at about 5–10 w% of PPgMA and above this point the MFI increases even higher than the neat PP. This tendency corresponds to an excess of PPgMA on the composite that acts as a lubricant [26] and therefore diminishing the shear stress during processing.

The values for the mechanical properties of these nanocomposites are presented in Table 2. Modulus and impact properties are highly improved for a material with 5 wt% of graft PP; otherwise, the mechanical properties diminish as the percentage of PPgMA increases. Consequently, from these studies, we can conclude that the optimal mechanical properties for PP-nanocomposites are obtained for a low percentage of graft polymer (5–10 %). These results suggest that the excess of graft PP produces a lubricant effect during the melt processing of the nanocomposite and consequently the nanoclays are not well dispersed, probably due to the higher reduction of viscosity in the melting state.

Table 2. Properties of the PP nanocomposites

Sample	MFI (g/10min)	Modulus (MPa)	Izod Impact Strength, notched (KJ/m^2)
PP	5.4	1887	2.35
PP-PPgMA-1	5.85	1327	2.05
PP-PPgMA-MMT-1	4.30	2064	2.54
PP-PPgMA-MMT-2	5.20	1973	2.39
PP-PPgMA-MMT-3	6.40	1938	1.29
PP-PPgMA-MMT-4	7.73	1788	1.05
PP-PPgMA-MMT-5	10.0	1568	1.05

Moreover, the percentage of MA in the graft PP also influences the properties of the nanocomposites. A higher degree of functionalization for the MA will allow to use a lower amount of PPgMA. Thus, the second study was focused to determine the best condition for the preparation of the nanocomposites with the optimal mechanical properties obtained. These samples were obtained by using two degrees of functionalization for the MA (1 %: Polybond 3200 and 4%: Epolene E-43) and two percentages of PPgMA according to the later results and bearing in mind that the best properties of these materials were obtained with low percentage of MA groups (0,1–0,5%) [27]. To study the influence of the degree of functionalization of the anhydride maleic polypropylene, a preblend of PP/PPgMA in relation 3/1 and the necessary amount of organoclay is prepared following the former method described. The composition of these nanocomposites is detailed in Table 3.The values for the mechanical properties of these nanocomposites are presented in Table 4. Modulus values are increased with respect to the neat PP in a high percentage for the samples grafted with PPgMA-1 (PP-PPgMA-MMT-6 and PP-PPgMA-MMT-7) showing a minimum of the MFI values and consequently, the best interaction between matrix and organoclays is produced. From the samples grafted with PPgMA-4, only the nanocomposite with 0.21 wt% of MA (PP-PPgMA-MMT-8) presents high modulus although a smaller impact value is detected. However the other nanocomposite with the highest presence of MA groups (PP-PPgMA-MMT-9) has the biggest MFI value and the smallest modulus.

Table 3. Characteristics of the PP nanocomposites with two maleic anhydride modified PP

Sample	MA oligomer (%)	% weight MA	TGA (% clays)
PP	–	–	–
PP-PPgMA-MMT-6	PPgMA-1 (7)	0.1	4.7
PP-PPgMA-MMT-7	PPgMA-1 (15)	0.21	4.6
PP-PPgMA-MMT-8	PPgMA-4 (4.6)	0.21	4.7
PP-PPgMA-MMT-9	PPgMA-4 (11.5)	0.53	4.4

Table 4. Properties of the PP nanocomposites with two maleic anhydride modified PP

Sample	MFI (g/10min)	Modulus (MPa)	Izod Impact Strength, notched (KJ/m^2)
PP	5.4	1887	2.35
PP-PPgMA-MMT-6	3.67	2524	1.95
PP-PPgMA-MMT-7	4.10	2428	1.55
PP-PPgMA-MMT-8	6.07	2552	1.05
PP-PPgMA-MMT-9	8.23	2266	1.08

We can conclude from these results that the optimal mechanical properties of PP-nanocomposite can be performed with a functionalization degree of the PP at about 1 % and a weight of MA around 0.1 % (PP-PPgMA-MMT-6).

Morphology of the nanocomposites was analysed by X-ray diffraction and TEM images. Figure 2 shows the X-ray patterns for the nanocomposites with different degrees of functionalization. The higher intercalation values have been produced on the clays in the nanocomposite with PPgMA of 4 wt% of MA groups like PP-PPgMA-MMT-8 and PP-PPgMA-MMT-9, where we have obtained peaks at 3.5 nm and 3.0 nm respectively. Otherwise in the nanocomposites produced with grafted PP with 1 wt% of MA groups only a slight increase of the intercalation size is produced (from 2.52 nm of the organoclays [17, 28]). A second peak at 1.71 nm and 1.58 nm is detected for the PP-PPgMA-MMT-8 and PP-PPgMA-MMT-9 which corresponds to the second harmonic. This means that an intercalated structure is formed. For the nanocomposite PP-PPgMA-MMT 6 a new peak at 1.84 nm is observed that is interpreted as a reduction of the original intercalation galleries of the organoclays due to a less favourable thermodynamic between polymer and organoclay and consequently repulsive interactions are present [29,30]. The smallest peaks situated at 1.06–1.08 nm ($2\theta = 8.2$ °) corresponds to the clays non modified with the surfactant.

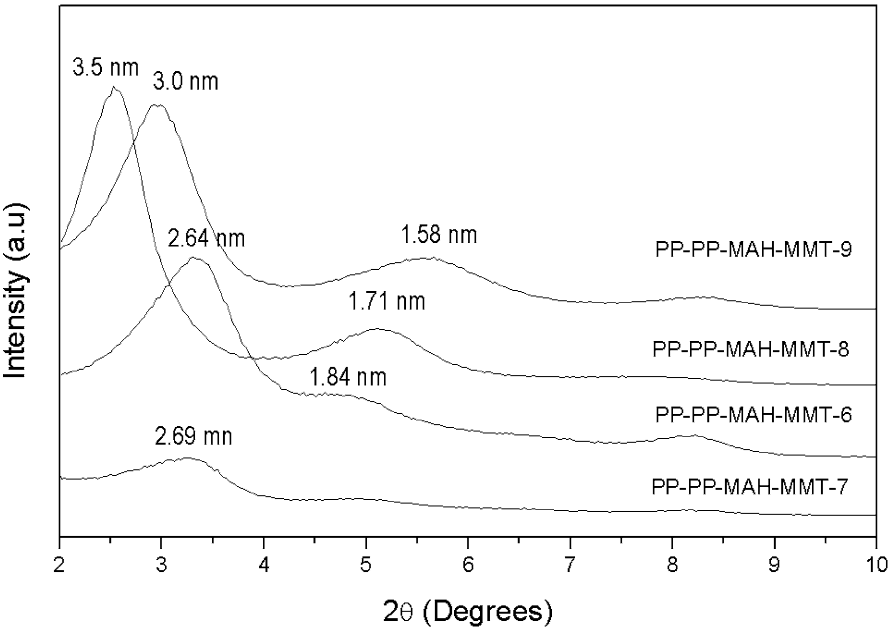

Figure 2. X-ray diffraction patterns of (a) PP-PPgMA-MMT-6; (b) PP-PPgMA-MMT-7; (c) PP-PPgMA-MMT-8; (d) PP-PPgMA-MMT-9

To complete the structural interpretation of the nanocomposites TEM photographs are shown in Figure 3. A tactoid-intercalated structure is mainly observed for the layer silicates in all the samples. Figure 3a shows different groups of intercalated clays formed by 10–15 silicate layers together with isolated layers. Similar picture was also observed for PP-PP-g-MMT-7. Figure 3b shows the microphotograph of the PP-PPgMA-MMT-8 with a homogeneous distribution of the organoclays in a tactoid-intercalated structure. PP-PPgMA-MMT-9 presented the higher intercalation distance by the X-ray analysis, but TEM photograph (Figure 3c) shows a dark area on the

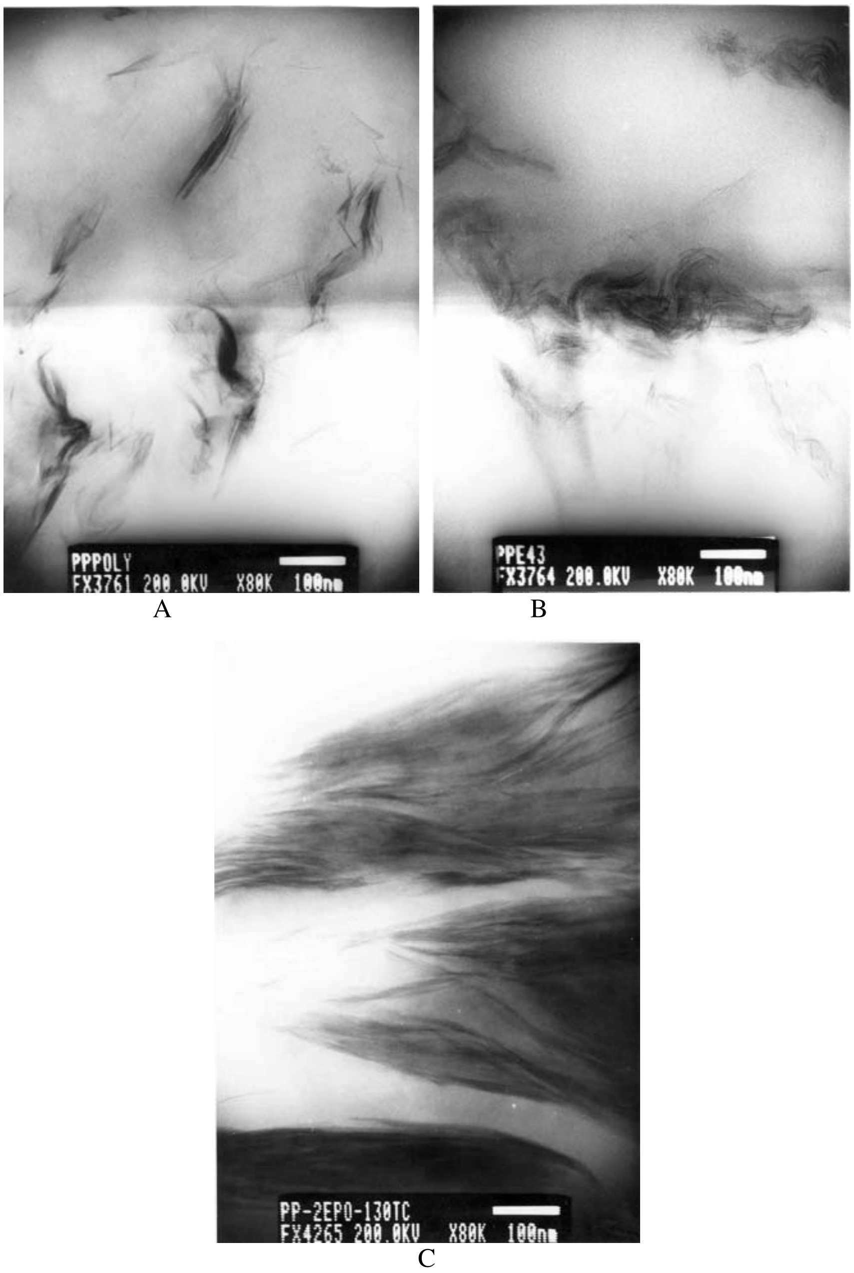

Figure 3. TEM images of (a) PP-PPgMA-MMT-6, (b) PP-PPgMA-MMT-8 and (c) PP-PPgMA-MMT-9 at x80.000

centre of the clay aggregates without polymer chains between the layers. Also, an external region with a higher intercalation distance with the polymer chain introduced between the galleries is observed. The great amount of MA groups introduced in this nanocomposite has produced a high interlayer separation but a lubricant effect (high

MFI values) prevents the destruction of the silicate aggregates during the process of preparation of the nanocomposites. The melt viscosity of this compound is lower than the later compound (hight MFI value) and therefore, an increase of the chain polymer intercalation on the PP-PPgMA-MMT-8 is produced with the improving of the modulus.

Conclusions

PP-PPgMA-MMT nanocomposites were successfully synthetized using melt interaction method in two steps; first, preparing a PPgMA/clay masterbach or a PP/PPgMA/clay preblend at low compounding speed; secondly, these masterbatch or preblend were mixed with the rest of materials at higher speed. The nanocomposites with about 4 %wt of MMT were obtained with different percentages of grafted PP.

PPgMA/clay relation has been optimized, succeeding in good mechanical properties with a minor relation than the normally used (3/1). In addition, whichever greater one is the degree of functionalization of the compatibilization agent, the PPgMA relation used can be smaller, since the properties of nanocomposites of PP are connected with the final percentage of MA groups. A percentage at about 5–10 %wt of PPgMA with 0.07–0.1 %wt of MA on the nanocomposite seems to be favourable to get the optimal mechanical properties. Moreover, the later percentages obtained with grafted PP with a functionalization degree at about 1–1.5 %wt allows to get a more intercalated structure and the best property balance with a high modulus and the lowest reduction in the impact strength.

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