

ORGANOPHILIC BENTONITES BASED ON ARGENTINEAN AND BRAZILIAN BENTONITES. PART 2: POTENTIAL EVALUATION TO OBTAIN NANOCOMPOSITES

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Abstract - This work describes the preparation of composites of polypropylene and organophilic bentonites based on Brazilian and Argentinean bentonites. During the processing of the samples in a twin screw microextruder, torque and pressures of the extruder were accompanied and the viscosity values were calculated. No significant changes in the torque, pressure and viscosity were found for composites prepared with different bentonites. The samples were characterized by XRD and TEM to evaluate the structure and dispersion of the organophilic bentonites. Composites with exfoliated, partially exfoliated and intercalated structures were obtained and correlations between the intrinsic properties of the sodium clays and organophilic bentonites and their influence on the composites were studied. The cation exchange capacity of the sodium bentonites and the swelling capacity of the organophilic bentonites were the most important properties to obtain exfoliated structures in composites. All bentonites showed the potential to obtain polymer nanocomposites, but the ones from Argentina displayed the best results.

Keywords: Bentonite; Polypropylene; Nanocomposite.

INTRODUCTION

Polymeric nanocomposites are a class of materials composed of one reinforcing agent with at least one dimension on the nanometric scale, dispersed in a polymer matrix within the nanometer range (Alexandre and Dubois, 2000; Beyer, 2002). The main applications of nanocomposites include the automotive and packaging areas, but also applications in other areas such as aerospace, electronic and biotechnological areas are important (Meenakshi *et al.*, 2011; Nguyen, 2011; Armentano *et al.*, 2010; Schmidt *et al.*, 2002; Gorrassi *et al.*, 2003; Luo and Daniel, 2003).

The most advanced and common systems are based on a polymer matrix and organophilic clays. Due to the interactions in the nanometer range, this kind of material can be produced with a small amount of filler compared to conventional composites and exhibit superior mechanical, thermal, barrier, and flame retardancy (Beyer, 2002). Several methods have been considered to prepare nanocomposites. Among these, melt intercalation is one of the most used. In this method, the mixture between organophilic clay and the polymer is done with the polymer in the molten state. As examples of the preparation of polymer nanocomposites by melt intercalation, the works of Okamoto *et al.* (2001),

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Kaspersma *et al.* (2002), Gorrassi *et al.* (2003), Kim *et al.* (2004), Ramos Filho *et al.* (2005), Nogueira *et al.* (2005), Zhang *et al.* (2006), Picard *et al.* (2007), Muksing *et al.* (2008), Sharma and Nayak (2009) and Morales *et al.* (2010), among others, can be mentioned. This method also allows nanocomposites to be formulated directly by using conventional compounding devices like extruders or mixers. Another important aspect is that the technique does not require the use of solvents, which makes it adequate from the environmental and industrial points of view (Alexandre and Dubois, 2000; Beyer, 2002; Zhu *et al.*, 2002; Pavlidou and Papispyrides, 2008). If the organophilic clay and the polymer are compatible, the polymer chains can migrate to the interlayer space of the clay to form a nanocomposite. The different levels of dispersion of the organophilic clay in the polymeric matrix can result in three structures: micro-composites in which the clay is not nano-dispersed; intercalated structures, in which single or more polymer chains are intercalated between the clay layers, resulting in an ordered multilayer structure of alternating polymeric and inorganic layers; and an exfoliated structure in which the clay layers are completely and uniformly dispersed in the continuous polymer matrix (Paiva *et al.*, 2007).

Aspects related to the influence of intrinsic properties of the pristine clays in nanocomposites are scarce in the literature; some correlations were found only in the works of Delbem (2005) and Chavarria *et al.* (2007). In our previous work (Paiva and Morales, 2012) the intrinsic properties of sodium bentonites were evaluated and correlated with their organophilization capacity. This work evaluates composites produced from these organophilic bentonites, which were modified by two different methodologies: in aqueous dispersion and semisolid medium. Correlations between the intrinsic properties of the organoclays and the composites properties were also established.

EXPERIMENTAL

Materials

The materials used to prepare the nanocomposites were the six bentonites modified by the two methodologies described in our previous work, Part 1 (Vulgel, TEC-09, Reminas, Soleminas Dye-10, Bentogel Patag and Brasgel PBS 50, designed as O1 for modification in aqueous dispersion, and O2 for modification in semisolid medium), the polypropylene

matrix (PP) [XM6150K from Quattor, MFI of 35g/10 min and density of 0.905 g/cm³] and the coupling agent polypropylene grafted with maleic anhydride [(PP-g-MA) Orevac CA100 from Atofina, MFI of 150-200 g/10 min and a high amount of maleic anhydride (the supplier did not inform the exact content)].

Preparation of Composites

The composites of PP/organobentonite were prepared through melt intercalation. The total composition was 80 wt% of PP, 15 wt % of PP-g-MA and 5 wt % of organobentonite. This mixture was processed in a twin screw HAAKE MiniLab II microextruder from Thermo Fischer Scientific, Figure 1. All mixtures were processed for 15 min after polymer melting. The screws operated in a co-rotating way at 100 rpm and the temperature of processing was 180 °C. Torque as well as entrance and exit pressures of the extruder were monitored. The samples were designated as Nano following the name of the respective organobentonite, for example, Nano_Vulgel O1.



Figure 1: HAAKE MiniLab II Microextruder.

Characterization Techniques

The dispersion of the organobentonites in the composites was evaluated by measuring the basal spacing of the (001) plane of the clay by X-ray diffraction (XRD). Analyses were carried out directly on pieces of the extruded composites (approximately 1 mm in thickness) using a Shimadzu Model SRD 700 X-ray diffractometer, Cu K α , $\lambda = 0.15406$ nm, current 30 mA, voltage 40 kV, at angles between $1.4 < 2\theta < 10.0^\circ$.

The dispersion of the organobentonites in the PP matrix and the structures formed were also evaluated by transmission electronic microscopy. Samples 50 nm in thickness were produced in a Leica model Reichert Ultracut FC4 microtome. Analyses were carried out on a Philips model CM120 microscope at 120 kV.

RESULTS AND DISCUSSION

An example of the visual aspect of the extruded samples can be seen in Figure 2. All samples showed translucence and brown coloration characteristic of the bentonite. No agglomerate particles of clay were observed. The translucency and brown coloration were also observed in our previous work (Paiva, 2007), for nanocomposites with the same matrix and compatibilizing agent and the commercial organophilic clay Cloisite® 20A.



Figure 2: Example of a sample of nanocomposite prepared in the microextruder (Nano_Vulgel O2).

Evaluation of the Viscosity During Processing of the Nanocomposites

The torque and pressure inside the microextruder were monitored during the whole process. They were measured at three processing times: five, ten and fifteen min. From these results the viscosity values were calculated using the equipment software.

The viscosities of the composites were very similar, as shown in Table 1. There is a tendency for viscosity reduction during processing. This behavior has already been observed and can be explained by the alignment of the clay due the shear (Tang *et al.*, 2010; Durmuş *et al.*, 2007; Százdi *et al.*, 2007; Ali Dadfar *et al.*, 2011). It was more evident for Nano_Vulgel O1, Nano_Vulgel O2, Nano_TEC-09 O1, Nano_Brasgel PBS50 O1 and Nano_Brasgel PBS50 O2. Although not studied in this work, differences in the aspect ratio could be the cause for

those differences between the samples, since the clay treatment, polymer matrix and processing conditions were kept unchanged.

Table 1: Viscosity of the samples during processing.

Nanocomposite	η (Pa.s)		
	5 min	10 min	15 min
Nano_Vulgel O1	40.2	38.6	36.7
Nano_Vulgel O2	39.9	37.6	36.3
Nano_TEC-09 O1	44.1	41.5	41.9
Nano_TEC-09 O2	38.9	38.9	38.0
Nano_Reminas O1	40.2	40.2	38.9
Nano_Reminas O2	38.6	38.3	37.3
Nano_Soleminas Dye-10 O1	41.2	39.6	40.2
Nano_Soleminas Dye-10 O2	41.2	42.2	42.2
Nano_Bentogel Patag O1	39.9	37.6	38.0
Nano_Bentogel Patag O2	40.9	40.2	40.2
Nano_Brasgel PBS50 O1	42.5	40.2	36.0
Nano_Brasgel PBS50 O2	41.5	37.6	34.7

Among all composites, the highest viscosity was 44.1 Pa.s for Nano_TEC-09 O1 after five min of processing, while the lowest was 34.7 Pa.s for Nano_Brasgel PBS50 O2 after fifteen min of processing. These values show that all organophilic bentonites can be processed under the same conditions; the data were not compared with other data from literature because similar studies were not found.

Evaluation of the Nanocomposite Structures by X-Ray Diffraction

A strong indication for a nanocomposite formation is the shift of the diffraction peaks of the organophilic clays to lower angles, as a result of the increase of the basal spacing, which can indicate the formation of an intercalated structure, or even the disappearance of the diffraction peaks attributed to the formation of an exfoliated structure. In the second case, the layer structure of the clay mineral is completely destroyed and, therefore, no diffraction peaks appear. However, it is also possible that a large basal space that is not detected in the evaluated range, generally below 1° or 2° (2θ), is produced. Figures 3(a) to 3(d) show examples of the XRD patterns of composites and their respective organophilic bentonites. Some samples had the same characteristic X-ray diffraction as the organophilic clays, i.e., the appearance of three diffraction peaks, but with larger basal spacing. In others samples, the diffractions peaks disappeared. The values of the basal spacing related to the main diffraction peak (001) are shown in Table 2 and the discussion of the structures focused in these values.

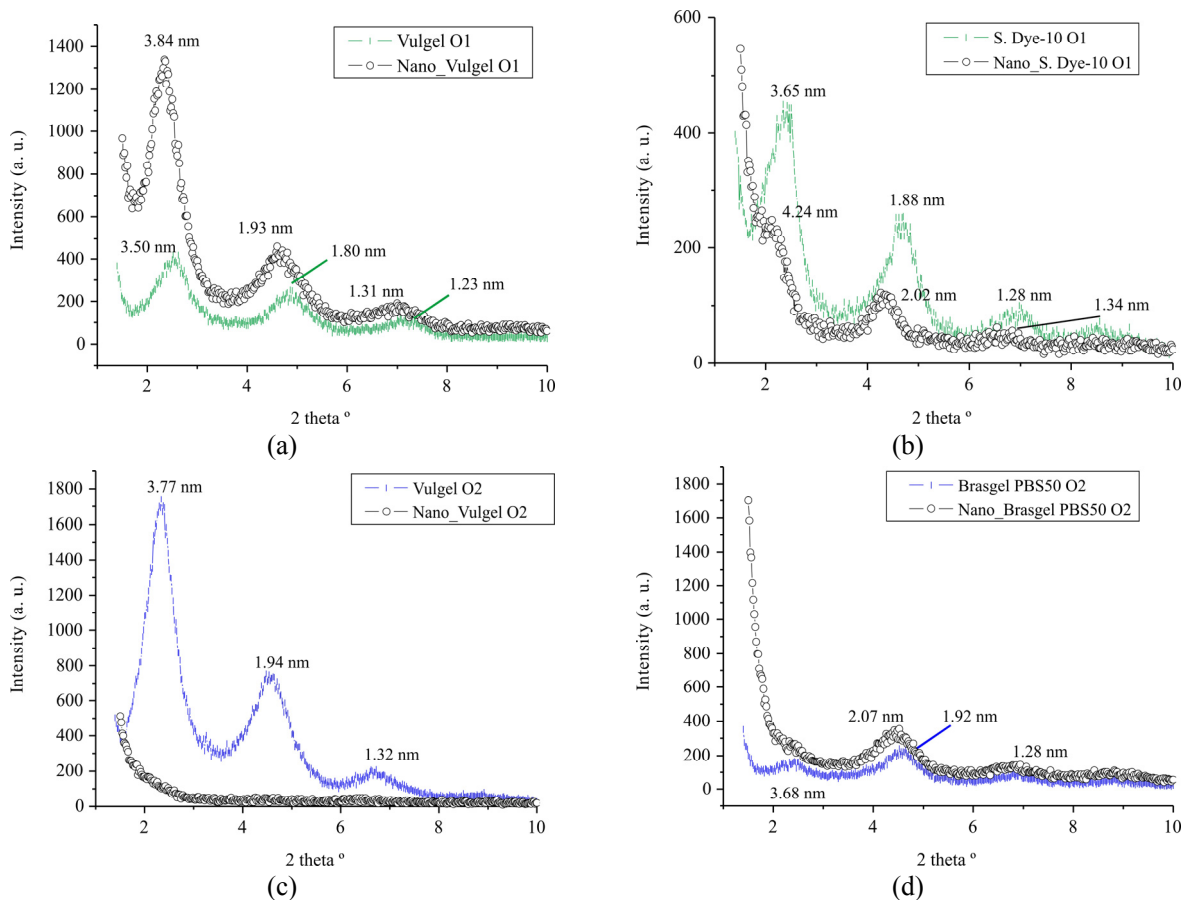


Figure 3: X-ray diffraction patterns of organophilic bentonites (a) Vulgel O1, (b) Soleminas Dye-10 O1, (c) Vulgel O2 and (d) Brasgel PBS50 O2 and their respective nanocomposites.

Table 2: Basal spacings of the (001) reflections of organophilic bentonites and their respective nanocomposites.

Bentonite/nanocomposite	d (nm)
Vulgel O1	3.50
Nano_Vulgel O1	3.84
Vulgel O2	3.77
Nano_Vulgel O2	-
TEC-09 O1	3.62
Nano_TEC-09 O1	3.80
TEC-09 O2	3.80
Nano_TEC-09 O2	4.24
Reminas O1	3.84
Nano_Reminas O1	4.20
Reminas O2	3.87
Nano_Reminas O2	4.08
Soleminas Dye-10 O1	3.65
Nano_Soleminas Dye-10	4.24
Soleminas Dye-10 O2	3.77
Nano_Soleminas Dye-10 O2	4.20
Bentogel Patag O1	3.45
Nano_Bentogel Patag O1	3.87
Bentogel Patag O2	3.53
Nano_Bentogel Patag O2	4.08
Brasgel PBS50 O1	3.74
Nano_Brasgel PBS50 O1	4.16
Brasgel PBS50 O2	3.68
Nano_Brasgel PBS50 O2	-

Among the composites prepared with the organophilic bentonites modified in aqueous dispersion, the samples Nano_Vulgel O1, Nano_TEC-09 O1, Nano_Reminas O1 e Nano_Brasgel O1 showed X-ray diffraction patterns similar to the organophilic bentonites, but with larger basal spacings. This suggests that intercalation of the polymer chains occurred, but the clay structure was preserved. The possibility of partial exfoliation exists, but only the structurally ordered fraction is detected by this technique. The sample Nano_Soleminas Dye-10 O1 did not show a well-defined diffraction peak in the region of $2\theta = 2^\circ$, but instead a “shoulder” at 2.08° was observed that corresponds to a basal spacing of 4.24 nm, while in the organophilic bentonite the diffraction angle was 2.42° and the basal spacing was 3.65 nm. The same behavior was observed for Nano_Brasgel PBS50 O1, which showed a basal spacing of 4.16 nm. The results suggest that structures with some degree of disorder were obtained, but it is possible that partially intercalated and exfoliated structures occurred. For the composites from organophilic bentonites modified in aqueous dispersion, considering the main diffraction peak, the highest basal spacing was obtained for Nano_Soleminas Dye-10 O1, 4.24 nm, while the lowest was for Nano_TEC-09 O1, 3.80 nm. Among the composites from the organophilic bentonites modified in semisolid medium, disappearance of all diffraction peaks occurred for the Nano_Vulgel O2, which is a strong indication that an exfoliated structure was formed. The composites Nano_TEC-09 O2, Nano_Reminas O2, Nano_Soleminas Dye-10 O2 and Nano_Bentogel Patag O2 also did not show well-defined diffraction peaks in the region of $2\theta = 2^\circ$ as observed in the respective organophilic bentonite. The results again suggest the formation of structures with some degree of disorder with the possibility of the existence of partially intercalated and exfoliated structures. Nano_Brasgel PBS50 O2 did not show a diffraction peak in the region of $2\theta = 2^\circ$ which suggest that the bentonite was partially exfoliated. For the composites prepared with the organophilic bentonites modified in semisolid medium, the highest basal spacing was for Nano_TEC-09 O2, 4.24 nm, and the lowest was for Nano_Reminas O2 and Nano_Bentogel Patag O2, 4.08 nm (slightly lower, but not a significant difference). The two hypotheses discussed for the occurrence of the three diffraction peaks in the organophilic bentonites (previously discussed in Part 1 of this work) can be considered for the composites. The first hypothesis is based on the existence of different levels of intercalation of organic cations between the clay

layers, promoting different expansions of the basal planes; therefore, it is possible that the intercalation of polymer chains occurs in the three regions and that, for this reason, the structure of the organophilic bentonite was maintained. However, it is not very probable that the polymer chains would adopt the same configuration as the organic cations to maintain the structure of the organophilic clay. So this hypothesis does not explain the results well. It is more probable that the intercalation of polymer chains occurred in the region of higher basal spacing, while no intercalation occurred in the other two regions, as suggested by Barbosa *et al.* (2006). The second hypothesis considers that the three diffraction peaks are reflections of the (001), (002) and (003) planes, suggesting that intercalation of the polymer chains occurred, increasing the basal spacing of the (001) planes, represented by the diffraction peak of the $2\theta = 2^\circ$ region. Consequently, the reflections of the (002) and (003) planes also increase. However, the values are not exact because there are different levels of intercalation between the clay layers. This hypothesis is more convincing and explains better the fact that some of the samples showed the same structure of the organophilic clay. Besides, it is the more probable hypothesis for the occurrence of the three diffraction peaks discussed previously in Part 1 of this work (Paiva and Morales, 2012). Zhang *et al.* (2005) also observed the presence of three diffraction peaks in the X-ray patterns of organophilic clays and nanocomposites of polyethylene and PP, where the original structure of the organophilic clay was preserved. However, the authors only refer to the diffraction peak at the lower angle as a reflection of the (001) plane. The nanocomposites showed a basal spacing between 4.2 nm and 4.4 nm, while the basal spacing of the organophilic clay was 3.8 nm. These results are similar to the ones found in the present work. Mandalia and Bergaya (2006) also found similar results for nanocomposites prepared with polyethylene and EVA as matrices. The authors considered the existence of reflections of the (001), (002) and (003) planes for the three regions. By comparison with other work in the literature, there are some divergences in the interpretation of the existence of more than one diffraction peak in the patterns of composites. The results show that the polymer chains were intercalated between clay mineral layers and that composites with intercalated and partially intercalated and exfoliated structures were formed, depending on the sample. Furthermore, the composites were formed with organophilic bentonites obtained using two methodologies of modification and did not show significant differences

in the structures. This is one more indication of the efficiency of modification of bentonites by semisolid methodology and show that the bentonites modified by this method can be employed to obtain polymer nanocomposites. The potential to obtain nanocomposites with the studied bentonites is another aspect to be considered.

Evaluation of the Dispersion of Organophilic Bentonites in PP by Transmission Electronic Microscopy

To complete the characterization of the composites; TEM micrographs are presented in Figures 4 and 5. In the micrographs, dark regions with lamellar form with different thicknesses

attributed to the organophilic clay phase can be observed. The thinner regions suggest the presence of individual layers or tactoids with few layers of clay minerals, while the thicker ones must be agglomerates of clay particles or even impurities. The TEM micrographs show that dispersion of the clays occurred in all samples, but at different levels. It is possible to observe the existence of different phases. Different levels of basal spacings were observed by X-ray analysis and some exfoliation should be expected. A limitation of this analysis is that the observation field of TEM is small and the interpretation must be careful. In order to interpret the results, a classificatory scale was used, which takes into account the observed aspects, as explained in the next paragraphs.

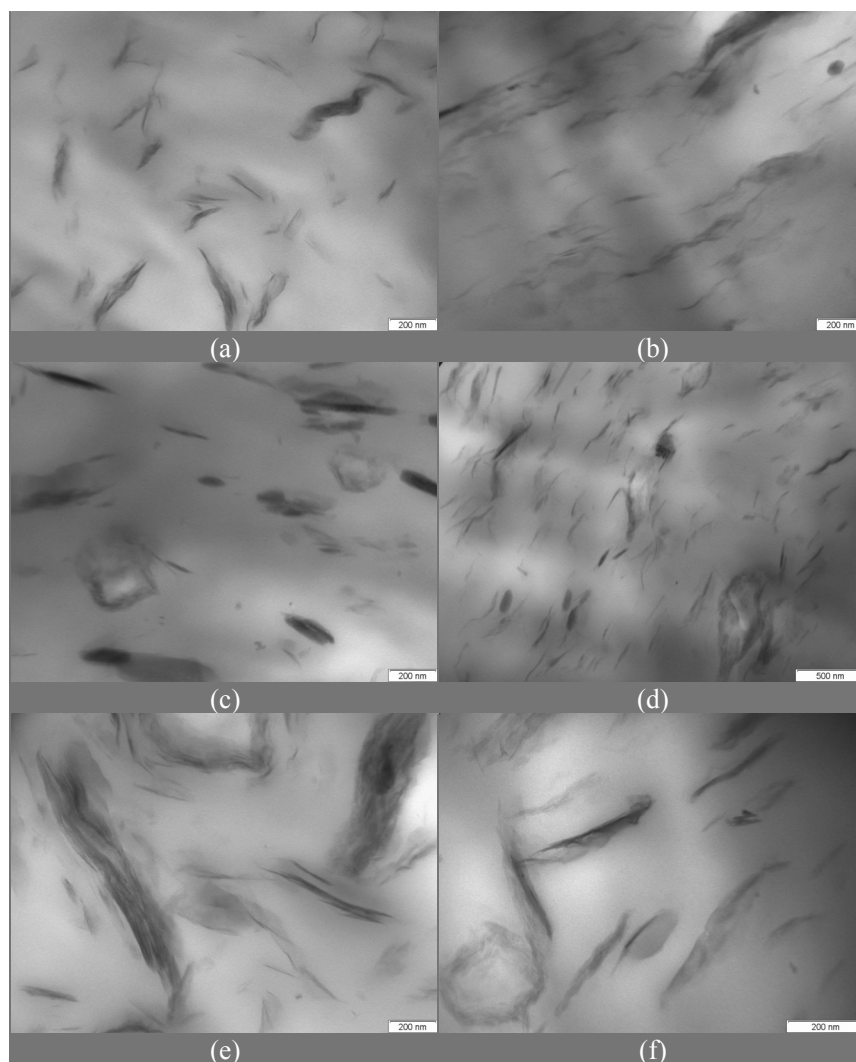


Figure 4: TEM micrographs: (a) Nano_Vulgel O1, (b) Nano_TEC-09 O1, (c) Nano_Reminas O1, (d) Nano_Soleminas Dye-10 O1, (e) Nano_Bentogel Patag O1, (f) Nano_Brasgel PBS50 O1.

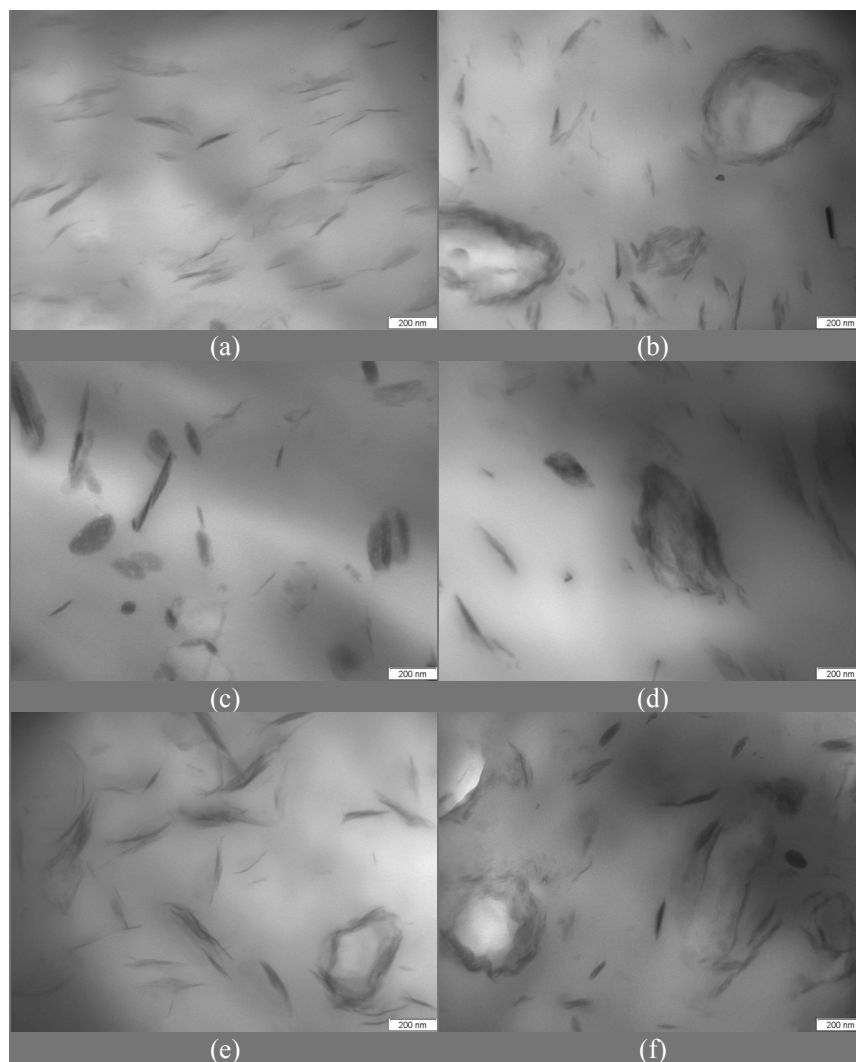


Figure 5: TEM micrographs: (a) Nano_Vulgel O2, (b) Nano_TEC-09 O2, (c) Nano_Reminas O2, (d) Nano_Soleminas Dye-10 O2, (e) Nano_Bentogel Patag O2, (f) Nano_Brasgel PBS50 O2.

Class 10

Predominance of a dispersed phase with flexible layers highly spread in all extension, with clear color. Absence of non-dispersed particles, agglomerates or impurities. Good dispersion with predominance of exfoliation - Sample: Nano_Vulgel O2

Class 8

Existence of mixture:

1. Dispersed phases with the characteristic of flexible layers highly spread in all the extension, with clear color;
2. Dispersed phases with stacked layers and dark color. Presence of non-dispersed particles, absence of agglomerates or impurities. Good dispersion with a mixture of intercalation and exfoliation - Samples:

Nano_Vulgel O1, Nano_Bentogel Patag O1 and Nano_Bentogel Patag O2.

Class 6

Presence of non-dispersed and dark particles, agglomerates or impurities, with a morphology as described in Class 10. Medium dispersion with partial intercalation and exfoliation, non-intercalated particles or impurities - Samples: Nano_TEC-09 O1 and Nano_TEC-09 O2.

Class 4

Dispersed phase with stacked layers and dark color. Presence of non-dispersed particles, agglomerates or impurities. Low dispersion, with predominance of intercalation, and few exfoliated regions - Samples:

Nano_Soleminas Dye-10 O1, Nano_Soleminas Dye-10 O2, Nano_Brasgel PBS50 O1 and Nano_Brasgel PBS50 O2.

Class 2

Presence of many dark particles, agglomerates or impurities, with a morphology as described in Class 4. Very low dispersion, intercalation, and non-intercalated particles or impurities - Samples: Nano_Reminas O1 and Nano_Reminas O2.

In some cases, regions with fractions of clay of round or ellipsoidal shapes with a clear aspect in the center with intercalated/exfoliated appearance can be observed. This characteristic can be associated with particles of organobentonite that opened but were not totally dispersed due to an insufficient shear; or can be fractions of organophilic bentonite near the polar regions of the maleic anhydride used as the coupling agent.

The results showed that there is not a well-defined and unique structure, but a distribution of phases, where intercalated, exfoliated and agglomerate regions co-exist. However, there is the presence of fractions with a good separation of the layers of the organophilic clay, mainly for organophilic bentonites from the Argentinian sodium bentonites, Vulgel O1, Vulgel O2, Bentogel Patag O1 and Bentogel Patag O2.

The existence of intercalated, exfoliated and agglomerate phases in nanocomposites was also observed by Chow *et al.* (2005) for polyamide-6/PP and organophilic clay nanocomposites.

Hedayati and Arefazar (2009) evaluated the dispersion of commercial organophilic clay modified with similar quaternary ammonium salts in a PP-g-MA matrix and also observed a non-uniform dispersion of the clay in the matrix, besides some indistinct tactoids. The micrographs also showed intercalated and partially exfoliated phases.

It is not possible to make a precise identification of the structures only by the TEM or XRD techniques, because the techniques are different. While TEM allows the observation of different phases and also some impurities and particles shape, XRD allows an evaluation of the basal spacing between layers of the clay. For this reason, the results of both techniques are complementary. As an example, the analyses made with Nano_Vulgel O1 where the diffraction peaks showed an intercalated structure can be mentioned; however, the micrograph showed an intercalated and exfoliated structure. For Nano_Vulgel O2, the XRD analysis showed an exfoliated structure that was confirmed by TEM. In conclusion, compared to other results found in the literature, similar microstructures for nanocomposites with exfoliated, partially exfoliated and intercalated and intercalated structures were obtained.

Properties Correlation

In this section, some correlations between the properties of sodium or organophilic bentonites and the properties of composites are presented. The purpose is to complement the correlations of properties presented in Part 1 of this work and to finish the evaluation of the potential use of bentonites to obtain polymer nanocomposites.

The results showed that there is a strong tendency of sodium bentonites with higher cation exchange capacity (CEC) in the organophilic form to better disperse in the polymer matrix. This can be observed in the sodium bentonites Vulgel S and Bentogel Patag S; they had the higher CEC and their respective composites had the better classification as evaluated by TEM. The bentonite Reminas S had the lowest CEC and the respective composites showed the worst classification by TEM. This correlation is shown in Figure 6. The higher CEC conferred better organophilic characteristics on the bentonites and thus promoted a better dispersion of the bentonites in the composites. Chavarria *et al.* (2007) also observed that lower values of the CEC resulted in a low degree of exfoliation of organophilic clays in nanocomposites with polyamide-6 and PP/PP-g-MA.

In Figures 7(a) and 7(b) the influence of basal spacing of the organophilic clays on the basal spacing of composites can be analyzed. There is a dependency, which can be considered partial, of a higher basal spacing of organophilic bentonites leading to a higher basal spacing of the composites, considering the intercalated phases. All samples prepared with bentonites modified in aqueous dispersion showed a (001) reflection; however, among the samples prepared with the bentonites modified in semisolid medium, Nano_Vulgel O2 did not show any basal reflection. Besides, this composite was not derived from the organophilic bentonite with the highest basal spacing, but resulted in an exfoliated structure. This indicates that a good intercalation or exfoliation does not necessarily occur for organophilic clays with high basal spacing. A similar behavior was observed for Nano_Brasgel PBS50, in which the main basal reflection disappeared, but did not show the highest basal spacing. Delbem (2005) also observed that the high basal spacing in organophilic clays is not the main parameter that contributes to the formation of intercalated or exfoliated structures.

The correlation of swelling capacity of organophilic clays in xylene and the classification of nanocomposites by TEM, Figures 8(a) and 8(b), showed a tendency of the bentonites with higher swelling capacity in xylene to have a better classification by TEM, which can be attributed to a better dispersion in the polymer matrix.

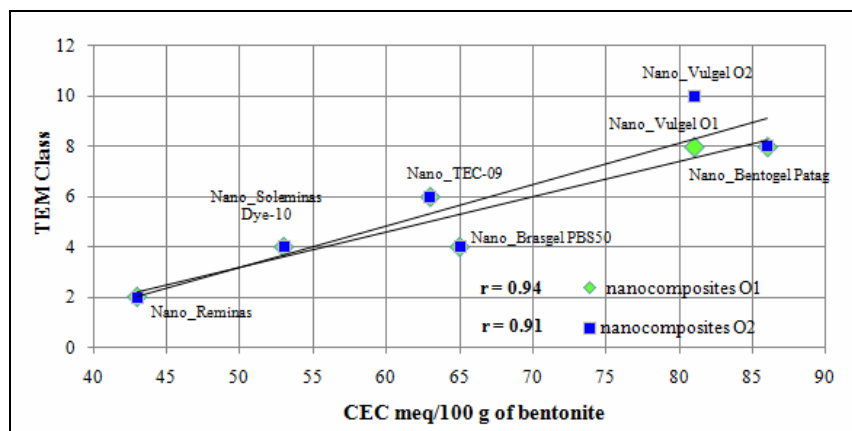
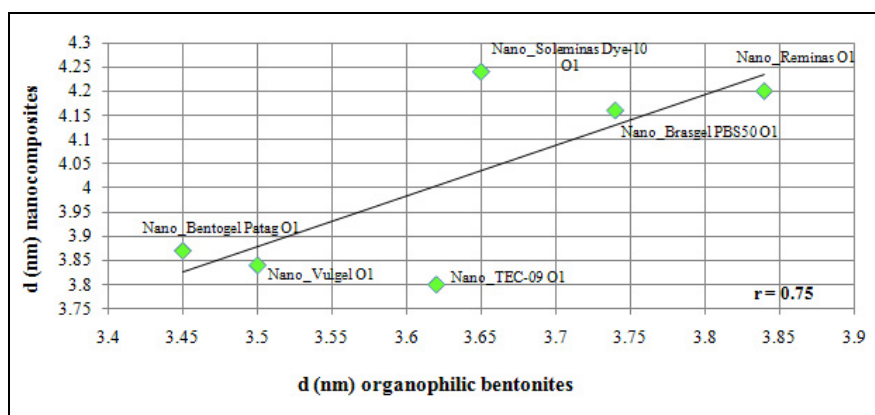
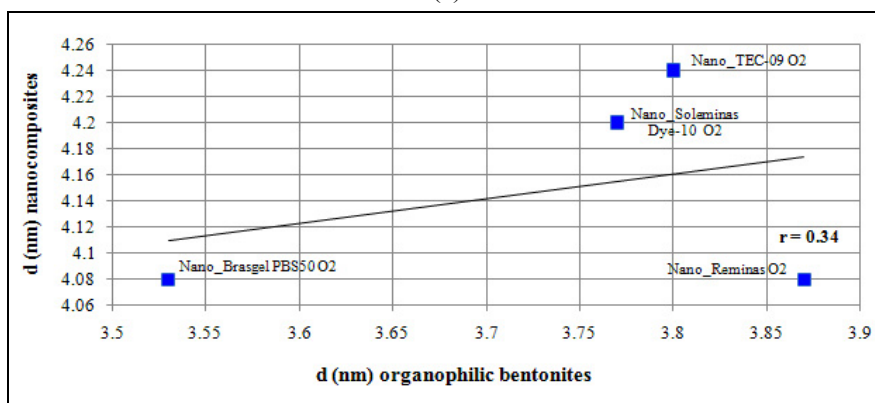


Figure 6: CEC of sodium bentonites versus TEM class micrographs.

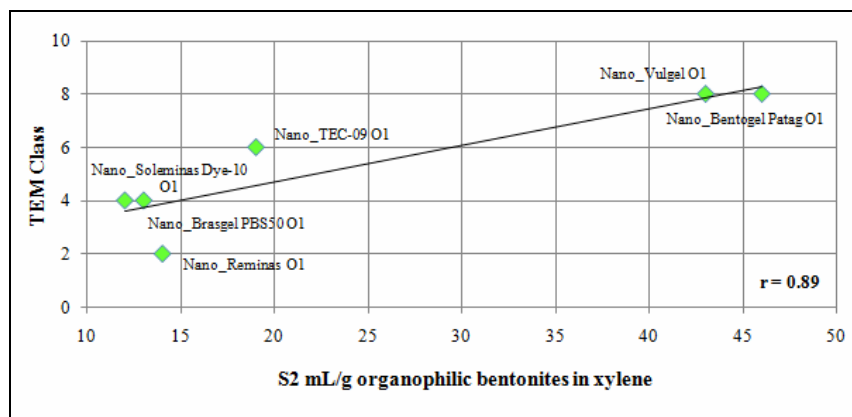


(a)

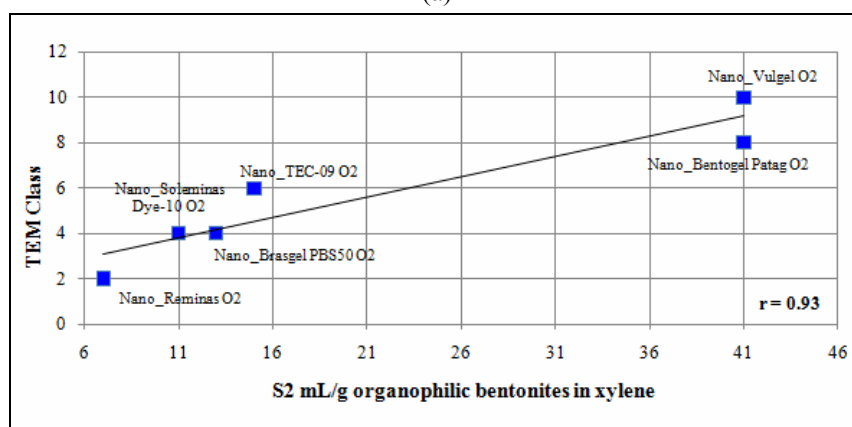


(b)

Figure 7: Basal spacing of organophilic bentonites versus basal spacings of their respective nanocomposites: (a) organophilic clays O1 (modified in aqueous dispersion); (b) organophilic clays O2 (modified in semi-solid medium).



(a)



(b)

Figure 8: Swelling capacity in xylene (after stirring and standing 24 h) of organophilic bentonites versus TEM class micrographs of their respective nanocomposites: (a) organophilic clays O1 (modified in aqueous dispersion); (b) organophilic clays O2 (modified in semi-solid medium).

In all curves the correlation coefficient, r , is presented. Except for the correlation between basal spacing of organophilic bentonites and the basal spacing of the composites, Figure 7, the values of r indicate moderate to strong correlation.

Based on these analyses, it was observed that for nanocomposites obtained from organically modified bentonites the structures of the nanocomposites were strongly dependent on several properties of the sodium bentonites. Among these properties, swelling capacity in water and cation exchange capacity (CEC) were the most significant. In summary, higher swelling capacities and higher CEC produce organophilic bentonites with more pronounced organophilic characteristics which in turn contribute to a better dispersion of the bentonites in the PP matrix.

CONCLUSION

The organophilic bentonites studied showed good performance in the preparation of the composites. The composites showed exfoliated, partially exfoliated and intercalated, and intercalated structures, depending on the bentonite grade. The results were similar to those found in other works in the recent literature, which show that the systems obtained are promising.

The capacity of intercalation and exfoliation and the type of structure of the composites were strongly influenced by the cation exchange capacity of the sodium bentonites and by the swelling capacity in xylene of the organophilic bentonites. Although all bentonites presented a good behavior, the grades from Argentina showed higher potential to obtain PP nanocomposites.

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