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Characterization of HDPE /Polyamide 6/ Nanocomposites Using Scanning-and Transmission Electron Microscopy

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Summary: Preparation and morphology of high density polyethylene (HDPE)/ polyamide 6 (PA 6)/modified clay nanocomposites were studied. The ability of PA 6 in dispersing clays was used to prepare modified delaminated clays, which were then mixed with HDPE. Mixing was performed using melt processing in a torque rheometer equipped with roller rotors. After etching the materials with boiling toluene and formic acid at room temperature, the morphology was examined by SEM analyses, showing that the PA 6 formed the continuous phase and HDPE the dispersed phase. X-ray diffraction patterns show that the (001) peak of the clay is dramatically decreased and shifted to lower angles, indicating that intercalated/exfoliated nanocomposites are obtained. TEM analyses confirmed the typical structure of exfoliated nanocomposites. A scheme for the mechanism of exfoliation and/or intercalation of these HDPE /PA 6/ /organoclay nanocomposites is proposed.

Keywords: clay; morphology; nanocomposites; polyamide; polyethylene

Introduction

The synthesis of clay-based nanocomposites by conventional polymer processing operations requires strong interfacial interaction between the polymer matrix and the clay to generate shear forces of sufficient strength to obtain adequate dispersion. This is readily achieved with high surface energy polymers such as polyamides, which polarity and hydrogen-bonding capacity generate considerable adhesion between the polymer and clay phases.

Interest in polyolefin nanocomposites has emerged due to their promise of improved performance in packing and engineering applications. However, materials with low surface energy such as polyethylene weakly interact with mineral surfaces, making the synthesis of polyolefin nanocomposites by melt compounding considerably more difficult.[1,2]

On the other hand, it is well known how the properties of one-component polymer systems can be improved by adding another polymer. PA 6 is one of the most widely used engineering polymers, but it has some disadvantages such as brittleness, high moisture absorption and poor dimensional stability. To overcome these disadvantages PA 6 is frequently blended with polyethylene, although they are incompatible.

When incompatible polymers are blended, they usually form multiphase morphologies. This characteristic is also shown in polyethylene and PA6 blends.[3,4]

Several papers have reported on the effects of organoclays on the properties of polymer blends.[5] In this work the interfacial adhesion and morphology of HDPE/

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PA 6/modified clay nanocomposites were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Experimental Part

Materials

An Argentinean montmorillonite (MMTAr) from Minarmco S.A. was used in this study. HDPE with a melt flow index (MFI) (190 °C/5 kg - ASTM D 1238) 0.41 g/10 min, density (ASTM D 792) 0.9530 g/cm^3 and softening point (ASTM D1525) 127 °C was provided by Polisur. PA 6 (Nylodur) with $[NH_2] = 55$ meq/kg, Mw = 32,600 g/mol, Tm = 212–220 °C and Tc = 173 °C was provided by DeMillus. Hexadecyl trimethyl ammonium chloride (HDTAM) (GENAMIN/CTAC) and ε-caprolactam were kindly supplied by Pharma Special and Braskem, respectively.

Clay Modification

Two modified clays were prepared: one modified with ε-caprolactam and one modified with HDTAM. Montmorillonite intercalated with ε-caprolactam (MMTArInt) was prepared using the Kojima Method.[5] The modification with HDTAM (MMTAr-HDTAM) was carried out according to Valenzuela technique.[6]

HDPE/PA 6/ Organoclay Nanocomposite Preparation

Mixing was performed using melt compounding by processing the components in a Haake torque rheometer Rheocord 9000, equipped with a mixing chamber and roller rotors. Composites were prepared with 3 wt% of filler. Blends containing 57% PA 6 and 43% HDPE were prepared at 245 °C, 10 min and 60 rpm.

Film Preparation

Films were manufactured by compression molding in a Carver press, heating at 240 °C and cooling the film in a cold press at room temperature. These films presented thickness of approximately 350 μm.

HDPE/PA 6/ Organoclay Nanocomposite Characterization

Modified clays and blends were characterized using a Shimadzu DRX 6000 diffractometer with a nickel filter and CuKα radiation ($\lambda = 1.54$ Å), operating at 40 kV and 30 mA. Data were recorded at 2θ rates of 2° per minute. Bragg's law ($\lambda = 2\ d \sin\theta$) was used to calculate the gallery spacing of the organoclay.

Characterization of blend morphologies was performed in a scanning electron microscope JEOL JSM-5600. The fractured surfaces of the nanocomposites for SEM imaging were prepared by cryogenic frac-

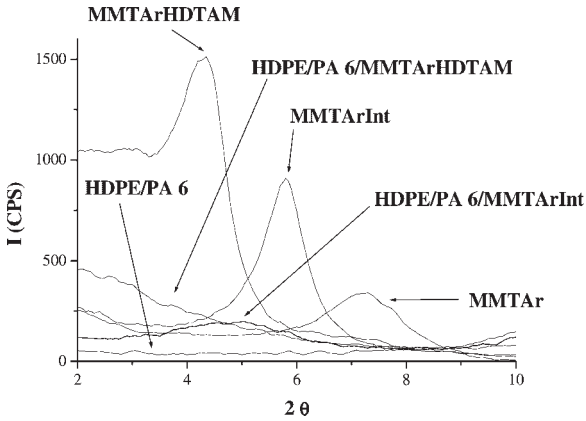


Figure 1.
XRD patterns of MMTAr, MMTArHDTAM, MMTArInt and HDPE/PA 6/organoclay nanocomposites.

Table 1.
Interlayer spacing of the different clays and blends.

Sample	2θ (°)	Basal spacing (Å)
MMTAr	7.30	12.3
MMTArInt	5.70	15.5
HDPE/PA 6/MMTArInt	4.95	17.8
MMTArHDTAM	4.29	20.8
HDPE/PA 6/MMTArHDTAM	2.82	31.4

turing in liquid nitrogen and then sputter-coating with Au. Samples were vapour phase-etched with boiling toluene in order to remove HDPE, and with vapour of formic acid at room temperature to remove PA 6.

Transmission electron microscopy (TEM) was carried out in a JEOL TEM-1210 using an accelerator voltage of 60 kV. Ultrathin sections of the composites with a thickness of approximately 50 nm were prepared in a Reichert ultramicrotome Ultracut S50 equipped with a diamond knife. Samples were analyzed without any staining.

Results and Discussion

Two organoclays were prepared to formulate HDPE/PA 6/ organoclay nanocomposites: 1) the filosilicate was intercalated with a quaternary ammonium salt derived from ε-caprolactam and 2) the clay was modified by mixing with hexadecyl trimethyl ammonium chloride. Thus, the effect of montmorillonite clay chemical modifications on the morphology of HDPE/ PA 6/ organoclay nanocomposite systems was investigated.

Figure 1 shows XRD patterns for MMTAr, MMTArHDTAM, MMTArInt and HDPE/PA 6 based blends containing 3 wt% of the organoclays. In both HDPE/ PA 6 materials, PA 6 seems to have a significant influence in the reduction of the

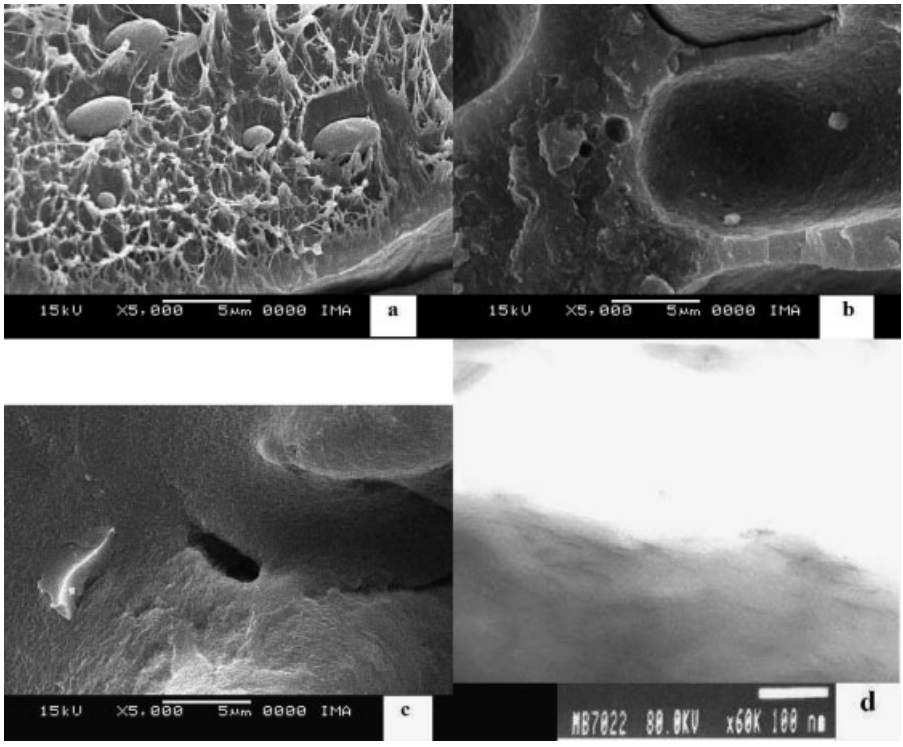


Figure 2.
SEM and TEM of HDPE/PA 6/ MMTArHDTAM: a) SEM HDPE/PA 6, b) SEM HDPE/PA 6/MMTArHDTAM etched with toluene vapor, c) SEM HDPE/PA 6/ MMTArHDTAM etched with formic acid vapor at room temperature, d) TEM HDPE/PA 6/ MMTArHDTAM.

clay characteristic diffraction peak intensity. A shifting of the (001) peak to lower angles could be also observed.

The d-spacing of silicate layers in the nanocomposites were measured using XRD. Table 1 shows that the organic species were efficiently intercalated with MMTAr. The higher interlayer spacing was obtained for MMTArHDTAM. In this case, the basal spacing corresponds approximately to the length of alkyl chains. The new interlayer spacing in MMArInt agrees with ε-aminocaproic acid dimension.

When the modified clays were mixed with PA 6 and HDPE as described above, in both cases mixed intercalated/exfoliated morphology of the silicate layers seemed to have taken place, resulting in nanocomposite structures.

HDPE/PA 6/ Organoclay Nanocomposite Morphology

For morphological investigation, the nanocomposites were examined by SEM and TEM analyses. The morphology of PA 6/HDPE blends is presented in Figure 2 and 3. The images clearly show that in these blends containing 57% PA 6, 40% HDPE and 3 wt% organoclay two phases are well separated due to the HDPE - PA 6 poor compatibility.

SEM images on Figure 2 are in agreement with what was expected for HDPE/PA 6/ MMTArHDTAM. Figure 2b shows hollows resulting from the HDPE removed by extraction with toluene vapour and Figure 2c shows polyamide phase extracted by formic acid.

Figure 3a shows HDPE/PA 6 morphology in which also two phases can be distinguished. SEM micrograph of Figure 3b shows holes on PA 6 surface corresponding to HDPE removed with toluene. The extraction of PA 6 with formic acid is observed in Figure 3c.These pictures state the presence of HDPE domains in the continuous phase.

TEM analyses confirmed the typical structure of the nanocomposites for HDPE/PA6/MMTArHDTAM (Figure 2d) and

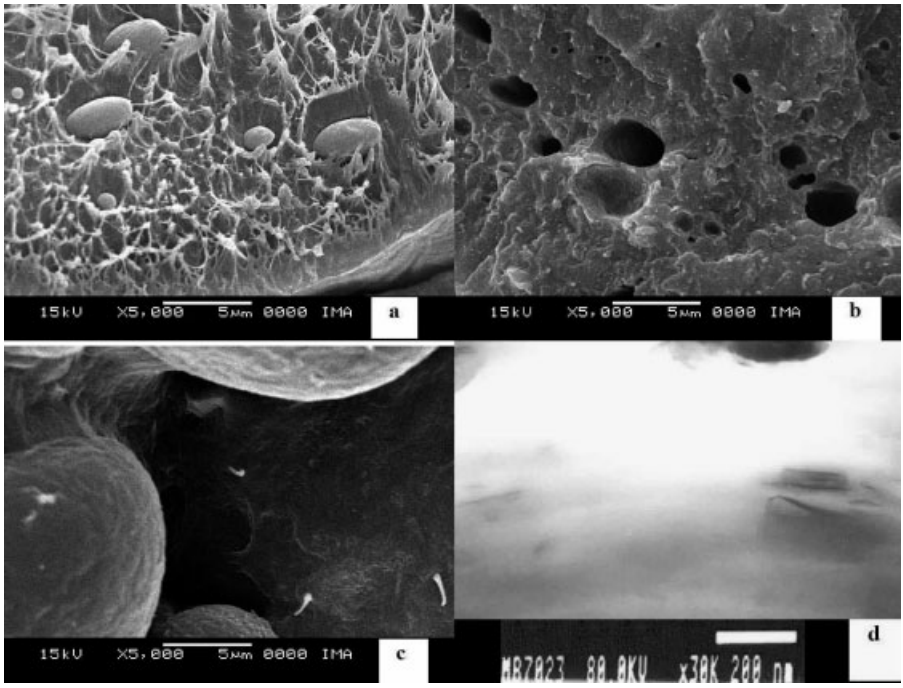


Figure 3.
SEM and TEM of HDPE/PA6 /MMTArInt: a) SEM HDPE/PA6, b) SEM HDPE/PA6/MMTArInt etched by toluene vapor, c) SEM HDPE/PA6/MMTArInt etched by formic acid vapor at room temperature, d) TEM HDPE/PA6/ MMTArInt.

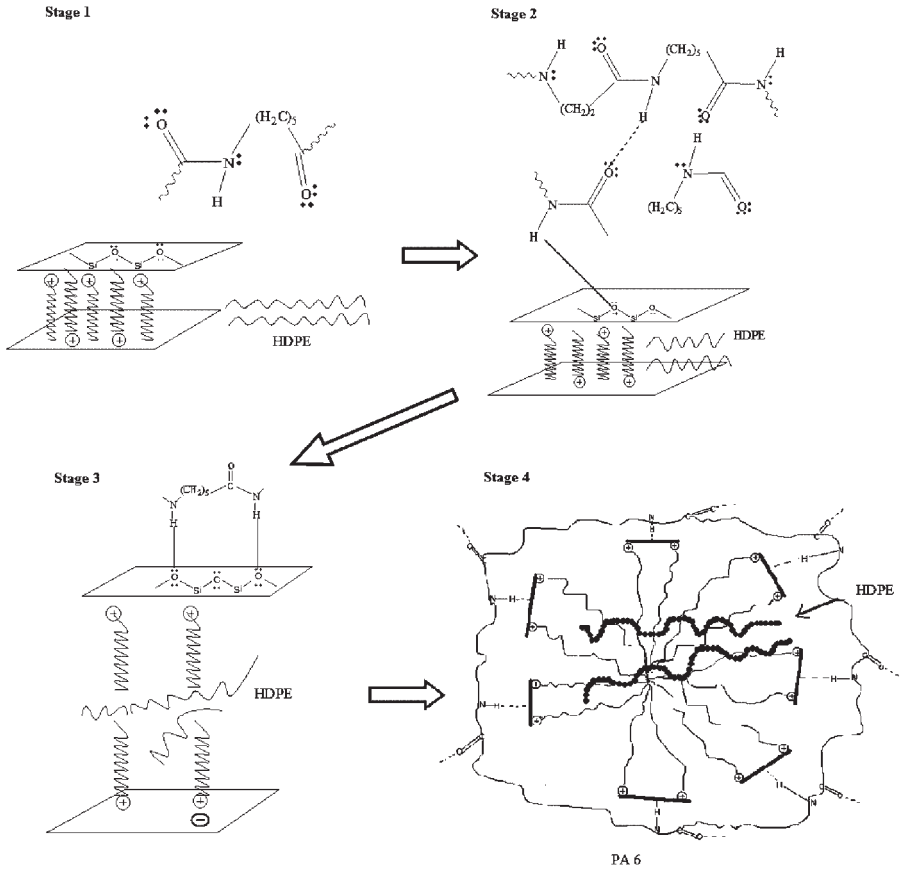


Figure 4.
Schematic illustration of HDPE/PA 6/MMTArHDTAM nanocomposites formation.

HDPE/PA6/MMTArInt (Figure 3d). The dark lines correspond to intersecting layers in the PA 6 matrix.

It was considered that these results would be due to intercalation and /or exfoliation of the organoclay added to the blend system, as the following mechanisms proposed bellow.

HDPE/PA 6/ MMTArHDTAM System

The process of nanocomposites formation from organophilic clays could be under-

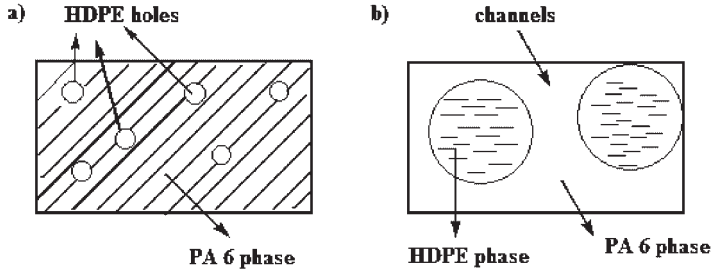


Figure 5.
Schematic diagram of HDPE/PA 6/MMTAHDTAM system a) etched with toluene vapour and b) etched with formic acid vapour.

stood considering the intermolecular forces that take place in each system. HDPE/ PA 6/ MMTArHDTAM system can be explained by the process showed in the scheme presented in Figure 4.

The organophilic clay is brought into contact with the non polar HDPE and PA 6, a molecule with a permanent dipole due to amide groups and peptide bonds (stage 1). PA 6 is able to form hydrogen bonds between polymer chains and the oxygen polar sites on the surface of the silicate. At the same time, HDPE chains are driven into the layers of clay in which the medium contains non polar chains from de hexadecyl group. The environment is non-polar and decreases the interaction between the layers, allowing the entrance of the HDPE (stage 2).

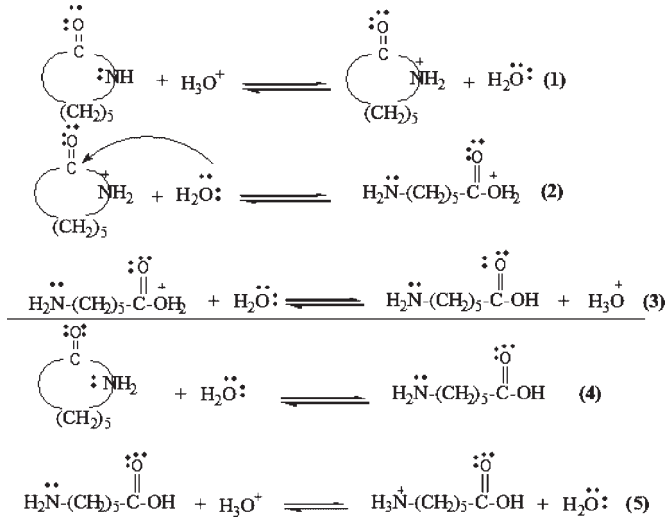
This process leads to the exfoliation of the silicate as this is the energetically preferred state. On the other hand, charges in the silicate are ionically bound to ammonium ions, and the outer layers of the silicate are bound to PA6 through hydrogen bonding. In addition, the non-polar chains of the ammonium ion have the tendency to interact with the HDPE chains by Van der Walls-type interactions (stage 3). This type of interaction would be possible if some degree of miscibility in the molten state took place during the melt processing.

This leads to the formation of clay-reach domains (a kind of micelles) at the interface of the continuous PA 6 phase/HDPE. In turn, the chains are also strongly bonded by hydrogen bonds (stage 4).

The morphologies of HDPE/PA 6 blends were studied by SEM. SEM images of samples etched with toluene vapour show the voids left by HDPE on the PA6 phase. However, when PA 6 is etched with formic acid vapour, a more homogeneous material results (with small voids). This morphology seems reasonable since the extraction takes place from PA 6 chains in the continuous phase. Figure 5 shows a schematic diagram of both samples, etched with toluene vapour and formic acid.

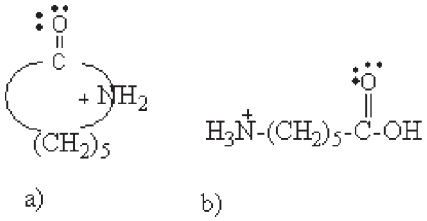
HDPE/PA 6/ MMTArInt System

In order to have a good better insight on the MMT- ε-caprolactam system, it is necessary to define carefully the ionic species in the reaction medium. Under the conditions in which the ionic exchange takes place (in chloridric acid), the ε-caprolactam solution contains the following species:



The medium catalyzes ε-caprolactam hydrolysis (1) and the formation of a cationic form of ε-aminocaproic acid (5).

As a consequence, the exchange of (Na+, K+, Ca++) of MMT can take place with two types of ammonium ions:



So, there is then the possibility of forming two organophilic clays as shown in Figure 6.

In the case of the MMTArInt clay, it is reasonable to assume that PA 6 molecules form hydrogen bonds with the outer edge of the silicate layer, and that they can also form hydrogen bonds with the OH part of the COOH group and the same groups of the silicate. The results obtained by Usuki et al.[7] suggested that *the chain axes of ω-amino acids with a carbon number of eight or less were parallel to the silicate layers, and that the chain axis of those with the carbon number of 11 or more were slanted to the layers*. A continuous phase appears comprised of PA 6 and exfoliated clay. In this polar medium, HPDE forms non polar domains that do not interact with the continuous phase (Figure 6c).

SEM images clearly showed this process. Figure 7 shows a schematic diagram of both samples, etched with toluene vapour and formic acid. In Figure 7a, which corresponds to the extraction with toluene, voids from the lixiviation of HPDE are observed, whereas Figure 7b shows the results after formic acid extraction. In this case, can be observed the remnant HDPE phase separated by channels containing the phase with PA 6 and exfoliated and/or intercalated clay.

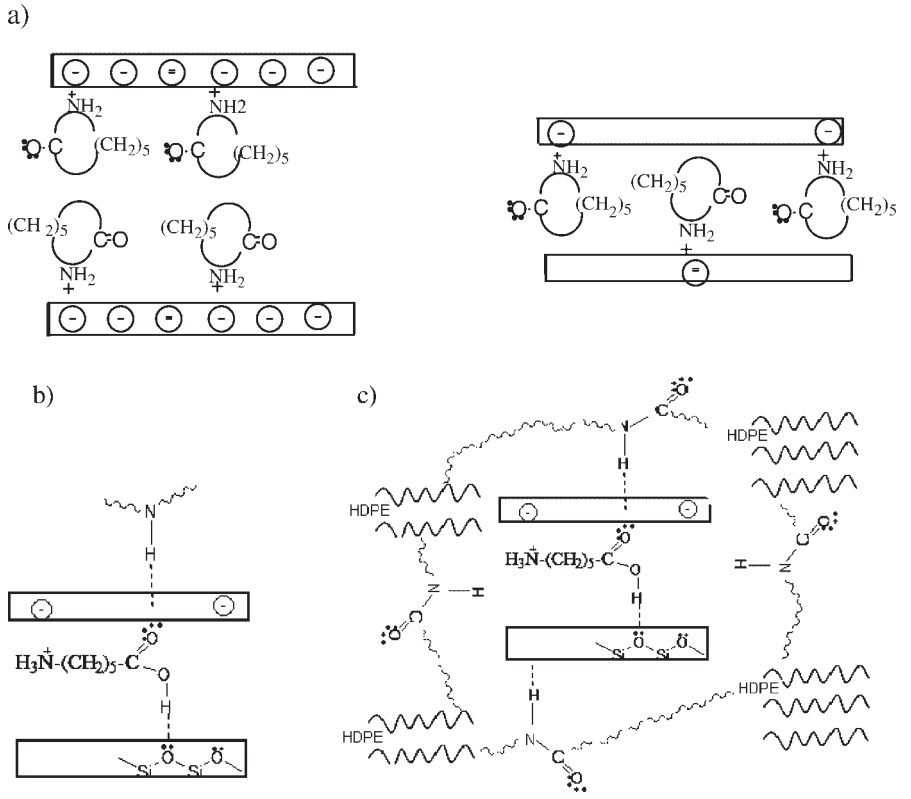


Figure 6.
Schematic illustration of HDPE/PA 6/MMTArInt nanocomposite formation.

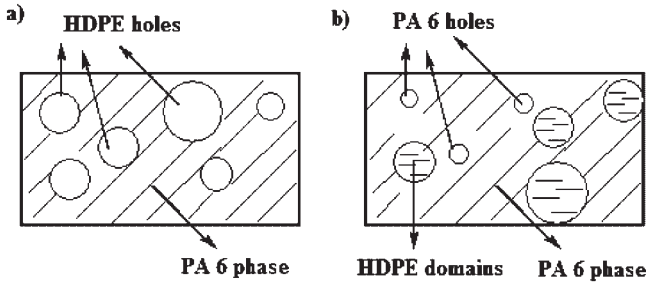


Figure 7.
Schematic diagram of HDPE/PA 6/MMTAInt samples a) etched with toluene vapour and b) etched with formic acid vapor.

The XRD patterns of Figure 1 clearly showed that the exchange of MMTAr with HDTMA shifts the (001) peak towards smaller angles ($2\theta = 4.29^\circ$) which correspond to a larger interlayer spacing d = 20.8 Å than that observed when the exchange is conducted with ε-caprolactame ($2\theta = 5.7^\circ$ and d = 15.5 Å). In the former case, the interlayer separation corresponds to the size of the molecule of hexadecylammonium, whereas in the second case the separation corresponds to the thickness of the silicate layers and the diameter of the ε-aminocaproic acid molecule.

The two organoclays were mixed with HDPE/PA 6, and in both cases mixed morphology of intercalated and/or exfoliated nanocomposites were obtained. Nevertheless, the diffractograms show an intercalation length of d = 17.8 Å for HDPE/PA 6/ MMTArInt, and d = 31.4 Å for HDPE/PA 6/MMTArHDTAM. These results are in accordance with our previous explanations and are supported by SEM and TEM data.

Conclusion

HDPE/PA6 /MMTArHDTAM and HDPE/PA 6/MMTArInt nanocomposites were successfully prepared via melt compounding method and characterized by XRD, SEM and TEM analyses. The morphology of the HDPE/PA 6/organoclay nanocomposites studied by these techniques showed that phase separation takes place, but the organoclay is well dispersed in the polymer blend matrix, forming the typical structure of nanocomposites. The proposed mechanisms for nanocomposites formation are in accordance with the results obtained from these different characterization techniques and took into consideration the strong interaction of PA 6 and the filosilicate filler.

[1] H. R. Dennis, D. L. Hunter, D. Chang, S. Kim, J. L. White, J. W. Cho, D. R. Paul, *Polymer* **2001**, *42*, 9513.
[2] T. G. Gopakumar, J. A. Lee, M. Kontopoulou, J. S. Parent, *Polymer* **2002**, *43*, 5483.
[3] A. Halldén, M. Deriss, B. Wesslén, *Polymer* **2001**, *42*, 8743.
[4] M. Y. Gelfer, H. H. Song, L. Liu, B. S. Hsiao, B. Chu, M. Rafailovich, M. Si, V. Zaitsev, *J. of Polym. Sci., Part B: Polym. Phy.* **2003**, *41*, 44.
[5] Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, T. Kurauchi, O. Kamijaito, *J. Polym. Sci.,Part A: Polym. Chem.* **1993**, *31*, 983.
[6] F. Valenzuela Diaz, *Key Engineering Materials* **2001**, *189–191*, 203.
[7] A. Usuki, M. Kawasumi, Y. Kojima, A. Okada, T. Kurauchi, O. Kamigaito, *J. Mater. Res.* **1993**, *8*, 1174.

