

PREPARATION AND CHARACTERIZATION OF MIX MATRIX MEMBRANES POLYMER BASED SILANE-TRATED CLAY REINFORCED POLYCARBONATE NANOCOMPOSITES.

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Abstract

In this work an argentinian sodium montmorillonite (MMT) was used as a starting materia. The first step was a cation exchange with hexadecyltrimethylammonium for obtain an organophilic clay. Then, this clay was mixed with dimethyldichlorosilane in a process involving the generation of the silane oligomers due to hydrolysis reaction and subsequent polymerization. Characterization of these clays by X-ray diffraction shows the intercalation of modifiers species. In adition, the results of TGA show different profiles of thermal decomposition of clays.

These additives were used to modify the structure of polymeric matrix of polycarbonate; the final materials were characterized by X-ray diffraction and thermal analysis; transport properties were evaluated by the pervaporation technique, using distilled water. The results show that the hydrophobic character of the silanized material affects the PC polymeric matrix by changing the molecular mobility of species, enabling their use in separation processes of alcohol-water mixtures.

1 Introduction

A typical biomass fermentation process produces 3-8 wt % ethanol and requires further purification up to >99.5 wt % as pure ethanol, [1]. Conventional ethanol fermentation systems usually make use of batch operation and the concentration of ethanol is very low, because fermentation is inhibited by the ethanol that is produced. This leads to high cost directly in the production of biomass ethanol. Pervaporation is a promising membrane-based technique for the separation of liquid chemical mixtures, especially in azeotropic or close-boiling solutions, [2-5].

In the last decade there has been significant progress in the performance of polymeric membranes and their separation properties of low molecular weight compounds due to the large number of studies with the systematic change of the molecular mobility of the polymer matrix. These membranes are obtained from the addition of a permeable rigid second phase of a nanometer dimensions within the polymer matrix, resulting in a combination of the separation properties of polymers with rigid porous materials, [6].

Polycarbonate is an attractive material for the use of membranes due to its thermal and mechanical stability. Although several studies on the transport properties of this polymer so far not been found in the literature reports studies of the composite membrane of polycarbonate / nanoclay, [7]. The adequacy of the transport properties of polycarbonate for the separation of liquid mixtures of polar species (alcohol / water, acetone / water, methanol / tert-butyl ether) involves modifying the chemical compatibility and chain mobility in order to facilitate the process of pervaporation and the selectivity. In these systems in which the molecular differences are sometimes subtle and difficult to implement in a membrane is important the selection of modifier agent that has versatility in the availability of functional groups to modify the chemical affinity with the permeant and the polymeric matrix.

In this regard the compounds derivatives of silanes result adequate. Process for obtaining modified clays with different functional silanes have proven their applicability to the modification of properties of polyethylene [8, 9, 10], this interesting perspective is what leads to consider the use of silylation processes for the modification of clays polycarbonates properties for application in separation operations.

A membrane to be efficient for a specific separation, it is always desirable to have good permeability and selectivity. However, the hydrodynamic conditions the movement of flows. The separation by pervaporation is governed by the chemical substance, the nature of the macromolecules that make up the membrane, the physical structure of the membrane, the physicochemical properties of mixtures that are separated and the interactions between the substance and the membrane [11, 12].

In this work an argentinian sodium montmorillonite (MMT) was used as a starting material, which underwent a cation exchange with solutions of hexadecyltrimethylammonium bromide (H) obtaining an organophilic clay (MMTH). The clays were characterized by X-ray diffraction and thermogravimetric analysis (TGA). The X-ray results show the intercalation of organic cations between the layers of mineral clay. DTG curves for these organophilic clays show the degradation steps. The organophilic clay was modified with dimethyldichlorosilane: $(\text{CH}_3)_2\text{SiCl}_2$, the modification procedure is in situ generation of oligomers by hydrolysis and condensation reactions.

These additives were used to modify the structure of the polymer matrix of polycarbonates, the final materials were characterized by X-ray diffraction and thermal analysis and transport properties were evaluated by the pervaporation technique.

2 Materials and testing methods

2.1 Materials

Hexadecyltrimethylammonium Bromide was purchased from Aldrich; dimethyldichlorosilane was purchased from Aldrich; Ethylic Ether VETEC; Na-Montmorillonite was obtained from Minarmco S.A., its CEC is between 70-80 meq/100 g values.

Table 1 describes chemical analysis performed on this clay.

	SiO ₂	Al ₂ O ₃	MgO	Na ₂ O	CaO	K ₂ O	Fe ₂ O ₃	Others
% w/w	62.0	18.0	3.0	3.5	2.0	1.0	7.0	3.5

Table 1. Percentage composition of natural clay

2.2 Preparation of modified clays

2.2.1 Preparation of organophilic clay, MMTH

Organophilic clay was synthesized by ionic exchange reaction between natural clay and ammonium salt (H), in an aqueous solution. MMT-Na was dispersed in a solution containing H with an excess of 50% compared to cation exchange capacity, [13]; this process was carried-out in a shaker at 353 K for 2h. The organo-modified montmorillonite (MMTH) was recovered by vacuum filtration using a funnel with a sintered glass filter, washed several times with distilled water, until bromide ions were absent in the supernatant (tested with 0,1 N AgNO₃ solution).

2.2.2 DMS intercalation into org-MMT

The silane (DMS) was mixed with the organophilic clay in a relation mass 1:1, in ether. Later, the solvent was evaporating and then distilled water was added to the solid, in a molar ratio 1:20 (water / silane), allowing to react overnight at room temperature; finally, the silanized clay (MMTH-DMS) was washed until neutral pH value and dried in a vacuum oven.

2.3 Films preparation of PC / clay composites

The membranes of polymer-modified clays were obtained by casting: modified clays were mixing with polymer matrix using dichloromethane as solvent; the load of clay was 3%. The composites materials were named: PC/MMTH and PC/MMTH-DMS.

2.4 Characterization

Clay samples powders were analyzed in a spectrometer Perkin Elmer, Spectrum 6X model, using pressed KBr disks, at 2 cm⁻¹ frequency resolution. For films, the spectra were obtained on a Varian 640-IR, with a resolution of 4 cm⁻¹. In both cases, the spectra were run between 4000 and 400 cm⁻¹ frequency.

X-ray diffraction (XRD) experiments were conducted on clay powders and polymer composite specimens at a scan rate of 2°/min, with CuK α X-ray radiation ($\lambda=1,54056 \text{ \AA}$) using a Rigaku Geiger-Flex model diffractometer, operating at 40 kV and 30 mA.

Thermogravimetric characterization (TG-DTG) was performed from 25°C to 900°C, at a heating rate of 20 K/min, under N₂ flow, with a thermal analyzer T.A. Instruments, TGA Q50 model. This procedure was used for both clay and PC composite materials.

Scanning electron microscopic (SEM) analysis was made on a JEOL JSM-6480 LV apparatus on polymer samples fractured under liquid nitrogen and coated with gold. Accelerate voltage of 15kV was used.

Pervaporation experiments were performed in a standard pervaporation equipment at 30°C using PC composite films. Vacuum at the downstream side was maintained using a vacuum pump. Liquid nitrogen was used as cooler in order to collect all permeated vapors. A peristaltic pump was used to re-circulate the solvent used (water). A gravimetric method was used to measure the rate of pervaporation.

3 Results and Discussion

3.1 Clays analysis

3.1.1 XRD analysis

Shifts of diffraction peak (001) reflection to lower angles suggest that basal spaces were increased. This is due to the presence of hexadecyltrimethyl ammonium ions interchanged and molecules of dimethyl silane intercalated in the pristine clay. Table 2 shows that the minimum interlamellar space of 12.30 Å corresponds to MMT while the maximum value of 20.80 Å corresponds to clay modified by exchange of quaternary ammonium salt (MMTH). The

interlayer space for the species MMTH-DMS has an intermediate value between those indicated.

Materials	2 θ	d (Å)
MMT-Na	7.10	12.30
MMT-H	4.80	20.80
MMTH/DMS	5.10	17.30

Table 2 Results extracted from XRD analysis

Several authors have reported a lateral bilayer arrangement for HDTA chains [14, 15] which agrees with the dimensions showed on Tables 2 and 3 for this ion. Others [8, 9] have indicated that the main oligomer generated in the hydrolysis of dimethyl silane is a tetramer (OMCTS). This oligomer can introduce in to the clay galleries because the alkylic chains of ammonium ion provide hydrophobic sites inside MMT, favorable for entry. The interlayer spacing does not change significantly compared to the value of organophilic clay, because the molecular size of OMCTS (Table 3) is lower than org-MMT interlamellar space.

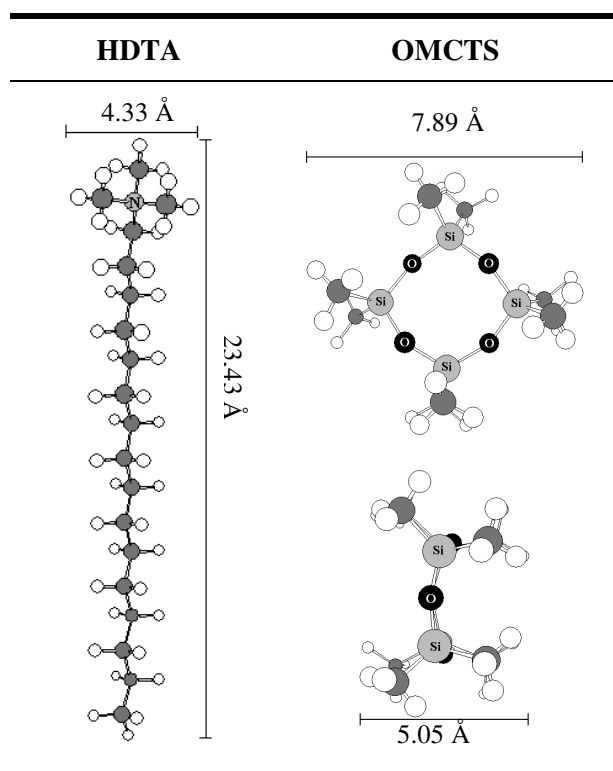


Table 3. Molecular dimensions of clay modifiers (Molecular simulation performed with CS Chem3D Pro software).

3.1.2 FTIR analysis

Infrared spectra on Figure 1 show the stretching vibration of isolated –OH group at 3638 cm⁻¹ for unmodified and modified clays. These clays also present the band at 3438 cm⁻¹ corresponding to H-bonded water and the Si-O stretching band at 1042 cm⁻¹. Except for MMT-Na, CH₂ symmetric stretching vibration (2853 cm⁻¹), CH₂ asymmetric stretching vibration (2926 cm⁻¹) and CH₂ bending vibration (1475 cm⁻¹) bands are present in all modified clays due to the presence of these functional groups in the organic compounds used as clay modifiers, and org-MMTH-DMS showed the asymmetric stretching vibration CH₃ band (2962 cm⁻¹). The H-O-H deformation band (~1630 cm⁻¹) was observed in all materials indicating the presence of water moisture.

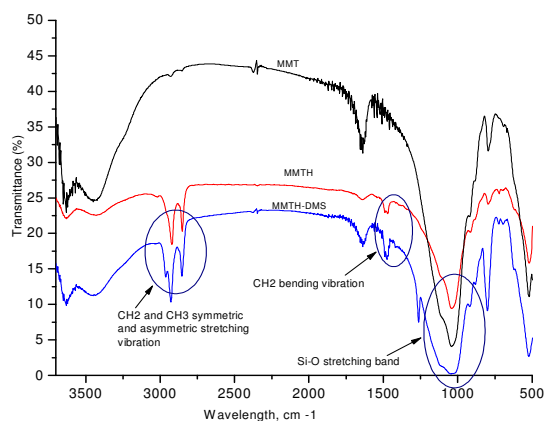


Figure 1. FTIR spectra of modified clays.

3.1.3 TG-DTG analysis

Figure 2 shows the TG-DTG thermograms of clays modified. It is observed that the modified clays have a lower percentage residual at 700 °C compared with natural clay, because there is a considerable loss of labile organic material (Figure 2a). Although the mechanisms of degradation are different for each material obtained (Fig. 2b) can be identified in all cases three distinct zones: a zone of loss of surface water, at temperatures below 200 °C, an intermediate zone between 250 and 450 °C where thermal degradation occurs modifiers of clay, and finally the zone above 450 °C, which would produce the dehydroxylation of the clay structure, [16, 17].

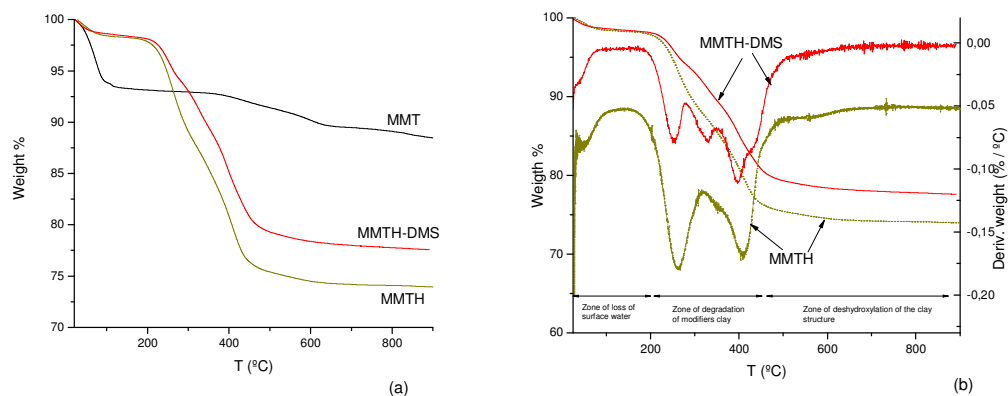


Figure 2. TG and DTG of the clays employed in PC modification.

3.2 PC-clay materials analysis

3.2.1 XRD analysis

RX diffractograms of polymeric materials prepared by casting show a similar profile as the pure polymer matrix (Figure 3). In the region of low angle ($2\theta < 10^\circ$) does not observe the diffraction peak characteristic of the modified clays; this could be due to a possible exfoliation of the layered structure of clays, which should be corroborated by other analytical methods.

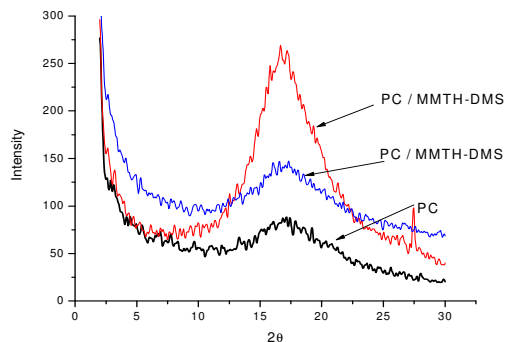


Figure 3. XRD patterns of PC/clay hybrids.

3.2.2 Morphological analysis

Figure 4 shows the morphologies of pure PC and after the addition of treated clay. Although clay surface modifiers were small quantities (3%), they affected the interfacial behavior clay/polymer matrix. MMTH-DMS contains rings (tetramers of DMS) with side groups (CH₃) similar to PC. Consequently, it presents better clay dispersion than PC/MMTH but some nanosheets remain agglomerated.

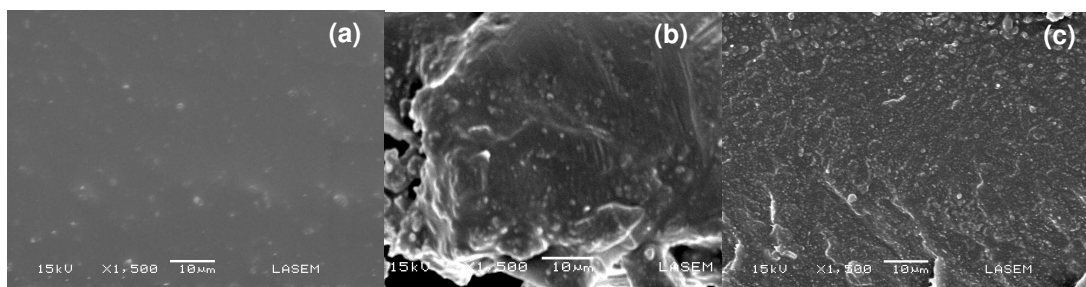


Figure 4. SEM microphotographs: (a) PC; (b) PC / MMTH; (c) PC / MMTH-DMS.

3.2.3 Thermogravimetric analysis

Non-oxidative thermal degradation presents different behaviors for each composite. Figure 5 shows the TGA curves and Table 4 summarizes the results: onset and endset temperature (T_{onset} , T_{endset}) of the degradation process, and temperature of maximum rate of weight loss (T_d). All hybrids have higher onset temperatures than unmodified PC.

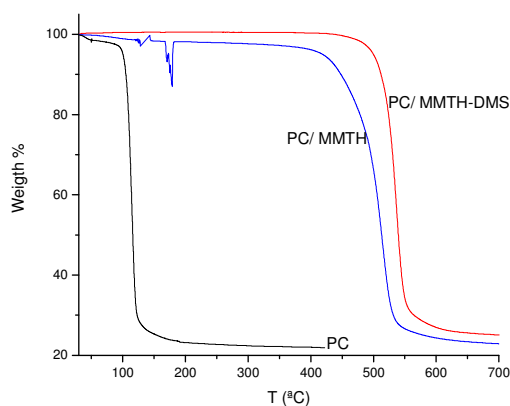


Figure 5. TGA curves of PC /clay hybrids.

Samples	T _d [°C]	T _{onset} [°C]	T _{endset} [°C]	T (50%) [°C]	T (95%) [°C]	% Residue at 700°C
PC	113	98,4	123	116,9	102,9	21,7
PC / MMTH	513	466,5	536	512	422,9	23,00
PC / MMTH-DMS	537,4	503,7	556	538	498	25,44

Table 4. Information obtained from TGA curves.

Throughout the weight loss of filled PC samples, it was noticed that degradations occurred at higher temperatures than pure PC. The polymer filled with silanized clay has better thermal properties than the polymer matrix, significantly differing thermal decomposition profile. This can be associated with the degradation of org-MMT/DMS fill alone.

Accordingly with observations on polymer-clay systems, the higher degradation temperatures compared to the corresponding pure polymer are caused by the phyllosilicate sheets that prevent the diffusion of degradation products outside the material [16-18]. In addition, it was observed that the modifying species caused different effects on the behavior of the polymer matrix. One hypothesis may be that the fragments from clay modifiers generated during degradation process affect PC chains scission in different ways.

3.2.4 Transport properties

Pervaporation experiments were carried out with water and ethanol, employing membranes of PC y PC / MMTH-DMS. Table 5 summarizes the results of water pervaporation. It was found that flux to ethanol is five time higher than to water, suggesting that both solvents permeate in the state vapor, and the membrane PC / MMTH-DMS is water-repellent, allowing to pass more ethanol than water through the membrane.

Membrane	Solvent	T [°C]	J [Kg / h.m ²]
PC	Water	30	2.8
PC / MMTH-DMS	Water	30	40.7

Table 5. Pervaporation results of PC and PC/silanized clay.

4 Conclusions

It has been shown that the hydrophobic character of the silanized clay affects the structure of the polymeric matrix of PC, being more favorable the passage of ethanol than water in pervaporation experience using these pure solvents. It is hoped that these composite materials will have good selectivity for the separation of alcohol in alcohol-water mixtures, especially for low concentrations of ethanol, similar to those obtained in industry preparation of ethanol from biomass.

This work also enables the projection of future studies that provide for the analysis of the flow rate and selectivity in separating mixtures of water-ethanol using membranes silanized clay-filled PC with other silanes such as dichloromethylphenylsilane and dichlorodiphenylsilane, and varying the percentage loading of these fillings.

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