

Nylon 6/Brazilian Clay Membranes Prepared by Phase Inversion

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ABSTRACT: Microporous membranes were synthesized from a polymer nanocomposite material, intercalated montmorillonite clay/nylon 6, by an immersion-precipitation method in a water bath. This membrane was skinless and was composed of cellular pores and sheaflike crystallites, which were interwoven into a bicontinuous structure. In contrast, pure nylon 6, precipitated under the same conditions, yielded a skinned asymmetric membrane. The X-ray diffraction patterns showed that the nanocomposites and the membranes exhibited exfoliated structures. By differential scanning calorimetry, it was

observed that the clay probably acted as a reinforcing filler, increasing the crystallinity degree of the nanocomposites, but it was practically unchanged in the membranes. Through photomicrographs obtained by scanning electron microscopy, it was possible to verify that all the membranes exhibited an asymmetric morphology with a well-defined porous structure and a tight skin with a cellular sublayer. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1488–1493, 2009

Key words: membranes; nanocomposites; nylon; X-ray

INTRODUCTION

Polymer/layered silicate nanocomposites have attracted a great deal of interest over the last few years as a result of the potentially superior properties that these materials can exhibit in relation to conventional composites.¹ These materials present excellent properties such as thermal stability and flammability. Small amounts of organoclays (<10 wt %) used in the polymer matrices significantly influence the mechanical, thermal, optical, electrical, and dimensional properties and also the flammability and barrier properties because of the large contact area between the polymer and clay on a nanoscale.^{2,3} Because of their easy preparation and properties, polymer/silicate nanocomposites form an important group. In general, to facilitate the intercalation of the silicate layers with the polymer, the clay is modified by quaternary ammonium salts through a cation-change reaction because the ammonium salt changes the surface of the clay from hydrophilic to organophilic.^{3–6} For instance, adding montmorillonite clay to nylon 6 increases the modulus, yield strength, and heat distortion temperature and also improves the barrier and ablative properties.⁷ Nylon 6 is particularly unique because exfoliated nanocomposites

have been formed by melt processing; this technique is attractive because of its versatility and compatibility with the existing processing infrastructure.⁸

Since the beginning of the 1970s, in addition to the classic separation process, new techniques have appeared that use synthetic membranes as selective barriers. Synthetic membranes appear to be a way to copy natural membranes, particularly with respect to the unique characteristics of selectivity and permeability. Studies of the membrane separation process and its applications are relatively recent.⁹

The use of synthetic membranes in separation processes in purification, fractionation, and concentration is increasing in a wide variety of industries, such as chemical, pharmaceutical, textile, paper, and food industries. The membrane separation process has as its main advantages (in relation to the classic techniques of separation) low energy consumption, a lower number of processing steps, great efficiency in separation, simple operation, and final products of high quality.^{9–12}

Membranes consist of an extremely thin selective layer (0.1–0.2 μm) backed by a porous substructure in which fingerlike cavities can sometimes be present.¹³ Polymer membranes have been developed for a variety of industrial applications. Examples of industrial applications include microfiltration, ultrafiltration, reverse osmosis, and gas separation.^{14,15}

Microporous membranes are often manufactured by a phase-inversion process in which a homogeneous polymer solution is induced to separate into

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polymer-rich and polymer-poor phases. The polymer-rich phase eventually forms the matrix, whereas the polymer-poor phase forms the membrane pores. Generally, the phase separation is induced by an immersion-precipitation process, in which a polymer solution is cast onto a support and then immersed into a coagulating nonsolvent bath. The rapid diffusive efflux of the solvent and influx of the nonsolvent quickly lead to the formation of a precipitated membrane. This process can involve liquid-liquid phase separation.^{9,16,17}

The aim of this work was to prepare porous polymer membranes from nylon 6/montmorillonite clay nanocomposites by a phase-inversion technique and to characterize them with X-ray diffraction (XRD), scanning electron microscopy (SEM), and differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

Nylon 6 (Technyl C216; number-average molecular weight = 10,500 g/mol, intrinsic viscosity = 134 mL/g) was supplied by Rhodia (São Paulo, Brazil). Pure clay sodium montmorillonite (Boa Vista, Paraíba, Brazil) was supplied by Bentonit União Nordeste with a cation-exchange capacity of 90 mequiv/100 g, and the interlayer spacing (d_{001}), obtained by XRD, was 12.5 Å. Montmorillonite was dried at 60°C for 48 h before use. The clay was modified with a quaternary ammonium salt and was named *organoclay*. Originally, this clay was a polycationic clay, and it was modified by the industry with sodium carbonate to transform it into sodium montmorillonite. This Brazilian clay is not applied commercially to make nanocomposites.

To prepare the membrane by phase inversion, formic acid from Synth (São Paulo, Brazil) (99%) was used as a solvent.

Nanocomposite preparation

In the nanocomposite preparation, before any processing step, all the materials with nylon 6 were dried in an oven with circulating air at 80°C for 1 h. After this step, these materials were kept in an oven *in vacuo* at 80°C for 24 h.

Nylon 6/organoclay nanocomposites, containing 3 wt % clay, were melt-compounded in a counter-rotating twin-screw extruder (torque rheometer; Haake, Karlsruhe, Germany) operating at 240°C in all zones and at 60 rpm. To ensure a better dispersion of the fine clay powder in the nylon polymer, a 1 : 1 nylon 6/clay master batch was previously produced in a Haake torque rheometer with an internal mixer at 240°C and 60 rpm for 10 min.

Membrane formation

The dried materials were dissolved in formic acid to make a clear and homogeneous solution. The membranes were prepared via the spreading of this solution on a glass plate and were rapidly immersed in a nonsolvent bath (distilled water). After the precipitation time, the membranes were removed, washed with distilled water, and dried at $60 \pm 5^\circ\text{C}$ for 2 h according to the method reported by Cheng et al.¹⁸

Characterization

The structures of nylon 6 and its nanocomposites were characterized with XRD, SEM, and DSC. The XRD measurement was performed with a Shimadzu (Kyoto, Japan) XRD-6000 diffractometer operating at 40 kV and 30 mA with a 2θ scan range of $2\text{--}30^\circ$ at room temperature at a scanning speed of $2^\circ/\text{min}$ with Cu $K\alpha$ radiation (wavelength = 0.154 nm).

The top and cross-section surfaces of the membranes were characterized with SEM (JSM-6360, JEOL, Tokyo, Japan) at 15 kV. All samples were coated with gold.

The DSC scans for nylon 6, its nanocomposites, and its membrane samples were performed to obtain the melting point and the heat of fusion. All experiments were carried out in aluminum pans with heating from room temperature to 260°C at a rate of $10^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Structure of the nylon 6/clay nanocomposites and membranes

Figure 1 presents the X-ray patterns of the nylon 6, clay, organoclay, and nylon 6/clay and nylon 6/organoclay nanocomposites. The characteristic peak related to the polymer matrix is present in the system diffractograms. For the pure clay, the characteristic peak (ca. 7°) can be observed at a basal distance of $d_{001} = 12.5$ Å. The characteristic peak of the organoclay, that is, the sample treated with a quaternary ammonium salt, is displaced toward lower angle values, and the interlayer spacing obtained from the corresponding XRD patterns is 21.4 Å. The results indicate that the quaternary ammonium salt was intercalated between the layers of the organoclay, leading to an expansion of the interlayer spacing. In the nylon 6/organoclay nanocomposite, the absence of the characteristic peaks from the organoclay can be observed, and this could indicate a nanocomposite with an exfoliated structure type according to Araújo and coworkers^{2,17} and Fornes et al.⁸ However, a new broad diffraction peak, related to the angle of 10.60° , which is close to the angle of 7° , can also be noticed for the nylon 6/clay and nylon

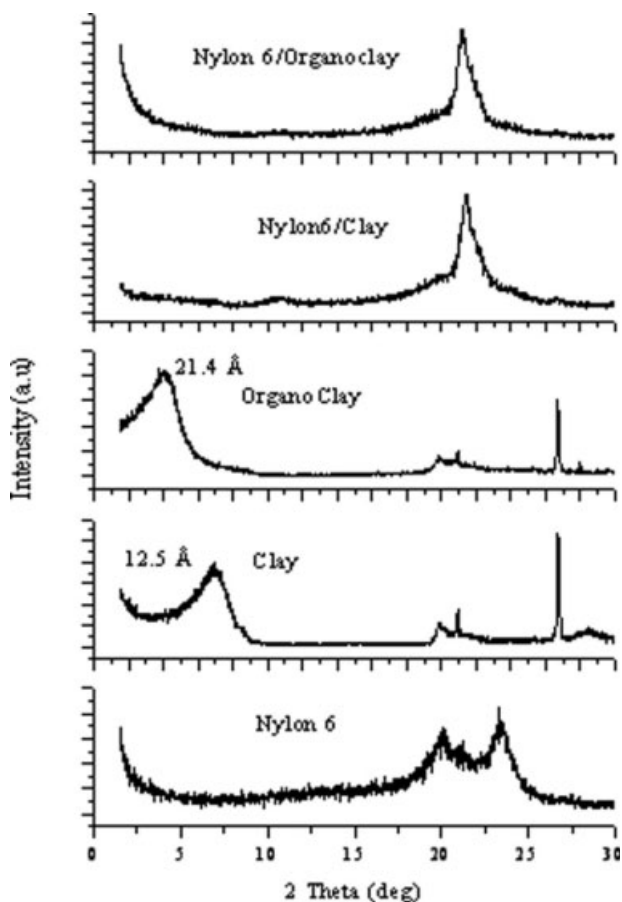


Figure 1 XRD patterns of nylon 6 and its nanocomposites.

6/organoclay nanocomposites. This can be related to the original peak of the clay, indicating that an increase in the basal spacing did not occur and that these nanocomposites presented partially exfoliated structures. The interlayer distance was determined from the diffraction peak by the X-ray method with the Bragg equation.

Figure 2 shows the X-ray patterns of the membranes of nylon 6 and its nanocomposites. In all the samples, the presence of peaks close to 20 Å (related to α -type crystals of nylon 6) and close to 24 Å (related to β -type crystals of nylon 6) can be observed. The XRD diffractograms of the nylon 6/clay and nylon 6/organoclay membranes are similar to those of the pure nylon 6 membranes. Because of the absence of peaks, this could be evidence of the fact that an exfoliated structure was obtained for the membranes. This change can be attributed to the dissolution and precipitation of the nanocomposites during the membrane preparation, which can provide a better dispersion of the particles in the polymer matrix, or to the segregation of these particles to form agglomerates, which make their identification by XRD difficult. These membranes need to be

characterized by transmission electron microscopy to confirm these results.

Morphologies of the membranes

Top surface

Figure 3 presents SEM photomicrographs of the top surfaces of nylon 6, nylon 6/clay, and nylon 6/organoclay membranes. The image of the pure nylon 6 membrane [Fig. 3(a)] shows a porous structure with interconnected spherical pores with a 2.5- μm size and a uniform distribution. In Figure 3(b), for the nylon 6/clay membrane, a structure with a low porosity can be observed with a small pore size close to 0.2 μm , a nonuniform distribution, and a heterogeneous arrangement. In Figure 3(c), for the nylon 6/organoclay membrane, a homogeneous structure with small open pores with a pore size close to 1.5 μm can be seen. Thus, the presence of the untreated and treated clays with a quaternary ammonium salt provides a significant change in the structure/morphology of the pores and porosity of the membranes, with big pores and a uniform distribution for the pure

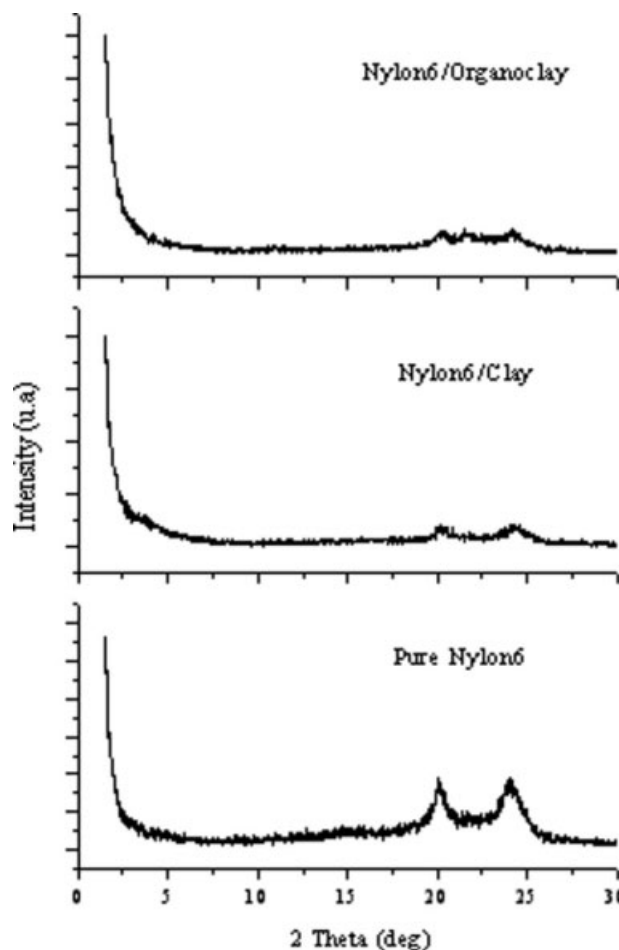


Figure 2 XRD patterns of nylon 6 and its nanocomposite membranes.

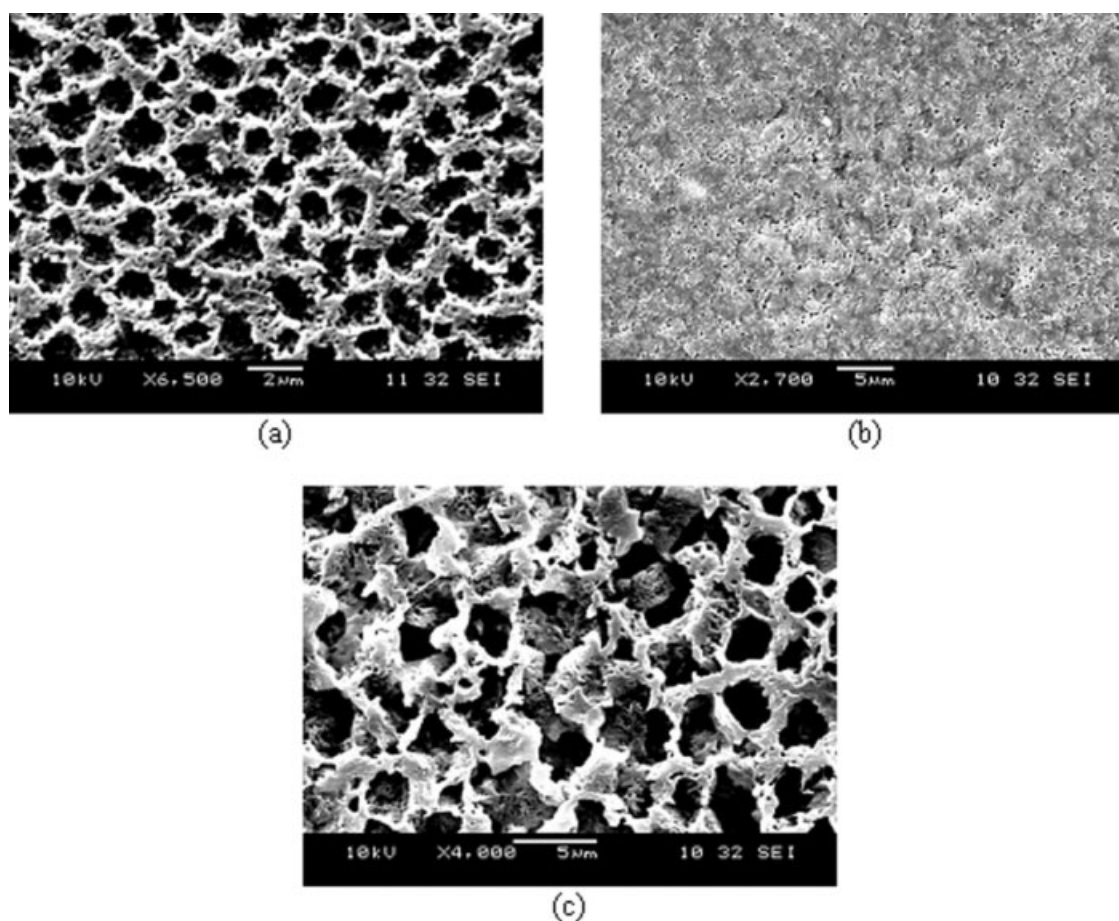


Figure 3 SEM images from the top surfaces of (a) nylon 6, (b) nylon 6/clay, and (c) nylon 6/organoclay membranes.

matrix and small pores and porosity for the membrane with clay. By a comparison of the clay and organoclay, it can be observed that the smallest pore size was achieved in the presence of clay.

Cross sections

In Figure 4, cross sections of the nylon 6, nylon 6/clay, and nylon 6/organoclay membranes can be seen. They had an asymmetric structure, consisting of a thin dense skin, a cellular bulk, a thin selective layer, and a porous support. The pores are approximately spherical with a decrease in size from the top to bottom, and they are interconnected. The cellular morphology results from nucleation and growth of a polymer-lean phase, typically for liquid–liquid phase separation. This morphology is ordinarily observed in amorphous polymer membranes prepared by the immersion–precipitation procedure.

DSC analysis

DSC data were used to complete the qualitative analysis and to determine the whole crystallinity

value and the relative proportion of each crystalline phase in the different membranes and pellets.

Table I shows the melting parameters for pure nylon 6 and nylon 6/clay systems, that is, for nylon 6, nylon 6/clay, and nylon 6/organoclay pellets and for nylon 6, nylon 6/clay, and nylon 6/organoclay membranes. For the pellets, an increase in the heat of fusion and the degree of crystallinity of the nanocomposites in relation to pure nylon 6 can be observed. The clay probably acts as a nucleation agent, increasing the crystallinity degree of the nanocomposite, according to Chavarria et al.,¹ Araújo et al.,² and Fornes et al.⁸ The melting temperature and enthalpy of fusion of the membranes are lower than those of nylon 6 in its pellet form. This suggests that the crystal structure might have changed during the immersion–precipitation procedure. For this reason, the level of crystallinity of the membranes decreased. In general, this can be attributed to the perfection of metastable crystals during heating and/or melting of crystallites in different crystal forms and bimodal or multimodal crystal size distribution in the sample.¹⁹ However, this requires further research (DSC, wide-angle X-ray diffraction,

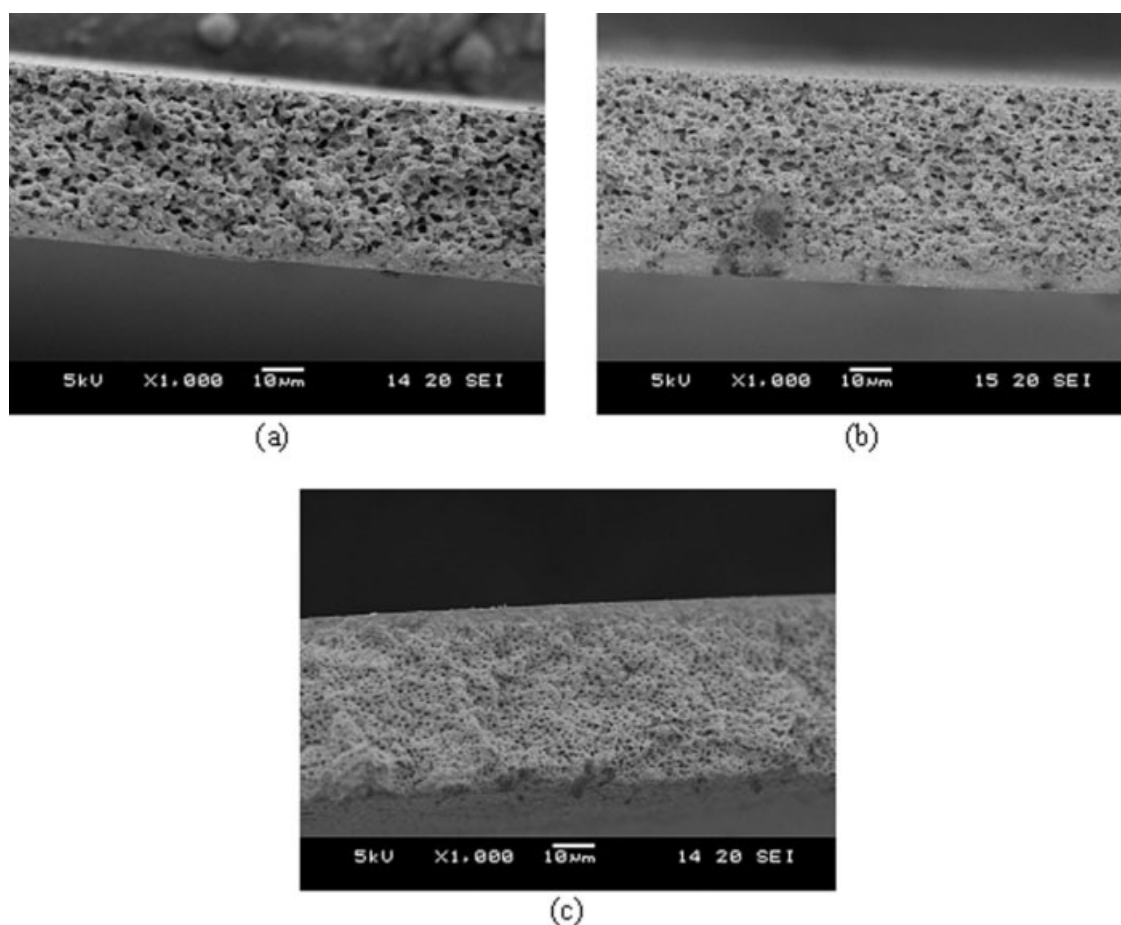


Figure 4 SEM images from cross sections of (a) nylon 6, (b) nylon 6/clay, and (c) nylon 6/organoclay membranes.

small-angle X-ray scattering, etc.) that is beyond the scope of this work.

CONCLUSIONS

Porous membranes were obtained from nylon 6/clay nanocomposites by an immersion-precipitation

method in water. The XRD patterns confirmed that exfoliated nanocomposites were obtained. It was also observed that the presence of clay and organoclay caused a significant alteration in the porous structure/morphology and porosity of the membrane. Large, well-distributed pores were obtained for the polymer matrix of nylon 6, and small pores were obtained in the presence of clay. All the membranes exhibited an asymmetric morphology with a tight skin and a cellular sublayer. The data obtained by DSC showed that the membranes had lower crystallinity than nylon 6 and its nanocomposites in pellet form. These nanocomposite membranes could have applications in gas separation, electro dialysis, microfiltration, and liquid-liquid separation.

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TABLE I
Melting Parameters for Pure Nylon 6 and Nylon 6/Clay Systems Obtained by DSC

| Sample | T_m (°C) | ΔH_f (J/g) | X_c (%) |
|--------------------|------------|--------------------|-----------|
| Pellets | | | |
| Pure nylon 6 | 224.28 | 37.53 | 19.96 |
| Nylon 6/clay | 226.02 | 40.05 | 21.96 |
| Nylon 6/organoclay | 221.10 | 45.51 | 24.95 |
| Membranes | | | |
| Pure nylon 6 | 217.73 | 20.85 | 11.09 |
| Nylon 6/clay | 219.03 | 21.03 | 11.53 |
| Nylon 6/organoclay | 220.17 | 17.32 | 9.49 |

ΔH_f = heat of fusion due to nylon 6 melting (measured through the melting peak); T_m = melting temperature taken at the melting peak; X_c = degree of crystallinity ($X_c = \Delta H_f / \Delta H_{F_0}$, where ΔH_{F_0} is the heat of fusion for 100% crystalline nylon 6, i.e., 188 J/g¹⁹).

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