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Thermal properties from membrane of polyamide 6/montmorillonite clay nanocomposites obtained by immersion precipitation method

A. M. D. Leite · L. F. Maia · R. A. Paz ·
E. M. Araújo · H. L. Lira

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Abstract The aim of this work was to obtain membranes from polyamide 6/montmorillonite clay nanocomposites through the phase inversion technique. The nanocomposites and membranes from polyamide 6/montmorillonite clay were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC). Microporous and asymmetric membranes were successfully obtained from nanocomposites and the results showed that the salts were incorporated by intercalation between the organoclay layers and, apparently that the nanocomposites and membranes were thermally more stable than the pure polyamide.

Keywords Polyamide 6 · Membranes · Nanocomposites

Introduction

Polymer layered silicate nanocomposites have a great interest over the last few years as a result of the potentially superior properties of these materials compared to conventional composites. Several studies have shown that a very low percentage of layered silicates can lead to a significant enhancement of many properties such as barrier-, heat resistance-, flame retardance- and mechanical properties [1, 2]. The property improvements are attributed to the high stiffness and strength of the clay particles and the interaction of the polymer chains with the exfoliated lamella [3, 4]. The dimensions of the polymer chain and the crystal structure of polyamide 6 are comparable to the dispersed clay-plates, which have a thickness around 1 nm and an average size of 100 nm [5].

Due to their excellent mechanical and thermal properties polyamides are widely used materials. Polyamide 6 and polyamide 66 are used in the majority of the commercial polyamide production and application. Amongst others these polyamides are physically differ from the others in terms of the melting point, glass-transition temperature, crystallinity, and tensile modulus. Reports in the literature have shown that these differences in the end group configuration can lead to significant differences in the morphology and properties with functionalized polymers made from these materials [1].

From the beginning of 70s, in addition to the classic separation process new techniques have appeared in which synthetic membranes are used as a selective barrier. Synthetic membranes came out in order to improve the natural membranes, particularly in relation to the unique characteristics of selectivity and permeability. Studies on the separation process and their applications are relatively recent [6]. Addition of inorganic nanoparticles into polymeric materials to improve their membrane filtration properties has attracted broad attention in the development of membrane science. Several works indicated that adding proper inorganic nanoparticles in polymeric casting solution could control the formation and growth of macrovoids, increase the number of small pores and run-through pores, improve the porosity, hydrophilicity and permeability with almost unchanged retention and enhance the mechanical and the anti-fouling performance [7].

There are several ways to prepare porous polymer films such as sintering, stretching, track etching and phase separation process. The final morphology of the membranes obtained will greatly depending on the properties of the

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A. M. D. Leite (✉) · L. F. Maia · R. A. Paz ·
E. M. Araújo · H. L. Lira
Departamento de Engenharia de Materiais,
Universidade Federal de Campina Grande, Paraíba, Brazil
e-mail: amandamelissa.lins@yahoo.com.br

materials and the process conditions. The majority of membranes are prepared by controlled phase separation of polymer solutions into two phases: the first with a high concentration and the second one with a low polymer concentration. The concentrated phase solidifies soon after the phase separation and forms the membranes [8]. The preparation of porous membranes by immersion precipitation consists in a polymer solution is cast as a thin film on a support and is subsequently immersed in a nonsolvent bath. Precipitation can occur because the solvent in the polymer solution is exchanged by nonsolvent one [8].

The aim of this work is to obtain membranes from polyamide 6/montmorillonite clay nanocomposites by phase inversion technique. The nanocomposites and the membranes were characterized by X-ray diffraction (XRD), Thermogravimetry (TG), Differential Scanning Calorimetry (DSC) and Scanning Electron Microscopy (SEM).

Experimental

Materials

Polyamide 6 (PA6) was supplied by Rhodia/Brazil. The pure clay Na-Montmorillonite (MMT, Brasgel PA, Boa Vista/Paraíba, Brazil) was supplied by *Bentonit União Nordeste* and the used quaternary ammonium salt for the modification of MMT was hexadecyltrimethylammonium chloride (Genamin) supplied by Clariant/Brazil.

To prepare the membrane by phase inversion it formic acid from Synth, 99% for solvent was used.

Preparation of organoclay

The preparation of the organophilic montmorillonite with Genamin salt can be resumed as follow: the Na-MMT was mixed in distilled water with stirring to form a homogenously dispersed suspension. The suspension was stirred for 20 min after all the clay has been added. Then, organic salt equivalent to 1:1 CEC (Cation Exchange Capacity) of Na-MMT was added to the dispersion. The mixture was stirred for more 20 min. After 24 h the mixture of montmorillonite and the salt were washed with distilled water for several times to remove the salt excess and it was dried at 60 °C for 48 h, and finally, passed in a sieve 200 mesh detailing of the procedure is described by Araújo et al. [9–12].

Nanocomposites preparation

In the nanocomposite preparation, before any processing step, all the materials with PA6 were dried in an oven with circulating air at 80 °C for 1 h. Afterwards, these materials were kept in an oven under vacuum at 80 °C for 24 h.

PA6/organoclay nanocomposites, containing 3 mass% of clay were melted in a counter-rotating twin-screw extruder (Torque Rheometer Haake) operating at 240 °C and 60 rpm. In order to assure a better dispersion of the fine clay powder in polyamide a 1:1 PA6/organoclay master was previously produced in a Torque Rheometer Haake with internal mixer at 240 °C and 60 rpm for 10 min.

Preparation of membranes

The dried materials were dissolved in formic acid to obtain a homogeneous solution. The membranes were prepared by spreading this solution on a glass plate and rapidly immersed in a non-solvent bath (distilled water). After the precipitation time the membranes were removed, washed with distilled water and dried at 50 °C for 2 h.

Characterization

The thermal stability was investigated by DSC using a DSC50 Shimadzu equipment. The heating rate was $10^{\circ}\mathrm{C}\ \mathrm{min}^{-1}$ from room temperature to 300°C and at air. To the thermogravimetry (TG) analysis it was also used a TGA 51 Shimadzu equipment, operating at rate $10\ ^{\circ}\mathrm{C}\ \mathrm{min}^{-1}$, from room temperature up 900 °C, under air with flow rate of $50\ \mathrm{mL\ min}^{-1}$. The sample masses were 5.0 ± 0.5 mg. The TG curves were analyzed with the aid of the TASYS software from Shimadzu. XRD measurements were performed at room temperature by a XRD-6000 Shimadzu diffractometer (40 kV, 20 mA) using the CuK_{α} radiation (wavelength of 0.154 nm) at the rate of $2^{\circ}\ \mathrm{min}^{-1}$, in the range from 2 to 30°. The structures of the membranes were characterized by SEM SSX 550 Superscan—Shimadzu, operating with 15 kV. All samples were gold sputtered.

Results

X-ray diffraction results

Figure 1 shows the XRD patterns for the unmodified Brasgel PA clay and modified with the quaternary ammonium salt, Genamin, PA6/unmodified clay and PA6/modified clay nanocomposites and membranes obtained from nanocomposites. It can be observed that the unmodified clay (MMT) has a peak corresponding to an interlayer spacing $d_{001} = 12.5$ Å. This interlayer spacing for the sample treated with Genamin is 22.34 Å. The results indicated that quaternary ammonium salt was intercalated between two basal planes of MMT leading to an expansion of the interlayer spacing. The diffraction patterns for the PA6/MMT and PA6/OMMT-Gen show the absence of characteristic peak of MMT, indicating that apparently all

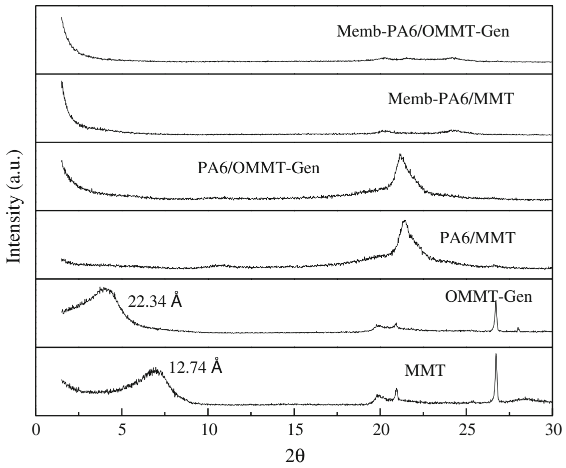

Fig. 1 XRD patterns of unmodified montmorillonite (MMT) and modified montmorillonite (OMMT-Gen), nanocomposites and membranes

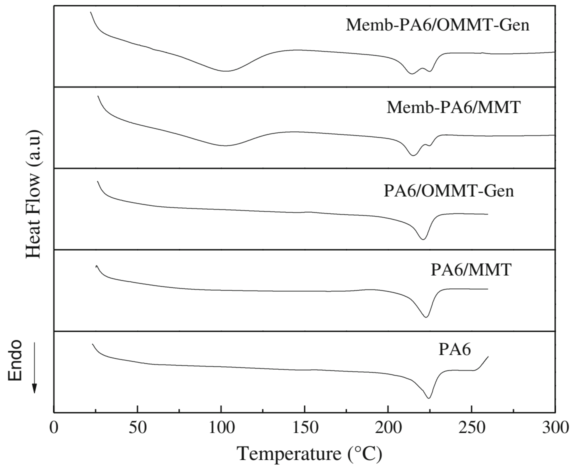

Fig. 2 DSC curves for pure polyamide, nanocomposites and membranes

nanocomposites present morphologies with particles partially exfoliated and intercalated by the polymer. The diffraction patterns for the membranes exhibit the same behavior of nanocomposites indicating the exfoliated morphology.

Thermal behavior

Figure 2 shows the DSC curves of polyamide, nanocomposites and membranes (PA6, PA6/MMT, PA6/OMMT-Gen, Memb-PA6/MMT and Memb-PA6/OMMT-Gen). The DSC curves of the PA6 and its nanocomposites showed the same behavior, showing that the melting point temperature is in the same 214–224 °C temperature range. The DSC curves of the membranes show a broad endothermic peak around 100 °C which is related to the evaporation of formic acid. Two consecutive peaks can also be seen related to the γ- and α-crystalline phases in the polyamide. Table 1 presents the thermal properties of PA6, its nanocomposites and membranes (melting temperature $T_{m,}$ heat of ΔH_m, and the degree of crystallinity X_c). It can be seen that in all the samples the melting point temperatures are very close. It was also observed that the degree of crystallinity of nanocomposites was lower when compared to the pure polyamide, indicating that the presence of clay influenced the crystallinity.

Table 1 Thermal properties of the PA 6 matrix, nanocomposites and membranes

Samples	T_m/°C	ΔH_m/J g^{-1}	X_c/%
PA 6	224.2	45.7	24.3
PA 6/MMT	222.7	43.6	22.5
PA 6/OMMT-Gen	221.1	45.5	23.4
Memb-PA 6/MMT	215.1–224.6	31.0	16.4
Memb-PA 6/OMMT-Gen	214.3–224.8	35.2	18.2

T_m melting temperature taken at the melt peak, ΔH_m heat of fusion, calculated from the melting peak, X_c degree of crystallinity obtained by DSC, taken from $\Delta H_{m/}\Delta H_o$, ΔH_o heat of fusion for PA6, 100% crystalline, 188 J/g

Figure 3 shows the TG and DTG curves of unmodified montmorillonite, treated montmorillonite, nanocomposites and membranes at air. It can be observed that the unmodified clay presents the first stage of degradation between 70 and 110 °C due to the loss of adsorbed water. For the sample treated with quaternary ammonium salt, two thermal decomposition stages are presented, first related to the mass loss in a temperature range from 220 to 400 °C with maximum at 265 °C attributed to the initial decomposition of quaternary ammonium salt and the second is attributed to the final decomposition of the organic salt. For the nanocomposites and membranes the same behavior is observed, but at higher temperatures.

Scanning electron microscopy

Figure 4 shows the morphology obtained by SEM for: (a) PA6 membrane, (b) PA6/MMT membrane and (c) PA6/OMMT-Gen. Figure 4a presents polyamide membrane and shows a structure with small porous and irregular distribution. In Fig. 4b it can be seen that the incorporation of the clay changed the structure of the membrane which displays different morphology of polyamide 6. In this case the surface is a less continuous skin consisting of irregular pores. Figure 4c shows a porous structure similar to Fig. 4a. It was observed that the membranes obtained from nanocomposites presented a larger quantity of pores and more uniform distribution when compared to polyamide membrane.

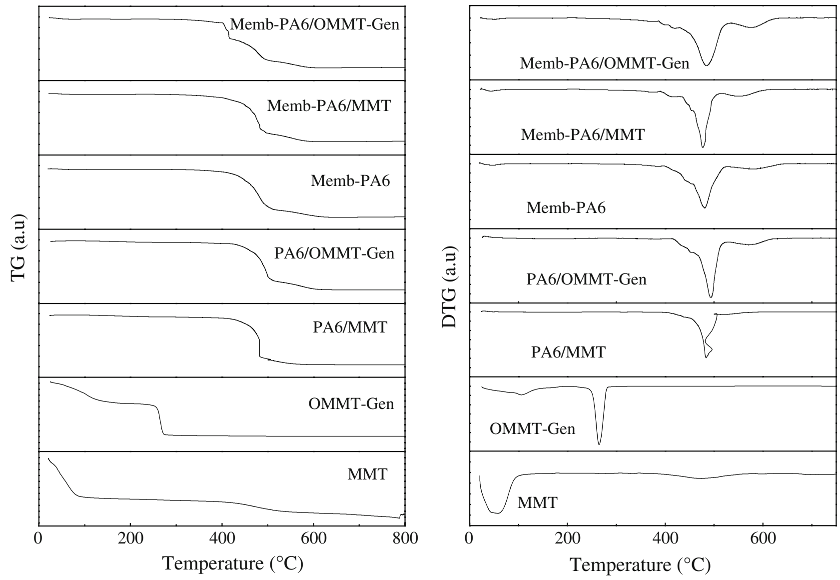

Fig. 3 TG and DTG curves of unmodified montmorillonite (MMT), clay modified with Genamin (OMMT-Gen), nanocomposites and membranes

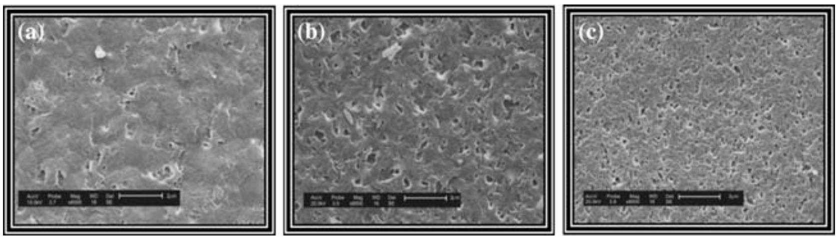

Fig. 4 SEM images from the top surface of **a** polyamide 6 **b** polyamide 6/unmodified clay and **c** polyamide 6/modified clay

Conclusions

Membranes were obtained from the polyamide 6 and polyamide 6/clay nanocomposites. By using XRD method a partially exfoliated and/or intercalated structure was observed. Also it can be seen that the degree crystallinity of the nanocomposites did not alter but the crystallinity of the membranes decreased in relation to PA6. According to the SEM studies one can conclude that the obtained membranes from nanocomposites presented a larger porous quantity and more uniform distribution when compared to polyamide membrane.

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