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Coagulation Bath in The Production of Membranes of Nanocomposites Polyamide 6/Clay

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Membranes of polyamide 6 and its nanocomposites with 3 and 5% of clay were obtained by the phase inversion method using distilled water and solvent as the coagulation bath, 10 and 30% of acid was used, in order to change the membranes morphology/porosity. By XRD analysis, the obtained nanocomposites showed an exfoliated and/or partially exfoliated structure, it was also seen two characteristics peaks of the polyamide 6 phases (α and γ). For the membranes, the characteristic peak γ of the membrane disappeared, being evident the peaks α_1 and α_2. By SEM the PA6 membrane almost doesn't have pores in its surface, with an addition of clay had an increase in the quantity of surface pores. In the cross section of the PA6 membrane, an extremely thin selective layer, adding the clay the selective layer became thicker and a better defined porous support was obtained. From the acid in the coagulation bath the PA6 membrane continued with a few pores structure. For the nanocomposites there was an increase in size and a better uniformity of the pores. In the cross section the presence of the bath decrease the membrane filtering, also modifying a uniformity of the pores.

Keywords: *membrane, nanocomposite, polyamide 6, clay, coagulation bath*

1. Introduction

Membranes are filter media, which are usually produced from polymeric material, which have pores with different dimensions. The pores are responsible for the various properties that can make them viable for a particular application, both to separate particles and to fractionate molecules of different molar masses. The membranes can act as a selective barrier like a filter, they can separate materials that with a regular filter would not be possible because it lacks adequate capacity for this type of process[1,2].

The phase inversion is the method that is being very used to obtain polymeric membranes, which a polymer solution is spread as a thin film on a glass plate or extruded as a hollow fiber, and then precipitated in a non-solvent bath[3-5]. The membrane is formed by the destabilization of the solution and the polymer precipitation. This technique allows large morphological change from small variations made in parameters used during the membranes preparation process[6]. This process allows to obtain membranes with a wide variety of morphology and a large number of applications.

The polymeric membranes have several advantages, and they have been used in various applications in industrial processes, such as in processes of separation, purification and fractionation of various industrial branches[3,7]. The main processes in which membranes are being used are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (HI), dialysis (D), gas permeation (GP) and pervaporation (PV). The efficiency and application of the membranes will depends on the morphology that it will present and as well as the nature of the material that constitutes[8-10].

For greater efficiency in production and application of the membranes, the surface modification is an approach that has been widely exploited to improve the fouling resistance in water purification from membranes. Thus, it is necessary to introduce an agent that can improve the characteristics and efficiency of the membrane, such as the inorganic fillers[11].

Polyamides are materials of fatigue resistance, high tensile strength, abrasion and good toughness. These properties is improved with the addition of clay when compared to pure polymer[12,13]. Polyamide membranes offer the advantage of being a hydrophilic material, and for this reason do not require a wetting agent used in applications microfiltration[14-16].

In recent years, polymer nanocomposites have caused great interest from both industry and academia[17-19], as they are hybrid materials in which particles of nanometric dimensions are dispersed in a single polymer matrix[20]. The reinforced polymers with low percentages mass of clay (1-5%) have raised interest in academic and industrial environment, due to considerable improvement of physical and mechanical properties, in addition to allow processing from conventional techniques such as extrusion and/or injection[21].

Nanocomposite materials are systems that have a polymeric matrix and a second inorganic phase (not

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necessarily particles) in nanometer scale dispersed in the matrix. The inorganic particle that is commonly used is the phyllosilicates a clay minerals of the family 2:1, its crystalline structure consists of an octahedral layer of aluminum hydroxide or magnesium hydroxide, between two tetrahedral layers of silicon oxide[22,23].

The addition of inorganic nanoparticles (clay) considerably improves the filtration of membrane controlling the formation and growth of macrovoids, increasing the number of small pores improving hydrophilicity, porosity, permeability, mechanical properties and antifouling properties[22,24,25].

Teimoori[26] studied the impact of several alkanes as additives in coagulation bath, on the structural parameters and the morphologies of flat PES membranes. The asymmetric membranes was also fabricated by phase inversion method. It was expected that two distinct phase inversions to be occurred since both the polymer and the additives were insoluble in the coagulation bath. In conclusion, it was revealed that the coagulation bath had a major impact on the membranes structure in order to achieve the enhanced properties.

Taking into consideration what were exposed, the objective of this work is to study the addition of acid in the coagulation bath in the morphology of membranes of polyamide 6 and its nanocomposites.

2. Materials and Methods

2.1 Materials

The polymer matrix used was polyamide 6 Polyform B300, viscosity IV = 140-160 mL/g as white colored granules. The clay used was Brasgel PA, with cation exchange capacity (CEC) of 90meq / 100g, supplied by Bentonit União Nordeste, located in the city of Campina Grande - PB, in the form of powder, used as nanofiller. To obtain the membranes the formic acid was used with 99% purity, and for the coagulation bath the acid with 85% purity, both made by Vetec.

2.2 Methods

Initially all materials containing polyamide 6 were dried in a vacuum oven for a period of 24 hours at 80ºC.

To obtain nanocomposites of polyamide 6/clay, a polymer/clay concentrate (1:1) by mass was obtained using a high speed homogenizer, model MH-50H of the brand *MH Equipamentos*. The obtained concentrate was ground and incorporated into the polyamide 6 matrix in amounts representing nominal of 3 and 5% contents, in weight, of clay in a Werner-Pfleiderer ZSK 18 twin-screw extruders, with L/D 40 mm, with screw rotation speed of 250 rpm and temperature profile of 260 ºC for all zones. Figure 1 illustrates the extruder screw profile used for the production of nanocomposites.

For the membranes preparation by the phase inversion method, polyamide 6 and its nanocomposites were dissolved in formic acid (99% purity) in a proportion of 20:80% by weight of polymer:acid, under constant stirring for a period of 24 hours until there was complete dissolution of the polymer.

After preparation of the solution, it was spread on a glass plate with a glass stick, then immediately immersed in a precipitation bath containing distilled water, after precipitation the membrane was removed, washed with distilled water and dried at room temperature. This procedure is in accordance with the literature[27].

The membranes were also obtained using a precipitation bath containing distilled water and formic acid (85% purity) with different contents (20 and 30%), the procedure has already been described previously.

2.3 Characterizations

The polymer nanocomposites and membranes were characterized by X-ray diffraction (XRD), using a Shimadzu XRD 6000 equipment, with CuKα radiation (λ = 1.5418 Å), 40 kV, 30 mA, and scanning 2θ from 1.5º to 30º at a scanning rate of 2º/min. The membranes were characterized by scanning electron microscopy analyzes were performed on a Superscan - Shimadzu SSX 550 equipment, operating at 15kV. The surface and cross-section of the membranes were evaluated. For the cross section analyzes, the samples were fractured in liquid nitrogen to prevent plastic deformation. The surfaces of the samples were coated with gold, in order to avoid the accumulation of negative charge. The thickness and the pore sizes measurements of the surface and cross-section of the membranes were made on the equipment itself.

3. Results and Discussion

Figure 2 illustrates the results from X-ray diffraction of clay, polyamide 6 and the nanocomposites with contents of 3 and 5% of clay mass.

It is noticed that the characteristic peak of the clay disappears when it is incorporated to the polymeric matrix, presenting an exfoliated and/or partially exfoliated structure[29] indicating that a nanocomposite with this type of structure was obtained.

It can also be seen the presence of two peaks in the range of 2θ = 20 º and 23 º, corresponding to reflections related to the crystalline planes (200) and (002) of the α phase of polyamide 6. In the literature, these crystalline planes were also observed[27,28,30,31]. It is possible to observe that the PA6 curve presents a behavior slightly different from the other curves, with the appearance of the crystalline plane (001) corresponding to the phase γ of the polymer. According to[32] the polyamide 6 can assume two crystallographic forms, monoclinic α and monoclinic or pseudo-hexagonal γ.

Figure 3 shows the XRD diffractograms of membranes prepared from polyamide 6 and its nanocomposites. As in Figure 2, the absence of the characteristic peak of the clay for the membranes obtained from the nanocomposites can also be highlighted.

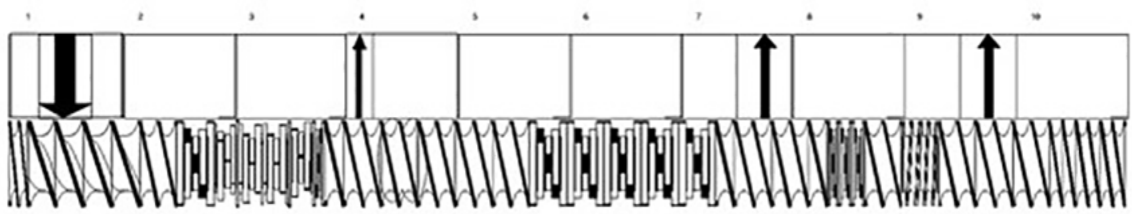

Figure 1. Extruder screw profile.

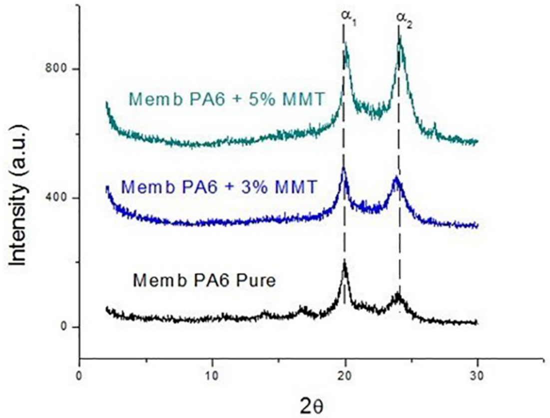

Figure 2. XRD patterns of clay, PA6 and its nanocomposites with different clay content (3 and 5%)

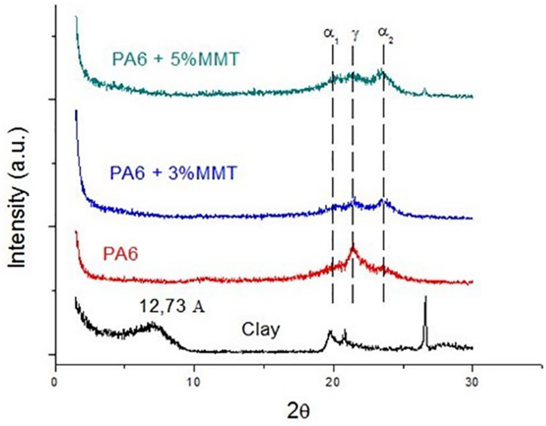

Figure 3. XRD patterns of the membranes PA6 and its nanocomposites with different clay content (3 and 5%)

Unlike the nanocomposites, the membranes presented an important characteristic in the diffractograms. It can be observed the presence of the phases α_1 and α_2 with more intensity for all the membranes produced[33]. In Figure 2, it is almost impossible to visualize the presence of these two crystalline phases of polyamide 6, and it is possible to affirm that the presence of formic acid influenced the crystallinity of the polymer, also making the phase γ disappear in the membranes, due to the solvent that changed the crystalline character of the material. The appearance of both peaks is related to the formation of two different crystallographic forms (α_1 and α_2) of the polyamide[34].

SEM images of the surfaces of PA6 membranes and their nanocomposites with and without a coagulation bath are shown in Figures 4 to 6. The PA6 membrane has a dense structure and a small number of pores. It is also observed that the presence of clay with contents of 3 and 5% in the membranes of PA6 provided a greater amount of pores and a better distribution throughout the surface. Increasing the percentage of clay also increased the amount of pores. Thus, it was evident the presence of the clay changes the quantity and uniformity of the pores. As observed by Medeiros[35], the addition of clay particles in the membrane structure modifies the pore morphology on the membrane surface.

With the presence of 10% of formic acid in the precipitation bath (Figure 5), it is observed that the PA6 continues to have a dense structure. In the nanocomposite membranes, the pores became larger and irregularly shaped, being this more pronounced for the membrane with 5% of clay, when compared to the membranes without the presence of acid in the precipitation bath of Figure 4.

For the precipitation bath containing 30% of formic acid, Figure 6, the PA6 membrane continued to have a dense structure, but there was an increase in the pores size presents on the surface. Membranes obtained with 3 and 5% of MMT had a morphology similar to that seen in the membranes with 10% of acid. However, the pores were larger, but less uniform in all the surface of the membrane. Thus, the introduction of 10% formic acid favored a better pores size uniformity.

For membranes produced with 10% and 30% solvent, it was possible to observe the presence of white particles throughout the membrane porous support, where this can be due to the poor dissolution of the polymer.

In Table 1 we have the pore size values for the membrane surface produced from the three different modes. Initially it was seen that clay had a direct influence on the size and distribution of membrane pores. The clay acted as a porogenic agent, increasing the amount of pores but decreasing the size of the pores throughout the membrane surface. With the presence of the acid, there was an increase in the pore size of the membranes containing clay, being attributed to a possible interaction between MMT and formic acid.

Figures 7 to 9 show the cross sections images of the PA6 membranes and their nanocomposites.

It was observed that, in general, the obtained membranes presented an asymmetric morphology formed by a selective

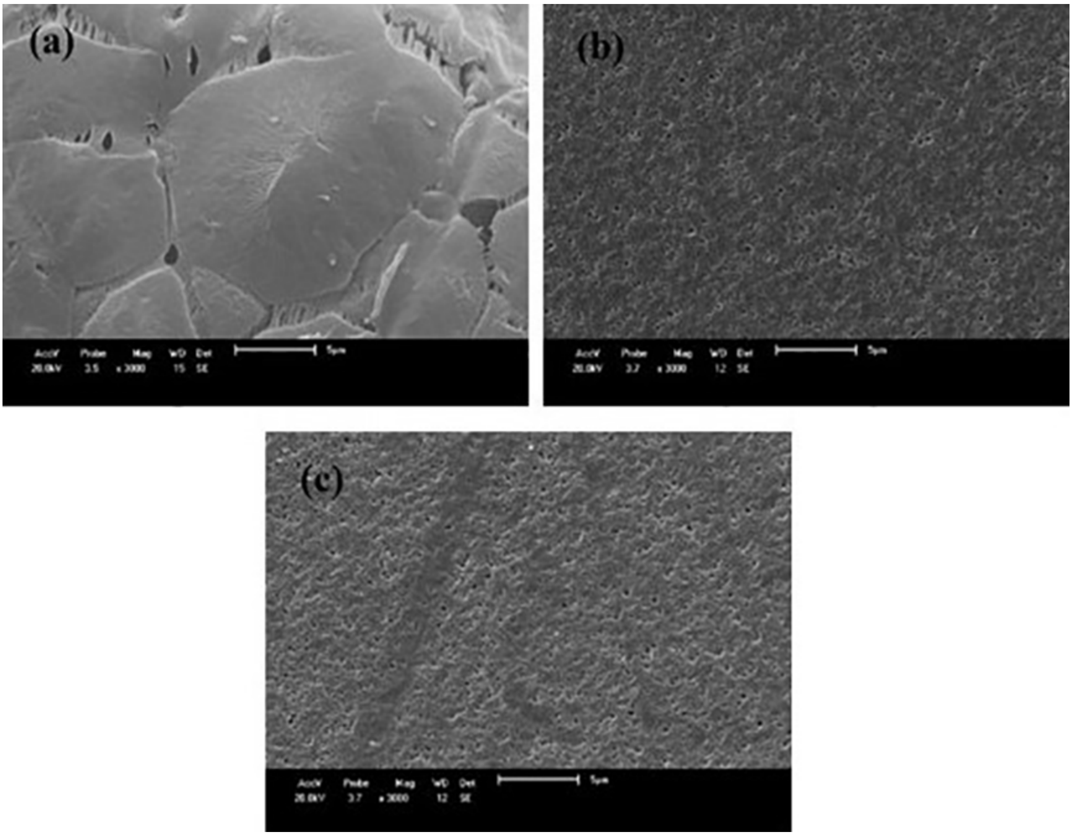

Figure 4. SEM images of the membranes surface of: (a) PA6; (b) PA6 + 3% MMT; and (c) PA6 + 5% MMT

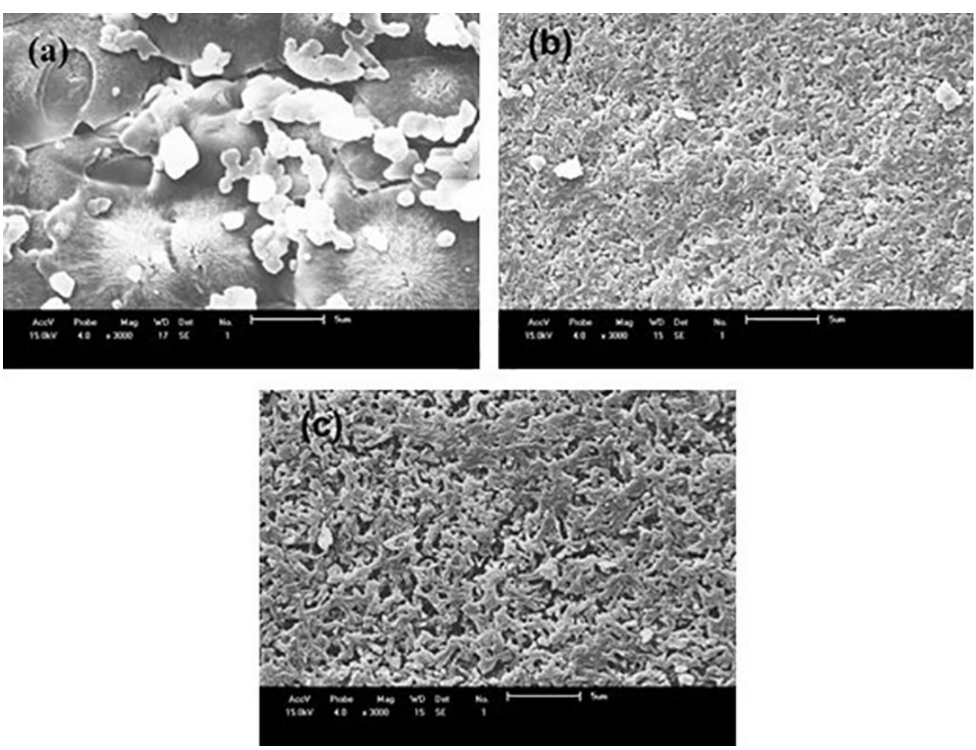

Figure 5. SEM images of the membranes surface with precipitation bath with 10% of formic acid: (a) PA6; (b) PA6 + 3% MMT and (c) PA6 + 5% MMT

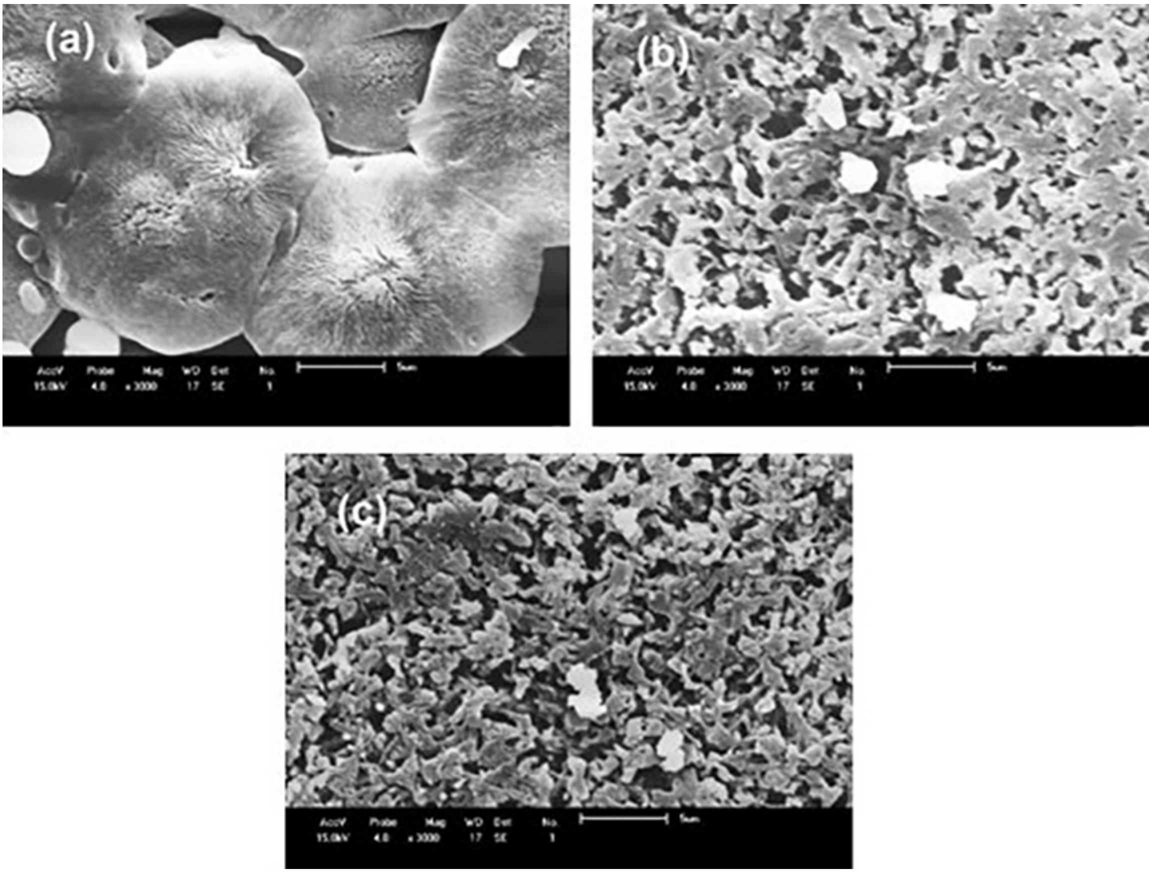

Figure 6. SEM images of the membranes surface with precipitation bath with 30% of formic acid: (a) PA6; (b) PA6 + 3% MMT and (c) PA6 + 5% MMT

Table 1. Pore size at the surface to all the membranes produced.

Membranes	No bath	10% acid	30% acid
PA6	1,161 μm	0,874 μm	1,632 μm
PA6 + 3%	0,304 μm	0,336 μm	0,679 μm
PA6 + 5%	0,277 μm	0,471 μm	0,673 μm

layer and a porous support, this structures is characteristic of the technique of obtaining the membranes that was the inversion of phases. It is possible to observe that the PA6 membranes presented a thin selective layer and the porous support with uniform and interconnected pores. The membranes with 3 and 5% of clay contents presented a better defined selective layer and a support with the presence of *"fingers"* interconnected and very close to the selective layer, these pores can be related to a possible delayed precipitation as a function of the presence of clay in the polymer solution. The "*fingers*" can also be related to the presence of a larger volume of trapped gases in the polymer solution, probably occurring a slower precipitation when were obtained these membranes[36].

The clay also influenced the regularity and the shape of the porous, leaving them more spherical. The PA6 membranes and its nanocomposites had a total thickness of 109, 152 and 230 μm respectively, also having an increase in the thickness of the selective layer. In view of this, it can be observed that the presence of clay significantly changed the morphology of the membranes.

The structure analysis of a membrane through the cross section is as determinant as the top surface, since it is responsible for the productivity of the membrane, where it will determine the permeability characteristics of it[37].

With the presence of 10% of formic acid in the precipitation bath, Figure 8, the PA6 membrane presented a decrease of the filtering skin in relation to PA6 membrane without the presence of acid, showing the influence of it. For the membranes with nanocomposites, it is observed that a considerable decrease occurred in the selective layer, being this more pronounced for the membrane with 5% of clay. The acid present in the bath favored a reduction in the amount and size of the *"fingers"*, evidencing that the acid retards the pores formation and they can have a greater uniformity throughout the porous support[38].

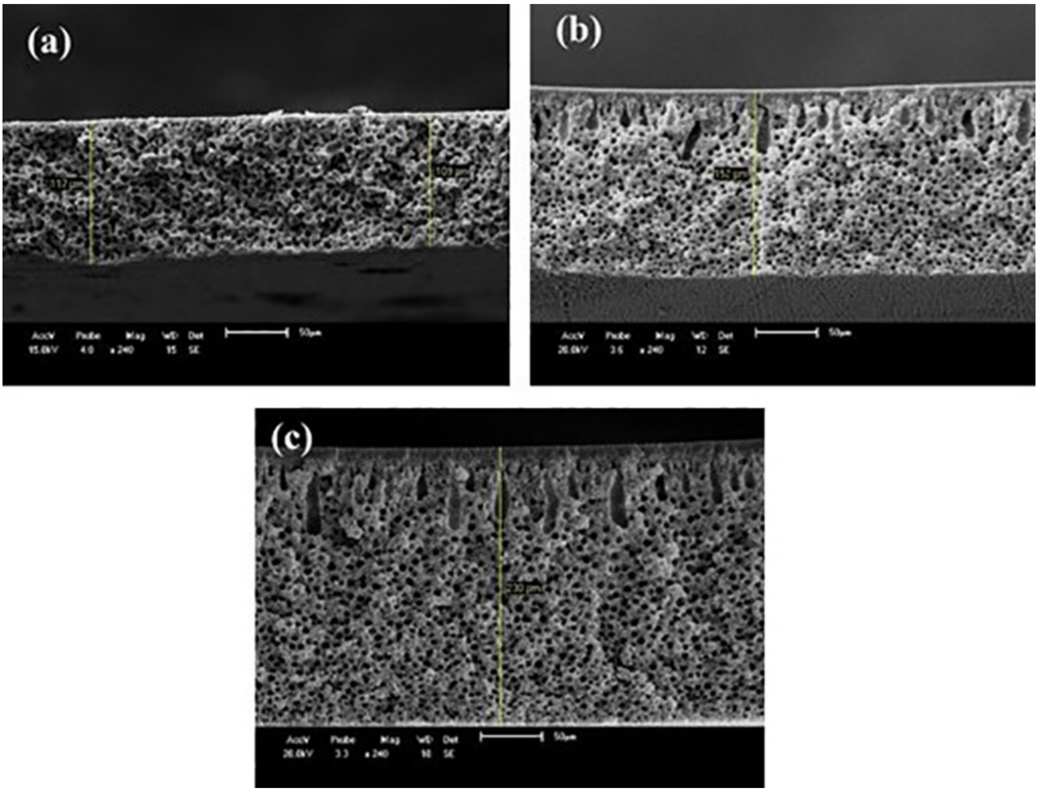

Figure 7. SEM cross-sectional images of the membranes of: (a) PA6; (b) PA6 + 3%MMT; and (c) PA6 + 5%MMT

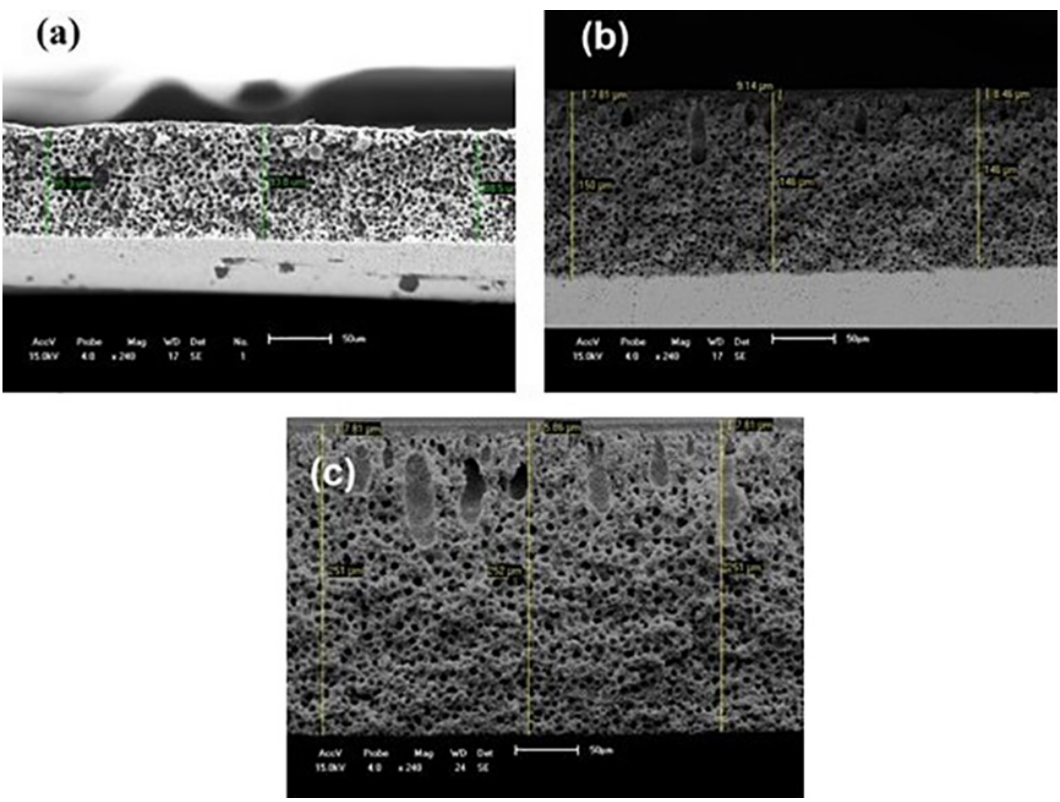

Figure 8. SEM cross-sectional images of the membranes with precipitation bath with 10% of formic acid: (a) PA6; (b) PA6 + 3%MMT and (c) PA6 + 5%MMT

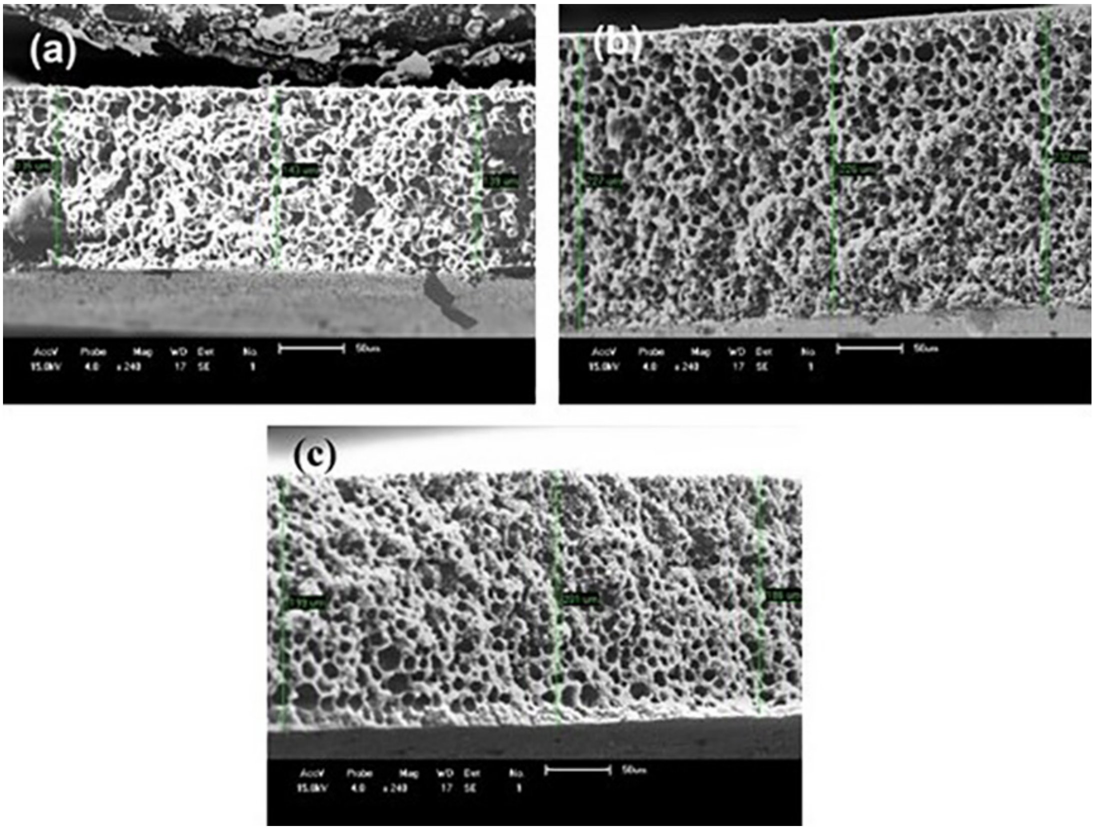

Figure 9. SEM cross-sectional images of the membranes with precipitation bath with 30% of formic acid: (a) PA6; (b) PA6 + 3%MMT and (c) PA6 + 5%MMT

In the precipitation bath with 30% of formic acid, Figure 9, it was visible that for all the membranes the filter skin reduced significantly, being confused with the porous support. There was an increase in size and as well in the uniformity of the pores throughout the porous support for the three membranes under study. In those that contain clay it was observed the absence of the *"fingers"*, due to the large percentage of acid in the bath, showing the direct influence of it on the formation of this macropore when compared to the membranes produced with 10% acid (Figure 8)[38]. It was also possible to visualize that the presence of clay left the pores with more spherical appearance and smaller for the content of 30% of acid.

With these parameters studied it was possible to evaluate that the clay and the presence of the acid in the coagulation bath provided changes in the membrane morphology. The presence of the acid changes the solvent output and the non-solvent input, so the membrane does not form a thick selective layer as in the membranes produced without the coagulation bath, leaving the membrane completely porous. It was clearly seen that the addition of clay in the polymer matrix significantly changed the amount and uniformity of the pores, acting as a porogen, as can be observed by Leite[23].

4. Conclusions

The influence of different acid levels in the coagulation bath on the membranes morphology was investigated. Based on the results obtained and presented in this study, it was seen that by XRD possibly nanocomposites were obtained with exfoliated and/or partially exfoliated structures, as well as the presence of characteristic peaks of the α and γ phases was observed, and also that the nanocomposites formation altered the crystallinity of polyamide 6. By SEM, it was evident that the clay directly influenced the formation and morphology of pores on the membrane surface, when compared to the polyamide 6 membrane, occurring the appearance of macropores in *"fingers"* shapes. With the presence of formic acid in the bath, it was possible to visualize a significant change in the formation and also in size of the membrane surface pores, where the reduction of the membrane selective layer occurred, there was a decrease in the number of fingers on the porous support and also an increase in size of the pores interconnected to the filtering skin.

With this, it was evident that the content of 10% of acid along with the presence of clay favored a greater uniformity in morphology throughout the membrane region.

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