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Development of Kevlar-Supported Novel Polypropylene Membranes: Effect of the Concentration of the Nucleating Agent on the Properties and Performance

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ABSTRACT: Novel membranes were fabricated with woven Kevlar fabric sandwiched between two isotactic polypropylene layers and with various concentrations of adipic acid as the nucleating agent (NA). A thermally induced phase-separation dip-coating method was adopted to generate and control the microporosity in the developed membranes. Scanning electron microscopy and atomic force microscopy were used to directly observe and confirm the morphologies and micropores in the fabricated membranes. We observed that with an increase in the concentration of the NA in the fabricated membranes, both the pore density and pore size decreased. The average pore sizes were observed to be 1.686, 0.925, 0.372 μm, respectively, for 0.3, 0.5, and 0.7 pphr concentrations of the NA, respectively. The flux characteristics of the prepared membranes were also tested at various pressures with water, methanol, ethanol, and isopropyl alcohol as solvents in a custom-made filtration cell. The results obtained indicate the dependence of the flux on the type of solvent, pressure, and membrane. The flux for the solvents was observed to decrease with increasing concentrations of NA in the prepared membranes and was attributed to the decrease in the pore density and pore size. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 2821–2831, 2013

KEYWORDS: adipic acid; flux rate; thermally induced phase separation (TIPS); membrane; microporosity; nucleating agent; polypropylene; water

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INTRODUCTION

One of the most pressing challenges of the present day is the availability of clean water through various treatment processes to meet the demand for global fresh water for various purposes, including drinking, irrigation, and industry.[1,2] Keeping in view the continuous decrease of clean water supplies, researchers are actively exploring new technologies to treat and purify water to cope with its increasing demand. In this direction, polymer membrane separation processes are expected to play an important role in achieving future water cue sustainability, as continuing population growth and industrialization require substantial and global improvements in the efficiency of water use. Thus, because technological improvements result in lower costs, membrane water-treatment processes based on polymeric materials have grown steadily both in terms of scale and market share, such that they now compete economically with conventional water-treatment technologies in certain applications.[3] The widespread applications of membrane separations on scales sufficient to realize global sustainability will require substantial reduction in operating costs and improved performance of the membranes. In view of this fundamental objective, the fabrication of new high-performance polymer membranes continue to attract the attention of researchers. One basic requirement that ultimately determines the performance of any polymer membrane is the polymeric material itself. In this regard, many polymeric materials have been used to prepare membranes with different properties and performances.[3]

Among the different polymeric materials, polymer membranes based on isotactic polypropylene (IPP) have been widely used.[4–10] IPP is one of the most important commercial thermoplastics because of its relatively low cost, versatility, recyclability, and good mechanical performance in engineering applications, including microporous membrane preparation. Polypropylene (PP) microporous membranes are widely used in the

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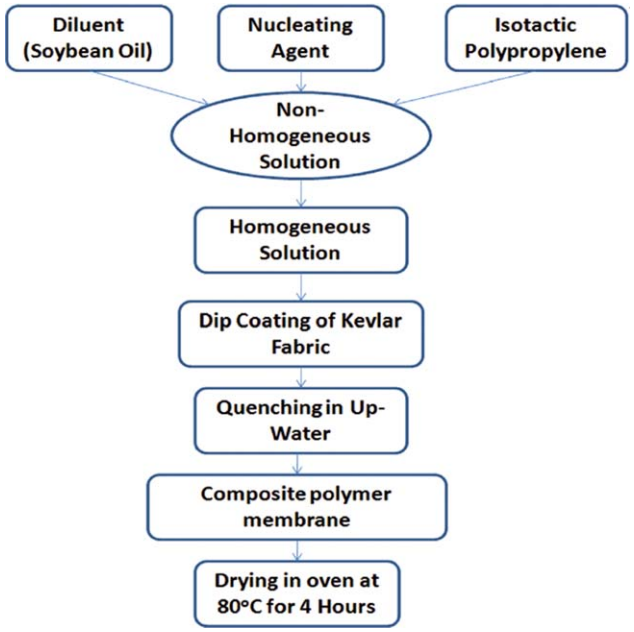

Figure 1. Schematic of the selective main steps adopted to fabricate Kevlar-supported IPP membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

manufacturing of lithium batteries and artificial lungs, chemical separation, and textile industry and for water purification.[4–10] Many techniques have been used for IPP membrane preparation, such as melt spinning and cold stretching, blending stretching, sintering, and thermally induced phase separation (TIPS). Among these, however, the TIPS process is a versatile technique for making semicrystallized polymer membranes. In this method, the polymer can be dissolved in the diluent at a high temperature and form a homogeneous solution, whereas phase separation is induced by a decrease in the temperature.[8–16]

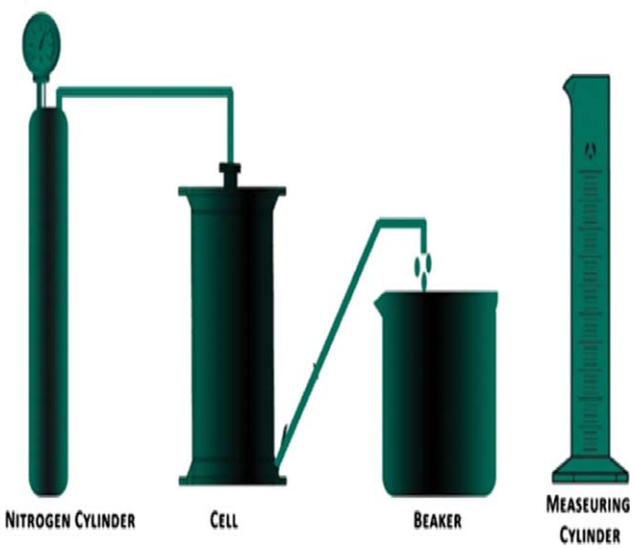

Figure 2. Schematic of the filtration process used to test the performance of the fabricated IPP membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

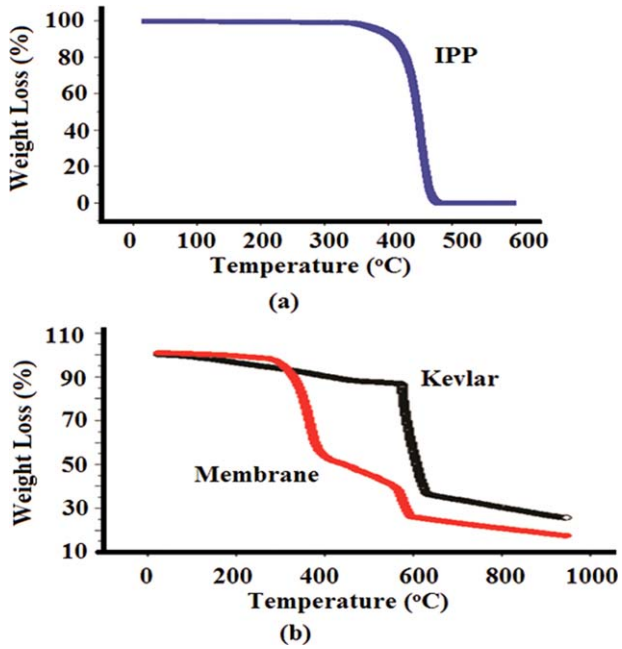

Figure 3. Thermal decomposition of (a) IPP and (b) the Kevlar fabric and one of the fabricated membranes with a 0.3 pphr NA concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

After the diluents are removed, microporous membranes can be obtained. Many studies have shown that the microstructure of membranes results not only from the effects of the diluent, quenching temperature, and coarsening[6,10,11,15] but also from

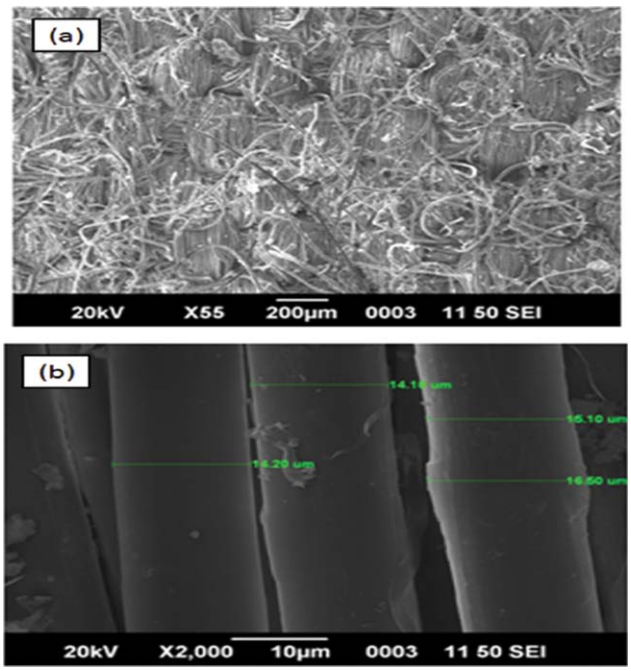

Figure 4. SEM images of the (a) Kevlar fabric and (b) the measurement of the fiber's average diameter employed for the fabrication of the membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

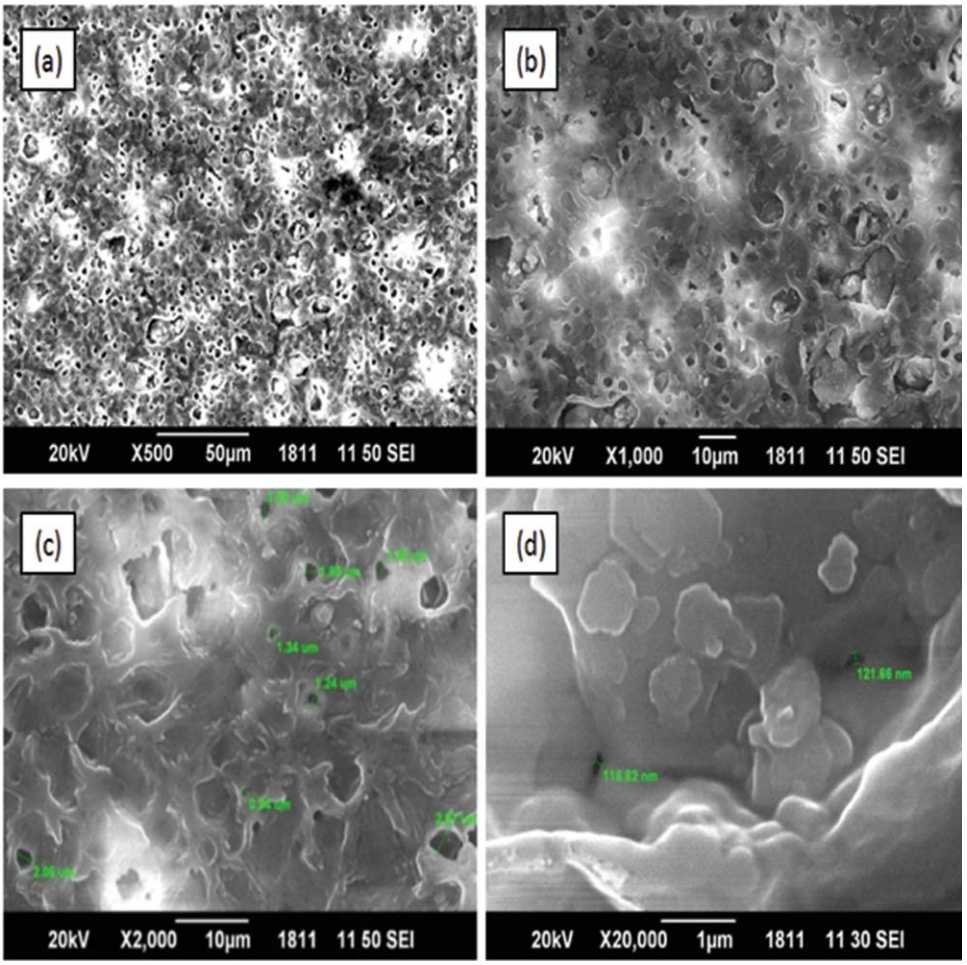

Figure 5. SEM micrographs at (a) 500, (b) 1000, (c) 2000, and (d) 20,000× magnifications of the fabricated membranes with 0.3 pphr adipic acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the nucleating agents (NAs).[9,17–22] The NA addition has a significant influence on the crystallization rate, crystallization temperature, and crystallization. Nucleating effects for semicrystalline polymers have been much investigated for pure polymer systems such as the IPP system. The addition of NA can influence the initiation of the crystallization at higher temperatures compared to the nonnucleated system. The addition of NAs, PP crystals with a center of NAs, is called heterogeneous nucleation. Because of a large enhancement of the crystal nucleus, the sizes of spherulites change to influence changes in the microstructural features.

In view of the importance of the influence of NA on the properties of the polymer membranes, in this study, we specifically focused on the incorporation of the various concentrations of the NA adipic acid on the characteristics, structures, morphologies, and performance of the novel membranes with woven Kevlar fabric (WKF) sandwiched between two IPP layers by employing the versatile technique of the TIPS dip-coating method to generate and control the microporosity in the developed membranes. Three different concentrations of the NA adipic acid were used in the preparation of PP microporous membranes. The effects of various concentrations of 0.3, 0.5, and 0.7 pphr of the NAs of adipic acid on the properties of the IPP microporous membranes prepared via TIPS were studied. To determine the performance and efficiency of the prepared membranes, flux rate analysis was also performed. For this purpose, water, methanol, ethanol, and isopropyl alcohol liquids were used; these which possessed different structures, polarities, and most importantly, sizes.

EXPERIMENTAL

Materials

The reagents used to fabricate the membrane were used as received. The membranes were fabricated from IPP with a melt flow index of 14.2 g/10 min. Adipic acid (Sigma-Aldrich), pure soybean oil, and *n*-hexane were also used. To support the membrane, WKF (DuPont International) was used.

Fabrication of the Membranes

The membranes were fabricated with a TIPS procedure and a dip-coating method. A typical example of the procedure is described later and is presented in Figure 1. In the first step, a suitable amount of soybean oil was placed in a 500-mL beaker, and then, IPP was added. Three concentrations of adipic acid (0.3, 0.5, and 0.7 pphr) as the NA were used. For example, 0.3

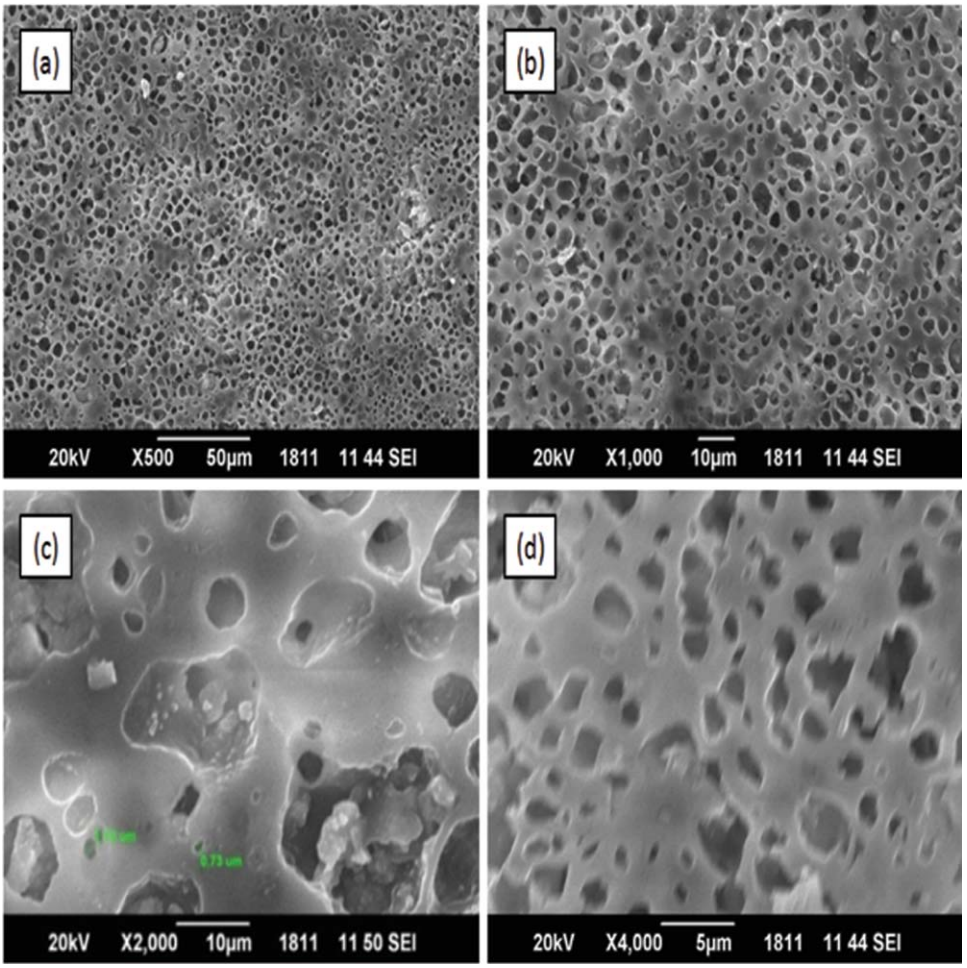

Figure 6. SEM micrographs at (a) 500, (b) 1000, (c) 2000, and (d) 4000× magnifications of the fabricated membranes with 0.5 pphr adipic acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

pphr adipic acid was placed into the soybean and IPP solution. This solution was placed on a hot plate and stirred for several hours to melt and homogenize the IPP resin with soybean oil. After the formation of the solution, the dried WKF with an approximate diameter of 8 cm was dipped in the prepared solution. We then quenched it in ultrapure water at room temperature. *n*-Hexane was used to extract the soybean oil from the IPP-coated WKF for several hours. The prepared membranes were then dried in an oven at 80°C for several hours. This process resulted in the formation of a homogeneous white IPP film on both sides of the WKF.

Characterization of the Membranes

The characteristics and performance of the prepared membranes were investigated with various techniques.

Thermogravimetric Analysis (TGA) Studies. TGA/differential thermal analysis studies of the prepared membranes were carried out with a PerkinElmer SDT Q600 instrument with a simultaneous TGA/differential thermal analysis analyzer at a heating rate of 10°C/min under a nitrogen atmosphere. The TGA thermal characteristics were determined from the corresponding curves.

Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) Analyses. The morphology and microstructure of the prepared membranes were studied with the aid of SEM (JEOL JSM 6490A) and AFM (JEOL JSPM-5200). For SEM analyses, the membranes were sputtered with a gold coating in a custom-made setup assembly. SEM was performed on the Kevlar-supported IPP membranes. The membrane samples were cut into 0.25-cm^2 (0.5 × 0.5 cm^2) pieces and subsequently immersed in a liquid nitrogen reservoir for 5 s. The broken membrane pieces were mounted on metal plates with carbon paste and were gold-coated before use. The cross sections of the resulting membranes at the broken parts were observed by SEM. In addition to SEM analyses, we also investigated the membrane surfaces with AFM by operating the instrument in the Alternating Current (AC) or tapping mode.

Flux Experiments. A custom-made stainless steel cell was used to test the permeation characteristics of the fabricated membranes. The schematic of the process is shown later in Figure 2. The performance of the prepared membranes was tested at different pressures for the permeation behavior of different solvents, such as water, methanol, ethanol, and isopropyl alcohol.

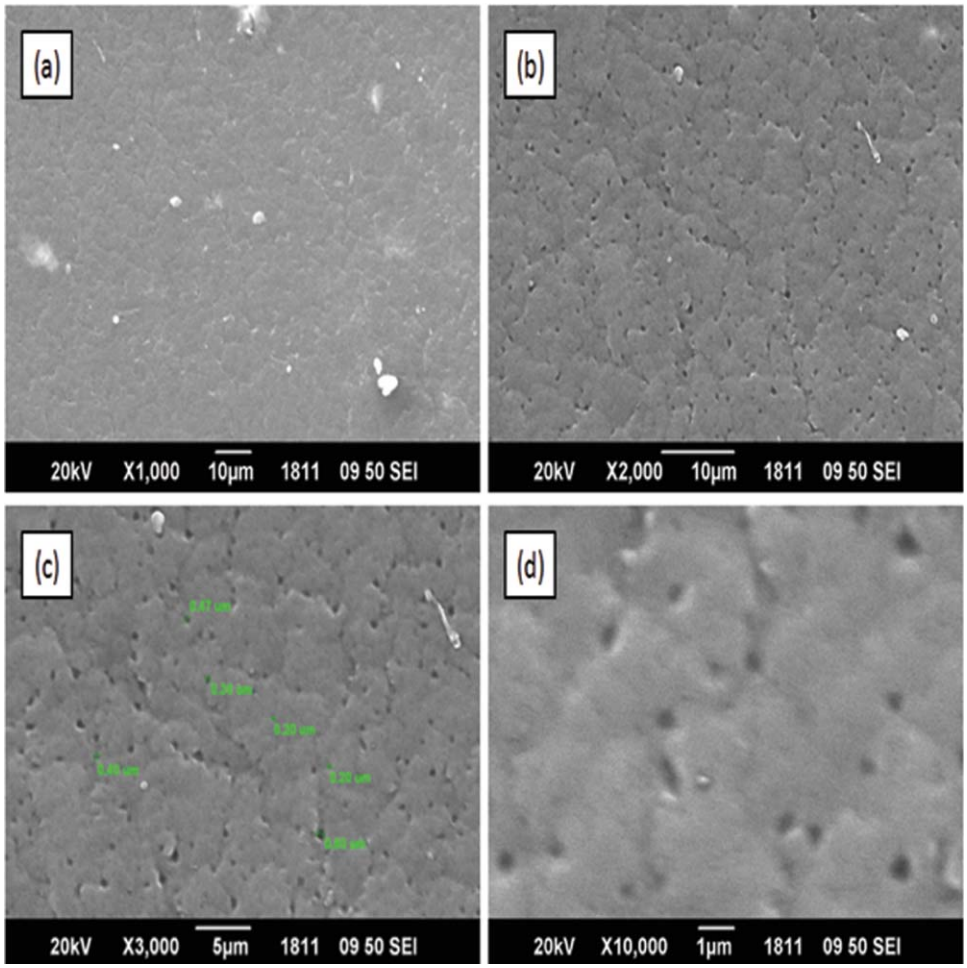

Figure 7. SEM micrographs at (a) 1000, (b) 2000, (c) 3000, and (d) 10,000× magnifications of the fabricated membranes with 0.7 pphr adipic acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For this purpose, a filtration membrane cell was attached to a nitrogen gas cylinder to obtain desirable pressure to permeate the liquid through the prepared porous membranes. For each experiment, 500 mL of liquid was placed in the cell and then subjected to the desirable pressure. The fabricated samples of the membranes were subjected to the permeation experimentation for the pure solvent at a constant flow rate (1.5 L/min) and a variable pressure of N_2 gas (13, 26, 39 psi) to measure the pure solvent permeability (P_{SP}; L m^{-2} bar^{-1} h^{-1}), which was calculated with the following equation:

$$P_{SP} = Q/PA \quad (1)$$

where Q is the volumetric flow rate (L/h) for the solvent permeation, A is the effective filtration area (m^2), and P is the transmembrane pressure drop (bar). The flux of pure water and other solvents λJ [L/(m^2 h)]ρ of the membrane was determined by the direct measurement of the permeate volume, which was calculated by the following equation:

$$J = V/At \quad (2)$$

where V is the volume of the permeated solvent, A is the effective membrane area, and t is the permeation time.

RESULTS AND DISCUSSION

TGA Studies

Figure 3 represents the effect of the temperature on the thermal degradation of the materials and the prepared membranes. The effects of the temperature change on the IPP, Kevlar fabric, and IPP membrane indicated the temperature at which the polymeric materials and prepared membranes could undergo thermal degradation. Figure 3 also shows the thermal degradation expressed in terms of weight loss as a function of the temperature for the IPP, Kevlar fabric, and membranes prepared with NA at a concentration of 0.3 pphr.

Figure 3(a) indicates that the weight loss of IPP in N_2 started around 350°C. Although the onset of the weight loss of PP began at 230–250°C, the breakdown leading to volatile products started only above 300°C. Intramolecular radical-transfer and propagation processes accounted for the volatile products above 300°C in PP. From the TGA of Kevlar [see Figure 3(b)], we observed that decomposition took place in three unique steps. In the first step, plain Kevlar fabric showed some weight loss between 20 and 580°C that could be attributed to the presence of moisture. In the second step, a very sharp decomposition

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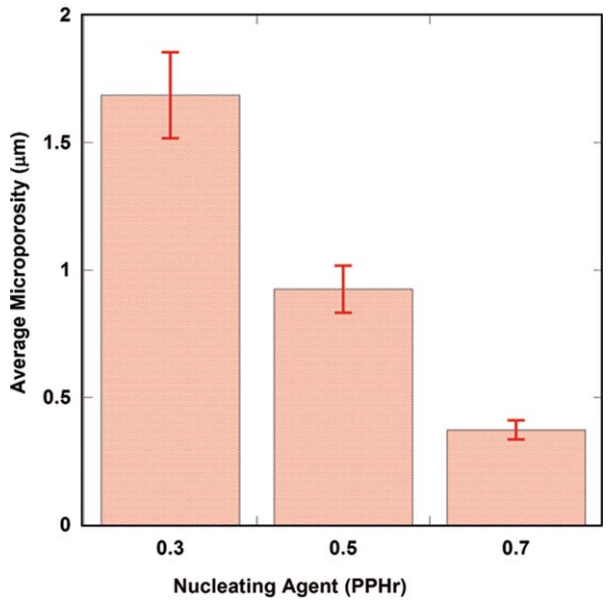

Figure 8. Effect of the adipic acid (NA) concentration on the average porosity of the fabricated IPP membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

took place around 620–630°C with a significant weight loss of about 60%. In the third step, there was another weight loss of about 20% from 630 to 950°C. Both second and third stage were probably due to the main thermal decomposition and/or the carbonization of the decomposed products to ash of the Kevlar chains. The TGA study of the prepared membranes indicated slightly different behavior. It was evident that the decomposition took place in four unique steps. In the first step, the membrane showed a slight weight loss of around 5% between 20 and 300°C that may have again been due to the presence of volatile components. In the second step, a very sharp decomposition took place around 300–400°C with a significant weight loss of about 40%. In the third step, there was another weight loss of about 25% from 400 to 600°C. In the final stage of step 4, another 10% loss in weight was observed between 600 and 950°C. As in the case of Kevlar, the thermal analysis for the membranes suggested that the main thermal decomposition was due to the carbonization of the decomposed products to ash of the polymer chains.

SEM Analysis

SEM was used to study the surface morphology of the prepared membranes. SEM images of the Kevlar fabric were also obtained. Figures 4–7 represent and compare the surface morphologies and extents of pore generation at various

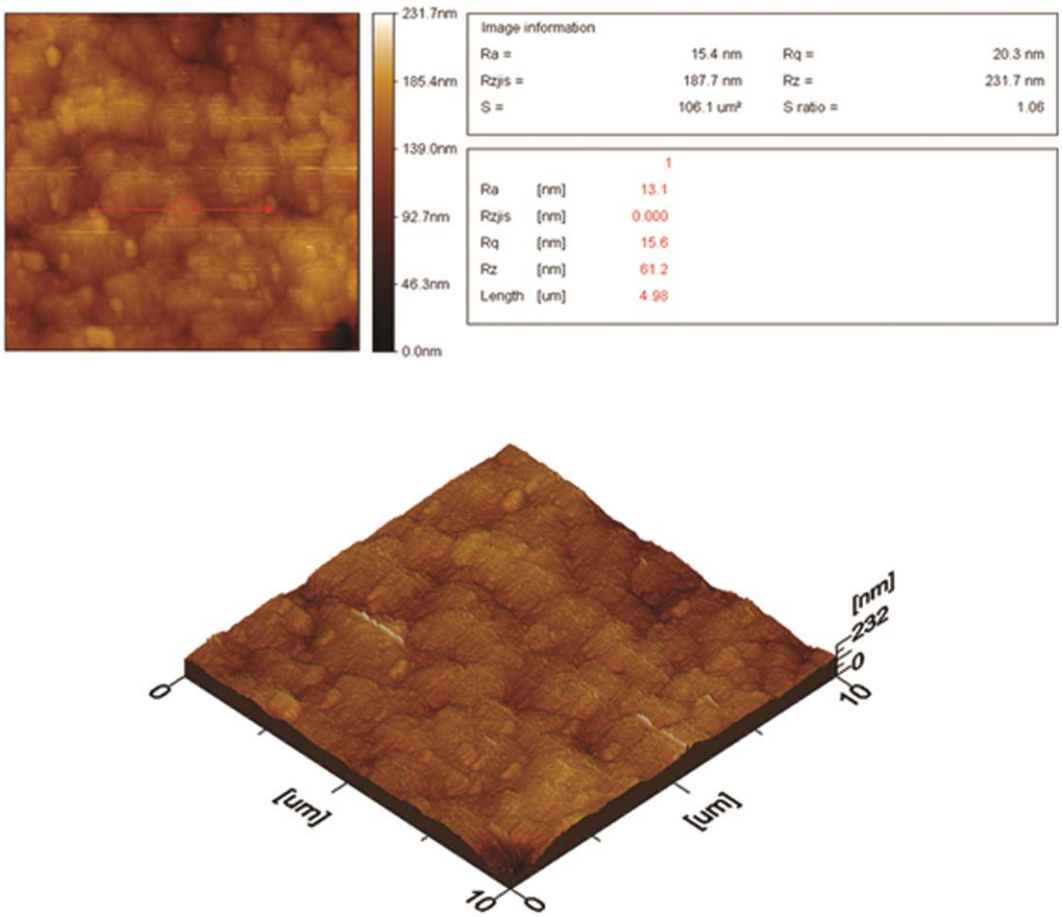

Figure 9. AFM topographical images of the membranes along with the IPP film thickness on the supported fabric prepared with an NA concentration of 0.3 pphr. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

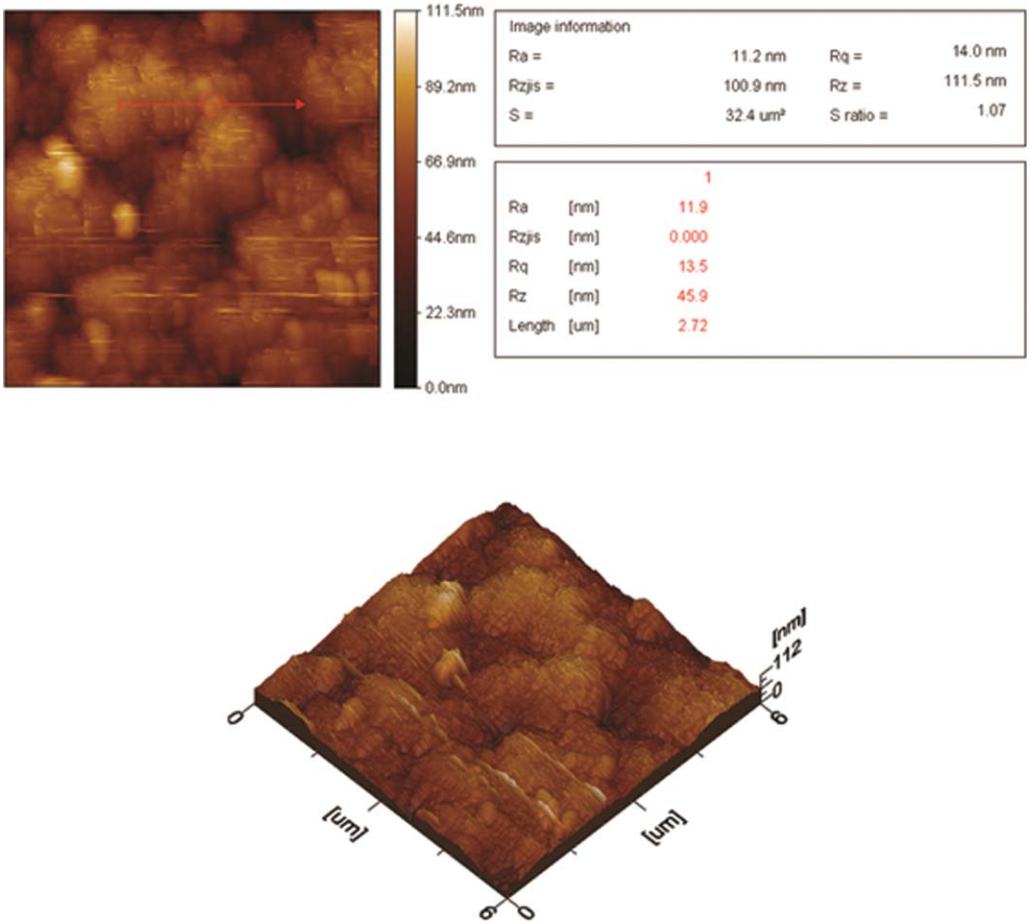

Figure 10. AFM topographical images of the membranes along with the IPP film thickness on the supported fabric prepared with an NA concentration of 0.5 pphr. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

magnifications for the three different membranes made with three different concentrations of adipic acid: 0.3, 0.5, and 0.7 phr.

The SEM results clearly indicate that the concentrations of NA significantly influenced the morphologies, pore structures, and porosities. The average sizes of the pores were found to be higher at lower NA concentrations. The average pore sizes observed from the SEM micrographs were found to be approximately 0.9–2.07 μm for 0.3 pphr, 1.12–0.73 μm for 0.5 pphr, and 0.2–0.6 μm for 0.7 pphr concentrations of NA. The effect of the NA concentrations on the average porosity of the fabricated IPP membranes is shown in Figure 8. The addition of NA also provided a large number of nuclei, which significantly modified the mechanism of the crystallization behavior of the IPP.[8–16,23,24] In this study, the average porosities of the membrane prepared with the highest concentration of NA adipic acid was found to be the smallest, and this observation was in good agreement with some of the previous studies, which also suggested that NA promotes the formation of narrow pore sizes.[9] These characteristics could be attributed to the spherulitic sizes in the prepared membranes because their morphology, pore sizes, and pore density are known to largely decrease under the influence of NA. Furthermore, the driving force for solid–liquid TIPS is the difference in the chemical potential of

Table I. Summary of the Properties of Liquids Used to Test the Performance of the Prepared IPP Membranes[27]

Property	Water	Methanol	Ethanol	Isopropyl alcohol
Chemical Abstracts Service (CAS) Registry Number	7732-18-5	67-56-1	64-17-5	67-63-0
Molar mass (g/mol)	18.01528	32.04	46.07	60.1
Size (nm)	0.26	0.41	0.44	0.48
Density at 20°C (g/cm^3)	1.0	0.7918	0.789	0.786
Dipole moment (D)	1.85	1.69	1.69	1.66
Viscosity at 20°C (Pa s)	0.001	0.00059	0.0012	0.00286

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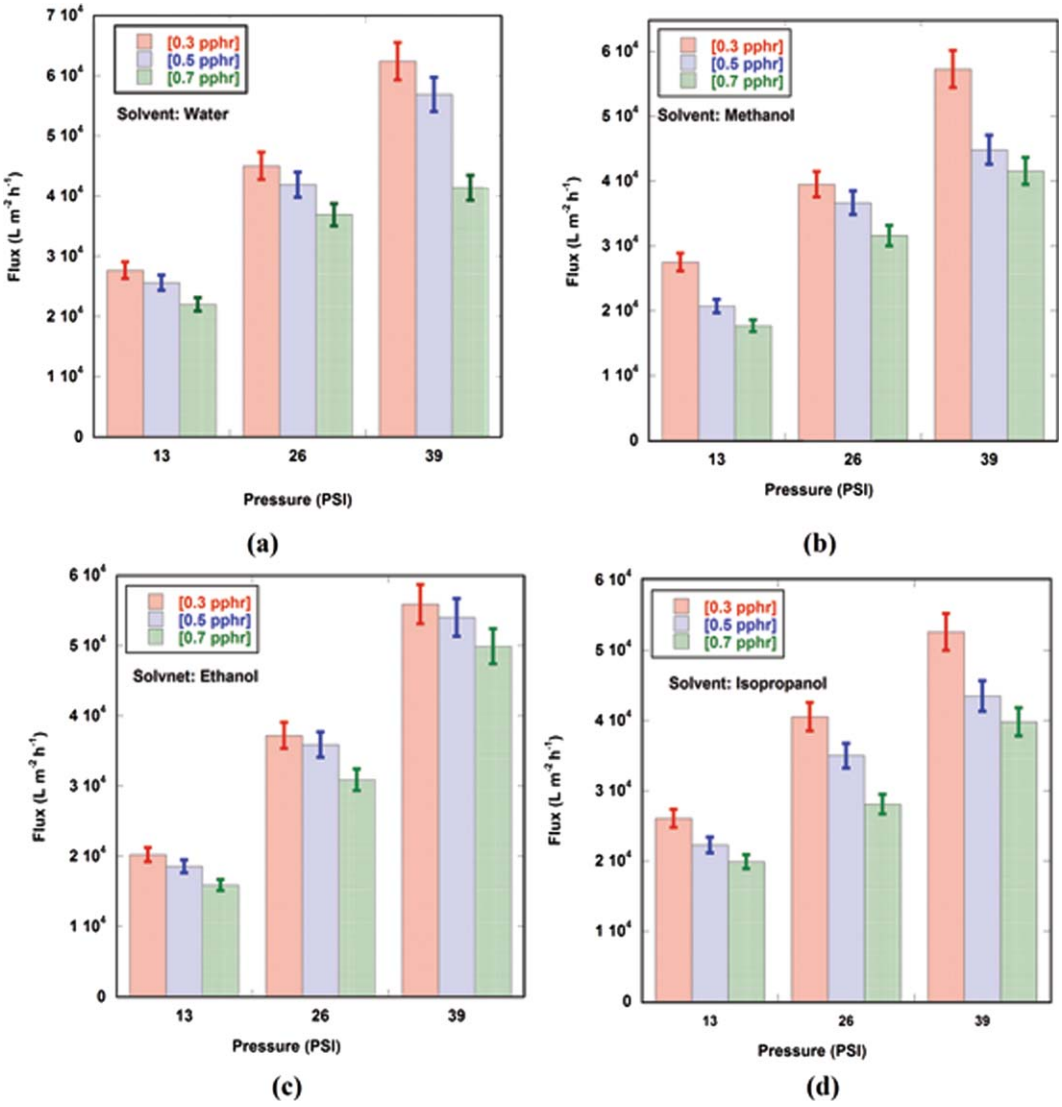

Figure 11. Effect of the NA concentration of adipic acid on the flux behavior of (a) water, (b) methanol, (c) ethanol, and (d) isopropyl alcohol solvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymer in the crystalline and solution phases.[23,24] Therefore, with this taken into consideration, the addition of NA could influence the magnitude of this driving force, as this is directly proportional to the difference between the equilibrium melting temperature of the diluted polymer and the imposed crystallization temperature. This difference in temperature is known as the *degree of supercooling*. Its greater value is known to result in a faster conversion of amorphous polymer to the crystalline state, the faster rate of increase in the size of individual spherulites, and the greater the number of nuclei sites formed at which spherulites can grow.[23,24] The addition of NA can increase the overall crystallization rate because of an increase in nucleation density. Upon increasing addition of NA, there is a possibility of a decrease in the spherulitic dimensions and an increase in the formation of the crystallinity regions.[25] The addition of NA can significantly influenced the crystallization of PP as multinuclei sites to generate more spherulites of smaller sizes.[9] Furthermore, the driving force for crystallization can increase due to heterogeneous nucleation to restrict the coarsening of droplets of the polymer-lean phase and thus result in smaller pore sizes.[8–16,23–25]

AFM Analysis

AFM images were acquired to directly observe and confirm the morphologies and micropores in the fabricated IPP membranes. Figures 9 and 10 show the AFM images of the membranes prepared with NA concentrations of 0.3 and 0.5 pphr, respectively. As supported by SEM analyses, we reconfirmed that with increasing concentration of the NA in the fabricated membranes, both the pore density and pore size decreased.

Flux Rate Studies

To test the performance and efficiency of the prepared membranes, flux rate analysis was performed. For this purpose, four different liquids were used; these possessed different structures,

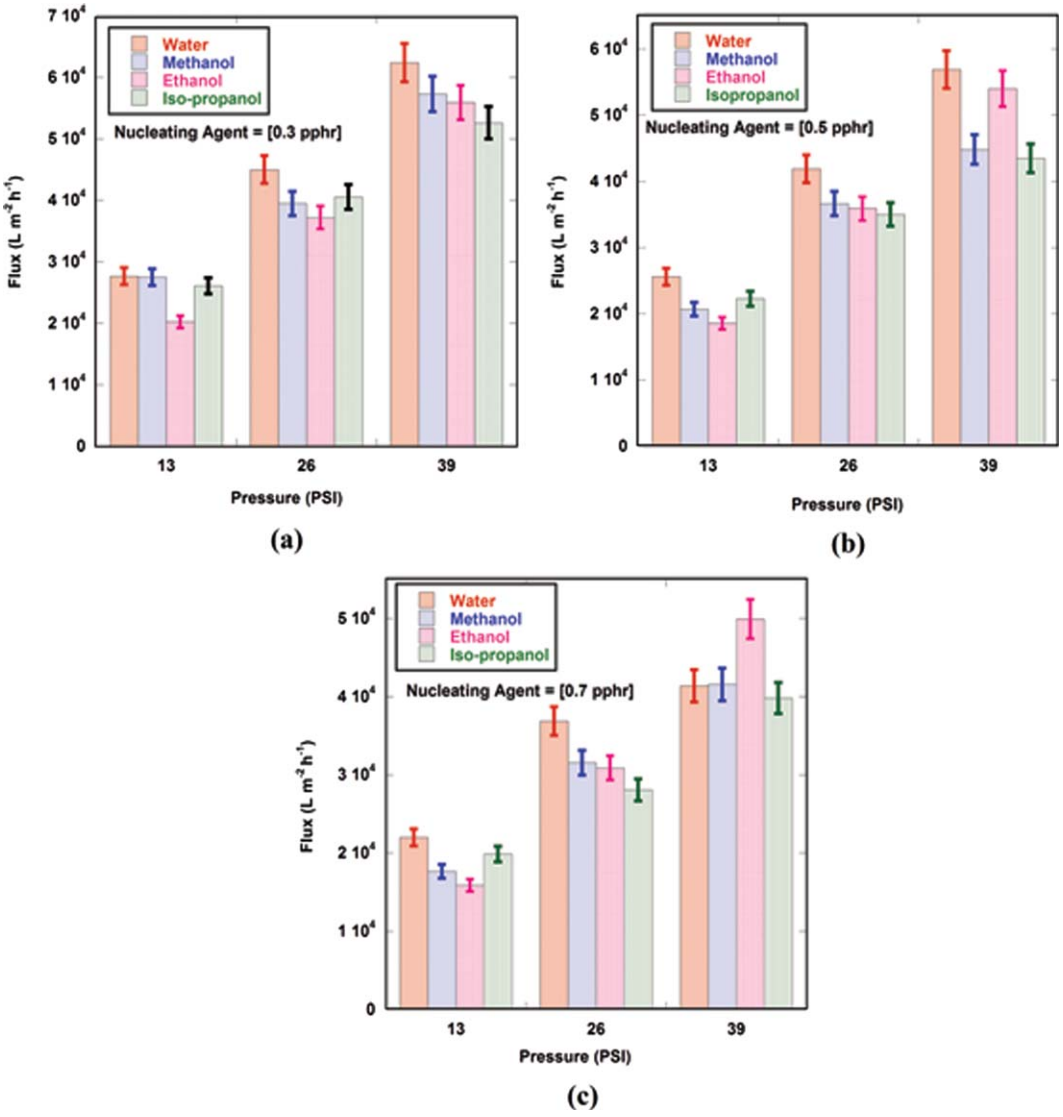

Figure 12. Effect of the type of solvents and NA concentration on the flux behavior through the various prepared membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polarities, and most importantly, sizes. These liquids were water, methanol, ethanol, and isopropyl alcohol. Before the permeation behavior of these solvent is discussed, it is appropriate to consider their various properties. Table I summarizes the salient features of the solvents tested for their flux rates analyses. In accordance to the data given in Table I, the sizes of the solvent molecules were categorized as follows: Water < Methanol < Ethanol < Isopropyl alcohol. Thus, water had the smallest and isopropyl alcohol had the biggest molecular size among these solvents. In addition, as the data given in Table I indicate, these solvents were also different in terms of other characteristics, such as density, dipole moment, and viscosity. The correlation of these parameters with the performance of the prepared membranes will be the subject of future work. In this study, our main focus was to interpret the data in accordance with the size of the solvent molecules. Figures 11–13 represent the flux rate of the four different solvents at different concentrations of NA (0.3, 0.5, and 0.7 pphr adipic acid, respectively) for the prepared membranes. We observed that with increasing pressure, the flux rate of all of the solvents increased as expected. Furthermore, we noted that in general water had the maximum flux rate, and isopropyl alcohol had the minimum flux rate. This could have been correlated with the size of the liquid droplets used in this study.

During the course of the experimental work, nitrogen gas pressures of 13, 26, and 39 psi were also applied, and graphs between the applied pressure and the flux rate were recorded. Because of the reduction of the pore density of the prepared membranes at higher adipic acid concentrations, the permeation of the diverse solvents through the porous medium was also influenced accordingly. The flux characteristics of the prepared membranes were also tested at various pressures with water, methanol, ethanol, and isopropyl alcohol as solvents in the filtration cell. The results obtained indicated the dependence of the flux on the type of solvent, pressure, and fabricated membranes. We observed that the flux for the solvents being

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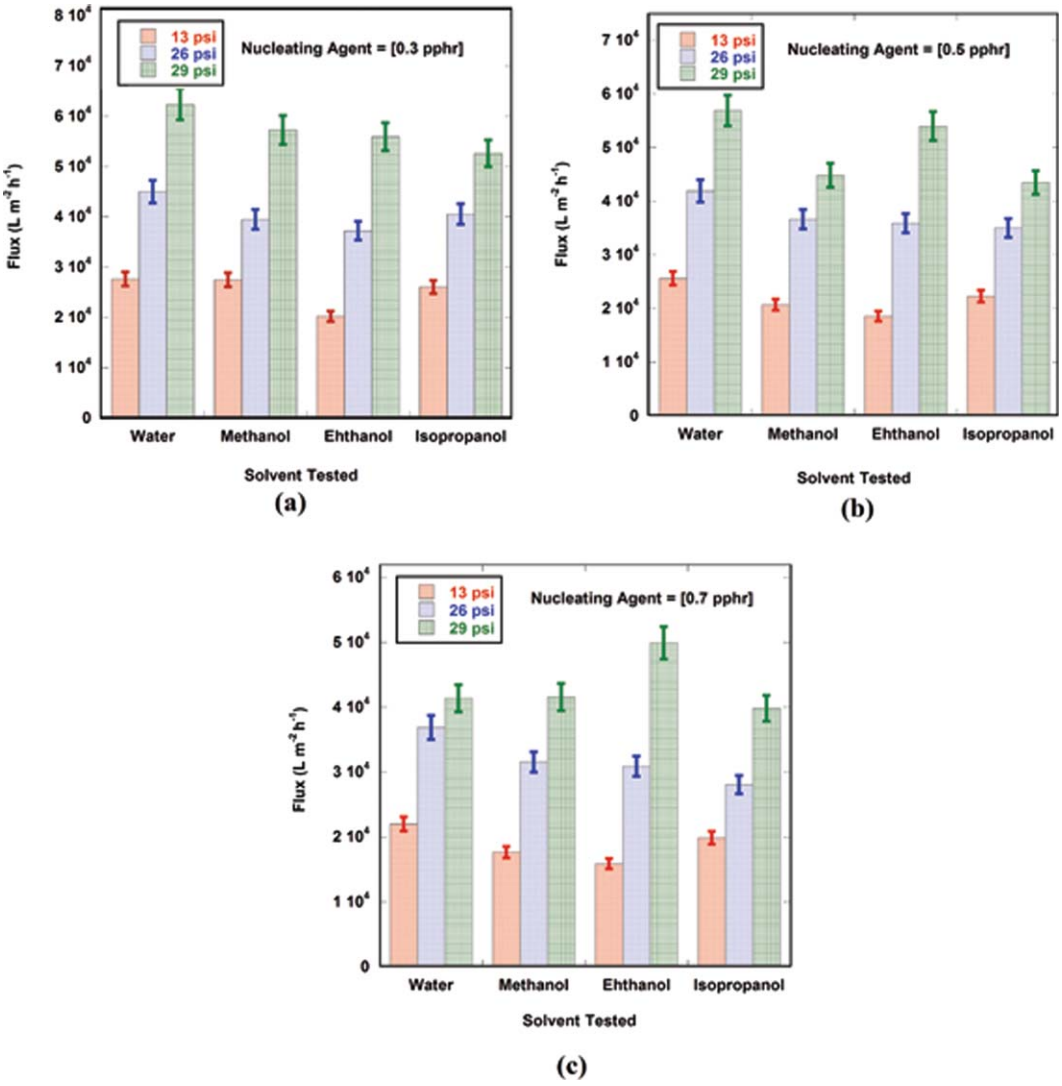

Figure 13. Effect of the degree of pressure on the flux behavior of the solvents for various membranes prepared at different NA concentrations of adipic acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tested decreased with increasing concentrations of NA in the prepared membranes, and this could be attributed to the decreases in the pore density and pore size. As discussed earlier, the NA provided a large number of nuclei, which could significantly modify the crystallization behavior of IPP. The observed results of the flux rate analyses were in good agreement with those of SEM analyses for the prepared membranes studied here. As revealed by the SEM analyses, increasing NA concentrations resulted in lower porosities in the prepared membranes, and therefore, accordingly, these also exhibited the lowest flux rate.

CONCLUSIONS

Microporous IPP membranes were prepared on WKF by a TIPS technique. During the fabrication, all parameters were kept constant except the NA concentration. The properties of the fabricated membranes were investigated with SEM, AFM, and TGA. The permeation of various solvents (water, methanol, ethanol, and isopropyl alcohol) were tested with a custom-made filtration cell. We observed that with increasing concentrations of NA in the fabricated membranes, both the pore density and pore size decreased. The average pore sizes were observed to be 1.686, 0.925, and 0.372 μm, respectively, for the 0.3, 0.5, and 0.7 pphr concentrations of NA. The flux characteristics of the prepared membranes were also tested at various pressures for different solvents in the filtration cell. The flux for water was observed to be the highest, whereas that of isopropyl alcohol was relatively lower. This observation was explained by consideration of the smaller size of the water molecules relative to those of the other solvent molecules tested in this study. We also observed that with increasing pressure, the flux also increased.

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