Preparation and Characterization of Membranes Obtained from Blends of Acrylonitrile Copolymers with Poly(vinyl alcohol)

Teodor Sandu,[1] Andrei Sârbu,[1] Celina Maria Damian,[2] Adela Marin,[3] Silviu Vulpe,[4] Temenuzhka Budinova,[5] Boyko Tsyntsarski,[5] M. Ferhat Yardim,[6] Ahmet Sirkecioglu[6]

[1]National Research-Development Institute for Chemistry and Petrochemistry—ICECHIM, Bucharest 060021, Romania
[2]Department of Bioresources and Polymer Science, University "Politehnica" Bucharest 010072, Romania
[3]Department of Anatomy, Animal Physiology and Biophysics, Faculty of Biology, University of Bucharest, Bucharest 050095, Romania
[4]Faculty of Physics, University of Bucharest, Măgurele, Ilfov 077125, Romania
[5]Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
[6]Department of Chemical Engineering, Technical University, Maslak, Istanbul 34469, Turkey
Correspondence to: A. Sârbu (E-mail: andr.sarbu@gmail.com)

ABSTRACT: New microfiltration and ultrafiltration membranes were obtained using acrylonitrile-vinyl acetate copolymers in mixture with poly(vinyl alcohol) (PVA). Thus, a blend polymer solution was prepared in dimethylsulfoxide (DMSO) and used to obtain bicomponent polymer membranes by phase inversion. The rheological behavior of the DMSO polymer solutions was, mostly, dilatant at low shear gradients and pseudo plastic with quasi Newtonian tendency at higher gradients. Membranes were characterized by Fourier transform infrared spectrometry (FTIR), optical microscopy, atomic force microscopy, thermal gravimetric analysis-differential thermal gravimetry, and pure water flux (PWF). FTIR spectra displayed the characteristic bands for acrylonitrile, vinyl acetate, and PVA. The morphology and the porosity can be tailored by the preparation conditions. PVA allows controlling the size of the pores and enables, in principle, to use the resulted membranes as supports for enzyme immobilization. PVA content influences the thermal stability. PWF values depend on the copolymer, on the content in PVA, but also on the coagulation bath composition. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41013.

INTRODUCTION

Membranes are often used for separations, such as microfiltration (MF) and ultrafiltration (UF), reverse osmosis, and electro dialysis, because these processes are based only on the membrane transport selectivity, without any additives or high temperatures. Membranes are, also, used in toxic chemicals removal or in enzyme immobilization.[1–11] Phase inversion, a commonly used technique in asymmetric membranes preparation, involves the casting of a homogeneous polymer solution on a suitable support followed by immersion in a coagulation bath containing a nonsolvent of the polymer, the solvent in the cast solution film being exchanged with bath liquid and phase separation process occurs in the film. Asymmetric membranes usually exhibit a dense top layer and a porous sub-layer.[6,12,13]

Polyacrylonitrile (PAN) and its copolymers are widely used in membranes obtaining because of their good thermal, mechanical and chemical stability, good solubility in polar solvents, excellent film-forming behavior, and good biocompatibility. PAN-based membranes combine enhanced chemical stability with good membrane performance in filtration applications, being widely used in water treatment, seawater desalination, dialysis, UF, and pervaporation.[14–33] PAN copolymers are more often used rather than the homopolymer, because this one is not suitable for enzyme immobilization because of its low biofouling resistance.[20,22,24] Use of vinyl monomers for acrylonitrile (AN) copolymerization as well as blends between AN copolymers and other polymers could provide reactive groups for enzyme immobilization or improve several properties (mechanical strength, solvent resistance, pervaporation, permeation flux, anti-fouling, and biocompatibility).[27] The use of maleic anhydride, acrylamido methylpropane sulfonic acid, 2-dimethylamino ethyl methacrylate, acrylic, polyethylene oxide, and of poly(vinyl chloride), as comonomers, has been reported.

Polymer blending enables to easier obtain new membranes, with designed properties.[20–22,34,35] On the other hand, poly(vinyl alcohol) (PVA) is widely used in many fields, including membranes, due to its lack of toxicity, hydrophilicity, water solubility, and excellent biocompatibility.[15]

In this work, MF and UF polymer membranes, useful for water treatment, were prepared using three acrylonitrile-vinyl acetate (AN-VA) copolymers in mixture with PVA. PAN is a rigid polymer (due to hydrogen bonds), so that the use of VA, as comonomer, was thought to increase copolymer flexibility. The use of two polymers is also advantageous because of their quite different coagulation rates, which could ensure a proper porosity. PVA provides —OH groups (available in enzymes immobilization) and improves the membrane hydrophilic character (which becomes an important parameter, water providing the required enzyme microenvironment). To the best of our knowledge, a membrane obtained from this polymer blend has not been reported before. First, a blend polymer solution was prepared by dissolving different copolymer-PVA mixtures in dimethylsulfoxide (DMSO) and then used to obtain bicomponent membranes by phase inversion in different water-isopropyl alcohol (IsOH) mixtures. The flow of the DMSO solutions was, mostly, dilatant at low shear gradients and pseudo plastic with quasi Newtonian tendency at higher gradients. Membranes were characterized by Fourier transform infrared spectrometry (FTIR), optical microscopy (OM), and thermal gravimetric analysis (TGA). Swelling degree values (SDs) and pure water flux (PWF) values were also determined for various membrane samples. FTIR spectra revealed the occurrence of characteristic peaks (belonging to AN, to VA, and to PVA). Morphology, porosity, thermal stability, and PWF values depend on membrane preparation conditions. The pores size, the thermal behavior, and SDs are also influenced by the PVA amount. PWFs depend on the content in VA or in PVA, but also on the coagulation bath.

EXPERIMENTAL

Materials

Monomers. Acrylonitrile (AN) and vinyl acetate (VA) were supplied by Merck (Darmstadt, Germany) and distilled out to remove the inhibitor. Redox initiation system components: Potassium peroxydisulfate (KPS) and sodium metabisulfite (sodium pyrosulfite, MS), pro analysis, supplied by "Reactivul" (Bucharest, Romania) were used as received. Azobisisobutyronitrile (AIBN, p.a. Merck, Darmstadt, Germany), initiator for poly(vinyl acetate) (PVAc) preparation, was used without further purification. Solvents and nonsolvents: DMF (N,N'-dimethylformamide), DMSO (solvents), methanol (MeOH), and IsOH (nonsolvents) were supplied by Merck (Darmstadt, Germany) and used without further purification. Sulfuric acid was provided by "Reactivul" (Bucharest, Romania) and used as received to ensure proper pH for the copolymerization reaction.

Synthesis of Polymers and Membrane Preparation

Copolymers Synthesis. In order to prepare polymer membranes, three AN-VA copolymers were synthesized by emulsion polymerization without emulsifier. Monomer content in aqueous dispersion was 15%. Copolymerization was performed for 2

h at 45°C, in acid pH in range of 2–3 (provided with H_2SO_4), in N_2 atmosphere, using a redox system: 1 : 1 (weight ratio) KPS: MS. Redox system concentration was 0.5% (calculated on monomer content). Monomer mixtures with different VA content (10%, 20%, and 30%, respectively) were used. These copolymers are designated as C1, C2, and C3, respectively. Conversion was about 80%, in all cases. All percents in this article are expressed by weight.

Poly(vinyl alcohol) Synthesis. The synthesis of PVA was carried out in two stages: synthesis of PVAc and the reaction between PVAc and MeOH. Synthesis of PVAc consisted of radical polymerization of VA in MeOH medium at 65°C, under refluxing, using AIBN as initiator. It was used a VA : MeOH ratio of 90/10 and the AIBN amount was 0.5% of the VA amount. Polymerization was stopped at a conversion of about 60% and followed by demonomerization.

To prepare PVA, the methanolysis of a 35% PVAc MeOH solution took place in the presence of NaOH as a catalyst (1.5% NaOH calculated to PVAc) at 45°C. It was obtained PVA with a polymerization degree of 920, a hydrolysis degree of 99.2% and containing 1.73% sodium acetate. Hydrolysis degree (HD) represents the percent of acetate radicals (—OCOCH$_3$) that have been transformed into hydroxyl (—OH) radicals. When total hydrolysis occurs, the HD value is 100%. This degree may be indirectly determined using the ester index which is known as saponification index and represents the number of KOH milligrams which are necessary for the complete saponification of 1 g substance (PVA). For pure PVA, the maximum SI value of 651.8 is reached. The following correlation exists between HD and SI:

$$HD = 100 - \frac{7.851 \times SI}{100 - 0.07492 \times SI} \qquad (1)$$

Copolymer Solutions Preparation in DMSO. Copolymer solutions of various concentrations were prepared in DMSO using all three copolymers (C1, C2, and C3) together with PVA. Polymer dissolution took place at 90°C, until the polymers were completely dissolved.

Membranes Preparation. Polymer solution was cast at room temperature on a glass plate (150 mm, 200 mm, 3 mm), and a draw-down technique was used to produce films with a wet thickness of 200 μm. After a few seconds, the plate was immersed in the coagulation bath composed of water–IsOH mixtures. It was chosen this kind of coagulation bath because preliminary tests have shown that in this case the membrane structure is more suitable for water treatment than in the case of mono component bath: water, MeOH, or IsOH.

Sample Characterization

Investigation of Copolymers Elemental Chemical Composition. The elemental composition was determined using a CHNS/O analyzer Perkin Elmer 2400 Series II (Bridgeville, USA). For all copolymers, the elemental composition was determined twice. For each element, it was made an average of percentage values obtained in the two determinations.

Determination of Copolymers Molecular Weight. The molecular weight was determined for all copolymers on an Agilent

Table I. Elemental Composition of Copolymers

Copolymer	C (%)	H (%)	N (%)	S (%)	O (%)
C1	65.8	6.1	24.3	0.9	2.9
C2	65.0	6.2	22.5	0.8	5.5
C3	64.1	6.5	20.6	0.9	7.9

Technologies 1200 Series Gel Permeation Chromatograph (Santa Clara, California, USA) with a PLgel Mixed-C column (300 × 7.5 mm) and an Agilent 1200 differential refractometer. Copolymers solutions of 0.1% concentration (wt %) in DMF were prepared and analyzed at room temperature, under a constant flow rate of 1 mL/min. Calibration was made with polystyrene standards.

Relative Viscosity Determination for the Three Copolymers. The relative viscosities were determined at 25°C, from 0.3% copolymer solutions in DMF.

Rheological Characterization of Copolymer Solutions. Study of rheological behavior of various polymer solutions consisted of determining the dynamical viscosity variation with shear gradient, at 25°C and 70°C, using a RHEOTEST 2.1 (Jena, Germany) device, with coaxial cylinders.

Investigation of Membranes Chemical Composition by Fourier Transform Infrared Spectrometry. FTIR spectra of membranes were recorded on a Bruker Vertex 70 (Ettlingen, Germany) device using 32 scans and 4 cm^{-1} resolution in 4000–400 cm^{-1} region.

Membrane Porosity Analysis by Optical Microscopy. OM images were recorded for membranes prepared by coagulation either in different solvent mixtures or in the same solvent mixture, but using polymer solutions with different composition. It was used an Axio Observer Inverted Microscope, Carl Zeiss, Germany. In this way, the effect of preparation conditions on the membranes morphology was determined. Pictures were taken with a photo camera Avio Com Mru type (Carl Zeiss, Germany). OM is more suitable than scanning electron microscopy, because the latter requires drying of membrane which leads to changes in its structure and porosity.

Membrane Surface Quality Investigation by Atomic Force Microscopy (AFM). Surface quality and roughness were investigated for membranes prepared under different conditions. AFM images were recorded with a NTEGRA Aura (from NT-MDT, Moscow, Russia) device, using the semi-contact mode. Cantile-

Table II. Monomers Content for Each Copolymer

Copolymer	Substrate monomer content		Copolymer content of monomers	
	AN (%)	VA (%)	AN (%)	VA (%)
C1	90	10	90,7	9.3
C2	80	20	82,5	17.5
C3	70	30	74,8	25,2

ver tip (NSG model, from NT-MDT) has a radius of 10 nm and a resonance frequency of 84.4 kHz.

Investigation of Membrane Thermal Behavior by TGA and DTG (Differential Thermal Gravimetry). The TGA and DTG results were obtained simultaneously on a Q 500 TA Instrument (New Castle, DE). A typical sample was heated from 20 to 520°C at a heating rate of 10°C/min under a constant nitrogen flow rate.

Swelling Studies. In order to further investigate the influence of the C3/PVA ratio on the membrane hydrophilicity and thermal behavior, swelling studies were conducted on the same samples which were characterized by TGA. A known volume (100 mL) of water was poured onto a piece of membrane at room temperature, without stirring. Water is changed daily until membrane reaches to constant weight ($m_{swelled}$). The swelled membrane is then dried to constant weight (m_{dried}). The SD is calculated according to eq. (2).

$$SD = \frac{m_{swelled} - m_{dried}}{m_{dried}} \times 100 \qquad (2)$$

Pure Water Flux Determination for Membranes. PWF were determined for membrane samples prepared under different conditions. PWF values were calculated by adapting the method of Mei et al.[20] PWFs of the membranes were measured at 175 mmHg residual pressure at room temperature. PWF was calculated by eq. (3):

$$J = \frac{V}{S * t} \qquad (3)$$

where J is the permeation flux through the membrane [L m^{-2} s^{-1}], V is the quantity of permeate [L], S is the membrane area [m^2], and t is the time [s]. Three samples belonging to each membrane were measured, and their average result is reported.

RESULTS AND DISCUSSION

Copolymers Characterization
Investigation of Copolymers Chemical Composition. Elemental compositions of each copolymer are shown in Table I.

Monomer composition (wt %) can be determined for each copolymer considering the fact that nitrogen is found only in AN and oxygen occurs almost entirely in VA (a small oxygen amount may be found in the SO$_3$H groups of initiator, which are linked to the polymer chain). Monomer content is given for all three copolymers in Table II.

Comparing the values from Table II, one may notice that for C1 the copolymerization was nearly azeotropic, whereas for C2 and for C3, the VA content is decreasing compared to the substrate content with the increase in the VA content in the initial monomer mixture. A possible explanation for this phenomenon consists of the difference occurring between monomers reactivity.

The values reported in literature[36,37] for reactivity ratios, r_1 (corresponding to AN) and r_2 (corresponding to VA), are given in Table III. The AN reactivity ratio is considerable higher than that of VA. This difference leads, during polymerization, to a decrease in the VA content in the copolymer compared with

Table III. The Reported Values of Reactivity Ratios [36,37]

r_1 (AN)	r_2 (VA)	Temperature (°C)
4.05 ± 0.3	0.061 ± 0.013	60
6.00 ± 0.2	0.020 ± 0.020	60
6.00 ± 0.9	0.070 ± 0.010	70

Table V. Molecular Characteristics of the Synthesized Copolymers

Sample	Mn (g/mol)	Mw/Mn
C1	6,451,500	1.40
C2	8,934,800	1.74
C3	4,088,100	1.23

substrate content. This effect becomes more intensive for higher contents in VA. However, reactivity ratios are relevant only in low conversions range. In our case, these ratios are less relevant, because all copolymerizations were stopped at a conversion of about 80%. For this reason, there is not a significant difference between the initial and the final monomer composition (Table II).

Relative Viscosity Determination for the Three Copolymers. The relative viscosity values are given in Table IV.

From Table IV, it can be seen that for C1 and C3 (containing in the monomers mixture 10 and 30% VA, respectively), the viscosity values are very close, but for C2 relative viscosity is higher, despite the redox initiation system concentration was the same. A possible explanation could be the gel effect (Trommsdorff-Norrish effect) which occurs, within polymer grains, at C2 synthesis.

Determination of Copolymers Molecular Weight by Gel Permeation Chromatography (GPC). In order to further investigate the copolymerization process, the synthesized copolymers were characterized by GPC in terms of number average molecular weight (Mn) and polydispersity (Mw/Mn, where Mw is the weight average molecular weight). The molecular characteristics are given in Table V for all copolymers.

Polydispersity indices show, for all copolymers, low values (Mw/Mn < 2) which show a quite well controlled process (Table V). As it can be noticed in Figure 1, the molecular weight distributions were monomodal for C1 and bimodal for C2 and C3. From Table V, one may notice that C2 shows the highest Mn value and the highest polydispersity (a little lower than 2). These results are in a good agreement with the determined relative viscosity values (Table IV). This further confirms the occurrence of Trommsdorff-Norrish effect during C2 synthesis.

Rheological Characterization of Copolymer Solutions. There were performed four series of experiments. In each series, rheological behavior was investigated for 8% solutions, prepared using DMSO (as solvent) and copolymer-PVA binary mixtures (with a different content in PVA). It was set a concentration of 8% because preliminary tests (carried out using 6, 8, 10, and 12%, respectively) have proven that this is the optimal level in

Table IV. Relative Viscosity Values of the Three Copolymers

Copolymer	$\eta_{relative}$
C1	1.58
C2	2.59
C3	1.48

terms of polymer dissolution. Moreover, at this concentration, the optimal membrane casting is achieved. In the first series of experiments (Figure 2), solutions based on C1 were analyzed.

From Figure 2, one may notice that the flow was dilatant at low shear gradients, while at higher gradients it was slightly pseudo plastic, with a quasi Newtonian tendency. For all these solutions, the dynamic viscosity was about three times higher at 25°C than at 70°C. The rheological behavior depends also on the content in PVA. Up to content in PVA of 20%, the viscosity is not influenced by the PVA amount, being quite similar.

In the second series of experiments, the rheological behavior was studied for C2-based solutions (Figure 3).

For solutions prepared using a polymer blend composed of 90% C2–10% PVA, viscosity was too high, which did not allow to perform rheological measurements. For solution prepared from a mixture composed of 85% C2–15% PVA, measurements were performed only at 70°C, because at 25°C the viscosity was too high. At low shear gradients, the flow was strongly dilatant, whereas at higher gradients it is pseudo plastic with quasi Newtonian tendency.

For solution prepared from a mixture composed of 80% C2–20% PVA, measurements were made at 25, but also at 70°C. At low shear gradients, the flow was strongly dilatant, whereas at higher gradients the flow is strongly pseudo plastic at 25°C and pseudo plastic with quasi Newtonian tendency at 70°C. As it can be noticed from Figure 3(b), an increase in the PVA content from 15 to 20%, results in a significant decrease in viscosity.

In the third experiment series, the rheological behavior was studied for C3-based solutions (Figure 4).
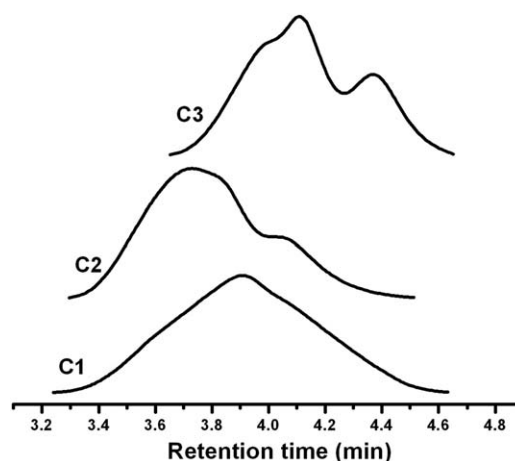
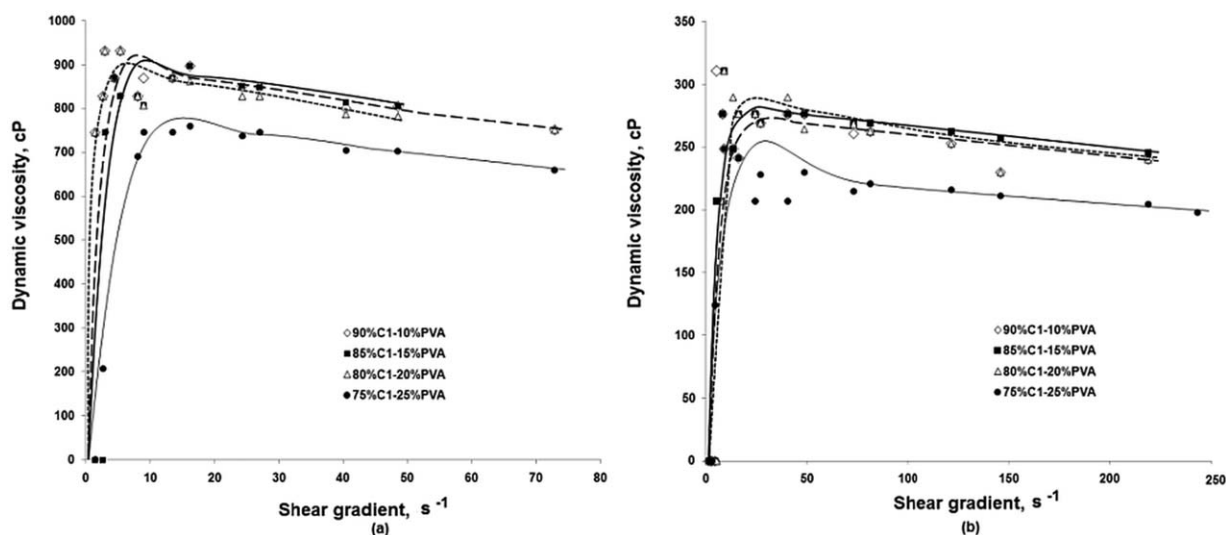**Figure 1.** GPC traces of the obtained copolymers.

Figure 2. Rheological behavior at 25°C (a) and 70°C (b), respectively, of 8% solutions prepared using various C1-PVA polymer mixtures.

No significant changes may be noticed in the rheological behavior of these solutions. At low shear gradients, the flow was strongly dilatant, whereas at higher gradients the flow is pseudo plastic with quasi Newtonian tendency. In this series, no correlation occurred between the PVA content and viscosity. A possible explanation for this phenomenon consists of the changes occurring in the polymer–solvent interactions.

In the fourth series of experiments, the time dependence of the rheological characteristics has been checked. The dynamic viscosity was determined while increasing the shear gradient, as well as in the regime of the decreasing of the shear gradient. In this way, it was possible to see if a hysteresis (indicating time dependence) occurs.

In Figure 5, the rheological behavior of a 8% C1 solution at 25°C is shown for both cases (increase and decrease of the shear

gradient). As it can be noticed, no hysteresis appears, so the solutions did not exhibit viscosity time dependence.

Polymer Membranes Characterization
Investigation of Membranes Chemical Composition by Fourier Transform Infrared Spectrometry. In order to identify the bands that are characteristic to the three copolymers and to the PVA, FTIR spectra were recorded for these samples.

In Figure 6, one may notice for all copolymers the occurrence of two characteristic peaks at 2230–2240 cm^{-1} (assigned to C—N bond from the nitrile group contained by AN) and at 1730 cm^{-1} (assigned to C═O bond of vinyl acetate). The characteristic peak for PVA appears at 3348 cm^{-1}, being assigned to —OH groups.

As it can be noticed from Figure 7, all samples exhibit peaks which are characteristic to AN ($\sim$2240 cm^{-1}), to VA

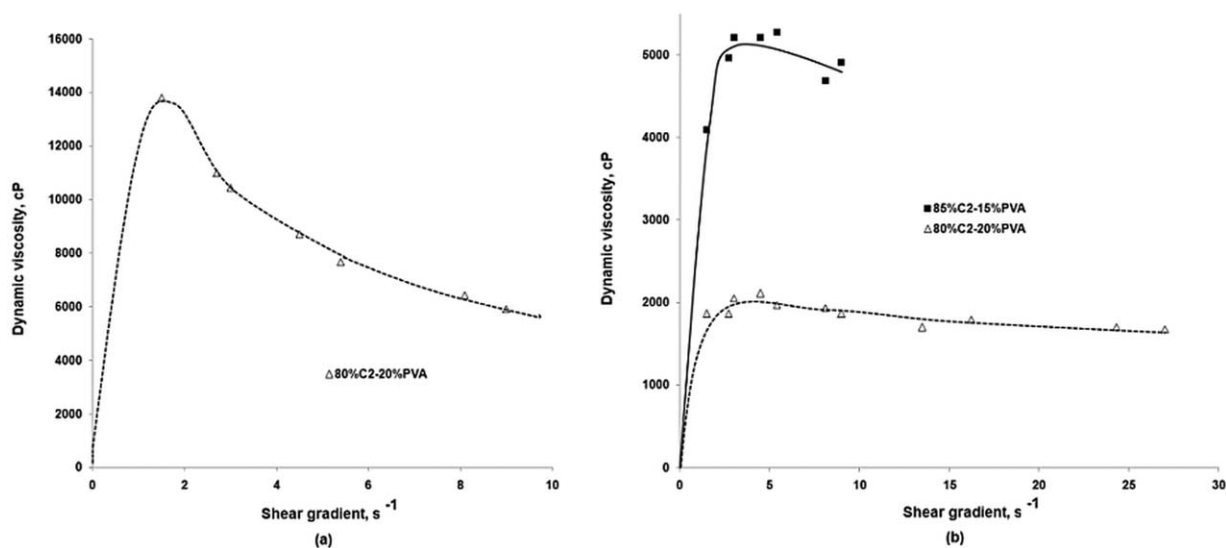**Figure 3.** Rheological behavior at 25°C (a) and 70°C (b), respectively, of 8% solutions prepared using various C2-PVA polymer mixtures.
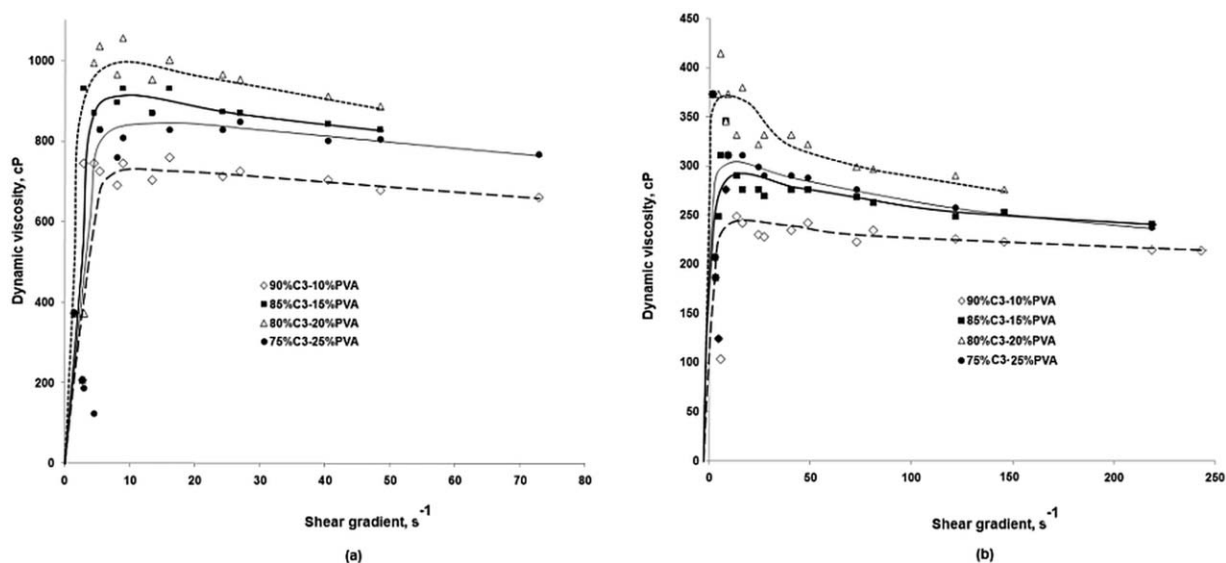
Figure 4. Rheological behavior at 25°C (a) and 70°C (b), respectively, of 8% solutions prepared using various C3-PVA polymer mixtures.

($\sim$1730 cm^{-1}), and to PVA ($\sim$3415 cm^{-1}). For M3, the peak assigned to —OH groups (3415 cm^{-1}) is less intense than for M1 and M2, presumably, because for this membrane it was used the lowest water amount in the coagulation bath. However, comparing the FTIR spectrum of M2 (40% H$_2$O) to that belonging to M1 (50% H$_2$O), one may notice that the peak from 3415 cm^{-1} is more intense for M2 despite that for this one it was used a lower water amount. This difference may be assigned to the differences in porosity, the optimal porosity occurring for M2. The porosity of M2 allows for a higher water volume retention, even after membrane drying. At higher or lower pore sizes (M1 and M3), a lower water amount is retained by the membrane. This highlights the importance of coagulation bath composition.

FTIR spectra were, also, recorded for other membranes (M4 ÷ M15) prepared under different conditions. All these membranes displayed the characteristic peaks to AN, to VA, and to PVA, respectively. In three membrane series (M7 ÷ M9, M10 ÷ M12, and M13 ÷ M15, respectively), the peak occurring at around 3400 cm^{-1} (assigned to —OH groups) was more intensive in case of higher water volumes in the coagulation bath. The wavenum-

bers of characteristic peaks as well as the membrane preparation conditions are given for each sample in Table VI.

Membrane Porosity Analysis by OM. In order to elucidate the effect of VA content in the acrylic copolymer, of PVA amount in the polymer blends and of the inversion bath composition on the membrane pore size, membrane porosity was studied by high performance OM. The most relevant images are presented. The images corresponding to membranes prepared from the same polymer mixture (80% C1–20% PVA) by coagulation in different water–IsOH mixtures are shown in Figure 8. Comparing these images, one may notice that M1 is very porous. An increase in the IsOH amount has led to a decrease in porosity, M2 being less porous than M1. A further increase in the amount of IsOH resulted in a complete porosity loss that is why M3 is almost completely nonporous membrane or its pores are very small. These images prove that the intensity of —OH peak in FTIR spectra could be influenced by the differences in porosity.

Comparing the images from Figure 9, for membranes prepared from a mixture 75% C3–25% PVA, in three different coagulation baths, one may notice that the morphology of M7 is
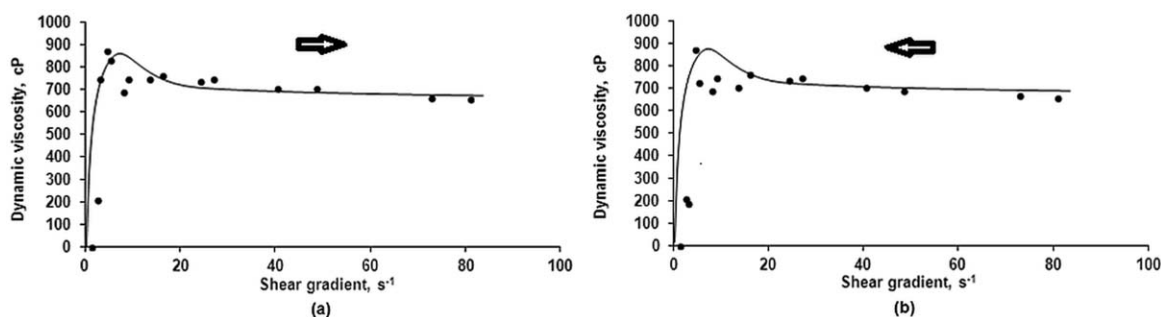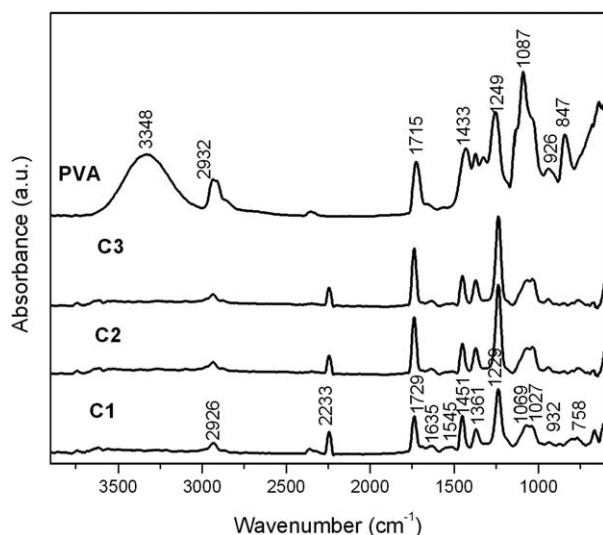

Figure 5. Rheological behavior of a 8% solution composed of a mixture consisting of 75% C1–25% PVA at 25°C for both cases: shear gradient increase (a) and decrease (b), respectively.

Figure 6. FTIR spectra for the three copolymers and for pure PVA.

different from the two other membranes, because of the different water/IsOH ratio. No significant difference may be noticed in the morphology corresponding to M8 and M9 samples.

In Figure 10, OM images are given for three membranes prepared using the same polymer mixture (80% C3–20% PVA) but different coagulation baths. The morphology is similar for all three images and pores are smaller for a water content of 30% in the coagulation bath.

As it can be noticed from Figure 11, for the mixture (90% C3–10% PVA), the morphologies corresponding to M13 and M14 samples are similar, but different from the morphology of M15 sample. Because of their morphology the size of pores is difficult to be estimated for M13 and M14. Only M15 exhibits almost regular round pores. Because for M13-M15 samples it
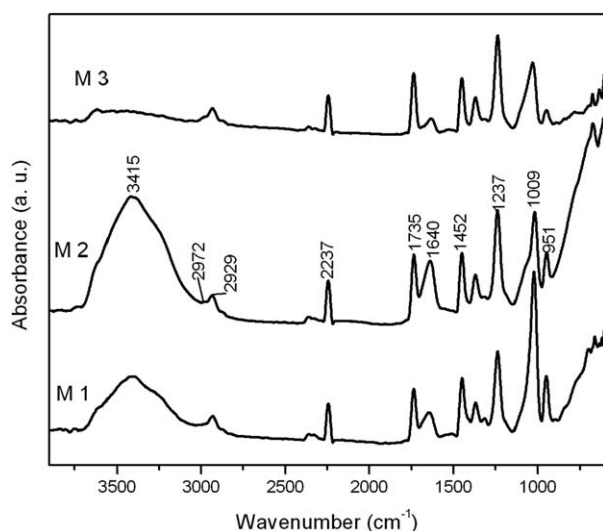
Figure 7. FTIR spectra for three membranes (M1, M2, M3) prepared using the same polymer mixture (80% C1–20% PVA) but coagulated in different coagulation baths (M1–50% IsOH-50% water; M2–60% IsOH-40% water; M3–70% IsOH-30% water).

was used the lowest PVA amount (10%), this difference in morphology shows on one hand the role of PVA in the pores formation and, on the other hand, the importance of the water content in the coagulation bath, even at low content in PVA.

Membrane Surface Quality Investigation by AFM. For a better comparison of the morphology of membranes prepared under different conditions, AFM images (2D and 3D) were recorded for these samples.

Comparing the AFM images from the two experimental series (Figures 12 and 13) and roughness values in Table VII, one may notice that, in case of C2 copolymer in mixture with 20% PVA, a decrease in the water amount in the coagulation bath leads to a pore size reduction. Conversely, for C3 in mixture with 10% PVA, a decrease in the water amount in the coagulation bath leads to a pore size increase.

At the same time, a decrease in the water amount leads to an increase in the membranes roughness. A possible explanation for this phenomenon could be that, when a part of PVA is dissolved in the water from the coagulation bath, this leads to holes (pores) formation.

Investigation of Membrane Thermal Behavior by TGA. To check the preparation conditions influence on the thermal behavior of the membranes, the TGA and DTG curves were recorded for three membrane samples: M7, M10, and M13. TGA tests were performed on vacuum dried samples. A proper samples drying is required for rigorous comparison, given that it is necessary to ensure the same moisture content for all samples. These three samples were prepared using various C3/PVA ratios by coagulation in the same inversion bath composition (50% IsOH-50% water). For a more accurate evaluation of the influence of the C3/PVA ratio on the membrane thermal stability, it was necessary to determine the relative stability of C3 and PVA. Thus, TGA and DTG curves were also recorded for pure C3 and pure PVA.

TGA and DTG results [Figure 14(a,b)] reveal that C3 is more thermal stable than PVA because the final weight loss is lower for C3 (66.6 instead of 96.8%). Moreover, for C3, the thermal degradation occurs only in one stage (the maximum degradation speed is reached at about 346°C), whereas for PVA exhibits a four-step degradation pattern (four peaks appear at about 302, 352, 427, and 443°C, respectively). From Figure 14(c,d) and from Table VIII, it can be observed that all samples exhibit peaks at temperatures lower than 100°C (assigned to water evaporation), but also in 300–500°C range with a maximum at 340°C (assigned to polymers degradation). A decrease in the PVA content leads to a decrease in the temperature assigned to the first peak, but to an increase in the weight loss assigned to this peak. A decrease in the content in PVA, which is a hydrophilic polymer, should lead to a water content decreasing and the weight loss should be smaller. This inconsistency shows once again that the morphology and porosity have a more important influence on the thermal behavior than the PVA content.

The second peak, with weight loss values in range of 56–64%, shows that a decrease in the PVA content leads to a decrease in

Table VI. Characteristic Peaks for Membrane Samples

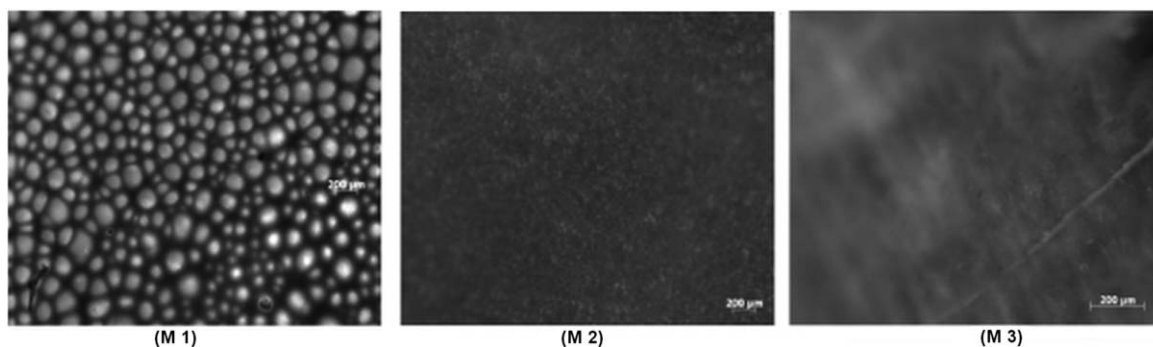| Sample	Polymer mixture and coagulation bath	Characteristic peaks (cm^{-1}) to		
		AN	VA	PVA
M1	80% C1–20% PVA 50% IsOH-50% H_2O	2246	1728	3425
M2	80% C1–20% PVA 60% IsOH-40% H_2O	2237	1735	3415
M3	80% C1–20% PVA 70% IsOH-30% H_2O	2248	1730	3452
M4	80% C2–20% PVA 50% IsOH-50% H_2O	2248	1730	3396
M5	80% C2–20% PVA 60% IsOH-40% H_2O	2243	1730	3400
M6	80% C2–20% PVA 70% IsOH-30% H_2O	2235	1735	3391
M7	75% C3–25% PVA 50% IsOH-50% H_2O	2243	1743	3404
M8	75% C3–25% PVA 60% IsOH-40% H_2O	2243	1735	3608
M9	75% C3–25% PVA 70% IsOH-30% H_2O	2243	1735	3574
M10	80% C3–20% PVA 50% IsOH-50% H_2O	2243	1739	3404
M11	80% C3–20% PVA 60% IsOH-40% H_2O	2235	1739	3548
M12	80% C3–20% PVA 70% IsOH-30% H_2O	2248	1743	3591
M13	90% C3–10% PVA 50% IsOH-50% H_2O	2243	1743	3491
M14	90% C3–10% PVA 60% IsOH-40% H_2O	2243	1739	3613
M15	90% C3–10% PVA 70% IsOH-30% H_2O	2239	1739	3430

the weight loss assigned to this peak. This further confirms that PVA is less thermal stable than C3.

Swelling Degrees Determination for Membranes Characterized by TGA. Since the membranes were stabilized in the same drying conditions before TGA tests, swelling studies (to determine SD values) were conducted on the same samples (M7, M10, M13). This allows for a more detailed investigation of the water-membrane components interactions. SD values are given in Table IX.

The SD values are influenced by the content in PVA. Thus, the use of large PVA amounts in the polymer mixture (25 and 20%) results in high SD values (>1000%). After an important reduction in the PVA amount (from 20 to 10%), an important SD decrease occurs (for M13, SD is lower than 900%). SD values cannot be correlated with the weight loss of the first peak from TGA, but with the temperature assigned to that peak (Table VIII). The temperature corresponding to M7 and M10

are considerably higher than that corresponding to M13. Therefore, temperature varies in the same manner as SDs. A correlation may be also made between SDs and porosity. OM images are given for M7, M10, and M13 in Figures 9–11, respectively. From these figures, one may notice that a decrease in the PVA amount leads to a decrease in the size of the pores, but to an increase in their number.

SDs show elevated values for M7 and M10 because of the high overall porosity (achieved either by few large pores or by many small pores). It seems that M13 shows the lowest overall porosity because the pores are very small, which results in the lowest SD value for M13. Because of this small water amount retention, a low temperature is required for its evaporation. Due to the small size of pores, the water retention is less intense, but as a consequence of the capillary effect, evaporation takes place at a lower temperature (56°C, Table VIII). So, SDs fit both with TGA and OM tests.
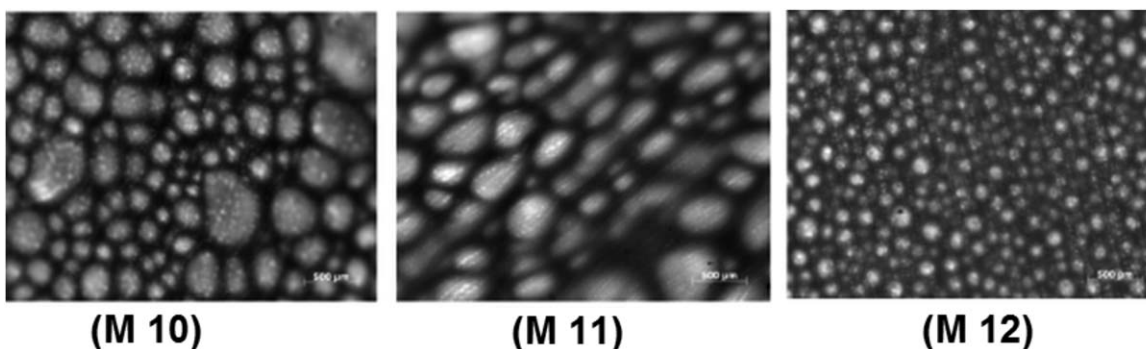

Figure 8. OM images recorded at 200 μm for three different membranes (M1, M2, and M3) prepared using the same polymer mixture (80% C1–20% PVA) but coagulated in different coagulation baths: M1: 50% IsOH-50% water; M2: 60% IsOH-40% water; M3: 70% IsOH-30% water.
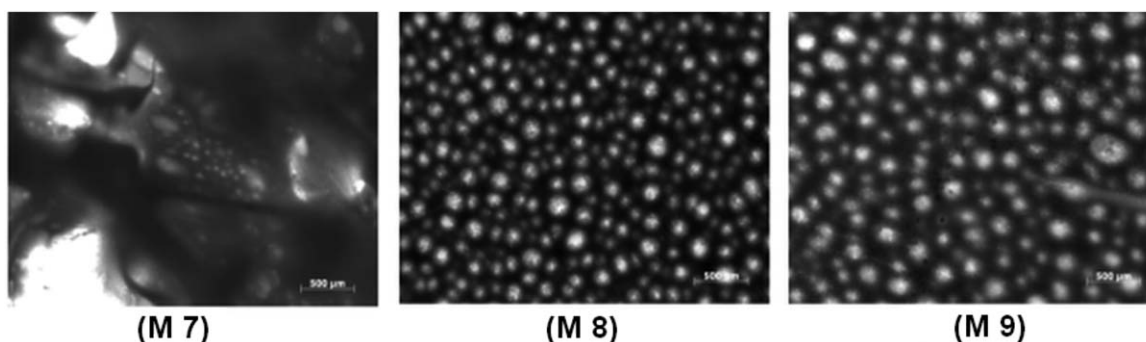
Figure 9. OM images recorded 500 μm for three different membranes (M7, M8, M9) prepared using the same polymer mixture (75% C3–25% PVA) but different coagulation baths: M7: 50% IsOH-50% water; M8: 60% IsOH-40% water; M9: 70% IsOH-30% water.
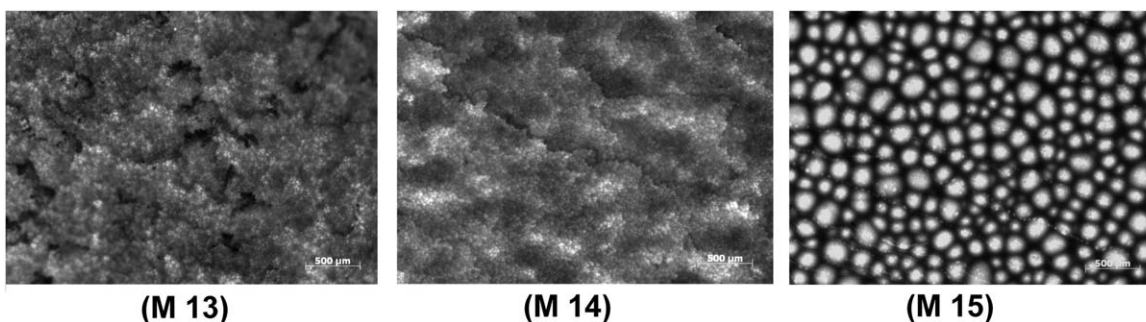

Figure 10. OM images recorded at 500 μm for three membranes (M10, M11, and M12) prepared using the same polymer mixture (80% C3–20% PVA) but different coagulation baths: M10: 50% IsOH-50% water; M11: 60% IsOH-40% water; M12: 70% IsOH-30% water.

Pure Water Flux Determination for Membranes. In order to check the influence of the membrane preparation conditions on their transport capacity, PWF values were determined for various membrane samples prepared under different conditions.

These values are given in Table X. In fact, two studies were conducted. For the first study, there have been used membranes prepared using a different copolymer but the same copolymer/PVA ratio (80/20). The second study consisted of the determination of the PWF values for membranes prepared using the same copolymer (C3) but different C3/PVA ratios (80/20 and 90/10, respectively).

Comparing the values from Table X, the following features are revealed: for C1 and C3, a decrease in water content of the inversion phase leads to a decrease in the PWF value. Conversely, for C2, PWFs are higher for low water content in coagulation bath. For C3, a decrease in the PVA content in the polymer blend results in lower PWFs. Thus, comparing the PWFs from the first series, corresponding to M1, M2, and M3, one may notice that these values are in a good agreement with OM images (Figure 8). The porosity decreases in the following order: M1, M2, M3. PWFs decrease in the same order, which is normal, because the more porous is the membrane, the shorter is the time for water stagnation on membrane. In the second series, AFM images in Figure 12 (M4, M5, M6) show that a

Figure 11. OM images recorded at 500 μm for three membranes (M13, M14, and M15) prepared using the same polymer mixture (90% C3–10% PVA) but different coagulation baths: M13: 50% IsOH-50% water; M14: 60% IsOH-40% water; M15: 70% IsOH-30% water.
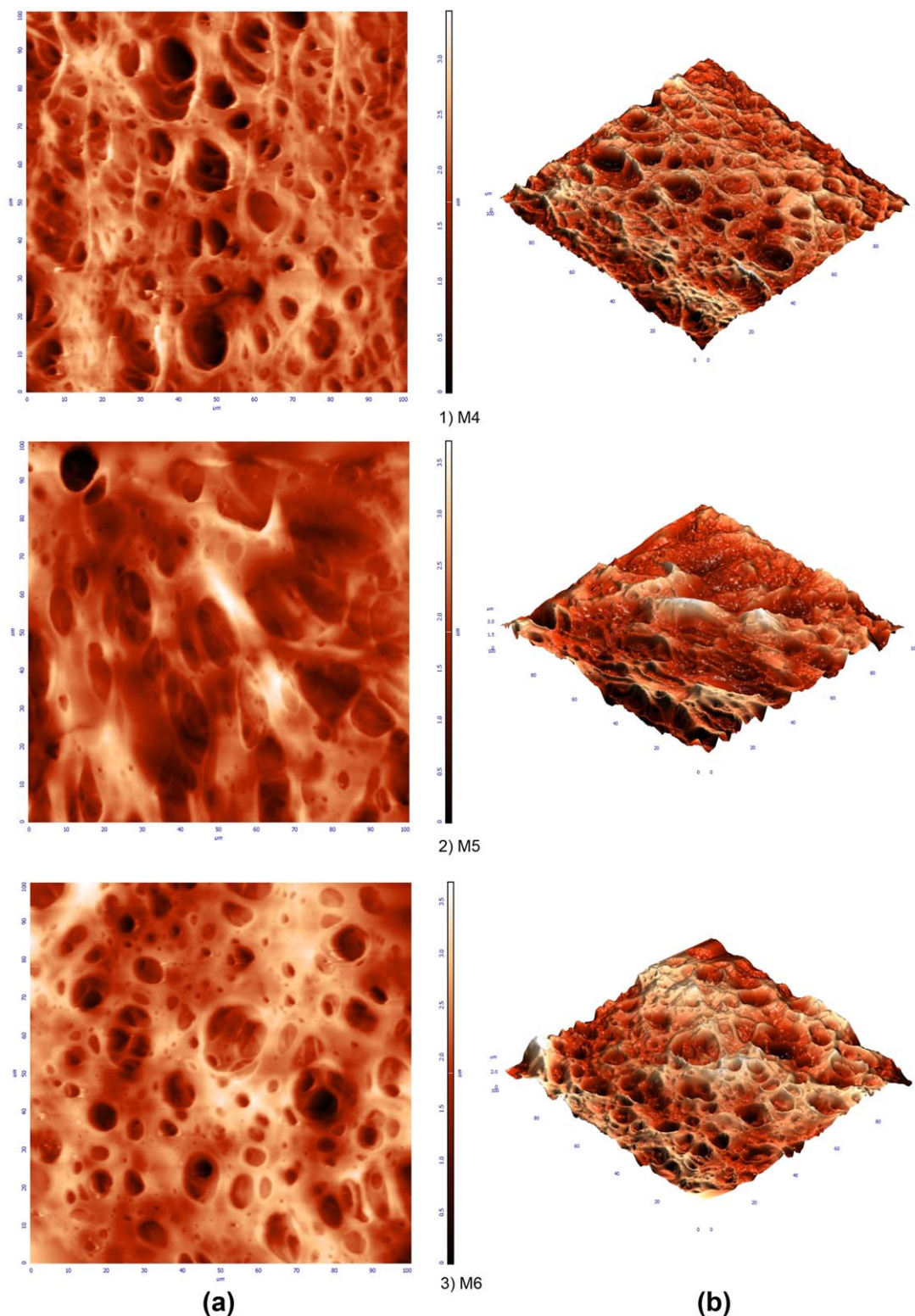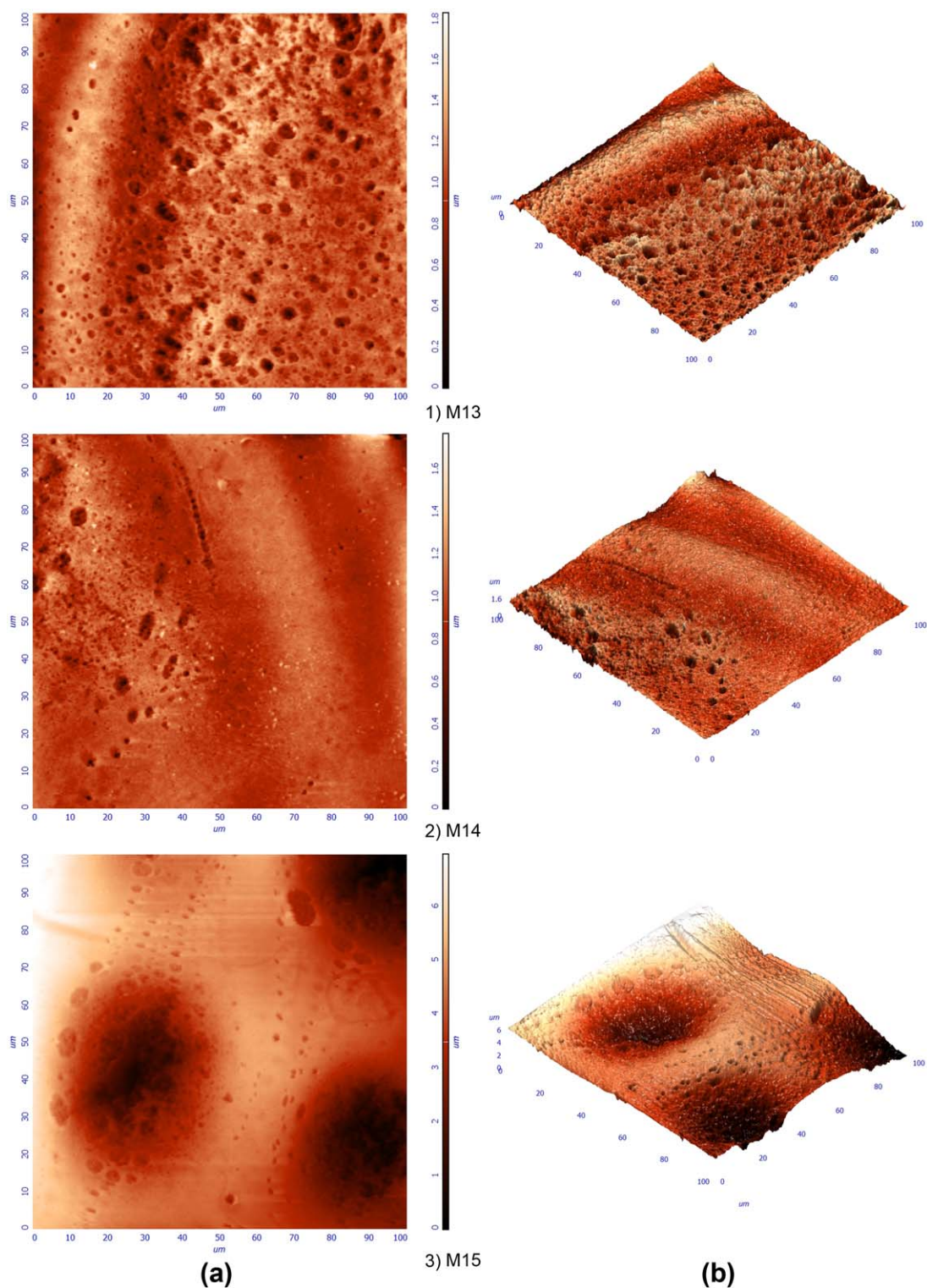
Figure 12. AFM bidimensional (a) and tridimensional (b) images (100 μm $\times$ 100 μm) for three membrane samples (M4, M5, M6) prepared using the same polymer mixture (80% C2–20% PVA) but different coagulation baths (M4–50% IsOH-50% water; M5–60% IsOH-40% water; M6–70% IsOH-30% water). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

water content reduction causes a pore size reduction. However, even though pores are smaller, the number of pores is higher which results in shorter times for water filtration and higher

PWFs. In the third and the fourth series (M10 ÷ M12 and M13 ÷ M15, respectively), PWFs are, also, in a good agreement with the microscopy results. In the latter of these series, PWF

Figure 13. AFM bidimensional (a) and tridimensional (b) images (100 μm $\times$ 100 μm) of three membrane samples (M13, M14, M15) prepared using the same polymer mixture (90% C3–10% PVA) but different coagulation baths (M13–50% IsOH-50% water; M14–60% IsOH-40% water; M15–70% IsOH-30% water). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

results are correlated both with OM and AFM. The highest PWF value was found for M10. This value is normal taking into account the considerable number of pores that may be found on M10 surface. The PWF corresponding to M11 was lower than for M10. Despite that M11 exhibits bigger pores than M10, the number of pores is lower for M11 that is why PWF is lower. There is no significant difference in PWFs corresponding to M11 and M12. Despite the number of pores

Table VII. Average Roughness Value Corresponding to Different Membrane Samples

Sample	M4	M5	M6	M13	M14	M15
Average roughness (nm)	679	892	1442	102	732	950

corresponding to M11 is lower than for M12, M11 exhibits bigger pores, so for these two membranes the overall filtration surface is almost the same.

A similar morphology may be observed for M13 and M14 both by OM and AFM (Figures 11 and 13), explaining the close PWFs corresponding to these membranes. However, the number of pores is higher for M13, which leads to a higher PWF value. For M15, the pores number is not high, no matter that they are very big. This results in a considerably lower PWF value.

CONCLUSIONS

The study of the copolymer solutions rheological behavior shows that, almost in all cases, the flow is dilatant at low shear gradient values, whereas at higher gradients the flow is pseudo plastic with quasi Newtonian tendency. The rheological behavior depends both on the VA content in the copolymer but also on the PVA content in the polymer blend. No time dependence of rheological features occurred.

FTIR spectra of bicomponent membranes showed the presence of the peaks which are characteristic to AN ($\sim$2240 cm^{-1}), VA ($\sim$1730 cm^{-1}) and to PVA ($\sim$3400 cm^{-1}), respectively.

Generally, the membranes which were coagulated in water/IsOH mixtures exhibit pores. The pore size and the morphology of membranes depend on the chemical composition and on the coagulation conditions. So, the morphology and the porosity of the membranes can be tailored by modifying the preparation conditions.
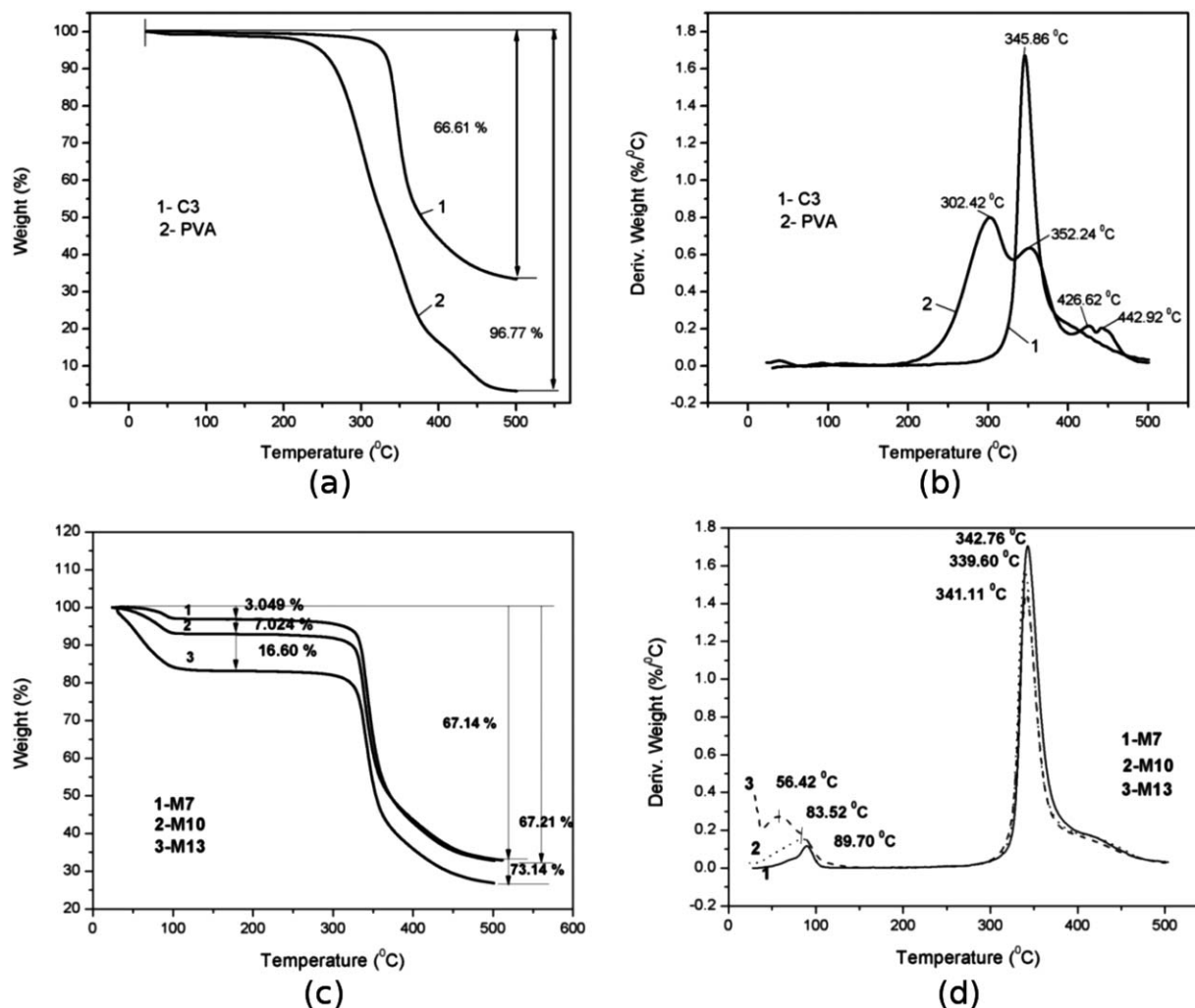
Figure 14. TGA (a, c) and DTG (b, d) curves for pure C3, pure PVA, and for three membranes prepared by coagulation in the same solvent mixture (50% water-50% IsOH) but using different copolymer/PVA weight ratios (%/%):(M7): C3/PVA = 75/25, (M10): C3/PVA = 80/20, (M13): C3/PVA = 90/10.

Table VIII. Thermal Decomposition Data for Three Membranes Samples (M7, M10, M13)

Sample	Polymer content (C3/PVA), %/% (weight ratio)	Peak 1		Peak 2	
		Temperature (°C)	Weight loss (%)	Temperature (°C)	Weight loss (%)
M7	75/25	89.70	3.049	342.76	64.16
M10	80/20	83.52	7.024	343.72	60.11
M13	90/10	56.42	16.60	341.11	56.54

Table IX. SD Values for Three Membrane Samples (M7, M10, M13) Prepared by Coagulation in the Same Coagulation Bath (50% IsOH-50% water)

Sample	C3/PVA (wt %/wt %)	SD (%)
M7	75/25	1049
M10	80/20	1071
M13	90/10	873

Reducing the water content in the coagulation bath leads to a decrease in the size of the pores. A decrease in water content leads, also, to an increase in membranes roughness.

The prepared membranes exhibit a very good thermal stability because the maximum degradation speed is reached at 340°C (at a high temperature). PVA reduces the thermal stability of the membranes. PVA content also influences the swelling behavior of the membrane. So, both thermal stability and SD of the membrane may be adjusted by modifying the amount of PVA.

The determined PWF values show that these membranes may be further used for filtration. PWF values depend not only on the copolymer nature but also on the copolymer/PVA ratio and on the composition of the coagulation bath. The determined PWF values can be correlated either with OM or with AFM results because they match very well with microscopic images.

Table X. PWF Values for Various Membrane Samples

Sample	Polymer mixture and coagulation bath	PWF [L m^{-2} s^{-1}]
M1	80% C_1−20% PVA; 50% IsOH-50% H_2O	0.373
M2	80% C_1−20% PVA; 60% IsOH-40% H_2O	0.215
M3	80% C_1−20% PVA; 70% IsOH-30% H_2O	0.081
M4	80% C_2−20% PVA; 50% IsOH-50% H_2O	0.138
M5	80% C_2−20% PVA; 60% IsOH-40% H_2O	0.202
M6	80% C_2−20% PVA; 70% IsOH-30% H_2O	0.706
M10	80% C_3−20% PVA; 50% IsOH-50% H_2O	1.028
M11	80% C_3−20% PVA; 60% IsOH-40% H_2O	0.800
M12	80% C_3−20% PVA; 70% IsOH-30% H_2O	0.772
M13	90% C_3−10% PVA; 50% IsOH-50% H_2O	0.787
M14	90% C_3−10% PVA; 60% IsOH-40% H_2O	0.720
M15	90% C_3−10% PVA; 70% IsOH-30% H_2O	0.458

This is normal because the water permeation properties are correlated both with size and number of pores.

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