Synthesis and Characterization of Semi-Interpenetrating Networks Based on Poly(dimethylsiloxane) and Poly(vinyl alcohol)

Rosalva S. Marques,¹ Tatiana C. O Mac Leod,² Inez Valéria Pagotto Yoshida,³ Valdir Mano,¹ Marilda D. Assis,² Marco A. Schiavon¹

¹Departamento de Ciências Naturais, Universidade Federal de São João Del Rei, UFSJ, Campus Dom Bosco, São João Del Rei, MG 36301-160, Brasil ²Departamento de Química, FFCLRP-Universidade de São Paulo, Av. Bandeirantes 3900, Ribeirão Preto, SP 14040-901, Brasil ³Instituto de Química, Universidade Estadual de Campinas, UNICAMP, Campinas, SP 13083-970, Brasil

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ABSTRACT: Semi-interpenetrating networks (Semi-IPNs) with different compositions were prepared from poly(dimethylsiloxane) (PDMS), tetraethylorthosilicate (TEOS), and poly (vinyl alcohol) (PVA) by the sol-gel process in this study. The characterization of the PDMS/PVA semi-IPN was carried out using Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and swelling measurements. The presence of PVA domains dispersed in the PDMS network disrupted the network and allowed PDMS to crystallize, as observed by the crystallization and

INTRODUCTION

Hybrid organic-inorganic materials obtained from a mixture of organic and inorganic components are more attractive for the development of new materials with specific properties compared to materials derived from single organic or inorganic constituents.^{1,2} The sol-gel method has been widely employed for the preparation of hybrid organicinorganic materials^{3,4} that can be synthesized at relatively low temperatures, thereby preserving the organic component and allowing the tailoring of material properties by choosing an appropriate combination of components.⁵

One area of recent interest in the field of organicinorganic hybrids has been the synthesis of materials having both hydrophilic and hydrophobic behaviors, which allows for interesting applications in a myriad of fields⁶ Materials having both hydrophilic and hydrophobic morphologies can be prepared using melting peaks in the DSC analyses. Because of the presence of hydrophilic (-OH) and hydrophobic (Si $-(CH_3)_2$) domains, there was an appropriate hydrophylic/hydrophobic balance in the semi-IPNs prepared, which led to a maximum equilibrium water content of ~ 14 wt % without a loss in the ability to swell less polar solvents. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 158–166, 2010

Key words: poly(dimethylsiloxane); poly(vinyl alcohol); semi-interpenetrating networks (semi-IPN); hydrogels; swelling

interpenetrating polymer networks (IPN)⁶ and block copolymers.⁷

A semi-IPN system is defined as a combination of two or more polymers in which one or more polymers are cross-linked and one or more polymers are linear or branched. Unlike copolymers, most IPNs do not blend on a molecular scale, but rather form phases that are continuous on a macroscopic scale. Usually semi-IPNs form finely divided phases, only a few nanometers in size. In semi-IPN, one of the polymers can be synthesized in the immediate presence of another.8 The phase morphology in a semi-IPN system is stable against environmental changes because at least one component in the system is fixed by crosslinking. Thus, if one of the polymers is hydrophilic, the resulting semi-IPN could form a hydrogel. Hydrogels exhibit the ability to swell in water, retaining a significant fraction of water within their structure without dissolving,^{9,10} and have been studied for various applications in the fields of medicine, pharmacy, biotechnology, and the controlled release of drugs.^{11–13}

Poly(vinyl alcohol) (PVA), is a polymer that has been intensively studied as a hydrogel¹⁴ due to its chemical stability, film-forming ability, high hydrophilicity, biocompatibility, and processability.

Correspondence to: M. A. Schiavon (schiavon@ufsj.edu.br). Contract grant sponsors: FAPEMIG, CNPq, CAPES.

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Diffusive permeabilities of solutes in PVA gel membranes and their applications in separation processes have been reported in several studies.¹⁵

On the other hand, poly(dimethylsiloxane) (PDMS), a hydrophobic polymer, is one of the most important polymers in silicon chemistry because of its excellent thermal and chemical stabilities,¹⁶ which allow it to be used in a wide variety of technological applications, including membranes for gas separation processes¹⁷ and supports in catalytic systems.¹⁸ One interesting example is the use of PDMS-based membranes as supports for the immobilization of oxidation catalysts, such as metalloporphyrins¹⁹ and Mn(salen).²⁰ These so-called Catalytic Polymeric Membranes (CPM) can be successfully used in the catalysis field to keep two liquid reagent phases (substrate and oxidant) apart, thus completely eliminating the use of a solvent. However, due to the highly hydrophobic character of the PDMS-based membrane, the swelling of hydrophilic substrates and oxidants is a drawback of this system. As previously observed by us,²¹ the use of a clean oxidant such as H₂O₂, which is an environmentally-friendly alternative to traditional inorganic oxidants, is precluded when using PDMS-based membranes; as this oxidant cannot be sorbed into the PDMS network by polarity forces. Therefore, efforts to develop new catalytic materials that are able to allow this polar oxidant to be sorbed into PDMS-based membranes are an interesting and important advancement in this field.

The synthesis and characterization of hybrids based on PDMS and PVA have been studied to overcome the difficulty that results from the poor hydrophilic character of PDMS, and to improve its swelling behavior and other physicochemical properties. The Tezuka group carried out the most complete study of PVA-PDMS copolymers.²²⁻²⁵ Recently, Ganachaud and coworkers.⁷ reported the direct synthesis of PVA-g-PDMS copolymers in an aqueous microsuspension. The method used was a direct reaction between epoxy-terminated PDMS and some pendant alcohol groups in P(VA-co-VAc). Semi-IPN hydrogel copolymers composed of PVA and PDMS, crosslinked with chitosan using 2,2-dimethyl-2-phenylacetophenone (DMPAP) as a photoinitiator under ultraviolet irradiation, were also described by Kim and coworkers.⁹ The same authors have also described the preparation of hydrogels based on PVA and PDMS crosslinked with methylenebisacrylamide (MBAAm) by thermal crosslinking, using DMPAP as a free-radical initiator.¹⁰ In both cases, the equilibrium water content (EWC) ranged between 65 and 95 wt %.

In this study, the syntheses of semi-interpenetrating networks (semi-IPNs) based on PDMS and PVA are reported. The semi-IPNs were prepared by crosslinking of the hydroxyl-terminated PDMS chains with tetraethylorthosilicate (TEOS) in a catalyzed reaction by the sol-gel process concomitant with the addition of PVA into the system, aiming to prepare polymeric materials suitable for usage in CPM systems in which H_2O_2 can be used as an oxidant. Characterization of the PDMS/PVA semi-IPNs was carried out by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and swelling measurements. The relationships between composition, microstructure and swelling properties of the resulting PDMS/ PVA semi-IPNs were discussed

EXPERIMENTAL

Materials

Commercially available PVA with 99.8% hydrolyzed groups and $M_w = 85,000-124,000$ g/mol was purchased from Aldrich Chemical Co. Hydroxy-terminated (PDMS-OH) with an average molecular weight of 2200 g/mol, and tetraehylorthosilicate (TEOS) were obtained from Dow Corning (Brazil). The dibutyltin–dilaurate complex (5 wt % in hexane; Sn catalyst) was purchased from Gelest. Isopropyl alcohol (99.7% purity) was obtained from Synth (Brazil). All materials were used as received.

Preparation of PDMS/PVA membranes

PVA/PDMS membranes were synthesized by the following procedure. PVA, 5 wt %, was dissolved in distilled water and heated at 85°C to produce a solution. Appropriate amounts of PDMS-OH were mixed with TEOS and the Sn-catalyst (0.1% of the total mass) in isopropyl alcohol (10 mL) and magnetically stirred for 30 minutes. This precondensed precursor mixture was added to the PVA aqueous solution and, after complete mixing, heated at 85°C for 7 hours. The low-viscosity dispersions were subsequently cast onto TeflonTM Petri dishes and left to stand for up to 14 days at room temperature. The self-supported membranes produced were then subjected to an isothermal treatment at 70°C for 48 hours. The composition of the membranes is reported in Table I. A membrane with PDMS crosslinked with TEOS, without any PVA, was also prepared for comparison purposes.

Characterization techniques

TGA analyses were performed using a TA instrument, model 2950, equipped with an alumina tube furnace and alumina crucibles. Analyses were performed with about 20 mg of sample under an argon

TABLE I		
Composition of the PDMS/PVA	Semi-IPN	Prepared
DVA		II TE

	PVA		PDMS-OH	TEOS	
Semi-IPN	g	wt % ^a	g	g	
PDMS/PVA 01	0.50	10	4.50	0.50	
PDMS/PVA 02 PDMS/PVA 03	0.75 1.00	15 20	4.50 4.50	0.50 0.50	

^a Based on the initial weight, without considering the hydrolysis reaction of TEOS.

flow (100 mL/minute) at a heating rate of 10°C/minute up to 980°C. DSC was conducted using a Perkin-Elmer Diamond calorimeter. Both heating and cooling processes were measured using aluminum pans at a 10°C/minute scanning rate under helium flow, and the data obtained in the second heating scan were used to eliminate any thermal history. The first scan was from 25 to 180°C, followed by a cooling scan to -180° C, and finally, the second heating cycle was from -150 to 130°C. After each ramp, a dwell time of 3 minutes was set to stabilize the temperature. The glass-transition of the materials was determined with the half-point method. The FTIR were obtained by using an Attenuated Total Reflectance (ATR) accessory with a ZnSe crystal in a FTIR Perkin-Elmer Spectrum GX, operating between 4000 and 650 cm^{-1} with a resolution of 2 cm^{-1} . Microstructural characterization was performed by SEM in a microscopy Zeiss EVO50 operating with an accelerating voltage of 20 kV. The microscope was equipped with an energy-dispersive X-ray spectroscopy (EDS) IXRF Systems Sphinx 130, allowing multiple chemical analysis. The samples were previously covered with a thin Au layer using a BAL-TEC-SCD050 sputtering instrument.

For swelling measurements, dried sample sheets were immersed in distilled hexane, dichlromethane, methanol or deionized water and left to equilibrate at room temperature. The swelling was monitored until the film reached a constant weight. Samples were withdrawn from the solvent at specified times and weighed after the removal of surface solvent by lightly blotting them with a piece of filter paper. The measurements were made in triplicate using a Mettler Toledo analytical balance, and the error was estimated to be 10%. Experiments were carried out for 120 hours, then all pieces were dried and weighed again.

RESULTS AND DISCUSSION

The semi-IPNs based on PDMS and PVA were synthesized by crosslinking PDMS-OH with TEOS, catalysed by a Sn-catalyst with the concomitant addition of a PVA solution. The crosslinking reactions between the hydroxy-terminated PDMS and TEOS units are represented in Figure 1, with the nodes of the PDMS network constituted by SiO₄ units. TEOS and PDMS-OH can react practically with all reactive functional groups, namely the four Si-OEt groups in TEOS and two Si-OH groups in PDMS. The crosslinking reaction between the hydroxy-terminated PDMS and TEOS, catalysed by the Sn-catalyst, is based on hydrolysis/condensation reactions with the formation of ethanol derived from TEOS. Such reactions are wellknown in the sol-gel chemistry process.²⁶ Many attempts were performed to find the optimized preparation conditions of the PDMS/PVA semi-IPNs described here, since slow changes in temperature or the prehydrolysis of PDMS and TEOS time and media led to phase segregation. Following the conditions stated here, the resulting PDMS/PVA membranes were flexible and crack-free.

FTIR spectra of the semi-IPNs, PDMS and PVA in the range between 1700 and 700 cm^{-1} are displayed in Figure 2. As expected, the spectra of semi-IPNs and PDMS are similar, and the main bands are assigned to PDMS, the major component in all samples. Indeed, the spectrum of PVA is mainly characterized by bands due to OH (stretching) and C-H (stretching), which were also present in PDMS. The most prominent absorption peaks are related to Si(CH₃)₂ groups at 1258 (δ C–H) and 782 cm⁻¹ $(\delta C-H; vSi-C)$. In addition, Si-O bonds of the siloxane network give rise to the absorption at 1080 and 1007 cm⁻¹ (stretching) (vSi–O).²⁷ The relative intensity of the bands decreases with increasing amounts of PVA in the semi-IPN samples. In addition, the measured spectra from the top and bottom sides of the membranes were similar (in position and intensity of bands), indicating a uniform distribution between the domains of the components in the membranes and no phase segregation.

TGA curves of PDMS/PVA 01, PDMS/PVA 02, PDMS/PVA 03, and PVA and PDMS network samples were recorded under an argon flow and their



Figure 1 A scheme showing the crosslinking of PDMS-OH with TEOS to generate a semi-IPN based on PDMS/PVA (*www indicates a chain growth in that position*).



Figure 2 FTIR spectra of PDMS/PVA semi-IPNs, PVA, and PDMS obtained using the Attenuated Total Reflectance (ATR) technique.

corresponding DTG curves are shown in Figure 3. The two-step degradation observed in the TG/DTG curves of the PVA sample with T_{MAX} at 332 and 418°C (T_{MAX} is the temperature at which the mass flux from the solid to vapor phase is maximum, corresponding to a peak in the DTG curves) has been the subject of several publications, $^{28-30}$ and the data is consistent with the elimination of side-groups at lower temperatures, followed by a breakdown of the polymer backbone at higher temperatures, as observed during thermal degradation in the molten state.²⁸ On the other hand, the one broad-step degradation ranging from 350 to 570°C with T_{MAX} at 488°C observed in the TGA curve of the PDMS network sample is due to thermal depolymerization, which started at around 350°C, involving mainly the siloxane backbone, with the participation of the remaining Si-OH end groups.^{31,32} The mechanism of this depolymerization is based on interchain and intrachain reactions, the main products of which are cyclic and linear volatile oligomers, such as D₃ and D₄.^{32,33} In addition, the Si-OH end groups can promote "back-biting" through a nucleophilic attack on a Si atom of the main chain. Although the PDMS chains were crosslinked with TEOS, the higher mobility of the chains and the remaining Si-OH groups from either the end of the chains or from the hydrolyzed TEOS was enough to lead to an almost complete degradation of the network.

The TGA curve of the PDMS/PVA 01 membrane displayed one main degradation step, with T_{MAX} at 433°C. The TGA curve of the PDMS/PVA 02 membrane displayed two degradation steps at T_{MAX} 280 and 432°C, while the TGA curve of the PDMS/PVA 03 membrane displayed three degradation steps at T_{MAX} 281, 437, and 518°C. The main degradation

peak observed in all membranes at T_{MAX} around 430°C is related to the degradation of both PVA and PDMS chains. Indeed, such peaks are more intense than those observed from the pure components. In addition, the breakage of crosslinking points by the thermal degradation or by the presence of PVA in the PDMS network could shift the T_{MAX} to lower values. For the PDMS/PVA 02 and PDMS/PVA 03 samples, a degradation step at around T_{MAX} 280°C is probably attributed to the degradation of PVA. Although T_{MAX} from the first step degradation in plain PVA was around 332°C, the dispersion of some PVA chains in the network could be responsible for the reduction in T_{MAX} of the PVA chains. This is reasonable to suppose since dispersion of some PVA chains into the PDMS network could led to the loss of hydrogen bonding, which reduces the melting point of the polymer chains, and hence leads to a thermal degradation similar to the thermal



Figure 3 TG and DTG curves of PVA, PDMS, PDMS/ PVA 01, PDMS/PVA 02, and PDMS/PVA 03 semi-IPN. (Recorded at 10°C/minute, under a nitrogen atmosphere).

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Figure 4 DSC thermograms of pure PVA, PDMS network, PDMS/PVA 01, PDMS/PVA 02, and PDMS/PVA 03 semi-IPNs.

degradation in the molten state²⁸ once we used a nonisothermal analysis method. Additionally, the reduction of T_{MAX} compared with plain PVA supports the above explanation of the increasing area in this event with increasing amounts of PVA in the semi-IPNs (as observed in the DTG curves in Fig. 3), even if low amounts of this polymer were used in each composition (see Table I).

It is interesting to notice that the PDMS/PVA 03 membrane displayed a third degradation step at a $T_{\rm MAX}$ of 518°C, which is mainly related to PDMS chain degradation. Although this sample has more PVA, it promotes more intense phase segregation, which is responsible for the appearance of degradation steps of both phases, PVA and PDMS, at a $T_{\rm MAX}$ of around 280 and 518°C, respectively.

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All of the membrane samples displayed small amounts of residue (less than 5 wt %) at temperatures higher than 700°C, while PDMS and PVA showed no residue beyond 600 and 675°C, respectively. The residues are probably constituted by silica from the PDMS network and also some free carbon from PVA degradation.

Figure 4 shows DSC thermograms of the PDMS/ PVA semi-IPNs and PVA and PDMS network. Upon heating, the PDMS network exhibited a glass transition, $T_{g'}$ at -124.4° C, in agreement with the literature.³⁴ PVA exhibited a typical T_g at 83.0°C.³⁵ Such events were not clearly observed for the semi-IPN. On the other hand, for the PDMS/PVA semi-IPNs an endothermic peak was observed upon heating at -53.1° C, along with an exothermic peak at -90.6° C, which is due to melting and crystallization events, respectively, of the PDMS chains.³⁴ It is interesting to note that there is a slight change in the temperature of melting with the change in the PVA content. The crystallization/melting of PDMS were observed even for crosslinked PDMS chains. However, these events can depend on both the type and density of the crosslinking.³⁴ According to classical crystallographic models, the presence of constraints that reduce the mobility of the chains leads to a reduction in the crystallization rate, resulting in a lower degree of crystallinity at a given cooling rate. Therefore, the appearance of crystallization and melting peaks in the semi-IPNs suggests that the crosslinking density of the PDMS chains had decreased, allowing them to crystallize to some extent. As expected, the crystallinity of the PVA phase would be reduced as a result of semi-IPN formation. Indeed, Kim's group¹⁰ followed the sharp endothermic peak of PVA at 219.5°C and found that its crystallinity was decreased when immersed in a PDMS network. DSC thermograms of membranes aged for 10 months (not shown here) displayed similar behaviors, suggesting that the semi-IPN networks prepared were stable with respect to crystallization.

The morphological characterization of PVA/ PDMS semi-IPN has not been described in the literature since the focus has been the swelling behavior of these materials. To address the lack of these studies in the literature, Figure 5 shows micrographs of the PDMS/PVA 01 semi-IPN at different magnifications. It can be seen in the low magnification micrographs [Fig. 5(A,B)] that the PVA phase is segregated in the PDMS matrix, forming circular dispersed domains from ~ 1 to 30 μ m in diameter. The driving force for segregation of the dispersed PVA domains is the different characteristics between the polar PVA and nonpolar PDMS network. Such domains are uniformly distributed in the PDMS matrix. At higher magnification [Fig. 5(C)], it can be seen that both phases are continuous, with no cracks



Figure 5 SEM micrographs of the surface of the PDMS/PVA 01 semi-IPN at different magnifications.

or pore formation, and having good adhesion at interfaces, probably associated with dispersion of some PVA chains into the PDMS network. This observation agrees with our interpretation of the observed shift of the first T_{MAX} of PVA (Fig. 3) to lower values due to some PVA dispersion into the PDMS network. The highest magnification registered [Fig. 5(D)] shows a continuous phase without any



Figure 6 SEM micrograph of the PDMS/PVA 01 semi-IPN with the corresponding energy dispersive X-ray spectra of two selected areas. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Water Swelling (%) 9 PDMS/PVA 01 6 3 PDMS 0 80 120 0 20 40 60 100 Time (h)

PDMS/PVA 03

PDMS/PVA 02

·· 3

.7

Figure 7 The water swelling kinetics of PDMS/PVA 01, PDMS/PVA 02, PDMS/PVA 03, and PDMS, at room temperature.

important morphological details, as usually observed for PDMS networks.³⁶ Such features were identical to those found in the bulk of the membranes, which were analyzed by the surface fracture of the membranes (micrographs not shown).

The elemental composition of the phases was confirmed by SEM and energy dispersive X-ray spectroscopy. Figure 6 shows the micrograph of the PDMS/PVA 01 semi-IPN together with the corresponding energy dispersive x-ray spectra of the selected areas. It can be seen from the EDS spectra that the intensity of the Si peak is higher than in the dispersed domains due to the PDMS phase. The relatively more intense C and O peaks in the dispersed domains are due to the high percentages of these elements in PVA.

The affinity of solvents for the polymeric membrane can be easily determined by their sorption in the membrane. The swelling process of polymeric materials involves the diffusion of the liquid phase into the bulk of the membrane, which is made possible by the mobility of the polymeric chains and the free-volume among chains. The molecules of the liquid remain entrapped in these free spaces up to an equilibrium point, as determined by both polymersolvent interactions and the elasticity of the material. In a swollen polymer, the segments are forced to assume an elongated conformation. In addition, the more a polymer swells in a specific solvent, the higher its affinity is for that compound.¹⁹

Figure 7 shows the water swelling kinetics of PDMS, PDMS/PVA 01, PDMS/PVA 02, and PDMS/PVA 03, at room temperature. The EWC values were 0.65, 5.27, 12.1, and 14.0 wt %, respectively. The increase in water sorption is related to the increase in the amount of PVA dispersed domains in the membranes, which





Figure 8 The solvent swelling kinetics of PDMS/PVA 01, PDMS/PVA 02, PDMS/PVA 03, and PDMS in: (A) Dichloromethane, (B) Hexane, and (C) Methanol. At room temperature.

15

12



Figure 9 SEM micrographs of dried PDMS/PVA 01 semi-IPN surfaces after water swelling.

the lower amount of PVA in the present system. It has also been reported that the addition of chitosan in a PDMS/PVA semi-IPN can lead to an EWC of up to 93 wt %.⁹ Similar results to that were described for a system based on PVA, in which the blending of chitosan with PVA increased the water uptake of the resulting material by up to 150 wt %.¹⁵ Although our results seem quite slow for EWC when compared to similar systems from the literature, it is important to keep in mind that this semi-IPN behavior fits well with the desirable EWC for a catalytic polymeric membrane, where the polar oxidant (H₂O₂) should be sorbed in relatively small amounts to avoid catalyst or polymer self-oxidation.

Interestingly, while the swelling capacities of the semi-IPN membranes in dichlromethane were similar, they swelled less than the PDMS network in hexane, as can be seen in Figure 8(A,B). In addition, when methanol, a polar solvent that does not swell the PDMS network, was used, a swelling of up to 119 wt % was obtained in the semi-IPN, as shown in Figure 8(C). Therefore, the semi-IPNs prepared showed a hydrophylic/hydrophobic balance, in which the amount of hydrophylic/hydrophobic phases from PDMS and PVA polymer chains determine the swelling properties of the semi-IPNs. Such results also agree with the solubility parameters.

Figure 9 shows the microstructure of dried PDMS/PVA 01 semi-IPN surfaces after swelling in water. This semi-IPN showed similar morphologies before and after the swell/dry processes, indicating that the material has a good dimensional stability, probably promoted by the dispersion of PVA domains in an elastic PDMS matrix. The lines observed in the globular hydrophilic domains are due to the drained solvent. The behavior is typical of PDMS membranes, as previoulsy reported in the PDMS-based catalytic polymeric membranes.¹⁹ After

swelling, the semi-IPNs displayed no significant weight loss or shrinkage, suggesting that there was no release of PVA or possible uncrosslinked PDMS chains during swelling.

The results presented here showed that PDMS/ PVA semi-IPNs appear to be good candidates for utilization as catalytic polymeric membranes. The preparation of such CPM, in which the catalyst is occluded into these PDMS/PVA semi-IPNs, is underway in our laboratory.

CONCLUSIONS

Semi-IPNs based on PDMS, TEOS, and PVA were prepared by the sol-gel process in this study. The conditions stated here were effective in dispersing hydrophilic PVA domains in a nonpolar PDMS matrix. The semi-IPNs showed reasonable thermal stability, with mixed characteristics between the plain PVA and PDMS network. Results from DSC showed the crystallization of PDMS chains. The semi-IPN exhibited both hydrophilic and hydrophobic characteristics. Increasing EWC values was obtained when the amount of PVA was increased, with no loss in the swelling capacity when less polar solvents, such as dichloromethane and hexane, were used. These results show promise for the use of these semi-IPNs as catalytic polymeric membranes.

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