

Membrane Properties of Microporous Structures Prepared from Polyethylene/Polymethacrylate IPN

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ABSTRACT: Polyethylene/polymethacrylate interpenetrating polymer networks (PE/PMA IPN) form a matrix-particle or a co-continuous morphology that can be adjusted by the composition and synthesis conditions. Based on the fact that PMA degrades whereas PE crosslinks when they are exposed to energetic irradiation, we developed a new approach to create a porous structure by electron beam irradiation. IPN systems that differ in the methacrylate components and composition were studied. One system contains poly(butyl methacrylate-co-methyl methacrylate) (BMA-co-MMA) and the other contains poly(dodecyl methacrylate-co-ethyl methacrylate) (DMA-co-EMA) as the PMA phase. After electron beam irradiation followed by extraction with

xylene, both IPN systems have a porous structure that is permeable to water. However, the structure and size of the pores depend on the PMA components and the synthesis conditions. PMAs with long aliphatic side chains degrade less than PMAs containing only short aliphatic pendant groups. Therefore, the PE/BMA-co-MMA IPN forms bigger pores than PE/DMA-co-EMA, resulting in a higher water flux. The molecular cutoffs of the IPN are characteristic for microfiltration or ultrafiltration. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1976–1982, 2003

Key words: membranes; polyethylene (PE); IPNs; electron beam irradiation; morphology

INTRODUCTION

Polymer membranes have been applied in various fields, ranging from desalting of sea water to the production of super pure water for the microelectronic industry.¹ According to their pore size, porous membranes can be classified as reverse osmosis membrane, ultrafiltration membrane, and microfiltration membrane.^{1,2} To match different requirements for different applications, various methods to acquire porous structures have been developed. Among others, the method most often used both in industry and in the laboratory is the phase inversion process.² In this process, a polymer sol is formed by dissolving the polymer in a solvent or a mixture of solvent and non-solvent. (A polymer may also be used as the non-solvent²). When evaporating the solvent, a sol-gel transformation occurs, and the gel still contains some solvent (and, if present, the non-solvent). Pores are formed during the phase inversion, which is caused by an exchange of the solvent with a precipitant and by the extraction of the remaining pore-forming non-solvent.

Another method to create pores is by mechanical stretching of crystalline polymers in a direction perpendicular to the extrusion direction.² Porous membranes of polyethylene (PE), polypropylene (PP), and polytetrafluoroethylene (PTFE) can be produced in this way. Membranes with evenly distributed pore sizes have also been prepared by exposing inorganic or organic materials to radioactive sources to create narrow trails. The subsequent etching out of the radiation-damaged material along the traces of energetic atoms results in a porous structure (e.g., 'Nucleopore').² Macroporous materials can also be obtained by chemically induced phase separation, which has been described by Kiefer et al.³

Most kinds of materials available are suitable for membrane processes. The selection of materials, however, remains empirical because of the complicated physicochemical relationships in the membrane process.⁴ In addition to natural materials, such as cellulose acetate, that are conventionally used in the membrane preparation, synthetic polymer materials of various kinds are also applied. Some of these synthetic polymers like polyaryls and aromatic polyamides have high mechanical performances.⁵

Low cohesive energy and excellent chemical stability are characteristics of PE, one component of the interpenetrating polymer network (IPN) material studied in this work. Membranes of PE are used to remove microparticles in microelectronic industry, where membranes have to withstand critical chemical conditions like exposure to sulfuric acid, nitric acid, or

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TABLE I
Composition of the Membranes

IPN system	Molar PMA composition	Peroxide wt % ^a	BDDM mol % ^b	PE content wt %	Gel content wt % ^c
PE/BMA-co-MMA	BMA/MMA = 50:50	1	0.1	18.8	21
PE/BMA-co-MMA	BMA/MMA = 50:50	1	1	18.6	45
PE/BMA-co-MMA	BMA/MMA = 60:40	1	1	18.1	(> 45) ^d
PE/DMA-co-EMA	DMA/EMA = 20:80	3	0	16.5	80
PE/DMA-co-EMA	DMA/EMA = 20:80	1	1	16.3	68

^a Related to (PE + PMA).

^b Related to PMA.

^c 800 kGy; extracted once with xylene.

^d Estimated from the BMA/MMA = 50:50 composition.

hydrofluoric acid. Polymethacrylates (PMAs), the other IPN component, possess a wide variability in properties, like polarity, acidity, or basicity. Moreover, the properties can be tailored by chemical modification. This versatility explains the great amount of attention paid to PMAs as a membrane material.⁶

The formation of IPNs allows the combination of even very incompatible polymers to create materials with technically suitable properties. The morphology of the IPN and, therefore, the separation characteristics of the final membrane can be adjusted to special demands by varying the composition and preparation conditions. In amphoteric membranes for liquid separation, the selectivity is enhanced because the neighboring nontransporting phase hinders the swelling of the transporting phase, thus restricting the so-called plasticization effect.⁷ In this work we used IPNs based on PE and PMA, which are very incompatible with each other and typically show a two-phase morphology.⁸⁻¹² The development of membrane materials from this type of IPN was accomplished by taking advantage of the different behavior of the IPN components under irradiation. With exposure of the IPN to high-energy irradiation, the PE phase crosslinks and the PMA phase degrades (at least partially). By following removal of the degraded material, the IPN becomes porous, which was observed both at the surface and in the bulk phase. Primary membrane properties, such as water flux and molecular cutoffs, were determined for two different PE/PMA IPN materials.

EXPERIMENTAL

Materials

Methyl (MMA), ethyl (EMA), and butyl (BMA) methacrylates (Aldrich) were freed from inhibitor by distillation under reduced pressure shortly before use. Dodecyl methacrylate (DMA) was washed with aqueous sodium hydroxide (4%) and then with distilled water. DMA was then dried with anhydrous calcium chloride and stored over 4 Å molecular sieves. Low-density polyethylene (PE, Bralen RA 2-19, non-stabilized, Slovnaft), butanediol dimethacrylate (BDDM,

Aldrich), 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane (Trigonox-101, Akzo), polypyrrolidone (Kollidon 30, $M_w = 55,000$ g/mol, BASF), and Dextran T2000 ($M_w = 2,000,000$ g/mol, Pharmacia AB) were used as received.

Preparation of IPN membranes

The IPN films were prepared by an *in situ* method.¹³ PE was dissolved in the methacrylate mixture containing BDDM as crosslinking agent for the methacrylates at ~ 105 °C. Trigonox-101 was added as initiator to the clear solution, and the solution was poured into a PTFE plate reactor composed of two PTFE plates, which were stabilized by two metal plates, and a PTFE frame of ~ 0.3 mm. The polymerization reaction was conducted at 115 °C for 6 h followed by 1 h at 160 °C. A detailed description of the procedure is given elsewhere.¹²

For the synthesis of the IPN thin films, the molar ratio of repeating units ethylene/methacrylate was kept constant at 1:1 in all investigated samples, whereas the monomer compositions and the contents on BDDM crosslinker and peroxidic initiator were varied (Table I). To study the influence of the nature of the contact surface of the reactor to the polymerization solution on the final morphology of the membranes, the PTFE plates of the "PTFE reactor" were covered with aluminium foil in some experiments (called "Alu reactor").

The IPN films were irradiated by an electron accelerator EB ELV-2 (INP Novosibirsk) at radiation dose of 400 or 800 kGy in individual irradiation runs of 100 kGy to avoid overheating of the samples. After irradiation, the films were extracted with xylene (~ 100 -fold excess) at boiling for 10 h to remove the degraded methacrylate polymers. The gel contents of reference samples, given in Table I, were determined after drying samples in a vacuum at 50 °C for 10 h. The dried materials were too brittle for testing the membrane properties. Therefore, to test the membrane characteristics, the xylene that remained in the film after extraction was gradually replaced by acetone, and the acetone was then replaced by distilled water.

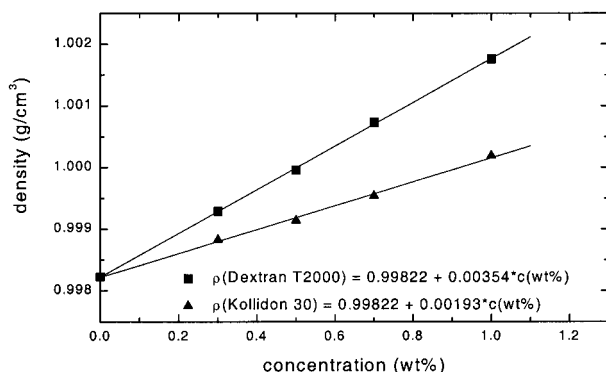


Figure 1 Calibration curves for the concentration determination of aqueous Kollidon 30 and aqueous Dextran T2000 solutions ($T = 20^{\circ}\text{C}$).

Morphology study

The morphology was studied on the extracted and dried samples with a low-voltage scanning electron microscope (SEM; DSM 982 GEMINI, Zeiss). The surfaces of the IPN films were studied directly, whereas the bulk morphology was determined after the IPN films were cryofractured in liquid nitrogen.

Determination of membrane characteristics

The water fluxes were determined at room temperature at a pressure of 2 bar according to $J = Q/A\Delta t$, where J is the flux, Q is the amount of water flowing through the membrane in the time period Δt , and A is the effective area of the membrane ($1.257 \times 10^{-3} \text{ m}^2$ in our experiments).

For the determination of the molecular cutoff at room temperature, 1 wt % solutions of the linear polymers Kollidon 30 and Dextran T2000 were used. Their densities as a measure of the polymer concentration were determined before and after the filtration on a density meter DMA 58 (AP PAAR, Austria) at 20°C . Solutions of Kollidon 30 and Dextran T2000, with concentrations of 0, 0.3, 0.5, 0.7, and 1 wt %, were prepared to create a calibration curve for the determination of the polymer content (Figure 1). The apparent rejection R was calculated according to $R = 1 - C_p/C_f$, where C_f and C_p are the concentrations of the solute in the feed and in the permeate, respectively.

RESULTS AND DISCUSSION

Morphology development during the IPN synthesis and membrane formation

In the phase inversion process, phase transitions take place during the evaporation of the solvent.² The final morphology of the product is dependent on the state at which the polymer exists during that process. If the macromolecules are present as a disperse phase and

the solvent forms a continuous phase, no membrane but only powder will be formed. Conversely, membranes with closed cells are obtained if the polymer component is the continuous phase.^{14,15} To acquire a membrane with interconnected porous structure, both the dissolved polymer and the solvent and/or non-solvent must exist in a continuous phase.

Methodologically, the method employed in the present work is similar to the phase inversion process. During the polymerization of the methacrylate phase, the original homogeneous PE methacrylate solution separates into a particle matrix or co-continuous morphology, caused by the incompatibility of PE and PMA. This phase separation occurs even though compatibilizing grafting reactions between both phases take place to a large extent during the IPN synthesis.^{9,16} Please note that phase separation and grafting between the two phases are not typical for an ideal IPN. Thus, such structures were called "IPN-like" material.¹³

Under irradiation and extraction conditions, the PMA phase of the phase-separated IPN serves as the pore-forming agent. Up to 80 wt % of the IPN may be extracted with xylene after electron beam irradiation (Table 1¹⁰). Previous results showed that the PE crosslinking is nearly complete after the IPN synthesis and electron beam irradiation.^{8-10,12} Therefore, the extractable content of the irradiated IPN consist almost only of degraded methacrylates.

It is reasonable that samples with a co-continuous morphology become permeable. However, in our previous works,⁸⁻¹² a matrix-particle morphology was observed for most of the studied IPN, especially for the PE/BMA-co-MMA IPN systems. Although PE is always the minor phase, it forms the matrix surrounding the closely packed PMA spheres as thin walls. It is expected that a membrane with closed cells will be created by degradation and extraction of the dispersed PMA phase.³ Nevertheless, most of the IPNs are permeable to water, as shown later, proving that interconnecting channels between the spheric pores must be generated during the process of synthesis, degradation, and extraction. We assume that the permeabilities are dependent on the degree of the destruction of the PE walls.

To prove that the extraction of degraded PE components does not result in additional pores, we prepared $\sim 260\text{-}\mu\text{m}$ -thick films by melt pressing. After irradiation with 400 or 800 kGy, the extractable contents (same conditions as for the IPN) were 19.4 or 14.1 wt %, respectively. Nonirradiated PE was completely soluble. The extractable amounts in the PE crosslinked by irradiation were much higher than those of materials additionally crosslinked by peroxide.¹⁰ After exchanging the solvent by acetone or acetone/water no signs of pore formation were observed by SEM at the

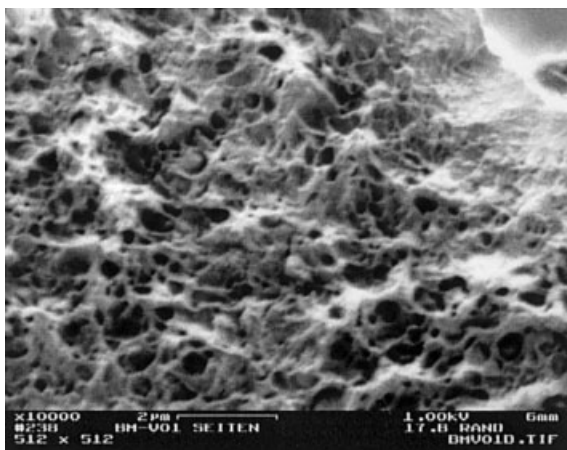


Figure 2 Porous structure of the cross-section of the PE/BMA-co-MMA IPN (PTFE reactor, BMA/MMA = 50:50, BDDM = 0.1 mol %, peroxide = 1 wt %, 800 kGy). A dense surface structure is visible in the right upper corner.

film surface on in the bulk phase. The extraction resulted in a shrinkage of the films only.

Morphology of the IPN

The morphology of the IPN was studied by SEM after electron beam irradiation and extraction with xylene. During the irradiation, a partial degradation of the PMA phase occurred. When extracting the degraded material, holes were formed, reflecting the original morphology of the PE/PMA IPN.

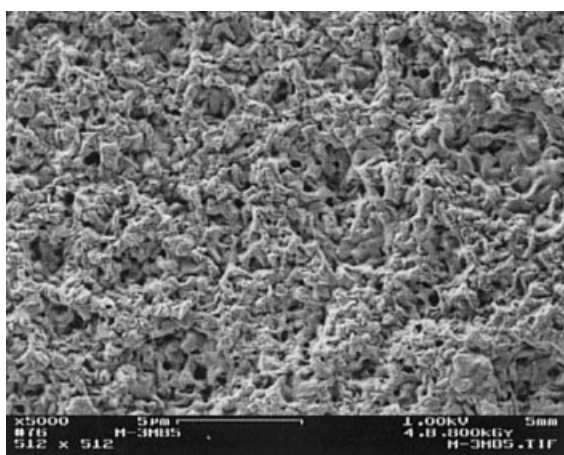
PE/BMA-co-MMA IPNs have a disperse two-phase morphology that can be adjusted by the synthesis conditions.⁹ Although PE amounts to only ~20 w %, it forms the matrix phase, and PMA appears as a disperse phase. Observations of the cross-section of a PE/BMA-co-MMA IPN, prepared with 1 wt % perox-

ide and 0.1 mol % BDDM with the PTFE reactor, reveal a similar morphology to the IPN described in our previous works that was prepared with a higher crosslinker degree.^{9,10} However, the morphology of the surface appeared different from the bulk phase (cross-section). A tight surface can be seen in Figure 2 (upper right corner), although the porous structure is obvious in the inner phase after irradiation and extraction with xylene. We assume that due to the nonpolar character of both the PTFE reactor surface and the PE dissolved in the polar methacrylate solution, PE adsorbs preferentially at the reactor surface, resulting in an IPN surface with an increased PE content compared with that of the bulk phase. Thus, the surface degrades less than the bulk phase under irradiation.

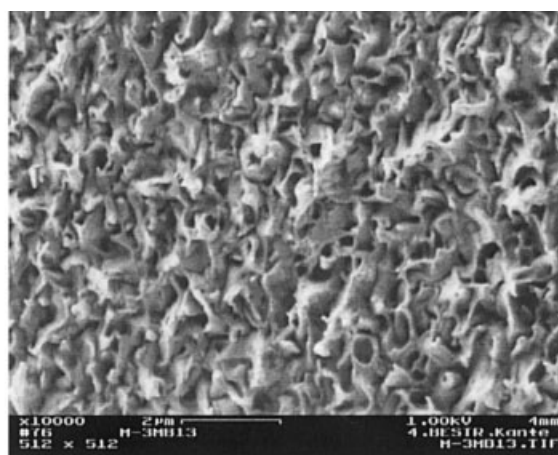
In contrast to the PE/BMA-co-MMA IPN but in agreement with observations of other DMA-containing IPN,^{8,9} a co-continuous morphology of the PE/DMA-co-EMA IPN prepared with 3 wt % peroxide but no crosslinker was observed both on the surface (Figure 3a) and on the cross-section (Figure 3b). In this IPN, the difference in the polarity between the PE and the methacrylates is reduced because of the long aliphatic side chain. The solubility of the PE in the methacrylates is increased. In the IPN, the dodecyl side chain acts as a compatibilizer to the PE phase.⁸ Therefore, we could not observe an enrichment of the PE phase on the IPN surface.

Influence of the reactor surfaces on the IPN morphology

The micrographs of structured PE/BMA-co-MMA IPNs (1 wt % peroxide, 1 mol % BDDM) that were synthesized with the Alu reactor are shown in Figures 4 and 5. Although regular surface morphologies can be seen, they seem to be charge dependent. The first



a)



b)

Figure 3 Porous (a) surface and (b) bulk morphology of the PE/DMA-co-EMA IPN (PTFE reactor, no BDDM, peroxide = 3 wt %, 800 kGy).

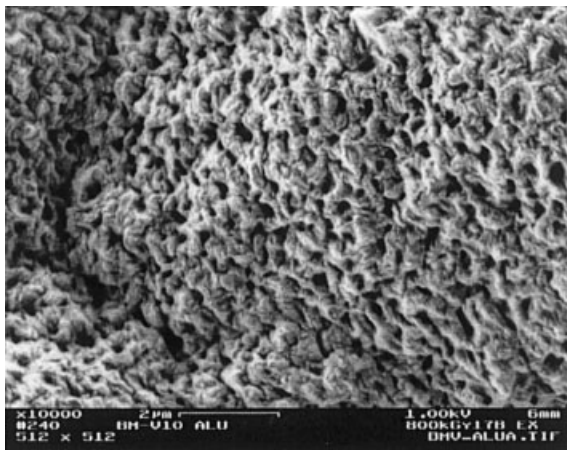


Figure 4 Porous surface structure of the PE/BMA-co-MMA IPN (Alu reactor, BMA/MMA = 50:50, BDDM = 1 mol %, peroxide = 1 wt %, 800 kGy).

kind of surface with a nominal pore size of 200 to 400 nm (Figure 4) appears less porous than the second one (Figure 5a), which has a pore size of 100 to 700 nm. In comparison to the morphology of the surface, the bulk phase of the second morphology possesses a rather porous structure (Figure 5b). The pore size corresponds to the category of microfiltration.¹ The matrix-particle morphology of the IPN can be clearly recognized.

The IPNs with the BMA/MMA molar ratio of 50:50 were brittle and thus difficult to handle when trying to test their membrane properties. Therefore, IPNs with 60 mol % BMA in the methacrylate phase were synthesized with the Alu reactor. As for the 50 : 50 composition a fine porous structure of the surface (Figure 6a) was obtained after the sample had been irradiated at 400 kGy and extracted with xylene. The micrograph of the cross-section (Figure 6b; the original membrane

surface is on the left-hand side) shows an evenly open porous structure without the tight skin that appeared in Figure 2. This structure is a prerequisite for the use of such membranes for microfiltration or ultrafiltration processes. As will be described later, this sample is permeable to water.

A similar porous surface structure was observed for the sample of PE/DMA-co-EMA, which was prepared with the Alu reactor in the presence of 1 mol % BDDM and 1 wt % peroxide (Figure 7). The irradiation dose was 800 kGy. In contrast to the PE/DMA-co-EMA IPN prepared without addition of crosslinker (Figure 3), the surface looks more like a particle matrix than a co-continuous morphology. This IPN is also permeable to water (vide infra).

Membrane properties

An interconnected porous structure is required for the microfiltration or ultrafiltration so that liquids to be separated can flow through the membrane material. The determination of the membrane properties was exclusively made on samples synthesized with the Alu reactor because the use of the PTFE reactor sometimes resulted in closed skin structures at the surface of the thin porous films. Samples synthesized under the same conditions and composition but from different batches were irradiated at 800 kGy and then extracted with xylene (Tables II–IV). To compare the effect of irradiation dose on the water flux, a sample irradiated at 400 kGy was also studied.

Samples of PE/BMA-co-MMA IPN (60 mol % BMA in the PMA phase) became permeable to water after irradiation and extraction with xylene (Table II). Their average water fluxes are ~ 100 L/h \cdot m² at 2 bar and seem not to be related to the irradiation dose. On the other hand, the samples of PE/DMA-co-EMA were

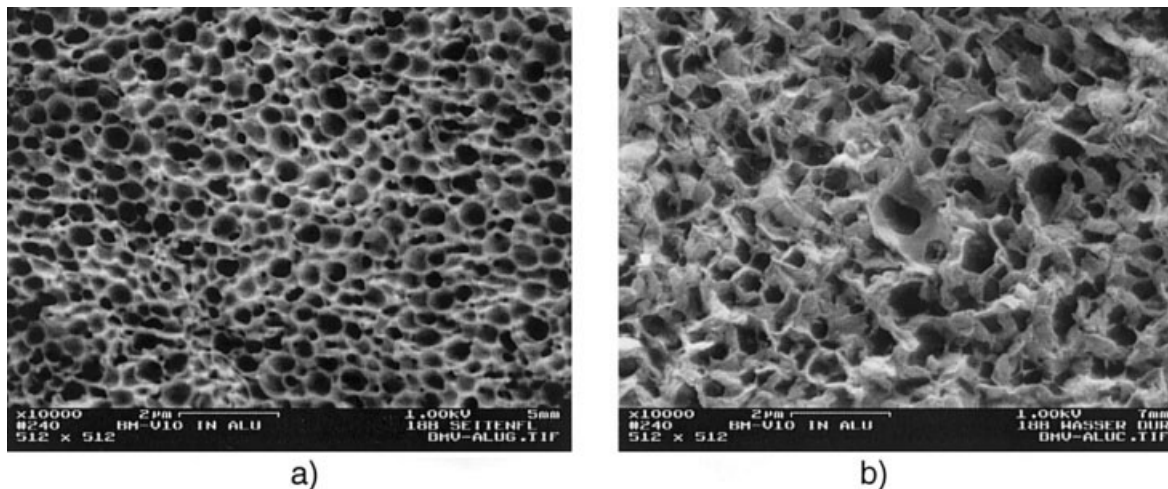


Figure 5 Porous (a) surface and (b) bulk morphology of the PE/BMA-co-MMA IPN (same material as in Figure 4, but different batch).

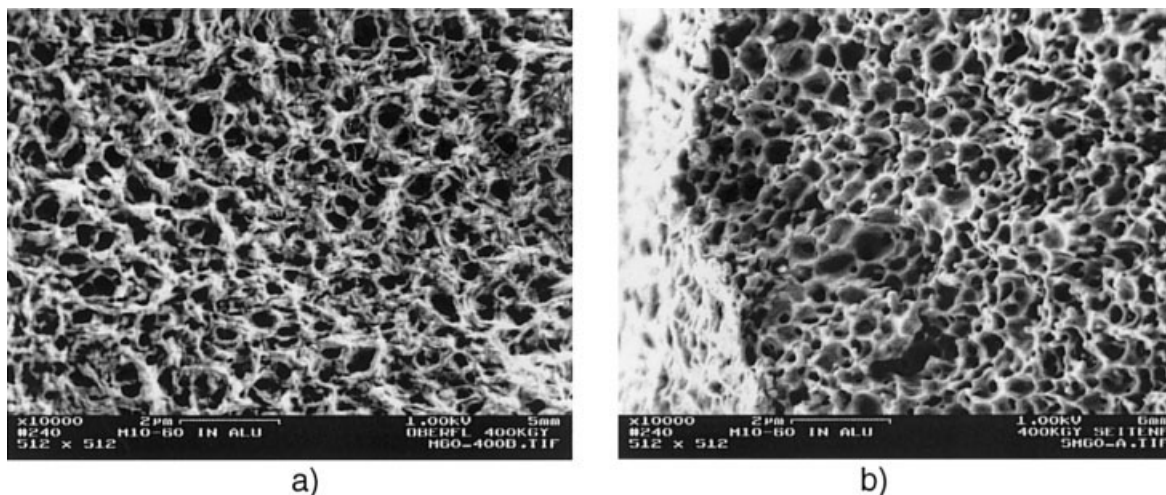


Figure 6 Porous (a) surface and (b) bulk morphology of the PE/BMA-co-MMA IPN (Alu reactor, BMA/MMA = 60:40, BDDM = 1 mol %, peroxide = 1 wt %, 400 kGy).

not permeable until they were extracted for a second time with boiling xylene. On the average, the water fluxes were lower than those of PE/BMA-co-MMA IPN. No water flux of the sample irradiated at 400 kGy could be obtained at 2 bar.

The differences in flux are attributed to two factors. One is the different radiation behavior of the polymethacrylates.¹⁷ The amount of radiation degradation of polymethacrylates depends on the length of their pendant groups. The longer the pendant groups are (as in the case of PE/DMA-co-EMA), the less is the degradation.^{10,12} Therefore, a smaller amount of PMA will degrade to extractable products, resulting in smaller pore contents. So, in the tested BMA-containing IPNs, the weight loss due to irradiation and extraction was >50%, whereas in the DMA-containing IPNs prepared under similar conditions with equal amounts of crosslinker and peroxide, only 33% could

be extracted. (Note: a gel content of 45 wt % was determined for the IPN with a methacrylate composition of BMA/MMA = 50:50, which was too brittle for testing the membrane properties. Because the amount of BMA in the IPN used for testing the membrane characteristics is only slightly higher, the gel content should be very similar). The compatibility of methacrylates with PE plays another part in the differing pore size. The good compatibility of DMA-containing PMA with PE results in a less pronounced phase separation, which leads to smaller domain size and therefore smaller pore size in the final membrane.

The determination of apparent rejection is one of the methods to characterize the pore size of membranes. Macromolecules, depending on their molecular weight, appear in a solution as do spherical coils. The coils that are larger than the pore size can not flow through the membrane under pressure but will be rejected at the feed side.¹ In the present work, linear macromolecules were used. Both IPN membranes

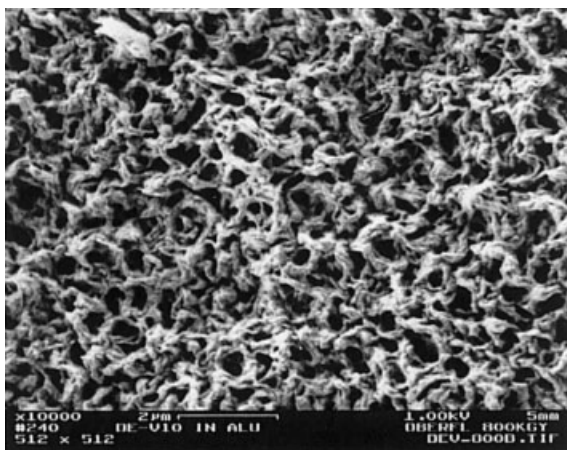


Figure 7 Porous surface structure of the PE/DMA-co-EMA IPN (Alu reactor, BDDM = 1 mol %, peroxide = 1 wt %, 800 kGy).

TABLE II
Water Flux of Membranes (800 kGy, 2 bar)

Batch no.	Flux, L/h · m ²	
	PE/BMA-co-MMA (BMA/MMA = 60:40)	PE/DMA-co-EMA (DMA/EMA = 20:80) ^a
1	30	8
2	97	8
3	100	46
4	57	26
5	99	12
6	165	42
7	107	0
8 ^b	110	0
Average	96 ± 40	18 ± 18

^a Extracted two times; 1 wt % peroxide; 1 mol % BDDM.

^b Irradiated at 400 kGy.

showed different molecular cutoffs. The PE/BMA-co-MMA membranes, which had higher fluxes, rejected no Kollidon 30, but they gave an apparent rejection of up to 44% to Dextran T2000 ($M_w 2 \times 10^6$) at 0.5 bar (Table III). This result means that this membrane has rejection properties that lie in the range of microfiltration.¹ In comparison, a rejection of up to 24.8% to Kollidon ($M_w 5.5 \times 10^4$) at 3 bar was found for the PE/DMA-co-EMA membranes (Table IV), which falls in the category of ultrafiltration. The results of both water flux and molecular cutoff show that the PE/BMA-co-MMA membranes possess a larger pore size than the PE/DMA-co-EMA membranes.

Unfortunately, the reproducibility of the membrane properties is still rather poor (Table II–IV). Although we tried to keep the preparation conditions constant, the water flux and the apparent rejection strongly varied, probably because of complexity and sensitivity of the overall membrane-forming process. Therefore, further work is necessary to improve the reproducibility of the membrane characteristics.

CONCLUSIONS

By partial degradation and extraction of the methacrylate phase in heterogeneous PE/PMA IPNs, an interconnected porous structure was formed that is permeable to water. The size of the obtained pores is dependent on the nature of the methacrylates used for the IPN syntheses and lies in the range suitable for microfiltration or ultrafiltration.

Although the reproducibility of the membrane characteristics is rather poor in this study, the results show that such PE/PMA IPNs are promising materials for

TABLE III
Apparent Rejection (R) of PE/BMA-co-MMA^a

Batch no.	R to Kollidon 30, %	R to Dextran T2000, %
1	2.1	11.4
2	1.1	14.9
3	1.1	1.7
4	1.9	32.0
5	2.8	6.6
6	0	1.4
7	0	1.9
8	0	24.3
9	0.5	18.0
10		44.0
11		29.0
Average	1.1 ± 1.0	16.8 ± 14.1

^a BMA/MMA = 60:40, 800 kGy, 0.5 bar.

TABLE IV
Apparent Rejection (R) of PE/DMA-co-EMA^a
to Kollidon 30^b

Batch no.	R to Kollidon 30, %
1	24.8
2	2.1
3	9.3
4	24.1
5	0.5
Average	12.2 ± 11.7

^a 1 wt % peroxide; 1 mol % BDDM.

^b 800 kGy; extracted twice; 3 bar.

the development of micro- or ultrafiltration membranes.

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