POLY(STYRENE-*CO*-DIVINYLBENZENE-*CO*-2-ETHYLH EXYL)ACRYLATE MEMBRANES WITH INTERCONNECTED MACROPOROUS STRUCTURE

POLI(STIREN-*KO*-DIVINILBENZEN-*KO*-2-ETILHEKSIL)AKRILATNE MEMBRANE S POVEZANO POROZNO STRUKTURO

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A combination of doctor blading and emulsion templating was used to prepare macroporous poly(styrene-*co*-divinylbenzene-*co*-2-ethylhexylacrylate) and poly(styrene-*co*-divinylbenzene) membranes with an interconnected porous structure. Water in oil high internal phase emulsions including monomers in the oil phase were cast onto a glass plate and polymerised at elevated temperature. After purification porous polyHIPE membranes were obtained. The volume ratio of aqueous phase (75 % or 85 %) and the molar ratio of divinylbenzene (2 % or 4 %) were varied, while the addition of chlorobenzene to the oil phase influenced the viscosity of the emulsions. A comonomer, 2-ethylhexylacrylate substantially improved the flexibility of the membranes. All yielding membranes were characterized by measuring their cast thicknesses and flow densities for deionised water. Scanning electron microscopy was used to study the morphological features of the membranes.

Keywords: membranes, porous polymers, polyHIPE, emulsions

Za pripravo makroporoznih poli(stiren-ko-divinilbenzen-ko-2-etilheksil)akrilatnih in poli(stiren-ko-divinil)benzenskih membran z odprto porozno strukturo smo uporabili kombinacijo nanosa z nožem in emulzij. Emulzije tipa voda v olju z visokim deležem notranje faze, z monomeri v oljni fazi smo nanesli na stekleno ploščo in polimerizirali pri povišani temperaturi. Po čiščenju smo pridobili porozne poliHIPE-membrane. Variirali smo volumski delež vodne faze (75 % ali 85 %) in molski delež divinilbenzena (2 % ali 4 %), medtem ko je dodajanje klorobenzena v oljno fazo vplivalo na viskoznost emulzije. Z dodatkom komonomera, 2-etilheksil akrilata so se elastične lastnosti membran bistveno izboljšale. Dobljene membrane smo okarakterizirali z merjenjem njihove končne debeline in merjenjem njihove pretočnosti za deionizirano vodo. Elektronsko vrstično mikroskopijo smo uporabili za študij morfoloških lastnosti membran.

Ključne besede: membrane, porozni polimeri, poliHIPE, emulzije

1 INTRODUCTION

Macroporous polymers with interconnected porous structure can be prepared by polymerising the continuous phase of a high internal phase emulsion. The most common definition of a high internal phase emulsion describes it as an emulsion where the volume fraction of the internal phase is very high, normally higher than 74 % (figure representing the maximum occupiable space by uniform spheres).[1] Polymers of this type are referred to as polyHIPEs.[2] Typically, hierarchically porous structure is obtained, with larger pores (referred to as cavities or voids) as the result of internal phase droplets and smaller connecting pores as a result of polymer shrinkage during the polymerisation. The most studied polyHIPE system is the styrene/divinylbenzene class material. Hydrophilic polyHIPE materials can also be prepared from HIPE emulsions.[3,4] Cooper *et. al* described the preparation of a number of polyHIPE materials using supercritical CO_2 in water (C/W) HIPE emulsions.[5] Other polyHIPE materials that have been investigated include those prepared from urea and

formaldehyde.[6] Monolithic polyHIPE materials from glycidyl methacrylate have also been described.[7,8] PolyHIPE material is suitable for a variety of applications, such as solid phase organic synthesis, separation of biomacromolecules, biocatalyst supports, water purification, sensors material, filtration, etc.[9] Due to relative simplicity of high internal phase emulsion preparation (although the issue of stability is frequently problematic) and its liquid form, a wide range of shapes and sizes of these porous materials can be prepared. It has been found that the nature of the mould substrate against which the polyHIPE material is prepared has a profound influence on its surface morphology and the degree of adhesion to the mould.[10] The influence of the substrate on the morphology of polyHIPE material is significant but not yet completely understood.[10,11] Problems with HIPE stability were encountered when using PVC as a mould substrate, which could be due to leaching of plasticizer. Even samples that did form tended to adhere to the substrate. Polypropylene did not result in adhesion, however, the surfaces polymerised against the substrate were largely of a closed-cell structure. This is probably

due to the presence of a surface film of monomer, caused by localised HIPE collapse at the HIPE-substrate interface. Different applications of polyHIPE materials require different materials properties, such as physical, mechanical, thermal, etc. Therefore good control over properties is desirable. One of these properties is elasticity. In order to increase flexibility, hydrophobic monomers, that produce low T_g polymers, such as 2-ethylhexylacrylate (EHA) and *n*-butyl acrylate (BA) are normally used.[12] In the case of using 2-ethylhexylacrylate, the lowering of T_g is the result of integration of the flexible 2-ethylhexylacrylate units into the polymer structure. The hydrophobicity of the plasticizing monomer ensures that emulsion stability is not compromised. Another very important characteristic of porous polyHIPE materials is their pore size. The average pore size can vary from about 1 μm to over 100 μm. It was noticed that increasing the DVB content in a styrene/DVB polyHIPE, from 0 % to 100 % DVB, caused a significant decrease in average void diameter from 15 μm to 5 μm.[13]

Most polyHIPE materials are prepared in a monolithic form following the shape of the mould. Thin films can be advantageous for numerous applications and in the case of polyHIPE membranes flexible mechanical properties are especially important. Furthermore, surface morphology is crucial for the performance of polyHIPE membranes.

In this paper, the preparation of styrene/divinylbenzene/ethylhexyl acrylate based polyHIPE membranes and the influence of monomer mixture, film thickness and added porogenic solvent on the morphology, is described.

2 EXPERIMENTAL

2.1 Materials and methods

Styrene (Merck), divinylbenzene (DVB, 80 %, tech.; Aldrich), 2-ethylhexylacrylate (EHA; Aldrich, 98 %) were purified by passing through basic alumina (Al₂O₃; Aldrich) to remove the inhibitors. Sorbitan monooleate (Span 80; Aldrich), chlorobenzene (CB; Aldrich), calcium chloride hexahydrate (CaCl₂ × 6H₂O; Merck), potassium persulphate (KPS; Fluka) were used as received.

Thicknesses of membranes were measured with MINIMER HD1 (Seltron), which is used for measurement of nonmagnetic coatings with accuracy 1 μm. Fluidity was measured with an ultrafiltration test cell AMICON, model 8400. Scanning electron micrographs were recorded on a Philips FEI XL30 ESEM.

2.2 Preparation of high internal phase emulsions and membranes

In a typical experiment, styrene, divinylbenzene and Span 80, 2-ethylhexylacrylate or chlorobenzene were placed in a 250 mL 3-neck round bottomed flask, and the mixture was stirred at 300 r/min with a glass stirring rod

fitted with a D-shaped polytetrafluoroethylene paddle, connected to an overhead stirrer motor. The aqueous phase was then added dropwise to the organic solution with continuous stirring. Once all the aqueous solution had been added, stirring was continued for further 30 min at 300 r/min to yield HIPEs. Both phases were degassed prior to use.

To prepare membranes, a doctor blade (slit 500 μm or 600 μm) was used to spread the HIPE emulsion onto a polished glass substrate ((300 × 300 × 15) mm). The spread of the emulsion was carefully covered with another glass plate ((300 × 280 × 3) mm) and heated to 60 °C for 24 h. After polymerisation, membranes were carefully retrieved from glass substrate, washed with deionised water and ethanol (both for 24 h) and then dried.

3 RESULTS AND DISCUSSION

Various methods can be used for the preparation of thin films of emulsions. With regards to polyHIPE membrane applications, the preparation method should be efficient and should offer the control of film thickness. Casting the emulsion onto a substrate using a doctor blade has already been demonstrated as an appropriate preparation procedure.[14] Doctor blades with different slits can be used to obtain films with various thicknesses.

Precursor emulsions with volume ratio of internal phase to continuous phase 7.5 to 2.5 and 8.5 to 1.5 were stabilised by sorbitan monooleate (Span 80, hydrophilicity lipophilicity balance number 4.3). Span 80 is a standard surfactant used for numerous water in oil high internal phase emulsions where hydrophobic monomers are used in the continuous phase and the amount of surfactant necessary for obtaining open porous structure is around mass fraction 20 % with regards to the continuous phase.[15] Emulsions A1, A2, A3 and A4 (**Table 1**) were prepared in that way, using mole fractions 2 % or 4 % of divinylbenzene in the continuous phase for crosslinking the styrenic chains. In our previous work, we have shown that higher degree of crosslinking reduces the flexibility of polymerised films to a degree that wrapping of membranes around a centimeter tube was not possible.[12] The casting of emulsions was done using a doctor blade on a polished glass substrate and it was found that a second glass plate was needed for retaining the emulsion stability until polymerisation. Generally, when preparing membranes from solution using doctor blading and subsequent polymer precipitation[16,17], the thickness of the resulting polymer membrane was close to the slit opening of the doctor blade used. In our work this was not the case and the resulting membranes were substantially thinner than the slit of the blade (**Table 2**). The explanation for this phenomenon lies probably in the viscous nature of the high internal phase emulsions. Since the shrinkage of polyHIPE with regards to precur-

Table 1: Preparation data for polyHIPE membranes
Tabela 1: Podatki za pripravo poliHIPE-membran

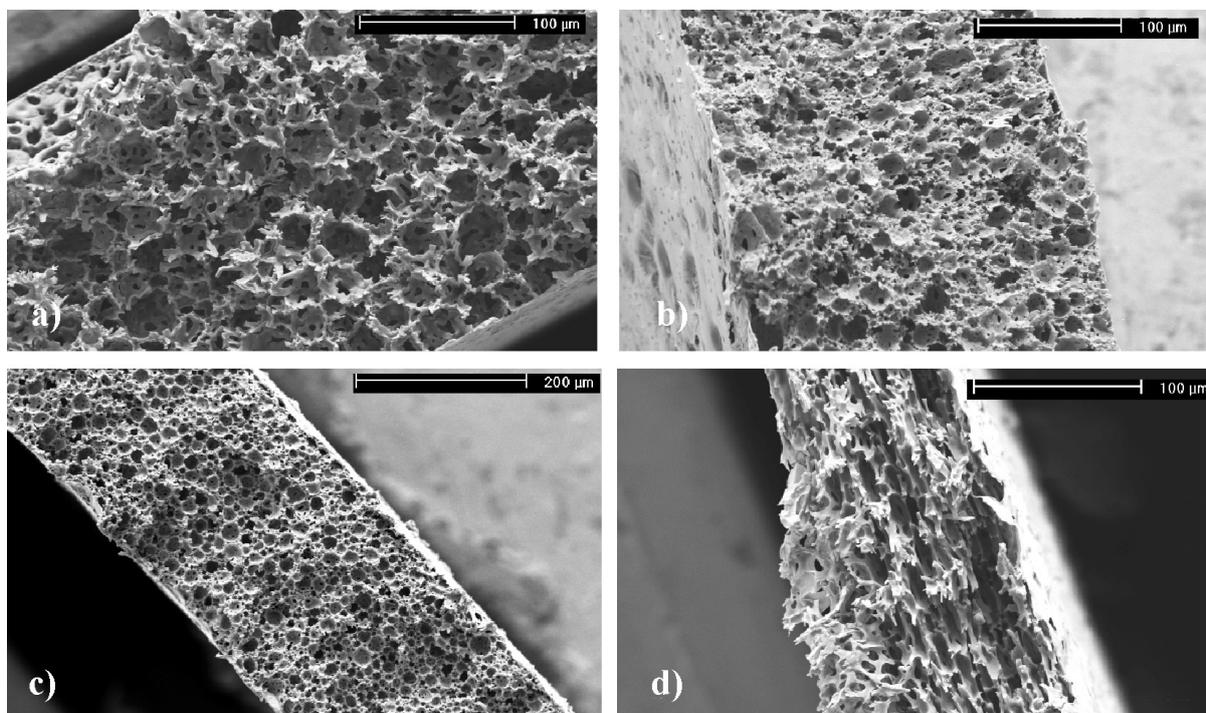| Membrane	PV^a/%	$X_{DVB}{}^b$/ %	$X_{EHA}{}^c$/ %	φ(porogen) /%	V (AP)^d/ mL	V (OP)^e/ mL	V (STY)/ mL	V (DVB) mL	V (EHA)/ mL	V (CB)/ mL
A1	75	2	0	0	12.1	4.87	3.91	0.13	0	0
A2	85	2	0	0	22.86	4.87	3.91	0.13	0	0
A3	75	4	0	0	12.18	4.81	3.81	0.25	0	0
A4	85	4	0	0	23	4.81	3.81	0.25	0	0
B1	75	2	10	0	13.08	5.16	3.51	0.13	0.73	0
B2	85	2	10	0	24.71	5.16	3.51	0.13	0.73	0
B3	75	4	10	0	13.16	5.19	3.41	0.25	0.73	0
B4	75	2	20	0	14.06	5.54	3.11	0.13	1.45	0
B5	85	2	20	0	26.56	5.54	3.11	0.13	1.45	0
B6	75	4	20	0	14.14	5.57	3.01	0.25	1.45	0
B7	75	2	30	0	15.04	5.93	2.71	0.13	2.18	0
B8	75	4	30	0	15.11	5.96	2.61	0.25	2.18	0
B9	85	2	30	0	28.41	5.93	2.71	0.13	2.18	0
C1	75	2	0	5	12.1	4.98	3.91	0.13	0	0.2
C2	75	4	0	15	12.18	5.42	3.81	0.25	0	0.61
C3	85	2	0	40	22.86	6.39	3.91	0.13	0	1.61
C4	85	4	0	50	23	6.84	3.81	0.25	0	2.03

^{a} pore volume (volume fraction of internal phase), ^{b} % mol of DVB, ^{c} % mol of 2-ethylhexylacrylate, ^{d} aqueous phase, ^{e}oil phase

Table 2: Thicknesses of membranes
Tabela 2: Debeline membran

Sample	A1	A2	A3	A4	B1	B2	B3	B4	B5	B6	B7	B8	B9	C1	C2	C3	C4
D^a/μm	500	500	500	500	600	600	600	600	600	600	600	600	600	500	500	500	500
$\overline{d}{}^b$/μm	231.5	253.6	174.7	286	380	397	344	305	407	403	223	251	115	78.3	162.2	174.4	340

^{a} slit opening on doctor blade, ^{b} average thickness of membrane

Figure 1: SEM images of the membranes A1 (a), B4 (b), B7 (c) and C1 (d)
Slika 1: SEM-posnetki membran A1 (a), B4 (b), B7 (c) in C1 (d)

sor emulsion is usually less than 10% (established from our work on monolithic polyHIPEs), we believe that the lower thicknesses of the resulting membranes are due to the thickness of the spread itself rather than subsequent shrinkage. However, a slight influence of emulsion composition on the final membrane thickness was also observed. Membranes A1 and A2 (same monomer composition, A1 with 75 % internal phase, A2 with 85 % internal phase) show a trend of increasing thickness with increasing pore volume. The same is true for membranes A3 and A4 and for the membranes including ethylhexyl acrylate (B1-B9). The reason again might be in different viscosity of emulsions with different phase volume ratios. Further experiments will however be needed to clarify this trend.

With regards to producing membranes with increased elasticity in order to meet the criteria of flexible films, a plasticizing comonomer, ethylhexyl acrylate (membranes B1-B9) was added to the oil phase of the emulsions. Visually, the emulsion stability was not compromised, using the same surfactant type and amount. The same can be concluded from SEM images (**Figure 1, b and c**). Together with a lower amount of crosslinking, the inclusion of EHA resulted in elastic membranes that could be easily wrapped around a one centimeter diame-

ter tube. However, permeability results have shown that a high degree of EHA content increases back pressure of the membranes so a compromise in mechanical and permeable characteristics needs to be reached with a specific application in mind.

Scanning electron microscopy inspection of cross sections of membranes (**Figure 1**) revealed open porous structure in all cases. Larger pores, in diameter ranging from 18 μm (B4) to 32 μm (A1), are connected by a series of interconnecting smaller pores. The size of the bigger pores reflects the emulsion preparation and kinetic stability since the creation of large pores is the consequence of non monomer containing droplet phase and the size of the droplets guides the pore size. As we can see from **Table 3**, membrane B7 with the highest share of 2-ethylhexylacrylate has the least opened structure. We believe the reason for this is the stabilizing effect of this hydrophobic monomer on the emulsion. FTIR spectroscopy of membranes (typical examples shown in **Figure 2**) confirm the inclusion of 2-ethyl-hexylacrylate in the polymer matrix in the case of B samples. The signal at 1729 cm^{-1} represents the carbonyl group of acrylate ester and this signal is not present in the spectra of samples A and C which do not include 2-ethylhexylacrylate.

When comparing polyHIPE membranes to polyHIPE monoliths, more attention in the case of membranes has to be devoted to the surface since there is no possibility of removing a layer prior to application. The importance of casting substrate for open surface of polyHIPE membranes has already been demonstrated.[8] Images of membrane surfaces, in most cases, show the open

Table 3: Pore size data
Tabela 3: Velikosti por

	A1	B4	B7	C1
$\overline{D}^a$/μm	31.6	18.3	21.1	22.0
$\overline{d}^b$/μm	9.6	7.0	5.2	7.7
$(\overline{d}/\overline{D})$	0.30	0.38	0.24	0.34

[a] average pore diameter, [b] average interconnecting pore diameter; both determined from SEM images

Table 4: Permeability of the membranes for deionised water
Tabela 4: Prepustnosti membran za deionizirano vodo

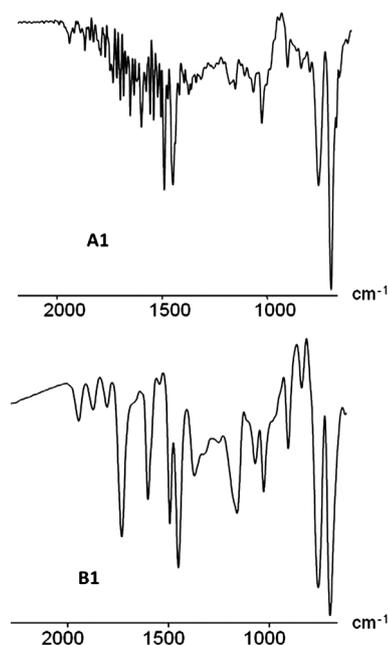| sample	p/bar	J (kg/m^2 h)	sample	p/bar	J (kg/m^2 h)
	0.5	36.9		0.5	2.9
A1	1	54.7	B4	1	2.9
	2	64.1		2	5.7
	0.5	25.25		0.5	0.8
A2	1	30.00	B6	1	1.0
	2	48.87		2	1.9
	0.5	87.1		0.5	4.75
A4	1	66.8	B7	1	6.79
	2	95.7		2	7.74
	0.5	32.6		0.5	0.8
B1	1	468	B8	1	0.8
	2	550		2	0.8
	0.5	36.2		0.5	-
B2	1	48.2	B9	1	4.8
	2	64.2		2	6.8
	0.5	3.8		0.5	117.4
B3	1	4.9	C4	1	127.9
	2	16.7		2	138.2

Figure 2: FTIR spectra of membranes A1 (no 2-ethylhexylacrylate) and B1 (10% 2-ethylhexylacrylate)
Slika 2: FTIR-spektra membran A1 (brez 2-etilheksil akrilata) in B1 (10 % 2-etilheksil akrilata)

polyHIPE morphology also on the surface of the membranes. This finding is important especially for applications where convective mass transfer is preferred. The high viscosity of the emulsions was occasionally causing inhomogeneous cast on the substrate. In order to address this issue, we attempted to reduce the viscosity by the addition of an organic solvent, namely chlorobenzene (CB). Improved homogeneity of the spread was observed, especially when the share of the solvent as high as the volume fraction of 40 % (in relation to oil phase) had been used.

To characterize the permeability properties of poly-HIPE membranes, the flux of deionised water through the membranes at a given pressure was measured (see **Table 4**). Membranes including ethylhexyl acrylate (B1-B9) have a lower flow density than the basic membranes (no 2-ethylhexylacrylate) and, generally, their flow density decreases with the increasing share of 2-ethylhexylacrylate. The results of flow properties are not in evident relation to pore sizes as measured from SEM images. However, the actual flow characteristics were measured from membranes immersed in water while SEM images were taken from dry samples and real "wet" morphology can differ from what is evident from SEM.

4 CONCLUSIONS

Results of this work have shown that high internal phase emulsions with internal phase volume ratio up to 85 % including styrene, divinylbenzene and ethylhexyl acrylate in the continuous phase, can be used for templating the porosity in thin polymer films. Addition of a plasticizing monomer enabled the tailoring of flexibility and did not compromise the precursor emulsion stability. Resulting membranes were between 80 μm and 407 μm thick and had an open porous structure which enabled the flow through applications; furthermore, by changing the monomer composition, the flow could be substantially affected.

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