Effect of Soxhlet Extraction and Surfactant System on Morphology and Properties of Poly(DVB)PolyHIPE

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Summary: Poly(Divinylbenzene)PolyHIPE (Poly(DVB)PolyHIPE) was successfully prepared by using two different systems of three-component surfactants (S20M and S80M) and toluene as porogenic solvent. Phase morphology, mechanical properties and surface area measurements of the obtained Poly(DVB)Poly HIPE were investigated. After polymerization of continuous phase followed by extraction process, the porous materials (open cellular structure with interconnections) were obtained. The cell size and surface area were found to be improved: this is due to the ability of porogenic solvent and mixture of the surfactants to prevent the Ostwald ripening (coalescence) of the emulsion droplet system. Moreover, the surface area and mechanical properties of the resulting materials were found to be depended on the Soxhlet extraction time. It was demonstrated that the usage of Soxhlet extraction technique for Poly(DVB)PolyHIPE improved surface area of the obtained materials by 107% as compared with the unextracted PolyHIPE. However, when the extraction time was longer than 12 hours, the properties of the obtained materials became poor. It was concluded that the suitable Soxhlet extraction time for Poly(DVB)PolyHIPE was 6–12 hours and at this condition, high surface area with the highest mechanical properties of the porous material were obtained.

Keywords: high internal phase emulsion; Poly(DVB)PolyHIPE; PolyHIPE; porogenic solvent; three-component surfactant

Introduction

PolyHIPE (Polymerized High Internal Phase Emulsion) is a novel porous polymer produced by polymerization of the continuous phase in a two phase system, which consists of organic or continuous phase and the aqueous or droplet phase.[1–3] The organic phase, generally less than 26% of the total volume, composes of a monomer, a suitable surfactant and a cross-linking comonomer. The aqueous phase (droplet phase) is usually contained water with

water soluble initiator and stabilizer. By introducing droplets of aqueous phase in the organic mixture under mechanical stirring, an emulsion is produced. During the polymerization of the continuous phase, this leads to the formation of highly porous material with interconnections and very low density. Due to PolyHIPEs many outstanding properties, they are employed in many applications such as Poly(S/DVB)PolyHIPE modified with bioactive molecules can offer an alternative used as a scaffold for biomedical applications[4–7] and Poly(GMA/EGDMA)PolyHIPE are used as a separation medium.[8] Additionally, PolyHIPE porous materials are used as ion exchange membranes,[9] catalyst supports[10] and a filtration media,[11] where high surface area is required. Previous studies reported that the use of a mixture

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of nonionic, anionic and cationic surfactants led to the increase in surface area and reduce in the cell sizes of PolyHIPE materials.[2] This is because of the effectiveness of the mixture of surfactants to form strong interfacial film around each emulsion droplet, leading to the enhance emulsion stability and prevent Ostwald ripening (destabilization mechanism) of the system. Moreover, results from the literatures reported that there are other ways to improve surface properties of PolyHIPE polymer; the cell size and surface area of PolyHIPE materials were strongly affected by the concentration of crosslinking comonomer,[12–13] amount of surfactant[14] and type of inert diluent solvent (porogen).[1,12,15] High surface properties of PolyHIPE will be obtained when secondary pore structures are generated within the cell walls by combination of three factors i.e. porogenic solvent, high level of crosslinking comonomer and suitable surfactant concentration.[12,15–16] Generally, PolyHIPE polymer with closed-cell type is also formed because the internal aqueous phase including toxic monomers, residual surfactants and porogenic solvent is trapped within the cellular structure of PolyHIPE porous polymer. This leads to PolyHIPE materials with low surface properties. To overcome this problem, the Soxhlet extraction technique is needed to remove the residual materials out from pore structure of PolyHIPE then the resulting materials with high surface properties are obtained.[17]

Furthermore, PolyHIPE morphology was found to be affected by the nature of surfactant used in the preparation.[18–19] The resulting properties of PolyHIPE prepared from different surfactants would not be the same. PolyHIPE with Span80 as a surfactant produced stable emulsion droplets and uniform cell size, similar to that of Span20, a surfactant with a high HLB balance (HLB 8.6) was able to form emulsion with small cell size and uniform size distribution.[18] Conversely, Williams *et al.*[19] also reported that Span80, a surfactant with low HLB balance (HLB

4.3) could act as the most suitable surfactant to produce stable emulsion for Poly(S/DVB)PolyHIPE system.

As part of our work, nature of surfactant on the characteristic of PolyHIPE was studied, PolyHIPE materials containing divinylbenzene were synthesized by using three different systems of surfactant including S80 (single surfactant), S80M and S20M (mixed surfactant; three-component surfactant) in order to investigate the effect of different systems of mixed surfactant. Effect of Toluene as porogenic solvent on the characteristic of the obtained PolyHIPE was also carried via the comparison between polyHIPE prepared with the addition toluene (T) as porogenic solvent (S80M_T and S20M_T) and PolyHIPE prepared without toluene as porogenic solvent (S80M and S20M). To further improve the surface properties and mechanical properties of the obtained PolyHIPE, studies of the effect of Soxlet extraction on the characteristic of PolyHIPE was carried out. Soxhlet extraction was applied on the obtained PolyHIPE by varying extraction time from 0–48 h.

Results from the experiments suggested that cell size and surface area were improved by using a three-component surfactant system with toluene as porogenic solvent. Additionally, Soxhlet extraction technique on PolyHIPE polymer was found to have an effect on the surface area and mechanical properties. The removal of residual monomer, surfactant and porogenic solvent by extraction technique resulted in the improvement of PolyHIPE properties such as surface area of the obtained PolyHIPE increased by 107% as compared with unextracted PolyHIPE.

Experimental Part

Materials

Divinylbenzene (DVB, Merck) was used as monomer to produce PolyHIPEs. Surfactants used in the study were cetyltrimetylammonium bromide (CTAB, Fluka Chemie), sorbitant monooleate (Span80; S80),

sorbitant monolaurate (Span20; S20) and dodecylbenzenesulfonic acid sodium salt (DDBSS), all surfactants were purchased from Sigma-Aldrich Chemical. The initiator and stabilizer used in the experiments were potassium persulfate ($K_2S_2O_8$, purity $\geq$98% (RT), Fluka Chemie) and calcium chloride ($CaCl_2$, purity $\geq$97% (KT), Fluka Chemie) respectively. Toluene (T) and isopropanol were used as received.

PolyHIPE Preparation

Poly(DVB)PolyHIPEs were prepared by polymerization of organic phase as described by Barbetta *et al.* and Hainey *et al.*[2,12] Single surfactant (S80) and two different mixtures of surfactant systems which were S80M (Span80, CTAB and DDBSS) and S20M (Span20, CTAB and DDBSS) were studied in this work. Toluene (T) was used as porogenic solvent (S80M_T denotes the Poly(DVB)Poly-HIPE prepared with toluene as porogenic solvent using S80M system as surfactant and S20M_T denotes the Poly(DVB)Poly-HIPE prepared with toluene as porogenic solvent using S20M system as surfactants). By added the aqueous phase (water; 90 ml, $K_2S_2O_8$ (0.2 g) and $CaCl_2$ (1.0 g)) drop-wise to an organic mixture (10 ml; contained monomer and porogen (1:1 ratio by volume)) with mechanical stirring to form PolyHIPE emulsion. The resulting mixture was placed in a water bath at 60 °C for 48 h for polymerization. After that the obtained solid materials was removed from mold and the remaining solvents were extracted with isopropanol by varying Soxhlet extraction time (0, 1, 3, 6, 12, 24, 48 h) before drying in a vacuum oven at 60 °C until a constant weight was obtained.

Characterization

Surface Properties

N_2 adsorption/desorption isotherms were obtained at -196 °C on a Quantachrome Autosorb I using a BET model. Samples were degassed at 100 °C for 12 hours in a vacuum furnace prior to analysis. Surface areas were calculated using the BET equation and pore volumes were determined by the t-plot method of De Boer. The pore size distributions were constructed based on Barrett, Joyner and Halenda (BJH) method using the adsorption branch of the nitrogen isotherm.

Morphology

Scanning electron microscope used in the morphology study of the obtained samples was JEOL (MP 152001 Model), operated at 15 kV and 500× and 1000× magnification. The specimens were coated with gold under vacuum before analysis. Transmission electron microscopy was also used in this studied to observe the morphology of the obtained materials. TEM micrographs was taken on a Tecnai G2 Sphera electron microscope with an accelerating voltage of 80 kV to observe the pore structure and secondary pore in the cell wall of Poly (DVB)PolyHIPE. Micrographs were recorded at magnifications of 3500× and 7800× magnification. TEM samples were prepared by embedding PolyHIPE in a support resin and sectioning on an ultra-thinmicrotome. The thin sections were supported on 300 mesh copper grids.

Mechanical Properties

A Lloyd Universal testing machine was used to measure mechanical properties of the obtained PolyHIPEs. The tests were carried out according to ASTM D822. The test specimens were prepared with 2.54 cm diameter ×2.54 cm high cylinders. A speed of 1.27 mm/min and 500 KN load cell were used for all measurements. The value of the compression strength and Young's modulus were determined.

Results and Discussion

Effect of 3-Component Surfactants on Phase Morphology and Surface Properties of Poly(DVB)PolyHIPE

Figure 1 shows SEM micrographs of Poly(DVB)PolyHIPE prepared by a single (S80) surfactant (Figure 1a) and three-component surfactants (S20M and S80M)
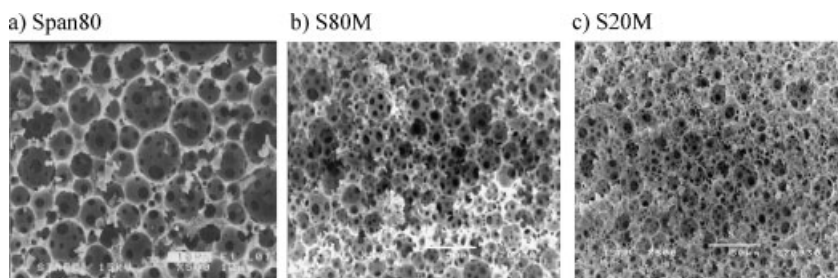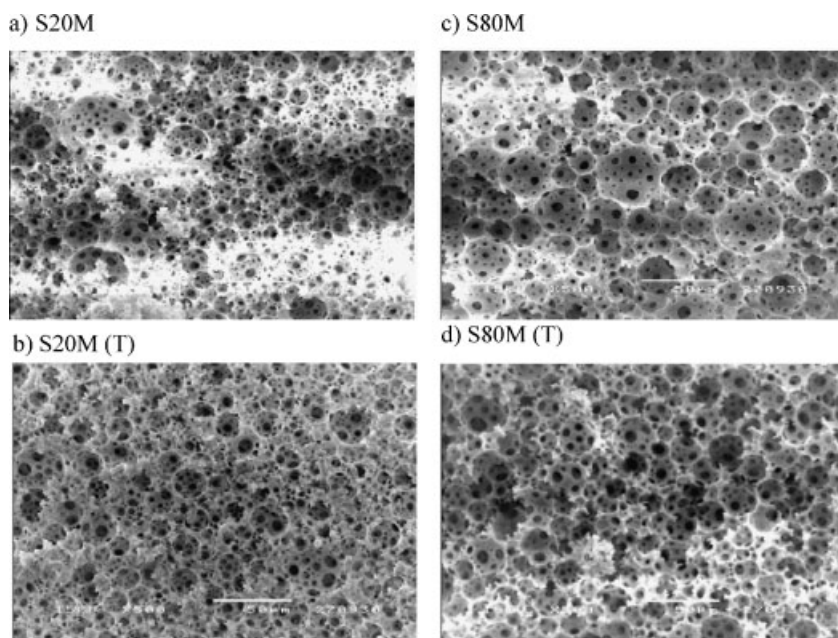
Figure 1.
Selected scanning electron micrographs of Poly(DVB)PolyHIPE; a) Span80 (single surfactant), b) S80M (three-component surfactant) and c) S20M (three-component surfactant).

(Figure 1b and 1c respectively). Morphology of the two different materials prepared from three-component surfactant systems (S20M and S80M) gave a relatively similar appearance. The cell sizes of Poly (DVB)PolyHIPE were found to reduce when a mixed surfactant was applied. This may due to the formation of a strong interfacial film around the emulsion droplet by the mixed surfactant leading to the prevention of Ostwald ripening (coales-cence) and an increase in stability of the system.[1–2]

SEM micrographs of Poly(DVB)Poly-HIPE with porogenic solvent; toluene (T) are shown in Figure 2. S20M was use as surfactant system in Figure 2(a-b) whereas in Figure 2(c-d) S80M surfactant system was used. The morphology of PolyHIPEs obtained from these two different surfactant systems were relatively similar, the results also showed that the cell sizes were
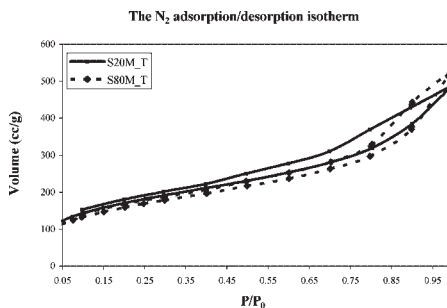

Figure 2.
Scanning electron micrographs of Poly(DVB)PolyHIPE; a-b S20M was used as surfactant (2a is the sample without toluene as porogenic solvent and 2b is the sample with toluene as porogenic solvent) whereas c-d S80M was used as surfactant (2c is the sample without toluene as porogenic solvent and 2d is the sample with toluene as porogenic solvent).

reduced with the presence of many pores was observed. These observations indicated the ability of both porogenic solvent and mixed surfactant systems to increase emulsion stability of the system.[1,2,12] Surface areas of the obtained materials tended to increase, from 10.49 to 568.7 m^2/g, when a three-component surfactant systems (both S20M and S80M) with toluene (non polar solvent) were used. This might be due to the enhancement of emulsion stability and formation of secondary pore structure within the cell wall of Poly(DVB)Poly-HIPE (see Table 1). The N$_2$ adsorption/desorption isotherm of Poly(DVB)Poly-HIPE after extraction are shown in Figure 3 and the parameters of which they were prepared are listed in Table 1. The isotherms of S80M_T and S20M_T system were found to be relatively similar. The shape of isotherms for both PolyHIPEs prepared from the different surfactant systems (S20M_T and S80M_T) shows a hysteresis loop which may belongs to a type IV BET isotherm according to the BDDT classification. The BET specific surface area of the extracted Poly(DVB)PolyHIPEs with toluene as porogenic solvent were between 560–570 m^2/g. It could be noted that both phase morphology and specific surface area of Poly(DVB)PolyHIPE tended to increase with the use of both the three-component surfactant (S80M and S20M) and the inert porogenic solvent.

Effect of Soxhlet Extraction Time on Surface Area, Phase Morphology and Mechanical Properties of Poly(DVB)PolyHIPE.

The effect of Soxhlet extraction time on phase morphology of Poly(DVB)Poly-HIPE is shown in Figure 4. Figure 4a shows

Figure 3.
N$_2$ adsorption/desorption isotherm of Poly(DVB)Poly-HIPE.

Poly(DVB)PolyHIPE prepared using S20M as surfactant system and toluene as porogenic solvent and Figure 4b shows Poly(DVB)PolyHIPE prepared using S20M as surfactant system with toluene as porogenic solvent that had been subjected to Soxlet extraction. The morphology of these two samples (Figure 4a and 4b) were found to be quite similar. However, SEM micrograph of Poly(DVB)PolyHIPE with Soxhlet extraction technique (Figure 4b) shows a more open cellular morphology than Poly(DVB)PolyHIPE prepared without Soxhlet extraction (Figure 4a). This observation was supported by surface area measurement which showed an increased in surface area by 58–107% when the Soxhlet extraction was applied (see Table 2). This observation could be further confirmed by TEM micrographs which show clear evidence of secondary pore structures within the cell wall of PolyHIPE when Soxhlet extraction technique was used (see Figure 5).
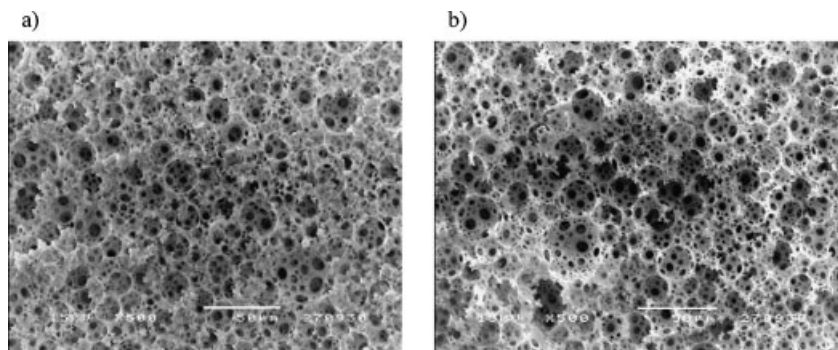
In this study, Poly(DVB)PolyHIPE was extracted with isopropanol by varying extraction time from 0 to 48 hours (0, 1,

Table 1.
Surface properties of Poly(DVB)PolyHIPE prepare with and without toluene as porogenic solvent.

Sample type Poly(DVB)PolyHIPE	Specific Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
S20M	10.49	0.006	1.53
S20M_T	568.70	0.510	1.36
S80M	11.16	0.007	1.39
S80M_T	564.97	0.810	1.35

Figure 4.
Scanning electron micrographs of Poly(DVB)PolyHIPE; a) S20M_T without Soxhlet extraction, b) S20M_T with Soxhlet extraction.
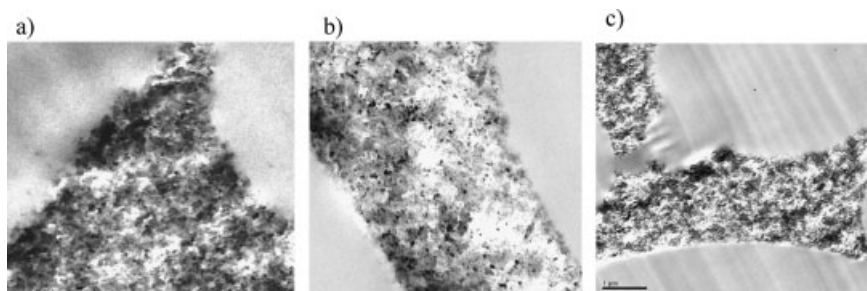
Table 2.
Surface properties of Poly(DVB)PolyHIPE with various Soxhlet extraction times.

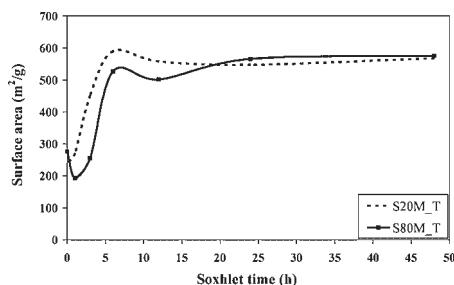| Surfactant system	Soxhlet time (h)	Specific surface areas (m²/g)	Surfactant system	Soxhlet time (h)	Specific surface areas (m²/g)
S20M_T	48	568.70	**S80M_T**	48	564.97
	24	547.60		24	539.25
	12	558.50		12	498.60
	6	590.20		6	526.50
	3	451.05		3	247.05
	1	270.25		1	186.80
	0	284.23		0	277.30

3, 6, 12, 24, 48 h). Although, preliminary results suggested that in preparation of PolyHIPE polymer, the extraction process is needed to remove the residue starting materials from pore structures which in turn would increase the surface properties of the obtained materials. However, when extraction time was longer than 12 hours, properties of the obtained materials were found to be reduced. It was found that the

structure of Poly(DVB)PolyHIPE foam could not be maintained and the mechanical properties of the material were reduced. From this observation, the optimum Soxhlet extraction time, to achieve the good properties (both surface area and mechanical properties) of Poly(DVB) PolyHIPE, was investigated. The extracted Poly(DVB)PolyHIPEs were dried and fabricated for mechanical property tests
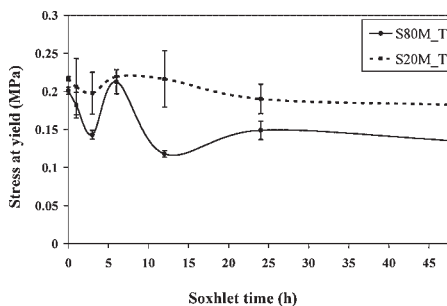

Figure 5.
TEM micrographs of Poly(DVB)PolyHIPE; a) without Soxhlet extraction, b) S20M_T with Soxhlet extraction 6 h, c) S80M_T with Soxhlet extraction 6 h.

and surface area measurements. Table 2 shows that surface area of both S20M_T and S80M_T system were depended on Soxhlet extraction time. At low extraction time (1–3 h), the results indicated that it was insufficient to remove the residual materials from pores of the obtained polyHIPEs. The surface area of Poly(DVB)PolyHIPE was low due to some residual materials remained and trapped within the pores structure of the obtained polyHIPEs. For S20M_T system the optimum extraction time to achieve the highest surface area was 6 h (surface area increased by 107% compared with the sample that had not been subjected to extraction process) whereas S80M_T system needed around 12–24 h (surface area increased by 95% compared with sample that had not been subjected to extraction process) to remove nearly all the residue materials from the obtained PolyHIPE (see Figure 6). The difference in the optimum extraction time could be due to the different nature of surfactants; Span80 in S80M had longer alkyl chain and was also less polar than Span 20 in S20M system, therefore the residue solvent tended to adsorb onto the polymer much stronger in the S80M system and made it more difficult to remove from the pore structures. Therefore, longer Soxhlet extraction time was required to remove the residue solvent from S80M system when compared with S20M system. Additionally, the mechanical properties of Poly(DVB)PolyHIPE were also found to rely on Soxhlet extraction time. The longer the extraction time used, the higher the
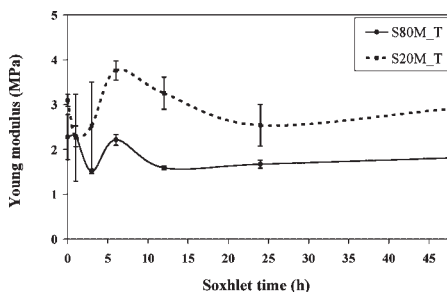

Figure 7.
Effect of Soxhlet extraction time on compression stress of Poly(DVB)PolyHIPE.

reduction of the mechanical properties of the resulting materials. This might be due to the damage to the structure of PolyHIPE by solvent extraction process. Figure 7 and 8 represent compressive stress and Young's modulus of PolyHIPE respectively. The results showed that both compressive stress and Young's modulus were highest at Soxhlet extraction time of 6 h. Therefore, it might possible to conclude that the optimum condition for Soxlet extraction using isopropanol on Poly(DVB)PolyHIPE was 6–12 hours. At this condition, Poly (DVB)PolyHIPE with high surface area and high mechanical properties would be obtained for both S80M_T and S20M_T system.

Conclusions

Poly(Divinylbenzene)PolyHIPE prepared from a single surfactant (Span80; S80),

Figure 6.
Effect of Soxhlet time on surface area of Poly(DVB) PolyHIPE.

Figure 8.
Effect of Soxhlet extraction time on Young modulus of Poly(DVB)PolyHIPE.

two different systems of three-component surfactants (S20M and S80M), with and without toluene as porogenic solvent were carried out. After polymerization of the continuous phase, the porous materials with interconnected pores were obtained. Morphology of the resulting materials was improved when a three-component surfactant (S20M or S80M) was employed. In addition, the use of S20M and S80M as a three-component surfactant with toluene as porogenic yielded Poly(DVB)PolyHIPE with substantially increased surface properties. This situation could be due to the formation of secondary pore structures within the cell wall of the resulting materials. Samples prepared using S20M and S80M surfactants with toluene as porogenic solvent showed relatively similar characteristics which indicated the effectiveness of the two three-component surfactants for use in preparation of Poly (DVB)PolyHIPE. Highest surface area of poly(DVB)PolyHIPE was achieved when materials was further subjected to Soxlet extraction process. The optimum Soxlet extraction time to achieve the highest surface area with the best mechanical properties for both S20M and S80M systems was Soxhlet around 6–12 hour. Surface area of Poly(DVB)PolyHIPE subjected to 6–12 hours of Soxlet extraction was found to increase by 95–107% when compared with samples which did not undergo of extraction process.

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