

Functionalised Macroporous Films via Emulsion Templating: Preparation, Processing and Applications

Qixiang Jiang

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Department of Chemical Engineering
Imperial College London

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Declaration

I declare here that the work presented in this thesis is my own investigation carried out in Imperial College London during the period from December 2008 to August 2012. Every work, which is not my own has been properly acknowledged.

Content

Declaration	2
Abstract.....	6
Acknowledgment.....	8
List of Symbols and Abbreviations.....	9
List of Figures	13
List of Tables	16
Chapter 1 Introduction	17
Chapter 2 Literature Review.....	19
2.1 Porous polymers	19
2.2 Hydrogel Membranes.....	22
2.2.1 Introduction	22
2.2.2 Preparation of hydrogel membranes.....	23
2.2.3 Swelling behaviour of hydrogels.....	24
2.2.4 Applications of hydrogel membranes	25
2.3 Emulsion templating	27
2.3.1 Introduction.....	27
2.3.2 Preparation of macroporous polymers.....	28
2.3.3 Fundamental research of polyHIPEs	35
2.3.4 Applications of polyHIPEs	38
Chapter 3 Preparation of macroporous polymer films	44
3.1 Introduction	44
3.2 Experiment.....	45
3.2.1 Materials.....	45
3.2.2 Particle modification	46
3.2.3 Emulsion preparation	46
3.2.4 Film preparation and polymerisation	48
3.2.5 Characterisation	49
3.3 Results and discussion.....	50
3.4 Conclusions	64

Chapter 4 Hydrogel filled polyHIPEs via emulsion templates	66
4.1 Introduction	66
4.2 Experiment.....	67
4.2.1 Materials.....	67
4.2.2 Preparation of hydrogel filled St-DVB based polyHIPEs.....	68
4.2.3 Characterisation	70
4.3 Results and Discussion	71
4.4 Conclusion.....	80
Chapter 5 Poly(methacrylic acid) filled polyHIPEs and their applications as ultrafiltration membranes.....	82
5.1 Introduction	82
5.2 Experiment.....	84
5.2.1 Materials.....	84
5.2.2 Preparation of hydrogel filled EHA-St-DVB based polyHIPEs.....	84
5.2.3 Characterisation	86
5.3 Results and discussion.....	87
5.4 Conclusion.....	97
Chapter 6 Tough polyurethane foams prepared via emulsion templating.....	99
6.1 Introduction	99
6.2 Experiment.....	100
6.2.1 Materials.....	100
6.2.2 Preparation of polyH(M)IPEs	101
6.2.3 Characterisation	102
6.3 Results and Discussions.....	102
6.4 Conclusion.....	107
Chapter 7 Flexible polyHIPE films via UV polymerisation and their applications for pressure-sensitive devices	108
7.1 Introduction	108
7.2 Experiment.....	110
7.2.1 Materials.....	110
7.2.2 Modification of silica particles	111
7.2.3 Preparation of emulsion templates	111
7.2.4 Characterisation	112
7.3 Results and discussion.....	113

7.4 Conclusions	126
Chapter 8 Conclusions and recommendations for future work	127
8.1 Conclusions	127
8.2 Recommendations for future work.....	128
Reference	131
Appendix.....	139

Abstract

Polymerised high internal phase emulsions, or polyHIPEs, refer to the macroporous polymers prepared via emulsion templating. PolyHIPEs are usually characterised by high porosity and interconnectivity and low density, which make them applicable in tissue engineering, construction materials and catalyst supports. However, the exploration of polyHIPE films is very limited so far. Thus this thesis will describe the works on designing flexible and tough functionalised macroporous films that are for a variety of applications.

Poly(methacrylic acid) (poly(MAA)) and poly(dimethyl aminoethyl methacrylate) filled polyHIPEs were firstly prepared and characterised. The hydrogels were grafted on the surface of the pore walls in the polyHIPE scaffolds. Subsequently, poly(MAA) filled polyHIPEs were sliced into membranes and their performances were tested. The permeability and selectivity of the membranes are highly affected by the pH value of the feed solution due to the pH-sensitivity of poly(MAA). The membranes with 2% crosslinking degrees in poly(MAA) had a cut-off of 50K polyethylene glycol, suggesting applications for ultrafiltration.

In the following work, mechanical properties of macroporous monoliths and films were tailored. Polyurethane diacrylate (PUDA), which is a long chain crosslinker, was copolymerised within emulsion templates to modify the mechanical properties of polyHIPEs. These macroporous polymers based on PUDA and styrene were less brittle than the conventional poly(styrene-divinylbenzene)HIPEs and possessed enhanced elastic moduli and crush strengths compared to poly(styrene-polyethylene glycol dimethacrylate)HIPEs. The tough polyHIPEs are expected to be used as scaffolds for membranes or catalysts. Subsequently, very flexible macroporous films were prepared by casting and UV polymerising emulsion templates based on PUDA and ethylhexyl acrylate. The films possessed breaking strains up to 30%. Moreover, the films showed constant mechanical behaviour under relaxation tests and cyclic tests, suggesting the capability for long term use. The films will be further designed for pressure sensor applications.

A novel method to prepare macroporous films was developed in this project. Emulsion templates were printed either by rolling-pin or screen and UV polymerised subsequently, resulting in patterned macroporous films. The experiment showed that the printing process did not damage the porous structure of the films. Additionally, it is feasible to multilayer print the emulsion templates to create 3D or complex structure.

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List of Symbols and Abbreviations

Symbol	Parameter	Unit
A	Efficient surface area of membranes	m ²
C _p	concentration of solute at the permeate solution	g/L
C _r	concentration of solute at the rejected solution	g/L
E ₁	Elastic modulus of spring	MPa
E ₂	elastic modulus of spring in Standard Linear Solid model	MPa
F	water flux	L·m ⁻² ·h ⁻¹
HLB	Hydrophobic-lipophilic balance	-
LCST	lower critical soluble temperatures	°C
m	weight	g
m _d	Weight of dry samples	g
m _w	Weight of wet samples	g
Mw	molecular weight	Da or g/mol
P	Porosity	%
R	Rejection of membranes	%
r1 and r2	reactivity ratio	-
S	Water uptakes	%
t	time	s or min
T _g	Glass transition temperature	°C
UCST	upper critical soluble temperatures	°C
V	volume	cm ³
V _p	Volume of water collected from permeate side	cm ³
Δσ	Stress decay	MPa
Δσ _{max}	Maximum stress decay	MPa
ε	strain	-
ε ₀	initial strain	-

η	viscosity of damp in Zener model	Pa·S
ρ_m	Matrix density	g/cm^3
ρ_f	Foam density	g/cm^3
σ	stress	MPa
σ_0	initial stress	MPa
τ	decay constant	s

Abbreviations

AA	acrylic acid
Aam	acrylamide
APS	ammonium persulfate
ATRP	atom transfer radical polymerisations
BA	butylacrylate
CNTs	carbon nanotubes
DMAEMA	dimethyl aminoethyl methacrylate
DVB	divinylbenzene
EGDMA	ethylene glycol dimethacrylate
EHA	2-ethylhexyl acrylate
EHMA	2-ethylhexyl methacrylate
GMA	glycidyl methacrylate
HDDA	6-hexanediol diacrylate
HEMA	hydroxyethyl methacrylate
HIPEs	high internal phase emulsions
IPN	Interpenetrate networks
LIPEs	low internal phase emulsions
MAA	methacrylic acid
MBA	N,N' -methylene bisacrylamide
MIPEs	medium internal phase emulsions

MMA	methyl methacryl
MOFs	metal-organic frameworks
MPS	Methacryloxypropyltrimethoxysilane
NIPAM	N-isopropylacrylamide
o/w	oil in water
PCL	poly(ϵ -caprolactone)
PEG	poly(ethylene glycol)
PEGDMA	poly(ethylene glycol) dimethacrylate
PHEMA	Poly(hydroxyethyl methacrylate)
PHPMA	Poly(hydropropyl methacryl amide)
PMAAm	Poly(methacryl amide)
PNIPAM	Poly(N-isopropylacrylamide)
poly(LIPes)	polymerised low internal phase emulsions
polyAA	Poly(acrylic acid)
polyAAm	Poly(acrylamide)
polyHIPEs	polymerised high internal phase emulsions
polyMAA	Poly(methacrylic acid)
polyMIPEs	polymerised medium internal phase emulsions
POSS	polyhedral oligomeric silsesquioxane
PUDA	polyurethane diacrylate
PVA	poly(vinyl alcohol)
PVDF	Polyvinylidene fluoride
SEM	scanning electron microscopy
St	styrene
TEOS	tetraethylorthosilicate
TGA	Thermal gravity analysis
THF	tetrahydrofuran
UV	Ultraviolet
VBC	Vinylbenzyl chloride

VSQ	vinyl silsesquioxane
w/o	water in oil

List of Figures

Fig 2.1 Scanning electronic microscope images or molecular structure of representative porous polymers: (a) supermacroporous, obtained from Ref ⁸: Xiao, Q.; Wang, X.; Li, W.; Li, Z.; Zhang, T.; Zhang, H. *Journal of Membrane Science* **2009**, 334, 117. (b) macroporous, obtained from Ref ⁹: Sone, H.; Fugetsu, B.; Tanaka, S. *Journal of Hazardous Materials* **2009**, 162, 423. (c) mesoporous, obtained from Ref ¹⁰: Wan, Y.; Shi, Y.; Zhao, D. *Chemistry of Materials* **2007**, 20, 932. (d) microporous, obtained from Ref ¹¹: Kuhn, P.; Forget, A. I.; Su, D.; Thomas, A.; Antonietti, M. *Journal of the American Chemical Society* **2008**, 130, 13333.

Fig 2.2 Representative macroporous polymer prepared via emulsion templates with 85 vol% internal phase. Here the term ‘pores’ describes the spherical voids resulted from the droplets of the emulsions, while ‘pore throats’ describes the windows connecting two pores.

Fig 2.3 PolyHIPEs from a Pickering emulsion stabilised by titania. Obtained from Ref ¹²⁵: Menner, A.; Ikem, V.; Salgueiro, M.; Shaffer, M. S. P.; Bismarck, A. *Chemical Communications* **2007**, 4274.

Fig 3.1 Microscope image of the sieve for screen printing.

Fig 3.2 Structure of sliced polyHIPE films. (a) Cracks on the surface of films when the films are relatively brittle. (b) cross-section of films. (c) surface of cross-section of films. (d) High magnification of surface of films.

Fig 3.3 Surface structure of poly(EHA-St-DVB)HIPE (PE-cast) on different substrates.

Fig 3.4 SEM images of the control PUEDA-EHA based polyH(M)IPE samples. (a)PE1C; (b)PE2C; (c)PE3C; (d)PE4C.

Fig 3.5 (a) Scheme of formation of textures during rolling-pin printing. (b) Representative picture of printed films via rolling pin printing

Fig 3.6 SEM images of poly-surfactant-stabilised-emulsion films from rolling-pin printing. (a) PE1R1; (b)PE1R1; (c)PE1R2; (d)PE1R2; (e)PE1R3; (f)PE1R3.

Fig 3.7 SEM images of poly-Pickering-MIPE films from rolling-pin printing. (a) PE2R1; (b)PE2R1; (c)PE2R2; (d)PE2R2; (e)PE2R3; (f)PE2R3.

Fig 3.8 Representative picture of PE1S.

Fig 3.9 SEM images of the cross-section and surface of screen printed polyH(M)IPE films. (a) PE1S; (b) PE1S surface; (c) PE2S; (d) PE2S surface; (e) PE3S; (f) PE3S surface; (g) PE4S; (h) PE4S surface.

Fig 3.10 Representative picture of double layer printing with a Packman pattern.

Fig 3.9 SEM images of the cross-section and surface of screen printed polyH(M)IPE films. (a) PE1S; (b) PE1S surface; (c) PE2S; (d) PE2S surface; (e) PE3S; (f) PE3S surface; (g) PE4S; (h) PE4S surface.

Fig 3.12 SEM images of multilayer screen printed films. (a) PE1S/PE2S; (b) PE1S/PE2S; (c) PE3S/PE4S; (d) PE3S/PE4S.

Fig 4.1 Schema of setup for preparing polyHIPE-hydrogel composites

Fig 4.2 SEM images of poly(MAA) filled poly(St-DVB)HIPEs. a, b. control sample (C); c, d. 0% (M0); e, f. 1% (M1); g, h. 2% (M2); i, j. 5% (M5); k, l. 10% (M10).

Fig 4.3 SEM images of poly(DMAEMA) filled poly(St-DVB)HIPEs. a, b. control sample (c); c, d. 0% (D0); e, f. 1% (D1); g, h. 2% (D2); i, j. 5% (D5); k, l. 10% (D10).

Fig 4.4 Water uptakes of poly(MAA) filled poly(St-DVB)HIPEs (black square) and poly(DMAEMA) filled poly(St-DVB)HIPEs (red dot).

Fig 4.5 Scheme of water uptaking of hydrogel filled polyHIPEs.

Fig 4.6 Elastic moduli and Crush strengths of poly(MAA) filled poly(St-DVB)HIPEs and poly(DMAEMA) filled poly(St-DVB)HIPEs.

Fig 5.1 Scheme of dead-end cell

Fig 5.2 SEM images of poly(MAA) filled poly(EHA-St-DVB)HIPEs. a, b. control sample (Ec); c, d. 0% (EM0); e, f. 1% (EM1); g, h. 2% (EM2); i, j. 5% (EM5); k, l. 10% (EM10).

Fig 5.3 Water uptakes of poly(MAA) filled poly(EHA-St-DVB)HIPEs

Fig 5.4 Mechanical properties of wet poly(MAA) filled poly(EHA-St-DVB)HIPEs.

Fig 5.5 Water flux of poly(MAA) with 1% crosslinker filled poly(EHA-St-DVB)HIPE membrane (EM1M) against pH values.

Fig 5.6 Scheme of effect of hydrogels to water flux. a, collapse (protonated). b, expand (deprotonated).

Fig 5.7 PEG solution flux and rejections of EM1M. (a) 35K PEG solution flux and rejection at different pH. (b) Solutions of PEG with different molecular weights flux and rejections

Fig 5.8 Water flux of poly(MAA) with 2% crosslinker filled poly(EHA-St-DVB)HIPE membrane (EM2M) against pH values.

Fig 5.9 PEG solution flux and rejections of EM2M. (a) 35K PEG solution flux and rejection at different

pH. (b) Solutions of PEG with different molecular weights flux and rejections.

Fig 6.1 SEM images of polyM/HIPEs: (a) poly(St-DVB)HIPE; (b) polyHIPE0; (c) polyHIPE1; (d) polyHIPE2; (e) polyHIPE3; (f) polyMIPE4; (g) polyMIPE5; (h) polyMIPE6; (i) polyMIPE7.

Fig 6.2 Representative stress-strain curves of poly(St-DVB)HIPE, poly(PEGDMA-St)HIPE and poly(PUDA-St)H/MIPEs.

Fig 7.1 SEM images of cross-section structure of poly(PUDA 8402-EHA)MIPE films.

Fig 7.2 SEM images of cross-section structure of poly(PUDA 284-EHA)MIPE films.

Fig 7.3 SEM images of cross-section structure of polyH(M)IPE films based on PUDA 8402-EHA .

Fig 7.4 Flexible porous films rolled up to a cylinder with a diameter less than 10 mm.

Fig 7.5 Representative Stress-strain curves of poly(PUDA-EHA)H(M)IPE films (the rest of the curves are in Appendix II).

Fig 7.6 Scheme of Standard Linear Solid model and description of relaxation behaviour

Fig 7.7 Representative relaxation curves of porous films via emulsion templating (the rest of the curves are in Appendix III).

Fig 7.8 Representative cycle curves of porous films via emulsion templating (the rest of the curves are in Appendix IV).

Fig 7.9 Long-term cycle tests of PM1 and PM7.

List of Tables

Table 2.1 List of common hydrogels

Table 3.1 Recipes of sample emulsions for film preparation

Table 3.2 Properties of control samples PE1-PE4

Table 3.3 Properties of PE1 films from rolling-pin printing

Table 3.4 Properties of PE2 films from rolling-pin printing

Table 3.5 Properties of PE1-4 films from screen printing

Table 3.6 Pore size of multilayer polyH(M)IPE films (unit: μm)

Table 4.1 Formulation of hydrogel filled poly(St-DVB)HIPEs

Table 4.2 Pore sizes, pore throat sizes, densities and porosities of poly(MAA) filled polyHIPEs

Table 4.3 Pore sizes, pore throat sizes, densities and porosities of poly(DMAEMA) filled polyHIPEs

Table 5.1 Formulation of hydrogel filled poly(EHA-St-DVB)HIPEs

Table 5.2 Density and porosity of poly(MAA) filled poly(EHA-St-DVB)HIPEs

Table 6.1 Recipes for MIPEs and HIPEs based on St-PUDA

Table 6.2 Summary of the measured properties (matrix density, ρ_s ; foam density, ρ_f ; porosity, P ; pore size, d_p ; pore throat size, d_{pt} ; elastic modulus, E and crush strength, σ) of the samples.

Table 7.1 Recipes for polyH(M)IPEs prepared via copolymerising EHA and PUDA.

Table 7.2 Densities, porosities, pore sizes and pore throat sizes of poly(EHA-PUDA)H(M)IPE films

Table 7.3 Mechanical properties of PM1-PH9.

Table 7.4 Decay constants and initial residual stress of PM1-PH9.

Chapter 1 Introduction

Natural porous materials, such as woods, coconuts shell and etc, can be found everywhere in the world. Such porous structures possess amazing performance such as low-density, high strength and permeability. Synthetic porous materials also have a very long history in human-beings society. For example people started to make fabrics and porcelain a long time ago. In recent years, porous materials can be found in our daily life and are used by many industries, ranging from packaging pellets, lunch boxes and roof sealing to filtration membranes, absorbents etc. Porous materials can be synthesised via many methods, depending on the pore sizes and pore structures required (see Chapter 2). One important method to prepare macroporous polymers is emulsion templating, which was firstly explored in 1970s¹. Generally, high internal phase emulsions (HIPEs) with monomers in the continuous phase, are polymerised. After the polymerisation and removal of the internal phase, the products, namely polyHIPEs, become macroporous polymers. The resultant polyHIPEs copy the morphology of the emulsions, therefore this technique is named with 'emulsion templating'. There are many publications describing synthesis, properties and applications of polyHIPEs (see Chapter 2). Besides the excellent properties of the resultant polyHIPEs, such as low densities, high porosities and interconnectivities, the feature of emulsion templating is that it turns liquid into solid foams with well-defined dimensions. This is very different from traditional foaming process involving blowing agents. This feature allows us to mould the emulsion templates and obtain polyHIPEs with the desired shapes. So far the majority of polyHIPEs are produced as monoliths, which are convenient for characterisation or further processing. PolyHIPE films have also been reported²⁻⁴ but research on this topic is very limited. One challenge is the mechanical properties of polyHIPEs. Traditional poly(styrene-divinylbenzene)HIPEs are too brittle for making films. The polyHIPE films are expected be very tough and flexible, since polyHIPEs films are desired rather than polyHIPE 'crisps'. On the other hand, the applications of polyHIPEs films needed to be expanded. So far the applications of polyHIPEs films are only for pervaporation², cell culturing³ and chromatography⁵. These can be expanded where the other properties of polyHIPEs films can be utilised.

Therefore this four-year PhD project, aiming at further developing the preparation, processing and applications of polyHIPEs films, was carried out. In this thesis, following key aspects are addressed:

1. The first objective was to print emulsion templates to create macroporous films and to investigate the impact of printing on the morphology of the macroporous films.
2. Hydrogel filled polyHIPEs were synthesised and characterised. Moreover, membranes were prepared from such polyHIPEs and their applications for ultrafiltration applications were explored.
3. Flexible and largely deformable macroporous films, which were desired for pressure sensor applications, were prepared and their mechanical properties will be characterised.

After the brief introduction, Chapter 2 is a theoretical background, starting with reviews on porous polymers and hydrogel membranes. Afterwards the previous research on polyHIPEs is comprehensively reviewed. Chapter 3 summarises the approaches to make polyHIPEs films in our projects and the approaches are compared and evaluated. Chapter 4 describes the preparation and properties of hydrogel filled polyHIPEs, which are precursors for functionalised polyHIPEs films. Based on this chapter, preparation of hydrogel filled polyHIPEs films and their performance for filtration applications is reported in Chapter 5. In Chapter 6, polyurethane-styrene based polyHIPEs are reported, which is an attempt to incorporate polyurethane to prepare tough polyHIPEs. After that work, styrene is replaced by ethylhexyl acrylate and polyurethane diacrylate-ethylhexyl acrylate based polyHIPEs films are synthesised. The preparation and properties of these very flexible polyHIPEs films are reported in Chapter 7. Chapter 8 concludes the remarks achieved in this project and make suggestions for further research.

Chapter 2 Literature Review

2.1 Porous polymers

Porous polymers are a topic of long-standing interest, which have been widely studied, developed and tailored. Examples of natural porous polymers include woods, coconuts shell and etc. Synthesised porous polymers can be found in our daily life, such as the filter and seals of fridge doors, the packaging for fragile goods, the sport mats and running shoes⁶. Porous polymers are characterised by pore size, and therefore they are usually classified into microporous polymers (pore size less than 2 nm), mesoporous polymers (pore size range between 2 nm to 50 nm) and macroporous polymers (pore size larger than 50 nm) according to IUPAC⁷ (Fig 1 showed scanning electronic microscope images or molecular structure of representative porous polymers with different pore sizes). The pore sizes of porous polymers, to a certain degree, decide the preparation and applications of the materials, and therefore this part will review a variety of porous polymers according to the pore sizes.

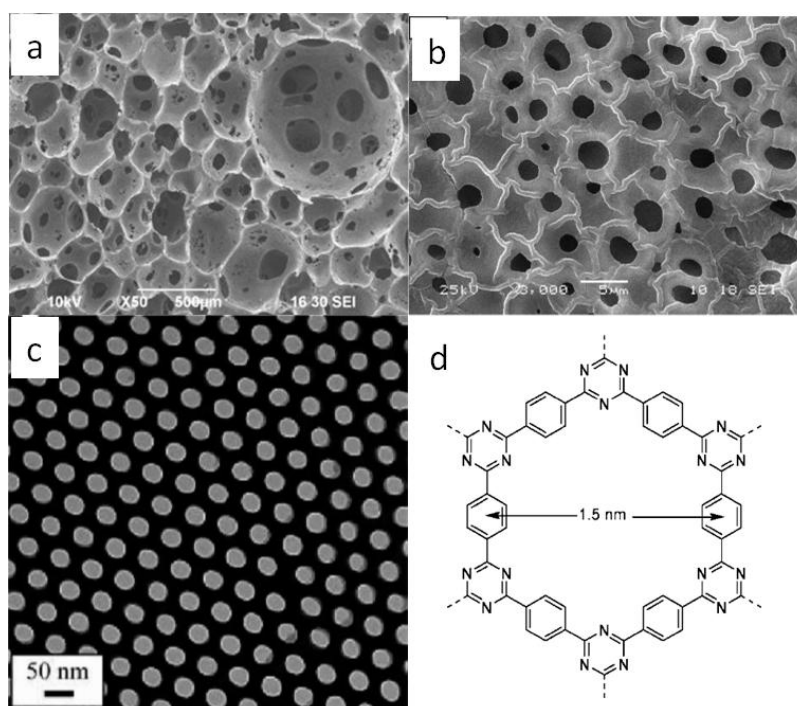


Fig 2.1 Scanning electronic microscope images or molecular structure of representative porous polymers: (a) supermacroporous, obtained from Ref⁸: Xiao, Q.; Wang, X.; Li, W.; Li, Z.; Zhang, T.; Zhang, H. *Journal of Membrane Science* **2009**, 334, 117. (b) macroporous, obtained from Ref⁹: Sone, H.; Fugetsu, B.; Tanaka, S. *Journal of Hazardous Materials* **2009**, 162, 423. (c) mesoporous, obtained from Ref¹⁰: Wan, Y.; Shi, Y.; Zhao, D. *Chemistry of Materials* **2007**, 20, 932. (d) microporous, obtained from Ref¹¹: Kuhn, P.; Forget, A. I.; Su, D.; Thomas, A.; Antonietti, M. *Journal of the American Chemical*

Since the knowing of porous structure of woods, the early stage porous polymers were also called 'plastic woods' or 'artificial wood'. The terminology did not only emphasize the similar structure of the porous polymers to woods, but also implied the applications of the material: replacement of woods, namely structural materials¹². These porous polymers are usually prepared using foaming agents. To prepare thermoplastic polymer foams physical foaming agents, which are volatile liquids or compressed gases, are usually used. The agents are mixed with polymers, which can be polystyrene, polyolefins, poly(vinyl chloride) and their derivatives, and the mixtures are consequently moulded, injected or extruded. Under a temperature or pressure drop, phase separation occurs in the bulk of the polymers, creating pores. Chemical foaming agents function via reacting with the polymers or oligomers. For example, water can foam polyurethanes by reacting with isocyanates to generate carbon dioxide. Other polymer foams using chemical foaming agents include polyphenylene oxide, polycarbonates, polyamide and so on. Sometimes these polymers are also foamed with physical foaming agents in addition of chemical foaming agents in order to obtain high porosities. The porous polymers via these techniques can have various pore sizes, which go up to several millimetres. These porous foams are usually applicable for structure materials, and depending on their applications, the foams can have various densities, strengths, moduli and thermal conductivities, aiming at light weight filling, energy adsorption, blocking, and heat isolation. Polyurethane foams can be divided into flexible foams and rigid foams depended on the isocyanates and polyols. The flexible foams are advantageous for energy adsorption, therefore highly applicable in automotive industry, including bumpers, arm rests, crash pads and seats. Rigid foams possess high stiffness, compared to the flexible polyurethane foams. They find applications in constructions, such as windows frames and roof drains. They are also applicable for furniture as they are not cold to the touch, and for electrical equipment, as their low heat distortion. Polystyrene foams and other polyolefin foams are applied in packaging due to the outstanding energy adsorptions. Moreover, they are also applied in house building and furniture, such as kitchen cabinetry, drawers, outer tank for washing machines, etc. The polymer foams are used to replace woods, metal or even unfoamed polymers, due to their low densities or reproducible, as well as the comparable mechanical properties, chemical resistance, etc^{6,12}.

Macroporous polymers with relatively small pores (i.e., 50 nm to 100 μ m) are prepared via many approaches. One well-established approach is phase separation¹³. The polymers are mixed with solvents. Due to the modest solubility of the polymers in the solvents, polymer-rich parts and polymer poor parts form in the bulk of the polymer solutions. Consequently, phase separation occurs under the conditions of freeze-drying¹⁴, solvent exchange¹⁵, or even crosslinking of polymers¹⁶, and polymers precipitate, forming a porous structure where the polymer-rich parts become polymer regions and the polymer-poor parts become pores. Another widely used method to prepare macroporous polymers is leaching¹⁷. In this technique, porogens are dispersed with polymer solutions. After the solidification of the polymers, the porogens are washed away from the bulk of the polymers, leaving pores within the polymers. Other methods to prepare macroporous polymers include sintering of polymer particles¹⁸, stretching of polymer films¹⁹, etc. These macroporous polymers are mainly applied in biotechnology and biomedicine, such as isolation of small molecules, separation of DNA or cells and scaffolds for tissue engineering²⁰, as well as industrial applications, including stationary phase in chromatography, supports for catalysts, sensors and adsorbents²¹.

Mesoporous polymers possess not only even smaller pore sizes than in macroporous polymers, but also narrow pore size distributions. The mesoporous polymers are synthesised with templates. The templates can be hard inorganic frames with mesopores, such as silica²². Polymers or monomers adsorb at the surface of the mesoporous templates, in prior to the solidification of the polymers. Afterwards the templates are dissolved, leaving mesoporous polymers which are the negative replicas of the templates. Another sort of templates is molecules, and this very technique is also called molecularly imprinting²³⁻²⁵. The templates are incorporated with monomers via functional groups, forming a template-binding group complex. Subsequently, the monomers are polymerised and in that case, the templates function as spacers. After the polymerisation, the templates are removed via specific trigger, leaving template-sized pores in the polymers. The advantage of the technique is sustaining functional groups on the polymer chains, which are used early for binding the templates, making the mesoporous polymers enzyme-like scaffolds²⁶. Highly ordered mesoporous polymers are prepared via molecule assembly^{10,27}. Amphiphilic molecules, such as surfactants or some copolymers, are used as templates. The templates interact with polymer precursors via hydrogen bonds or ion strengths and the interacting molecules are dispersed in solvents. Subsequently, the templates are

self-assembled via solvent evaporation. As a result the polymer precursors form ordered structures, for example, spherical shells or tubes. After the crosslinking of the precursors and the washing away of the templates, the mesoporous polymers are formed. The applications of mesoporous polymers include separation of small molecules^{25,28}, hydrogen storage²⁷ due to their high surface areas, drug delivery due to the enzyme-like properties of some mesoporous polymers²⁶, as well as electrical devices²⁷.

Microporous polymers are of even smaller pores, and in that case, they are usually characterised by high surface areas up to more than 4000 m²/g²⁹. The microporosity of polymers can be from extrinsic and intrinsic. Tsyurupa and Davankov³⁰ reported hypercrosslinked polystyrene. The chloromethylated polystyrene beads were swollen in solvent and crosslinked via a Lewis acid mediated Friedel-Craft alkylation, resulting in porous polystyrenes with surface areas of up to 2000m²/g. The microporosity was caused by the inert solvent acting as a spacer, which therefore was considered as extrinsic. Intrinsic microporous polymers compose of fused-ring components³¹⁻³². In order to prevent the collapse of the pores within the molecules, the components chosen are usually rigid (for example aromatic based). In addition, building blocks (one well-described building block is spirobifluorene) are used to maintain steric stability of the porous macromolecules³¹. Due to the high surface areas of microporous polymers, they are excellent candidate for gas adsorption³³ and storage³⁴. Other applications of these polymers include separation and catalysis³¹.

2.2 Hydrogel Membranes

2.2.1 Introduction

Hydrogels are hydrophilic polymers or copolymers which can adsorb large amounts of water. Due to the presence of chemical crosslinks or physical crosslinks, such as entanglement, crystals and hydrogen bonds, the polymers are not soluble in water. However, due to the swelling in water, hydrogels form three-dimensional networks. This networks present excellent properties in water, such as high permeability to hydrophilic matter and high fluidity, as well as outstanding bio-compatibility. Hence, hydrogels have found many applications in medicine, biotechnology and agriculture³⁵⁻³⁶.

Table 2.1 List of common hydrogels³⁵⁻³⁶

Polymer	Abbreviation	Polymer	Abbreviation
Poly(hydroxyethyl methacrylate)	PHEMA	Poly(hydropropyl methacryl amide)	PHPMA
Poly(N-isopropylacrylamide)	PNIPAAm	Poly(ethylene glycol)	PEG
Poly(vinyl alcohol)	PVA	Dextran	N/A
Poly(acrylic acid)	PolyAA	Chitosan	N/A
Poly(methacrylic acid)	PolyMAA	Poly(dimethyl aminoethyl methacrylate)	PDMAEMA
Poly(acrylamide)	PolyAAm	Poly(methacryl amide)	PolyMAAm

Hydrogels can be classified in many ways³⁵⁻³⁶. Depending on the charge of their pendant groups or their polymer chains, hydrogels can be neutral or ionic. Depending on the network structures, hydrogels can be either amorphous or semicrystalline. Hydrogels are porous after swelling in water; in terms of pore dimensions, they can be divided into microporous, macroporous or even nanoporous hydrogels. A well-known synthetic hydrogel is poly(hydroxyethyl methacrylate), which was firstly explored by Wichterle and Lim³⁷. Other polymers usually used as hydrogels are listed in Table 2.1.

2.2.2 Preparation of hydrogel membranes

Hydrogel membranes can be prepared via phase inversion or interfacial polymerisation. Phase inversion represents a process in which a liquid film is transformed into a solid state³⁸. Liquid films can be either a monomer solution or a polymer solution. For polymer solutions, taking PVA membranes as an example, PVA, crosslinkers, buffers, quenchers and catalysts were dissolved in solvents. The solutions were cast or moulded into membranes. Afterwards, the membranes were crosslinked and dried³⁹. For membranes prepared from monomer solutions, a similar process is used. Initially, monomers were dissolved into solvents, and other components such as quenchers, initiators and buffers are dissolved into the solutions as well. The solutions were processed into membranes, by means of casting or moulding. The monomers were then polymerized. Afterwards, crosslinkers were introduced into the membranes, allowing the membranes to crosslinked, and then the membranes were washed and dried. Usually many hydrogel membranes were prepared by polymerizing two

hydrophilic monomers to make hydrogel-hydrogel copolymers, such as PAAm-PAA⁴⁰, PMAAm-PMAA⁴¹, PNIPAAm-PMAA⁴² and PMAA-PAA⁴³.

Hydrogel composite membranes are prepared via grafting polymers or monomers onto porous supports. Porous matrices (usually membranes) are brought in to contact with solutions containing hydrophilic monomers or polymers. By means of chemical initiation or photo-initiation, the monomers or polymers are grafted onto the surface of the supports, forming hydrogel composite membranes. Xu et al.⁴⁴ reported the preparation of PVA / polyvinylidene fluoride (PVDF) composite membranes by functionalizing the PVDF membranes and grafting PVA on the surface of the PVDF membranes. Radiation-grafting of hydrophilic polymers or their monomers onto supports was studied by Hegazy et al.⁴⁵. They successfully grafted methyl methacrylate onto the surface of PTFE. The homopolymerisation inhibitor, dilute solvent and atmosphere were believed influencing the grafting efficiency. Similarly, DMAEMA was grafted onto surfaces of PVDF membranes initiated by electron irradiating. Adsorption of acidic and basic drug models on the resultant membranes were studied⁴⁶. Zhang et al.⁴² have reported the grafting of DMAEMA and NIPAAm onto the surface of nylon membranes via atom transfer radical polymerisations (ATRP), which was a living polymerisation. Using ATRP, PNIPAAm-PDMAEMA diblock copolymers were grafted on the surface of the nylon membranes. Besides hydrophobic membranes, such as PVDF and PTFE, hydrogels can also be grafted onto the surface of hydrophilic polymers such as hydrophilised polypropylene membranes⁴⁷, biomaterials, such as chitosan membranes⁴⁸ and inorganic membranes, such as silicon membranes⁴⁹.

2.2.3 Swelling behaviour of hydrogels

Many factors can influence swelling of hydrogels. Firstly, hydrogels with more hydrophilic groups can swell to a higher degree than the hydrogels with more hydrophobic groups. The more hydrophobic polymers collapse when contacting water, hence have less exposure to water. Crosslinking ratio is an important factor that determines the swelling ratios of hydrogels. The polymer chains of highly crosslinked polymers arrange closely, and hence highly crosslinked hydrogels swell less than lowly crosslinked polymers³⁶.

Besides the nature of hydrogels, the environment of hydrogels also influences the swelling ratios of

hydrogels. The swelling degrees of the hydrogels can vary, depending on pH and temperature. PH-responsive hydrogels contain either acidic or basic pendant groups. In a media with high (low) pH, acidic (basic) hydrogels can deprotonise or protonise, respectively, generating fixed charges on the polymer chains. Due to the electrostatic repulsions, the hydrogels are pushed apart and can therefore swell more solvents. Well-known pH-responsive hydrogels are PMAA, PAA, PAAm and their copolymers⁵⁰⁻⁵¹. Temperature-responsive hydrogels can be classified into positive temperature responsive and negative temperature responsive. Positive temperature responsive hydrogels have upper critical solution temperatures (UCST). Above the temperatures, the polymers are soluble in water, while below the temperatures, the polymers are gels. Negative temperature responsive polymers have lower critical solution temperatures (LCST). The polymers are soluble in the solvents under LCST, but gel when the temperatures are beyond LCST⁵². The best known temperature-responsive hydrogel is polyNIPAAm. Since its LCST is 34.3°C, which is near the human body temperature, it has been studied for bio-applications, such as drug delivery⁵³. There are also hydrogels sensitive to biomaterials. One example of bio-sensitive hydrogels is pH-sensitive hydrogels combined with glucose oxidases, showing glucose-sensitivity. When the hydrogels meet glucose in solutions, the glucose is oxidised to gluconic acid, hence lowering the pH in the environment. Due to the presence of the pH-sensitive hydrogels, the swelling degree, in turn the permeability, of the hydrogels changes⁵⁴.

2.2.4 Applications of hydrogel membranes

Usually, gases can hardly permeate through dry hydrogel membranes; however, the permeability of gases through swollen hydrogel membranes is much higher. Due to the favourable solubility of acidic gases in hydrogel membranes, acidic gases, such as CO₂, have even higher permeability in wet hydrogel membranes⁵⁵. Ito et al.⁵⁶ have investigated CO₂ permeating through chitosan membranes. The CO₂ from the feed side was wetted by water vapour. The results showed a selectivity of 70 for CO₂ / N₂ separation (here selectivity is the CO₂ / N₂ ratio in permeate side divided by the CO₂ / N₂ ratio in feed side). A similar experiment was conducted by Wu et al.⁵⁷. Wet cellulose membranes were used to separate CO₂ and N₂ and the selectivity was 50. Xu et al.⁴⁴ prepared PVA grafted PVDF membranes. Afterwards, the membranes were either carbonated or immobilised with enzymes. The resultant

membranes were employed to remove CO₂ from N₂. Liu et al.⁵⁵ investigated gas permeability of hydrogel membranes. They found that the water immobilised in the hydrogel formed the pathways for the gases and the content of water highly influenced the gases permeability. The gas permeability increased as the swelling degree increased.

Metal ions can coordinate with water-soluble complexing agents, such as chitosan, PVA and alginic acid, so hydrogel membranes composing of these agents have been employed to remove metal ions from water. Juang et al.⁵⁸ have studied the removal of divalent ions using cellulose membranes enhanced by chitosan. The results showed that the removal of Cu (II) was significant because of the outstanding coordination ability of Cu (II) with chitosan. Ethylene-cellulose-poly (ethylene glycol) composite membranes were used to separate Cu (II), Ni (II) and Fe (III) by using dextran and PVA as complexing reagents⁵⁹. PVA-AA / N-vinyl imidazole composite membranes were considered for practical use of separation Co (II) and Ni (II) at a pH higher than 4.5⁶⁰.

Because of the remarkable bio-compatibility, hydrogel membranes have found potential applications in biomaterials separations. Yang et al.⁶¹ have studied the permeability of creatinine, vitamin B₁₂, uric acid and 5-fluorouracil (5-FU) through chitosan / PVA blend membranes. It was found that all materials have linear increasing permeability with the chitosan ratio increasing in the blend membrane. However, the permeability of uric acid decreased when the chitosan ratio increased from 20% to 60% because of the interaction of uric acid with chitosan. The permeability of uric acid sharply increased when the chitosan ratio up to 80%. Obaidat et al.⁵⁴ have investigated glucose-sensitive membranes releasing model proteins (insulin and lysozyme). With the change of the glucose concentration in the environment, the membranes showed highly different permeation rates of the model proteins. The membranes not only worked as an 'on / off' switch, but controlled the permeation rate of the model proteins. Bayramoglu et al.⁴⁸ have studied the adsorption of alkaline trypsin onto a PolyMAA-chitosan membrane by means of ion exchange. The highest adsorption amount appeared at neutral. In addition, the adsorption process was a reversible process. 90% of the alkaline trypsin was desorped at pH 4.0. Salt-sensitive membranes were synthesised by grafting poly(N-vinyl lactam) onto PVDF membranes. The hydrophobicity of the membranes can be controlled by adjusting the salt concentration in environment. The membranes found potential applications in

adsorbing and desorbing antibodies, hence making them applicable in protein separation⁶². Hydrogel membranes were also used as membrane reactor. Crosslinked poly (NIPAAm-*N*-acryloxysuccinimide-HEMA) hydrogels on polyester nonwoven supports have been investigated by Chen and Chiu⁶³. Urease was immobilized onto the backbone of the hydrogel. Urea, passing through the membranes, hydrolysed into ammonia. The results showed the best hydrolysis achieved when there was a temperature swing, because the mass transfer through the membranes was enhanced in that case.

2.3 Emulsion templating

2.3.1 Introduction

An emulsion consists primarily of two immiscible liquid, usually an aqueous phase and an oil phase. One liquid phase is dispersed as droplets within another liquid phase to form either a water-in-oil (w/o) emulsion or an oil-in-water (o/w) emulsion. Emulsions can be used as templates to produce porous polymers. An emulsion template is prepared via dispersing an internal phase into a continuous phase, which contains monomers and emulsifiers, e.g. surfactants. After the polymerisation of the continuous phase and the removal of the internal phase, the resultant product is a macroporous polymer (Fig 2.2), characterised by high porosity and interconnectivity. The product maintains mostly the volume of the emulsion and copies the morphology of the emulsion. Therefore this technique is called emulsion templating. Usually the emulsions employed for the synthesis of porous polymers possess a high internal phase ratio, which is more than 74%, referring the volume percentage of close package of uniform-size spherical droplets. These emulsion templates are therefore called high internal phase emulsions (HIPEs), and the products from these emulsion templates are called polymerised high internal phase emulsions (polyHIPEs). Emulsion templating can be resourced back to Lissant¹, who solidified the continuous phase of HIPEs in order to study their morphology. In 1980s, Barby and Haq⁶⁴ patented the preparation of polyHIPEs and described their properties as low density. In the next three decades emulsion templating for making macroporous polymers have been widely studied.

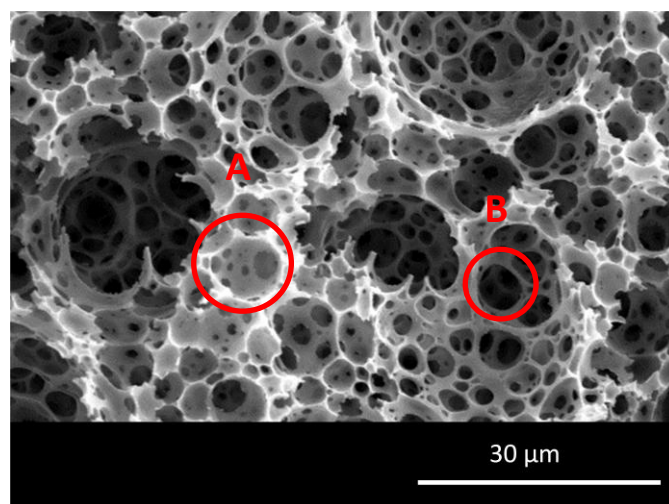


Fig 2.2 Representative macroporous polymer prepared via emulsion templates with 85 vol% internal phase. Here the term ‘pores’ describes the spherical voids resulted from the droplets of the emulsions (Red mark A), while ‘pore throats’ describes the windows connecting two pores (Red mark B).

2.3.2 Preparation of macroporous polymers

Emulsion templates are prepared by dispersing one phase into another immiscible phase. Usually an aqueous phase is dispersed in an organic monomer phase to make a water-in-oil (w/o) emulsion, while oil-in-water (o/w) emulsions were also reported by many researchers⁶⁵⁻⁶⁸. Based on the different internal phase volume ratios, emulsion templates can be classified as low internal phase emulsions (LIPEs, with less than 30 vol% internal phase⁶⁹), medium internal phase volumes (MIPEs, with 30 vol% to 70 vol% internal phase⁷⁰) and high internal phase emulsions (HIPEs, with more than 74 vol% internal phase). The setup to prepare a w/o emulsion template is usually a flask equipped with stirrer. The continuous phase, including monomers, initiators and surfactants are placed in the flask. The aqueous phase, which contains electrolytes and sometimes initiators, is slowly dropped into the continuous phase while stirring. After the addition of the internal phase, the emulsion is usually stirred for a while longer to produce a homogeneous emulsion. An alternative way is using two-syringe system to mix the two phases⁷¹. Two syringes are connected nozzle to nozzle by a tube. The components for emulsions are placed in one of the syringe and the emulsification is carried out by the motion of the plungers of the syringes, which drive the components pass through the connecting tube successively. Emulsion templates can be moulded, cast, or dispersed in immiscible solvents to produce monoliths^{70,72-73}, films⁴⁻⁵ or beads⁷⁴⁻⁷⁵. The emulsion templates are then placed into an oven to polymerise the continuous phase thermally, or placed under UV light for a photo-polymerisation⁷⁶.

After the polymerisation the polyHIPEs are washed and dried for further characterisations or applications.

The original polyHIPEs, which are also the mostly researched polyHIPEs, are based on styrene (St) and divinylbenzene (DVB)^{1,64,73}. The advantages of St-DVB based polyHIPEs can include the stabilities of the emulsion templates, ease of polymerisation and certain mechanical properties of the polyHIPEs⁷³. Therefore, St-DVB based polyHIPEs are studied as a model form of polyHIPEs. On the other hand, St-DVB based polyHIPEs are characterised as chemically inert, hydrophobic, as well as brittle and chalky⁷⁰, which may not be desired for real applications. Therefore researchers put their efforts to develop polyHIPEs, which possess either improved properties or fulfil a variety of functions. Vinylbenzyl chloride (VBC) has been used in preparing polyHIPEs⁷⁷. It is a hydrophobic monomer which guarantees stability of emulsion templates but also contains a benzyl chloride group suitable for post-polymerisation functionalisation. For example, the resultant VBC-based polyHIPEs can be functionalised with a variety of nucleophilic amines⁷⁸⁻⁷⁹, or the polyHIPEs can be further crosslinked using a Lewis acid⁸⁰. Conventional method to make St-DVB based polyHIPEs of hydrophilic surface is sulphating the polyHIPEs. In this case, the reagents need to be hydrophobic to achieve a high degree of modification⁸¹⁻⁸². In a more recent work styrenesulfonate was used to prepare polyHIPEs⁶⁷. The monomer is hydrophilic, thus an o/w was employed. The resultant polyHIPEs were hydrophilic, as demonstrated by the water adsorption tests. Although this method provides one-pot preparation of polyHIPEs with hydrophilic surface, due to the poor stability of such an o/w emulsion template, the direct synthesis of styrenesulfonate based polyHIPEs was not ideal, compared to the solphation of conventional St-DVB polyHIPEs.

Besides vinyl benzyl monomers, another group of monomers used in emulsion templating is acrylate monomers. Acrylate monomers like ethylhexyl acrylate⁸³⁻⁸⁵, ethylhexyl methacrylate⁸⁵ and butylacrylate (BA)⁸⁶ have been used with St and DVB to reduce the brittleness and chalkiness of original St-DVB based polyHIPEs. However, this led to a dramatic reduction in glass transition temperature (T_g) of the polyHIPEs⁸³⁻⁸⁵, turning them, depending on the co-monomer concentration, into elastomers. This can effectively limit their applicability. Alternatively, Menner et al. managed to use acrylate crosslinker, i.e. polyethylene glycol dimethylacrylate^{70,87} to make polyHIPEs. The resultant

polyHIPEs showed improved mechanical properties in terms of less brittleness and chalkiness, as well as non-reduced T_g ⁷⁰. Similar to VBC, some acrylate monomers can induce reactive groups into resultant polyHIPEs, making them multifunctional. 4-nitrophenyl acrylate⁸⁸ and 2,4,6-trichlorophenyl acrylate⁸⁹ were used to prepare polyHIPEs. The functional groups can be converted into acid groups or acid chloride groups, which are open for further functionalisations. Glycidyl methacrylate (GMA) has also been used in preparing polyHIPEs for post-polymerisation functionalisation^{5,90-91}. However, emulsion templates with GMA require usually extremely hydrophobic surfactants (i.e. Hydrophilic-lipophilic balance, HLB, value less than 0.5) due to the hydrophilicity of GMA⁹². Acrylic acid based polyHIPEs were synthesised by Krajnc et al. in o/w emulsions⁶⁵, which gave a one-pot method to prepare polyHIPEs with acid groups. Another motivation using some acrylate monomers in polyHIPEs is concerning their bio-compatibility. One example is modifying poly(ϵ -caprolactone) (PCL)⁹³⁻⁹⁵ and using it in emulsion templating. Commercial PCL is an oligomer terminated with diol groups. The product is modified with acryloyl chloride to make it vinyl-terminated⁹⁵. Afterwards the PCL-vinyl-terminated is used to prepare polyHIPEs which are potentially used for tissue engineering. Moreover, it is worth mentioning that polyPCL is degradable, which is advantageous for cell-culture applications. 2-Hydroxyethyl methacrylate (HEMA) based polyHIPEs were prepared by thermal polymerisation. Such polyHIPEs required o/w emulsion templates and surfactants with high HLB values, as the monomer is hydrophilic⁹⁶. N-isopropyl acrylamide (NIPAM) has also been used to make polyHIPEs⁹⁷. Due to the temperature-sensitivity of polyNIPAM, the polyHIPEs have controllable mesh size and dimensions at different temperature, thus can load and unload matters in a solution by controlling temperature. This is applicable in drug release.

There have been many monomers, which are not classified as vinyl benzyl or acrylate monomers, being used for polyHIPE preparation. A series of maleimide monomers were copolymerised with St to produce polyHIPEs⁹⁸. Due to the slight solubility of the monomers in the internal phase, the resultant polyHIPEs showed relatively large pores, but the polyHIPEs demonstrate remarkable thermal oxidative stabilities. 1-vinyl-5- amino tetrazole, which was synthesised from 5-amino tetrazole, was used as a monomer for preparation of polyHIPEs⁹⁹. Due to the hydrophilicity of the monomer, the polyHIPEs were formed from o/w emulsions. The polyHIPEs showed improved mechanical properties in terms of Young's moduli, compared to typical St-DVB polyHIPEs. Subsequently, polyHIPEs based on 1-Vinyl-1, 2,

4-triazole were synthesised via a similar route⁶⁸. The resultant polyHIPEs showed high Young's moduli even at low crosslinking degrees. Kovacic et al. reported the preparation of polyHIPEs via the ring-open polymerisation of dicyclopentadiene¹⁰⁰⁻¹⁰¹. The polyHIPEs had high Young's moduli under tensile tests, which can reach to about 150 MPa. PolyHIPEs prepared via step-growth polymerisation were also reported. David and Silverstein¹⁰² and Lépine et al.¹⁰³ have both reported the syntheses of polyurethane from isocyanates and polyols for making polyHIPEs.

Another important family of polyHIPEs are organic-inorganic polyHIPEs. Tai and Silverstein reported syntheses of Methacryloxypropyltrimethoxysilane (MPS)-St-DVB based polyHIPEs¹⁰⁴. Due to the polysilsesquioxane inorganic networks in addition of the crosslinking of St-DVB, the polyHIPEs obtained enhanced T_g , thermal stability, dimensional stability and mechanical properties. Other inorganic silsesquioxane, including polyhedral oligomeric silsesquioxane (POSS)¹⁰⁵⁻¹⁰⁶ and vinyl silsesquioxane (VSQ)¹⁰⁷⁻¹⁰⁸, were also used to prepare organic-Si polyHIPEs by the same group. In 2010, Hu et al.¹⁰⁹ reported a HIPE possessing a colloidal suspension of tetraethylorthosilicate (TEOS) as the continuous phase and mineral oil as the internal phase. The HIPE was simply 'cured' by immersing the HIPE in an amine media, which led to the condensation of TEOS and consequently to the formation of a solely inorganic macroporous network.

Metal-organic polyHIPEs were also been prepared. A two-step approach to make metal-organic frameworks (MOFs) polyHIPEs was described by Schwab et al.¹¹⁰. They prepared St-DVB-VBC polyHIPEs firstly. Afterwards, $\text{Cu}_3(\text{btc})_2$ was incorporated into the polyHIPEs via chemical bonding. The resultant MOFs polyHIPEs had increased surface area, which gave them potential applications in energy storage and as catalyst supports. A one-pot synthesis was used by Croix et al.¹¹¹ to prepare gold-organic polyHIPEs. Vinylphenyl(triethylphosphine)gold(I) was prepared in prior to the copolymerisation of organo-gold with St and DVB in an emulsion templating. The gold-organic polyHIPEs are applicable in inertial confinement fusion experiments.

Another methodology to tailor the properties of polyHIPEs or functionalise polyHIPEs is to make polyHIPE composites. St-DVB based polyHIPEs with rubber composites were prepared by Choi et al.¹¹². They dissolved polybutadiene rubber in the continuous phase in prior to the preparation of the

emulsion templates. The resultant polyHIPE composites showed much smaller pore sizes, but without reduction of mechanical properties. Polymer-polymer Interpenetrating networks (IPN) within polyHIPEs have been reported by Tai et al.¹¹³. They firstly prepared polyHIPEs based on St, DVB or EHA. Afterwards the foams were immersed in other monomers (St, DVB or EHA, which were not used in the earlier preparation of polyHIPEs), and placed in oven to polymerise the second group of monomers. The composites polyHIPEs showed modified mechanical properties without the increase in densities, when the foams precursors: monomers ratios were less than 1:1. Lépine et al.¹⁰³ reported a one-step preparation of IPN within polyHIPEs, in which urethane and St-DVB mixture was used as the continuous phase of emulsion templates and they were polymerised simultaneously. Although some compositions resulted in shrunken polyHIPEs, PU-PS polyHIPEs with an appropriate composition exhibited enhanced elastic moduli. PolyHIPE composites were also prepared via coating polymers on the walls of pores in polyHIPEs¹¹⁴. St-DVB based polyHIPEs were impregnated with furfuryl alcohol vapour which was then polymerised. The heterocycle polymer coating improved the mechanical properties of the polyHIPEs composites.

A conventional emulsion template usually contains monomers in the continuous phase, while the dispersed phase is inert, such as aqueous solution of electrolytes. Emulsion templates, which contain monomers in the continuous phase and other monomers in the dispersed phase, have also been used to prepare polyHIPEs. Ruckenstein et al. prepared emulsion templates with St in the continuous phase and acrylamide (AAM) in the aqueous phase¹¹⁵. After the polymerisation the products are St-based polyHIPEs with polyAAM composites in polyHIPEs. In addition, the emulsion templates with AAM in the continuous phase and St in the dispersed phase were also prepared and polymerised by the same group¹¹⁶. Moreover Ruckenstein et al. also prepared emulsions with sodium acrylate in the internal phase, resulting in St-DVB based polyHIPE composites with poly sodium acrylate¹¹⁷⁻¹¹⁸. It is worth mentioning that sodium acrylate is the deprotonated form of acrylic acid (AA), which is required for preparation of such emulsion templates. Moreover, in some of their works pre-polymerisation of continuous phase is necessary for stabilising the emulsions¹¹⁹. This indicates that such emulsion templates may be not as stable as conventional emulsion templates, due to the solubility of the monomers in the continuous phase and the dispersed phase. However, they mainly characterised the polyHIPE composites with regards to their separation performance, including their swelling behaviour,

permeability and selectivity. Gitli and Silverstein¹²⁰ also prepared polyHIPEs composites via emulsions with St and DVB in the continuous phase and AAm in the internal phase. They observed the morphology of the dried and hydrated composites under SEM and found that the polyAAm was filled in the poly(St-DVB)HIPE scaffolds. In addition they also studied the factors, such as the concentration of the AAm and locus of polymerisation, affecting the stability, morphology and mechanical properties of the hydrogel filled polyHIPEs.

Haibach et al.¹²¹ firstly prepared silica particle reinforced polyHIPEs. The emulsion templates contained up to 10% (mass to volume of monomers) silica particles in the continuous phase, as well as St, MPS and DVB. After the polymerisation, the composites with silica particles showed increases in the elastic moduli and crush strength, compared to the control samples. However, due to the reaction of methoxysilane groups with the hydroxyl groups on the silica particles, methanol was formed in the continuous phase during emulsion preparation and polymerisation, which led to the destabilisation of the emulsion templates. This caused the loss of the characteristic pore structure of polyHIPEs, as the particle concentrations exceeded 10%. In a subsequent work from the same group, the researchers grafted MPS on the surface of silica particles, and used the modified particles to prepare polyHIPE composites¹²². The modification of silica particles addressed the problem of formation of methanol. Therefore the foams with up to 60% silica particles still had polyHIPE structures. Although the report describes the improvement of mechanical properties of the polyHIPEs with silica particles, the maximum reinforcement was found at a particle concentration of about 60%. PolyHIPEs with carbon nanotubes (CNTs) composites were prepared via two routes by Hermant et al.¹²³. They found if CNTs were dispersed in the continuous phase of emulsion templates, the resultant polyHIPEs with CNTs did not have conductivity. On the other hand, the emulsion templates, which had CNTs suspended in the internal phase, led to the polyHIPEs with conductivity. However, suspending of CNTs required surfactants, which can result in the destabilising of the emulsion templates. Therefore this approach required an appropriate amount of surfactants in the internal phase.

Pickering emulsions refer to the emulsions stabilised by particles. The particles adsorb at the interface between the continuous phase and the internal phase of emulsions, forming a thin layer to hinder the coalescence of the droplets¹²⁴. Menner et al. firstly reported the successful preparation of high

internal phase Pickering emulsions stabilised by functionalised titanium particles and subsequently the poly-Pickering-HIPEs¹²⁵. The particles were firstly modified to obtain appropriate wettability. Only 1% (weight to volume ratio with respect to continuous phase) particles can stabilise emulsions with up to 80% internal phase. The feature of these poly-Pickering-emulsions is the closed-cell morphology (Fig 2.3). Silica-stabilised emulsions were reported by Ikem et al.. The silica particles were also functionalised prior to mixing in the continuous phase, and emulsions with up to 92% internal phase were stabilised by using such particles with 4% loading¹²⁶. CNTs-stabilised emulsions were also used to synthesise polyHIPEs. Menner et al.¹²⁷ studied the effects of the locus of CNTs in emulsion templates to the properties of the resultant products. The products can be open-cell foams, close-cell foams or even spheres rather than foams, depending on which phase the CNTs were dispersed in. Hermant et al.¹²⁸ also reported polyHIPEs resulted from CNTs-stabilised-emulsions. The CNTs were firstly assembled with polystyrene-poly(DMAEMA) surfactant prior to the preparation of the Pickering emulsions. They emphasise that the amount of the CNTs can affect the morphologies of the polyHIPEs: as the amount of CNTs increased, the resultant polyHIPEs turned from close-cell to open-cell. Additionally, they also demonstrated the good conductivity of the poly-Pickering-HIPEs from CNTs. Besides inorganic particles, polymer particles were also used for making poly-Pickering-HIPEs. Zhang and Chen¹²⁹ described the preparation of poly(St-methyl methacryl (MMA)-AA) particles and using the particles to stabilise MMA-based emulsion templates. The particles can partially dissolve in the continuous phase, therefore can stabilise the emulsions, and resulting in polyHIPEs with open and half-covered pores. On the other hand, Li and Ngai¹³⁰ reported Pickering o/w emulsion with up to 80% internal phase stabilised by poly(St-NIPAM) particles. Even without polymerisation, the HIPEs were dried and directly formed a porous structure. The SEM images of their samples revealed the pore walls were formed by dense package of particles. Poly(urethane urea) particles (aqueous dispersion) were prepared by Zhu et al.¹³¹⁻¹³². The particles were used to prepare both o/w and w/o emulsion templates. The o/w HIPEs based on AAm and methylenebisacrylamide (MBA) were stable at room temperature, and the resultant polyHIPEs showed open-cell structures. On the other hand, w/o HIPEs based on St and DVB required elevated temperature to enhance the hydrogen bonds in the particles to form stable emulsions. The resultant polyHIPEs showed closed-cell morphology.

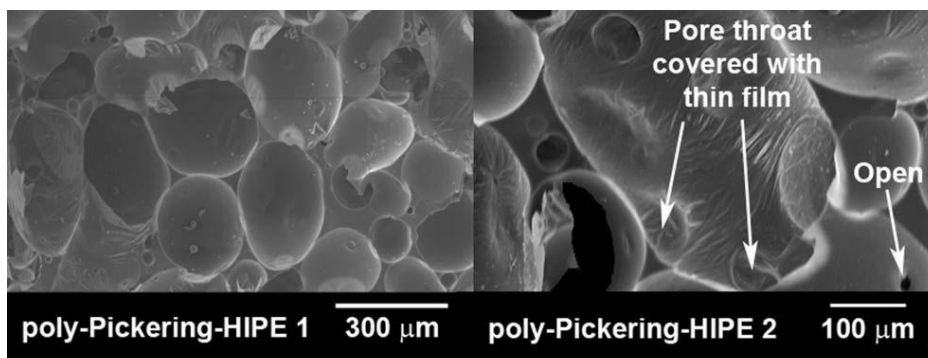


Fig 2.3 PolyHIPEs from a Pickering emulsion stabilised by titania. Obtained from Ref ¹²⁵: Menner, A.; Ikem, V.; Salgueiro, M.; Shaffer, M. S. P.; Bismarck, A. *Chemical Communications* **2007**, 4274.

2.3.3 Fundamental research of polyHIPEs

Stabilities are the most important factor to emulsions, which not only determine the probability of sedimentation, coalescence, creaming, phase separation and phase inversion of the emulsions, but also affect the droplet sizes of the emulsions. Therefore, stabilities of emulsion templates have a dramatic impact on the morphology and properties of the resultant polyHIPEs. In this section, earlier studies on the factors affecting the stabilities of emulsion templates, and how these factors influence the morphologies and properties of the resultant polyHIPEs will be reviewed. Williams and co-workers used St, DVB and sorbitan monooleate (SMO) as surfactant to build model HIPEs and consequently polyHIPEs, and studied the effects of the components on the morphology of the polyHIPEs by varying the amount of the components⁷³. They found that the morphology of polyHIPEs is more sensitive to the ratios of the surfactants to the monomer phases rather than the ratios of internal phase to the emulsions. As the surfactant increased from less than 5% to 10% with respect to the volume of the emulsions, the morphology of the polyHIPEs changed from a closed-cell porous structure to open-cell structure. As surfactant amount from the 10% to 50%, the polyHIPEs were all open-cell and the pore sizes decreased with the increase of the surfactant amount. A further increase of the surfactant to more than 70% resulted in products without porous structure. Moreover, the nature of the monomers also affected the morphology of the polyHIPEs. DVB, more hydrophobic than St, resulted in decrease in droplet size of the HIPEs and subsequently the pore sizes in polyHIPEs¹³³. Moreover, a large concentration of DVB in the monomer phase can also expand the range of surfactant amount which was required for open-cell polyHIPEs. Polar monomers, on the other hand, decrease the stability of emulsions, more likely leading to phase separation of the emulsion templates¹³⁴. Besides monomers

and surfactants, other components were also used to modify the morphology of polyHIPEs. Some chemically inert organic solvents also called porogens were mixed in continuous phase for making polyHIPEs. Cameron et al.¹³⁵ suggested some porogens, including toluene, chlorobenzene, 2-chloroethylbenzene, etc, can absorb with surfactant at the interface between the organic phase and the aqueous phase to reduce the interfacial tension. Thus the porogens lead to smaller droplets in emulsions and consequently smaller pores in the polyHIPEs. Moreover due to the solubility of the porogens in the monomers, the phase separation of the porogens and monomers can create microparticles during the polymerisation at the wall of the pores. The roughness of the walls thus increases the surface areas of the polyHIPEs. Butler et al.¹³⁶ studied the effects of PVA on the stabilities of emulsion templates (They studied supercritical carbon dioxide-in-water emulsions, therefore PVA was an additive in the continuous phase). The pore sizes of polyHIPEs reduced with the increase of the concentration of PVA, as the increase of the viscosity of the continuous phase. However, an over-viscous continuous phase formed with a further increase of the concentration of PVA. This made the stirring inefficient, resulting in larger droplet sizes. Adding solvents in aqueous phase of emulsion templates was also proved having effect to the stabilities of emulsions. Carnachan et al.¹³⁷ investigated the effects of a serial of solvents, including PEG with a molecular weight of 400, methanol and tetrahydrofuran (THF), on the stabilities of emulsions. They found PEG and THF destabilise the emulsions by enhancing Ostward Ripening effect, while methanol destabilise the emulsions by migrating the surfactants into the continuous phase from the interface between the continuous phase and internal phase. All the solvents led to large-pores and pore throats but still porous polyHIPEs, which suggested an approach to make macroporous polymers with large pores via controlled coalescence of the emulsion templates.

Apart from the components, emulsification conditions also proved to have an influence on the morphology of the resultant polyHIPEs. Abbasian et al.¹³⁸ investigated the influence of stirring speeds on the morphology of polyHIPEs. A vigorous stirring can decrease dramatically the droplet sizes of emulsion templates, leading to small pore sizes in the resultant polyHIPEs. Moreover, due to the strong stirring, the droplet shape was changed from spherical to more or less hexagonal. In contrast, a faster aqueous addition in to the continuous phase can lead to the increase of the pore sizes according to their research. Comparable to stirring speeds in a preparation of emulsion templates, the

energy input in an alternative method to prepare emulsion templates, namely two-syringe system, was considered as an important factor affecting the morphology of emulsion templates. Lépine et al.⁷¹ studied the influence of frequency of the plungers to the morphology of emulsion templates. They changed the frequency from 14min^{-1} to 27min^{-1} , resulting in a decrease in the droplet sizes in the emulsions and subsequently a decrease in pore size in the polyHIPEs. In addition, these affected in turn the pore throat sizes, making them decrease and wide-distributed as well. The shearing time was also investigated and they found at short shearing time (2 min), liquid drainage happened in the emulsion due to the low viscosity of the emulsion. The organic phase flowed from the films separating the droplets to the shared edges of the droplets, leading to polymer beams rather than walls delimiting the pores after the polymerisation. As the shearing time increased from 15 min to 300 min, the polyHIPEs had typical porous structure with decreases in pore sizes. It is notable that in their experiment with the varying in frequencies and shearing times, the emulsions were all stable during polymerisation.

Pore throats are an important feature of many polyHIPEs. Williams has discussed the factors determining the size of pore throats, such as surfactant amount which was reviewed above, and distribution of monomers in the continuous phase¹³⁹. The reasons for the formation of pore throat, however, were unknown. Cameron et al.¹⁴⁰ used cryo-scanning electronic microscopy (cryo-SEM) to observe the morphologies of emulsion templates during the polymerisation via freezing the emulsions in different periods during polymerisation. They claimed that the continuous phase of emulsion templates shrank during polymerisation due to the conversion of monomers into polymers, especially at the gel point. With the contraction of the monomer phase, the films between two droplets became thinner and pore throats started to form at the thinnest points which were the junctions of two neighbouring droplets. However, since one was already at or after the gel point, the continuous phase was strong enough to maintain the stability of the emulsions even with the interconnectivity of the droplets. On the other hand, Menner and Bismarck¹⁴¹ observed the morphologies of polyHIPEs from SEM and they found pore throats half-covered with thin films. They suggested along polymerisation, the solubility of surfactant in the monomer phase decreases. Thus a monomer-rich phase and a surfactant-rich phase are formed. The surfactant-rich phase locates at the liquid film between two adjacent droplets. After the polymerisation, the film composes of majority of surfactant and minority

of polymer network, which is therefore mechanically weak. During the washing and drying process, the films were burst, forming pore throats at the junctions of two droplets.

2.3.4 Applications of polyHIPEs

PolyHIPEs are characterised by tuneable porosities, interconnectivities and surface area, as well as the chemistry of the materials from which polyHIPEs are prepared. These properties gave polyHIPEs a variety of applications.

PolyHIPEs are excellent candidates as matrices for cell-growth due to their high porosities, which are required for nutrients to reach tissues and removal of waste products. In the very early stage, polyHIPEs were used as matrixes and cells were grown on the surface of the polyHIPEs. In that case, the compatibilities of the materials of the polyHIPEs with the cells and the polarities of the materials, which determine the degradation and environmental response of the polyHIPEs, are important. Busby et al. studied PCL⁹³ based polyHIPEs and poly(lactic acid)¹⁴² based polyHIPEs. Both polyHIPEs showed hydrophilicity as they swelled in polar solvents, suggesting they were suitable for tissue engineering. Skin cells were cultured on the surface of the polyHIPEs, the good adhesion, spread and proliferation of cells, as well as their maintained differentiation states indicated the outstanding bio-compatibilities of the polyHIPE matrixes. Akay et al.¹⁴³ studied poly(St-DVB)HIPEs with or without hydroxyapatite for osteoblast growth. They seeded the cells on the surface of the polyHIPEs and studied the penetration of the cells into the bulk. They found the incorporation of hydroxyapatite encouraged the penetration of the cells, letting them move in the depth of the polyHIPE supports. The pore sizes of polyHIPEs seemed on the other hand to have no effect on the movement of cells. In a following work, they developed peptide hydrogel-polyHIPEs hybrid materials for osteoblast growth¹⁴⁴. The peptide (RAD16-I)-cell solution was dynamically seeded within a poly(St-DVB)HIPEs. The physical crosslinking of the peptide within the pores was subsequently initiated via exposing the construct to a phosphate buffered saline, leading to the formation of the peptide-polyHIPE hybrid materials. Due to the excellent bio-compatibility of the peptide hydrogel, the osteoblast penetration in the polyHIPEs was strongly enhanced, compared to the polyHIPEs with hydroxyapatite. Moreover, they also reported the enhanced the distribution of the cells in the polyHIPEs due to the dynamic cell seeding, compared to static seeding used in their early works. Cell-growths on 2D and 3D polyHIPE scaffolds were compared

by Hayman et al.¹⁴⁵. They prepared St-DVB based polyHIPEs, and remarkably, they enlarged the pore size of the polyHIPEs by using THF to destabilise the emulsion templates. This ensured space for large cells or cell aggregations. The growths of neurons on such polyHIPEs were studied. The growth on 2D matrix (i.e. the surface of polyHIPEs) made the mature and stability of the cells relative fast. However, the 3D matrix enhanced the differentiation and made the cells form intricate networks, which was more desirable for neural cell culturing. They also grew liver cells on 2D and 3D polyHIPE scaffolds³. The results showed the cells on 3D polyHIPE scaffolds had enhanced functional activity, compared to cells on 2D polyHIPEs. Toxicological tests on such liver cells found that cells on 3D polyHIPEs provided more accurate data on the responses to cytotoxic compounds rather than cells on 2D polyHIPEs¹⁴⁶. This suggested the 3D cell culturing can provide accurate data on cell functional activity contributing to research.

One application of polyHIPEs which has drawn large interest is as supports for catalysts or reagents in organic chemical synthesis. In this case, polyHIPEs are pre- or post- polymerisation functionalised and thus catalysts are immobilised within the porous structure with or without chemical bonds. Pre-polymerisation functionalisation of polyHIPEs usually involves synthesis of monomers with functional groups. For example, N-(p-vinylbenzyl)-4,4-dimethylazlactone was synthesised and used for preparation of polyHIPEs by Lucchesi et al.¹⁴⁷. The resultant polyHIPEs showed capability of amine scavengers in batch and flow-through processes. Moreover, due to the reactivity of azlactone groups, the polyHIPEs can function as precursors for further modification. Mercier et al.¹⁴⁸ prepared polyHIPEs based on copolymers of St, DVB and 4-Ethyl-(2-dibutylchlorostannyl) styrene. The incorporated organotin functioned as a catalyst for the reduction of 1-bromoadamantane and the cyclisation of 1-Bromo-2-(prop-2-enyloxy) benzene. The reduction experiment showed the good activity and stability of the supports. The cyclisation experiment demonstrated excellent yield, which they believed due to the outstanding diffusion of the raw materials within the polymer matrix. One well-established polyHIPE support was prepared via post-functionalisation of VBC based polyHIPEs. Poly(VBC-DVB)HIPEs were functionalised with tris(2-aminoethyl)amine and other nucleophilic amines. The functionalised polyHIPEs were efficient in scavenging 4-Chlorobenzoyl chloride at ambient temperature⁷⁸. VBC-DVB based polyHIPEs were also used for Suzuki coupling reactions¹⁴⁹. The procedure included the synthesis of 4-iodobenzoic acid on polyHIPEs, Suzuki coupling of

4-methoxybenzeneboronic acid on the functionalised polyHIPEs and cleaves of biaryl compound. In the flow-through method, the polyHIPE system was compared to commercial porous bead supports. The polyHIPEs supports were believed more efficient than the porous beads, as the channel effects observed in the beads supports. VBC based polyHIPEs supports were optimised via enhancing the surface area of the porous structure⁸⁰. Hypercrosslinked poly(VBC)HIPEs was prepared, which possessed $700 \text{ m}^2 \text{ g}^{-1}$ surface areas compared to $6.4 \text{ m}^2 \text{ g}^{-1}$ of normal poly(VBC)HIPEs. The polyHIPEs were subsequently functionalised with 4-(N-methylamino) pyridine, and were used to catalysis the acrylation of 1-Methylcyclohexanol. Due to the surface area the activity of the hypercrosslinked polyHIPEs was much higher than that of the normal polyHIPEs. Moreover, this approach was superior to using porogens to create high surface area, as hypercrosslinking did not decrease the mechanical properties. Post-functionalisation of polyHIPEs with organo-metals were studied by Desforges et al.¹⁵⁰. Pd-polyHIPEs were prepared via a short route synthesis. The short route preparation was simply immersing polyHIPEs into a water/THF solution of K_2PdCl_4 and reduction of Pd (II) then occurred spontaneously or directed via reagents or UV light. The resultant Pd-polyHIPEs showed good activity in catalysis in the hydrogenation of allyl alcohol and reusability, which was comparable with commercial Pd-carbon supports. Au-polyHIPEs composites were prepared via a similar approach¹⁵¹. HAuCl_4 was dissolved in water/acetone mixture, and afterwards the solution was forced into a polyHIPE monolith. The reduction of the Au (III) occurred, forming Au nanoparticels with in the porous structure. The catalytic activity of the Au-polyHIPEs system was tested using the reduction of eosin. Due to the macroporous structure, which cannot perturb the diffusion of molecules, polyHIPEs were considered as good candidates for heterogeneous catalyst system. Another kind of porous catalytic system was prepared from polyHIPE precursors. SiC was mixed with St and DVB and consequently incorporated in polyHIPEs¹⁵². The polyHIPEs were then pyrolysed into SiC porous materials. The SiC 'polyHIPEs' were used with ceria to catalyse temperature programmed oxidation of methanol.

Many researchers have found the applications of polyHIPEs in bio-reactors in which cells or enzymes are immobilised within polyHIPEs and the systems are designed for chemical synthesis, conversion or removal. Griffiths and Bosley¹⁵³ described the immobilisation of *Citrobacter freundii* within St based polyHIPEs. The system showed a continuous biotransformation of glycerol to trimethylene glycol. Erhan et al.¹⁵⁴ reported *Pseudomonas syringae* immobilised within polyHIPEs based on St and DVB.

The system was made a fixed bed for phenol removal. The large pore size and pore throat size, compared with the cell size, ensured the penetration and proliferation of cells. However, the high proliferation rate made the cell particles quickly convert to biofilms, which hindered the transfer of nutrient and gas, and moreover limited the degradation of phenol at only the surface of the polyHIPEs. Due to the hydrophobic surface of cells, the adhesion between cells and polyHIPEs (which were also hydrophobic) were very well. This incorporating with the surface topology reduced the washout effects on cells, brought by fast dilution rates. Immobilisation of lipase on polyHIPEs and using the system for biodiesel production were developed by Dizge et al.¹⁵⁵⁻¹⁵⁷. The lipase was immobilised within a polyHIPEs based on St, DVB and poly(glutaraldehyde). The existence of aldehyde groups made the immobilisation of lipase efficient and it also ensured the activity of the enzymes for repeated uses and after storage. The system was mixed with many resources to produce biodiesel. The researchers reported that the hydrophobic surface caused by the copolymer of St and DVB prevented the inhibition of by-product glycerol, thus sustained the production of biodiesel. In addition, polyHIPE beads and powders appeared to be more efficient in biodiesel production as their better mixing with reactants, compared to polyHIPE monoliths.

The applications of polyHIPEs in membranes have been studied by Ruckenstein and co-workers. They prepared various polyHIPEs composites via emulsion templating containing monomers in both phases and used the composites for pervaporation. Poly(St-DVB)HIPEs filled with polyacrylamide were used for the separation of ethanol and water via pervaporation¹¹⁵. They found high water permeation through the membranes due to the hydrophilic pore surface of the polyHIPEs. The selectivity of the membranes depended on the composition of the feeding solution and temperature and the highest selectivity was 50, meaning the fraction of permeate water was 50 times larger than that of the permeate ethanol. Separation of ethanol and water was also carried out using a poly(DVB)HIPEs filled with poly(sodium acrylate) membranes¹¹⁸. After the preparation of emulsion templates, the emulsions were placed between two glass plates with a certain distance and polymerised to make membranes. The selectivity of the membranes ranged from 32 to 235, depending on the feeding composition and temperature. However, this membrane was also characterised by high brittleness due to the presence of DVB in the continuous phase and low permeation. In a following work, DVB in the continuous phase was changed to St and butyl acrylate⁸⁶. However, in this experiment, the researchers polymerised the

emulsion templates prior to grinding them into powders. Afterwards, the powders were hot-compressed into membranes. The presence of St-BA instead of DVB made the scaffold (resulting from the continuous phase) of the membrane elastic, which made the preparation of the membranes easier. Additionally due to the elasticity of the membrane the swelling degree in water increased. The permeation of the composite membrane was improved via adding porogen in the continuous phase¹⁵⁸. The presence of the porogen in the emulsion templates led to an increasing porosity in hydrophobic scaffold of the resultant polyHIPEs, thus increasing the permeation rate. However the porosity in the scaffold can actually increase the flow rate of both water and ethanol, therefore the addition of porogen decreased the selectivity of the membranes. On the other hand, poly(acrylamide)HIPEs filled with poly(St) were prepared via o/w emulsion templates through the sandwiching method¹⁵⁹⁻¹⁶⁰. The membranes were used for the separation of toluene and cyclohexane. Despite the feeding composition and temperature, the permeate rate and selectivity were also depended on the fraction of the poly(acrylamide) (Here it is the scaffold). The increase of poly(acrylamide) meant the unswollen parts of the membrane increasing, while the volume of the pathway for the solution reduced, therefore decreasing the permeate rate. Bhungara reported filtration media prepared from poly(St-DVB)HIPEs⁷². The cylinder-shape monolith was made to a filtration module via making channels across its thickness. The media showed good rejection to aragonite particles, however, the flow rate decreased and the pressure drop increased as the experiment was carried on, caused by the formation of particle cakes at the surface of channels. The rejection to cationic surfactant of a poly(St-DVB)HIPEs was modest. The rejection was improved via sulphonating the polyHIPEs. The sulphonated polyHIPEs provided negative charges at the surface of the channels, which attracted the cationic surfactant, therefore leading to a better rejection, compared to unmodified polyHIPEs. Krajnc et al.⁹⁰ reported using poly(GMA-EGDMA)HIPEs in chromatography for protein separation. They prepared chromatographic columns using polyHIPEs with up to 90% porosity, which was impossible for conventional method to prepare chromatographic columns. The separation ability of the polyHIPEs monolith was lower than the commercial ones, which they believed due to the high porosity of the polyHIPEs. In a following work, they prepared more flexible polyHIPE membranes (based on GMA-EGDMA-EHA) rather than monoliths⁵. The membranes were wrapped around and fit in a chromatography module. The system showed a high binding capacity for proteins.

In summary, the methods to produce porous polymers, with pore sizes ranging from macroporous to microporous pores were reviewed in this chapter. Emulsion templating provides an approach to prepare macroporous polymers, namely polyHIPEs, which are characterised by controllable porosity, pore size and interconnectivity, as well as other various functionalities, such as biocompatibility, capability of separation purpose, swelling behaviour, etc. Methods to produce polyHIPE films, casting and slicing, have been reviewed in this chapter. However, these methods seem not to be adequate to prepare polyHIPE films with complex patterns. Therefore, it is aimed to explore printing as a means to create sophisticated patterned films. Hydrogel filled polyHIPEs have been used as pervaporation membranes. It therefore seems to be a good strategy to make functionalised polyHIPEs for separation purposes. In this project, hydrogel filled polyHIPEs are also produced but was aimed for ultrafiltration membranes. Moreover, the challenge mentioned in the original publications, brittleness of their membrane support, is also solved in this project. For applications of polyHIPEs, for instance in pressure sensors, flexible porous films are required, so the films can withstand necessary deformations during their applications or processing. As learned from the literature review, some acrylate monomers can provide flexibility to polyHIPEs. Therefore, this can be inspiration to copolymerise proper acrylate monomers with optimised compositions within emulsion templates to make flexible macroporous films.

Chapter 3 Preparation of macroporous polymer films

Abstract

In this chapter, three methods to prepare polyHIPE films are discussed. Firstly, slicing polyHIPE monoliths using a microtome provides a way to prepare films with defined thickness. Moreover cutting a monolith into films will result in films with open surface and the structure of the surface is same as the bulk. Thus slicing is used in the PhD project to prepare symmetric polyHIPE membranes. Casting emulsion templates into films, which is then UV polymerised, is an alternative way to prepare polyHIPE films. This method is advantageous for fast preparation of macroporous films based on acrylate. Printing emulsion templates is newly developed, which provides a method to create patterned porous polymer films. Moreover, multilayer printing, which allows making 3D porous medium with complex structures, was also explored.

3.1 Introduction

Although most of polyHIPEs are prepared as monoliths, polyHIPE films have also been reported. Briefly polyHIPE films are prepared via slicing or casting. Bokhari et al. have reported slicing St-DVB based polyHIPE monoliths into films with a thickness of $120\text{ }\mu\text{m}$ ^{3,146}, which is designed for 3D cell cultural. The main reason for slicing polyHIPEs into films is for the open porous surface of the films, which allows the access and penetration of cells and nutrition and gases into the inner space. Casting refers to spreading emulsion templates into films on a substrate and polymerising subsequently. Ruckenstein and Park¹¹⁵ have reported preparation of hydrogel filled poly(St-DVB)HIPE films with a thickness of $150\text{ }\mu\text{m}$ via setting emulsion templates between two glass plates and thermal polymerising them afterwards. The membranes were used for separation of water and ethanol. However, Ruckenstein and Sun¹¹⁹ have also mentioned that the mechanical properties of such membranes are not satisfactory. Pulko and Krajnc⁴ have prepared polyHIPE films via casting emulsion templates between two glass plates and polymerising them subsequently. They prepared films with different thicknesses ranging from $30\mu\text{m}$ to up to $500\mu\text{m}$. Moreover, they displayed the open cell surface structure of the films. More recently, Pulko et al.⁵ prepared polyHIPE membranes via casting

for chromatograph applications.

An advanced method to make thin films, as compared to casting, is printing, in which inks are not only spread into thin layers, but also form patterns simultaneously. Printing is an important process in art and publishing, where it has been used for centuries. The principles of printing can be divided into planographic printing, relief printing, intaglio printing and stencil printing¹⁶¹. More recently, printing has been also applied in engineering, due to its advantage to form thin layers and create patterns on substrates simultaneously. The main printing processes for engineering applications include gravure printing¹⁶², screen printing¹⁶³⁻¹⁶⁶ and inkjet printing¹⁶⁷⁻¹⁶⁹, and they found applications in bio engineering¹⁷⁰, preparation of electric device^{162,164,169}, and solar cells^{163,165-166,171}. In the above processes, inks for printing usually are solutions, suspensions and pastes. Although emulsions (usually oil-in-water emulsions) have been used as inks for printing, the purposes to use emulsions as inks are for reducing the volatile of organic components¹⁷² and for the convenience to clean the printer¹⁷³, while printing emulsion templates to produce macroporous films have not been developed yet.

In this chapter the methods to prepare polyHIPE films are summarised and compared, which is very important considering the specific applications of polyHIPE films, such as supported membranes or pressure sensors (discussed in the following chapters). The formulation of emulsion templates will be optimised so they can be processed into films. Moreover, to make films with desired thickness (e.g. less than 400 μm for membrane tests) and surface morphology (e.g. open surface for membrane tests), the processing of polyHIPE films will be controlled. Printing emulsion templates to make macroporous polymer films is also described in this chapter, as it is advantageous for producing films with desired patterns. Initially, it is necessary to study if the printing process can affect the morphology of the emulsions and subsequently of the macroporous polymer films. Therefore, in this chapter, the morphology of printed macroporous polymer films is mainly investigated.

3.2 Experiment

3.2.1 Materials

Styrene (St), divinylbenzene (DVB), methacrylic acid (MAA), ethylhexyl acrylate (EHA), NaOH and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ as well as oleic acid, chloroform and methanol, which were used for modification of silica

particles, were purchased from Sigma-Aldrich (Gillingham, UK). Polyurethane diacrylate (PUDA, Ebecryl 8402) was kindly supplied by Cytec (Belgium). All the monomers were used as received. Hypermer B246, supplied by Croda (East Yorkshire, UK), was used as surfactant. Ammonium persulfate (APS, Sigma-Aldrich, Gillingham, UK) was used as thermal initiator. Darocur 1173, purchased from Ciba (Basel, Switzerland) was used as UV initiator. Silica particles with an average diameter of 20 nm were kindly provided by Ortwin Rave Produkte and Dienstleistungen (Koblenz, Germany).

3.2.2 Particle modification

Modification of silica particles was conducted as described elsewhere¹²⁶. Briefly, silica particles were mixed with oleic acid and chloroform in a ratio of 1g silica: 7ml oleic acid: 6ml chloroform. The mixture was stirred for 3 hours and then left overnight. The mixture was transferred into 50 ml centrifuge tubes and about 30 ml methanol was added to ease the precipitation of the particles. The mixture was centrifuged at 6000 rpm for 20 min. Afterwards, the supernatant above the modified particles was decanted. 10 ml chloroform was added into the pellet and the mixture was ultrasonicated for 30 min. Methanol was added in the mixture to fill up to 40 ml, and the mixture was centrifuged at 6000 rpm for 20 min. Then the liquid was disposed and the filtrate was placed in oven. The particles were dried at 110 °C under vacuum until the weight was constant.

3.2.3 Emulsion preparation

A reaction vessel equipped with a glass paddle rod connected to an overhead stirrer was used for preparation of emulsion templates. The internal phase of E-slice1 was aqueous solution of 10g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and APS. Monomers and surfactant were mixed in the vessel as the continuous phase. The internal phase was dropped into the continuous phase under stirring at a speed of 400 rpm. Afterwards, the emulsions were further stirred at a speed of 2000 rpm for 3 min to homogenise the emulsions further. The internal phase for E-slice2 was an aqueous solution containing 12 vol% MAA. The MAA was deprotonated by adding NaOH to the solution until pH 12 was reached. The internal phase was added dropwise into the continuous phase under stirring. Afterwards, the emulsions were stirred at a speed of 2000 rpm for 2 min. APS was dissolved into less than 0.5 ml water and added into the emulsion, then the emulsion was further stirred for 1 min.

E-cast, E1 and E2 were prepared following a same procedure. Monomers, surfactant and Darocur 1173 were mixed in the vessel. The internal phase, which was an aqueous solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, was dropped into the mixture under stirring at a speed of 400 rpm. After the addition of the internal phase, the emulsions were stirred at a speed of 2000 rpm for 3 min.

For Pickering emulsions (E2 and E4), the particles were dispersed within the monomers by homogenising at a speed of 20000 rpm for 30 min. The continuous phase was then transferred to the reaction vessel. The internal phase (aqueous solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) was added into the continuous phase under stirring at a speed of 500 rpm. After the addition of the internal phase, the emulsion was stirred for another 3 min at 500 rpm. Seven emulsion templates were prepared and the detailed recipes are summarised in Table 1. Here 'E' refers to the emulsion templates, while after polymerisation the corresponding samples were named 'PE'.

Table 3.1 Recipes of sample emulsions for film preparation

	E-Slice1	E-Slice2	E-Cast	E1	E2	E3	E4
Continuous phase (vol%)^a	20	20	20	40	40	25	25
EHA (vol%)^b	33.33	33.33	20	47.06	50	58.82	62.5
St (vol%)	41.67	41.67	40	-	-	-	-
DVB (vol%)	8.33	8.33	20	-	-	-	-
PUDA 8402 (vol%)	-	-	-	47.06	50	35.29	37.5
B246 (vol%)	16.67	16.67	20	5.88	-	5.88	-
Modified silica particles (w/v%)^c	-	-	-	-	7	-	10
Darocur 1173 (mol%)^d			2	2	2	2	2
APS (mol%)	1	1	-	-	-	-	-
Internal phase (vol%)	80	80	80	60	60	75	75

a. the continuous phase volume ratio is with respect to the whole volume of emulsion. b. the monomers volume ratio is with respect to the continuous phase. c. the particle weight percentage is with respect to the volume of continuous phase. d. initiator ratio is molar percentage of the amount of carbon-carbon double bonds in the monomers.

3.2.4 Film preparation and polymerisation

a. Slicing polyHIPE monoliths into films

PolyHIPE films were prepared via slicing from PE-slice1 and PE-slice2. The emulsions were charged into a mould with a diameter of 50 mm and a height of 30 mm. The mould was placed in oven and the emulsions were polymerised at 50°C for 48 hours. The monoliths were washed in a mixture of methanol and water for 24 hours and then sliced into films using a microtome (RM2245 Rotary Microtome, Leica Ltd, Milton Keynes, UK).

b. Casting emulsion templates

Emulsions were cast onto aluminium foils, polyvinylidene fluoride films and glass plates. Masking tapes were stuck layer by layer on the substrates to make two parallel blocks with a thickness of about 300 μm . Between the blocks E-cast was cast using a blade. Afterwards the cast layers were polymerised under an UV lamp (UVP-100, with highest power of $20\text{mW}\cdot\text{cm}^{-2}$, UVP, Cambridge, UK,).

c. Printing emulsion templates

Emulsion templates E1-E4 were printed by rolling-pin printing and by screen printing. A transparent polypropylene film was used as substrate. For rolling-pin printing, masking tapes and double side tapes were stuck on the substrate parallel as blocks. Using various layers of tapes, the thickness of the blocks was adjusted in order to print films with different thicknesses. A stainless steel rolling pin with a diameter of 1 cm and a length of 30 cm was placed on top of the blocks, and the emulsions were put before the pin. The rolling pin was rolled by hand forward and spread the emulsion on the substrates.

For screen printing, a woven screen with a mesh size of $250\ \mu\text{m}\times 250\ \mu\text{m}$ was used (Fig 1). The substrates to print on were placed under the screen; the emulsions were poured on top of the screen. A blade was used to spread the emulsion evenly on the screen and the substrate. Afterwards, the screen is removed leaving behind a thin emulsion layer on the substrate for subsequent polymerisation. For both rolling-pin-printing and screen printing, the substrates with the thin layers of emulsions were immersed in a bath which was an aqueous electrolyte solution of the same concentration as the internal phase of the emulsions. The emulsions were then polymerised in the solution under a UV lamp for 2 min. The polymerised H(M)IPE films will have a sample ID ending with

either 'R' for rolling-pin printing or 'S' for screen printing. In order to investigate the effect of printing process on the structure of the resultant porous films, control samples (non-printed samples) were prepared. E1-E4 were cast on a glass plate with blocks of 800 μm prior to UV polymerisation of the emulsion templates. The resultant polyH(M)IPEs were the control samples and the sample ID will end with 'C'.

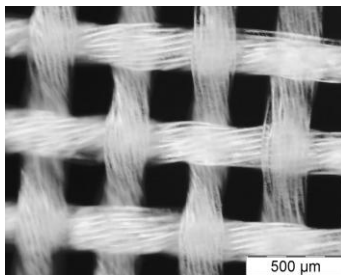


Fig 3.1 Microscope image of the sieve for screen printing.

3.2.5 Characterisation

a. Oleic acid loading of Silica particle

Thermal gravimetric analysis (TGA, TA Q500 TGA, TA instruments Intl., Delaware, USA) was used to measure the oleic acid loading on the silica particles. About 5mg silica particles were heated to 600 $^{\circ}\text{C}$ at a rate of 10 K/min. The weight loss of the particles, referring to the degradation of oleic acid, was plotted against the temperature (the curves are in the Appendix I). The ideal silica particles for stabilising emulsion templates were with 3.5 wt% oleic acid loading¹²⁶.

b. Morphology of the polyH(M)IPEs

The cross-section and surface of the macroporous films were observed using scanning electron microscopy (SEM, Hitachi S-3400N, Hitachi High Technologies, Germany). The samples for SEM were gold-coated to obtain sufficient conductivity prior to observation. The SEM was operated in secondary electron mode using a voltage of 15kV for the electron beam. The images were further analysed using software UTHSCSA ImageTool. To determine the pore size at least 200 pores were measured. However, the average pore size determined by this method underestimates the real pore size. The cross-section of a pore may not be across the middle of the pore but across randomly the pore, thus giving a smaller diameter. Another method to determine pore size, namely mercury porosimetry, was not used in this experiment, as it requires the samples to be permeable to mercury. However, some

of the samples, such as poly-Pickering-H(M)IPEs possessed a closed-cell structure, thus this measurement was not applicable.

c. Densities and Porosities

The matrix densities of the samples were measured using Accupyc 1330 (Micrometrics Ltd., Limited, Dunstable, UK). The samples were ground into powder. For each sample, about 0.5 g powder was placed into a chamber, whose volume has been measured by filling empty chamber with helium till 0.131 MPa reached. Helium was charged into the chamber with the samples until a pressure of 0.131 MPa was reached, the volume of the material was determined by the difference of the volume of the empty chamber and the chamber with the samples, thus the density of the material can be calculated. To measure the foam densities, the control samples or printed films were cut into small pieces with dimensions of 10 mm by 10 mm. The sample dimensions were measured after cutting and the pieces were weighed. The foam densities, ρ_f , were calculated as follows:

$$\rho_f = \frac{m}{V}$$

Where, m is the weight of the sample and V is the volume of the sample.

The porosities, P, of the samples were calculated by:

$$P = \left(1 - \frac{\rho_f}{\rho_m}\right)$$

Where, ρ_m is the matrix density.

3.3 Results and discussion

Slicing polyHIPE monolith into films was carried out using a microtome in this project. The samples are clamped on a sample holder. In one cycle, the blade on the microtome moves upward and cuts the sample and moves downward to its initial position. After each cycle, the sample holder move forward for a desired distance in the direction perpendicular to the moving direction of the blade. Therefore in the next cycle, the blade can section a film with desired thickness. Due to the angle between the blade and the sample, the sliced films tended to roll up. In that case, the films can crack if they are brittle. Therefore here wet monoliths, which are less brittle, were sliced. Poly(St-DVB)HIPEs films

prepared via slicing using a microtome has been reported³. However, the attempt to prepare such films failed as the poly(St-DVB) were too brittle and the sliced films cracked. Thereafter poly(St-DVB-EHA)HIPEs were prepared for slicing, as incorporating EHA into the poly(St-DVB)HIPEs can reduce brittleness⁸³. In PE-slice1, the DVB concentration was relatively low and the polyHIPE monoliths were successfully sliced into films. However, slicing the monoliths with double DVB concentration led to cracked films. PolyHIPEs with or without hydrogel filling in the pores were compared (PE-slice1 and PE-slice2, respectively). The sliced films with thickness of 200 μ m from both monoliths are satisfactory. However, 250 μ m films from the polyHIPEs without hydrogels (PE-slice1) contained fractures (Fig 3.2a), while films from the hydrogel filled polyHIPEs (PE-slice2) had good-quality. Since the produced polyHIPE films tended to roll up, thick films had to be softer to prevent cracking. PolyHIPEs with hydrogels may adsorb slightly water in the poly(St-DVB-EHA)HIPEs due to the copolymerization of MAA in the scaffold¹²⁰. Therefore, polyHIPE with hydrogels were softer than the one without hydrogels, hence resulting in good-quality films. Fig 3.2 (b) shows the SEM images of PE-slice2 films with a thickness of 200 μ m. The films have a uniform thickness and one can see that the surface structure (Fig 3.2 d) and the bulk structure (Fig 3.2 c) are identical. This is ideal for symmetric membranes which have surface morphology identical to the bulk morphology. Thus, in this PhD project, the symmetric polyHIPE membranes for filtration purpose are prepared via slicing.

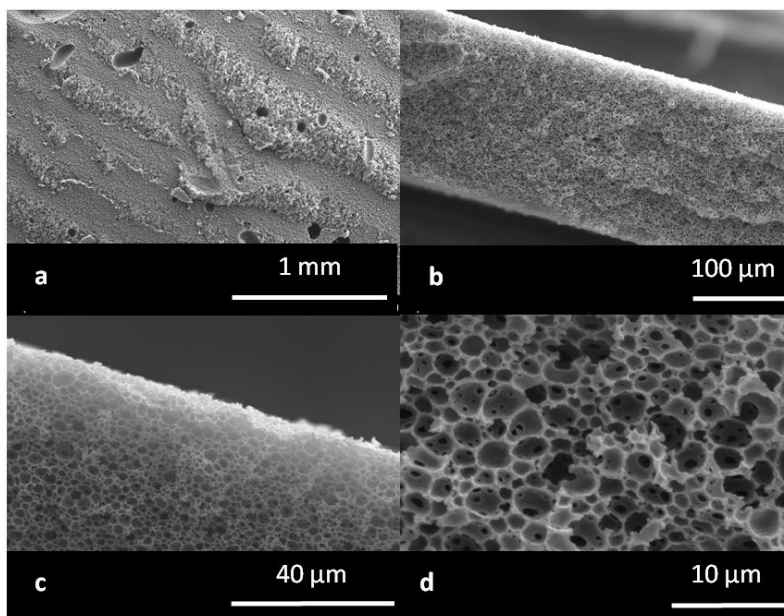


Fig 3.2 Structure of sliced polyHIPE films. (a) Cracks on the surface of films when the films are relatively brittle. (b) Cross-section of films. (c) Top of cross-section of films. (d) High magnification of surface of films.

Ruckenstein and Park have reported preparation of polyHIPE films between two glass plates¹¹⁵. In their case, the emulsion thin layer was sealed between two glass plates to prevent the emulsions contacting air and therefore the emulsion could thermally polymerise. In contrast, here the emulsion templates were cast on substrates but not covered (exposing them to air on one side) in order to simulate the conditions during large scale or continuous casting: applying a cover film or even glass would complicate and, therefore, increase the costs of a casting process. Thermal polymerisation of the emulsions will take hours and during that time it can accelerate the evaporation of the monomers in the emulsions, thus it is not suitable for the cast thin layer. To address this problem, UV polymerisation was used to polymerise the emulsions rapidly. The first preparation of St-DVB based polyHIPEs failed, as both monomers can hardly be initiated by UV radiation and the thin layer of emulsions evaporated under the UV lamp before polymerisation. However, E-cast based on EHA, St and DVB successfully polymerised within 15 min under the UV lamp and did not show any visible destabilisation during polymerisation. This may be due to the presence of EHA in the emulsions, which helped to initiate the polymerisation. E-cast was casted on different substrates and the surface structures contacting the substrates were investigated (Fig 3.3). The surface of the polyHIPEs exposed in air was a skin with few opened pores. Since air is a hydrophobic media, polyHIPEs with a skin are expected. The pores can be caused by the evaporation of the internal phase due to the heating during the polymerisation, or simply the skin cracking due to the shrinkage during polymerisation. The surface of PE-cast to glass plates was open-cell. The surface structure is similar to that reported by Pulko and Krajnc⁸¹, which consist of flat surface with large open-cell pores caused by coalescence of droplets. PolyHIPE films produced by polymerisation of HIPEs cast against aluminium foil had a similar surface structure as compared to the one polymerised against glass plates. The surface was flat with large open-cell pores since aluminium foil is a hydrophilic material. The pores are even larger compared to the polyHIPE surface against glass plate, which was probably due to the texture surface of aluminium foil, which helped the coalescence of droplets in the emulsions. The polyHIPEs surface against PVDF was completely open, which was typical polyHIPE structure. This is due to the skin was peeled off from the films when the film was removed from the PDVF substrate. However, since the PVDF films are not UV transparent, the emulsions cannot be polymerised between two PVDF films. Therefore it is difficult to obtain films with both sides of open cell structures. On the other hand,

casting and UV polymerisation is advantageous for fast curing of emulsion templates with the presence of acrylate in the templates. Therefore the flexible polyH(M)IPE films based on acrylate monomers are prepared via casting and UV polymerisation in this PhD project.

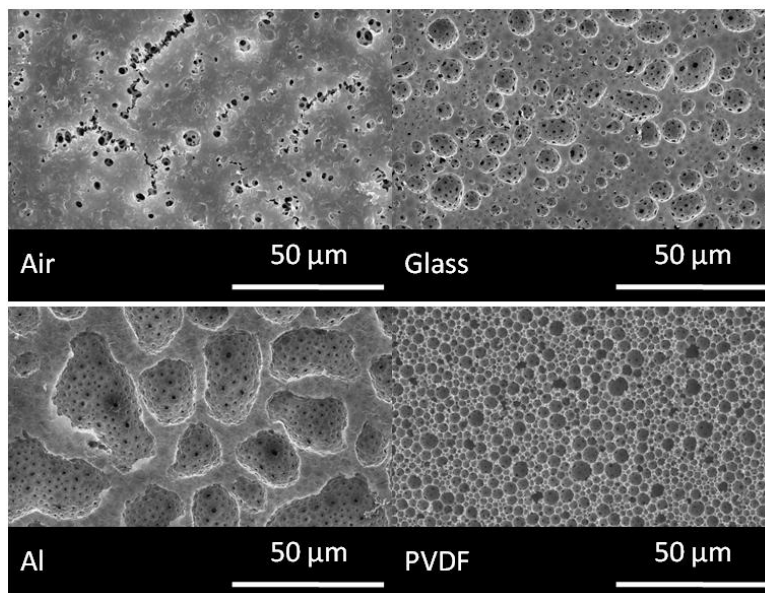


Fig 3.3 Surface structure of poly(EHA-St-DVB)HIPE (PE-cast) on different substrates.

E1 and E2 were two MIPEs with internal phase ratio of 60%, while E3 and E4 were HIPEs with 75% internal phase. The monomer ratios within the MIPE set and the HIPE set were identical but in each set, one MIPE and one HIPE were stabilised by particles, and the other ones were stabilised by surfactant. The monomers used in E1-E4 were all acrylate monomers. PUDA is an oligomer with long flexible backbone and encapped with two acrylate groups, therefore acts as crosslinker of the polyH(M)IPEs and provide flexibility of the polyH(M)IPEs. EHA is an elastomer that has been used in previous research to reduce the brittleness of typical St-DVB based polyHIPEs⁸³. The control samples were prepared by casting the emulsion templates into films with thicknesses of 0.8 mm and polymerising them under UV light. Because of the acrylate-based monomers of E1-E4, the UV polymerisation of the emulsions was completed within 2 minutes, which was much faster than that of E-cast. After polymerisation, the samples were washed and dried for characterisation. The matrix and foam densities, porosities and pore sizes are listed in Table 3.2. PE1C and PE2C had the same composition, only the emulsifiers were changed. Due to the presence of silica particle in PE2C, the matrix density of PE2C is slightly higher than that of PE1C. The foam densities of PE1C and PE2C are identical within error (about 0.46 g/cm³), and so are the porosities (approximate 60%). This is as

expected since PE1C and PE2C were prepared from emulsion templates with 60% internal phase. PE4C has a higher matrix density than PE3C, due to the addition of silica particles. The foam densities of the two samples are identical in range of error, approximate 0.32 g/cm^3 . The porosities of PE3C and PE4C are about 75%, as they were prepared from emulsion templates with 75% internal phase. Fig 3.4 shows the SEM images of PE1-4C. PE1 and PE3 were made from surfactant-stabilised emulsion templates. The polyHIPEs possess pores with diameters of 2.5 and $2.3 \mu\text{m}$ (Table 3.2), respectively, and pore throats connecting the pores. PE2 and PE4 are poly-Pickering-emulsions, which are characterised by large closed pores with diameters of $18 \mu\text{m}$ and $35 \mu\text{m}$, respectively (Table 3.2).

Table 3.2 Properties of control samples PE1-PE4

	Matrix density (g/cm^3)	Foam density (g/cm^3)	Porosity (%)	Pore size (μm)
PE1C	1.10 ± 0.01	0.46 ± 0.07	58 ± 9	2.5 ± 0.9
PE2C	1.140 ± 0.001	0.49 ± 0.03	57 ± 3	18 ± 7
PE3C	1.08 ± 0.01	0.32 ± 0.05	70 ± 11	2.3 ± 0.7
PE4C	1.14 ± 0.01	0.33 ± 0.04	71 ± 9	35 ± 11

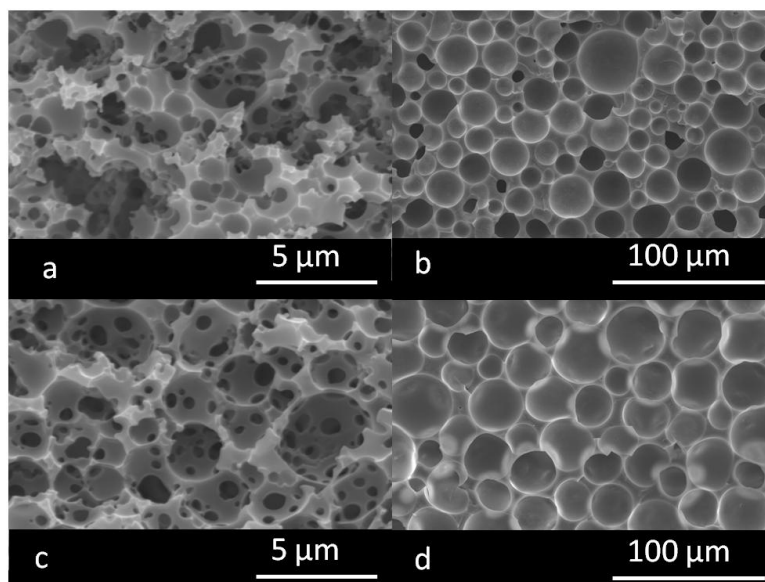
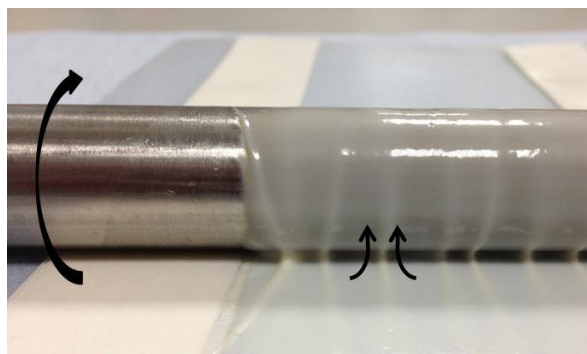


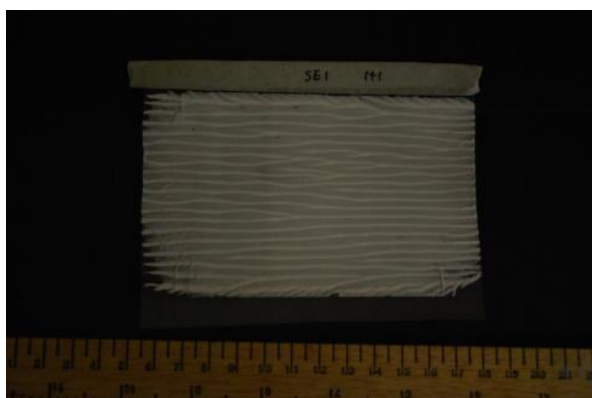
Fig 3.4 SEM images of the control PUHA-EHA based polyH(M)IPE samples. (a)PE1C; (b)PE2C; (c)PE3C; (d)PE4C.

E1 was printed using a rolling-pin on a polypropylene film. Tapes were stacked on the substrate as blocks and the emulsion was placed on the substrate between the two blocks. The rolling-pin perpendicularly sat on the blocks and moved along the blocks. By pushing the rolling-pin, the pin rolled forwards to spread the emulsion on the substrates. Due to the adhesion between the emulsion and the substrate, the emulsion stuck to the substrate and formed a thin layer. The thicknesses of the blocks were varied from 100 μm to 420 μm to prepare thin emulsion layers, subsequently polyMIEPE films, with varying thicknesses. The rolling-pin printed emulsion layers had uniform thicknesses in the rolling direction, meaning the blocks helped to maintain the thickness of the thin layer during printing in the rolling direction. However the layers had texture on the surfaces, parallel to the blocks, causing the thickness in the perpendicular to the rolling direction to vary. This surface texture was caused by the adhesion of the emulsion templates with the rolling-pin, the emulsions stuck at the rolling pin surface, and was dragged with it to form a peak shape on the rolling-pin surface when the rolling-pin surface was lifted off from the printed emulsion layer (Fig 3.5 a). As the emulsions sticking to the rolling-pin was continuously dragged up by the moving pin, the textures on the thin emulsion layers formed therefore in the rolling direction. UV polymerisation of the printed emulsions in air failed as the emulsions phase separated and evaporated before polymerisation due to the heat irradiated by the UV lamp. Therefore, the printed thin layers were polymerised in an aqueous electrolyte solution. The bath with the same electrolyte concentration as the internal phase of the emulsion template was used to suppress potential liquid transport between the internal phase and the bath. The polymerised films maintained the shape of the thin emulsion layer, resulting in a thin textured film (Fig 3.5 b). The SEM images reveal the textures of the PE1R1-3 films that are perpendicular to the rolling direction (Fig 3.6a, c and e). The thicknesses of the films were measured on the flat film parts. As the thicknesses of the blocks increased from 100 μm to 430 μm , the thickness of the films increased from 33 μm to 149 μm (Table 3.3). The decreases of the thicknesses of the films as compared to the blocks can be attributed to several reasons: Firstly, during the printing, the rolling-pin was pushed forwards. It is inevitable that the rolling-pin was pressed down onto the blocks compressing them. Moreover, the formation of the textures suggests the emulsions were dragged up by the rolling-pin during the printing. Thus the thicknesses of the flat film parts are lower than expected. The high magnification SEM images show that the films have porous structure (Fig 3.6b, d and f). The pore sizes of the printed PE1R1-3 films are 2.7 μm , 2.5 μm and 2.6 μm (Table 3.3), which are

identical within error to the control samples. Additionally the foam densities of PE1R1, PE1R2 and PE1R3 were also identical within error to the control sample (Table 3.3). This indicates the rolling-pin printing did not affect the droplet sizes and internal phase ratios of the emulsions, in turn the porous structures of the polymerised films.



(a)



(b)

Fig 3.5 (a) Scheme of formation of textures during rolling-pin printing. (b) Representative picture of printed films via rolling pin printing

Table 3.3 Properties of PE1 films from rolling-pin printing

	PE1R1	PE1R2	PE1R3
Blocks (μm)	100	210	430
Films thickness (μm)	33 ± 3	68 ± 5	210 ± 16
Pore size (μm)	2.7 ± 0.7	2.5 ± 0.7	2.6 ± 0.6
Foam densities (g/cm^3)	0.47 ± 0.07	0.48 ± 0.09	0.49 ± 0.08

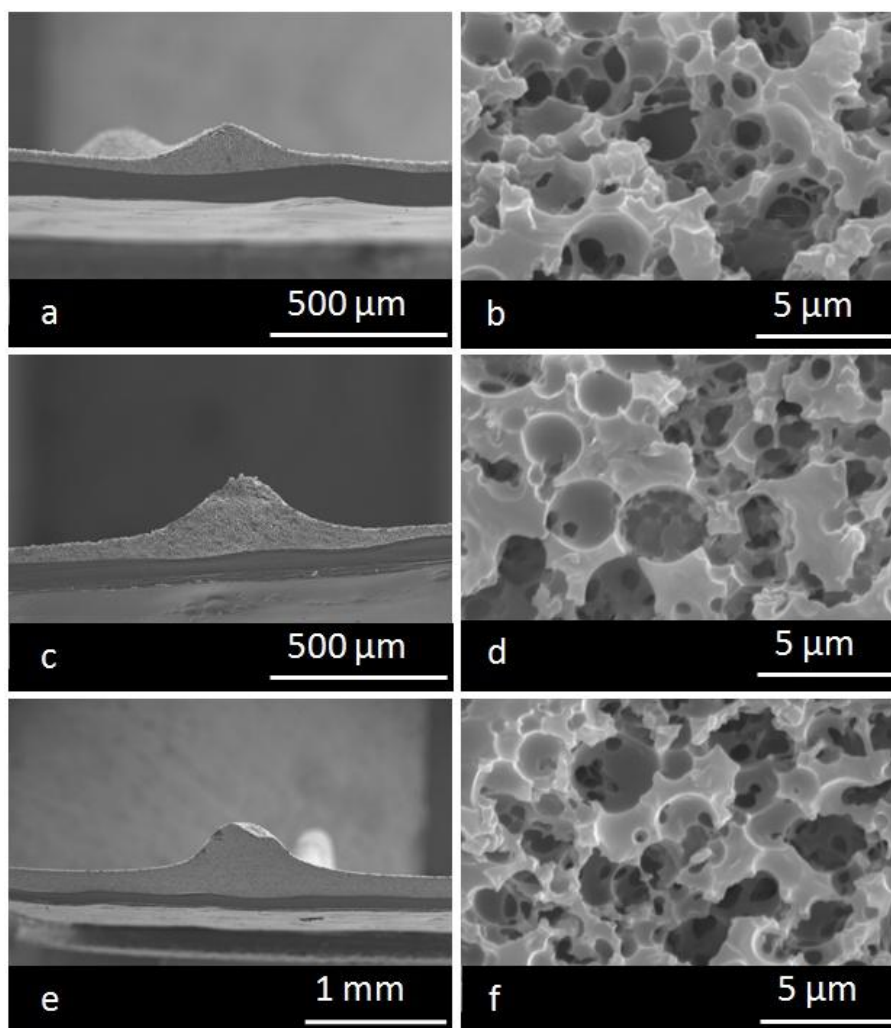


Fig 3.6 SEM images of poly-surfactant-stabilised-emulsion films from rolling-pin printing. (a) PE1R1; (b)PE1R1; (c)PE1R2; (d)PE1R2; (e)PE1R3; (f)PE1R3.

E2 having a lower viscosity than E1 was then rolling pin printed. The thin layer emulsion appeared to be evenly spread but was still with textured. Fig 3.7 shows the cross-rolling-direction images of PE2R1-3 films. The films consisted of plane parts with peak parts on the top, referring to the textures on the surface of films. Similar to PE1R, the texture was formed due to the emulsion dragged up when the rolling pin surface left the emulsion surface. However, the peaks are very broad, compared to PE1R1-3. This is caused by the lower adhesion of E2 to the rolling-pin, probably due to its lower viscosity than E1. As the pin rolled forwards, the emulsion did not stick too much to the pin. Thus the emulsions were not dragged up a lot by the pin. Therefore the textures on the surface of PE2R are not as pronounced as the one of the PE1R series, represented by the broad peaks from the SEM (Fig 3.7 a, c and e). As the block thicknesses increased, the thicknesses of PE2R1-3 increased from 20μm to

95 μm (Table 3.4). The factors that influenced the thicknesses are same to PE1R, which can be the compressed emulsion layers and the dragging of emulsions, reducing the overall thicknesses of the printed emulsion layers and in turn the films. The high magnification SEM images show the porous structures of the films (Fig 3.7b, d and f). The pore sizes of PE2R1-3 were 18 μm , 20 μm and 20 μm , which were identical within error to the control samples. The three samples also saw identical foam densities, which were 0.53 g/cm³, 0.49 g/cm³ and 0.52 g/cm³, compared to 0.49 g/cm³ of the control samples (Table 3.4). Pickering emulsions were successfully rolling-pin printed, without damaging the pore structures of the resultant polyH(M)IPE films.

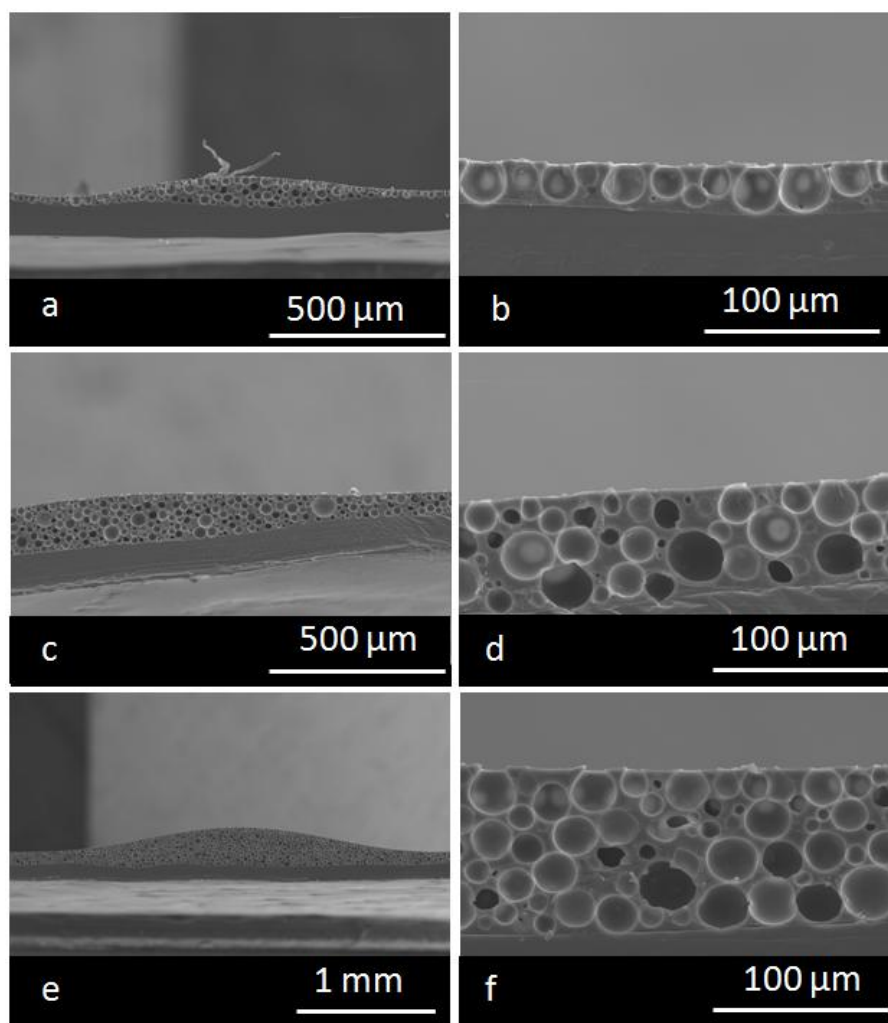


Fig 3.7 SEM images of poly-Pickering-MIPE films from rolling-pin printing. (a) PE2R1; (b)PE2R1; (c)PE2R2; (d)PE2R2; (e)PE2R3; (f)PE2R3.

Table 3.4 Properties of PE2 films from rolling-pin printing

	PE2R1	PE2R2	PE2R3
Blocks (μm)	100	210	430
Films thickness (μm)	20 ± 3	55 ± 3	95 ± 5
Pore size (μm)	18 ± 6	20 ± 8	20 ± 7
Foam densities (g/cm^3)	0.53 ± 0.09	0.49 ± 0.05	0.52 ± 0.04

In order to screen print emulsion templates, no blocks were stuck on the substrate to ensure the contact of the screen and the substrate. The screen was placed directly on top of the substrate and the emulsion was poured on the screen. A blade was used to spread the emulsion, pushing the emulsion through the screen, where the emulsion formed a thin layer adhering to substrate. After polymerisation, the thin emulsion layer became a flat polyH(M)IPE film (Fig 3.8).

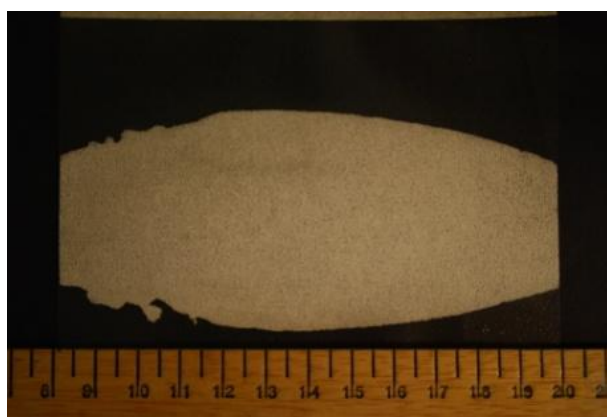


Fig 3.8 Representative picture of PE1S

A flat film of PE1S without peaks can be observed in the SEM image (Fig 3.9a). The thickness of PE1 was $32\mu\text{m}$ (Table 3.5). The film has porous structure with a pore size of $2.4\mu\text{m}$ and a foam density of $0.4\text{ g}/\text{cm}^3$ (Table 3.5), both are identical within error to the control sample PE1C. This suggests the screen printing did not damage the morphology of the emulsion, and subsequently the structure of the film. The bird's eye SEM image of PE1S (Fig 3.9b) revealed an open porous surface of the film. This is as expected since E1S was polymerised in an aqueous solution. PE2S film was obtained via a same way as PE1S, resulting in a film with a thickness of $35\mu\text{m}$ (Fig 3.9c). The pore size of printed PE2S was $13\mu\text{m}$ (Table 3.5), which was smaller than that of the control sample PE2C. This can be explained by the shearing of the emulsion during the printing, in which the relatively large droplets can be further

broken into smaller ones. The foam density of PE2S was 0.5 g/cm^3 , which was identical within error to the control sample. The bird's eye SEM image of PE2S reveals its closed cell surface (Fig 3.9d), which is caused by the silica particle stabilisation. The silica particles formed a very strong film, which stopped the breaking of the droplets on the surface. PUDA and EHA based HIPEs, namely E3 and E4, were screen-printed and polymerised to prepare porous films. PE3S was a flat film with a thickness of $36 \mu\text{m}$ (Fig 3.9e). The pore size and foam density of PE3S was $2.5 \mu\text{m}$ and 0.31 g/cm^3 , (Table 3.5), respectively, which were identical to the control sample PE3C. That means printing did not affect the pore structure of the films. The surface of PE3S is also open porous (Fig 3.9f), as the printed emulsion was polymerised in contact with an aqueous solution. PE4S had an open porous structure (Fig 3.9g) with a pore size of $30 \mu\text{m}$ (Table 3.5), which was identical with the control sample. The bird's eye SEM image showed that the surface of the PE4S (Fig 3.9h) was close-cell even the skin seems very thin (as the pore walls beneath the skin can be also seen). Besides, defects were also observed in the SEM image. Due to the relatively large droplet size, the emulsion was sheared during the screen printing. Some droplets were extremely big that were over the thickness of the film. Therefore the droplets formed as defects (marked in Fig 3.9h) on within the film after the polymerisation. Moreover, due to the defects, the foam density of PE4S was not applicable, as the volume of the film was not measurable.

Table 3.5 Properties of PE1-4 films from screen printing

	PE1S	PE2S	PE3S	PE4S
Films thickness (μm)	32 ± 6	35 ± 5	36 ± 3	52 ± 4
Pore size (μm)	2.4 ± 0.6	13 ± 7	2.5 ± 0.7	30 ± 7
Foam densities (g/cm^3)	0.4 ± 0.2	0.5 ± 0.2	0.31 ± 0.05	-

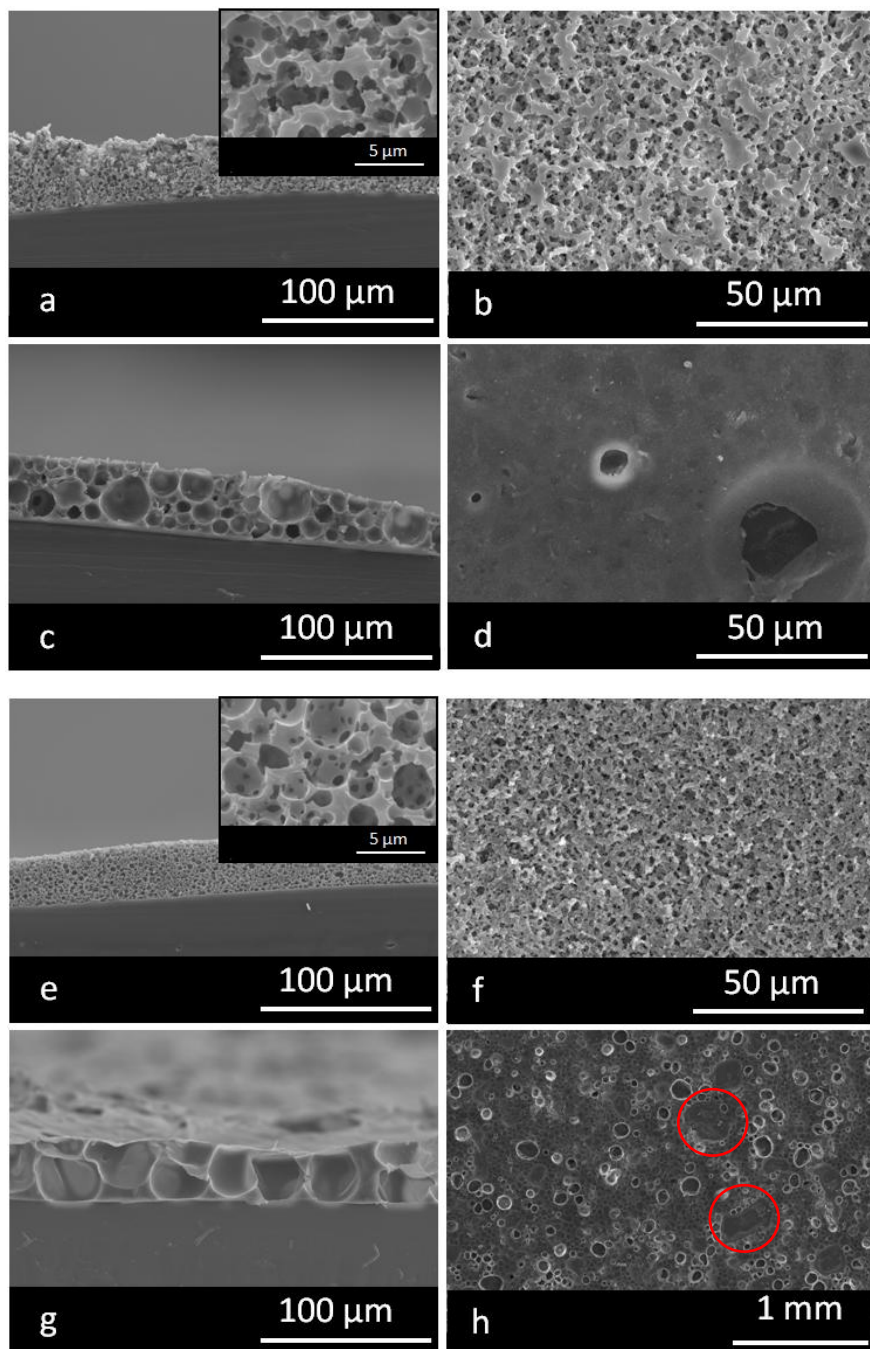


Fig 3.9 SEM images of the cross-section and surface of screen printed polyH(M)IPE films. (a) PE1S; (b) PE1S surface; (c) PE2S; (d) PE2S surface; (e) PE3S; (f) PE3S surface; (g) PE4S; (h) PE4S surface.

Following work was carried out on printing of emulsion templates on a printed polyH(M)IPE films, in order to make composite porous films. Here this method required the base layer to be flat, therefore screen printing was used in this experiment. E1 was screen-printed and polymerised as described before. After the drying of the PE1S, E2 was screen-printed on top of PE1S film in a 'Pacman' pattern and polymerised afterwards to create a double-layer porous film (Fig 3.10). The cross-section image of

the film shows a clear boundary of the two layers (Fig 3.11a). The top layer has a typical poly-Pickering-emulsion structure. However, the bottom layer does not have porous structure (Fig 3.11b). Instead, the bottom layer has many balls that are within the film. This indicates that E2 emulsion was imbibed into the PE1S film because of its high interconnectivity and open porous surface. Simultaneously the adsorbed E2 destabilised during the imbibing into PE1S film¹⁷⁴, resulting in the formation of polymer beads within the PE1S film after the polymerisation. To address this problem E4 was printed on a wet PE3S film, which was then polymerised. The SEM image of the two-layer film and the boundary distinguishing the two layers (Fig 3.11c) shows that the top layer has large and closed pores, which are typical for poly-Pickering-emulsions, while the bottom layer has small but open-cell pores. At the boundary the two films the porous structure of PE3S is observed (Fig 3.11d), which means E4 did not penetrate into the bottom layer, as the water occupied the pore space in the wet PE3S during the printing of E4. Moreover, the pore sizes of both layers are identical within error to those observed in single printed layers, suggesting that printing on open porous substrate did not affect the porous structure of the top layer (Table 3.6). On the other hand, a PE4S/PE3S double layer film was also prepared by printing E3 on wet PE4S films. The two-layer film has a clear boundary and porous structure in both layers. Due to the closed surface of PE4S, E3 could not penetrate into the porous PE4 film (Fig 3.11e and f). However E3 can possibly flow into the PE4S film through the defects of PE4S film, forming small porous structure within the large pores of PE4S (Fig 3.11e marked).

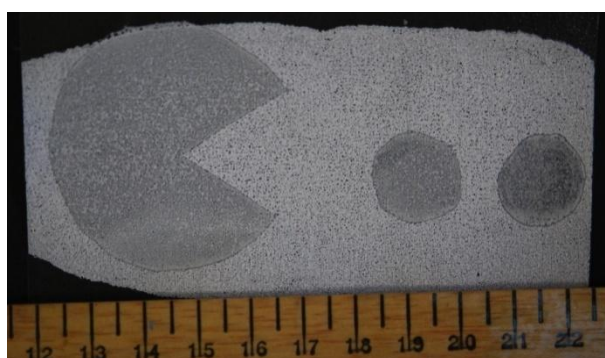


Fig 3.10 Representative picture of double layer printing with a Pacman pattern.

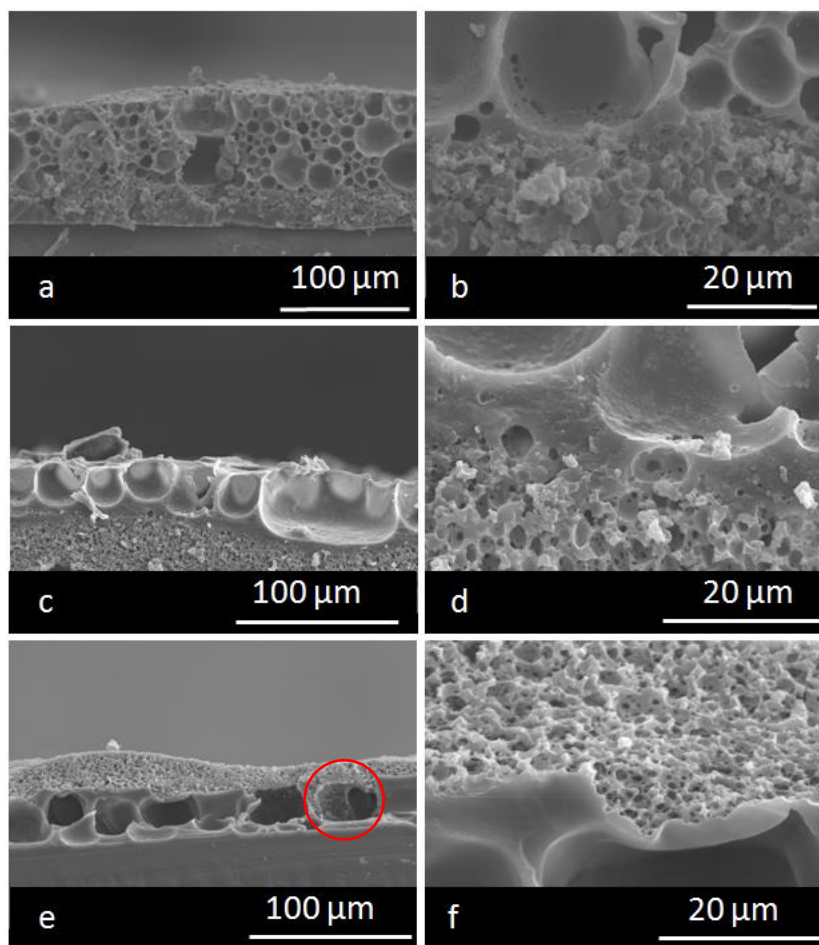


Fig 3.11 SEM images of double-layer screen printed polyH(M)IPE films. (a) PE2S on PE1S; (b) PE2S on PE1S; (c) PE4S on PE3S; (d) PE4S on PE3S; (e) PE3S on PE4S; (f) PE3S on PE4S.

Finally, multiple layer printing of emulsion templates was explored. A layer of emulsion template was printed and polymerised. Before it was dried, a second layer of emulsion template was then printed on top of it and polymerised. This process was repeated seven times to create a film. E1 and E2 were grouped to create a polyMIPE film and E3 and E4 were grouped to create a polyHIPE film. In order to observe the boundaries between the various layers, Pickering emulsions and surfactant stabilised emulsions were printed in sequence. The layers in the PE1S/PE2S and PE3S/PE4S films, which both consist of seven layers, can be easily distinguished by the different porous structures of each layer (Fig 3.12a and c). The high magnification SEM images show the porous structure of polymerised surfactant stabilised emulsions between two poly-Pickering-emulsions (Fig 3.12b and d). In addition, the pore sizes of both multilayer films are identical within error to their corresponding single layer films, suggesting the repeated printing of the emulsion templates to create multilayer films without

damaging the porous structures.

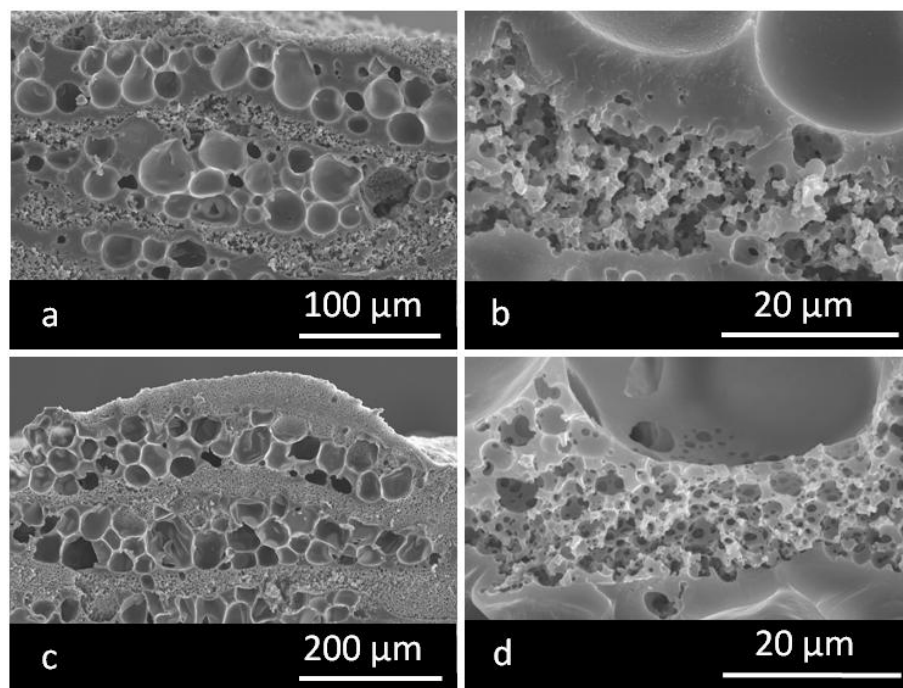


Fig 3.12 SEM images of multilayer screen printed films. (a) PE1S/PE2S; (b) PE1S/PE2S; (c) PE3S/PE4S; (d) PE3S/PE4S.

Table 3.6 Pore size of multilayer polyH(M)IPE films (unit: μm).

	PE2S on PE1S	PE3S on PE4S	PE1S/PE2S	PE3S/PE4S
	Double layer	Double layer	Multilayer	Multilayer
PE1S layer	Not measurable	-	2.5 ± 1.0	-
PE2S layer	14 ± 8	-	15 ± 7	-
PE3S layer	-	2.4 ± 0.7	-	2.5 ± 0.9
PE4S layer	-	33 ± 10	-	32 ± 9

3.4 Conclusions

In this chapter methods to prepare polyH(M)IPE films have been summarised and the reasons the methods being used for different macroporous films are justified. Slicing is an excellent method to prepare films with uniform thickness and with surface morphology identical to the bulk morphology, thus is applicable to prepare symmetric polyHIPE membranes. Casting emulsions and subsequent UV

polymerisation provide fast production of macroporous films, thus the acrylate based polyH(M)IPE films will be prepared via this route.

Printing emulsion templates to create porous films on substrates to create macroporous films was studied. Both rolling-pin and screen printing can be used to produce macroporous films without damages on the pore structures. In this specific case, screen printing was superior to rolling-pin printing as it led to a flat film surface rather than textures on the films surface. However, it might be possible to improve the quality of the rolling-pin printed films by using more sophisticated tools in the future. Furthermore, in this chapter, evidence has been provided that emulsion templates with large droplets (Pickering emulsions) and small droplets (surfactant-stabilised emulsions) are equally well suited as inks in the printing process. However, it is worth noting that the maximum droplet size of the emulsion template used as ink and, therefore, the maximum pore size of the macroporous films strongly depends on the printer. For example, the droplet size needs to be smaller than the mesh size of a printing screen, or the gap between the substrate and the screen or rolling-pin in order to prevent the destabilisation of the emulsion and defects in the film. Double layer printing was subsequently studied. It is found that printing emulsion templates on polyH(M)IPE films required the substrates to be wet to prevent the penetration of the emulsions into the substrates. Moreover multilayer printing was explored to create macroporous films with open porous structure alternative with closed cell structures. The success in multilayer printed films suggests the possibility of printing emulsion templates to produce macroporous films with complex and 3D structure.

Chapter 4 Hydrogel filled polyHIPEs via emulsion templates

Abstract

Poly(methacrylic acid) or poly(dimethyl amino ethyl methacrylate) filled poly(styrene-divinylbenzene)HIPEs are prepared via emulsion templates with monomers in both continuous phase and internal phase. Forming a polymer-polymer composite, the dry hydrogel filled polyHIPEs have higher elastic moduli and crush strengths than the control polyHIPE. The hydrogel filled polyHIPEs possess hydrophilic pore surface, therefore adsorb water. Moreover, the hydrogel loading and hydrogel network structures are highly related to the crosslinking degrees of the hydrogels. The mechanical properties and water uptakes of the hydrogel filled polyHIPEs can therefore be tailored via varying the crosslinking degrees of the hydrogels.

4.1 Introduction

Hydrogels refer to the crosslinked hydrophilic polymers or copolymers. They are characterised by their swelling behaviour in water or the other polar solvents. Additionally, many of them can also possess bio-compatibility and environmental sensitivity. Therefore, hydrogels are applicable in many fields, like medicine, biotechnology and agriculture (see Chapter 2). Hydrogels within a macroporous structure have been synthesised via emulsion templating by many researchers. One straightforward method is using oil-in-water (o/w) emulsions as templates to prepare hydrogel polyHIPEs. Krajnc et al.⁶⁵ reported poly(acrylic acid)HIPEs prepared by polymerising o/w emulsions. The purpose for the synthesis of the polyHIPEs was to induce acid groups in polyHIPEs in a one-step synthesis. Kulygin and Silverstein⁹⁶ have reported the preparation of poly(HEMA)HIPEs from o/w emulsions, and the porous hydrogels are expected to be applicable in tissue engineering and drug release. Butler et al.¹³⁶ prepared poly(acrylamide)HIPEs via a CO₂-in-water emulsion templates, in which supercritical CO₂ was used as internal phase for the emulsion templates. These polyHIPEs have potential applications in enzyme immobilisation. Grant et al.⁹⁷ prepared poly(N-isopropylacrylamide)HIPEs, which possessed temperature-responsive swelling. The polyHIPEs showed temperature-controlled uploading and release, which may be applicable in drug delivery and in smart coating. An alternative way to prepare

polyHIPEs incorporating hydrogels is using emulsion template with monomers in both phases, i.e., hydrophobic monomers in the continuous phase and hydrophilic monomers in the internal phase. Such bi-monomer phase emulsion templates result in hydrophobic polyHIPE scaffolds with hydrogels in the pores after polymerisation. Ruckenstein et al.^{115,118} reported poly(acrylamide) filled polyHIPEs and poly(sodium acrylate) filled polyHIPEs, both for pervaporation separation purposes. Gitli and Silverstein¹²⁰ have reported the preparation of polyacrylamide filled polyHIPEs and investigated the effect of the locus of initiation of polymerisation on the porous structures. Additionally, they also reported a stiffness reduction of the hydrated polyHIPEs due to the presence of polyacrylamide. In an article afterwards, they reported the loading and release of Eosin Y in polyacrylamide filled polyHIPEs, aiming to develop their drug release applications¹⁷⁵. Recently, Kovacic et al.¹⁷⁶ reported poly(acrylic acid) filled polyHIPEs and poly(N-isopropylacrylamide) filled polyHIPEs. They characterised the water flux at different pH values or temperatures through the porous monoliths.

The work in this chapter should be considered as a proof concept to demonstrate the preparation of poly(methacrylic acid) (MAA) filled poly(St-DVB)HIPEs and poly(dimethyl aminoethyl methacrylate) (DMAEMA) filled poly(St-DVB)HIPEs via emulsion templates with monomers in both phases. It is aimed to study the effect of the hydrogels on the properties of the polyHIPEs. Therefore, the water uptakes of the hydrogel filled polyHIPEs are measured to study if the hydrogels provide hydrophilic pore surface for the polyHIPEs. Additionally, the mechanical properties of the hydrogel filled polyHIPEs are determined to investigate if the hydrogels are reinforcement or softener for the polyHIPEs.

4.2 Experiment

4.2.1 Materials

Styrene (St), divinylbenzene (DVB), dimethyl aminoethyl methacrylate (DMAEMA), *N, N*'-methylenebisacrylamide (MBA), azobisisobutyronitrile (AIBN), ammonium persulfate (APS), NaOH, HCl (37.5 %) and CaCl₂·2H₂O were purchased from Sigma-Aldrich (Gillingham, UK). Methacrylic acid (MAA) was purchased from Acros (Geel, Belgium). Hypermer B246 was kindly supplied by Croda (Snaith, UK). All the chemicals were used as received.

4.2.2 Preparation of hydrogel filled St-DVB based polyHIPEs

The internal phases of the HIPEs were firstly prepared by dissolving 12 vol% MAA or DMAEMA and various amounts of MBA into deionised water. The MAA solutions were deprotonated via adding NaOH to reach a pH value of 14, while the DMAEMA solutions were protonated via adding HCl to reach a pH of 1. The setup for HIPE preparation consisted of a reaction vessel equipped with a glass paddle connected to an overhead stirrer (Fig 3.1). St, DVB, Hypermer B246 and AIBN were mixed in the reactor. The internal phase was placed in a dripping funnel and added dropwise into the continuous phase while stirring at a constant rate of 400 rpm. Afterwards the emulsion was stirred for 2 min (for MAA in the internal phase) or 9 min (for DMAEMA in the internal phase) at a speed of 2000 rpm to produce homogeneous emulsions. APS was dissolved in less than 1 ml deionised water and the solution was added into the emulsions as an aqueous phase initiator. In a preliminary experiment, it was found that dissolving APS directly in the alkaline internal phase containing deprotonated MAA could lead to the premature polymerisation of the monomers; gelation can occur before the internal phase can be added into the continuous phase. This might be due to the pH-sensitivity of APS, whose capability of initiation was accelerated at high pH values (pH 14). Therefore the APS was added after the dropping of the internal phase. The emulsions were subsequently stirred for another minute to disperse the APS evenly. Finally, the emulsions were transferred into centrifuge tubes and polymerised in an oven at 70 °C for 24 hours. Afterwards, the hydrogel filled polyHIPEs were purified by immersing them in mixtures of water and methanol (1:1 by volume) for 48 hours. The samples were dried at 70°C in air and under vacuum for 24 hours, respectively.

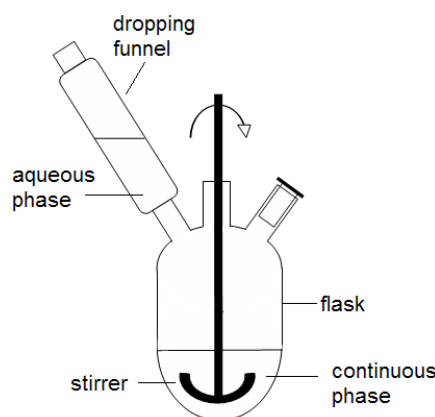


Fig 4.1 Schema of setup for preparing polyHIPE-hydrogel composites

A control sample, a poly(St-DVB)HIPE without hydrogels, was made via a same route. Instead, the internal phase was a water solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (1.25 g / 250 ml water) and APS was not used in this sample. The formulation of the samples are summarised in Table 4.1. C stands for the control sample. Sample codes starting with M represent the poly(MAA) filled poly(St-DVB)HIPEs, while sample codes starting with D represent the poly(DMAEMA) filled poly(St-DVB)HIPEs. The number behind M or D refers the molar ratio of MBA (crosslinker) with respect to MAA or DMAEMA.

Table 4.1 Formulation of hydrogel filled poly(St-DVB)HIPEs

	Continuous phase (20 vol%) ^a				Internal phase (80 vol%)		
	St (vol%) ^b	DVB (vol%)	B246 (vol%)	AIBN (mol%) ^c	Monomer	MBA (mol%) ^d	APS (mol%) ^e
C	60	20	20	1	-	-	-
M0	60	20	20	1	MA	0	1
M1	60	20	20	1	MA	1	1
M2	60	20	20	1	MA	2	1
M5	60	20	20	1	MA	5	1
M10	60	20	20	1	MA	10	1
D0	60	20	20	1	DMAEMA	0	1
D1	60	20	20	1	DMAEMA	1	1
D2	60	20	20	1	DMAEMA	2	1
D5	60	20	20	1	DMAEMA	5	1
D10	60	20	20	1	DMAEMA	10	1

a. Continuous phase and internal phase volumes were 20% and 80%, respectively, with respect to the total volume of emulsions. b. Monomer and surfactant volume ratios were with respect to the continuous phase volume. c. AIBN molar ratio was with respect to the molar number of double bonds in the monomers in continuous phase. d. MBA molar ratio was with respect to the molar numbers of aqueous phase monomers. e. APS molar ratio was with respect to the molar number of double bonds in the aqueous phase monomers.

4.2.3 Characterisation

a. Morphology of the polyHIPEs

The morphology of the samples was investigated using SEM, which was the same procedure as described in Chapter 3 (P49).

b. Density and porosity

Matrix density was measured using Accupyc 1330 (Micrometrics Ltd, Dunstable, UK), which has been described in Chapter 3 (P50). Foam density was measured using Geopyc 1360 (Micrometrics Ltd, Dunstable, UK). Graphite powder (with a diameter ranging from 20-200 µm) was placed in a chamber. The powder was compacted by a plunger connected to a stepping motor. By measuring how far the plunger can be driven by the motor into the chamber, the volume of the powder was measured (blank measurement). Afterwards, about 0.1 g of small sample pieces was mixed with the graphite powder in the chamber and the volume was determined via the route described. The external volume of the sample is calculated by the difference of the volume of the powder with samples and the blank measurement. The foam density can be obtained from the mass of the sample divided by its external volume. The porosity (P) was calculated from the equation below:

$$P = \left(1 - \frac{\rho_f}{\rho_m}\right)$$

where, ρ_f is the foam density, g/cm³ and ρ_m is the matrix density, g/cm³.

c. Water uptake

The samples were immersed in DI water until their weights did not change. Afterwards, the samples were taken out and the water on the surface was wiped using filter paper. The wet samples were weighed. Then the samples were dried again and weighted. The water uptake (S) can be calculated using the equation below:

$$S = \left(\frac{m_w - m_d}{m_d}\right) \times 100\%$$

where m_w is the wet sample weight, g, and m_d is the dry sample weight, g.

d. Mechanical properties

Mechanical properties of the hydrogel filled polyHIPEs were determined via compression, which represents the mode of deformation when samples are being used for separation purpose. Compression tests were carried out using a Lloyds EZ50 (Lloyds Instruments Ltd, Fareham, UK) with a 50 kN load cell. The disks for the test had a diameter of 25 mm and a height of 10 mm. The disks were compressed between compression plates at a speed of 1 mm/min and their stress-strain curves were recorded. The elastic modulus was determined from the slope of the initial linear region in the stress-strain curve. The crush strength was defined as the maximum strength at the end of the initial linear elastic region. The mechanical properties of wet and dry samples were measured and compared. Here the wet samples refer to those without drying.

4.3 Results and Discussion

In this experiment, the internal phases with MAA or DMAEMA needed to be deprotonated or protonated in order to prepare stable emulsion templates. The SEM images of the control sample and poly(MAA) filled poly(St-DVB)HIPEs are shown in Fig 4.2. The pore sizes, pore throat sizes, densities and porosities of the control sample and poly(MAA) filled St-DVB based polyHIPEs are listed in Table 4.2. The control poly(St-DVB)HIPEs consist of spherical pores, which are interconnected by pore throats. These are characteristic for polyHIPEs (Marked in Fig 4.2a, b). The pore size of the control sample is $4\pm1\ \mu\text{m}$ in diameter and the pore throats size is $1.5\pm0.4\ \mu\text{m}$ in diameter (Table 4.2). The matrix densities of M0-M10 are identical within error, which are $1.24\ \text{g/cm}^3$. The higher matrix densities of M0-M10 compared to the control are due to the high matrix densities of poly(MAA) hydrogels. The foam densities of M0-M10 are higher than that of the control poly(St-DVB)HIPEs. This indicates the presence of hydrogels, which occupies the pore volume. Moreover, the foam densities of M0-M10 increased gradually, corresponding to the decrease of their porosities. This may suggest that the hydrogel loading increases as the crosslinker concentration increases in the internal phase of the emulsions. This result is in good agreement to the work of Mika et al.¹⁷⁷ and Susanto and Ulbricht¹⁷⁸ on grafting polymers to porous media, in which the grafting amount increased with the crosslinking degrees of hydrogels. Briefly, the presence of crosslinker leads to side groups with double bonds in the polymerised chains, allowing more MAA polymerising on the grafted chains. Thus, the hydrogel loading increased with the increase in the crosslinker concentration. The SEM images of M0-M2 do

not show differences compared to the control sample: the pores are interconnected and rather empty. However, as can be seen in Fig 4.2d, f and h, some pore throats seem to be covered by light grey film, which suggests that the hydrogels formed thin layers and coated the surface of the pores. The SEM images of M5 and M10 show less open pore throats than the control, as some pore throats are covered by hydrogels. The formation of pore throats in typical polyHIPEs is caused by the contraction of the monomers while polymerising¹⁴⁰, in bi-monomer phase emulsion templates, however, can be related to the contraction of both hydrophobic monomers and hydrophilic monomers at the interface of the continuous phase and the internal phase. The reactivity ratios of St (1) and MAA (2) have been listed in a publication from Sahloul and Penlidis¹⁷⁹, which are roughly $r_1=0.2\sim0.3$ and $r_2=0.4\sim0.6$, depending on different polymerisation conditions. This means both radicals tend to react with the other monomers. In this case, one can imagine the monomer contractions for St and MAA at the interface are at a similar rate. Thus M0-M10 tended to have uncovered pore throats, though they have hydrogel coated on the wall of the pores.

Table 4.2 Pore sizes, pore throat sizes, densities and porosities of poly(MAA) filled polyHIPEs

	Pore size (μm)	Pore throat size (μm)	Matrix density (g/cm^3)	Foam density (g/cm^3)	Porosity (%)
Control	4 $\pm$ 1	1.5 $\pm$ 0.4	1.14 $\pm$ 0.05	0.15 $\pm$ 0.01	87 $\pm$ 1
M0	4 $\pm$ 1	1.3 $\pm$ 0.6	1.25 $\pm$ 0.01	0.24 $\pm$ 0.03	81 $\pm$ 2
M1	4 $\pm$ 1	1.2 $\pm$ 0.3	1.25 $\pm$ 0.01	0.27 $\pm$ 0.03	78 $\pm$ 2
M2	3 $\pm$ 1	1.2 $\pm$ 0.3	1.25 $\pm$ 0.01	0.25 $\pm$ 0.02	80 $\pm$ 1
M5	3 $\pm$ 1	0.8 $\pm$ 0.3	1.24 $\pm$ 0.01	0.35 $\pm$ 0.01	71 $\pm$ 1
M10	3 $\pm$ 1	1.0 $\pm$ 0.3	1.24 $\pm$ 0.01	0.37 $\pm$ 0.01	70 $\pm$ 1

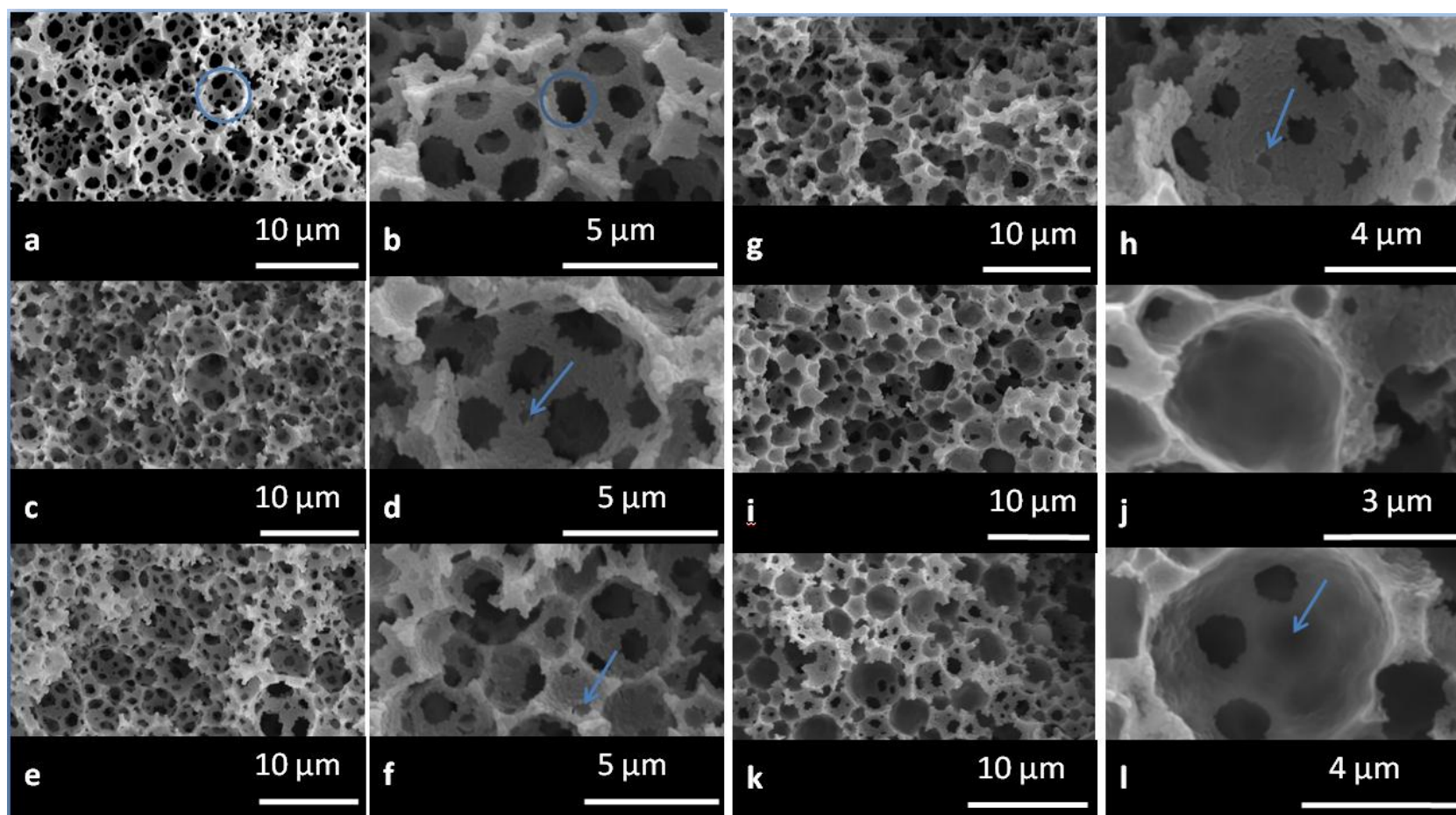


Fig 4.2 SEM images of poly(MAA) filled poly(St-DVB)HIPES. a, b. control sample (C); c, d. 0% (M0); e, f. 1% (M1); g, h. 2% (M2); i, j. 5% (M5); k, l. 10% (M10).

The matrix densities of D0-D10 are higher than that of the control sample, which is due to the higher densities of poly(DMAEMA) hydrogels (Table 4.3). The higher foam densities of D0-D10 as compared to the control sample suggest the presence of hydrogels in the polyHIPEs. Moreover, one can conclude the increase in hydrogel amounts in D0-D10, as the increase in their foam densities. The SEM images of D0-D10 show hierarchical pore structures possessing dramatic large pores and relatively small pores. This indicates that coalescence occurred in the emulsion templates (Fig 4.3). Coalescence of the droplets in emulsions can be a complex procedure involving many factors. In the elevated temperature at which the emulsions were polymerised, the solubility of DMAEMA in St may increase. Moreover, hydrochloride acid might evaporate at the temperature, which reduced the protonation of the DMAEMA. Both made DMAEMA slightly soluble in the continuous phase, therefore increasing the coalescence of droplets. The pore throat size of D0 is 0.8 μm , which is smaller than that of the control. Furthermore there are too few pore throats visible in the SEM image of D1-D10 to allow for a statistical relevant analysis. This indicates that the majority of pore throats of the poly(St-DVB) scaffolds for D1-D10 were covered by poly(DMAEMA) hydrogels (for D0, the pore throats were partially covered) (Fig 4.3). This can be also explained by the copolymerisation of St and DMAEMA at the interface of the continuous and internal phase. The reactivity ratios for the St (1)/DMAEMA(2) system are $r_1=1.74$ and $r_2=0.43^{180}$, meaning both monomers tend to polymerise with St. This resulted in a quick contraction of St at the interface where copolymerisation occurred. Thus, after the gel point, even pore throats formed as the contraction of St in the continuous phase, the ongoing polymerisation DMAEMA in the internal phase formed thin film on the wall and within pore throats that covered the pore throats.

Table 4.3 Pore sizes, pore throat sizes densities and porosities of poly(DMAEMA) filled polyHIPEs

	pore size (μm)	Pore throat size (μm)	Matrix density (g / cm^3)	Foam density (g / cm^3)	Porosity (%)
C	4 $\pm$ 1	1.5 $\pm$ 0.4	1.14 $\pm$ 0.05	0.15 $\pm$ 0.01	87 $\pm$ 1
D0	4-30	0.8 $\pm$ 0.2	1.2 $\pm$ 0.1	0.19 $\pm$ 0.03	84 $\pm$ 2
D1	3-28	-	1.20 $\pm$ 0.06	0.21 $\pm$ 0.03	83 $\pm$ 3
D2	3-30	-	1.2 $\pm$ 0.1	0.27 $\pm$ 0.01	78 $\pm$ 1
D5	2-46	-	1.21 $\pm$ 0.09	0.32 $\pm$ 0.03	73 $\pm$ 2
D10	1-50	-	1.2 $\pm$ 0.1	0.36 $\pm$ 0.01	70 $\pm$ 1

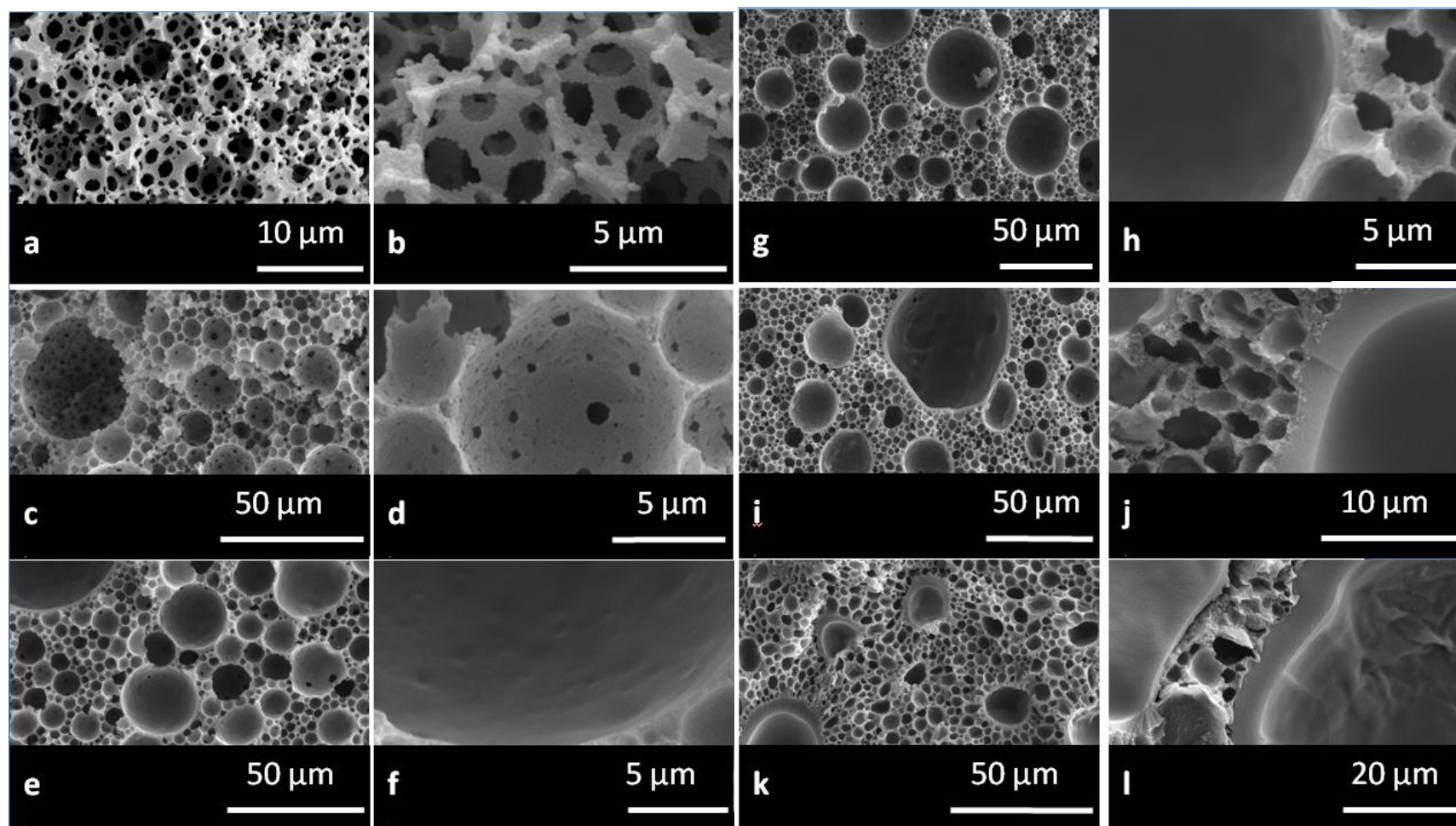


Fig 4.3 SEM images of poly(DMAEMA) filled poly(St-DVB)HIEs. a, b. control sample (c); c, d. 0% (D0); e, f. 1% (D1); g, h. 2% (D2); i, j. 5% (D5); k, l. 10% (D10).

The water uptake of polyHIPEs was measured by immersing the polyHIPEs in water statically and measuring the weight change of the samples. A decrease in water uptake with increasing crosslinking degrees of the PMAA and PDMAEMA hydrogels, respectively, can be observed for both groups of the polyHIPEs (Fig 4.4). The water went into polyHIPEs and took over the space where air had been. One can imagine that water went into the polyHIPEs via two routes at the beginning of water uptakes: diffusion through the hydrogel layers and passing through uncovered pore throats (Fig 4.5 left). In this stage, air can leave the pores through pore throats. As the hydrogels swelled, the pore throats were then covered by hydrogels completely, thus the water could only go into pores by diffusion and the air could not leave the pores easily as its poor permeation in hydrogels (Fig 4.5 middle). Therefore the entrapped air pressurised as the water continuously diffused into the pores. Finally the air pressure balanced with the back pressure of water, and an equilibrium state reached (Fig 4.5 right). The highly crosslinked hydrogels form much denser layers which hinder water diffusion through¹⁸¹. As a result, both hydrogels filled polyHIPEs exhibit decreased water uptakes as the crosslinking degrees of hydrogels increased. Pore throats are much easier routes for water to penetrate the pores compared to diffusion through hydrogels. Therefore, M1-M10, possessing uncovered pore throats, have higher water uptakes than the corresponding D1-D10. D0 has relatively high water uptakes compared to other poly(DMAEMA) filled polyHIPEs, due to the presence of the pore throats in D0. Dramatic decreases in water uptakes were found in D1-D10 compared to D0, as the pore throats were covered by hydrogels in these samples even the hydrogels were dry.

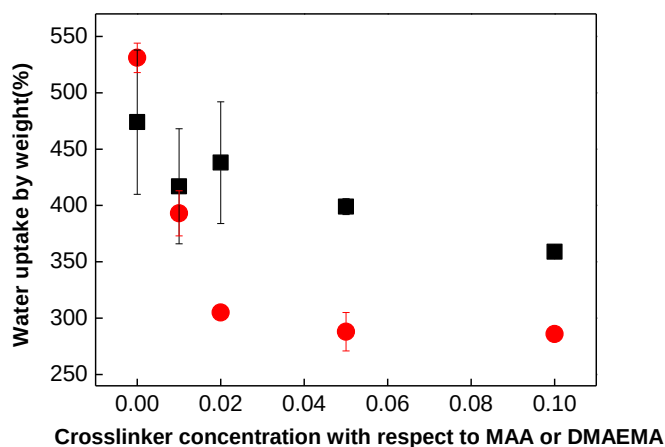


Fig 4.4 Water uptakes of poly(MAA) filled poly(St-DVB)HIPEs (black square) and poly(DMAEMA) filled poly(St-DVB)HIPEs (red dot).

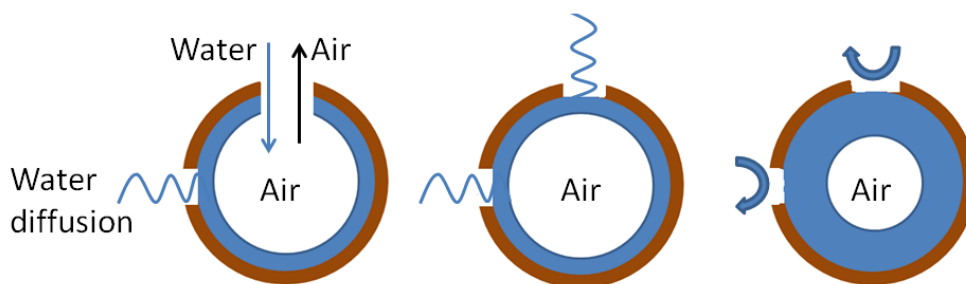
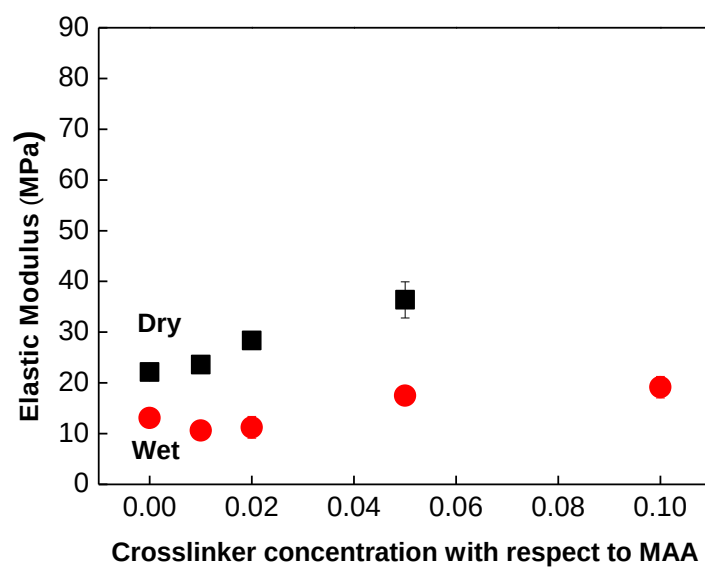


Fig 4.5 Scheme of water uptaking of hydrogel filled polyHIPEs.

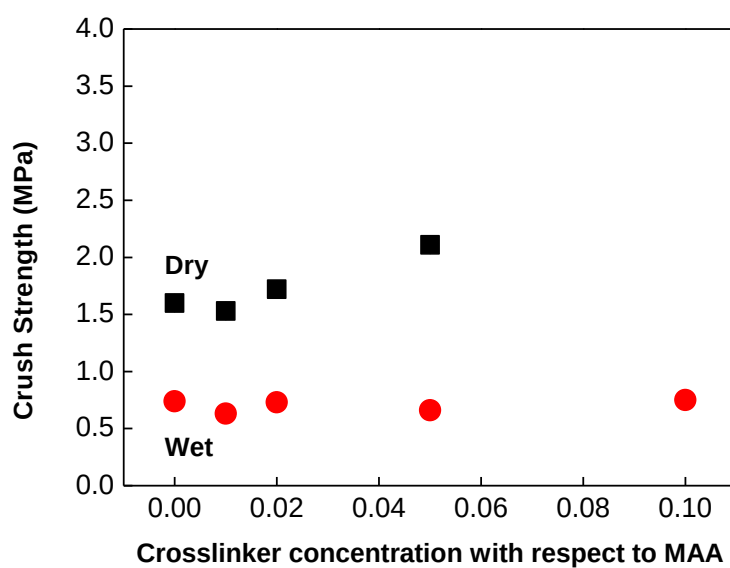
Elastic moduli and crush strengths of the control samples and the poly(MAA) and poly(DMAEMA) filled poly(St-DVB)HIPEs were tested. The tests were carried out on dry and wet samples. However, the wet control sample dried too fast, so the wet mechanical properties of the control sample were not available. M10, D5 and D10 broke after drying, as the polyHIPE scaffolds cannot stand the stress caused by the shrinkage of the hydrogels. Therefore, the mechanical properties of those dry samples were not measurable. The dry control sample has an elastic modulus of 14 ± 1 MPa and crush strength of 1.00 ± 0.08 MPa (Fig 4.6), which is comparable with the previous results from our group¹⁸². Dry M0 has a higher elastic modulus (22 MPa), as well as a higher crush strength (1.6 MPa) (Fig 4.6a), compared to the control. A further increase of elastic moduli and crush strengths of M1, M2 and M5 was also found (Fig 4.6a and b): the elastic moduli increased from 23 MPa (M1) to 36 MPa (M5) and the crush strengths increased from 1.5 MPa (M1) to 2.1 MPa (M5). This can be due to the increase in the foam densities of these samples, which increases the elastic moduli of the samples¹⁸³. The enhancement in the mechanical properties may also be explained by the grafting of dry poly(MAA) on the polyHIPEs scaffold, which formed a polymer-polymer composite to reinforce the polyHIPE scaffolds. Moreover, the hydrogels might be stiffer as the crosslinking degrees of the hydrogels increased, which provided a stronger reinforcement to the polyHIPE scaffolds. On the other hand, the elastic moduli and crush strengths of the wet poly(MAA) filled poly(St-DVB)HIPEs reduce dramatically, compared to their corresponding dry samples. The swollen hydrogels are mechanically weak and can, therefore, not reinforce the polyHIPE scaffolds. Furthermore, the fact that the mechanical properties of the wet samples are even lower than those of the control sample indicates that certain amount of St-DVB-MAA copolymers was formed at the oil/water interface¹²⁰. Such copolymers are hydrophilic

and can absorb a small amount of water, which weakens their mechanical integrity. Therefore, the wet samples can even be slightly softer than control sample. Nevertheless, wet M5 and M10 had higher elastic moduli than the other samples. As revealed by the SEM image, the pore throats are covered by hydrogels in M5 and M10. The swollen hydrogels can function as a spacer in the pore throats that locks the water in the pores during the compression, thus resisting the samples being compressed, leading to higher Young's moduli. However, the swollen hydrogels, which are far weaker than the scaffolds of the samples, crushed much earlier than the scaffolds. Therefore the crush strengths of M5 and M10 did not benefit from the hydrogel covering the pore throats (Fig 4.6 b).

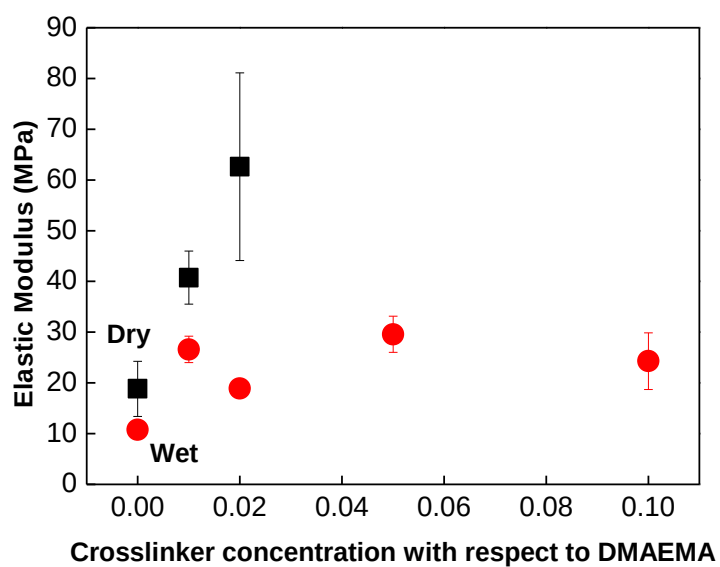
Dry D0 shows an improved elastic modulus and crush strength of 20 MPa and 1.2 MPa, compared to the control sample (Fig 4.6c and d), due to the reinforcement of the dry poly(DMAEMA) hydrogels. The elastic moduli of M1 and M2 undergo dramatically increase to 40 MPa and 63 MPa, respectively (Fig 4.6c), and the crush strengths improve to 2 MPa and 3.5 MPa, respectively (Fig 4.6d). That is, on one hand, due to the increase in the crosslinking degree in hydrogels, the hydrogels thus provide enhanced reinforcement. Moreover, this can be explained by the change of morphology of the hydrogel filled polyHIPEs. D0 is with open porous structure even with hydrogels in the pores, while D1 and D2 possess a mainly closed-cell structure since the pore throats are covered by hydrogels. The hydrogel layers with only a few pore throats in D1 and D2 provided better reinforcement, which lead to the dramatic improvements in mechanical properties observed for D1 and D2. On contrast, the wet samples show low elastic moduli and crush strengths, which are close to the elastic modulus and crush strengths of the control sample. That is, as discussed above, due to swollen hydrogels losing their reinforcement functions, and due to the presence of DMAEMA-St-DVB copolymers in the pore walls, which can absorb a little water, softening the polyHIPE scaffolds. The elastic moduli of D1-D10 are higher than that of D0 (Fig 4.6 c), again, due to the hydrogel covering the pore throats in these samples, which function as spacer to resist the compression of the samples. Similarly, as the wet hydrogels crushed earlier than the scaffolds of D1-D10, they did not provide high crush strengths for these samples (Fig 4.6 d).



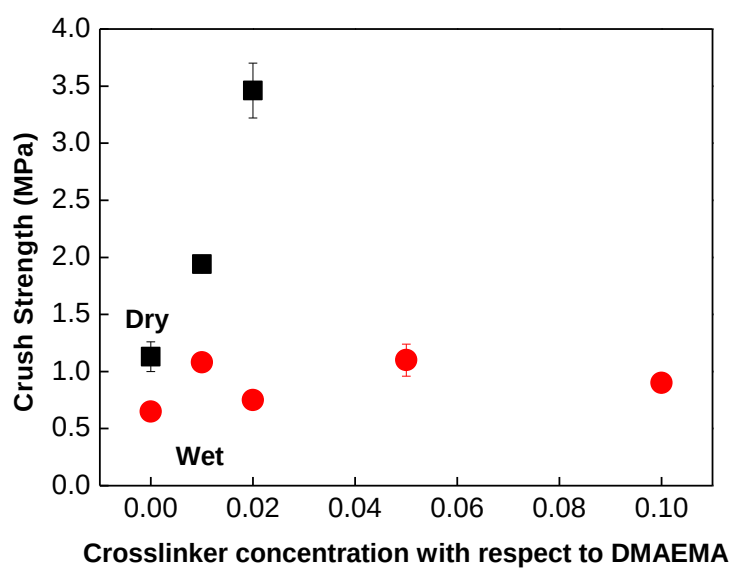
(a) Elastic moduli of poly(MAA) filled polyHIPEs.



(b) Crush strengths of poly(MAA) filled polyHIPEs.



(c) Elastic moduli of poly(DMAEMA) filled polyHIPEs.



(d) Crush strengths of poly(DMAEMA) filled polyHIPEs.

Fig 4.6 Elastic moduli and Crush strengths of poly(MAA) filled poly(St-DVB) and poly(DMAEMA) filled poly(St-DVB)HIPEs.

4.4 Conclusion

Emulsion templates with monomers in both phases were used in this experiment for preparation of poly(MAA) filled polyHIPEs and poly(DMAEMA) filled polyHIPEs. The SEM images revealed that the

hydrogel formed thin layers coating on the pore walls of the polyHIPE scaffolds. The presence of dry hydrogels in the polyHIPEs reinforces the samples, enhancing the elastic moduli and crush strengths of the samples. Moreover, the reinforcement from the dry hydrogels increases with the increase in the crosslinking degrees of the hydrogels. However the wet hydrogels within the polyHIPEs cannot reinforce the scaffold, resulting in polyHIPEs with modest mechanical properties. The presence of hydrogels in polyHIPEs provides the polyHIPEs hydrophilic inner surface, enabling them to absorb water. The water uptakes decreased as the increase in the crosslinking degrees of the hydrogels. The tuneable water uptakes of the hydrogel filled polyHIPEs may provide them potential application as membranes.

Chapter 5 Poly(methacrylic acid) filled polyHIPEs and their applications as ultrafiltration membranes

Abstract

In Chapter 4 the concept of making poly(methacrylic acid) filled polyHIPEs was discussed. The next logical step is to use this concept to develop polyHIPE supported hydrogel membranes. One engineering challenge is to reduce the brittleness of the polyHIPE scaffold to process the membranes. Therefore, the compositions of the continuous phase of the emulsion templates reported in chapter 4 were modified by replacing some of the styrene and DVB with ethylhexyl acrylate, which is known to introduce some elasticity in the resulting polyHIPE. The produced wet poly(methacrylic acid) filled poly(styrene-DVB-EHA)HIPEs were sliced into membranes. The membranes showed pH-dependent water flux and rejection. The water flux decreased as the pH increased from 2 to 10 due to the deprotonation of the hydrogel. The highest rejection for one membrane was also found at pH 10, where the hydrogel mostly deprotonated. Crosslinking degrees of the hydrogel affected the performance of the membranes dramatically. The membrane with 1% crosslinker has a 55% rejection to 100K polyethylene glycol, while the membrane with 2% crosslinker has a 90% rejection to 50K polyethylene glycol, suggesting that the membrane is for ultrafiltration application. However, the relatively high rejection came at expense of low water flux and high back pressure.

5.1 Introduction

Hydrogel membranes are usually prepared via 'crosslinking' and 'grafting'. Crosslinking methods are used to prepare unsupported hydrogel membranes. Obaidat and Park⁵⁴ reported preparation of poly(hydroxyethyl methacrylate) membranes via crosslinking the monomer with ethyleneglycol dimethacrylate in an aqueous solution. Post-crosslinking was used to prepare poly(N-isopropylacrylamide) membranes¹⁸⁴. The solution with monomers was polymerised to achieve a viscous solution. After the casting of the solution on a plate and drying, the membrane was soaked

in a solution of crosslinker where crosslinking took place. Poly(vinyl alcohol) membranes were prepared via casting a solution of poly(vinyl alcohol) with crosslinkers and catalysts on a glass plate¹⁸⁵. Subsequently, the solution was heated to allow the crosslinking of the polymer. Some blend hydrogel membranes were also prepared in this method^{55,61}. Grafting refers to the method to prepare hydrogel composite membranes or hydrogel modified membranes. Usually the grafting of monomers were carried out via irradiation, such as UV grafting⁴⁷ and ⁶⁰Co irradiation grafting¹⁸⁶⁻¹⁸⁷. Thermal or even room temperature grafting was also reported, but the membrane precursors required pre-grafting chemical treatment in that case¹⁸⁸⁻¹⁸⁹. Liang et al.¹⁹⁰ have reported UV polymerisation of NIPAM on the surface of polypropylene membrane. The resultant hydrogel grafted membranes showed temperature-sensitive behaviour: as the temperature increased from 20°C to 40°C, the water flux increased from 20 L·m⁻²·h⁻¹ to 1000 L·m⁻²·h⁻¹, while the rejection to 40K dextran decreased from 60% to 0%. Susanto and Ulbricht^{178,191} have reported grafting of poly(ethylene glycol) methacrylate and N,N-dimethyl-N-(2-methacryloyloxyethyl-N-(3-sulfopropyl) ammonium betaine onto polyethersulfone ultrafiltration membranes. The grafted membranes showed better anti-fouling as the hydrogel layer reduced the adsorption tendency of the solute on the membrane surface, preventing the formation of tight fouling cake. Besides of improving the membrane performance, hydrogel membranes have also showed capability to gain the membranes other functions. For example, some hydrogels have environmental-sensitivity and biocompatibility, which make them excellent candidates for drug release¹⁹² and membranes for biotechnologies¹⁹³⁻¹⁹⁴.

Emulsion templating provides a method to prepare supported hydrogel membranes in which the supports and the hydrogel membranes are synthesised simultaneously. Ruckenstein and Park have polymerised emulsion templates with hydrophobic monomers in the continuous phase and hydrophilic monomers in the aqueous phase to prepare hydrogels supported by polyHIPE scaffolds. They have successfully prepared poly(acrylamide) filled polyHIPEs and poly(sodium acrylate) filled polyHIPEs for separation of water and ethanol via prevaporation^{115-116,118}.

The previous chapter showed a proof concept of producing poly(methacrylic acid) filled polyHIPEs. In this chapter, the concept is applied to prepare polyHIPEs supported poly(MAA) and slice them into membranes for separation purposes. Since the poly(St-DVB)HIPE scaffold was too brittle to be sliced,

here poly(methacrylic acid) filled poly(EHA-St-DVB)HIEs polyHIEs are prepared and processed into membranes are prepared. The membranes are aimed to be suitable for ultrafiltration applications in aqueous solutions. Therefore, the membrane performances, including rejections and operating pressures, are tested using a dead-end cell. The supports are required to be able to withstand the operating pressure of ultrafiltration, namely ranging from 1 to 10 bar. Moreover, it is aimed that the membranes can have 90% rejections to solutes with molecular weight in the range of 10K to 100K to be suitable for ultrafiltrations. Since the swelling behaviour of poly(methacrylic acid) is pH-dependent, the poly(methacrylic acid) filled polyHIE membranes are also expected to show a pH-dependent membrane performance.

5.2 Experiment

5.2.1 Materials

Styrene (St), divinylbenzene (DVB), 2-ethylhexyl acrylate (EHA), *N, N'*-methylenebisacrylamide (MBA), ammonium persulfate (APS), NaOH, HCl (37.5 %), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and neutral and basic Al_2O_3 were purchased from Sigma-Aldrich (Gillingham, UK). Methacrylic acid (MAA) was purchased from Acros (Geel, Belgium). Hypermer B246 was kindly supplied by Croda (Snaith, UK). EHA, St and DVB were purified via filtering the monomers through neutral and basic Al_2O_3 powder to remove the inhibitor.

5.2.2 Preparation of hydrogel filled EHA-St-DVB based polyHIEs

The internal phase of the HIEs was firstly prepared by dissolving 12 vol% MAA and various amount of MBA into deionised water. The MAA solution was deprotonated via adding NaOH to adjust the pH value to 14. The setup for preparing HIEs was a reaction vessel equipped with a glass paddle stirrer. St, DVB, EHA and B246 were dissolved within the reactor. The internal phase was purged by nitrogen for 15 min, and was added dropwise into the continuous phase while stirring at a speed of 400 rpm. Afterwards the emulsion was stirred for 2 min at a speed of 2000 rpm to homogenise the emulsion. APS was dissolved into 1 ml deionised water then added into the emulsions as an initiator and the emulsion was further stirred at 2000 rpm for 1 min. A control sample, without monomers in the aqueous phase, was made using a same method. The internal phase in that case was a water solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (1.25 g / 250 ml water).

To prepare monoliths, the emulsions were transferred into centrifuge tubes and polymerised in an oven at 50 °C for 48 hours. Afterwards, the hydrogel filled polyHIPEs were purified by immersing them in mixtures of water and methanol (50 vol%:50 vol%) for 48 hours. The samples were dried using a freeze-drier.

To prepare hydrogel filled polyHIPE membranes, the emulsions were centrifuged at 3000 rpm for 5 min to remove any entrapped air bubbles. Subsequently, the emulsions were transferred into a mould with a diameter of 50 mm and a height of 30 mm. The mould was placed in oven to let the emulsions polymerise at 50 °C for 48 hours. After the polymerisation, the polyHIPEs filled with hydrogels were washed in a mixture of water and methanol (volume ratio 1:1) for 2 days. Afterwards the monoliths were sliced into membranes with a thickness of 150 µm using a microtome (RM2245 Rotary Microtome, Leica Ltd, Milton Keynes, UK). The formulations used to prepare poly(MAA) filled poly(St-DVB-EHA)HIPE are summarised in Table 5.1. Ec refers to the control sample. EM refers to the poly(MAA) filled poly(St-DVB-EHA)HIPEs, and the numbers represent the molar percentages of the crosslinkers for MAA. Sample ID with M at the end means membrane samples, for example, EM1M refers the membranes prepared from EM1 formulation.

Table 5.1 Formulation of hydrogel filled poly(EHA-St-DVB)HIPEs

	Continuous phase (20 vol%)				Internal phase (80 vol%)		
	St (vol%)	DVB (vol%)	EHA (vol%)	B246 (vol%)	MAA (vol%)	MBA (mol%)	APS (mol%)
Ec	41.7	8.3	33.3	16.7	0	0	1
EM0	41.7	8.3	33.3	16.7	12	0	1
EM1	41.7	8.3	33.3	16.7	12	1	1
EM2	41.7	8.3	33.3	16.7	12	2	1
EM5	41.7	8.3	33.3	16.7	12	5	1
EM10	41.7	8.3	33.3	16.7	12	10	1

a. Continuous phase and internal phase volumes count 20% and 80%, respectively, with respect to the total volume of emulsions. Monomers and surfactant volume ratios are with respect to the continuous

phase volume. MBA molar ratio is with respect to the molar numbers of aqueous phase monomers. APS molar ratio is with respect to the molar number of double bonds of the monomers in both continuous phase and internal phase.

5.2.3 Characterisation

The morphology, density and porosity, mechanical properties and water uptakes of the monoliths were determined using the same method as discussed for hydrogel filled poly(St-DVB)HIEs, which have been reported in Chapter 4 (P69). Membrane tests were carried out as described below. The dead-end cell is shown in Fig 5.1. The membrane, two hydrophilic filter papers and a metal porous matrix were stacked up in a sequence and placed on the bottom of the tube. Then the bottom of the testing tube was sealed with O-ring and clamps. Water or solutions were poured from the top of the tube. The top of the tube was then sealed with a lid, which was connecting to a nitrogen cylinder.

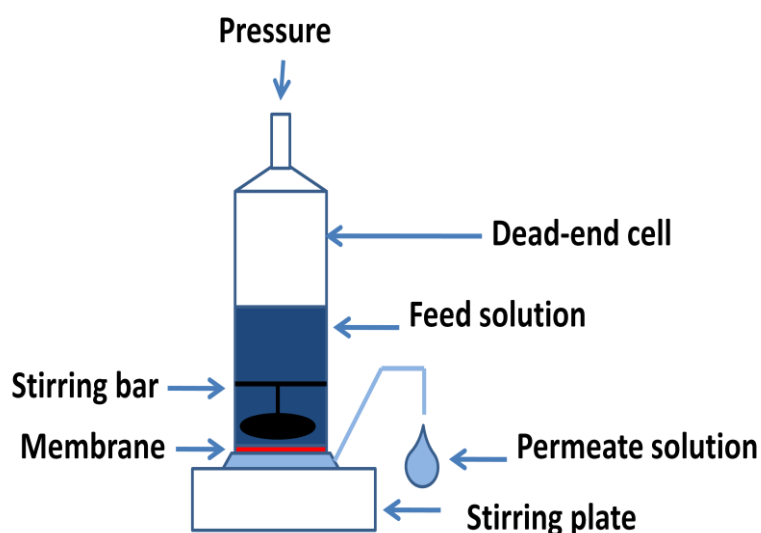


Fig 5.1 Scheme of dead-end cell

The membranes were tested in aqueous solutions under pH2, pH7, pH10 and pH12. For each pH values, the membranes were left in the solution with the certain pH value for one day prior to the test. To measure the flux, the solution with desired pH value was added into the tube. Amount of solution was allowed to pass through the membrane to reach an equilibrium flux. Afterwards the permeate water or solution was collected and the collection of the permeate solution was timed. The flux was calculated using equation:

$$F = \frac{V}{A \cdot t}$$

In which, F is the water flux, with unit $L \cdot m^{-2} \cdot h^{-1}$. V is the volume of the permeate solutions collected with unite of L. t is time for collecting the solutions with unit with h. A is the efficient surface area of the membrane with unit of m^2 .

The rejection measurement is carried out after the flux test. 50 ml 1g/L poly(ethylene glycol) (PEG) solution with desired pH value was added into the cell. After 25ml solution passing through the membrane, 2ml permeate solutions and the retention solutions were collected. The concentrations of PEG in the solutions were measured using Total Organic Carbon (TOC) and the rejection was calculated using equation:

$$R = (1 - \frac{C_p}{C_r})$$

In which, R is the rejection, %; C_p is the concentration of the solute in permeate solution, g/L; C_r is the concentration of the solute in retention solution, g/L. The rejections of the membranes for PEG with molecular weights of 10K, 20K, 35K, 50K and 100K were measured. Once the rejection of a membrane to a certain molecular weight PEG reaches 90%, this molecular weight is defined as the molecular weight cut-off of the membrane³⁸.

5.3 Results and discussion

Poly(MAA) filled poly(St-DVB)HIPEs have been reported in the previous chapter. Here EHA was added in the continuous phase, in order to achieve less brittle polyHIPEs⁸³, which is desirable for membrane preparation and applications as discussed in Chapter 3. APS was used as the only initiator for the emulsions rather than two initiators, namely AIBN and APS, as reported in the last chapter. It has been reported in a typical emulsion template, internal phase initiation for the polymerisation of the continuous phase can result in high toughness of the resultant polyHIPE¹³³. Therefore here only APS was used as initiator.

The matrix and foam density of Ec are $1.06 g/cm^3$ and $0.16 g/cm^3$, respectively, resulting in a porosity of 85%. The matrix density of EM0 is identical within error, and higher than that of Ec. This is as

expected since the density of poly(MAA) is higher than that of poly(St-DVB-EHA). The foam density of EM0 dramatically increases to 0.33 g/cm^3 , as compared to the control sample, which is due to the presence of the hydrogel in the pores. EM1-EM10 underwent shrinkage after drying: EM1 and EM2 shrank about 10 vol% and EM5 and EM10 shrank approximate 36 vol% to their wet samples. Due to the relatively low DVB concentration of the samples, the scaffolds of EM1-EM10 are of relatively low crosslinking degrees. During the drying, the hydrogels shrank and applied stresses on the poly(St-DVB-EHA)HIPE scaffolds. The scaffolds, with low crosslinking degrees, cannot withstand the stress, thus shrink as well. Moreover, as the crosslinking degrees of the hydrogels increased, the stresses of the hydrogels applied on the scaffolds were increasingly significant, thus leading to the increase in the shrinking degrees of EM1-EM10. The matrix densities of EM1-EM10 are identical, which are approximate 1.24 g/cm^3 . The foam densities of EM1-EM10 increases from 0.39 g/cm^3 to 0.60 g/cm^3 , resulting in the decrease in the porosities from 69% to 53% (Table 5.2). The increase in foam densities can be attributed to the shrinkage of the samples. Moreover, the hydrogel loadings in EM1-EM10 can increase as the increases in the crosslinker concentrations in the hydrogels, as discussed in Chapter 4, which leads to the increase in their foam densities. The SEM images show that Ec has a typical polyHIPE structure: spherical pores are interconnected by pore throats (Fig 5.2a). The pore size and pore throat size of Ec are $4 \text{ }\mu\text{m}$ and $0.8 \text{ }\mu\text{m}$, respectively (Table 5.2). From the low magnification SEM image, EM0 shows similar morphology as Ec. The high magnification SEM image, however, reveals a wrinkle surface of the pores, indicating the hydrogel coating on the walls of pores. Moreover, non-round pore throats are found in the high magnification SEM image, which can be caused either by pore throats partially covered by hydrogels or by deformation during shrinkage of the hydrogel. Nevertheless, the pore throat size of EM0 is identical within error to Ec (Table 5.2). EM1 and EM2 have wide-distributed and deformed pores (Fig 5.2e and g). This may suggest the samples undergo an uneven shrinkage during drying: some pore walls were stretched while their neighbouring pores were shrinking. Generally, the pore throats in E0-E2 are not covered by hydrogels, which is due to the similar contraction speeds of the hydrophobic monomers and hydrophilic monomers (as discussed in Chapter 4). EM5 and EM10 exhibit slightly decreases in pore sizes as compared to the control, caused by the shrinkage of the scaffolds (Table 5.2). Moreover one can hardly find pore throats from these two samples (Fig 5.2j, l). Since the scaffold shrank the surface of the pore walls reduced, therefore the hydrogel were sufficient to cover most of the pore throats.

Table 5.2 Density and porosity of poly(MAA) filled EHA-St-DVB based polyHIPEs

	Matrix density (g / cm ³)	Foam density (g / cm ³)	Porosity (%)	Pore size (μm)	Pore throat size (μm)
Ec	1.06±0.01	0.16±0.00	85±1	4 ±1	0.8±0.2
EM0	1.25±0.04	0.33±0.01	73±1	4±1	0.7±0.2
EM1	1.24±0.00	0.39±0.01	69±4	4±3	0.8±0.3
EM2	1.23±0.01	0.48±0.02	61±2	4±3	1.4±0.7
EM5	1.23±0.02	0.61±0.10	52±8	3±1	-
EM10	1.24±0.02	0.60±0.10	53±7	3±1	-

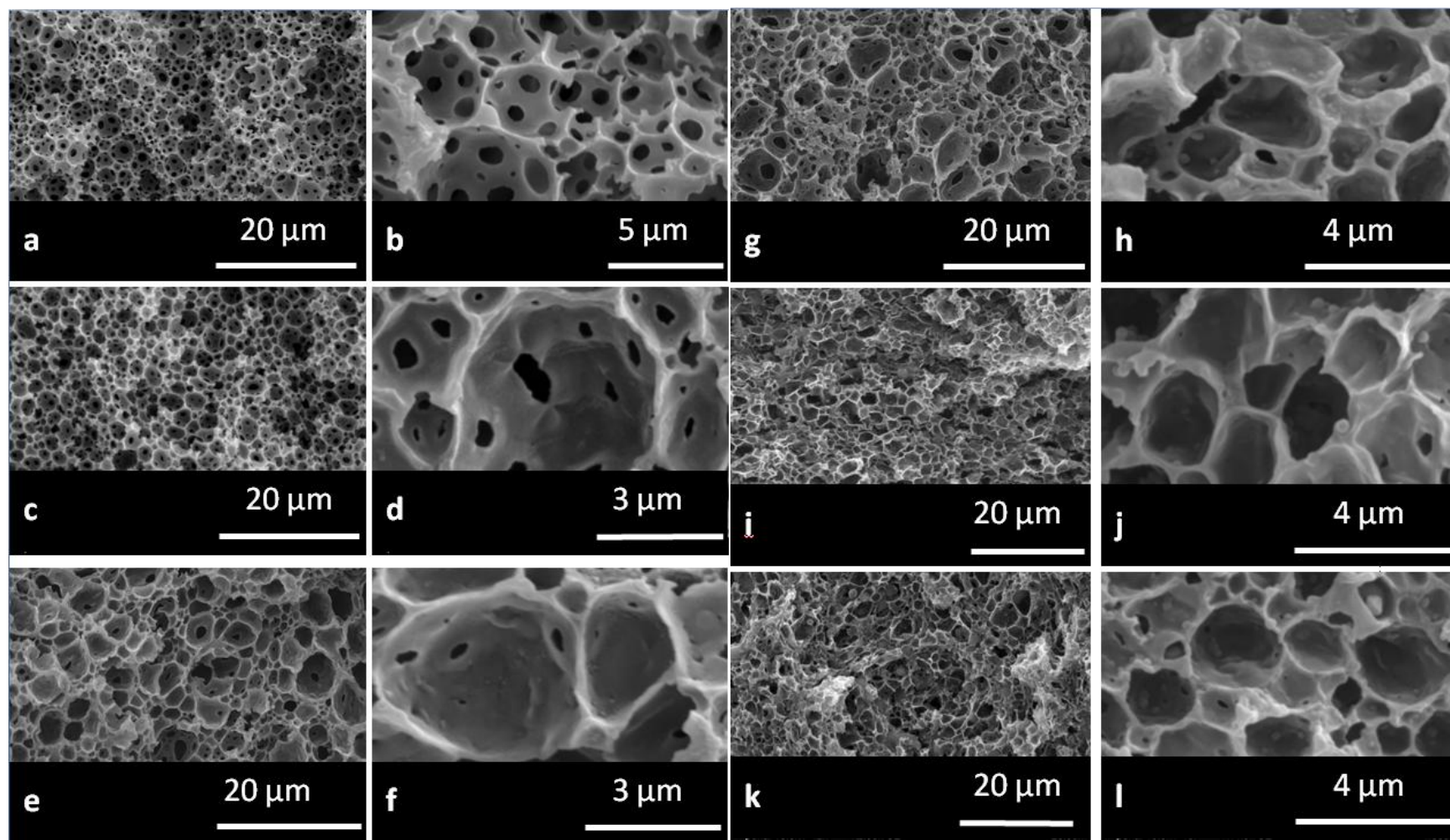


Fig 5.2 SEM images of poly(MAA) filled poly(EHA-St-DVB)HIPEs. a, b. control sample (Ec); c, d. 0% (EM0); e, f. 1% (EM1); g, h. 2% (EM2); i, j. 5% (EM5); k, l. 10% (EM10).

Fig 5.3 shows the water uptake of EM0-10. The mechanism of water uptakes in polyHIPEs has been discussed in the previous chapter: water transports into the pores of polyHIPEs either by diffusing through hydrogel layers and passing the pore throats. The water thereby, replaces the air in the pores. In the beginning, the air can escape from the pores through pore throats. However, after the hydrogels swell and cover the pore throats, or the pore throats are initially covered by hydrogels, the air was trapped in pores and impeded further water transport. The water uptakes of EM0-EM10 decreased as the hydrogel crosslinking degrees increases. Firstly the hydrogels with high crosslinking degrees formed dense network after swelling, suppressing the diffusion of the water. Moreover, the pore throats in EM0-EM10 turned from open to partially covered, and finally to covered by hydrogels. In this case, the air was trapped in the polyHIPEs with highly crosslinked hydrogels from the beginning of the water uptakes. Therefore the water uptake of the samples decreased.

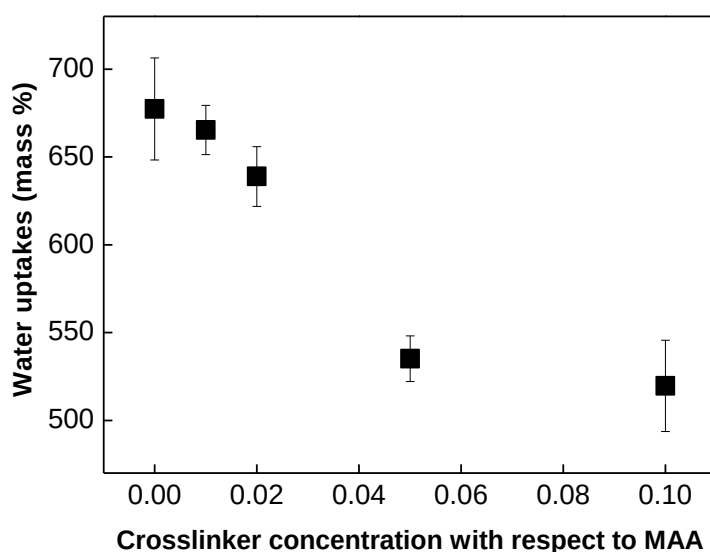


Fig 5.3 Water uptakes of poly(MAA) filled poly(EHA-St-DVB)HIPEs

Because of the shrinkage of the dry samples, the dimensions of the samples are not uniform. Therefore, the mechanical properties of the samples, which are highly affected by the dimensions, are not comparable. In addition, mechanical properties of wet samples are more meaningful in terms of membrane applications, as the membranes will be used in their wet stage. Hence in this study, only the mechanical properties of the wet samples of EM0-10 were measured (Fig 5.4). The elastic moduli of EM0-EM10 did not have a dramatic variation, which were about 11 MPa. Similarly, their crush

strengths were identical within error (0.5 MPa). This is as expected because they have scaffolds with same formulation. The hydrogels swollen and were soft if the samples were wet. Therefore they cannot provide any mechanical strength. The mechanical properties of the samples were from the scaffolds.

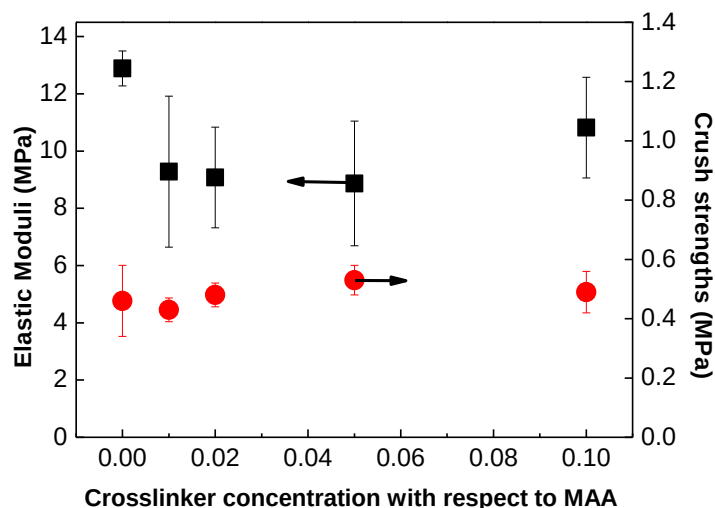


Fig 5.4 Mechanical properties of wet poly(MAA) filled poly(EHA-St-DVB)HIPes.

In order to produce defect free membranes, the emulsions were centrifuged to remove any air bubbles. After the polymerisation in a mould, the washed monoliths were sliced into membranes and kept in water in fridge before tests. Since poly(MAA) is a pH-sensitive hydrogel, the performance of the membranes were tested in varying pH solutions. The water flux of EM1M at pH 2 is $600 \text{ Lm}^{-2}\text{h}^{-1}$ at a back pressure of 1 bar (Fig 5.5). At a low pH value, poly(MAA) was protonated, the uncharged chains could pack close to each other. The hydrogel thus formed a thin layer, which was easy for water to diffuse through (Fig 5.6a). As the pH increased from 2 over 7 to 10, the water flux decreased dramatically. This is due to the deprotonation of the poly(MAA), which led to charged polymer chains. In this case, the hydrogel could adsorb a large amount of water and expand dramatically due to the repulsive force between the polymer chains, creating a thick layer for water transport. Therefore the water flux reduced dramatically. As the pH value further increased to 13, the water flux slight increased as compared to at pH 10 (Fig 5.5). Upon this pH value, the ion strength dominated the morphology of the hydrogel. The deprotonated poly(MAA) chains formed sodium poly(MAA) in the presence of sodium ions with high concentration. The uncharged sodium poly(MAA) collapsed as the

repulsive force reduced between the polymer chains and thus the hydrogel layer become thin again, which allowed the water diffuse through the hydrogel rapidly (Fig 5.6a). This phenomena has been reported by Osada et al.¹⁹⁵.

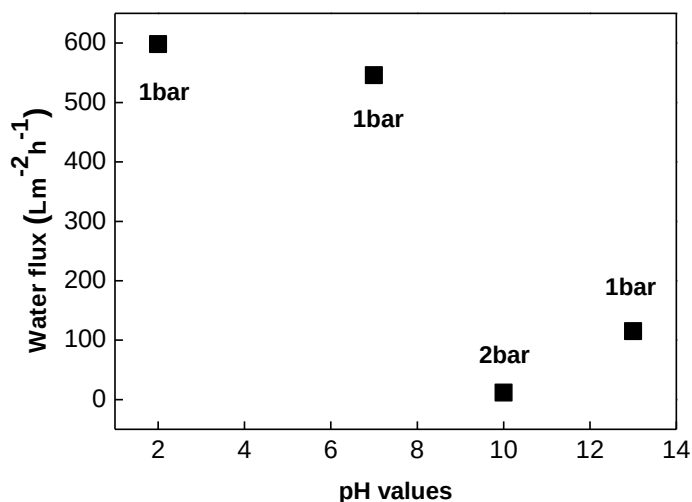


Fig 5.5 Water flux of poly(MAA) with 1% crosslinker filled poly(EHA-St-DVB)HIPE membrane (EM1M) against pH values.

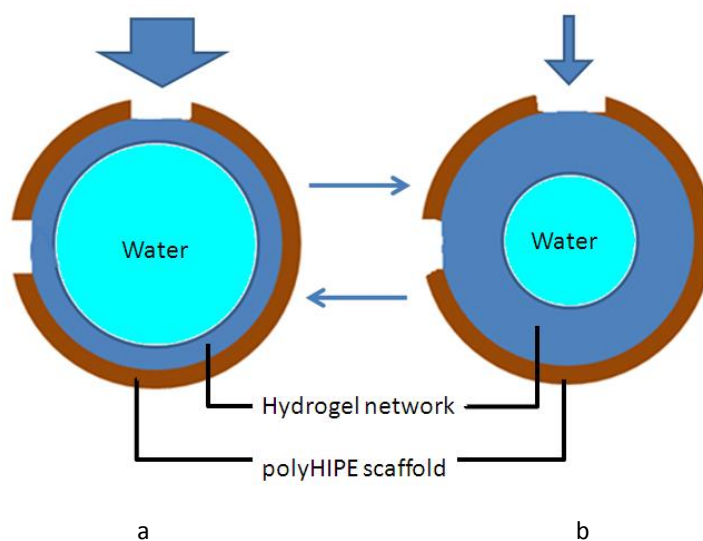
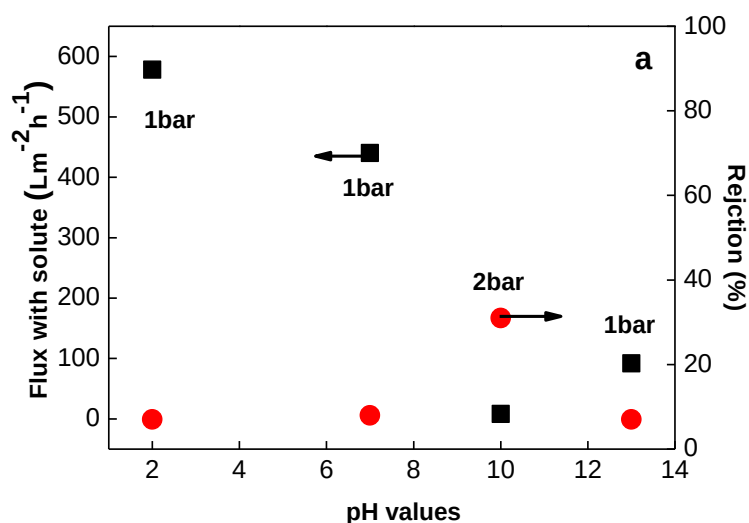


Fig 5.6 Scheme of effect of hydrogels to water flux. a, collapse (protonated). b, expand (deprotonated).

The rejections of EM1M under different pH values were tested using a 1g/L 35K PEG solution. The flux of PEG solutions have a similar trend as the water flux, which decreased as the pH value increased from 2 to 10 and rebounded at pH 13. At pH 2, pH 7 and pH13, EM1M showed no rejection to the polymer. The only rejection was found at pH 10, which was 30% to the 35K PEG (Fig 5.7a).

Solution-diffusion theory is usually used to explain the separation of matters in hydrogel membranes^{181,185,196}. The theory states that the swollen hydrogel membrane consists of polymer chains and water channels which are the meshes of the hydrogel network filled with water¹⁹⁷. The feed solution can only go through the water channel but the polymer chains are not permeable for both the solutes and the solvents. The separation of the solutes and solvents is determined by the different solubility and diffusion speed in the water channel: the fast-diffusing matter can pass through the membrane rapidly thus enrich in the rejection solution, while the slow-diffusing matter has lower concentration in the rejection solution¹⁹⁸. The undetectable rejection of PEG for EM1M at pH 2, pH 7 and pH13 is due to the thin hydrogel layer under these pH values, which resulted in relatively short water channel within the hydrogel membrane. Thus the PEG did not have enough time to separate from the water within such short retention times in the membrane. On the other hand, at pH 10, the hydrogels were deprotonated and expanded dramatically. Thus the water channel extended, which provided sufficient retention time for the separation of PEG from water, resulting in higher rejection than the other pH values. The rejections of EM1M to PEG with different molecular weights were tested in order to find a molecular weight cut-off of the membranes. The rejections of 35K, 50K and 100K PEG increased from 30% over 38% to 58% (Fig 5.7b). The increase in molecular weight of PEG resulted in a decrease of solubility and diffusion coefficient in water channel. This enlarged difference in transport speeds between the PEG and the water in the water channel thus enhanced the separation performance of the membrane.



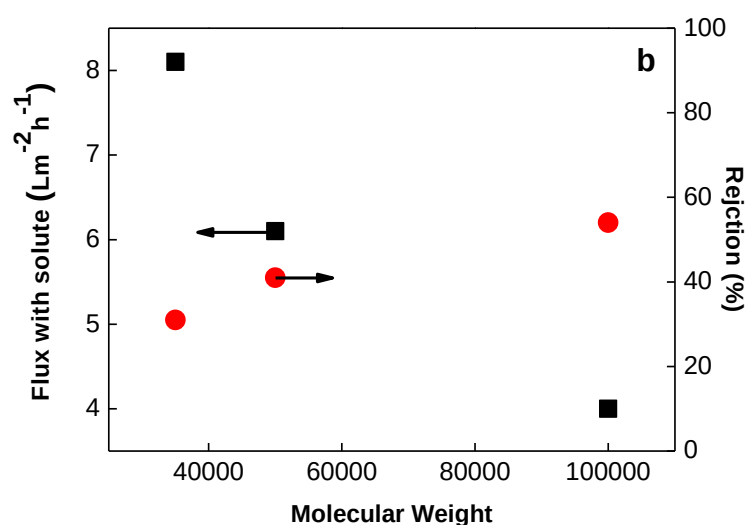


Fig 5.7 PEG solution flux and rejections of EM1M. (a) 35K PEG solution flux and rejection at different pH. (b) Solutions of PEG with different molecular weights flux and rejections

Thereafter, poly(MAA) filled poly(EHA-St-DVB)HIPEs with increased hydrogel crosslinking degree, namely EM2M, was tested. The variation of water flux as a function of pH values in EM2M followed a similar trend as for EM1M: a water flux of $31 \text{ Lm}^{-2}\text{h}^{-1}$ was obtained at pH 2. The flux decreased to $23 \text{ Lm}^{-2}\text{h}^{-1}$ at pH 7, and finally reduced to $5 \text{ Lm}^{-2}\text{h}^{-1}$ at pH 10 even under a back pressure of 9 bar. At pH 13, the flux of EM2M increased again as compared to pH 10. The explanation is the change of the thickness of the hydrogel layers as a function of pH values and ion strength, which has been discussed above. The rejections of EM2M under different pH values were measured using 1g/L 35K PEG. The rejections of PEG at pH 2 and pH 7 were about 10% and 20%, respectively. However the rejection of PEG at pH 10 increased to more than 85%, and the rejection reduced to 44% at pH 13. The rejection to 35K PEG as a function of pH values is as expected, which is again due to the different thickness of the hydrogel layers. The relatively thick hydrogel layer at pH 10 provided long time for the PEG separating from water. Furthermore, the water flux in EM2M is much lower than that in EM1M, but the rejection to PEG in EM2M is higher than that in EM1M. Due to the low crosslinking degree, the hydrogel network in EM1M was flexible. Thus the flowing water could easily deform the polymer chains to gain a rather straightforward water channel within the hydrogel network. On the other hand, the hydrogel network in EM2M was rather difficult to be deformed by the flowing water, thus the water could only detour around the polymer chains. This firstly increased the tortuosity (the length of the actual

pathway of water over the ideal pathway of water, namely, the thickness of the membrane) in EM2M, and also extended water channel in EM2M as compared to EM1M, thus leading to the decrease in water flux. On the other hand, the tortuosity in the water channel reduced the diffusion coefficient of PEG in EM2M. This, combining with the longer water channel in EM2M, enhanced the separation of PEG from water in EM2M. The rejections of PEG in EM2M as a function of PEG molecular weights are shown in Fig 5.9 b. As the increase in molecular weight, the PEGs have decrease in solubility in water and diffusion coefficient in water, leading to enhanced separation of PEG from water. The rejection of EM2M to 50K PEG was 91%, meaning that the molecular weight cut-off of EM2M was 50K, which is in range of cut-off of ultrafiltration membranes.

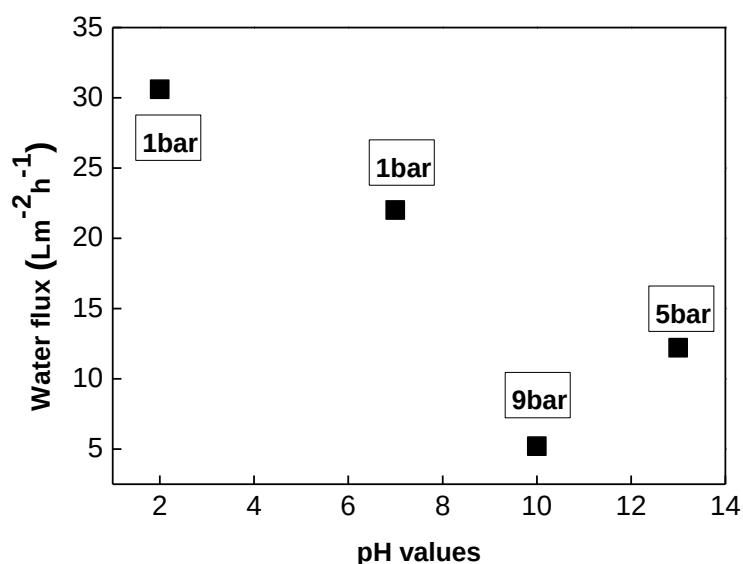


Fig 5.8 Water flux of poly(MAA) with 2% crosslinker filled poly(EHA-St-DVB)HIPE membrane (EM2M) against pH values.

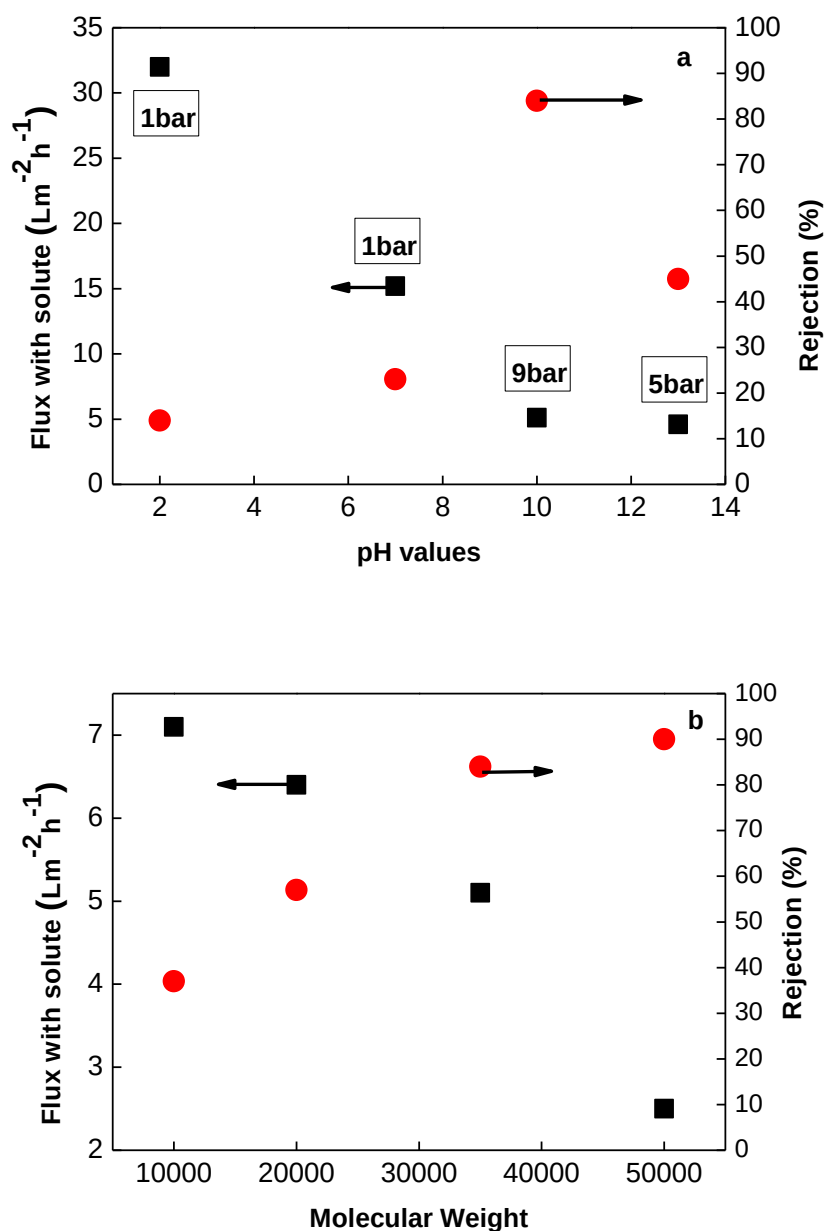


Fig 5.9 PEG solution flux and rejections of EM2M. (a) 35K PEG solution flux and rejection at different pH. (b) Solutions of PEG with different molecular weights flux and rejections

5.4 Conclusion

In this chapter supported hydrogel membranes were synthesised via a one-pot route. By polymerising St, EHA and DVB, and MAA in the continuous phase and internal phase, respectively, in emulsion templates simultaneously, the scaffold and the hydrogels of the membranes were prepared. The membranes had water flux depending on pH of the feeding solution. The water flux at pH 2 for the

membranes were very high, as the poly(MAA) was protonated and the hydrogels collapsed. The lowest water fluxes of EM1M and EM2M were found at pH 10, when the poly(MAA) was deprotonated and largely swollen. The water flux increased at pH 13, which due to the formation of sodium poly(MAA) under a very high concentration of NaOH. On the other hand, for both membranes the highest rejections to PEG were observed at pH 10. The EM2M had a higher rejection than EM1M due to the higher crosslinking degrees in the poly(MAA). Moreover, the EM2M possesses a cut-off of 50K PEG, which suggests the membrane is applicable for ultrafiltration.

Chapter 6 Tough polyurethane foams prepared via emulsion templating

Abstract

Urethane diacrylate oligomer and styrene were copolymerised within emulsion templates to make macroporous polymers that were not brittle and of high elastic moduli and crush strengths. Polyurethane diacrylate oligomer helped to reduce the droplet size of the emulsions, which therefore resulted in polyHIPEs with small pores as compared to control poly(polyethylene glycol dimethacrylate-styrene)HIPEs. Moreover the poly(urethane diacrylate-styrene)HIPEs also have higher elastic modulus and crush strengths than the control sample. This is attributed to the longer polymer chain of the urethane diacrylate. Moreover, it is also found that the mechanical properties of the macroporous polymers can be tailored by changing the ratio of styrene and polyurethane diacrylate.

6.1 Introduction

High internal phase emulsions (HIPEs) have been defined as emulsions with more than 74 vol% internal phase¹⁹⁹. The continuous phase usually contains monomers, surfactants and initiators (sometimes the initiators are in the internal phase), while the internal phase is an immiscible liquid dispersed in the monomer phase. After the polymerisation of the continuous phase and the removal of the internal phase, the resultant product becomes a macroporous polymer, which is termed polymerised high internal phase emulsions (polyHIPEs). PolyHIPEs have outstanding properties, such as low density²⁰⁰, high porosity and interconnectivity^{72,81}. Therefore they are considered for many applications, such as filter media^{2,115}, ion exchange modulus⁸¹ and scaffolds for tissue engineering^{144-145,201}. The most commonly studied polyHIPEs are based on styrene (St) and divinylbenzene (DVB)^{73,134}, which are brittle and chalky^{70,202} and, thus, not desired in their practical applications. Therefore research has been focused on improving the mechanical properties of polyHIPEs. Cameron et al.⁸³ reported using 2-ethylhexyl acrylate (EHA) and 2-ethylhexyl methacrylate (EHMA) incorporating with St and DVB to prepare elastomeric polyHIPEs. However, in this case, the decrease of brittleness of polyHIPEs was at the expense of reduction of their glass transition

temperatures^{83,85}. Our group has used polyethylene glycol dimethacrylate (PEGDMA) instead of DVB as crosslinker for emulsion templates^{70,87,122}. The resultant polyH(M)IPEs were less brittle and less chalky. Moreover, due to the high crosslinking degree, no glass transition was observed in the range of 20°C to 200°C. Polymerised medium internal phase emulsions (polyMIPEs) were also prepared by the researchers from our group. They reported reducing porosity of macroporous polymers resulting in much tougher materials^{70,121}.

Polyurethanes (PU) have been successfully synthesised within polyHIPEs. David and Silverstein¹⁰² prepared polyHIPEs solely based on polyurethane which was synthesised from 1, 6-diisocynatohehexane and poly(ϵ -caprolactone)). The polyHIPEs had porous structure resulting from the emulsion templates, as well as large bubbles caused by the CO₂ generated by the reaction of the diisocynate and the polyol. Lépine et al.¹⁰³ prepared PU-poly(St-DVB) interpenetrating network within polyHIPEs via polymerising isocynates and polyol as well as styrene and DVB in emulsion templates simultaneously. The interpenetrating networks were interconnected by a difunctional agent, i.e. hydroxybutyl methacrylate. The resultant polyHIPEs based on PU-PS had higher elastic modulus (38 MPa) and crush strength (about 2.5 MPa) than poly(St-DVB)HIPEs (elastic modulus of 9 MPa and crush strength of about 0.6 MPa). Their work is inspirational, as it suggests the possibility to prepare PU-PS polyHIPEs in an alternative way: why not let hydroxybutyl methacrylate react with isocynates to form urethane methacrylate, which can subsequently copolymerise with styrene? Therefore in this experiment, polyurethane diacrylate, which is a long chain crosslinker, was copolymerised with styrene within the continuous phase of emulsion templates to make macroporous polymers. The mechanical properties of the macroporous polymers are mainly studied. The aim of this work is to make macroporous polymers which are less brittle than poly(St-DVB)HIPEs, and possess high elastic moduli and crush strengths, so they can be used as structural materials or scaffolds employed usually at pressurised conditions.

6.2 Experiment

6.2.1 Materials

Styrene (St, purchased from Sigma-Aldrich, Gillingham, UK), divinylbenzene (DVB, purchased from Sigma-Aldrich, Gillingham, UK), polyethylene glycol dimethylacrylate (PEGDMA, kindly supplied by

Cognis, Southampton, UK) and polyurethane diacrylate (Ebecryl 284, was kindly supplied by Cytec, Belgium) were used as monomers. All monomers were used as received. Hypermer B246, supplied by Croda (East Yorkshire, UK), was used as surfactant. Ammonium persulfate (APS), purchased from Sigma-Aldrich (Gillingham, UK) was used as initiator. $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was purchased from Sigma-Aldrich (Gillingham, UK).

6.2.2 Preparation of polyH(M)IPEs

The internal phase was aqueous solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ with dissolved APS. The equipment used in the experiment was a reactor with a glass paddle rod connected to an overhead stirrer. Emulsion templates were prepared as follows: monomers and surfactant were mixed in the reactor to make the continuous phase, to which the internal phase was added dropwise while stirring at a speed of 400 rpm. Afterwards, the emulsions were further stirred at 2000 rpm for 3 min to produce homogeneous emulsions. The emulsions were transferred into free-standing centrifuge tubes and placed in oven at 70 °C. After polymerisation, the samples were washed in ethanol and in water for 24 h, respectively. The washed samples were dried at 70 °C in air until constant weight. The formulations of H(M)IPEs are summarised in Table 6.1.

Table 6.1 Recipes for polyH(M)IPEs based on St-PUDA

Sample	Continuous phase		Internal phase	
	St/DVB/PEGDMA/PUDA 284 (vol%/vol%/vol%/vol%) ^a	Surfactant B246 (vol%) ^b	APS (mol%) ^c	Internal phase volume fraction (vol%) ^d
HIPE(St-DVB)	50/30/0/0	20	1	75
HIPE0	50/0/30/0	20	1	75
HIPE1	50/0/0/30	20	1	75
HIPE2	55.6/0/0/33.3	11.1	1	75
HIPE3	58.8/0/0/35.3	5.9	1	75
MIPE4	70.6/0/0/23.5	5.9	1	60
MIPE5	58.8/0/0/35.3	5.9	1	60
MIPE6	47.05/0/0/47.05	5.9	1	60
MIPE7	35.3/0/0/58.8	5.9	1	60

a. Monomer volume fraction with respect to continuous phase; b. Surfactant volume fraction with respect to continuous phase; c. Initiator molar fraction with respect to molar number of double bonds in monomers; d. the internal phase was aqueous solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, the concentration for HIPE0 was 0.62mol/L, the concentrations for the other samples were 0.0775mol/L.

6.2.3 Characterisation

The morphology, density, porosity and mechanical properties of the samples were tested using the same methods as described in Chapter 4 (P69).

6.3 Results and Discussions

Table 6.1 summarises the formulations of all the samples. HIPE(St-DVB) containing styrene and DVB in the continuous phase was prepared as a control sample. A surfactant concentration of 20 vol%, commonly used in our group, was used and the internal phase ratio was set to 75 vol%. Poly(St-DVB)HIPE has a matrix and foam density of 1.08 g/cm^3 and 0.23 g/cm^3 resulting in a porosity of 78% (Table 6.2). This is typical for polyHIPEs made from emulsion templates with an internal phase of 75%¹²⁶. Poly(St-DVB)HIPE has an open porous structure (Fig 6.1a), characterised by an average pore and pore throat size of $2.6 \text{ }\mu\text{m}$ and $0.3 \text{ }\mu\text{m}$ (Table 6.2), respectively. The stress-strain curve of poly(St-DVB)HIPE under compression is composed by two regimes: an elastic regime and a stress decrease beyond the crush strength (Fig 6.2). This suggests the sample failed beyond the crush strength. This finding is consistent with our observation during the compression test: the sample broke during the test. Both suggest poly(St-DVB)HIPE was brittle. PolyHIPE0 was based on PEGDMA and St. The matrix and foam density is 1.13 g/cm^3 and 0.26 g/cm^3 , resulting in a porosity of 77% (Table 6.2). PolyHIPE0 has an open porous structure (Fig 6.1b) with a pore size of $3 \text{ }\mu\text{m}$ and pore throat size of $0.5 \text{ }\mu\text{m}$, which are identical with poly(St-DVB)HIPE within error. The stress-strain curve of polyHIPE0, however, is different from that of poly(St-DVB)HIPE (Fig 6.2): the elastic regime is followed by a stress plateau rather than a stress decrease, and the transition from the elastic regime to the stress plateau is smooth. This suggests the sample did yield during the compression test, thus crush strength exists, but did not fail. It was also observed that the sample only expanded but did not break after the test. This indicates polyHIPE0 was less brittle than poly(St-DVB)HIPE, which was consistent with previous findings from our group⁷⁰. The elastic modulus and the crush strength of polyHIPE0 were 22 MPa and

1.4 MPa, respectively (Table 6.2). The lower elastic modulus and crush strength of polyHIPE0 than the poly(St-DVB)HIPE was resulted from the low crosslinking degree of polyHIPE0.

Table 6.2 Summary of the measured properties (matrix density, ρ_m ; foam density, ρ_f ; porosity, P; pore size, d_p ; pore throat size, d_{pt} ; elastic modulus, E and crush strength, σ) of the samples.

Sample	ρ_m (g/cm ³)	ρ_f (g/cm ³)	P (%)	d_p (μ m)	d_{pt} (μ m)	E (MPa)	σ (MPa)
poly(St-DVB)HIPE	1.080 $\pm$ 0.010	0.23 $\pm$ 0.01	78 $\pm$ 1	2.6 $\pm$ 0.8	0.3 $\pm$ 0.1	70 $\pm$ 4	4.8 $\pm$ 0.1
polyHIPE0	1.130 $\pm$ 0.006	0.26 $\pm$ 0.01	77 $\pm$ 1	3 $\pm$ 1	0.5 $\pm$ 0.2	22 $\pm$ 2	1.4 $\pm$ 0.1
polyHIPE1	1.088 $\pm$ 0.006	0.25 $\pm$ 0.01	77 $\pm$ 1	1.2 $\pm$ 0.3	0.4 $\pm$ 0.1	31 $\pm$ 8	1.8 $\pm$ 0.1
polyHIPE2	1.093 $\pm$ 0.003	0.24 $\pm$ 0.01	78 $\pm$ 1	2.0 $\pm$ 0.5	0.4 $\pm$ 0.2	59 $\pm$ 4	2.9 $\pm$ 0.1
polyHIPE3	1.090 $\pm$ 0.010	0.23 $\pm$ 0.01	79 $\pm$ 1	3.3 $\pm$ 0.8	0.5 $\pm$ 0.2	65 $\pm$ 4	3.6 $\pm$ 0.3
polyMIPE4 ^a	1.094 $\pm$ 0.005	-	-	3.7 $\pm$ 0.9	0	-	-
polyMIPE5	1.110 $\pm$ 0.007	0.37 $\pm$ 0.01	66 $\pm$ 1	2.7 $\pm$ 0.8	0.3 $\pm$ 0.1	143 $\pm$ 3	7.0 $\pm$ 0.3
polyMIPE6	1.122 $\pm$ 0.004	0.38 $\pm$ 0.01	66 $\pm$ 1	2.5 $\pm$ 0.5	0.3 $\pm$ 0.1	111 $\pm$ 17	5.0 $\pm$ 0.2
polyMIPE7	1.148 $\pm$ 0.017	0.39 $\pm$ 0.02	66 $\pm$ 1	2.0 $\pm$ 0.4	0.3 $\pm$ 0.2	61 $\pm$ 9	3.1 $\pm$ 0.2

a. PolyHIPE4 could not be dried, therefore the foam density, porosity and mechanical properties could not be determined.

The first group of HIPEs (HIPE1-3) was prepared with constant ratio of St/PUDA 284. PUDA 284 was used because it can be easily copolymerised with St via radical polymerisation. HIPE1 was prepared with the same surfactant concentration, internal phase ratio and emulsification condition as HIPE(St-DVB) and HIPE0. The polyHIPE1 has a matrix density of 1.088 g/cm³ and a foam density of 0.25 g/cm³, leading to a porosity of 77% (Table 6.2). PolyHIPE1 is also open-porous (Fig 6.1c) with a pore size of 1.2 μ m and a pore throat size of 0.4 μ m (Table 6.2). Since the surfactant and emulsification conditions were the same for both HIPE0 and HIPE1, the smaller pore size of polyHIPE1 compared to polyHIPE0 must have been due to the presence of PUDA in HIPE1. The presence of PUDA in the continuous phase raised the viscosity of the continuous phase, which suppresses the tangential interfacial flow of the internal phase, hence hindering coalescence of droplets, resulting in smaller droplets¹³⁶. The stress-strain curve of polyHIPE1 has a similar trend as that of polyHIPE0 (Fig 6.2): the curve consists of an elastic regime, followed by a stress plateau regime. Additionally, the tested

polyHIPE1 sample did not break, suggesting that polyHIPE1 is not a brittle sample. PolyHIPE1 had an elastic modulus of 31 MPa and crush strength of 1.8 MPa, indicating that the presence of PUDA 284 in polyHIPE1 results in improved mechanical properties as compared to polyHIPE0. The longer chains of the PUDA crosslinker as compared to PEGDMA provided more flexible joints within the polymer network, reducing the potential residual stresses within the macroporous polymers. On the other hand, the elastic modulus and crush strength of polyHIPE1 is lower than those of poly(St-DVB)HIPE, which is due to the low crosslinking degree in polyHIPE1. Preparation of poly(St-DVB)HIPE with identical crosslinking degrees to polyHIPE1 failed, as the resultant poly(St-DVB)HIPE was of closed cells, which was thus incomparable with polyHIPE1.

Since PUDA 284 contributed to the formation of smaller droplets, lower surfactant concentrations were used in the following emulsion templates in order to increase the pore sizes and tailor the mechanical properties of the polyHIPEs. HIPE2 and HIPE3 were prepared with only 11.1 vol% and 5.9 vol% surfactant, respectively. PolyHIPE2 and polyHIPE3 have identical matrix and foam densities within the range of error and, therefore very similar porosities (78% and 79%, respectively, Table 6.2). As expected the matrix densities are identical, since the compositions of the monomers in these HIPEs were identical. The average pore size of polyHIPE2 is 2.0 μm and that of polyHIPE3 further increases to 3.3 μm , both larger than in polyHIPE1. However, the average pore throat sizes of the two polyHIPEs are 0.4 μm and 0.5 μm , respectively, identical within errors. The gradual increase of the pore sizes of polyHIPE1-3 can be explained by the reduced surfactant concentration in the HIPEs. The amount of coalescence of the emulsion droplets was possibly enhanced by reducing the surfactant concentrations, thus enlarging the droplet size and subsequently the pore sizes¹³³. Nevertheless, despite the lower surfactant concentration, HIPE2 and HIPE3 were visually stable during polymerisation, and polyHIPE2 and polyHIPE3 both have typical polyHIPE structures (Fig 6.1 d, e). The stress-strain curve of polyHIPE3 is representative to that of polyHIPE2: both have an elastic regime smoothly transiting to a stress plateau after the crush strength. The elastic moduli of polyHIPE1-3 increase from 31 MPa over 59 MPa to 65 MPa and the crush strengths from 1.8 MPa over 2.9 MPa to 3.6 MPa (Table 6.2). Since the monomer compositions in the HIPEs were same, the improvement of the mechanical properties of the polyHIPEs might be attributed to the decrease in surfactant concentration. Although the samples were washed, there can be traces of surfactants within the

polyHIPEs, which might act as plasticiser, softening the polyHIPEs⁷³. Thus, with the decrease in surfactant concentration used to stabilise the HIPE templates, which reduced the possibility of residual surfactant, the mechanical properties of the polyHIPEs increase. Moreover, due to the decrease in the surfactant concentration in HIPE1-3, the pore sizes of the samples increased, which may have influence on their mechanical properties. Maheo et al.²⁰³ have reported that the pore walls of polyHIPEs consists of a soft skin and a rigid core. The composition of the soft skins in the pore walls decreased with the increase in the pore sizes of polyHIPE1-3, which causes the enhancement in the mechanical properties of the polyHIPEs.

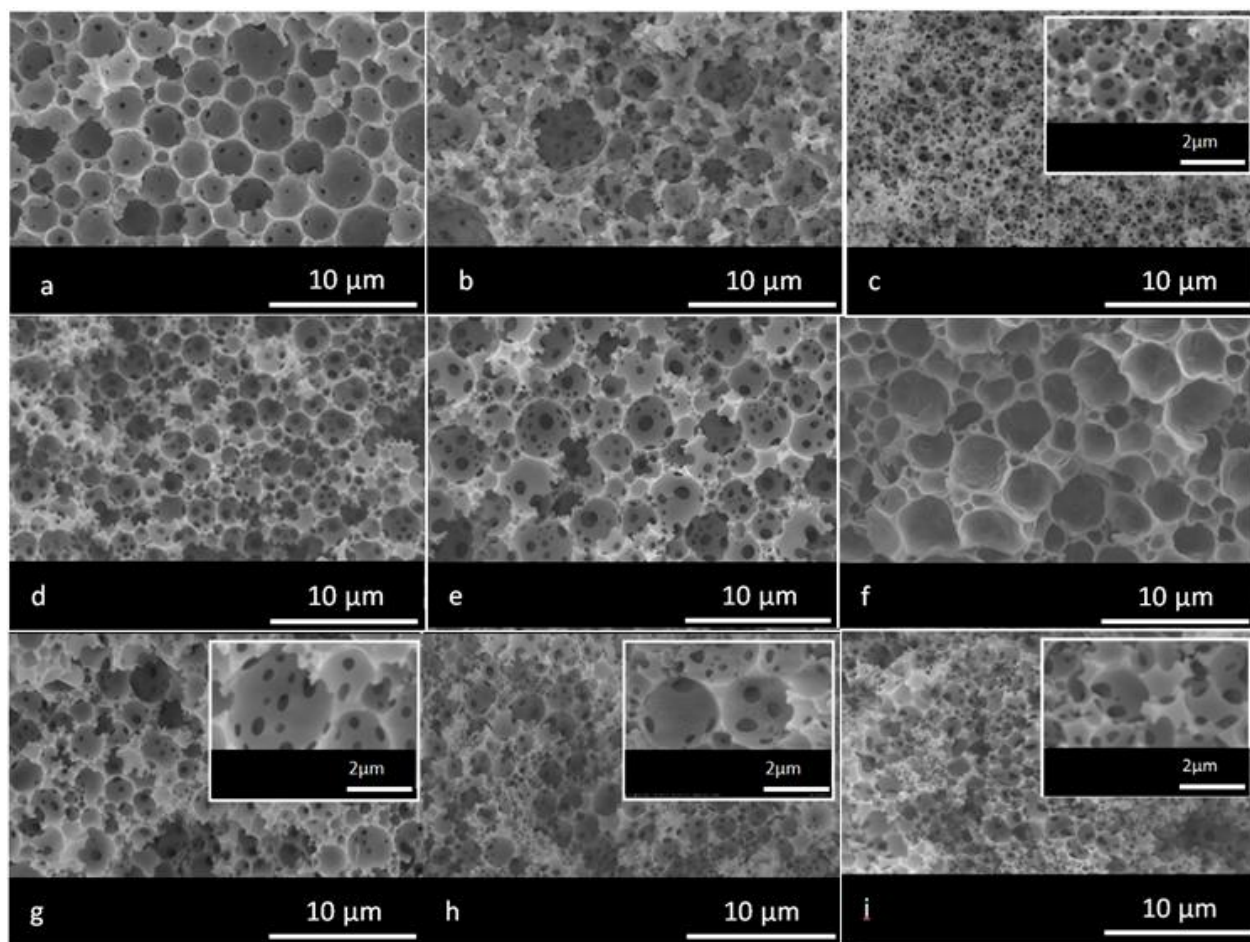


Fig 6.1 SEM images of polyH(M)IPEs: (a) poly(St-DVB)HIPE; (b) polyHIPE0; (c) polyHIPE1; (d) polyHIPE2; (e) polyHIPE3; (f) polyMIPE4; (g) polyMIPE5; (h) polyMIPE6; (i) polyMIPE7.

In order to investigate the effect of the St/PUDA 284 ratio in the HIPE on the mechanical properties of polyHIPEs, the surfactant concentration was kept at 5.9 vol% but the St/PUDA 284 ratio was varied (Table 6.1). A St/PUDA 284 ratio over 1:1 resulted in a very viscous continuous phase, which was not

suitable for the preparation of HPIEs. A group of MIPEs (MIPE4-7) was, therefore, prepared and polymerised. Small pieces and powder of polyMIPE4 were dried for SEM and determination of its matrix density, respectively. PolyMIPE4 has a matrix density of 1.094 g/cm^3 . It has a close-cell pore structure with an average pore size of $3.7 \text{ }\mu\text{m}$ (Fig 6.1f). The other properties of polyHIPE4 could not be determined as big pieces of sample could not be dried.

The matrix densities of polyMIPE5-7 increase slightly (Table 6.2) because of the increase in the PUDA 284 concentration, since PUDA 284 has a higher density than PS. The foam densities of polyMIPE5-7 are identical within error, resulting in identical porosities of polyMIPE5-7 (Table 6.2). The average pore sizes of polyMIPE4-7 decrease from $3.7 \text{ }\mu\text{m}$ to $2.0 \text{ }\mu\text{m}$, due to the increase in the PUDA 284 concentration in the corresponding MIPEs, where PUDA 284 played a part in creating smaller emulsion droplets during the emulsification process. In contrast to the closed celled polyMIPE4 (Fig 1f), polyMIPE5-7 are open-porous (Fig 6.1g-i), with average pore throat sizes identical in the range of error ($0.3 \text{ }\mu\text{m}$, Table 6.2). Surfactant concentration in an emulsion template determines the contact of emulsion droplets and subsequently the pore throat formation in polyHIPEs⁷³. The surfactant concentration was 5.9 vol% with respect to the continuous phase in MIPE4-7. However, PUDA has been revealed to act as co-stabiliser, which helped to form small droplets in emulsion templates. Thus in MIPE4, with the lowest PUDA 284 concentration, the total stabiliser (surfactant plus PUDA 284) concentration was relatively low, resulting in a closed-cell polyMIPE after the polymerisation. With increasing PUDA 284 concentrations from MIPE4 to MIPE5-7, the total stabiliser (surfactant plus PUDA 284) concentration increased, which therefore led to the formation of open-porous structure in polyMIPE5-7. The stress-strain curve of polyMIPE5 is representative to those of polyHIPE6 and polyHIPE7. Again, the samples yielded but did not break after the compression tests. The elastic moduli of polyMIPE5-7 decrease from 143 MPa to 61 MPa. In addition, the crush strengths of polyMIPE5-7 also decrease from 7.0 MPa to 3.1 MPa. The mechanical properties of polyMIPE5-7 are dominated by the increase in the PUDA 284 concentration in the emulsion templates. PUDA 284, possessing a very flexible backbone, forms the flexible parts in the polyMIPEs, while the polystyrene parts increase the stiffness of the polyMIPEs. Therefore, as the PUDA 284 concentration increased from 23.5% to 58.8% in MIPE5 to MIPE7, polyMIPE5-7 became less stiff, characterised by decreases in the elastic moduli and crush strengths. PolyMIPE5 and polyHIPE3 had same composition in the

continuous phase. The higher elastic modulus and crush strength of polyMIPe5 is caused by the higher foam density compared to polyHIPE3. This is consistent with some pervious findings^{69-70,202}.

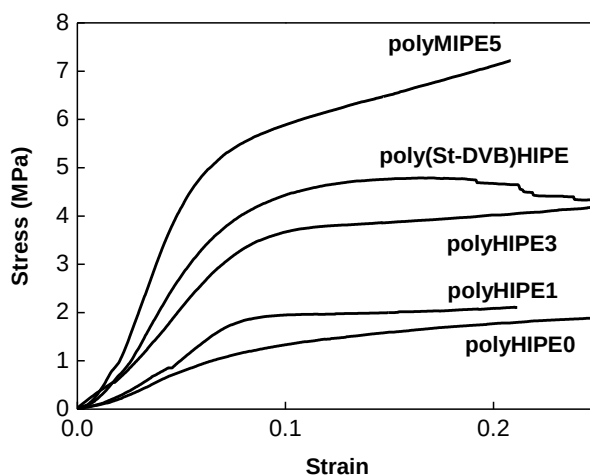


Fig 6.2 Representative stress-strain curves of poly(St-DVB)HIPE, poly(PEGDMA-St)HIPE and poly(PUDA-St)H/MIPEs.

6.4 Conclusion

Polyurethane diacrylate-St based polyHIPEs were prepared via emulsion templating, which are less brittle than the conventional St-DVB based polyHIPEs. As compared to a poly(PEGDMA-St)HIPE control, poly(PUDA-St)HIPE (polyHIPE1) had 41% higher elastic modulus and 29% higher crush strength. Moreover, PUDA was found to function as a co-stabiliser, as HIPE2 and HIPE3 were prepared with less surfactant than HIPE1 and still stable. The resultant polyHIPE2 and polyHIPE3 were with larger pore sizes and higher elastic moduli and crush strengths than polyHIPE1. On the other hand, since the PUDA forms flexible parts and poly(St) forms rigid parts in a poly(PUDA-St)MIPEs, the mechanical properties of those macroporous polymers can therefore be tailored by adjusting the PUDA/St ratios. Generally, the samples reported in this chapter have crush strengths ranging from 1.4 MPa to 7 MPa, and thus can have potential applications as supports for membranes applied within this pressure range.

Chapter 7 Flexible polyHIPE films via UV polymerisation and their applications for pressure-sensitive devices

Abstract

Poly(urethane diacrylate-ethylhexyl acrylate)H(M)IPE films are prepared via UV polymerising emulsion templates. The mechanical properties of the porous films are measured via tensile tests. The porous films have strains up to 30%. The poly-Pickering-emulsions have much higher Young's moduli compared to the poly-surfactant-stabilised-emulsions, but much lower strains. The films have more or less viscoelasticity, which have decay constants ranged from 67s to 146 s, according to the relaxation test. The cyclic tensile test of the films revealed the changes of the Youngs' moduli in each cycles. All the films reached steady Young's moduli within 2 cycles under 5% strain, and they also showed good repetitions on loading and unloading curves. The results suggest corresponding stress and strain within 5% strain, indicating their pressure-sensor applications in this strain range.

7.1 Introduction

Porous polymer films have been widely used in many electric devices, as they possess low dielectric constant as well as other notable properties such as low density, high flexibility, low elastic stiffness and high impact resistance compared to metal or ceramic films²⁰⁴. One application of porous polymer films is the diaphragm that separates two electrodes in a battery to prevent the short circuit between the electrodes²⁰⁵. The diaphragm needs to be permeable for electrolyte thus allowing the battery to charge and discharge. Additionally, a porous polymer diaphragm has chemical resistance to the electrolyte and mechanical strength to withstand physical variation of the battery. The films for this application are usually ion-exchange membranes or multilayer porous films with preferable pore size of 0.2 to 3 μm and porosity of 70% to 85%. Osmosis sensor has been designed by Chakraborty²⁰⁶. A porous polymer diaphragm is sealed in the middle of a chamber, separating two ionic solutions. The concentrations differential drives the flow of the solution across the porous film, which changes the dielectric constant of the film, thus generating electric signal representing the osmotic pressure.

Piezoelectric polymers refer to those with electromechanical response: the polymers can generate electric signals upon the application of mechanical deformation and vice versa²⁰⁴. Porous piezoelectric polymers have been significantly studied recently. The macroporous polymers, such as porous polypropylene²⁰⁷ and polyvinylidene fluoride²⁰⁸, can have electromechanical performance after space charging. Compare to non-porous ones, porous piezoelectric polymers have higher charging density and stability due to their larger inner surface area. Moreover the macroporous polymer films usually have low Young's moduli, which means that the electric induced strains are relatively large, resulting in enhanced electro-strain sensitivity²⁰⁹. Wegener et al. reported the Young's moduli of porous polypropylene films with porosities within range of 27% to 57%, which possess Young's moduli of from 14.3 MPa to 1.3 MPa²¹⁰. Paajanen et al. reported a porous polypropylene film, which was employed in loudspeaker, with a Young's modulus of about 2 MPa and a breaking strain of 17%²¹¹. The porous piezoelectric polymers are widely used as electrets in microphone²¹², loudspeaker²¹¹, and the other applications as pressure sensors in keyboard and floor sensor have already been on market²¹¹.

Emulsion templating provides an approach for preparing macroporous polymers, which has been described by researchers from Unilever²¹³. Usually, high internal phase emulsions (HIPEs) with more than 74 vol% internal phase (this value refers to the volume fraction of close packed uniform sized spheres¹³⁴) are employed in the approach. Being polymerised, the continuous phase of HIPEs are converted into solid, while after the removal of the internal phase, the droplets in HIPEs become spherical pores. The resultant polymerised high internal phase emulsions, or polyHIPEs, replicate the structure of the HIPEs at the gel point and, therefore, possess a well-defined porosity and pore diameter. The commonly prepared and studied polyHIPEs are based on styrene (St) and divinylbenzene (DVB), which result in brittle and chalky polyHIPEs⁷⁰. There have been many attempts to improve the mechanical properties, including using new monomers like ethylhexyl acrylate⁸³, butylacrylate⁸⁶ and polyethylene glycol dimethacrylate⁷⁰, reducing porosity (making polymerised medium internal phase emulsions, termed polyMIPEs)^{2,115}, making organic-inorganic networks within polyHIPEs^{104,107,122}, etc.

PolyHIPE films have been prepared using a variety of approaches and, because of the porosity, interconnectivity and permeability, polyHIPE films can have many applications^{2,4,115}. Bokhari et al.³

sectioned polyHIPE monoliths into films and used them as scaffolds for cell cultural. Ruckenstein et al.^{2,115} produced polyHIPE membranes for pervaporation separation purposes. Additionally, they also prepared butylacrylate-St-DVB based polyHIPE membranes to reduce the brittleness of original St-DVB based polyHIPE membranes⁸⁶. Pulko et al. attempted to use polyHIPE membranes for protein purification applications⁵. In their work, Glycol methacrylate-EHA-ethyl glycol dimethaylacrylate based polyHIPE films were prepared and the film could be rolled up and reversible after unfold.

The aim of this chapter is to produce macroporous polymer films via emulsion templating, which can be potentially used as the spring element in pressure sensors. The challenge is to prepare very flexible macroporous films, so the films can be deformed to a large degree to generate electric signals. As known from Chapter 6, polyurethane diacrylate (PUDA) provide flexibility to the polyHIPEs. Here macroporous films are prepared based on PUDA and ethylhexyl acrylate. The macroporous films are desired to possess porosities and mechanical properties comparable to the porous pressure sensor films reviewed above. Therefore, the porous structures and mechanical properties of films are determined. Moreover, as for long term pressure sensor applications, the responses of these films to constant loading and cyclic loading are also investigated.

7.2 Experiment

7.2.1 Materials

Ethylhexyl acrylate (EHA, purchased from Sigma-Aldrich, Gillingham, UK) and polyurethane diacrylate (Ebecryl 8402 and Ebecryl 284, kindly supplied by Cytec, Belgium) were used as monomers. Ebecryl 8402 (PUDA 8402) is a polyurethane diacrylate with a molecular weight of 1000 Da. Ebecryl 284 (PUDA 284) is a mixture of 88 wt% polyurethane diacrylate with a molecular weight of 1200 and 12 wt% of Hexanediol diacrylate (HDDA) as a reactive diluent. Hypermer B246, supplied by Croda (East Yorkshire, UK), was used as surfactant. Darocur 1173, purchased from Ciba (Basel, Switzerland) was used as UV initiator. $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was purchased from Sigma-Aldrich (Gillingham, UK). Silica particles with an average diameter of 20 nm were kindly provided by Ortwin Rave Produkte and Dienstleistungen (Koblenz, Germany). Oleic acid, chloroform and methanol were purchased from Sigma-Aldrich (Gillingham, UK). All the chemicals were used as received.

7.2.2 Modification of silica particles

Silica particles were modified as described in Chapter 3(P44).

7.2.3 Preparation of emulsion templates

A reaction vessel equipped with a glass paddle rod connected to an overhead stirrer was used for preparation of emulsion templates. The internal phase was prepared by dissolving 10g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in water. A surfactant-stabilised-emulsion template was prepared as follows: monomers, surfactant and initiator were mixed in the reaction vessel as the continuous phase. The internal phase was slowly dropped into the continuous phase whilst stirring at a speed of 400 rpm. Subsequent to the adding of the internal phase, stirring was continued for 2.5 min to produce homogeneous emulsions.

In order to prepare Pickering emulsion templates, the modified silica particles were dispersed within the monomers by homogenising at a stirring speed of 20000 rpm for 30 min in an ice bath. The mixture was then transferred to the reaction vessel with the addition of the initiator. The internal phase was added dropwise into the continuous phase whilst stirring at a speed of 500 rpm. After adding the internal phase, the emulsion was stirred for another 3 min at 500 rpm. The detailed recipes of the emulsion templates are summarised in Table 7.1.

Masking tapes were stuck on a glass plate and stacked up to make two parallel blocks with a distance of 50 mm and thicknesses of 380 μm . The emulsion templates were cast on the glass plate with a blade. Afterwards the emulsion template layer was immersed in an aqueous bath with 10g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and polymerised using a UV lamp (UVP-100, UVP, Cambridge, UK). The samples were washed in water for 24 h and subsequently in ethanol for 24 h. Afterwards the samples were dried in air at 70 °C. The emulsion templates were labelled as M1 to H9. The polymerised samples were labelled PM1 to PH9 (M1 becoming PM1, etc, with M and H referring to MIPEs and HIPEs and P referring to polymerised).

Table 7.1 Recipes for polyH(M)IPEs prepared via copolymerising EHA and PUDA.

	Continuous phase						Internal phase	Stirring
	8402	284	EHA	B246	Silica	Darocur 1173	volume ratio	speed
	(vol%) ^a	(vol%)	(vol%)	(vol%)	(w/v%) ^b	(mol%) ^c	(vol%) ^d	(rpm) ^e
M1	47.05		47.05	5.9		2	60	2000
M2	47.05		47.05	5.9		2	60	1000
M3	48.48		48.48	3.04		2	60	1000
M4		47.05	47.05	5.9		2	60	2000
M5		48.48	48.48	3.04		2	60	2000
M6		48.48	48.48	3.04		2	60	1000
M7	50		50		7	2	60	500
H8	35.29		58.81	5.9		2	75	2000
H9	37.5		62.5		10	2	75	500

a. The monomers and surfactant volume ratios are with respect to the volume of continuous phase.

b. Silica weight over volume ratio is with respect to the volume of the continuous phase.

c. The initiator molar ratio is with respect to the molar number of double bonds in the monomers.

d. Internal phase volume ratio is with respect to the volume of emulsion.

e. Stirring speed refers to that after the adding the internal phase.

7.2.4 Characterisation

The loading of the oleic acid on the silica particles was measured using TGA, which was same as described in Chapter 3 (P49). The morphology, densities and porosities of the polyH(M)IPEs were determined via the same methods as described in Chapter 3 (P49).

a. Tensile tests

Tensile tests were carried out using a Lloyds EZ50 (Lloyds Instrument, Fareham, UK) with a 20N load cell following the standard BS ISO 527²¹⁴. The films were cut into specimens with a width of 15mm and a length greater than 150 mm. The thickness of the films was about 0.35mm. The samples were marked towards their centre, across the width, with two lines separated by 10 mm. The samples were

clamped with two grips, and the distance between the two grips was initially 100mm. The crosshead displacement speed was 5mm/min. Valid fractures were at least 10 mm away from the grips²¹⁴. All the tests were recorded using a video camera. Afterward, the videos were analysed using the software Tracker (a project of Open Source Physics, OSP), the change in distance between the two markers as a function of time was obtained. From the curve the strains of the samples were calculated. The stresses of the samples were exported from the Lloyds machine and stress-strain curves were plotted. The breaking strain and breaking stress were directly read from the curves. The Young's modulus was defined as the slope of the initial relatively linear region of the stress-strain curve. Here the strain region of 0%-5% from the stress-strain curve was employed for the linear fitting and the Young's modulus was calculated.

b. Relaxation tests

Tensile relaxation tests were carried out using the Lloyds machine equipped with a 20N load cell. The specimens were prepared in the same way as specimens for tensile tests. The samples were loaded at a speed of 5mm/min to achieve predetermined machine strain of 0.05 which were then held constant for 10 minutes whilst the change in the stress was recorded. The stress decay as a function of time was plotted.

c. Cyclic Loading Tests

In the cyclic loading tests samples were strained to 5% at a speed of 5 mm/min and then unload at the same speed back to 0% strain. The samples were loaded and unloaded for at least 10 cycles and the stress-strain curves recorded. For long term cyclic test, PM1 and PM7 were loaded and unloaded for 430 and 550 cycles with in strain range from 0% to 5%.

7.3 Results and discussion

In previous research on polyurethane based polyHIPEs¹²¹, CO₂ bubbles were generated in the resultant polyHIPEs as the synthesis of the polyurethane from polyols and diisocyanates, which eliminated the pore structure of the polyHIPEs from emulsion templating. Polyurethane diacrylate has a long backbone with encapped acrylate groups, which make the polyurethane easy to be crosslinked via free radical polymerisation. Both polyurethane diacrylate, namely PUDA 8402 and PUDA 284, are

very viscous. Hence EHA functions as a monomer as well as a diluent. Nonetheless, at an EHA: PUDA volume ratio of 1:1 only MIPEs could be made owing to the relatively high viscosity of the continuous phase (M1-M7). In order to prepare HIPEs (H8 and H9), the concentration of EHA needed to be increased to reduce the viscosity of the continuous phase.

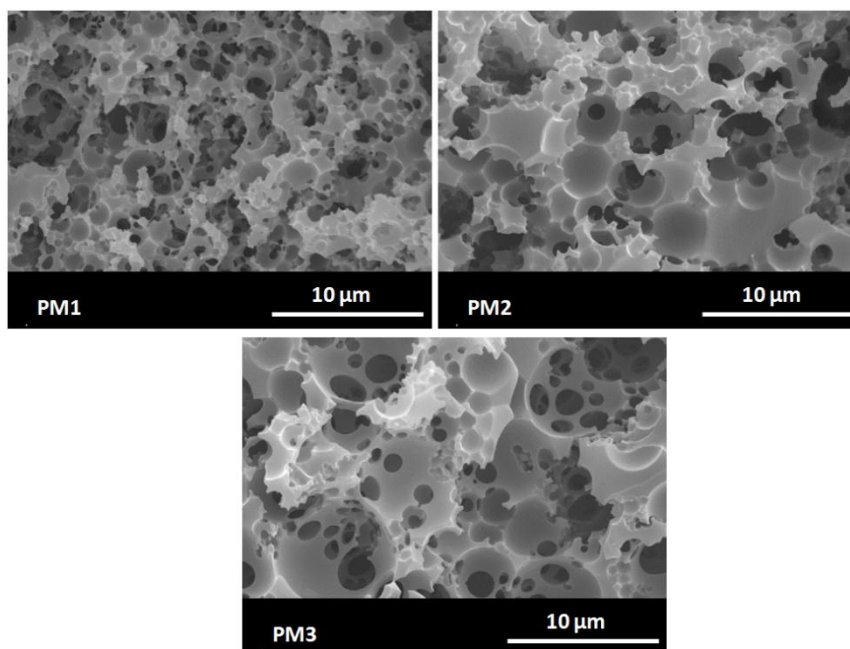


Fig 7.1 SEM images of cross-section structure of poly(PUDA 8402-EHA)MIPE films.

The polyH(M)IPE films have a thickness of about 350 μm . The first group of samples was based on EHA and 8402 (PM1-PM3). They had an identical monomer ratio and internal phase ratio, but the surfactant amounts and stirring speeds were varied to adjust the pore size. As expected, because the monomer composition and internal phase ratio of M1-M3 were identical, the matrix densities and the foam densities of PM1-PM3 are identical (Table 7.2). The porosities of PM1-PM3 are about 58%. The measured porosities are lower than the internal phase ratios, which can be caused by the negative systematic error on the samples' volumes resulting from the calliper measurement. However, using other pycnometry method to measure the foam density of the films, such as Geopyc 1360 (Micrometrics Ltd., Limited, Dunstable, UK) which is usually used in our group, would deform the films significantly, resulting in even larger systematic error. Thus here calliper was used to measure the dimensions and calculate the volumes and foam densities of the films. The SEM image of PM1 shows the typical pore structure of polyMIPEs (Fig 7.1): pores interconnected by pore throats. However, a non-homogenous pore structure with some small bulk polymer regions is observed in the SEM image.

In an emulsion, droplets do flocculate, especially in a medium internal phase emulsion, where the droplets are not closely packed, therefore resulting in local variations of porosity after polymerisation of the emulsions. PM2 was prepared from the emulsion template with the same surfactant concentration but using a lower stirring speed than M1, which resulted after polymerisation in larger pore size of about 3 μm (Table 7.2). PM3 was prepared with a reduced surfactant concentration and lower stirring speed, compared to PM1. Therefore, the pore size of PM3 increases even further to 4 μm (Table 7.2). Moreover, PM3 has more and larger pore throats than PM1 and PM2 (Table 7.2). This is due to the large droplets in M3, which allows large contact area between neighbouring droplets. For the above discussed reasons can local porosity variations also be found in the SEM images of PM2 and PM3.

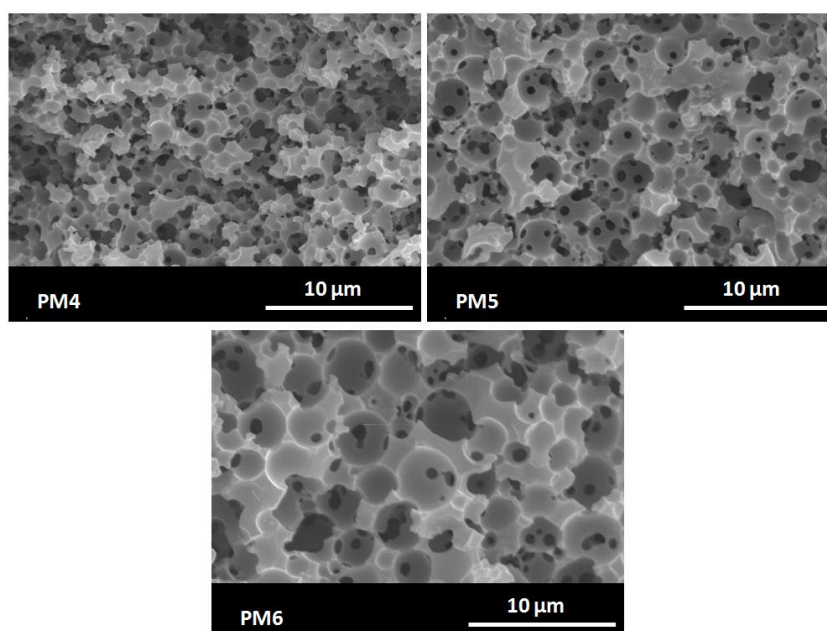


Fig 7.2 SEM images of cross-section structure of poly(PUDA 284-EHA)MIPE films.

PM4-PM6 are polyMIPEs based on PUDA 284 and EHA, and again the same internal phase ratio was used. Therefore, the matrix densities of PM4-PM6 are roughly 1.08 g/cm^3 , and the foam densities are approximately 0.46 g/cm^3 , resulting in porosities of 58% (Table 7.2). The SEM images of PM4-PM6 show the typical porous structure of polyMIPEs (Fig 7.2). The pore size of PM4 is 1.5 μm (Table 7.2). Due to the reduction of the surfactant concentration, the pore size of PM5 increases to 2.2 μm . The pore size of PM6 further increases to 2.9 μm due to the reduced stirring speed and surfactant amount, compared to PM4. Bulk polymer regions are rarely visible in the SEM images of PM4-PM6 (Fig 7.2).

This is due to the higher viscosity of the continuous phase as compared to M1-M3, which suppressed the movement of droplets, resulting in an even droplet and, subsequently, pore packing arrangement after polymerisation.

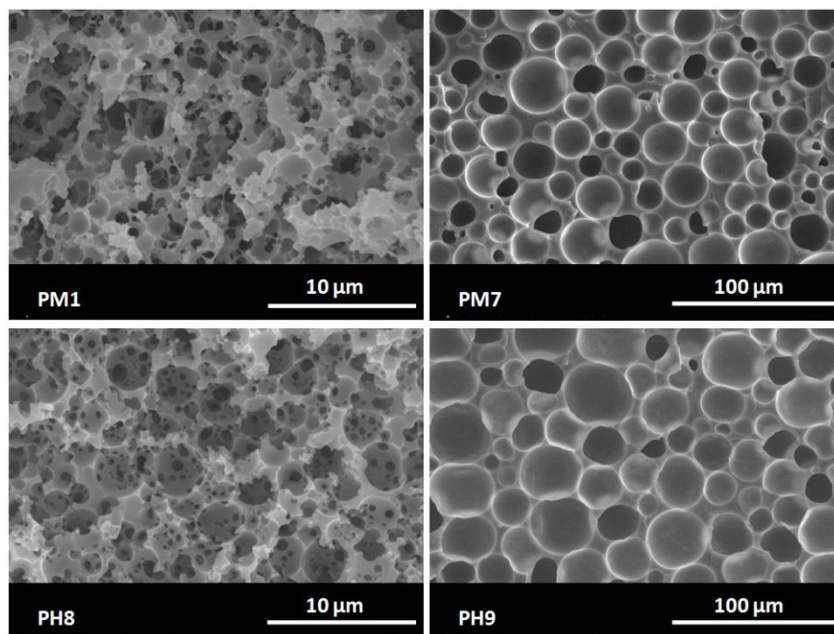


Fig 7.3 SEM images of cross-section structure of polyH(M)IPE films based on PUDA 8402-EHA .

PM7 was polymerised from a Pickering emulsion M7, which had the same monomer composition and internal phase ratio as M1. The matrix density of PM7 is slightly larger than that of PM1, due to the presence of silica particles. PM7 has a foam density of 0.49 g/cm^3 , resulting in a porosity of 57% (Table 7.2). PM7 has a typical closed cell poly-Pickering-MIPE structure (Fig 7.3) with much larger pores (18 μm , Table 7.2) than PM1. On the other hand, the pore size of PM7 is smaller than those poly-Pickering-emulsions reported before¹²⁶. The dramatically smaller average pore size was due to the viscosity of the continuous phase compared to the traditionally used St/DVB or St/PEGDMA continuous phase. The higher viscosity of M7 was caused by the presence of the high molecular weight crosslinker combined with the relatively high particles concentration. The highly viscous continuous phase firstly contributed to a more effective droplet break up during emulsification and secondly the high particle concentration combined with the highly viscous continuous phase counteracts limited coalescence. H8 and H9 are HIPEs based on EHA and PUDA 8402. The EHA:PUDA 8402 ratio was adjusted to 1.6/1 in order to reduce the viscosity of the continuous phase for preparing HIPEs. The resultant PH8 has a typical polyHIPE structure with an average pore size of 2.3 μm (Table

7.2). PH8 has a matrix density of 1.08 g/cm^3 and foam density of 0.32 g/cm^3 , resulting in a porosity of about 70%. PH9, which is a polymerised Pickering emulsion, has a typical closed cell structure (Fig 7.3) with an average pore size of $35\mu\text{m}$ (Table 7.2). PH9 possess a higher matrix density than PH8, due to the presence of the silica particles in the samples.

Table 7.2 Densities, porosities, pore sizes and pore throat sizes of poly(EHA-PUDA)H(M)IPE films

	Matrix density (g/cm^3)	Foam density (g/cm^3)	Porosity (%)	Pore size (μm)	Pore throat size (μm)
PM1	1.10 ± 0.01	0.46 ± 0.07	58 ± 9	2.5 ± 0.9	0.4 ± 0.2
PM2	1.083 ± 0.008	0.46 ± 0.02	57 ± 3	3 ± 1	0.5 ± 0.2
PM3	1.081 ± 0.009	0.47 ± 0.04	57 ± 3	4 ± 1	1.0 ± 0.4
PM4	1.098 ± 0.008	0.45 ± 0.04	59 ± 5	1.5 ± 0.4	0.4 ± 0.1
PM5	1.086 ± 0.009	0.46 ± 0.03	57 ± 3	2.2 ± 0.6	0.4 ± 0.1
PM6	1.08 ± 0.01	0.45 ± 0.03	59 ± 4	2.9 ± 0.8	0.6 ± 0.2
PM7	1.140 ± 0.001	0.49 ± 0.03	57 ± 3	18 ± 7	0
PH8	1.08 ± 0.01	0.32 ± 0.05	70 ± 11	2.3 ± 0.7	0.6 ± 0.2
PH9	1.14 ± 0.01	0.33 ± 0.04	70 ± 9	35 ± 11	0



Fig 7.4 Flexible porous films rolled up to a cylinder with a diameter less than 10 mm.

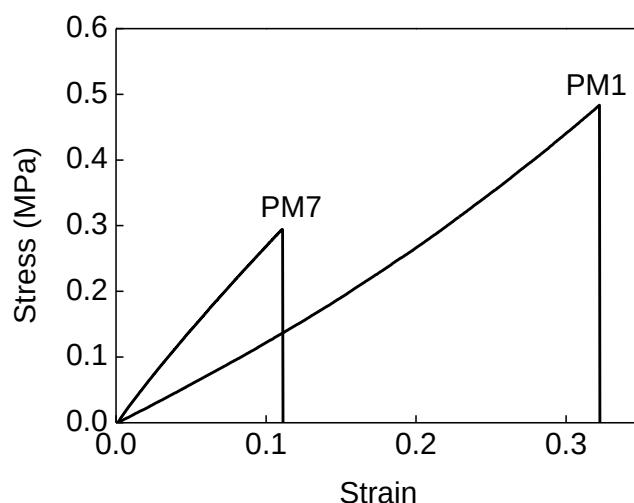


Fig 7.5 Representative stress-strain curves of poly(PUDA-EHA)H(M)IPE films (the rest of the curves are in Appendix II).

All polyH(M)IPE films produced by polymerising surfactant stabilised emulsion templates are very flexible; these films can be easily rolled up and unrolled without any visible damage (Fig 7.4). However, the poly-Pickering-H(M)IPEs, PM7 and PH9, are much stiffer, and can only be bent but not rolled up. The mechanical properties of the polyH(M)IPE films were measured by tensile tests carried out at a crosshead speed of 5mm/min. The representative stress-strain curves of polyH(M)IPE films are shown in Fig 7.5. The 0% to 5% strain regions on the curves were fitted and the correlation coefficient (R^2) of more than 95% were achieved. Thus those regions are defined as stress-strain linear, and Young's moduli for the samples were calculated from the fitting curves of those regions. The representative stress-strain curve for the polyH(M)IPE films produced from surfactant stabilised emulsions, bends slightly to the strain axis (Fig 7.5, PM1), indicating the viscoelastic behaviour of the film²¹⁴. PM1 and PM2 have identical breaking strains within error, which are approximately 30% (Table 7.3). Nevertheless, the Young's modulus and breaking strength of PM1 are relatively high (Table 7.3). M1 and M2 were prepared with same amount of surfactant and internal phase ratio. However, the larger droplet size in M2 indicates a low interfacial area as compared to M1, thus M2 needed less surfactant adsorbed at the interface. The adsorbed surfactant was subsequently removed after the polymerisation and the washing of the sample. Thus one can see the residual surfactant amount in PM2 is higher than that in PM1. The residual surfactant in PM2 cannot provide any strength to the

samples, leading to lower breaking stress and Young's modulus than PM1. The strain to failure for PM3 is lower at 19%. This can be explained by the large pore throats in PM3, which results in the higher openness of PM3. This very open porous structure of PM3 cannot maintain large deformations and ruptures at relatively low strain. Nevertheless, the breaking stress of PM3 is very close to that of PM2 even at a much lower breaking strain. Moreover, the Young's modulus of PM3 is higher than that of PM2. Since only half the amount of surfactant was used to prepare M3 as compared to M2, the residual surfactant in PM3 is much less, leading to higher Young's modulus than PM2.

PM4-PM6 have similar breaking strains (Table 7.3). Despite using different amounts of surfactant and stirring speeds, there is hardly any difference in the pore throat size for PM4-PM6, resulting in a similar openness of their porous structure. Nevertheless, PM5 possesses a higher breaking strength than PM4. Since PM5 was prepared from emulsions with a lower surfactant amount than PM4, the residual surfactant in PM5 is less than in PM4, thus resulting in higher breaking strength. PM5 has higher breaking strength than PM6. This is, as discussed above, due to the residual surfactant in the samples which may soften the samples. PM5, with smaller pore size, can have more surfactant adsorbed at the pore surface than PM6 after the polymerisation. The surfactant at the pore surface being washed away from the sample, the residual surfactant in PM5 is thus less than that in PM6, resulting in a higher breaking strength. On the other hand, despite the different residual surfactant amount, the Young's moduli of PM4-PM6 are identical within error. This can be explained by the relatively high crosslinking degrees in PM4-PM6 as compared to PM1-PM3: EHA/PUDA 284 ratio in M4-M6 was 1:0.32, while EHA/PUDA 8402 ratio in M1-M3 was 1:0.24. The relatively higher crosslinking degrees in PM4-PM6 make the impact of the residual surfactant on the Young's moduli less significant.

PM7 was made from a Pickering emulsion. A representative stress-strain curve is shown in Fig 7.3, where it can be seen the strain increases more rapidly than stress. PM7 film had a lower breaking strain and, thus, breaking strength as compared to PM1. The closed-cell structure of PM7 makes the sample difficult to deform. Therefore during the tensile test the pores walls ruptured rather than deformed, resulting in a low strain to failure for PM7. Additionally, the presence of silica particles can also make the film rupture rapidly¹²¹. Nevertheless, the Young's modulus of PM7 is much higher than

that of PM1. This suggests the silica particles reinforce the polyMIPE films^{115,122}. Moreover, the closed-cell structure may also provide stiffness of PM7 as compared to the open-cell structure of PM1. PH8 possesses a Young's modulus of 0.46 MPa and breaking strain of 33%. Based on the same materials as PH8 but with presence of silica particles, PH9 has a breaking strain of 14% (Table 7.3), compared to 33% of PH8. This is caused by the closed-cell structure of PH9. Nevertheless, due to the presence of the silica particles and the closed-cell structure, PH9 has a higher Young's modulus than PH8 (Table 7.3). Although with the presence of silica particles, PH9 has lower breaking strength than PH8 due to the rather low breaking strain.

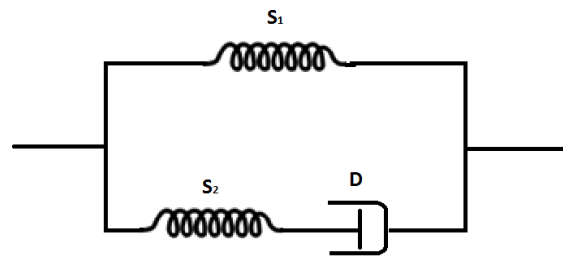
Table 7.3 Mechanical properties of PM1-PH9

	Breaking strain	Breaking Stress (MPa)	Young's modulus (MPa)
PM1	0.31±0.04	0.49±0.07	1.2±0.2
PM2	0.28±0.05	0.31±0.04	0.9±0.3
PM3	0.19±0.05	0.29±0.04	1.25±0.02
PM4	0.28±0.08	0.6±0.1	2.2±0.5
PM5	0.25±0.05	0.74±0.02	2.6±0.5
PM6	0.21±0.03	0.65±0.07	2.8±0.4
PM7	0.11±0.03	0.29±0.01	3.1±0.5
PH8	0.33±0.08	0.19±0.06	0.46±0.02
PH9	0.14±0.02	0.11±0.01	0.9±0.1

Generally, the breaking strains of the samples varied from 11% to 33% depending on the recipe. This is very step-forward results, as to our best knowledge there have not been any reports on breaking strains of flexible polyH(M)IPE films under tensile tests. Additionally, the electric induced strains of porous piezoelectric polymers are usually less than 10%²¹⁵, depending on the applied voltage. Thus the films are applicable for piezoelectric devices as the breaking strains of our samples are higher than those typical electric induced strains.

The macroporous films are intended for long term and repeatable applications, thus the mechanical

behaviour of the films as a function of time were investigated. The relaxation behaviour of the porous films was tested via stretching the films to 5% strain and holding for 10 min, and the stress decay against time was recorded. The samples were tested at this specific strain as this is the linear region of stress and strain. When used as electro-strain sensors, the electrically induced strain within this region can be linearly related to stress, which makes the sensors also electro-stress responsive. Therefore it is necessary to study the stress relaxation over time of the films within this stress-strain linear region. Fig 7.7 shows representative relaxation curves for PM1, PM4 and PM7 under 5% strain. The strain curves were fitted using the Standard Linear Solid model (Fig 7.6):



$$\sigma(t) = \sigma_{\infty} + (\sigma_0 - \sigma_{\infty})e^{-\frac{t}{\tau}}$$

Fig 7.6 Scheme of Standard Linear Solid model and description of relaxation behaviour

The Standard Linear Solid model is a combination of the Maxwell model and a parallel spring, offering a realistic representation of the actual materials behaviour²¹⁶. The spring (S_1 , characterised by modulus E_1) represents the non-relaxable parts in the polymer films. The spring (S_2 , characterised by modulus E_2) in the Maxwell arm represents the stress caused by the elongation of the system, which will decay over time. The dashpot (D , characterised by viscosity η) in the Maxwell arm represents viscous components in the polymer, which enables the stress relaxation. It is known that the stresses in the dashpot and spring S_2 are identical, and the deformation of the Maxwell arm is the sum of the deformations of the dashpot and the spring S_2 . After the system is stretched and held (total deformation is a constant), the dashpot, which is under a stress, elongates. This leads to the decrease in the deformation of the spring S_2 , the stress on the spring S_2 thus decays, resulting in the total stress decay. Moreover, the decrease in the stress on the Maxwell arm reduces the elongation rate of the dashpot, slowing the entire relaxation process over time. Therefore the stress relaxation follows an exponential decay. Simultaneously, the spring S_1 does not relax since its deformation does

not change. Therefore, after infinite time, the stress on the Maxwell arm decays to zero, and the total stress of the system is $\sigma_{\infty} = \sigma_{s1} = E_1 \times \epsilon$. In the equation, σ_0 is the initial stress, and the decay constant $\tau = \eta/E_2$. Here σ_{∞} and τ were achieved from the best fitting of the experimental data using the model. One can see from the equation that the residual stress is $\Delta\sigma(t) = \sigma(t) - \sigma_{\infty}$. In the beginning of the relaxation ($t=0$), the initial residual stress is $\Delta\sigma_0 = \sigma_0 - \sigma_{\infty}$, and decreases as a function of time. The decay constant τ represents the time needed for the residual stress $\Delta\sigma(t)$ to reduce to $1/e$ times of its initial value, namely, $\Delta\sigma(\tau) = (1/e) \cdot \Delta\sigma_0$, thus τ can represent the relaxation rate of the materials. Table 7.4 lists the $\Delta\sigma_0$ and τ of all the samples. The $\Delta\sigma_0$ of PM1-PM3 are about 1×10^{-3} to 2×10^{-3} MPa and the mean lifetimes τ are in the range of 110-160s. The initial residual stress $\Delta\sigma_0$ of PM1-PM3 are less than 3% to their initial stresses σ_0 , meaning that the stress decays are insignificant. However, PM4-PM6 have maximum decay stresses of about 10×10^{-3} MPa and mean lifetime of about 70-80s (Table 7.4). The different relaxation behaviour between the two groups of samples can be explained by the different crosslinking degrees. The PUDA 284 in M4-M6 provided higher crosslinking degrees in PM4-PM6 after polymerisation, compared to PM1-PM3. The higher crosslinking degrees in PM4-PM6 made the polymer chains being less mobile or deformable as compared to PM1-PM3. Therefore, during the elongation of the samples, the stresses induced by the deformation were higher in PM4-PM6, giving them higher residual stresses ($\Delta\sigma_0$) to decay during the relaxation than PM1-PM3. Moreover, the flexibility of PM1-PM3 indicates more mobile components in the polymer networks than PM4-PM6. According to the physical meaning of the mean lifetime $\tau = \eta/E_2$, it is expected that the τ for PM1-PM3 are longer than those of PM4-PM6. PM7 and PH9 have decay constants of 100s, which are slightly lower than the corresponding samples (PM1 and PH8). This is caused by the inextensibility of the particles. Since the particles can hardly be deformed, during the tensile test, the matrix in particle-incorporated-samples (PM7 and PH9) underwent larger strain than the matrix without particles (PM1 and PH8)²¹⁷⁻²¹⁸. Thus PM7 and PH9 had residual stresses higher than PM1 and PH8. As a result, they had higher relaxation rates than the samples without particles²¹⁸⁻²¹⁹. Despite the rapid relaxation behaviour of PM7 and PH9, their maximum decayed stresses are 8% and 13% to their initial stress (σ_0), respectively, which make their decayed stress a significant proportion to their initial stress. In real applications, once PM7 and PH9 films are used as electric-stress responsive sensors over time, the electric induced stress need to be calibrated.

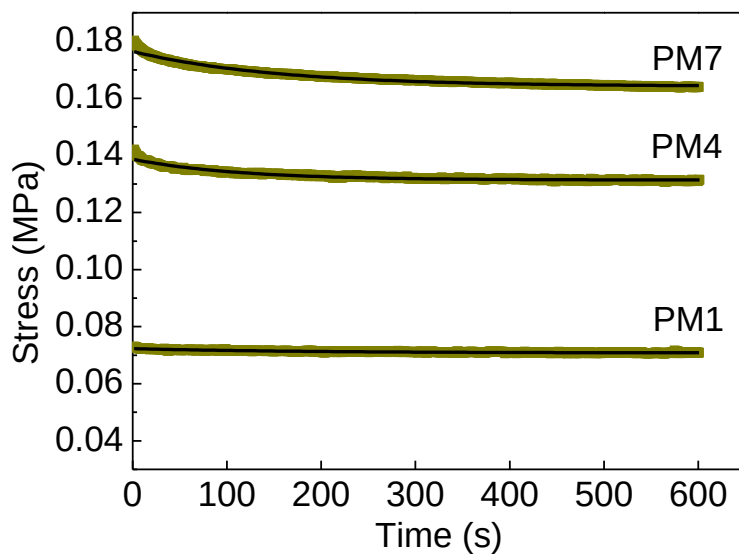


Fig 7.7 Representative relaxation curves of porous films via emulsion templating (the rest curves are in Appendix III).

Table 7.4 Decay constants and initial residual stress of PM1-PH9

	Initial Residual Stress, $\Delta\sigma_0$ ($\times 10^{-3}$, MPa)	Mean Life Time, τ (s)
PM1	2.3 $\pm$ 0.5	110 $\pm$ 30
PM2	1.3 $\pm$ 0.3	160 $\pm$ 70
PM3	1.1 $\pm$ 0.3	140 $\pm$ 70
PM4	10.2 $\pm$ 0.6	70 $\pm$ 10
PM5	10.4 $\pm$ 0.4	70 $\pm$ 10
PM6	11.2 $\pm$ 0.5	80 $\pm$ 10
PM7	15 $\pm$ 1	100 $\pm$ 3
PH8	1.2 $\pm$ 0.3	110 $\pm$ 20
PH9	7.6 $\pm$ 0.6	100 $\pm$ 4

Cyclic loading tests were carried out by loading and unloading the samples in the elastic region several times, in order to investigate the stress-strain curves under loading and unloading. These tests were also used to determine the number of cycles for the porous polymer films to reach a steady

stress-strain loop. PM1-PM3 and PH8 have a small difference between loading curve and unloading curve at a strain of about 5% (Fig 7.8, PM1), suggesting that the deformation of the samples is reversible within this strain. Moreover, the stress-strain curves of PM1-PM3 and PH8 follow the same loop as the first cycle. This is preferable for electric-strain or electric-stress response applications as the deformation and recovery of the samples upon electric charging and discharging will follow identical stress-strain curves. PM4-PM7 and PH9 have a more significant difference between the loading and unloading curves within the first cycle (Fig 7.8, PM7), which reveals the viscoelastic behaviour of the materials within the strain region²²⁰. The second loading curve is lower than the first, which suggests stress softening of the material. Nevertheless the stress-strain curves of PM4-PM7 and PH9 start to follow an identical loop from the second cycle, and the difference between the loading and unloading curves becomes less significant. Therefore the materials are also suitable for electromechanical sensitive applications where a preconditioning is required.

The long term mechanical performance of PM1 and PM7 were also investigated via cyclic tests. The samples were loaded and unloaded for 430 cycles and 550 cycles, respectively, in order to check the durability. The samples did not break during testing, and the stress-strain curves of PM1 and PM7 follow identical loops for 430 or 550 cycles, respectively. The samples were chosen as they have the same monomer compositions and internal phase ratio, the only difference is the method of stabilisation of the emulsion templates from which the samples were made. Moreover, PM1 has a relatively large breaking strain among the samples, while PM7 has the highest Young's modulus but lowest breaking strain. This suggests that the mechanical properties of the other samples are roughly within the range between PM1 and PM7. Although the intermediate samples have not been tested, the durability of the other samples can be expected as similar to PM1 and PM7.

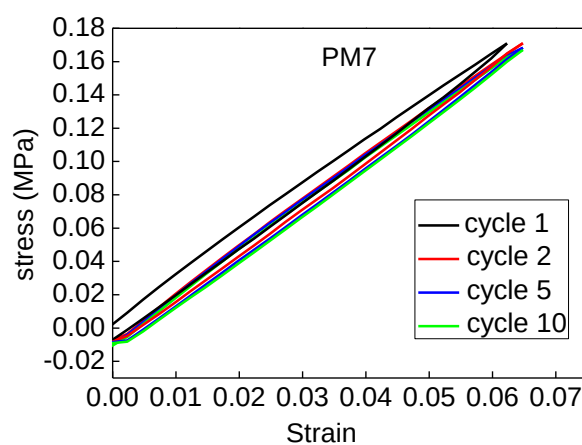
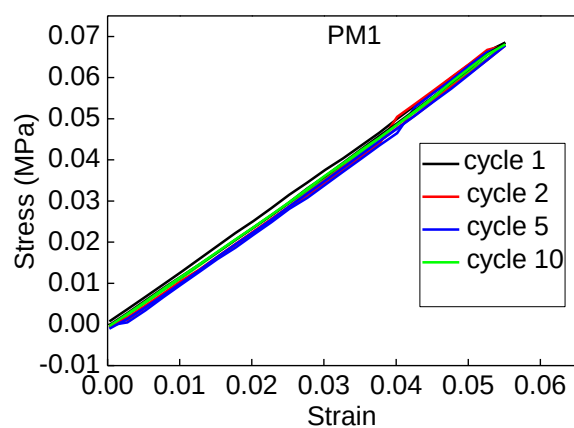
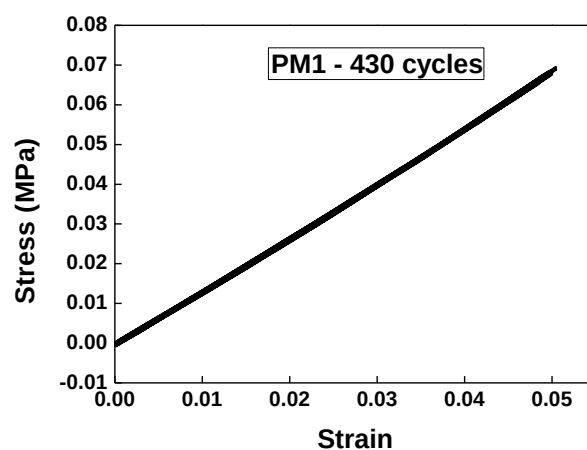


Fig 7.8 Representative cycle curves of porous films via emulsion templating (the rest of the curves are in Appendix IV).



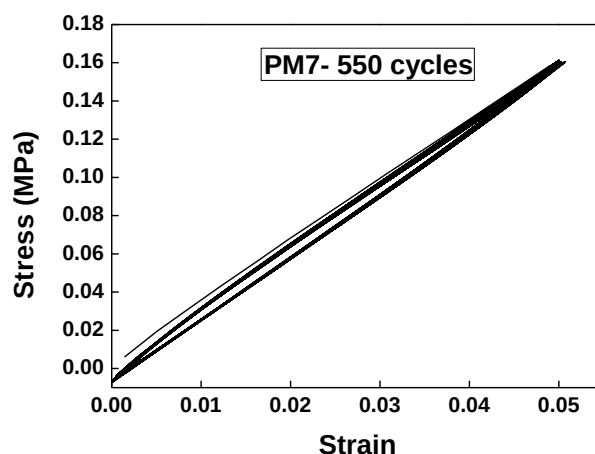


Fig 7.9 Long-term cycle tests of PM1 and PM7.

7.4 Conclusions

Rubbery macroporous films based on polyurethane-ethylhexyl acrylate were prepared via emulsion templating. The porous films demonstrate high flexibility, which can be stretched up to 30% strain. The films based on PUDA 284 had higher Young's moduli than those based on PUDA 8402 due to the higher crosslinking degrees. The Poly-Pickering-H(M)IPEs had much higher Young's moduli than the corresponding poly-surfactant-stabilised-H(M)IPEs, due to the reinforcement of the particles and their closed-cell structures. However, those samples showed much low breaking strains. The relaxation behaviour of the films depends on the crosslinking degrees of the films and presence of silica particles: the films with high crosslinking degrees or with presence of silica particles had large stress decay and rapid relaxation. The cyclic test suggests the deformation of the films is reversible and the films can be for long-term use within 5% strain. As compared to some porous piezoelectric polypropylene films, the porous films possess higher porosity but comparable mechanical properties. Thus In future work, the piezoelectric performance of the films will be tested and the films are intended to be used as electromechanical sensors.

Chapter 8 Conclusions and recommendations for future work

8.1 Conclusions

Macroporous polymers via emulsion templating have been studied for more than 40 years, however, such macroporous polymer films have not been widely studied. Therefore this PhD project focus on the development of macroporous polymer films via emulsion templating. Three aims were set and the sub-sections of the project were carried out based on the aims. In this final chapter conclusive remarks regarding to this project are presented, including recommendation for future work.

Firstly, macroporous polymer films were successfully prepared via rolling-pin printing and screen printing. The challenge to polymerise thin printed emulsion layers was solved by UV polymerising the layers in an aqueous bath. The films from both printing routes did not have damage on their porous structures. Printing emulsion templates on poly(H)MIPE substrates were explored. In that case, the substrates need to be wet while printing the second emulsion templates, in order to obtain double layer films with two distinguished pore structures. Moreover, multilayer films were prepared via alternatively printing surfactant emulsions and Pickering emulsions, suggesting the possibility to use printing to produce 3D objects with complex structures.

The second aim is to prepare and characterise functionalised polyHIPE membranes for ultrafiltration applications. To start this section, functionalised polyHIPEs were prepared using emulsion template with monomers in both phases. Poly(MAA) filled poly(St-DVB)HIPEs and poly(DMAEMA) filled poly(St-DVB)HIPEs were synthesised and characterised. The SEM images suggested the hydrogels were covering the wall of polyHIPEs scaffolds. Depending on the copolymerisation of the monomers in the continuous phase and the internal phase, the hydrogels can either cover the pore throats or not. The presence of the hydrogels affected many properties of the polyHIPEs. The dry hydrogels can reinforce the polyHIPE scaffolds, increasing their elastic moduli and crush strengths, while the wet hydrogels cannot. The hydrogels provide hydrophilic surface to the polyHIPEs, enabling them absorb water. The water uptakes decreased with the increase in the crosslinking degrees of the hydrogels. A following

work was carried out on preparing hydrogel filled polyHIPEs membranes. Poly(MAA) filled poly(EHA-St-DVB)HIPEs were prepared and subsequently sliced into membranes. Here EHA was copolymerised with St and DVB in the continuous phase to make the monoliths sliceable. Poly(MAA) filled poly(EHA-St-DVB)HIPE membranes showed pH-dependent performance. The water flux decreased as the pH values increased from 2 to 10, due to the deprotonation of poly(MAA). As the pH values increased further to 13, the charged poly(MAA) formed sodium poly(MAA) and the hydrogels collapsed, resulting in the increase in the water flux. The membranes showed the highest rejection to PEG at pH10. The membranes with 1% crosslinker in hydrogels showed a highest rejection of 58% to 100K PEG. The membranes with 2% crosslinker in hydrogels had a cut-off of 50K PEG at pH 10, which suggests their ultrafiltration applications.

Briefly, the third aim is to make very flexible polyH(M)IPE films. This work started with the preparation and characterisation of poly(PUDA-St)H(M)IPEs. Due to the presence of PUDA, the polyHIPEs are less brittle than typical poly(St-DVB)HIPEs, and, as compared to poly(PEGDMA-St)HIPEs, much tougher. This suggests the possibility to use PUDA as a monomer to make flexible polyH(M)IPE films. Therefore, following this work, PUDA-EHA based polyH(M)IPE films were prepared. The emulsions were firstly casted on a glass plates and then UV polymerised. The poly-surfactant-stabilised-emulsions were very flexible that can be rolled up without visual damage. The films had breaking strains ranging from 11% to 30% and Young's moduli ranging from 0.4 MPa to 3 MPa. The samples with higher crosslinking degrees had higher Young's moduli. The poly-Pickering-emulsions had much higher Young's moduli than the corresponding poly-surfactant-stabilised-emulsions, but much lower breaking strains. The relaxation test revealed the viscoelastic behaviours of the samples over time. The samples with higher crosslinking degrees or with the presence of silica particles showed larger stress relaxation and fast relaxation. The cyclic tests showed the good mechanical stability of the samples within a 5% strain range, and also suggest their capability for long term and repeatable applications.

8.2 Recommendations for future work

The work discussed in this thesis opens new approaches to the engineering of polyHIPEs. Further developments of this research work should focus on the following areas:

PolyHIPE supported membranes: One achievement of this project is the success in making poly(MAA) filled polyHIPE membranes: the polyHIPE scaffolds provided mechanical strengths and the supported hydrogel membranes demonstrated the capability for ultrafiltration. However, the morphology of the crosslinked poly(MAA) network is still underexplored. It is recommended to study the morphology of the network, such as the mesh size and distribution, in the future work. Based on that the network morphology can be optimised by controlling the polymerisation of MAA (e.g. steric polymerisation), which can possibly enhance the membrane behaviour. Moreover, the follow on work can involve making polyHIPE scaffolds filled with different hydrogels for a variety of applications. For example, poly(DMAEMA) filled polyHIPEs can be a good candidate for membranes which can have pH-dependent behaviour. Different from poly(MAA), poly(DMAEMA) swells highly at low pH values but lowly at high pH values. A polyHIPE filled with poly(DMAEMA) membrane thus can have an opposite pH-dependent performance to the poly(MAA) filled polyHIPE membranes reported in this thesis. In this project, poly(DMAEMA) filled polyHIPE membranes were not produced as such hydrogel filled polyHIPEs had wide pore size distribution with large pores of about 50µm to 100µm, which were considered as defects within macroporous structures. The large pores might be caused by the coalescence of droplets during the polymerisation. However, in Chapter 7, the efficiency of UV polymerising acrylate monomers within emulsion templates has been proven. Therefore, it is worth working on UV polymerising the emulsion templates with DMAEMA in the internal phase and acrylate monomers (e.g. EHA, PUDA and PEGDMA) in the continuous phase. The rapid polymerisation may suppress the formation of the large pores, so the poly(DMAEMA) filled polyHIPEs with small and narrow distributed pores may be processed into membranes without defects. Beside membrane applications, hydrogel filled polyHIPEs can be applicable depending the type of hydrogels. For example, PCL and peptide having excellent biocompatibility, PCL or peptide filled polyHIPEs can be prepared and applied for cell culture. Poly(NIPAM), the temperature-sensitive hydrogel, can be filled in polyHIPEs via the route explored in this thesis. The products can have temperature-dependent swelling behaviour, which are good candidate for temperature controlled filtration applications or release control.

Printing emulsion templates to make macroporous films with defined patterns has been demonstrated in this work. The advantage of this process is to create pattern and simultaneously

produce macroporous structure. The future work is to design a production line to make macroporous films or devices for a variety of applications by means of printing. Firstly, the emulsion templates used for printing need to be optimised in terms of droplet sizes. When emulsions pass through the printing devices (e.g. screens or nozzles), the droplets can be strongly sheared, leading to the destabilisation of the emulsion templates and subsequently the loss of the porous structure of the polymerised films. Thus, to reduce the possibility of the shearing of the droplets, it is advisable to make emulsion templates with very small droplets. Moreover, in order to print patterns with high resolution or films with low thickness, small droplets of the emulsion inks are required so the resultant films or device can have porous structures. Secondly, in order to build a production line for macroporous films, the printing machine is ideally to be fed with emulsion templates continuously. It is not ideal to feed the printing machines with batches of emulsions because of the potential quality difference. Therefore, it is worthy developing a continuous preparation protocol for emulsion templates to provide the printing process a supply line. Finally, the downstream products from the printing process are expected for these applications:

It was shown in Chapter 7 that the flexible macroporous films can be made via casting and UV polymerising emulsion template, and that such films have adequate mechanical properties and porosities for pressure sensor applications. The next step is to print out such macroporous films to make pressure sensors. For example, the emulsion template can be printed on an electrode used as substrate and polymerised subsequently. Afterwards, a layer of electrode can be coated on top of the macroporous films to make an electrode-macroporous films-electrode sandwich composite for tests or applications.

Multilayer printing of emulsion templates has been reported in this project. It seems to be a good method to assemble different macroporous structures into one device in a desired sequence for a variety of functions. One idea is to print a hybrid polyHIPE reactor, which has designed channels (open porous polyHIPEs), walls or scaffolds (poly-Pickering-emulsions), reaction chamber (polyHIPEs containing catalysts), switch and separation device (hydrogel filled polyHIPEs), so the reactor can fulfil a various functions including mixing, reacting, sensing and separating.

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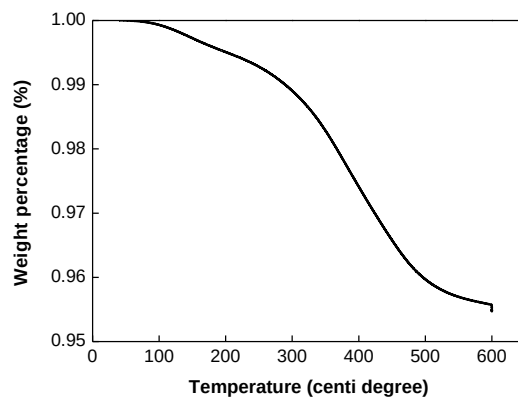
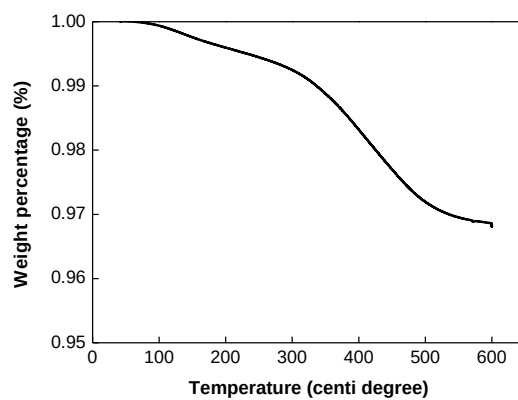
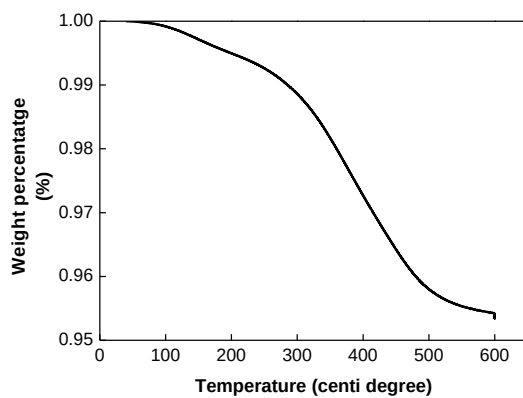
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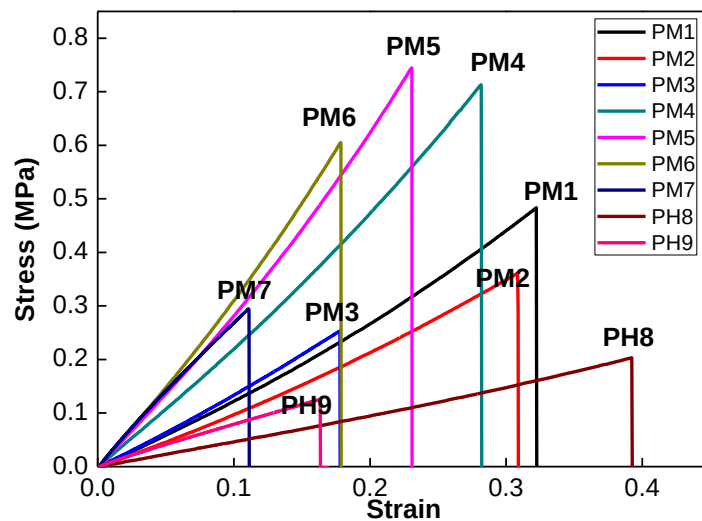
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Appendix

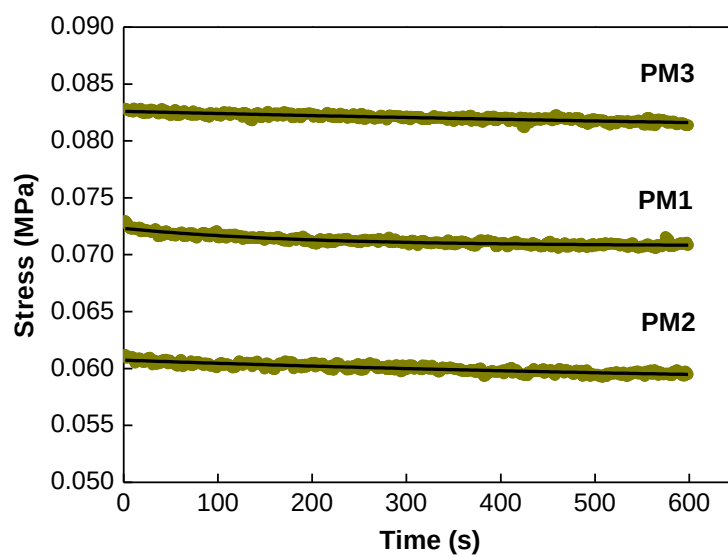
Appendix I Loading of oleic acid on silica particles, determined using TGA

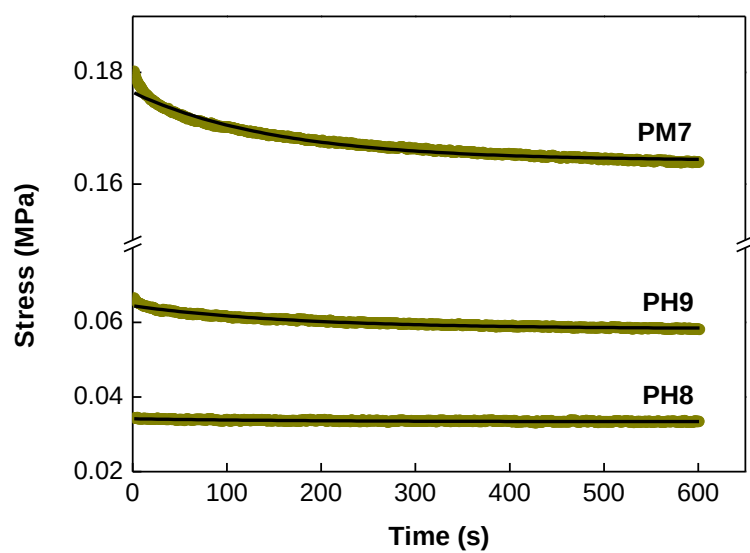
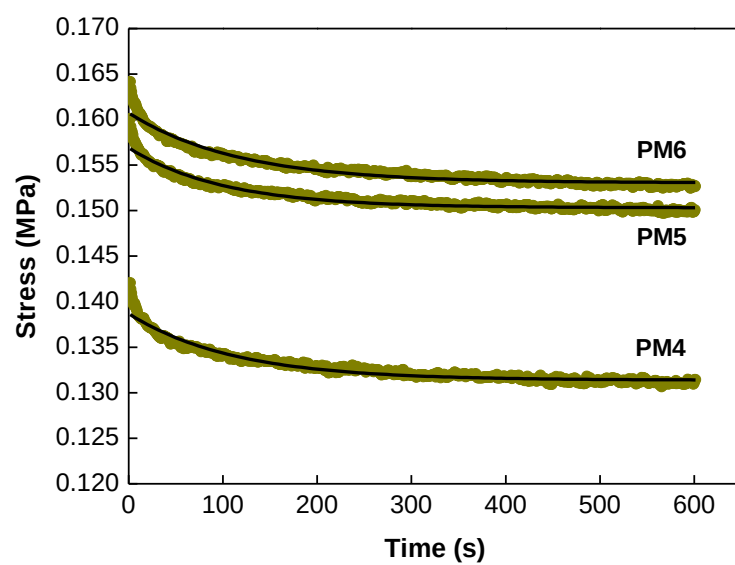


Appendix II Stress-strain of flexible polyH(M)IPE films, determined via tensile tests



Appendix III Stress relaxation curves of flexible polyH(M)IPE films





Appendix IV Stress-strain curves of flexible polyH(M)IPE films via cyclic test

