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**FOAM TEMPLATED MACROPOROUS POLYMERS
AND POLYMER COMPOSITES**

by

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Doctor of Philosophy

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Declaration of Originality

I declare that this report and the work presented in it are my own and has been generated by me as the result of my own research. Where I have consulted the published work of others, this is always clearly attributed; where I have quoted the work of others, the source is always given. This work was done wholly in candidature for a research degree at Imperial College London.

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Abstract

A blowing agent and stabiliser free method – foam templating method – has been introduced to manufacture bio-based epoxy foams. In order to widen the potential applications of the foam templated macroporous polymers, three major challenges have been successfully addressed in this thesis: (i) increase the porosity of the foam templated macroporous polymers above the state of the art; (ii) enhance the fracture resistance and impact toughness of the foam templated macroporous polymers; and (iii) improve the mechanical performance of the foam templated macroporous polymers.

The thesis starts from increasing the porosity of foam templated macroporous polymers. By using heat-induced bubble expansion, the porosity has been successfully increased from 71% to 85% without introducing any blowing agents or stabilisers. Correspondingly, the compressive modulus and strength decrease from 231 MPa and 5.9 MPa to 58 MPa and 1.9 MPa. The influence of the curing conditions on the mechanical properties and the deformation of the pores based on in-situ SEM micro-compression test are also discussed.

Hollow elastomeric microspheres are used to enhance the fracture resistance and impact toughness of the foam templated macroporous polymers. A 15% increase in critical stress intensity factor and 33% increase in Charpy impact strength are achieved, and the failure behaviour of the epoxy foams changes from catastrophic failure to progressive failure. More importantly, the compressive properties of the toughened epoxy foams are not compromised.

Short carbon fibres are used to improve the mechanical properties of the foam templated macroporous polymers. After short mixing time of 20 s, the carbon fibres are still mostly in tow form, and 58% and 10% increase in compressive modulus and strength along the fibre orientation direction are observed. By optimising the mixing process and prolonging the mixing time to 2 min, the single carbon fibres are successfully individualised from the original fibre tows, leading to more significant improvement – 165% and 53% increase in compressive modulus and strength. The highest compressive modulus and strength achieved are 845 MPa and 14.8 MPa.

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Contents

Declaration of Originality	2
Copyright Declaration	3
Abstract.....	4
Acknowledgements.....	6
Contents	7
List of Figures	10
List of Tables	16
List of Publications.....	18
Chapter 1 Introduction	20
1.1 Objective of this project	21
1.2 Structure of this thesis	22
Chapter 2 Literature review.....	23
2.1 Introduction	23
2.2 Manufacturing methods of epoxy foams	24
2.2.1 Blowing agent foaming method	25
2.2.2 Syntactic foaming method.....	27
2.2.3 Emulsion templating method	28
2.2.4 Foam templating method.....	32
2.3 Pore formation and pore structure	35
2.3.1 Pore formation in liquid foams	36
2.3.2 Pore evolution in liquid foams	38
2.3.3 Pore size and structure	40
2.4 Mechanical properties of macroporous polymers	43
2.4.1 Gibson and Ashby model	43

2.4.2	Influence of pore size and structure on mechanical properties	47
Chapter 3 Heat-induced bubble expansion as a route to increase the porosity of foam templated macroporous polymers..... 51		
3.1	Introduction	51
3.2	Experimental.....	51
3.2.1	Materials.....	52
3.2.2	Heat-induced bubble expansion of foam templated macroporous polymers	52
3.2.3	Preparation of bulk polymers cured at different conditions.....	53
3.2.4	Characterisation of the foam templated macroporous polymers.....	54
3.2.5	Characterisation of the resin-hardener mixture and the bulk polymers cured at different conditions	56
3.3	Results and discussion.....	59
3.3.1	Density, porosity, and morphology of the macroporous polymers	59
3.3.2	Compressive properties of the macroporous polymers	63
3.3.3	In-situ SEM micro-compression test of the macroporous polymers.....	68
3.3.4	Discussion: The effect of different curing conditions on the compressive properties of foam templated macroporous polymers.....	70
3.4	Concluding remarks.....	72
Chapter 4 Enhancing the fracture resistance and impact toughness of epoxy foams with hollow elastomeric microspheres 74		
4.1	Introduction	74
4.2	Experimental.....	76
4.2.1	Materials.....	76
4.2.2	Manufacturing of (hollow elastomeric microsphere filled) epoxy foams	76
4.2.3	Characterisation of the (hollow elastomeric microsphere filled) epoxy foams	77
4.3	Results and discussion.....	81

4.3.1	Morphology of the (hollow elastomeric microsphere filled) epoxy foams..	81
4.3.2	Fracture toughness of the (hollow elastomeric microsphere filled) epoxy foams	84
4.3.3	Charpy impact toughness of the (hollow elastomeric microsphere filled) epoxy foams	88
4.3.4	Compressive properties of the (hollow elastomeric microsphere filled) epoxy foams	89
4.4	Concluding remarks.....	91
Chapter 5 Transversely isotropic porous material from liquid foam templates: Short carbon fibre reinforced epoxy foams		92
5.1	Introduction	92
5.2	Experimental.....	93
5.2.1	Materials.....	93
5.2.2	Preparation of (short carbon fibre reinforced) epoxy foams	94
5.2.3	Characterisation of the (sCF reinforced) epoxy foams	96
5.3	Results and discussion.....	98
5.3.1	Structure and morphology of the (sCF reinforced) epoxy foams	98
5.3.2	Fracture toughness of the (sCF reinforced) epoxy foams	103
5.3.3	Compressive properties of the (sCF reinforced) epoxy foams.....	108
5.4	Concluding remarks.....	111
Chapter 6 Conclusion and future work.....		112
6.1	Conclusion.....	112
6.2	Future work	113
6.2.1	Optimising the foam templated macroporous polymers	113
6.2.2	Cost analysis on the foam templated macroporous polymers	114
References		115

List of Figures

Figure 2-1. Chemical reaction between epoxide group and amine group.....	25
Figure 2-2. Scanning electron micrographs of emulsion templated epoxy foam. Obtained from Ref. [67] with kind permission of John Wiley and Sons.....	30
Figure 2-3. The porosity of the emulsion templated epoxy foams as a function of the volume fraction of the internal aqueous phase. Obtained from Ref. [68] with kind permission of Elsevier.....	31
Figure 2-4. Scanning electron micrograph of foam templated acrylated epoxidised soybean oil based macroporous polymers. Obtained from Ref. [9] with kind permission of Royal Society of Chemistry.....	33
Figure 2-5. Scanning electron micrograph of foam templated epoxy foam. Obtained from Ref. [10] with kind permission of Royal Society of Chemistry.....	34
Figure 2-6. An Ashby-plot of the foam templated epoxy foams and the commercial engineering foams. Obtained from Ref. [10] with kind permission of Royal Society of Chemistry.....	35
Figure 2-7. Schematic diagram of an air-in-liquid dispersion (e.g. a foam).....	37
Figure 2-8. Schematic illustration of Ostwald ripening.....	38

Figure 2-9. Schematic diagram of a single bubble in (a) Patel model and (b) Amon and Denson model.....	39
Figure 2-10. The ideal polyhedral structure (the structure with lowest surface energy): (a) Kelvin structure and (b) Weaire-Phelan structure. Obtained from Ref. [90] with kind permission of The American Society of Mechanical Engineers.	41
Figure 2-11. Schematic illustration of Feret, Martin and Image Sheared diameters.	42
Figure 2-12. The idealised pore structure used in the derivation of the Gibson and Ashby model. Obtained from Ref. [99] with kind permission of Cambridge University Press.	44
Figure 3-1. Scanning electron micrographs of the foam templated macroporous polymers. Sample 0 : cure at room temperature for 24 h and post-cure at 40 °C for 24 h. 1 and 2 represent standing time at room temperature of 1 h and 30 min after initial mixing, respectively. A , B and C represent polymerising temperature of 80 °C, 100 °C and 120 °C, respectively. The scale bar represented by the solid line is 500 µm.	60
Figure 3-2. Viscosity (η) of the resin-hardener mixture polymerised at different conditions. (a) cure at room temperature, corresponding to sample 0 . (b), (c) and (d) cure at room temperature for 1 h and post-cure at 80 °C, 100 °C and 120 °C, respectively, corresponding to samples 1-A , 1-B and 1-C , respectively. (e), (f) and (g) cure at room temperature for 30 min and post-cure at 80 °C, 100 °C and 120 °C, respectively, corresponding to samples 2-A , 2-B and 2-C , respectively.	62

Figure 3-3. Representative compressive stress (σ) – strain (ε) curves of the foam templated macroporous polymers. 64

Figure 3-4. Viscoelastic properties of the bulk polymers polymerised at different conditions. E' and T represent storage modulus and temperature, and $\tan \delta$ is the ratio of loss modulus to storage modulus. 66

Figure 3-5. SEM images of in-situ micro-compression test on (a) sample **0** and (b) sample **2-C**. The black arrow represents the loading direction and the white arrow indicates the cracks and corrugations. The scale bar represented by the white solid line is 500 μm . 69

Figure 3-6. Deformation of pores with different diameter. F_h and F_v denote horizontal and vertical Feret diameter. A F_h/F_v value of unity and zero correspond to perfect spheres (as-fabricated pore) and a line (fully crushed pore), respectively. D_{pore} is the average pore diameter. 72

Figure 4-1. Scanning electron micrographs of the fabricated samples and hollow elastomeric microspheres used in this work. (a) Sample **M0** (neat and un-filled epoxy foam), (b) sample **M0.5** (0.5 wt.-% hollow elastomeric microsphere filled epoxy foam), (c) sample **M1** (1.0 wt.-% hollow elastomeric microsphere filled epoxy foam) and (d) hollow elastomeric microspheres. The scale bar represented by the solid line is 200 μm 82

Figure 4-2. Pore size distribution of the fabricated samples and microsphere size distribution of the hollow elastomeric microspheres used in this work. (a) Sample **M0** (neat and un-filled epoxy foam), (b) sample **M0.5** (0.5 wt.-% hollow elastomeric

microsphere filled epoxy foam), (c) sample **M1** (1.0 wt.-% hollow elastomeric microsphere filled epoxy foam) and (d) hollow elastomeric microspheres. The bin size is 20 μm 83

Figure 4-3. Representative load (P)-displacement curves of fracture toughness test (single edge notched specimens loaded in three-point bending mode). (a) Sample **M0** (neat and un-filled epoxy foam), (b) sample **M0.5** (0.5 wt.-% hollow elastomeric microsphere filled epoxy foam), (c) sample **M1** (1.0 wt.-% hollow elastomeric microsphere filled epoxy foam). 85

Figure 4-4. Fracture surfaces of samples **M0**, **M0.5** and **M1** after fracture toughness test. The vertical dash lines represent the initial crack tip and the crack propagation direction is to the right of the vertical dash lines. The circles with dash line and solid line denote textured microflow and crack pinning, respectively. The arrows with solid lines, dash lines and dotted lines denote fractured, debonded and deformed microspheres, respectively. 86

Figure 4-5. Critical stress intensity factor (K_{1c}) as a function of crack opening (Δa) of the (hollow elastomeric microsphere filled) epoxy foams. 87

Figure 4-6. SEM images of the fracture surfaces of the samples after Charpy impact tests. 89

Figure 4-7. Representative compressive stress-strain curves of the (hollow elastomeric microsphere filled) epoxy foams. 90

Figure 5-1. Scanning electron micrographs of the (sCF reinforced) epoxy foams. (a) Sample **0-A**, (b) sample **0-B**, (c) sample **1** (2.5 wt.-% sCF reinforced), (d) sample **1** (5.0 wt.-% sCF reinforced), (e) sample **2** (2.5 wt.-% sCF reinforced) and (f) sample **2** (5.0 wt.-% sCF reinforced). The scale bar represented by the solid line is 200 μm 99

Figure 5-2. Representative cross-sections of (a) sample **1** (2.5 wt.-% sCF reinforced) and (b) sample **2** (2.5 wt.-% sCF reinforced)..... 100

Figure 5-3. Pores size distributions of the (sCF reinforced) epoxy foams. (a) Sample **0-A**, (b) sample **0-B**, (c) sample **1** (2.5 wt.-% sCF reinforced), (d) sample **1** (5.0 wt.-% sCF reinforced), (e) sample **2** (2.5 wt.-% sCF reinforced) and (f) sample **2** (5.0 wt.-% sCF reinforced). The bin size is 20 μm 102

Figure 5-4. Representative load-displacement curves of fracture toughness test. (a) Sample **1** loaded in the out-of-plane direction and (b) sample **1** loaded in the in-plane direction, relative to sample **0-A**; (c) sample **2** loaded in the out-of-plane direction and (d) sample **2** loaded in the in-plane direction, relative to sample **0-B**. The inset diagrams showed preparation of the test specimens (represented by the dark grey) from the original sample (represented by light grey). 104

Figure 5-5. Exemplary fracture surfaces of the sCF reinforced epoxy foams after fracture toughness test. (a) & (b) Sample **1** (2.5 wt.-% sCF reinforced) test in out-of-plane direction, and (c) & (d) sample **2** (2.5 wt.-% sCF reinforced) tested in out-of-plane direction..... 105

Figure 5-6. Representative compressive stress-strain curves of (a) sample **1** loaded in the out-of-plane direction and (b) sample **1** loaded in the in-plane direction, relative to sample **0-A**, (c) sample **2** loaded in the out-of-plane direction and (d) sample **2** loaded in the in-plane direction, relative to sample **0-B**, respectively. The inset diagrams showed the loading direction of the test specimens (represented by the dark grey) relative to the original samples (represented by light grey). 109

List of Tables

Table 3-1. Density, porosity and morphological properties of the macroporous polymers. ρ_f , P , O_V , D_{pore} , T_{wall} , D_{throat} and f_{throat} denote foam density, porosity, open cell content, average pore diameter, mean pore wall thickness, average pore throat diameter and pore throat frequency, respectively	59
Table 3-2. Compressive properties of the foam templated macroporous polymers. E_{cf} and σ_{cf} denote the compressive modulus and compressive strength	65
Table 3-3. Viscoelastic properties of the bulk polymers. E' , E'_R , T_g and M_c denote the storage modulus at room temperature, the storage modulus of the rubbery plateau evaluated at $T_g + 40$ K, the glass transition temperature and the molecular weight between crosslinks, respectively	66
Table 3-4. Mechanical properties of the bulk polymers. E_C , σ_C , E_T , σ_T , E_F and σ_F denote compressive modulus and strength, tensile modulus and ultimate strength, flexural modulus and ultimate strength, respectively	67
Table 3-5. Normalised compressive properties of the foam templated macroporous polymers. E_{cf} , σ_{cf} and ρ_f denote compressive modulus, strength and foam density of the macroporous polymers, respectively.....	70
Table 4-1. Physical and morphological properties of the (hollow elastomeric microsphere filled) epoxy foams. ρ_f , P , D_{pore} , N_p and N_m denote the foam density, porosity, average pore diameter, pore density and microsphere density, respectively.....	81

Table 4-2. Mechanical properties of the (hollow elastomeric microsphere filled) epoxy foams.. K_{1c} , a_{cU} , E and σ denote the critical stress intensity factor, Charpy impact strength, compressive modulus and compressive strength, respectively 85

Table 5-1. The true density of the pore wall material (ρ_s), envelope density (ρ_f), porosity (P) and the average pore diameter (D_{pore}) of the (sCF reinforced) epoxy foams. 101

Table 5-2. In-plane and out-of-plane critical stress intensity factor (K_{1c}), normalised critical stress intensity factor ($\tilde{K}_{1c}$), compressive modulus (E) and compressive strength (σ) of the (sCF reinforced) epoxy polymers. 107

List of Publications

Peer-reviewed Journal Paper

1. Song, W., Kevin, B., Lee, K.-Y., Heat-induced bubble expansion as a route to increase the porosity of foam-templated bio-based macroporous polymers, *Polymer* **118** (2017), 97-106.
2. Song, Y., Li, Y., Song, W., Yee, K., Lee, K.-Y., Tagarielli, V. L., Measurements of the mechanical response of unidirectional 3D-printed PLA, *Materials & Design* **123** (2017), 154-164.
3. Song, W., Tagarielli, V. L., Lee, K.-Y., Enhancing the fracture resistance and impact toughness of mechanically frothed epoxy foams with hollow elastomeric microspheres, *Macromolecular Materials and Engineering* (2018), 1800363.
4. Song, W., Konstantellos, G., Li, D., Tagarielli, V. L., Lee, K.-Y., Transversely isotropic porous material from liquid foam templates: Short carbon fibre reinforced epoxy foams, (2018) in preparation.

Conference Presentation & Proceeding

1. Song, W., Kevin, B., Lee, K.-Y., Heat-induced bubble expansion as a route to increase the porosity of foam-templated bio-based macroporous polymers. Nordic Polymer Days (NPD), May 2016, Helsinki, Finland.

2. Song, W., Lau, T., Wong, L. C., Bismarck, A., Lee, K.-Y., Tailored for simplicity: Foam-templated bio-based macroporous polymers. International Symposium on Bioplastics, Biocomposites and Biorefining (ISBBB), June 2016, Guelph, Canada
3. Li, D., Song, W., Tagarielli, V. L., Lee, K.-Y., UHMWPE fibre yarn established continuous wavy network construction reinforced epoxy foam composite. European Conference on Composite Materials (ECCM), June 2018, Athens, Greece

Chapter 1 Introduction

Macroporous polymers are lightweight materials of great commercial importance, with an estimated global market value of US\$172 billion by 2021 [1]. The most commonly used macroporous polymers are made from polyurethane, polystyrene and poly(vinyl chloride). Together, they represent ~90 % of the market share for macroporous polymers in 2015 [2]. Among the macroporous polymer families, epoxy foams possess excellent specific mechanical property, good thermal stability and high chemical and moisture resistivity [3]. Therefore, they are often employed in demanding applications where weight saving is critical, such as core material for sandwich-structured composites used in wind turbine blades, naval constructions and aeronautical components [4].

Numerous methods can be used to produce epoxy foams. Epoxy resin can be foamed during its curing process with the use of physical or chemical blowing agents. Physical blowing agents are mainly low boiling points hydrocarbons, such as pentane, toluene and hexane [5]. They are added into the epoxy resin as liquid at room temperature and vaporised upon heating during the curing of the resin to produce cellular structures. Chemical blowing agents generate gaseous products via chemical reactions upon heating. Ammonium carbonate [6], azodicarbonamide [7] and sodium borohydride [8] are used as chemical blowing agents to produce epoxy foams.

Syntactic epoxy foams can be produced by dispersing hollow microspheres, typically made from glass or phenolic, into the liquid epoxy resin, followed by curing of this resin. The porosity of syntactic foams is controlled by the concentration of hollow

microspheres in the resin. While it is desirable to increase the concentration of hollow microspheres to increase the porosity of syntactic foams, excessive microspheres will result in a dramatic increase in the viscosity of the resin-microspheres dispersion, leading to processing difficulties.

A blowing agent and stabiliser free, foam templating method have recently been developed to produce macroporous polymers derived from bio-based epoxy resin [9, 10]. This was achieved by first creating an air-in-resin liquid foam template using mechanical frothing, followed by curing of this liquid foam template to produce the epoxy foams. The epoxy foams can be feasibly moulded into desired shapes due to the liquid status of the foam templates. The compressive modulus and strength of these epoxy foams were found to be 163 MPa and 4.9 MPa. This green, simple and versatile manufacturing method has the potential to provide a new generation of epoxy foams that meet the stringent requirements for future materials.

1.1 Objective of this project

The main aim of this thesis is to use foam templating method to develop a new generation of epoxy foams and to widen the potential applications of the foam templated macroporous polymers. In order to achieve this, three major challenges need to be addressed: (i) the porosity of foam templated macroporous polymers need to be increased; (ii) the brittleness stemming from the inflexibility of epoxy resin need to be reduced; and (iii) higher mechanical performance of the foam templated macroporous polymers is desirable. Based on these challenges, three objectives are determined:

- 1) To produce and characterise high porosity foam templated macroporous polymers above the state of the art;
- 2) To enhance the fracture resistance and impact toughness of the foam templated macroporous polymers;
- 3) To manufacture and characterise short carbon fibre reinforced foam templated macroporous polymers.

1.2 Structure of this thesis

This thesis is divided into 6 chapters. The first chapter provides a short introduction to the thesis. The literature review describing and discussing the background and prior art of epoxy foam and foam templating method is summarised in Chapter 2. Each chapter in chapters 3-5 is a stand-alone article that can be read independently. Chapter 3 introduces heat-induced bubble expansion as a route to increase the porosity of foam templated macroporous polymers and discusses the influence of pore structures on the mechanical properties of the fabricated macroporous polymers with the aid of in-situ SEM micro-compression test. Chapter 4 reports foam templated macroporous polymers toughened by hollow elastomeric microspheres. Fracture toughness and impact toughness results are presented and the toughening mechanism is discussed. Chapter 5 investigates the reinforcing performance of short carbon fibre to the foam templated macroporous polymers. The conclusions are summarised in the last chapter (Chapter 6), where future work is also included.

Chapter 2 Literature review

2.1 Introduction

Macroporous polymers, also known as polymer foams, plastic foams or cellular plastics, refer to substances which contain a gaseous phase within a polymer matrix. Both the gaseous phase and polymer matrix may consist of more than one component depending on the manufacturing processes. The key feature for macroporous polymers is the reduced density compared to the pure polymer material. Numerous macroporous polymers are available today with their density ranging from about 1.6 kg m^{-3} to over 960 kg m^{-3} [11], and they can be used for a variety of applications.

There are several classification methods for macroporous polymers. Firstly, macroporous polymers can be categorised by their polymer components. The most widely used ones include polyurethane (PU or PUR) foam, polystyrene (PS) foam, polyvinyl chloride (PVC) foam, and polyolefin foam which mainly consists of polypropylene (PP) foam and polyethylene (PE) foam. Together they represent a market share of approximately 95% in 2015 [2]. Secondly, based on the molecular structures of the polymers, macroporous polymers can be divided into thermoplastic foams and thermoset foams. Thermoplastic foams mainly have long molecular chains which slide past each other when heated. Therefore, thermoplastic foams can be melted and remoulded into other shapes by thermal treatment. The molecular structures of thermoset foams are crosslinked to form a 3D network. The crosslinked network restricts the molecules from sliding apart from

each other upon heated. Thermoset foams usually have better mechanical performance and heat resistance.

Macroporous polymers can also be divided into open- and closed-pore foams based on the pore structures. Closed-pore macroporous polymers possess lower permeability to gas or liquid, lower absorptive capacity for water and moisture, and more effective insulation abilities for either heat or sound compared to open-pore macroporous polymers. Closed-pore macroporous polymers are often used for thermal insulating [12-14], sound damping [15, 16] and water proofing applications [17, 18], while open-pore structure is needed for water and gas adsorbing and filtration [19-21], as well as tissue engineering [22-24].

Macroporous polymers can be classified as flexible foams and rigid foams based on their rigidity. Flexible foams could recover to the original shape rapidly and completely when the external force was removed. Rigid foams have very low flexibility and high ratio of load bearing to density, and they retain some permanent deformation after loading. Flexible foam is one of the most versatile materials that is widely used, such as in cushioning for furniture and bedding, and in packaging for delicate devices [25-27]. Rigid foams are widely applied in load bearing applications due to their exceptional specific mechanical properties [28-30].

2.2 Manufacturing methods of epoxy foams

Epoxy foams are typically closed-pore, rigid thermoset foams which possess excellent mechanical properties, chemical and corrosion resistance and thermal stabilities. Epoxy

foams are made from epoxy resins, which are chemicals containing epoxide groups. The epoxide groups can react (crosslink) with different curing agents (hardeners) through ring-opening polymerisation. One major type of hardener is amine-based hardener. As shown in Figure 2-1, the epoxide group can react with the primary amine and form a hydroxyl group and secondary amine. This reaction is a polyaddition process which is free of by-products. Therefore, in order to fabricate epoxy foams, the gaseous phase needs to be added. Different manufacturing methods will be introduced and discussed in this section.

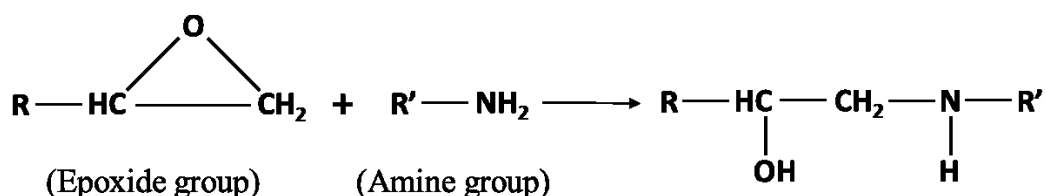


Figure 2-1. Chemical reaction between epoxide group and amine group.

2.2.1 Blowing agent foaming method

Blowing agent foaming is a universal method used for the manufacturing of various types of macroporous polymers. Physical blowing agents are either liquid materials with low boiling points or liquefied gases at high pressures. They are typically added and mixed with polymers in a liquid state, and transformed to gaseous state upon heating or depressurising to foam the polymers. For example, pentane, hexane, benzene, xylene, carbon tetrachloride (CCl_4) and trichlorofluoromethane (CCl_3F) have been used to

manufacture epoxy foams [5]. It is worth mentioning that CCl_4 and CCl_3F , as well as other blowing agents in chlorofluorocarbon (CFCs) and hydrochlorofluorocarbon (HCFCs) families, have been banned globally due to their ozone depletion potential and greenhouse effect [31-33]. In addition, some other hydrocarbons with low boiling point, such as butane and tertiary butanol [34], can also be used to fabricate epoxy foams. Another widely studied physical blowing agent is pressurised or supercritical carbon dioxide (CO_2) [35-37]. Stringent conditions are required to mix the polymer with CO_2 . For example, to dissolve the CO_2 into epoxy resin, Ito et al. [37] used an autoclave at 35 °C and 5 MPa for 60 h.

Chemical blowing agent foaming involves chemical reactions to generate gases, normally by decomposing the chemical blowing agents at elevated temperatures. The chemical blowing agents include low alkoxyboroxines, such as trimethoxyboroxine, triethoxyboroxine and tripropoxyboroxine. They react with water and form boric acid and corresponding alkanols, and their application in epoxy foam manufacturing was first patented by Shell company in 1962 [38]. Since then, a variety of chemical blowing agents have been used to foam epoxy systems, such as siloxane [39], ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) [6], sodium bicarbonate (NaHCO_3) [40], azodicarbonamide (ADCA) [7] and p,p'-oxybis (benzenesulfonyl hydrazide) (OSBH) [41]. Generally, the temperatures required for decomposing chemical blowing agents are higher than the boiling points of physical blowing agents which are typically around 60-80 °C. For instance, 140 °C was applied for NaHCO_3 foamed epoxy systems [42], and 185 °C [43] and 230 °C [7] were used for decomposing ADCA. In addition to the temperature requirement, another concern when using chemical blowing agents is the forming of hazardous by-products.

For example, $(\text{NH}_4)_2\text{CO}_3$ decomposes into ammonia, carbon dioxide and water, and ADCA generates ammonia, nitrogen and isocyanic acid [44]. Extra measures need to be taken to prevent the hazardous chemicals from endangering the operational staff and end users.

2.2.2 Syntactic foaming method

Unlike blowing agent foaming method, syntactic foaming is mainly employed for epoxy foam manufacturing. Hollow microspheres (also termed as microballoons or cenospheres) are added into the epoxy-hardener mixture by gentle mixing, followed by crosslinking. The pores or porosity in syntactic epoxy foams stem from the added hollow microspheres. It should be noted that the entrapment of air bubbles is undesirable. Therefore, to limit the amount of entrapped air bubbles, the hollow microsphere filled epoxy-hardener mixture is usually degassed before curing.

The most widely used hollow microsphere in syntactic epoxy foams is glass microspheres [45]. In addition, phenolic microspheres [46], carbon microspheres [47] and thermoplastic microspheres [48] have also been used. The diameter and true density of the hollow glass microspheres used in syntactic foaming normally vary from 10 μm to 150 μm and 0.2 g cm^{-3} to 0.6 g cm^{-3} , respectively [49-51]. Due to this high density in comparison to air or any other blown gases, the resulting syntactic epoxy foams also possess higher foam density compared to gas blown epoxy foams with the same porosities. For example, syntactic foam with 60 vol.-% of hollow glass microspheres had density of 0.9 g cm^{-3} [52], whereas the theoretical density of epoxy foam with 60 vol.-% of air is about 0.5 g cm^{-3} . It should be noted that the volume fraction of the microspheres

that can be added into epoxy-hardener mixture is often limited to ~60 vol.-% [52-54] due to the dramatic increase of viscosity.

Syntactic epoxy foams have great mechanical performance and the mechanical properties normally increase with reducing the volume fraction of the added hollow microspheres because of the increase in densities. Gupta et al. [55] reported that the compressive strength of syntactic foams with 67 vol.-% glass microspheres was ~20 MPa. Qiao et al. [53] prepared syntactic foams with 50% volume fractions of glass microspheres and found the corresponding compressive modulus and strength was ~1.9 GPa and ~76 MPa. Zhu et al. [52] studied syntactic foams with the same volume fraction (50%) of different types of glass microspheres. They found that epoxy foams with one of the studied glass microspheres, S60HS from 3M Ltd., outperformed the bulk epoxy plastics. The compressive modulus and strength reached ~2.5 GPa and ~130 MPa. Syntactic foams are often brittle foams as well stemming from the inflexibility of the glass microspheres and epoxy resin. For example, instead of undergoing plastic deformation after initial linear elastic region, Bardella [56] reported a nearly elastic-brittle failure of syntactic foam at ~5% strain under compression test.

2.2.3 Emulsion templating method

Templating methods provide the benefit of being able to tune the pore structures of the final macroporous polymers by altering the templates. Emulsions, which are made up of two or more immiscible liquids, have been well-studied as templates to make macroporous polymers. The early attempts date back to at least the 1960s [57, 58], and attracted much attention when Williams and his team studied the technique extensively

around 1990 [59-62]. The manufacturing process starts from an emulsion template, normally by adding water drop-wise into an oil phase which contains monomers, surfactants and initiators. Continuous stirring is required during the mixing to disperse the water homogeneously. The emulsion template is then exposed to either heat or UV light to initiate the polymerisation reaction of the monomers. The polymerised emulsions are then washed to remove unreacted monomers and surfactants. The foam is finally obtained after a drying step to remove the water phase.

The pores in the final foams are formed from the space occupied by the water, i.e. the internal phase of the emulsion template. As a result, the porosity of final foam is expected to be close to the volume fraction of the internal water phase. Lissant [63] classified the emulsions with >70 vol.-% water phase as high internal phase emulsions (HIPEs), with <20 vol.-% as low internal phase emulsions (LIPEs), and between 20-70 vol.-% as medium internal phase emulsions (MIPEs). In emulsion foam manufacturing, attention has mainly been on HIPEs because of their potential to deliver low-density foams. In addition to overall porosity, it is also possible to alter the individual pore size and structure of the final foams using emulsion templating. The pores are mostly interconnected due to the water evaporation process, which makes them favourable for applications requiring permeability, e.g. filtration or tissue engineering [64-66].

Most of the polymerised high internal phase emulsions (polyHIPEs) are based on styrene and divinylbenzene monomer system. Nevertheless, epoxy foams manufactured using emulsion templating have also been reported in the literature. Wang et al. [67] studied polyHIPEs prepared from water-in-epoxy emulsions. A colloidal silica suspension was used as the aqueous phase instead of pure water, because it provided more steric repulsion

which improves the emulsion stability. Prior to adding the aqueous phase, the oil phase, which contained diglycidyl ether of bisphenol-A (DGEBA) as epoxy resin, polyamide as curing agent, nonyl phenol polyoxyethylene ether (NPE-4) as surfactant and 4-methyl-2-pentanone as solvent, was precured at 60 °C for about 1 h to gain higher viscosity that helped stabilise the prepared emulsions. The aqueous phase was dropwise added into the oil phase with the volume fraction ranging between 74% and 86%. One exemplary foam was made by curing and drying the emulsion with 74% internal phase and the scanning electron micrographs are shown in Figure 2-2. The images show the interconnected pore structure of emulsion templated epoxy foams.

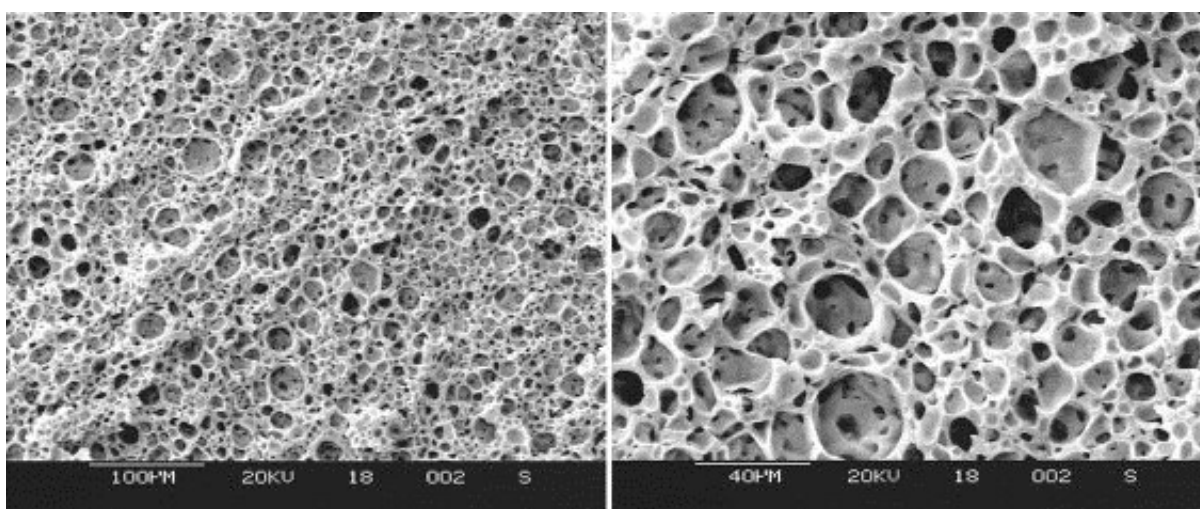


Figure 2-2. Scanning electron micrographs of emulsion templated epoxy foam. Obtained from Ref. [67] with kind permission of John Wiley and Sons.

In another paper published by the same group [68], different surfactants were investigated to find the optimum hydrophile–lipophile balance (HLB) for stabilising the epoxy resin-based emulsions. The relationship between the volume fraction of the aqueous phase and the porosity of the resulting foams were also studied. Similar

procedure as in Ref. [67] were applied to prepare the emulsions and the optimum HLB value was found to be 8.6. The viable candidates included Span 20, NPE-4, and Span 80/Tween 80 at weight ratio of 3/2. The prepared emulsions were cured at 60 °C for 8 h, subsequently washed by acetone 3 times, and finally dried in a vacuum oven at 80 °C until the weight became constant. The porosity of the fabricated foams was much lower than the initial volume fraction of internal aqueous phase as shown in Figure 2-3. The authors ascribed the inconsistency between the volume fraction of the internal phase and the final foam porosity to pore collapse during curing and drying.

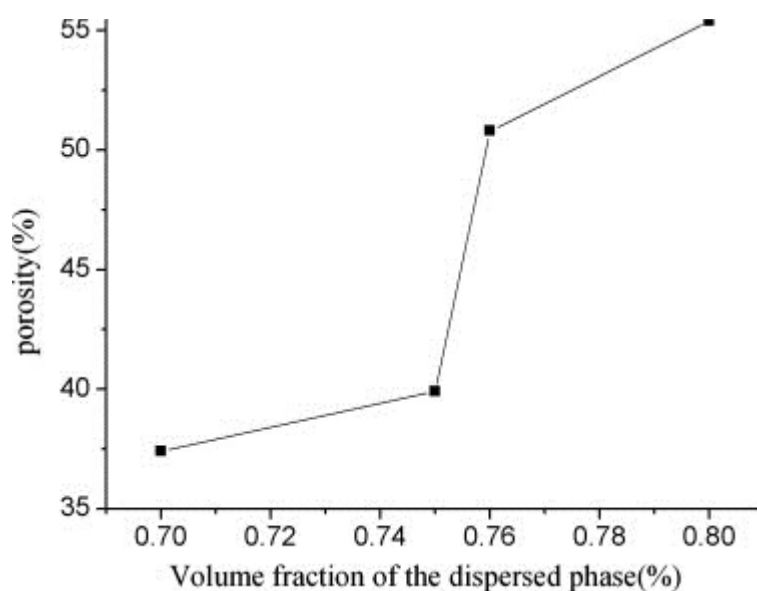


Figure 2-3. The porosity of the emulsion templated epoxy foams as a function of the volume fraction of the internal aqueous phase. Obtained from Ref. [68] with kind permission of Elsevier.

2.2.4 Foam templating method

In addition to the emulsion, liquid foam can also be used as a template to manufacture macroporous polymers. Liquid foams can be prepared via mechanical frothing, and since gas, mostly air, is used to create the liquid foam template, the drying step is no longer needed. Also, if the viscosity of the liquid polymer is high enough to stabilise the liquid foam, no surfactants, or washing step is needed. Therefore, the foam templating method has great simplicity and is easy to operate. It also has low environmental impact because it is blowing agent and stabiliser free.

Mechanical frothing had been used to fabricate macroporous polymers since 1970s. Marlin et al. [69] used this method to produce polyurethane foams. They achieved quasi two-dimensional (2D) foams with thickness of ~ 6 mm. The foam had a density of 0.48 g cm^{-3} and tensile strength of 2.0 MPa. Deanin et al. [70] employed this technique to manufacture polyvinyl chloride foams. The thickness was doubled to ~ 12 mm, and the frothing time varied from 6 min to 55 min. With the frothing time of 55 min, foam with lowest density of 0.34 g cm^{-3} was achieved, and its tensile strength was 0.06 MPa. These fabricated foams found several applications, such as for the production of carpets, sport surfaces and shoe inner soles [71].

In 2011, Lee et al. [9] fabricated three-dimensional monolithic foams using this method and termed it foam templating. They prepared the liquid foam template by frothing acrylated epoxidised soybean oil (AESO) and lauroyl peroxide (as initiator) mixture for 5 min. The foam template was subsequently polymerised under microwave irradiation, washed by ethanol and water, and dried at 40°C overnight. The resulting density and

porosity were 0.44 g cm^{-3} and 59%. The pores were mostly closed and irregular in shape, as shown in Figure 2-4. The compressive modulus (E) and strength (σ) was 111 MPa and 0.34 MPa. Bacterial cellulose (BC) was added to improve the mechanical properties, and it was found that with 0.5 wt.-% addition, the E and σ changed to 166 MPa and 0.25 MPa, though the porosity decreased slightly to 54%.

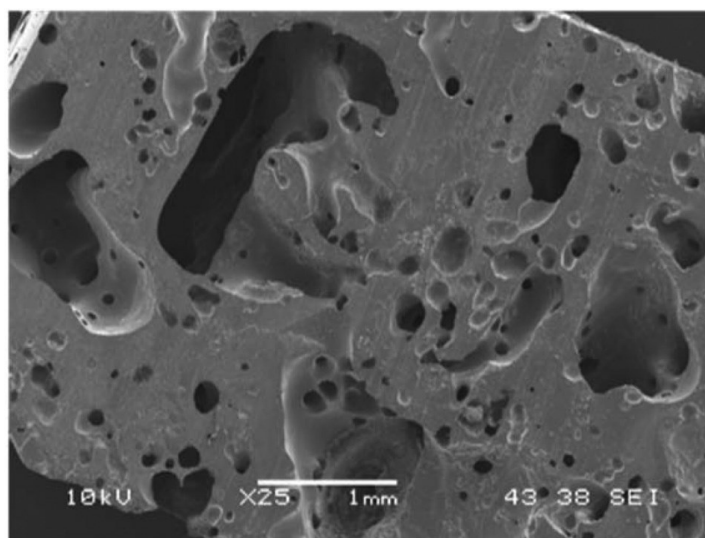


Figure 2-4. Scanning electron micrograph of foam templated acrylated epoxidised soybean oil based macroporous polymers. Obtained from Ref. [9] with kind permission of Royal Society of Chemistry.

The same research group has applied foam templating on a bio-based epoxy resin system [10]. The epoxy foams were produced simply by curing the mechanically frothed liquid foam templates. No blowing agents or stabilisers were added to the epoxy resin and hardener. No washing or drying steps were required. The influence of frothing periods and curing conditions on the epoxy foams were studied. It was found that all the samples had spherical closed pore structures as shown in Figure 2-5, which means the trapped air bubbles reached equilibrium with the surrounding resin during the curing step. The

average pore size decreased from $\sim 250\ \mu\text{m}$ to $\sim 180\ \mu\text{m}$ with increasing the frothing time from 10 min to 30 min. This was attributed to the extended frothing time suppressing the coalescence of the trapped air bubbles prior to the gelation of the surrounding resin. The best compressive property achieved was $E = 163\ \text{MPa}$ and $\sigma = 4.9\ \text{MPa}$, with foam density and porosity of $0.29\ \text{g cm}^{-3}$ and 75%. This property made the fabricated foam comparable to the commercial engineering foams as can be seen from the Ashby plot in Figure 2-6.

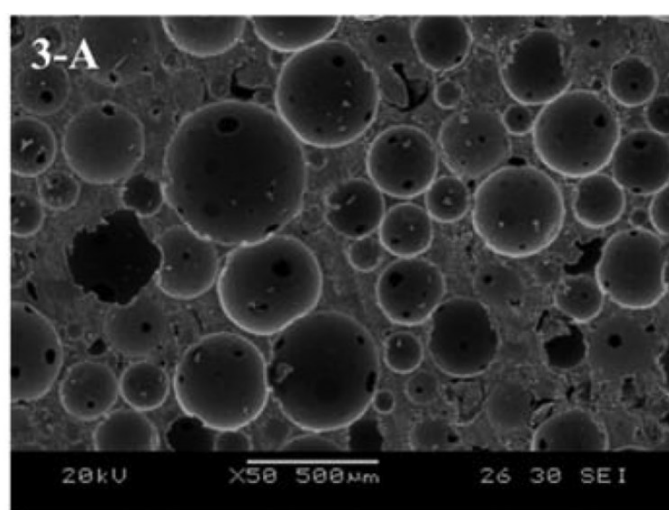


Figure 2-5. Scanning electron micrograph of foam templated epoxy foam. Obtained from Ref. [10] with kind permission of Royal Society of Chemistry.

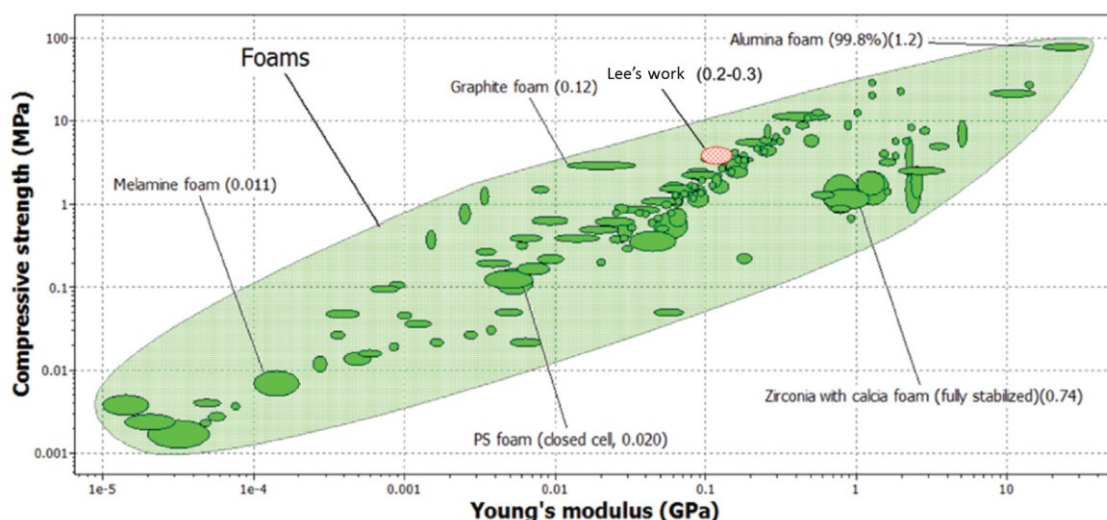


Figure 2-6. An Ashby-plot of the foam templated epoxy foams and the commercial engineering foams. Obtained from Ref. [10] with kind permission of Royal Society of Chemistry.

2.3 Pore formation and pore structure

Pores are vital for porous materials as not only is the porosity directly determined by the pores, also many other properties are related to the pore structures. For example, the permeability and thermal insulation property of macroporous polymers is related to the interconnectivity of the pores [72]. The adsorption behaviour is influenced by the pore sizes [73]. For foam templated macroporous polymers, the pore structure in the final products is determined by the dispersed air bubble structure in the liquid foam template if the polymerisation process does not disrupt the air bubble structure. In this section, the formation in liquid foam system is firstly discussed, followed by pore evolution and pore size and structure characterisation of macroporous polymers.

2.3.1 Pore formation in liquid foams

While some liquid foam can remain stable for several months or even years, all liquid foams are thermodynamically unstable [74]. The stability of a liquid foam can be influenced by numerous factors, such as the drainage rate, surface tension gradient, surface diffusion, the presence and concentration of surfactants and external disturbance. There are three well established procedures to prepare liquid foams [75]: (i) introduce air directly into a liquid by mechanical shaking or whipping; (ii) disperse gas through an orifice; and (iii) nucleate gas bubbles from oversaturated solutions. The last one corresponds to blowing agent foaming method and the first one to foam templating method, which will be focused on in this thesis.

When air bubbles are introduced into a liquid, gravity initially drives the liquid to drain downwards. This drainage causes the thinning of the films between the adjacent pores. As shown in Figure 2-7, the thin films between pores are referred to as lamella, and the junction area of two or more lamellae are known as Plateau borders. Once this structure is formed, capillary suction effect takes over and further drains the liquid from the lamella region to the Plateau border [76]. The drainage caused by either gravity or capillary pressure is a major factor which leads to phase separation. Overall, liquid flows downwards and air bubbles float to the top surface. This destabilisation process is also known as creaming. The air bubbles in the top surfaces are more susceptible to rupture by vibration or temperature shock, which leads to bubble coalescence and/or collapse and finally perishing of the liquid foams.

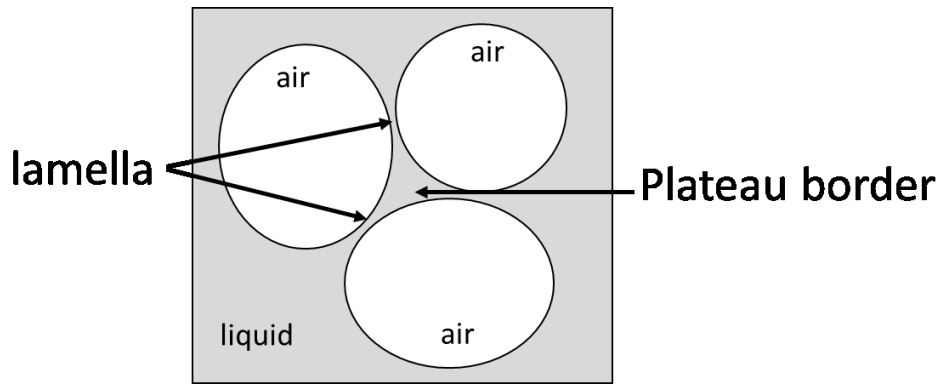


Figure 2-7. Schematic diagram of an air-in-liquid dispersion (e.g. a foam).

In addition to drainage, gas diffusion also plays a key role in pore formation in liquid foam systems. According to Young-Laplace equation, the Laplace pressure inside a spherical bubble (ΔP) is related to the surface tension (γ) and the radius of curvature (R)

$$\Delta P = \gamma \frac{2}{R} \quad (2.1)$$

Due to the smaller radius of small bubbles, the pressure in small bubbles is higher than that in the big ones. As a result of the higher pressure, the gas in small bubbles becomes more soluble. Hence, it tends to dissolve, then diffuse in the liquids and eventually redeposit into the big bubbles. Consequently, with time, the small bubbles will disappear and the big ones become even larger. This process, as schematically drawn in Figure 2-8, is known as Ostwald ripening or disproportionation. It should be noted that, although bubble coalescence gives similar outcome – larger sized bubbles, they are different in fundamental mechanisms. Ostwald ripening is realised by gas diffusion whilst bubble coalescence is only achieved by film rupture.

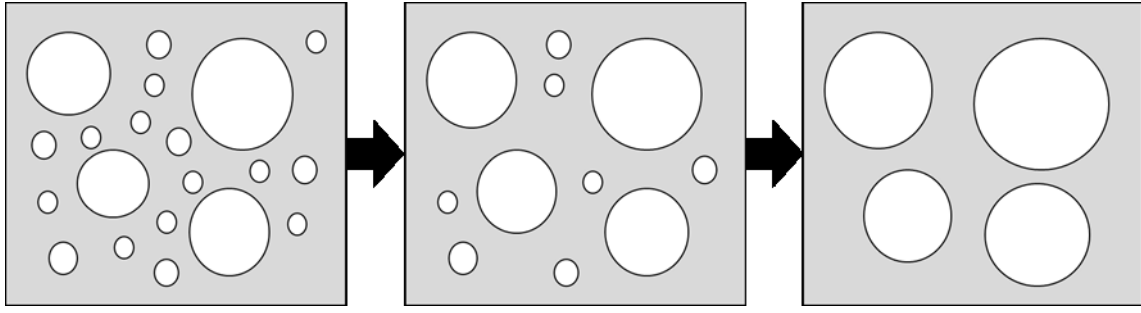


Figure 2-8. Schematic illustration of Ostwald ripening.

2.3.2 Pore evolution in liquid foams

Several papers have discussed pore evolution in specific situations. For example, Ramesh et al. [77] conducted experimental and numerical study of bubble growth during the microcellular foaming process; Villamizar and Han [78] studied the bubble dynamics during injection moulding process; and Fan et al. [79] simulated bubble growth during extruding process. Also, several researchers studied bubble evolution in more general situations. Patel [80] discussed bubble growth in a viscous Newtonian fluid system. It was assumed that an isolated spherical bubble was in an infinite isothermal Newtonian fluid (refer to Figure 2-9 (a)), and the bubble growth rate is expressed as:

$$\frac{dR}{dt} = R \left(\frac{P_g - P_a - 2\sigma/R}{4\eta_0} \right) \quad (2.2)$$

where R is the radius of the gas bubble; t is time; P_g is the gas pressure inside the bubble; P_a is the atmospheric pressure; σ is the surface tension; and η_0 is the liquid viscosity.

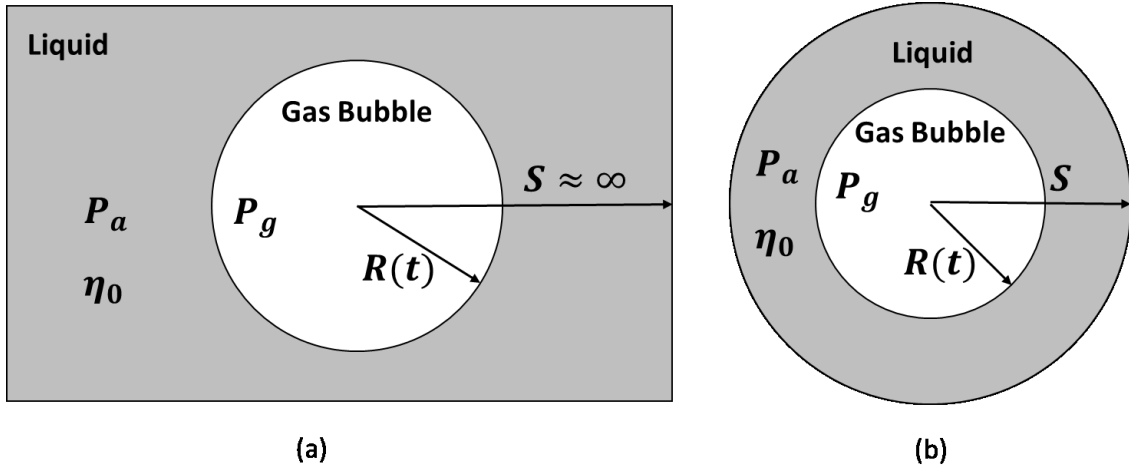


Figure 2-9. Schematic diagram of a single bubble in (a) Patel model and (b) Amon and Denson model.

Later, Amon and Denson [81] developed the model which considered the limited surrounding liquid for each gas bubble. They assumed each single gas bubble is surrounded by a liquid envelope and these bubbles expand in close proximity to one another (refer to Figure 2-9 (b)). The bubble growth rate equation then becomes:

$$\frac{dR}{dt} = R \left(\frac{P_g - P_a - 2\sigma/R}{4\eta_0} \right) \left(\frac{S^3}{S^3 - R^3} \right) \quad (2.3)$$

where S is the radius of the liquid envelope. The term $\frac{\eta_0(S^3 - R^3)}{S^3}$ can be regarded as effective viscosity (η_e) of the liquid envelop [82], and the surface tension effect has been found to be negligible by Amon and Denson and many researchers [79, 83, 84], so the term $\frac{2\sigma}{R}$ can be omitted in the equation:

$$\frac{dR}{dt} \approx R \left(\frac{P_g - P_a}{4\eta_e} \right) \quad (2.4)$$

Bubble growth rate is positively correlated with the pressure inside the bubble and negatively correlated with liquid viscosity. Therefore, higher gas pressure and lower liquid viscosity are favourable for bubble growth. Also, higher gas pressure can be acquired by elevating the ambient temperature, under which conditions, liquid viscosity is normally reduced. This could be used to increase the gas volume fraction in a liquid foam system, which corresponds to a higher porosity of foam templated macroporous polymers. Although in real cases, the temperature should be cautiously selected and the condition should be controlled as thermal treatment could also lead to destabilisation of the liquid foams.

2.3.3 Pore size and structure

The shape of the pores is very diverse in macroporous polymers. When only small quantity of gas is introduced, the pores tend to form spherical shapes to minimise surface energy, because a sphere has the lowest surface area to volume ratio. Theoretically, the maximum gas volume fraction of a foam packed with equally-sized spherical pores can reach 74% [85]. The equally-sized pore structure is also referred as monodispersed pore structure, which is hardly achievable in reality. When the gas volume fraction exceeds 74%, the pores must be either in different sizes, namely polydisperse, or deformed into polyhedral structures [86]. The ideal polyhedral structure, i.e. the structure with lowest surface energy, was once thought to be Kelvin structure (shown in Figure 2-10 (a)) [87] for over a century, until disproved by Weaire and Phelan in 1994 [88, 89]. The Weaire-Phelan structure, as shown in Figure 2-10 (b), is made up of six tetrakaidecahedron and two dodecahedra per unit, and has a lower surface energy than Kelvin structure. Similar

to the monodispersed pore structure, the Weaire-Phelan structure or Kelvin structure can rarely be observed in real foam systems as well.

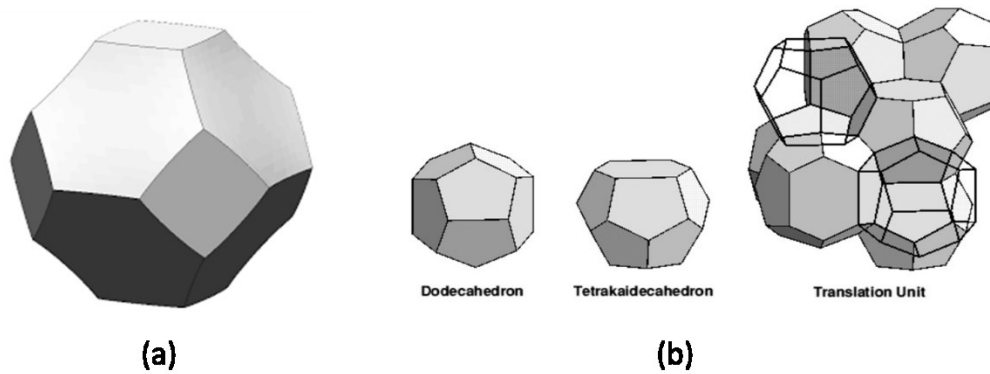


Figure 2-10. The ideal polyhedral structure (the structure with lowest surface energy): (a) Kelvin structure and (b) Weaire-Phelan structure. Obtained from Ref. [90] with kind permission of The American Society of Mechanical Engineers.

One fundamental parameter for individual pore is its size. It is simple to define the pore size given a spherical shape, e.g. the diameter is used in most cases. However, when the pores are not in spherical shape, the definition of pore size becomes less straightforward. A commonly used concept is the equivalent spherical diameter. For example, it can be defined as the diameter of a sphere having the same volume, or projected area etc., as the pore in question. Also, in microscope analysis, there are three frequently used diameters: Feret, Martin and Image Sheared [91]. As shown in Figure 2-11, the Feret diameter is determined as the distance between two parallel tangents of the pore. Normally the tangents are drawn horizontally or vertically, and the corresponding Feret diameter is named as vertical Feret diameter and horizontal Feret diameter, respectively. The Martin diameter refers to the length of a line bisecting the pore. The choice of the direction of

the line is arbitrary, but it should remain constant for all measurements. The Image Shear diameter is determined by shifting the image of a pore to the point that it is just touching the edge of the original image. The shifting distance is the Image Shear diameter and it is normally done by computer.

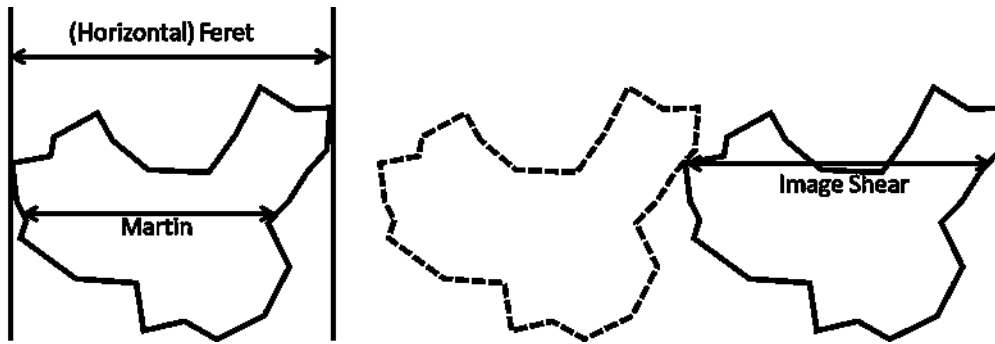


Figure 2-11. Schematic illustration of Feret, Martin and Image Sheared diameters.

Once the pore size is determined, some other important parameters can be attained subsequently. For example, the pore density, defined as number of pores per unit volume (N) can be calculated using the following equation:

$$N = \frac{6P}{\pi D^3} \quad (2.5)$$

where P is the porosity and D is the average pore size of the macroporous polymers. Another useful parameter is pore wall thickness (T_{wall}), and according to Aleksandrov's formula [92], the relation between T_{wall} and D is

$$T_{\text{wall}} = D\left(\frac{1}{\sqrt{P}} - 1\right) \quad (2.6)$$

2.4 Mechanical properties of macroporous polymers

The mechanical property of macroporous polymers is very important, not only for foams used in load bearing applications, but also for those not primarily used in mechanical situations. For example, for foams used for thermal insulation or filtration, it is still vital to know their strength and fracture behaviour. Many researchers have contributed to the exploration and explanation of the relationship between the mechanical properties of macroporous polymers and pore structures [93-95]. Among them, the most well-established model is described by Gibson and Ashby [96-98], which will be introduced in this section, followed by discussion of the influence of pore size and structure on the mechanical properties of macroporous polymers.

2.4.1 Gibson and Ashby model

The pore structure of macroporous polymers in Gibson and Ashby model is constructed as cubic array of equal-length and -size pore edges where the edges of the adjacent pores meet at the midpoints. As shown in Figure 2-12, the closed pore structure resembles the open one whilst it has membranes for each face of the pores. It should be noted that, although this pore structure is rarely seen in real foams, the results stay valid as long as the foam deforms and fails following the same mechanism as discussed here. They also pointed out that, the small strain linear elastic response of a foam in tension is the same as that in compression, which means the compressive modulus should be equal to the tensile modulus.

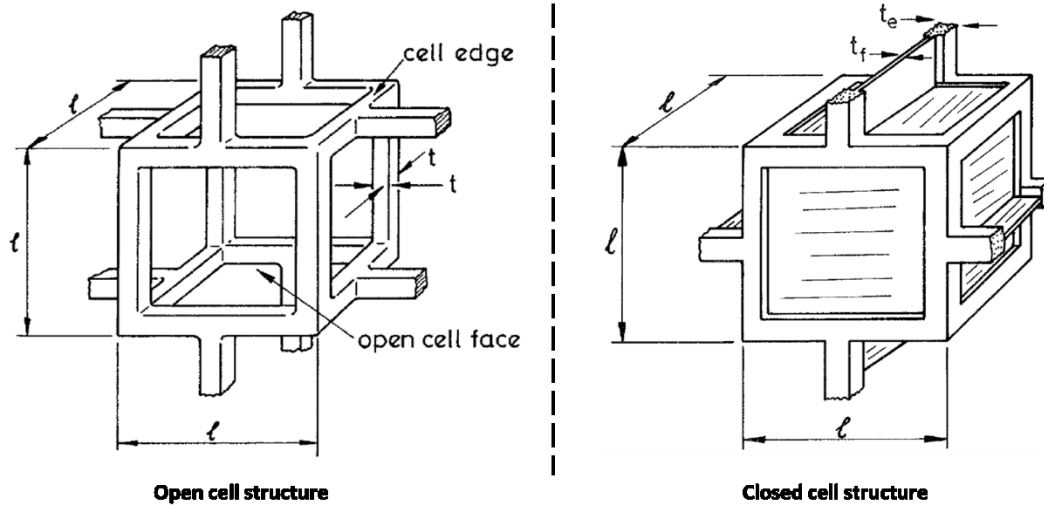


Figure 2-12. The idealised pore structure used in the derivation of the Gibson and Ashby model. Obtained from Ref. [99] with kind permission of Cambridge University Press.

For open pore foams with low relative densities (less than 0.1), the foam deformation mechanism in linear elastic region is primarily pore-wall bending [100]. It was found that the stiffness of the foam is proportional to the stiffness of the matrix material and the relative density to the power of 2, as shown in the equation:

$$E_f = C E_s \left(\frac{\rho_f}{\rho_s} \right)^2 \quad (2.7)$$

where E_f and E_s is the modulus of the foam and the matrix material, respectively; ρ_f and ρ_s is the density of the foam and the matrix material, respectively; and C is a constant, which was found, by fitting this equation with experimental data, to be close to 1.

For closed pore structures, in addition to the pore wall bending mechanism, two more factors may also contribute to the stiffness of the foams: the stretch of the pore faces and

the compression of the enclosed gas. The equation then becomes (constants have been fitted):

$$E_f \approx \varphi^2 E_s \left(\frac{\rho_f}{\rho_s}\right)^2 + (1 - \varphi) E_s \frac{\rho_f}{\rho_s} + \frac{p_0}{3(1 - \rho_f/\rho_s)} \quad (2.8)$$

where φ is the volume fraction of the solids that is contained in the pore edges, and thus $(1 - \varphi)$ is the fraction of the solids contained in the pore faces; and p_0 is the initial gas pressure inside the pore. The three parts in this equation correspond to the afore-discussed three factors. It should be noted that, when p_0 equals to atmospheric pressure (p_{at}), which is the case for foam templated macroporous polymers, the third contribution is very small and can be neglected [101].

The linear elastic region for macroporous polymers is typically limited to less than 5% of strain. Beyond that, the foam deforms either elastically but non-linearly (e.g. elastomeric foams), or plastically (e.g. rigid polymer foams). Epoxies are rigid polymers, so the following discussion will focus on plastic deformation only. Also, the deformation mechanism beyond linear elastic region becomes different for compression and tension situations. For an open pore foam under compression, the plastic deformation starts when the forces applied on the pore walls exceed their fully plastic bending moment. It was found that, the compressive strength of the foam (σ_{fc}) is proportional to the yield strength of the matrix material (σ_{ys}) and the relative density to the power of 1.5:

$$\sigma_{fc} \approx 0.3 \sigma_{ys} \left(\frac{\rho_f}{\rho_s}\right)^{1.5} \quad (2.9)$$

It should be noted that this equation is only valid for low density foams ($\rho_f/\rho_s < 0.3$), because at high relative densities, the foam is better to be modelled as a solid with holes and thus the pore walls yield axially instead of bending. For closed pore foams, the two aforementioned factors need to be considered again, and the equation is:

$$\sigma_{fc} \approx 0.3\sigma_{ys}\varphi^{1.5}\left(\frac{\rho_f}{\rho_s}\right)^{1.5} + 0.4(1 - \varphi)\sigma_{ys}\frac{\rho_f}{\rho_s} + (p_0 - p_{at}) \quad (2.10)$$

It can be seen that, for foams containing atmospheric-pressure gases, the third contribution becomes 0.

Under tensile forces, macroporous polymers behave differently. For macroporous polymers made from epoxy resin, due to the inherent brittleness of epoxy resins, they would fail and fracture catastrophically instead of yielding plastically as in compression. The tensile strength (σ_{ft}) is then found to be related to the fracture strength of the matrix material (σ_{fs}) and the relative density:

$$\sigma_{ft} \approx 0.2 \sigma_{fs} \left(\frac{\rho_f}{\rho_s}\right)^{1.5} \quad (2.11)$$

Similarly, for closed pore foam, pore face stretching needs to be included as well. However, the influence of the enclosed gas does not need to be considered in this case, since the foam fractures before any plastic deformation occurs. Hence, the tensile strength of a brittle closed pore foam is

$$\sigma_{ft} \approx 0.2 \sigma_{fs} \varphi^{1.5} \left(\frac{\rho_f}{\rho_s}\right)^{1.5} + (1 - \varphi)\sigma_{fs}\left(\frac{\rho_f}{\rho_s}\right) \quad (2.12)$$

2.4.2 Influence of pore size and structure on mechanical properties

As can be seen from the equations in last section, the Gibson and Ashby model predicts that the mechanical properties of macroporous polymers are independent of the specific pore size and structures. Macroporous polymers made from the same matrix material and with the same relative densities would possess the same mechanical properties even if their pore size and structures are different. However, this model assumes that all the pores undergo the same deformation process, which in reality, is not always true. The deformation mechanism might be different when the pore structures change. In addition, the existence of flaws and pre-cracks in the macroporous polymers will also affect the failure mechanisms. The influence of pore size and structures on the mechanical properties of macroporous polymers have been widely observed by many researchers and will be discussed here.

Schmitt's research group studied the influence of pore size on the mechanical properties of emulsion templated macroporous polymers [102-104]. Macroporous polymers were prepared from styrene and divinylbenzene as monomers and sorbitan monooleate as surfactants. The total volume fraction of the internal phase in the emulsions was kept the same while varying the drop size of the internal phase, so that foams with the same porosities (78%) but different pore sizes were fabricated. The compression test results showed that both compressive modulus and strength increased with increasing the pore size from 1.8 μm to 14 μm . This was caused by the heterogeneity of the pore walls. The authors found that independent of the pore sizes, a fixed-thickness layer of surfactant material was always on the surface of the pore walls, and the mechanical properties of

the surfactant were inferior compared to the main polymers. Also, for foams with the same porosities, the pore wall thickness increases with increasing the pore sizes. Therefore, macroporous polymers with larger pore sizes had a better mechanical performance.

For foams having homogenous pore walls, most researchers found a different relationship between pore sizes and foam mechanical properties. Alonso et al. [105] fabricated aramid fibre reinforced epoxy foams using polydimethylsiloxane as a chemical foaming agent. They credited the improvement in compressive properties partially on the reduced pore sizes caused by the introduced fibres. Pellegrino et al. [106] observed that the failure of glass bubble filled syntactic polyurethane foam always initiated from the larger pores. Huang and Li [107] further analysed the failure mechanism in syntactic epoxy foams filled with hollow glass microspheres using finite element modelling. The results suggested that the failure was most likely to originate at the biggest pores as well.

In addition to macroporous polymers, similar results have been widely reported for metallic foams. Xu et al. [108] fabricated magnesium alloy foams with the same porosity of 87% and different pore sizes between 0.9 mm and 1.6 mm. The results showed that both compressive modulus and strength increased with decreasing pore size. Bekoz and Oktay [109] used carbamide particles as physical blowing agent to prepare steel alloy foams with porosity of ~50% and average pore size of ~400 μm , 500 μm and 900 μm . They observed that foams with smaller pores possessed higher compressive modulus strength. Li et al. [110] prepared nickel foams following colloidal crystal template-assisted electrodeposition method. The porosity of the foams remained at 74% while the

pore sizes varied from 0.3 μm to 1.2 μm . It was found that both the elastic modulus and hardness of the nickel foams decreased with increasing the pore sizes. Taherishargh et al. [111] fabricated expanded perlite particle filled syntactic aluminium foams. The porosities of the fabricated foams were all around 60% and the particle size ranged from 1 mm to 5.6 mm. It was found that the aluminium foams with smaller pores exhibited higher plateau stress and more significant strain hardening effect. The cause of this phenomenon was discussed by these researchers, which mainly included: (i) smaller pores result in a refined pore structure which has less imperfections and defects; (ii) the homogeneity of the pore size increases as the pore size decreases; and (iii) the load upon foams with smaller pores is shared by more pores.

In addition to the average pore size, the pore arrangement and pore structure was also reported to have influence on the macroporous polymer mechanical properties. Wong et al. [112] prepared emulsion templated polystyrene foams using both particles and surfactants as emulsifiers. They fabricated foams with constant porosity of 79% but various pore structures, among which, they defined the pore structure where the big ones were surrounded by many smaller ones as hierarchical pore structure. They reported that these foams possessed more than double the compressive modulus and strength of the ones with more uniform size pores. The same group further studied the relationship between hierarchical pore structure and foam mechanical properties [113]. They synthesised poly(styrene-co-divinylbenzene) foams with the same porosity of 84% following the emulsion templating method. Foams with different pore structures were achieved by altering the concentration of surfactant from 1% to 20%, and found a maximum of 80% improvement in both compressive modulus and strength for foams

having hierarchical pore structures. They claimed that hierarchical pore structures are more efficient for load transfer in macroporous polymers. This was also supported by Hus and Krajnc's work [114], where ~70% improvement in tensile modulus and ~80% in tensile strength was observed on poly(methyl methacrylate) foams with hierarchical pore structures manufactured by emulsion templating method.

Chapter 3 Heat-induced bubble expansion as a route to increase the porosity of foam templated macroporous polymers

3.1 Introduction

Foam templating method is a blowing agent and stabiliser free method to produce epoxy foams. The epoxy foams are fabricated by first mechanical frothing to create an air-in-resin liquid foam template, and then curing this liquid foam template. While this method is green, simple and versatile, the density and porosity of these foam templated macroporous polymers are limited to $\sim 0.29 \text{ g cm}^{-3}$ and $\sim 70\%$ [9, 10]. In order to widen the applications of these foam templated macroporous polymers, it is desirable to further reduce the density and increase the porosity.

Therefore in this chapter, a simple method to increase the porosity of the foam templated macroporous polymers based on air bubble expansion is presented. By using heat, the air bubbles trapped within the air-in-epoxy resin liquid foams can be expanded, thereby increasing the porosity of the resulting foam-templated bio-based macroporous polymers. The morphology and mechanical properties of these bio-based macroporous polymers are characterised and the influence of the pore structures on the measured compression properties of the macroporous polymers is also discussed.

3.2 Experimental

3.2.1 Materials

A high biomass content epoxy resin (Greenpoxy 56, biomass carbon percentage = 56 ± 2 %, $\rho = 1.20 \pm 0.01$ g cm⁻³, $\eta = 2500$ mPa s at 15 °C) and an amine-based hardener (GP 505, biomass carbon percentage = 58 ± 3 %, $\rho = 0.99 \pm 0.01$ g cm⁻³, $\eta = 2600$ mPa s at 15 °C) were purchased from Matrix Composite Materials Company Ltd (Bristol, UK), and used as the bio-based epoxy resin for the preparation of foam templated macroporous polymers.

3.2.2 Heat-induced bubble expansion of foam templated macroporous polymers

Foam templated macroporous polymers were prepared by mechanical frothing a mixture of epoxy resin and hardener following previously described methods [10]. Briefly, 75 g of bio-based epoxy resin and 30 g of amine-based hardener were poured into a Pyrex glass bowl and this mixture was mechanically frothed using a hand-held mixer (HM730B, Sainsbury's, London, UK) operated at maximum power output of 200 W for 20 min to produce an air-in-resin liquid foam. The liquid foam was then poured into self-standing Falcon® tubes (25 mm in diameter and 115 mm in height) and left to cure at room temperature for 24 h, followed by a post-curing step at 40 °C for another 24 h (sample **0**). To increase the porosity of the foam templated macroporous polymers, the prepared air-in-resin liquid foam was left at room temperature for only 40 min (**1**) or 10 min (**2**),

followed by a curing step at elevated temperatures of 80 °C (**A**), 100 °C (**B**) and 120 °C (**C**) in a pre-heated oven for 24 h. The samples left at room temperature for 40 min (samples **1**) and 10 min (samples **2**) correspond to 1 h (20 min of mechanical frothing, followed by 40 min of standing time at room temperature) and 30 min (20 min of mechanical frothing, followed by 10 min of standing time at room temperature) after the initial mixing of the bio-based epoxy resin and hardener.

3.2.3 Preparation of bulk polymers cured at different conditions

As the macroporous polymers were fabricated by curing the air-in-resin liquid foams at different time after initial mixing and temperatures, the changes in curing conditions could affect the mechanical performance of the resulting pore wall materials and hence, the overall mechanical performance of the resulting macroporous polymers. Therefore, bulk polymers without air bubbles were also prepared and tested. 75 g of bio-based epoxy resin and 30 g of hardener were mixed for 10 min in a paper cup using a wooden stick. The stirring of the mixture was kept slow and gentle to avoid trapping air bubbles in the resin-hardener mixture. To prepare compression test specimens, the well-mixed resin-hardener mixture was poured into Falcon® tubes with diameter and height of 15 mm and 115 mm. Tensile test specimens were prepared by pouring the well-mixed resin-hardener mixture into silicon rubber-based dumbbell shaped moulds, whereby the dumbbells possessed an overall length and thickness of 75 mm and 1.5 mm. The narrowest part of the dumbbells was 5 mm. To fabricate flexural test specimens, the resin-hardener mixture was poured into a $240 \times 80 \times 5 \text{ mm}^3$ metal mould coated with PTFE release agent. All the samples were cured following the conditions previously described.

3.2.4 Characterisation of the foam templated macroporous polymers

3.2.4.1 Structure and morphology of the macroporous polymers

The internal structure of the foam templated macroporous polymers was investigated using scanning electron microscope (SEM) (Hitachi S-3700N, Tokyo, Japan) operating at an accelerating voltage of 15 kV. Prior to SEM, the macroporous polymers were cut into cylinders (diameter = 25 mm and height = 5 mm) and broken into two halves by hand to reveal the internal structure of the macroporous polymers. The samples were then mounted onto aluminium stubs using carbon tabs, followed by Au coating (Agar Auto Sputter Coater, Essex, UK) at 40 mA for 1 min. The average pore diameter (D_{pore}), average pore throat diameter (D_{throat}) and pore throat frequency (f_{throat}) were determined from these SEM images with a population size of 600 pores. The mean pore wall thickness (t_{wall}) was calculated using the Aleksandrov's equation [92]:

$$t_{\text{wall}} = D_{\text{pore}} \left(\frac{1}{\sqrt{1 - \rho_f / \rho_s}} - 1 \right) \quad (3.1)$$

where ρ_f and ρ_s are the density of the macroporous polymers and the bulk polymers.

3.2.4.2 Density, porosity and open cell content of the macroporous polymers

Prior to determining the foam density of the macroporous polymers (ρ_f), the prepared samples were lathed and cut to produce cylindrical samples with uniform diameter (d) and height (h). ρ_f was then calculated from the measured d , h and the mass (m) of the cylindrical samples using the equation:

$$\rho_f = \frac{4m}{\pi d^2 h} \quad (3.2)$$

The true density of the bulk polymers (ρ_s) was determined using He pycnometry (Accupyc II 1340, Micromeritics Ltd, Hexton, UK). The porosity (P) of the macroporous polymers was calculated using:

$$P = \left(1 - \frac{\rho_f}{\rho_s}\right) \times 100\% \quad (3.3)$$

The open cell content (O_V) of the macroporous polymers was determined in accordance to ASTM D6226–15 using He pycnometry (Accupyc II 1340, Micromeritics Ltd, Hexton, UK). Rectangular specimens with dimensions of $12 \times 12 \times 25 \text{ mm}^3$ were prepared to determine the skeletal density (ρ_{skel}), and the open cell content was calculated using:

$$O_V = \left(1 - \frac{\rho_f}{\rho_{\text{skel}}}\right) \times 100\% \quad (3.4)$$

3.2.4.3 Compressive properties of the foam templated macroporous polymers

The compressive properties of the macroporous polymers were determined in accordance to ASTM D1621–10 using an Instron universal tester (Model 5969, Norwood, USA) equipped with a 50 kN load cell. Cylindrical compression test specimens with both diameter and height of 24 mm were compressed between two flat and parallel polished plates at a crosshead displacement speed of 1 mm min^{-1} . A total of five specimens were tested for each sample at room temperature. The compliance of the compression test equipment was found to be $1.8 \times 10^{-5} \text{ mm N}^{-1}$.

3.2.4.4 In-situ SEM micro-compression test of the foam templated macroporous polymers

In-situ SEM micro-compression test was performed using a micro-compression tester (Deben Microtest Stage, Suffolk, UK) equipped with a 5 kN load cell placed in an SEM chamber (Hitachi S-3700N, Tokyo, Japan). Prior to the test, cubic specimens of the macroporous polymers with dimensions of $10 \times 10 \times 10 \text{ mm}^3$ were cut and coated with Au (Agar Auto Sputter Coater, Essex, UK) at 40 mA for 1 min. The test specimens were then compressed at a crosshead displacement speed of 0.5 mm min^{-1} and the morphology of the compressed cubic test specimens were imaged every 30 s.

3.2.5 Characterisation of the resin-hardener mixture and the bulk polymers cured at different conditions

3.2.5.1 Viscosity of the resin-hardener mixture

The rheology of the resin-hardener mixture as a function of temperature and time after initial mixing was determined using a rotational rheometer (HAAKE MARS 60, Thermo Fisher Scientific, Hemel Hempstead, UK) equipped with a plate-plate (35 mm diameter) geometry. Prior to the test, the resin and hardener were mixed gently in a paper cup to avoid trapping air bubbles. Approximately 1 g of resin-hardener mixture was then placed between two parallel disposable aluminium plates and the gap between the plates was set to be 1 mm. Rheological characterisation was conducted in oscillatory mode at frequency and strain of 1 Hz and 0.5 %.

3.2.5.2 Compressive properties of the bulk polymers

The compressive properties of the bulk polymers were determined in accordance to ASTM D695–15 using an Instron universal tester (Model 5969, Norwood, USA). The load cell and crosshead displacement speed used were 50 kN and 1 mm min⁻¹. Prior to the test, the previously prepared cylindrical bulk polymer specimens were lathed and cut into cylinders with diameter and height of 12 mm and 24 mm. The test specimens were loaded in compression between two flat and parallel polished plates. A video extensometer (Imetrum Video Gauge, Bristol, UK) was used to monitor the strain of the test specimens. A total of five specimens were tested at room temperature for each sample.

3.2.5.3 Tensile properties of the bulk polymers

The tensile properties of the bulk polymers were determined in accordance to ASTM D638–14 using an Instron universal tester (Model 5969, Norwood, USA) equipped with a 1 kN load cell. The dumbbell-shaped test specimens possessed a gauge length of 25 mm. A total of five specimens were tested at room temperature for each sample at a crosshead displacement speed of 1 mm min⁻¹. The strain of the test specimens was monitored using a video extensometer (Imetrum Video Gauge, Bristol, UK).

3.2.5.4 Flexural properties of the bulk polymers

The flexural properties of the bulk polymers were determined in accordance to ASTM D790–15 using an Instron universal tester (Model 5969, Norwood, USA) equipped with a 1 kN load cell at room temperature. Prior to the test, the previously prepared bulk polymers were cut into rectangular specimens with dimensions of 100 × 9 × 5 mm³. The

span length used was 80 mm and the test specimens were loaded in 3-point bending mode at a crosshead displacement speed of 2 mm min⁻¹.

3.2.5.5 Molecular weight between crosslinks of the bulk polymers

The average molecular weight between crosslinks (M_c) of the bulk polymers cured at different conditions was estimated from the glass transition temperature (T_g) and the storage modulus of the rubbery plateau (E'_R) using the following equation [115]:

$$M_c = \frac{3\varphi\rho_s R(T_g + 40)}{E'_R} \quad (3.5)$$

where φ is the mean-square end-to-end chain distance in the polymer network over the chain distance in free space, which was found to be very close to 1 for cured epoxy resin [116]. R , T_g and E'_R are the universal gas constant (8.31 J mol⁻¹ K⁻¹), the glass transition temperature (based on the temperature at the peak of the $\tan \delta$ curve) [117] and the storage modulus of the rubbery plateau evaluated at $T_g + 40$ K, respectively. The viscoelastic properties of the bulk polymers were determined using dynamic mechanical thermal analysis (DMTA) (RSA-G2, TA Instruments, New Castle, UK) conducted on test specimens with dimensions of 30 × 5 × 1.5 mm³ in 3-point bending mode (span = 25 mm). The test specimens were heated from 25 °C to 150 °C at a rate of 5 °C min⁻¹. The frequency and strain amplitude used were 1 Hz and 0.005%.

3.3 Results and discussion

3.3.1 Density, porosity, and morphology of the macroporous polymers

The SEM images of the foam templated polymers cured at various conditions are shown in Figure 3-1 and the foam density (ρ_f), porosity (P), open cell content (O_v), average pore diameter (D_{pore}), mean pore wall thickness (t_{wall}), average pore throat diameter (D_{throat}) and pore throat frequency (f_{throat}) of the fabricated macroporous polymers are summarised in Table 3-1. Spherical pores can be observed for all samples, which is a direct result of the trapped air bubbles reaching equilibrium with the surrounding resin prior to gelation as spherical shape minimises surface tension.

Table 3-1. Density, porosity and morphological properties of the macroporous polymers. ρ_f , P , O_v , D_{pore} , t_{wall} , D_{throat} and f_{throat} denote foam density, porosity, open cell content, average pore diameter, mean pore wall thickness, average pore throat diameter and pore throat frequency, respectively

Sample	ρ_f (g cm ⁻³)	P (%)	O_v (%)	D_{pore} (μm)	t_{wall} (μm)	D_{throat} (μm)	f_{throat} (%)
0	0.35 ± 0.02	71 ± 2	2 ± 1	152 ± 114	28 ± 1	18 ± 6	4
1-A	0.31 ± 0.01	74 ± 1	15 ± 1	181 ± 135	30 ± 1	23 ± 9	13
1-B	0.28 ± 0.01	77 ± 1	16 ± 1	187 ± 144	27 ± 1	31 ± 14	17
1-C	0.26 ± 0.02	78 ± 1	24 ± 1	187 ± 143	26 ± 1	36 ± 28	20
2-A	0.21 ± 0.01	82 ± 1	30 ± 1	229 ± 161	25 ± 1	56 ± 34	28
2-B	0.20 ± 0.01	83 ± 1	28 ± 1	248 ± 159	26 ± 1	56 ± 34	24
2-C	0.18 ± 0.01	85 ± 1	29 ± 1	352 ± 277	33 ± 1	89 ± 53	27

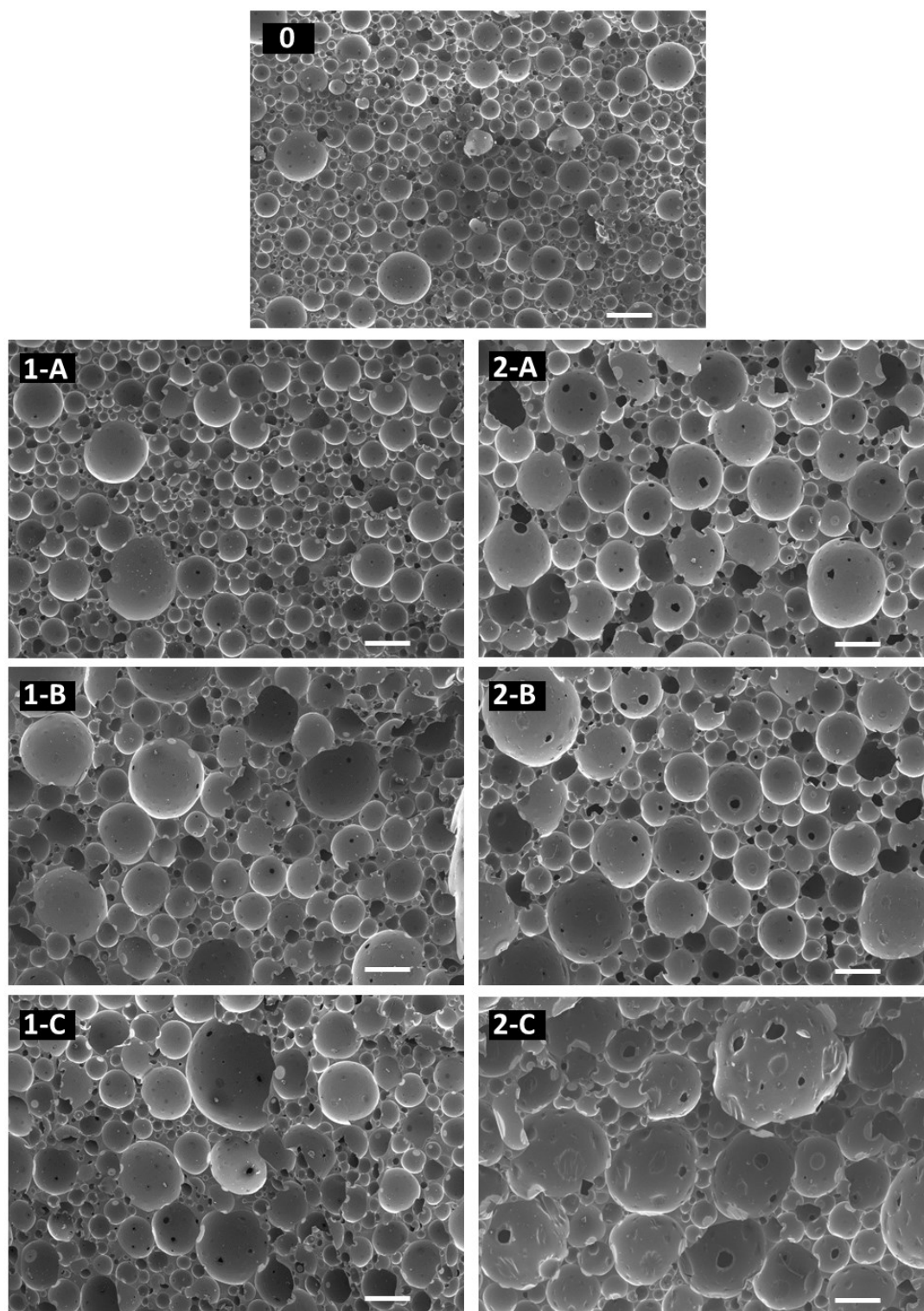


Figure 3-1. Scanning electron micrographs of the foam templated macroporous polymers. Sample **0**: cure at room temperature for 24 h and post-cure at 40 °C for 24 h. **1** and **2** represent standing time at room temperature of 1 h and 30 min after initial mixing, respectively. **A**, **B** and **C** represent polymerising temperature of 80 °C, 100 °C and 120 °C, respectively. The scale bar represented by the solid line is 500 μm .

Air-in-resin liquid foam cured at room temperature for 24 h followed by post curing at 40 °C for another 24 h (sample **0**) possessed a porosity of 71 % and average pore diameter (D_{pore}) of 152 μm . By reducing the time after initial mixing of the air-in-resin liquid foam at room temperature to only 1 h before curing at elevated temperatures of 80 °C (sample **1-A**), 100 °C (sample **1-B**) and 120 °C (sample **1-C**), the porosity of the resulting macroporous polymers increased up to 78 %. This is accompanied by an increase in D_{pore} of the macroporous polymers from 152 μm for sample **0** to 187 μm for sample **1-C**.

A further reduction in the time after initial mixing of the air-in-resin liquid foam to only 30 min before curing at elevated temperatures of 80 °C (sample **2-A**), 100 °C (sample **2-B**) and 120 °C (sample **2-C**) increased the porosity of the resulting macroporous polymers further up to 85%, with a D_{pore} of 352 μm (sample **2-C**). These results can be attributed to the air-in-resin liquid foams 30 min and 1 h after initial mixing have not reaching their gelation point prior to heating, as well as the increase in pressure inside the air bubbles of the liquid foams upon heating. This leads to the expansion of the air bubbles trapped in the air-in-resin liquid foam, producing macroporous polymers with higher porosity and larger D_{pore} .

In addition to this, the viscosity of the resin also decreased upon heating of the air-in-resin liquid foam prior to gelation (see Figure 3-2). The viscosity of the resin-hardener mixture left to cure at room temperature (Figure 3-2(a), correspond to sample **0**) increased exponentially after initial mixing. This increase is consistent with the viscosity of epoxy resin systems as a function of time reported in the literature [118-120]. The

viscosity of resin-hardener mixtures dropped sharply upon heating initially, followed by vitrification of the resin (a sharp increase in viscosity). The initial decrease in viscosity further aided the expansion of the air bubbles at elevated temperatures. Phase separation of liquid foams could potentially occur upon heating as the viscosity of the liquid decreases, leading to air bubble coalescence. Nevertheless, this was not observed due to the short time (less than 8 min) between viscosity decrease upon heating and the vitrification of the resin system. This prevented the complete phase separation of the air-in-resin liquid foam prior to resin vitrification.

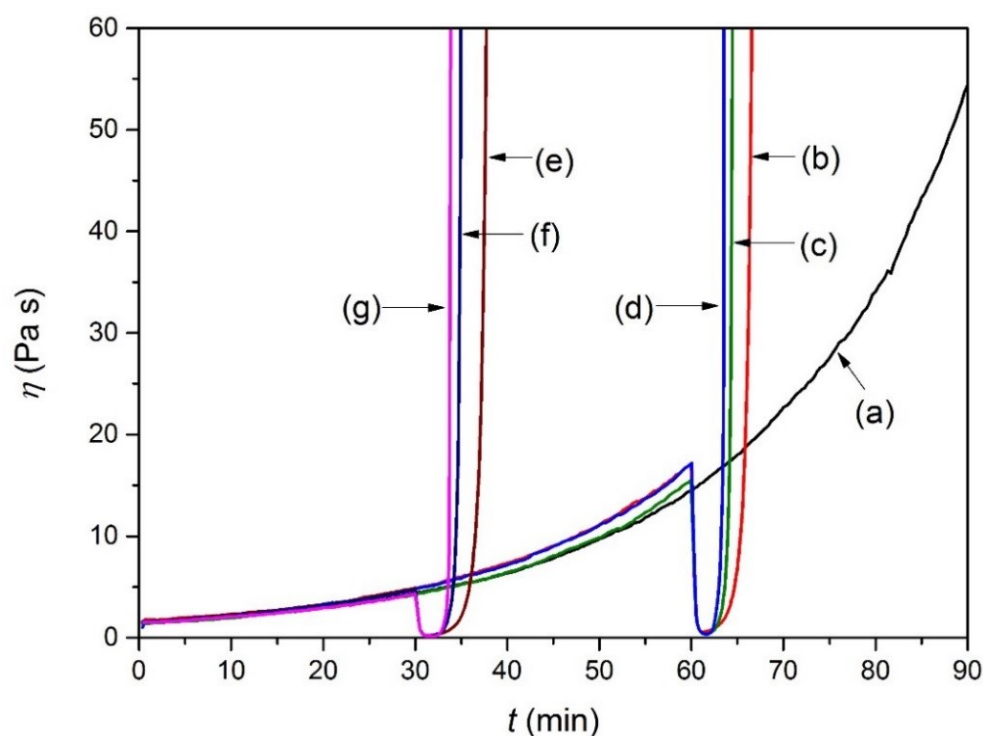


Figure 3-2. Viscosity (η) of the resin-hardener mixture polymerised at different conditions. (a) cure at room temperature, corresponding to sample **0**. (b), (c) and (d) cure at room temperature for 1 h and post-cure at 80 °C, 100 °C and 120 °C, respectively, corresponding to samples **1-A**, **1-B** and **1-C**, respectively. (e), (f) and (g) cure at room temperature for 30 min and post-cure at 80 °C, 100 °C and 120 °C, respectively, corresponding to samples **2-A**, **2-B** and **2-C**, respectively.

Pore throats can also be observed on all samples. A pre-requisite for pore throat formation is the rupture of the thin pore walls between two adjacent pores [121, 122]. The formation of pore throats in foam templated macroporous polymers can also be attributed to the incomplete coalescence of two air bubbles during curing [10]. Sample **0** possessed a pore throat diameter (D_{throat}) and pore throat frequency (f_{throat}) of 18 μm and 4%. By reducing the time after initial mixing to 1 h followed by curing at elevated temperatures, D_{throat} and f_{throat} increased to 23 μm and 13 % for sample **1-A**, 31 μm and 17 % for sample **1-B** and 36 μm and 20 % for sample **1-C**. The open cell content (O_V) also increased from 2% (sample **0**) to ~20% (samples **1**). This is due to the expansion of air bubbles at elevated temperatures, causing the adjacent bubbles to touch and coalesce. As the viscosity of the resin decreased only for a short period of time before resin vitrification occurred, the coalescence of the air bubbles was incomplete, leading to the formation of pore throats and an increase in D_{throat} and f_{throat} , as well as an increase in the open cell content of the macroporous polymers. Comparing samples **1** and **2**, D_{throat} , f_{throat} and O_V of samples **2-A**, **2-B** and **2-C** increased as the resin viscosity of samples **2** upon heating was lower (due to shorter time after initial mixing) than samples **1** and **0**. It should be noted that the macroporous polymers fabricated were not air permeable as the pores observed were only partially interconnected.

3.3.2 Compressive properties of the macroporous polymers

The representative compression stress-strain curves of the foam templated macroporous polymers are shown in Figure 3-3. All the curves possess three characteristic regions: (i) a linear elastic region of up to ~5 % strain, (ii) a plateau region where the stress remained

almost constant with increasing strain and (iii) a densification region where the compressive stress increased rapidly again. In the linear elastic region, the macroporous polymers deformed reversibly via pore wall bending [99]. When the force applied on the pore walls (struts) exceeded the plastic moment, the macroporous polymer yielded [123, 124]. At this point, the pore walls (struts) were bent plastically and the deformation of the macroporous polymers was no longer recoverable upon removal of the applied stress. After yielding, the compressive stress of the macroporous polymers stayed constant with increasing strain. This indicates that the presence of air trapped in the pores has little or no effect on the compressive properties of these macroporous polymers [99]. In the densification region of the stress-strain curves, most of the pores were completely crushed and the porous polymers behave like bulk polymers, causing the steep increase of stress with increasing strain.

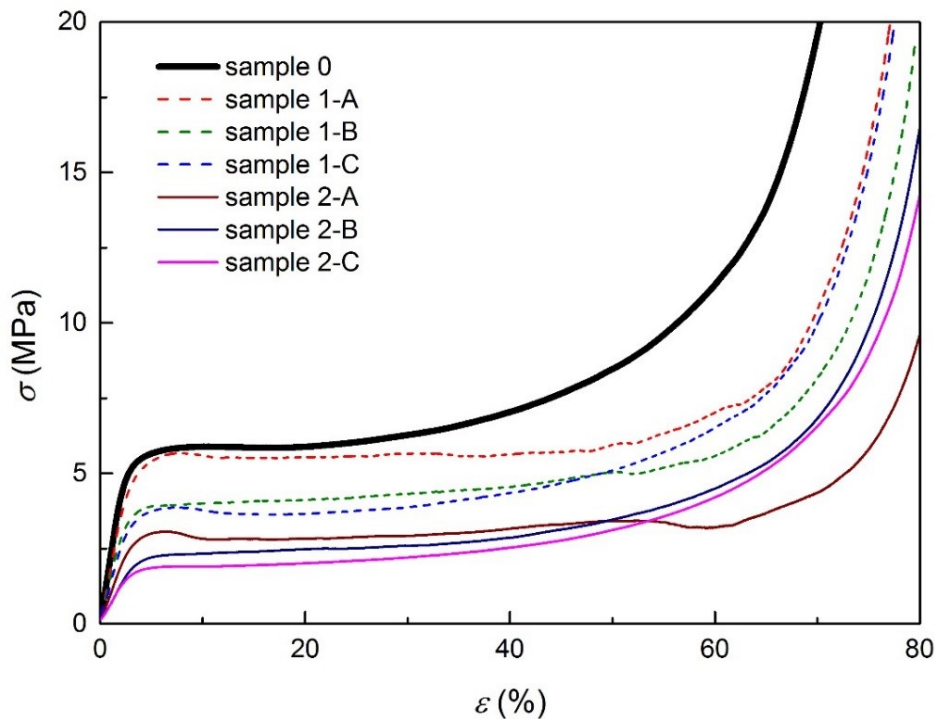


Figure 3-3. Representative compressive stress (σ) – strain (ε) curves of the foam templated macroporous polymers.

The compressive properties of the macroporous polymers cured at different conditions are summarised in Table 3-2. Sample **0** possessed compressive modulus (E) and strength (σ) of 231 MPa and 5.9 MPa. By reducing the time after initial mixing to 1 h before curing at elevated temperatures, the compressive properties of the resulting macroporous polymers decreased to $E = 125$ MPa and $\sigma = 3.8$ MPa (sample **1-C**). A further reduction of the time after initial mixing to only 30 min before curing at elevated temperatures further reduced the compressive properties of the macroporous polymers to $E = 58$ MPa and $\sigma = 1.9$ MPa (sample **2-C**).

Table 3-2. Compressive properties of the foam templated macroporous polymers. E_{cf} and σ_{cf} denote the compressive modulus and compressive strength

Sample	E_{cf} (MPa)	σ_{cf} (MPa)
0	231 ± 17	5.9 ± 0.7
1-A	184 ± 10	5.4 ± 0.3
1-B	146 ± 4	4.5 ± 0.1
1-C	125 ± 16	3.8 ± 0.5
2-A	95 ± 3	2.7 ± 0.2
2-B	73 ± 11	2.2 ± 0.3
2-C	58 ± 10	1.9 ± 0.1

To ascertain whether the changes in the curing conditions of the air-in-resin liquid foam affected the compressive properties of the foam templated macroporous polymers, the degree of crosslinking of the bulk polymers cured at different conditions was evaluated. The average molecular weight between crosslinks (M_c) of the bulk polymers were estimated from the viscoelastic properties (see Figure 3-4). M_c reduced with increasing polymerisation temperature (see Table 3-3). This is also accompanied by an increase of the glass transition temperature (T_g) of sample **0** from ~ 65 °C to ~ 91 °C for the rest

samples. This is due to the formation of more crosslinks when the curing temperature was increased and a higher degree of crosslinking results in a higher T_g and a lower M_c .

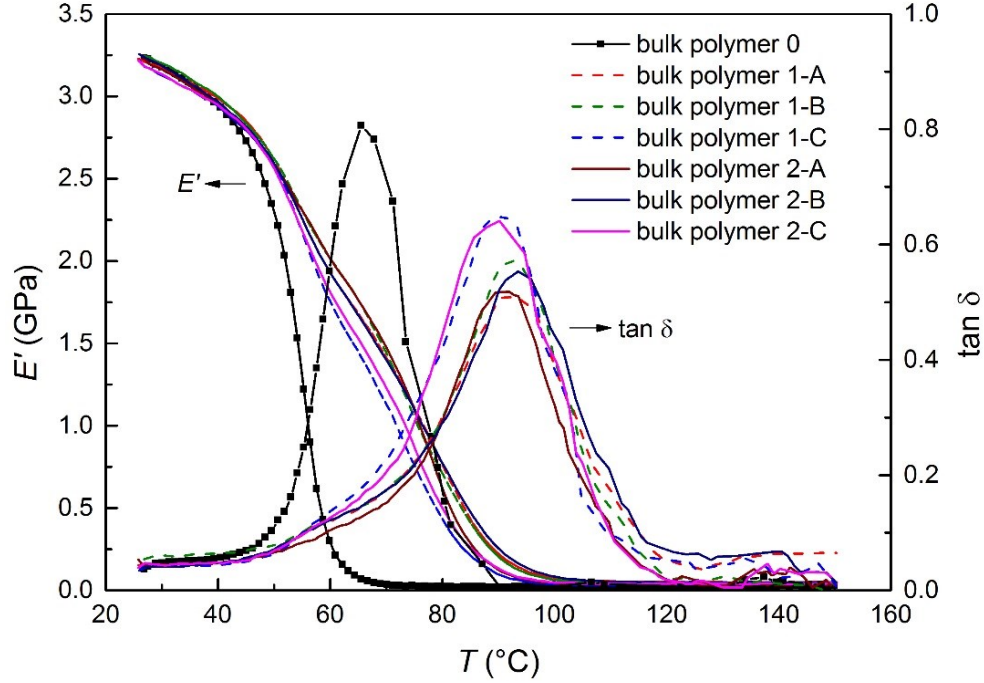


Figure 3-4. Viscoelastic properties of the bulk polymers polymerised at different conditions. E' and T represent storage modulus and temperature, and $\tan \delta$ is the ratio of loss modulus to storage modulus.

Table 3-3. Viscoelastic properties of the bulk polymers. E' , E'_R , T_g and M_c denote the storage modulus at room temperature, the storage modulus of the rubbery plateau evaluated at $T_g + 40$ K, the glass transition temperature and the molecular weight between crosslinks, respectively

Sample	E' (GPa)	E'_R (MPa)	T_g (° C)	M_c (g/mol)
0	3.23 ± 0.02	26.9 ± 1.6	65.8 ± 0.2	416 ± 25
1-A	3.08 ± 0.29	44.2 ± 5.9	92.8 ± 0.1	273 ± 37
1-B	3.10 ± 0.20	45.5 ± 5.2	92.3 ± 0.1	264 ± 30
1-C	3.13 ± 0.17	37.1 ± 3.9	89.3 ± 0.9	321 ± 33
2-A	2.92 ± 0.23	43.2 ± 2.1	91.0 ± 0.7	276 ± 13
2-B	2.96 ± 0.48	44.9 ± 5.2	93.1 ± 0.1	268 ± 31
2-C	3.05 ± 0.29	38.0 ± 4.5	91.3 ± 0.9	316 ± 36

Nevertheless, the difference in M_c was not significant amongst all samples. This is also consistent with the mechanical properties of these bulk polymers (see Table 3-4). Sample **0** possessed compressive modulus and strength of 3.2 GPa and 82 MPa, tensile modulus and strength of 2.6 GPa and 52 MPa, and flexural modulus and strength of 2.5 GPa and 70 MPa. By curing the bulk polymers at various conditions, no significant differences in the mechanical properties of the bulk polymers can be observed. This further ascertains that the mechanical properties of the pore wall materials of the foam templated macroporous polymers cured under different conditions are also similar to each other.

Table 3-4. Mechanical properties of the bulk polymers. E_C , σ_C , E_T , σ_T , E_F and σ_F denote compressive modulus and strength, tensile modulus and ultimate strength, flexural modulus and ultimate strength, respectively

Sample	E_C (GPa)	σ_C (MPa)	E_T (GPa)	σ_T (MPa)	E_F (GPa)	σ_F (MPa)
0	3.2 ± 0.1	82 ± 1	2.6 ± 0.1	52 ± 1	2.5 ± 0.1	70 ± 2
1-A	3.2 ± 0.2	84 ± 1	2.5 ± 0.1	57 ± 1	2.6 ± 0.1	89 ± 1
1-B	2.9 ± 0.1	81 ± 1	2.5 ± 0.1	55 ± 1	2.5 ± 0.1	80 ± 2
1-C	3.0 ± 0.1	79 ± 1	2.6 ± 0.1	54 ± 1	2.6 ± 0.1	85 ± 2
2-A	3.2 ± 0.2	83 ± 1	2.5 ± 0.1	56 ± 1	2.8 ± 0.1	90 ± 2
2-B	2.9 ± 0.1	80 ± 1	2.5 ± 0.1	55 ± 1	2.5 ± 0.1	72 ± 4
2-C	3.1 ± 0.2	80 ± 1	2.5 ± 0.1	52 ± 1	2.7 ± 0.1	85 ± 2

3.3.3 In-situ SEM micro-compression test of the macroporous polymers

The mechanical properties of porous materials are also influenced by their pore structures [108-111, 125, 126]. Therefore, in-situ SEM micro-compression test was carried out to investigate the micro-deformation process of the fabricated macroporous polymers. Exemplarily images of samples **0** and **2-C** are shown in Figure 3-5(a) and (b), respectively. When the strain of the test specimens was low, both samples deformed elastically and no visible cracks can be seen (Figure 3-5(a-1) and (b-1)). As the strain increased, small cracks can be observed in Figure 3-5(a-2) and (b-2) (see arrows). Corrugations on the pore walls of sample **2-C** can also be seen. A further increase in strain of the samples led to the propagation and joining of cracks, forming localised crack lines (Figure 3-5(a-3) and (b-3)). The previously observed corrugation in sample **2-C** fractured. At this point, both samples started to yield due to the irreversible displacement along the localised crack lines. The propagation of the cracks continued and the localised crack lines joined together throughout the samples (Figure 3-5(a-4) and (b-4)). Beyond this specimen strain, the pores along the crack lines were crushed and these crack lines became crush bands. These bands are generally perpendicular to the compression direction [127, 128].

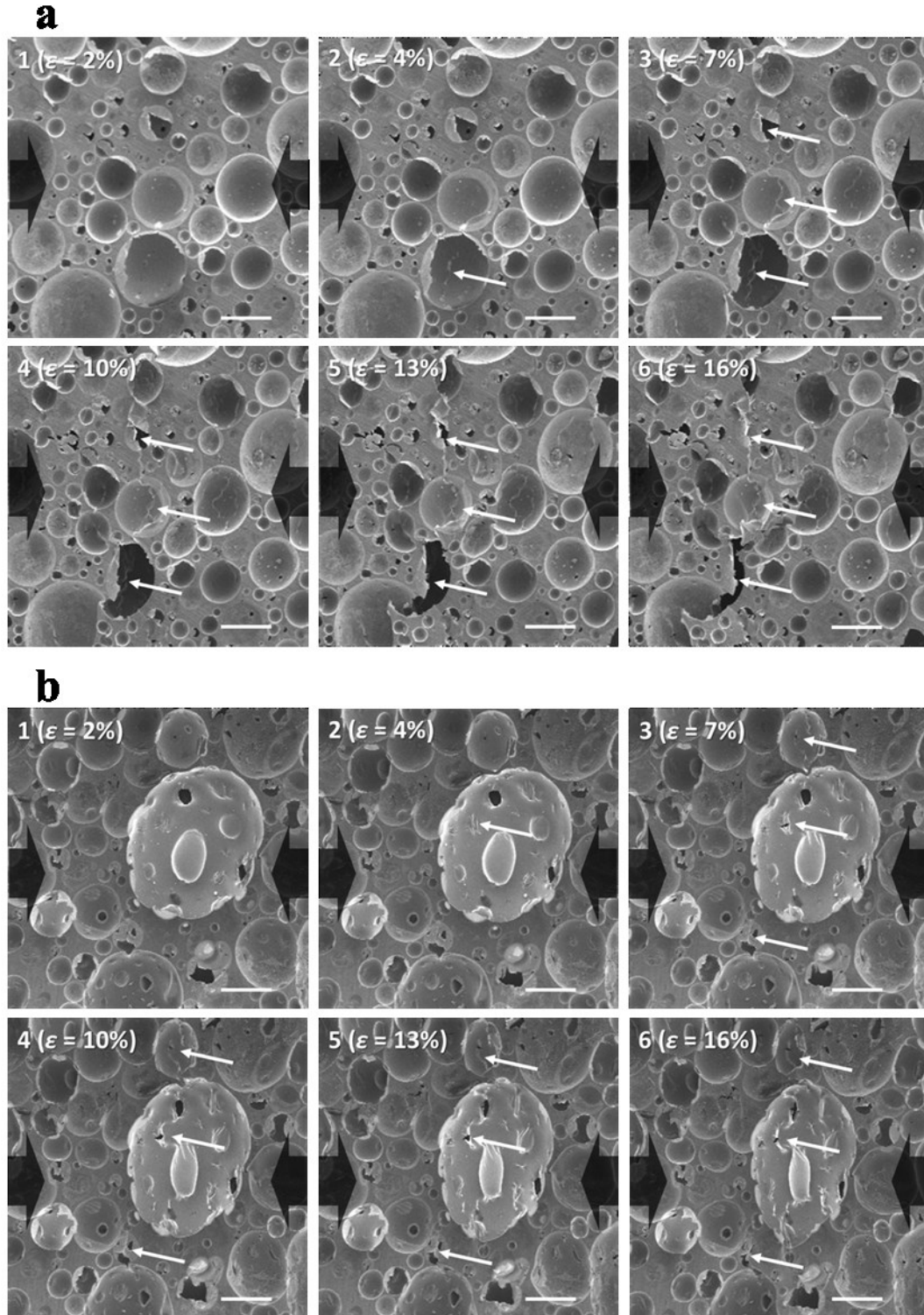


Figure 3-5. SEM images of in-situ micro-compression test on (a) sample **0** and (b) sample **2-C**. The black arrow represents the loading direction and the white arrow indicates the cracks and corrugations. The scale bar represented by the white solid line is 500 μm .

3.3.4 Discussion: The effect of different curing conditions on the compressive properties of foam templated macroporous polymers

Different curing conditions of the initial air-in-resin liquid foams led to the fabrication of macroporous polymers with different foam densities, pore throat frequencies and pore diameters. Ashby-Gibson model showed that the compressive properties of macroporous polymers are dependent only on the relative density, ρ_f/ρ_s , of the macroporous polymers. Table 3-5 summarises the normalised compressive properties of the fabricated foam templated macroporous polymers. The compressive modulus and strength of the macroporous polymers are normalised against ρ_f^2 and $\rho_f^{1.5}$, respectively [99]. It can be seen from this table that the normalised compressive properties of the macroporous polymers are similar for all samples. As no significant difference was observed in the mechanical properties of the pore wall materials, the reduction in the compressive properties of the fabricated macroporous polymers can be mainly attributed to the reduction in the density of the macroporous polymers.

Table 3-5. Normalised compressive properties of the foam templated macroporous polymers. E_{cf} , σ_{cf} and ρ_f denote compressive modulus, strength and foam density of the macroporous polymers, respectively.

Sample	$\frac{E_{cf}}{\rho_f^2} (\text{MPa cm}^6 \text{ g}^{-2})$	$\frac{\sigma_{cf}}{\rho_f^{1.5}} (\text{MPa cm}^{4.5} \text{ g}^{-1.5})$
0	1908 ± 133	28.4 ± 0.8
1-A	1951 ± 64	31.8 ± 0.5
1-B	1872 ± 99	30.8 ± 0.6
1-C	1830 ± 363	28.3 ± 1.7
2-A	2139 ± 93	27.7 ± 1.2
2-B	1778 ± 188	24.3 ± 1.9
2-C	1713 ± 259	24.4 ± 0.9

In addition to this, the reduction in compressive properties of the macroporous polymers cured at different conditions can also be attributed to the increase in pore throat frequency when the time after initial mixing of the air-in-resin liquid foam is reduced and the curing temperature is increased. Pore throats can be regarded as flaws on the pore walls and cracks can easily form and propagate from the pore throats. Many of the cracks observed in sample **2-C** (Figure 3-5b) were initiated from pore throats and the crack line passed through these pore throats. Since the pore throat frequency increased with increasing the porosity of the macroporous polymers, the presence of pore throats further reduced the compressive properties of the fabricated macroporous polymers.

The pore deformation of the foam templated macroporous polymers was also studied. Figure 3-6 shows the degree of pore deformation, defined as the ratio between the horizontal and vertical Feret diameters of the pores, F_h/F_v , for 2 different pore sizes of all samples. A F_h/F_v value of unity and zero correspond to perfect spheres (as-fabricated pore) and a line (fully crushed pore), respectively. It can be seen from this figure that larger pore deformed more compared to smaller pores. Several pore deformation mechanisms have been proposed, including pore wall buckling, stretching and bending [129, 130]. Considering the relatively high foam density ($\sim 0.3 \text{ g cm}^{-3}$) of the fabricated macroporous polymers, pore wall bending is considered to be the dominant pore deformation mechanism [131]. It can be anticipated that the deflection of the pore wall materials at a given load will be larger for larger pores. This implies that macroporous polymers with larger D_{pore} will deform easier than macroporous polymers with smaller D_{pore} . Similar observations were also observed by other researchers [106, 107], whereby the fracture of a macroporous polymer initiates from pores of larger diameter.

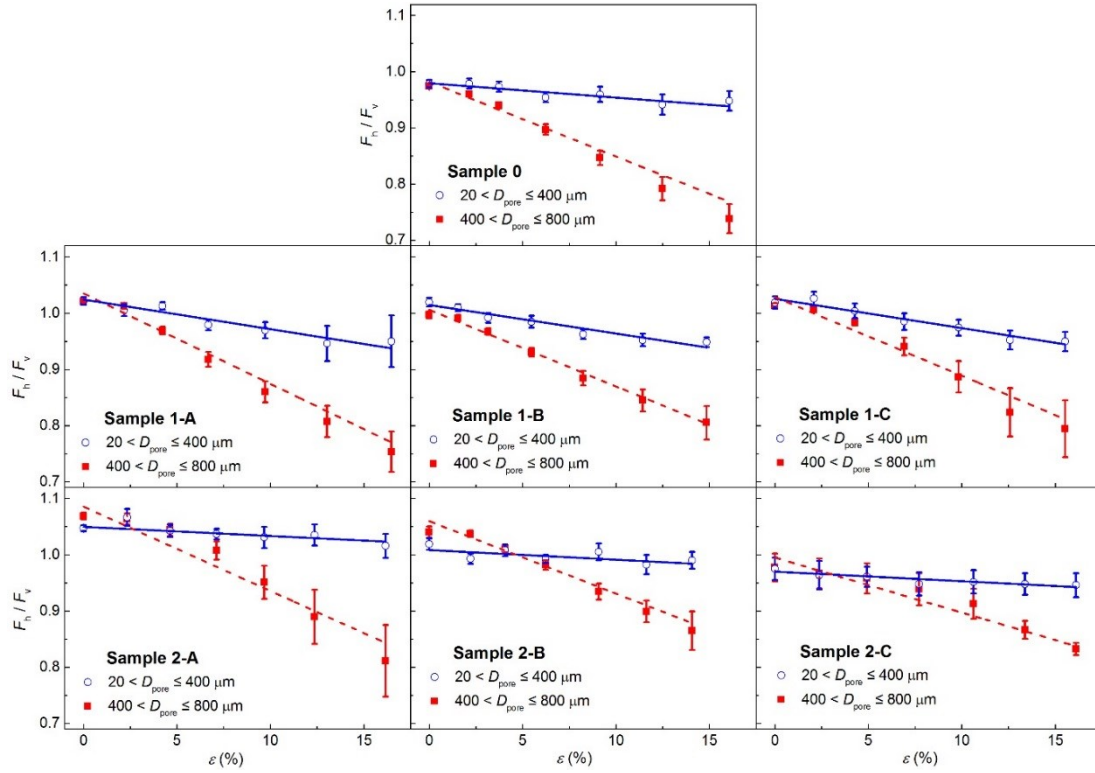


Figure 3-6. Deformation of pores with different diameter. F_h and F_v denote horizontal and vertical Feret diameter. A F_h/F_v value of unity and zero correspond to perfect spheres (as-fabricated pore) and a line (fully crushed pore), respectively. D_{pore} is the average pore diameter.

3.4 Concluding remarks

High performance macroporous polymers can be produced using a simple blowing agent- and stabiliser-free foam-templating method. In this chapter, the porosity of the foam templated macroporous polymers has been successfully increased from 71% to as high as 85% by heating the air-in-resin liquid foam prior to its gelation. The heating of this liquid foam decreased the viscosity of the resin surrounding the air bubbles and increased the pressure inside the air bubbles, leading to the isotropic expansion of air bubbles trapped within the liquid foam. It was also observed that the increase in porosity of the

macroporous polymers was also accompanied by an increase in average pore diameter and pore throat frequency.

The fabricated macroporous polymers also possessed high compressive properties. Macroporous polymers with a porosity of 71% possessed compressive modulus and strength of 231 MPa and 5.9 MPa. The compressive modulus and strength of macroporous polymers decreased to 58 MPa and 1.9 MPa, when the porosity was increased to 85%. The average molecular weight between crosslinks, compression, tension and flexural properties of the pore wall materials were found to be similar for all samples. In situ SEM micro-compression tests showed larger pores deformed more compared to smaller pores and the cracks were more likely to initiate from the pore throats of the macroporous polymers. Therefore, the decrease in compressive properties of the foam templated macroporous polymers is due to the decrease in foam density and the increase in pore throat frequency.

Chapter 4 Enhancing the fracture resistance and impact toughness of epoxy foams with hollow elastomeric microspheres

4.1 Introduction

In the previous chapter, the porosity of the foam templated macroporous polymers has been successfully increased from 71% to 85%. The increase in porosity led to a decrease in the compressive properties from $E = 231$ MPa and $\sigma = 5.9$ MPa to $E = 58$ MPa and $\sigma = 1.9$ MPa. These epoxy foams can be used for structural applications, and one major concern is the inherent brittleness stemming from the inflexible and highly cross-linked epoxy network [132]. Therefore, it is necessary to reduce the brittleness of epoxy foams, and this challenge will be addressed in this chapter.

Various research effort has been poured into enhancing the toughness of epoxy foams. Typically, a second phase consisting of soft and non-porous elastomeric particles [44, 133, 134] is added into the epoxy foams to reduce their brittleness and increase their fracture toughness or fracture resistance. However, the increase in toughness and fracture resistance of non-porous elastomeric particle filled epoxy foams is often at the expense of their quasi-static compressive properties. For instance, the addition of 2 vol.-% 40 μm and 75 μm rubber particles derived from tire waste improved the compressive fracture strain and energy absorption (evaluated from the area under the compressive stress-strain curves) of syntactic epoxy foam compared to un-filled foam at the same relative density

[135]. The quasi-static compressive modulus and strength of these rubber particle filled syntactic epoxy foams, on the other hand, decreased by 50% and 10% compared to unfilled syntactic epoxy foams. Similar results were also observed for poly(dimethylsiloxane) (PDMS) particle [136] filled syntactic epoxy foams. The toughness (evaluated from the area under the flexural stress-strain curves) of syntactic epoxy foams filled with 7 vol.-% PDMS particles improved by up to 2.5 times but their compressive strength decreased by 20% compared to unfilled syntactic epoxy foams. This is a direct result of using soft and non-porous elastomeric particles which are inherently inferior in compressive properties, leading to a significant reduction in the quasi-static compressive properties of the elastomeric particle filled epoxy foams.

Therefore, a new strategy to enhance the fracture resistance and impact toughness of epoxy foams without sacrificing their quasi-static compressive properties is needed. Due to the higher specific surface area per unit mass of hollow elastomeric microspheres compared to their non-porous counterparts, which is an essential energy-absorbing feature to enhance the fracture toughness/resistance of materials via filler-epoxy matrix de-bonding, it can be envisaged that hollow elastomeric microspheres will also serve as excellent toughening agent for epoxy foams. Moreover, the hollow microspheres will form part of the pore structures, instead of reducing the mechanical properties of the pore wall material of the epoxy foams, so the quasi-static compressive properties should be preserved. Therefore, in this chapter, the epoxy foam was toughened by hollow elastomeric microspheres and the fracture resistance and Charpy impact toughness enhancement was reported.

4.2 Experimental

4.2.1 Materials

Epoxy resin with 56 % biomass content (Greenpoxy 56, $\rho = 1.20 \pm 0.01 \text{ g cm}^{-3}$, $\eta = 2500 \text{ mPa s}$ at $15 \text{ }^{\circ}\text{C}$) and amine-based hardener with 58 % biomass content (GP 505 v2, $\rho = 0.99 \pm 0.01 \text{ g cm}^{-3}$, $\eta = 1800 \text{ mPa s}$ at $15 \text{ }^{\circ}\text{C}$) were purchased from Matrix Composite Materials Company Ltd (Bristol, UK) and used as received. A commercial lightweight hollow poly(acrylonitrile-co-methacrylonitrile) elastomeric microsphere (Expancel 920 DE 40, $35 < D_{0.5} < 55 \text{ }\mu\text{m}$, $\rho = 0.03 \pm 0.01 \text{ g cm}^{-3}$) was kindly provided by AkzoNobel (Sundsvall, Sweden) and used as the toughening agent for epoxy foams.

4.2.2 Manufacturing of (hollow elastomeric microsphere filled) epoxy foams

Epoxy foams were prepared using foam templating method following a previously described procedure [137]. Briefly, 70 g of epoxy resin and 29.4 g of amine-based hardener were added into a 2 L Pyrex glass bowl and mechanically frothed using a hand mixer (HM730B, Sainsbury's, London, UK). To prepare the control sample (sample **M0**), the epoxy resin and amine-based hardener were mechanically frothed for 20 min at maximum power output of 200 W. The air-in-resin liquid foam was then poured into either self-standing Falcon[®] tubes of 25 mm in diameter and 115 mm in height, or rectangular mould with dimensions of $110 \times 100 \times 25 \text{ mm}^3$ and left to cure at room temperature for 24 h.

To produce lightweight hollow elastomeric microsphere filled epoxy foams, the resin-hardener mixture were first mechanically frothed for 15 min at maximum power output of 200 W, followed by the addition of the lightweight hollow elastomeric microspheres and further frothed for another 5 min at lower power output of 80 W to produce 0.5 wt.-% and 1 wt.-% hollow elastomeric microsphere filled epoxy foams. These foams were transferred to the same moulds and cured at the same conditions as control sample. These samples were designated as samples **M0.5** and **M1**, respectively

4.2.3 Characterisation of the (hollow elastomeric microsphere filled) epoxy foams

4.2.3.1 Density and porosity of the (hollow elastomeric microsphere filled) epoxy foams

The envelope density of the epoxy foams (ρ_f) was calculated by dividing the mass of each specimen by its envelope volume, calculated from the measured diameter and height of cut cylindrical specimens. To obtain the true density of the solid epoxy matrix (ρ_s), the fabricated epoxy foams were milled into powder using a jet mill (Picojet 40 AFG, Hosokawa Alpine, Augsburg, Germany) with 5 bar of compressed air. ρ_s was then determined using a He pycnometry (Accupyc II 1340, Micromeritics Ltd, Hexton, UK) and the porosity (P) of the fabricated epoxy foams was calculated using:

$$P = \left(1 - \frac{\rho_f}{\rho_s}\right) \times 100\% \quad (4.1)$$

4.2.3.2 Structure and morphology of the (hollow elastomeric microsphere filled) epoxy foams

The structure and morphology of the (hollow elastomeric microsphere filled) epoxy foams were investigated using a scanning electron microscope (SEM) (Hitachi S-3700N, Tokyo, Japan) operating at an accelerating voltage of 5 kV. Prior to SEM, the epoxy foams were cut into cylinders (diameter = 25 mm and height = 5 mm) and broken by hand to reveal the internal structure. The specimens were then mounted onto aluminium stubs using carbon tabs and sputter coated with Au (Agar Auto Sputter Coater, Essex, UK) at 40 mA for 1 min. The average pore diameter (D_{pore}) was determined from these SEM images with a population size of 300 pores. The pore density (N_{p}) of the fabricated epoxy foams, defined as the number of pores per unit volume of foam, was calculated using:

$$N_{\text{p}} = \frac{6P}{\pi D_{\text{pore}}^3} \quad (4.2)$$

The microsphere density within the epoxy foam (N_{m}) was defined as the number of the hollow elastomeric microspheres per unit volume of foam, and was calculated using:

$$N_{\text{m}} = \frac{6\varphi}{\pi D_{\text{m}}^3} \cdot \frac{\rho_{\text{f}}}{\rho_{\text{m}}} \quad (4.3)$$

where φ is the weight ratio of the added microsphere to the resin and hardener; D_{m} is the average diameter; and ρ_{m} is the density of the hollow elastomeric microsphere.

4.2.3.3 Fracture toughness of the (hollow elastomeric microsphere filled) epoxy foams

The fracture toughness of the epoxy foams was determined in accordance to ASTM D5045–14 on single edge notched beam (SENB) specimens loaded in 3-point bending mode with a span length of 80 mm. Prior to the test, the samples were cut into rectangular test specimens with dimensions of $100 \times 20 \times 10 \text{ mm}^3$. An initial crack of $\sim 10 \text{ mm}$ was introduced to the rectangular test specimens such that the initial crack length (a) to width (w) ratio fulfil the requirement of $0.45 \leq a/w \leq 0.55$. The initial crack length was created by cutting the first 8 mm with a band-saw and the last 2 mm with a sharp scalpel. The precise crack length value (a) was determined from analysis of the fracture surfaces after the fracture toughness test. The test was conducted using an Instron universal tester (Model 5969, Norwood, USA) equipped with a 1 kN load cell. The crosshead displacement speed was set to 1 mm min^{-1} . A total of five specimens for each sample were tested and the critical stress intensity factor (K_{1c}) was calculated using:

$$K_{1c} = \left(\frac{P_C}{bw^{0.5}} \right) f(a/w) \quad (4.4)$$

where P_C is the load at crack initiation, b is the thickness of the specimen, and $f(a/w)$ is given by:

$$f(a/w) = 6 (a/w)^{0.5} \frac{[1.99 - a/w(1-a/w)(2.15 - 3.93a/w + 2.7(a/w)^2)]}{(1+2a/w)(1-a/w)^{1.5}} \quad (4.5)$$

4.2.3.4 Charpy impact strength of the (hollow elastomeric microsphere filled) epoxy foams

Charpy impact test was used to quantify the impact strength of the (hollow elastomeric microsphere filled) epoxy foams. The test was conducted in accordance to ISO 179-1:2010 using a Charpy impact tester (Zwick 5102.100, Ulm, Germany) equipped with a 0.5 J pendulum. The impact velocity is 2.93 m s^{-1} . Unnotched rectangular specimens with dimensions of $50 \times 10 \times 10 \text{ mm}^3$ were placed on the supports with a span length of 40 mm. A total of 5 specimens were tested for each sample. The frictional loss was found to be 0.007 J.

4.2.3.5 Compressive properties of the (hollow elastomeric microsphere filled) epoxy foams

The compressive properties of the (hollow elastomeric microsphere filled) epoxy foams were determined in accordance to ASTM D1621–10 using an Instron universal tester (Model 5969, Norwood, USA) equipped with a 50 kN load cell. Cylindrical specimens with both diameter and height of 25 mm were placed between two flat and parallel polished plates, and compressed at a crosshead displacement speed of 2.5 mm min^{-1} . A video extensometer (Imetrum Video Gauge, Bristol, UK) was used to monitor the strain in the test specimens. A total of 5 specimens were tested for each sample.

4.3 Results and discussion

4.3.1 Morphology of the (hollow elastomeric microsphere filled) epoxy foams

The envelop density (ρ_f) and porosity (P) of un-filled epoxy foam **M0** and hollow elastomeric microsphere filled epoxy foams **M0.5** and **M1** are identical at $0.37 - 0.40 \text{ g cm}^{-3}$ and $66-68\%$, respectively (see Table 4-1), as the weight fractions of the added hollow elastomeric microspheres were low. The internal morphology of the fabricated epoxy foams and their respective pore size distributions are presented in Figure 4-1 and Figure 4-2, respectively. Un-filled epoxy foam **M0** possessed a polydispersed spherical pore structure, characterised by a broad pore size distribution with an average pore diameter (D_{pore}) of $114 \pm 75 \text{ }\mu\text{m}$ (see Table 4-1). The spherical pore structure is a direct result that the introduced air bubbles achieving equilibrium with the surrounding liquid epoxy resin prior to the gelation, as spherical-shaped air bubbles minimises surface tension.

Table 4-1. Physical and morphological properties of the (hollow elastomeric microsphere filled) epoxy foams. ρ_f , P , D_{pore} , N_p and N_m denote the foam density, porosity, average pore diameter, pore density and microsphere density, respectively

Sample	$\rho_f \text{ (kg m}^{-3}\text{)}$	$P \text{ (\%)}$	$D_{\text{pore}} \text{ (}\mu\text{m)}$	$N_p \text{ (mm}^{-3}\text{)}$	$N_m \text{ (mm}^{-3}\text{)}$
M0	372 ± 14	68 ± 1	114 ± 75	854 ± 98	0
M0.5	400 ± 7	66 ± 1	70 ± 56	3660 ± 522	2533 ± 394
M1	388 ± 8	67 ± 1	56 ± 55	7402 ± 1116	4876 ± 759

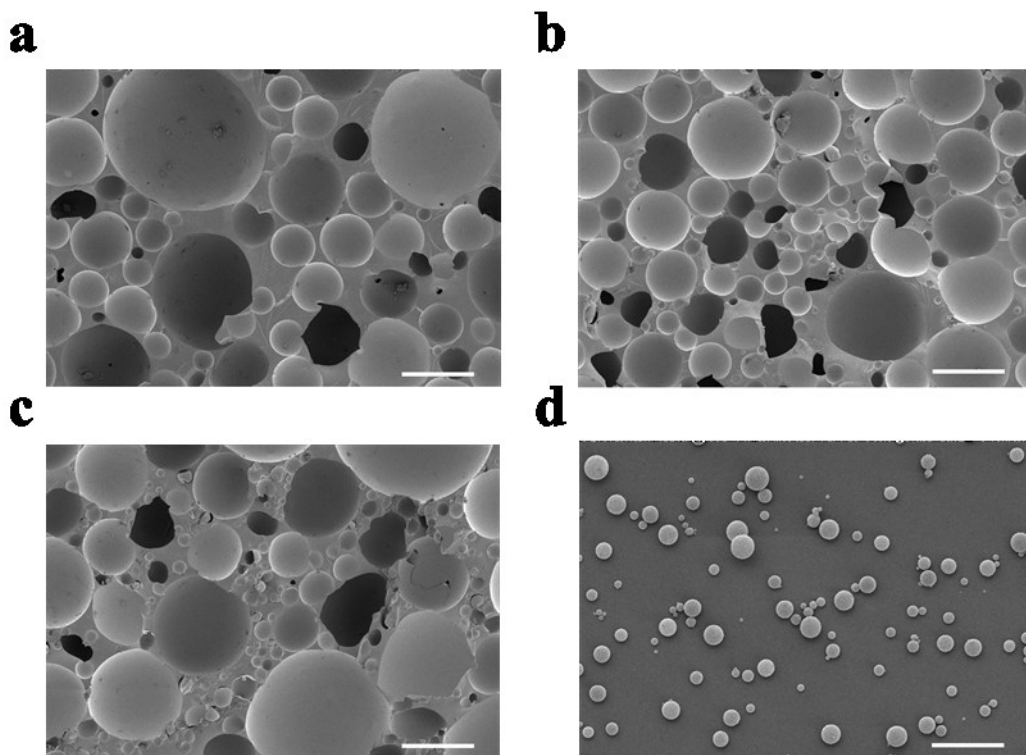


Figure 4-1. Scanning electron micrographs of the fabricated samples and hollow elastomeric microspheres used in this work. (a) Sample **M0** (neat and un-filled epoxy foam), (b) sample **M0.5** (0.5 wt.-% hollow elastomeric microsphere filled epoxy foam), (c) sample **M1** (1.0 wt.-% hollow elastomeric microsphere filled epoxy foam) and (d) hollow elastomeric microspheres. The scale bar represented by the solid line is 200 μm .

When the epoxy foams were filled with 0.5 wt.-% (**M0.5**) and 1.0 wt.-% (**M1**) hollow elastomeric microspheres, the spherical pore morphology was preserved but D_{pore} decreased to $70 \pm 56 \mu\text{m}$ and $56 \pm 55 \mu\text{m}$ (see Table 4-1). This is due to the addition of the hollow elastomeric microspheres, which possessed an average microsphere diameter of only $37 \pm 17 \mu\text{m}$. The number of hollow elastomeric microspheres added per unit volume of epoxy foam (N_m) into **M0.5** and **M1** was estimated to be $2533 \pm 394 \text{ mm}^{-3}$ and $4876 \pm 759 \text{ mm}^{-3}$ (see Table 4-1). This value is significantly higher than the pore density (defined as the number of pores per unit volume of the epoxy foam) of **M0** (see

Table 4-1), resulting in a decrease in pore size, as well as narrowing of the pore size distributions of **M0.5** and **M1**. However, due to the large N_m into **M1**, agglomeration of the hollow elastomeric microspheres could also be observed (see Figure 4-1(c)). It should be noted that no significant agglomeration of hollow elastomeric microspheres was observed in sample **M0.5**.

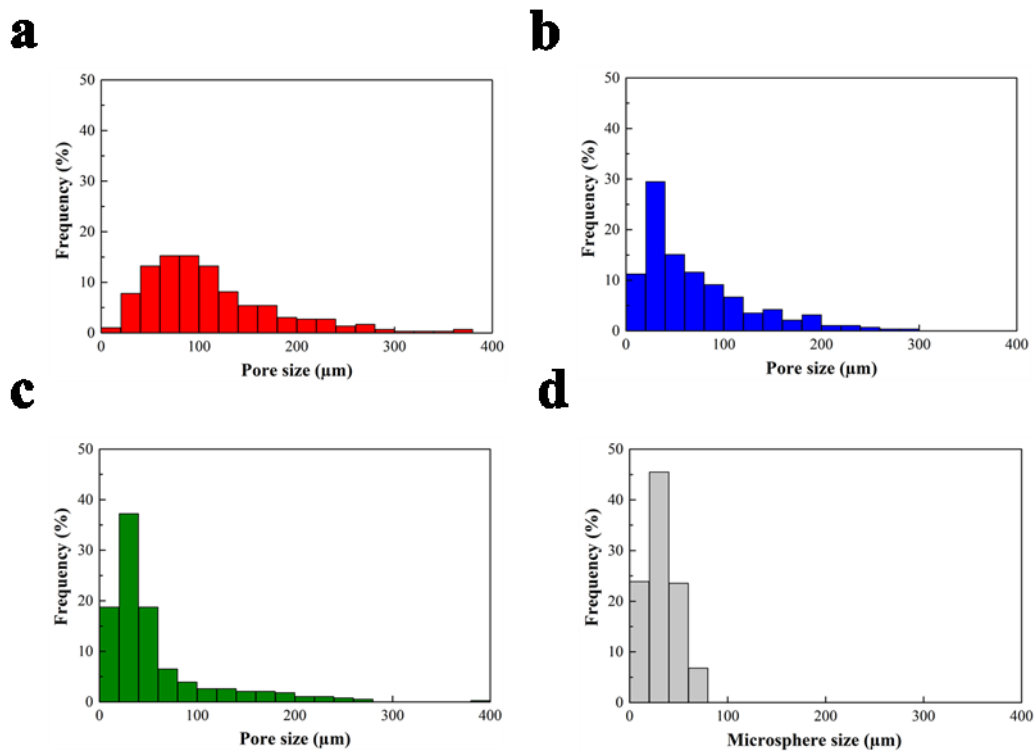


Figure 4-2. Pore size distribution of the fabricated samples and microsphere size distribution of the hollow elastomeric microspheres used in this work. (a) Sample **M0** (neat and un-filled epoxy foam), (b) sample **M0.5** (0.5 wt.-% hollow elastomeric microsphere filled epoxy foam), (c) sample **M1** (1.0 wt.-% hollow elastomeric microsphere filled epoxy foam) and (d) hollow elastomeric microspheres. The bin size is 20 μm.

4.3.2 Fracture toughness of the (hollow elastomeric microsphere filled) epoxy foams

The fracture toughness of the (hollow elastomeric microsphere filled) epoxy foams was measured from single-edge notched test specimens loaded in three-point bending mode. Their representative load-displacement curves are shown in Figure 4-3. The initial linear part of the load-displacement curves corresponded to an elastic response while the softening part indicated crack propagation. It can be seen from this figure that compared to samples **M0** which failed catastrophically, hollow elastomeric microsphere toughened **M0.5** and **M1** exhibited a more progressive failure, indicating that the added microsphere does reduce the brittleness and improve the fracture toughness of the resulting epoxy foams.

The critical stress intensity factors (K_{1c}) of samples **M0**, **M0.5** and **M1** are summarised in Table 4-2. Un-filled epoxy foam **M0** possessed K_{1c} of $0.33 \text{ MPa m}^{0.5}$. When the epoxy foams were filled with 0.5 wt.-% hollow elastomeric microspheres, K_{1c} increased by 15% to $0.38 \text{ MPa m}^{0.5}$ for sample **M0.5**. However, a further increase in the concentration of hollow elastomeric microspheres to 1.0 wt.-% (sample **M1**) led to a slight decrease in K_{1c} to $0.35 \text{ MPa m}^{0.5}$. This can be attributed to the agglomeration of the added hollow elastomeric microspheres, which is postulated to lead to insufficient wetting of the added microspheres in sample **M1**. As a result, sub-critical flaws around the vicinity of the agglomerated microspheres could form, leading to the lowering of K_{1c} values for **M1**. Similar results were also observed for syntactic epoxy foams toughened with thermoplastic poly(ether ether ketone) [138] and nano-clay particles [139].

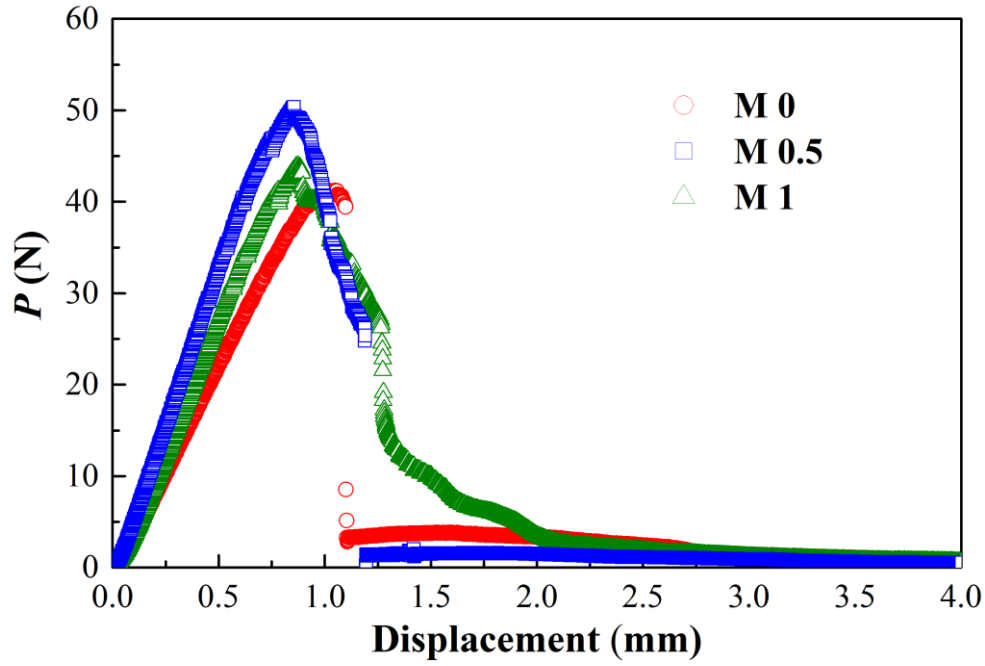


Figure 4-3. Representative load (P)-displacement curves of fracture toughness test (single edge notched specimens loaded in three-point bending mode). (a) Sample **M0** (neat and un-filled epoxy foam), (b) sample **M0.5** (0.5 wt.-% hollow elastomeric microsphere filled epoxy foam), (c) sample **M1** (1.0 wt.-% hollow elastomeric microsphere filled epoxy foam).

Table 4-2. Mechanical properties of the (hollow elastomeric microsphere filled) epoxy foams.. K_{1c} , a_{cU} , E and σ denote the critical stress intensity factor, Charpy impact strength, compressive modulus and compressive strength, respectively

Sample	K_{1c} (MPa m ^{0.5})	a_{cU} (kJ m ⁻²)	E (MPa)	σ (MPa)
M0	0.33 ± 0.02	0.79 ± 0.09	290 ± 51	8.0 ± 0.3
M0.5	0.38 ± 0.01	1.05 ± 0.09	290 ± 30	8.1 ± 0.4
M1	0.35 ± 0.01	0.93 ± 0.04	295 ± 25	7.8 ± 0.3

Fractographic analysis was conducted on the fracture surfaces of single edge-notched bending test specimens to investigate the origin of the toughening and crack resistance mechanisms of the (hollow elastomeric microsphere filled) epoxy foams (see Figure 4-4). Textured micro-flow was observed on the fracture surfaces of sample **M0**, indicating a

brittle fracture process [140-142]. This is consistent with the load-displacement curve, whereby sample **M0** failed catastrophically when peak load was reached. The fracture surfaces for samples **M0.5** and **M1**, on the other hand, displayed (i) microsphere debonding, (ii) microsphere deformation and fracture and (iii) crack pinning (due to the hollow elastomeric microspheres causing the crack to deflect and bow out); all these mechanisms contribute to the improvements in fracture toughness of the hollow elastomeric microsphere filled epoxy foams [54, 143-145].

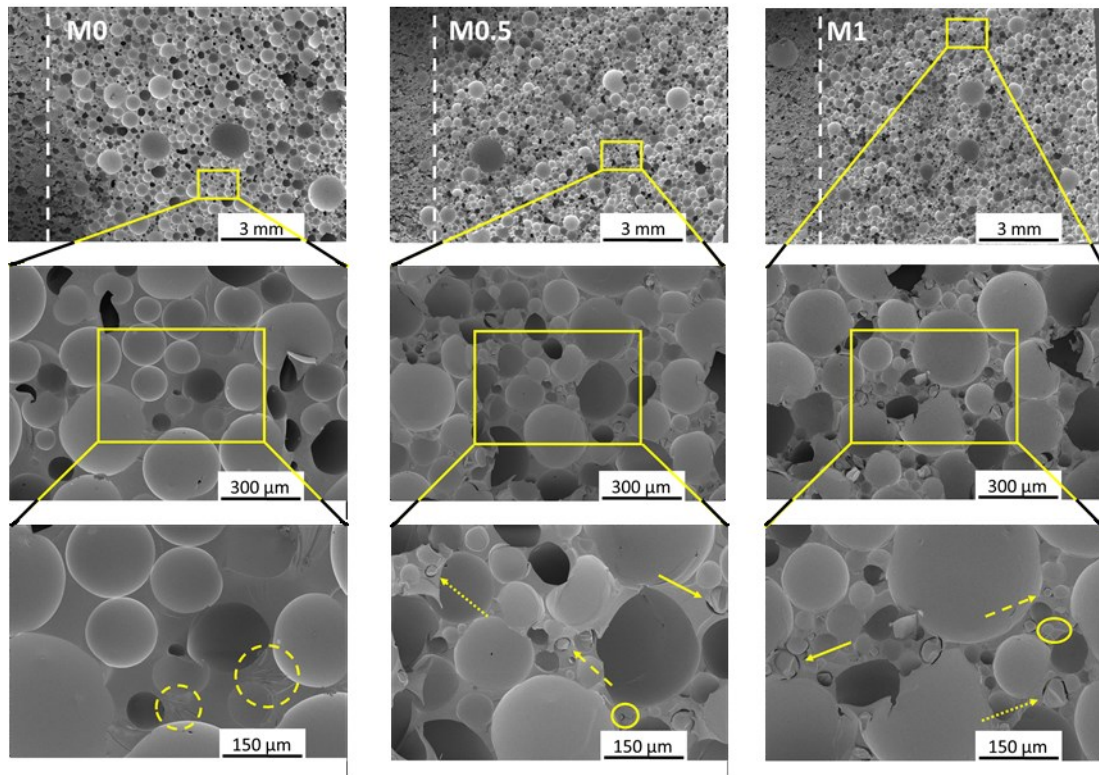


Figure 4-4. Fracture surfaces of samples **M0**, **M0.5** and **M1** after fracture toughness test. The vertical dash lines represent the initial crack tip and the crack propagation direction is to the right of the vertical dash lines. The circles with dash line and solid line denote textured microflow and crack pinning, respectively. The arrows with solid lines, dash lines and dotted lines denote fractured, debonded and deformed microspheres, respectively.

To further evaluate the resistance of the (hollow elastomeric microsphere filled) epoxy foams to crack growth, a plot of K_{1c} as a function of crack opening (Δa) is shown in Figure 4-5. This crack resistance curve is more commonly known as R-curve. Since sample **M0** failed catastrophically, it is assumed that K_{1c} of sample **M0** is independent of Δa (represented by the dash line). It can be seen from this figure that epoxy foams containing hollow elastomeric microspheres showed enhanced crack resistance during crack propagation, characterised by an increase in K_{1c} as a function of Δa . This implies that the crack front encountered resistance in crack propagation stemming from the added hollow elastomeric microspheres and more energy is required to propagate the crack.

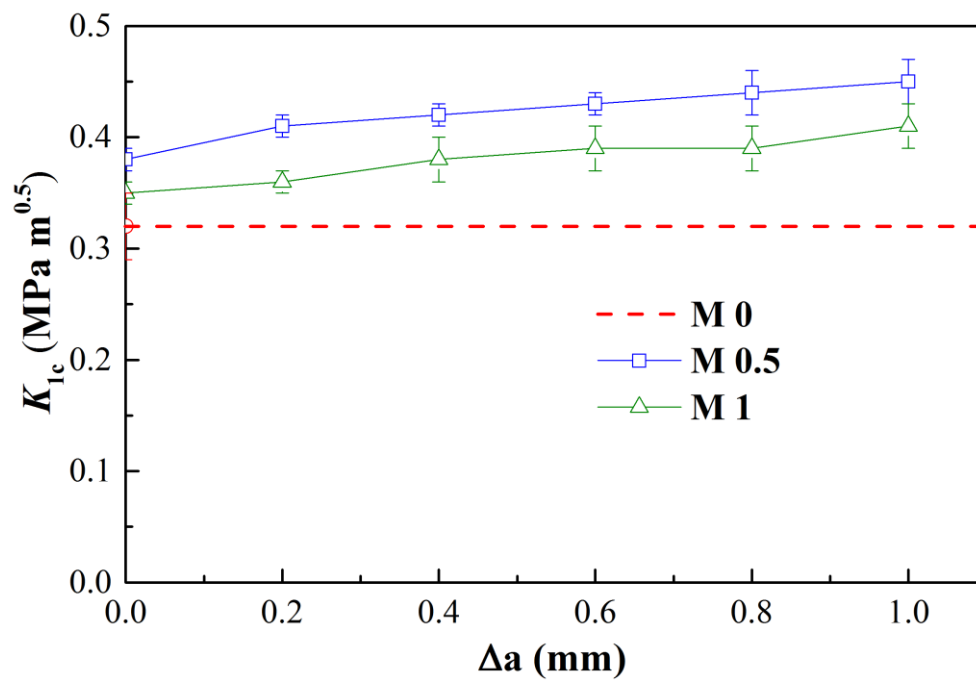


Figure 4-5. Critical stress intensity factor (K_{1c}) as a function of crack opening (Δa) of the (hollow elastomeric microsphere filled) epoxy foams.

4.3.3 Charpy impact toughness of the (hollow elastomeric microsphere filled) epoxy foams

Charpy impact test was further conducted to investigate the impact toughness of the (hollow elastomeric microsphere filled) epoxy foams (see Table 4-2). Un-filled epoxy foam **M0** possessed a Charpy impact strength (a_{cU}) of 0.79 kJ m⁻². Similar to K_{1c} , the addition of the hollow elastomeric microspheres increased a_{cU} of sample **M0.5** to 1.05 kJ m⁻² but a further addition of hollow elastomeric microspheres to 1 wt.-% (sample **M1**) decreased a_{cU} to 0.93 kJ m⁻². These results further demonstrated the toughening effect of the hollow elastomeric microspheres on epoxy foams at 0.5 wt.-%, but agglomeration occurred at higher microspheres concentration of 1 wt.-%, leading to a decrease in impact toughness. The previously discussed fractographic features could also be observed for samples after Charpy impact test specimens (see Figure 4-6).

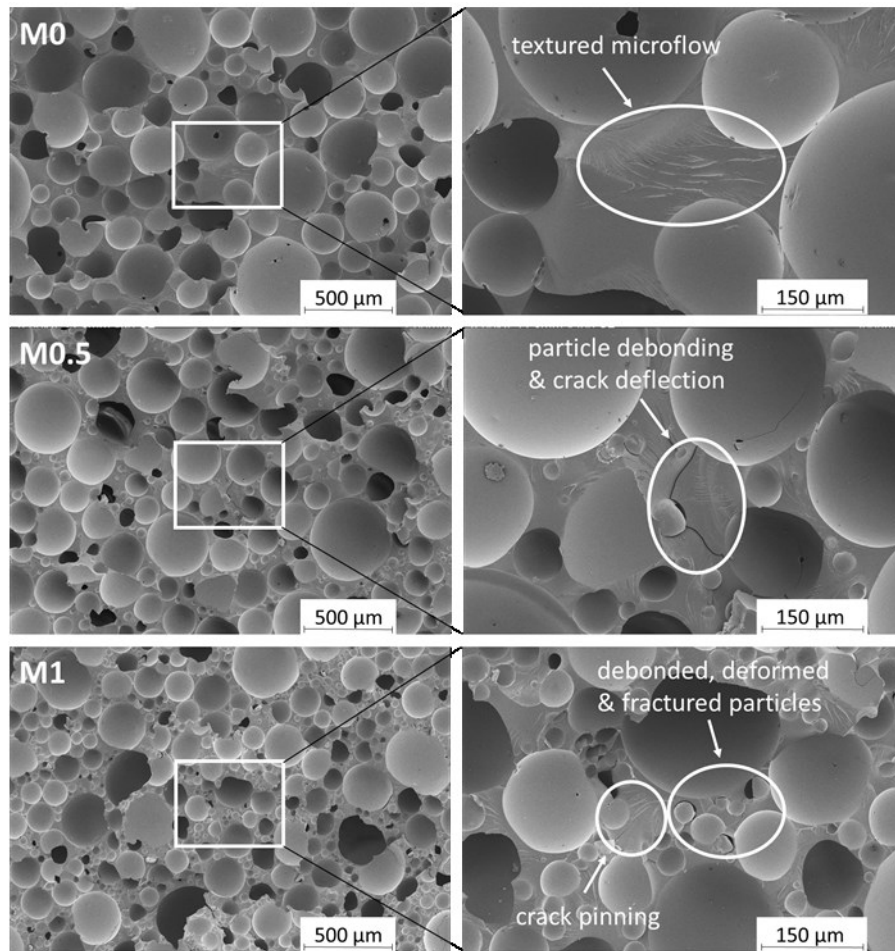


Figure 4-6. SEM images of the fracture surfaces of the samples after Charpy impact tests.

4.3.4 Compressive properties of the (hollow elastomeric microsphere filled) epoxy foams

To ascertain whether the added hollow elastomeric microspheres lowered the compressive properties of the epoxy foams, quasi-static compression test was conducted. The representative compressive stress-strain curves of the (hollow elastomeric microsphere filled) epoxy foams are shown in Figure 4-7. All samples exhibited similar

mechanical response under uniaxial compressive load. The initial linear elastic region of the compressive stress-strain curves correspond to elastic bending of the pore wall material. Yielding of the foam occurs by plastic deformation of the pore walls, resulting in an approximately constant plateau stress. At large strains densification occurred, with self contact of the pores and the consequent increase in stress.

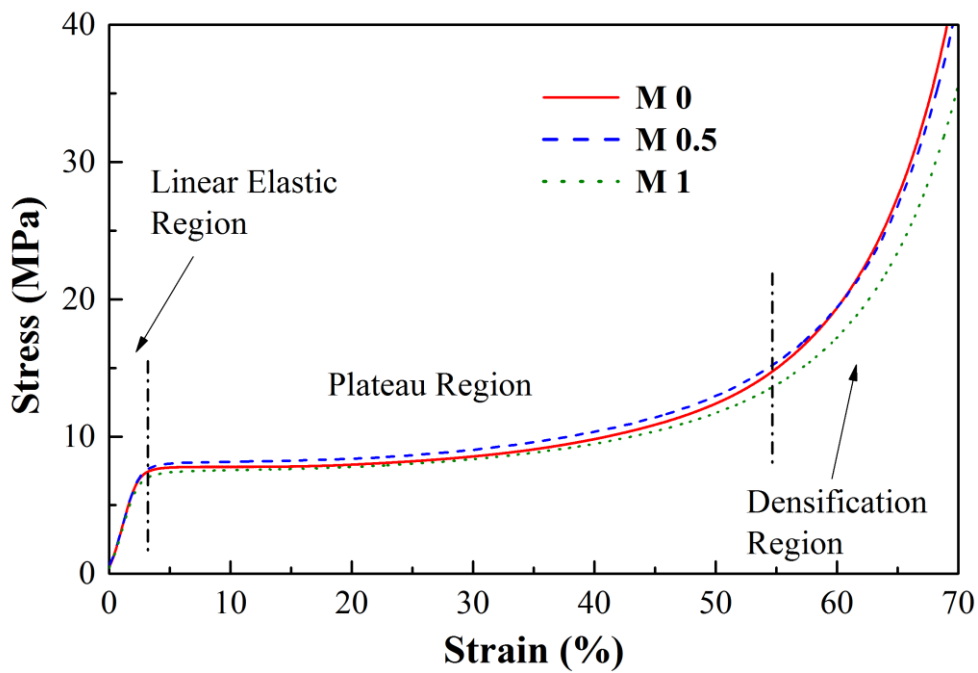


Figure 4-7. Representative compressive stress-strain curves of the (hollow elastomeric microsphere filled) epoxy foams.

The compressive modulus (E) and strength (σ) of the (hollow elastomeric microsphere filled) epoxy foams are summarised in Table 4-2. The values of E and σ range between ~290 MPa and ~8 MPa, independent of the addition of the hollow elastomeric microspheres. This confirms that the use of hollow elastomeric microspheres as

toughening agent does not reduce the quasi-static compressive stiffness and strength of the epoxy foams.

4.4 Concluding remarks

The fracture resistance and impact toughness of the foam templated macroporous polymers have been successfully enhanced without sacrificing the quasi-static compressive properties. This was achieved by using hollow elastomeric microspheres instead of conventional non-porous elastomeric particles as toughening agent for epoxy foams. All epoxy foams fabricated possessed similar density of $0.37 - 0.40 \text{ g cm}^{-3}$. The quasi-static compressive modulus and strength of the epoxy foams were $\sim 290 \text{ MPa}$ and $\sim 8 \text{ MPa}$, independent of the addition of the hollow elastomeric microspheres, indicating that hollow elastomeric microspheres do not weaken the mechanical properties.

Both the fracture resistance based on initial stress intensity factor (K_{1c}) and impact toughness based on Charpy impact strength (a_{CU}) of the hollow elastomeric microsphere filled epoxy foams were found to improve over unfilled epoxy foam. These improvements are attributed to the introduction of additional energy absorbing mechanisms: microsphere-epoxy resin debonding, deformation and fracture, as well as crack deflection by microspheres. The strategy of toughening brittle epoxy foams with hollow elastomeric microspheres without sacrificing their compressive properties provides an exciting opportunity to employ high performance epoxy foams in applications where toughness and quasi-static compressive properties are both critical.

Chapter 5 Transversely isotropic porous material from liquid foam templates: Short carbon fibre reinforced epoxy foams

5.1 Introduction

High specific mechanical properties are crucial for rigid macroporous polymers employed in structural applications. The aim of this work is to further improve the mechanical performance of foam templated macroporous polymers. This can be achieved by reinforcing the pore wall of the macroporous polymers. For example, with the addition of 4.5 vol.-% glass fibre into glass microsphere filled syntactic epoxy foam, a 50% and 35% improvement in flexural modulus [146] and strength [147], as well as a 64% and 33% increase in compressive modulus [148] and strength [149] were observed.

Compared to glass fibres, carbon fibres normally present better reinforcing performance because of their superior mechanical properties. It was found that the flexural modulus of hollow glass microsphere filled epoxy foam with density of 0.79 g cm^{-3} increased from 1.8 GPa to 2.4 GPa when the reinforcing materials was substituted from 0.9 vol.-% of glass fibre to 0.9 vol.-% of carbon fibre [150]. Similar results were also reported for rigid polyurethane foams [151]. 3 wt.-% of carbon fibre reinforced rigid polyurethane foam exhibited an 80% improvement in both tensile modulus and strength compared to 3 wt.-% of glass fibre reinforced polyurethane foam with the same density of 0.45 g cm^{-3} .

To manufacture fibre reinforced macroporous polymers, the fibres are normally introduced and dispersed into the bulk polymers first by intensive mixing prior to foaming, e.g. a homogenizer operating at 4500 rpm was used to disperse carbon fibre into phenolic resin [152], and a dispersator operating at 10^5 rpm was applied for the mixing of carbon fibre with polypropylene. During these intensive mixing steps, the entrainment of air bubbles is almost inevitable, but often undesirable. As a result, a degassing step is often employed to remove the unwanted air bubbles.

It is advantageous to fabricate fibre reinforced macroporous polymers using foam templating method, because intensive mixing is desirable for both foaming (mechanical frothing) step and fibre mixing/dispersing step. Therefore, in this chapter, the short carbon fibre is introduced to the epoxy foam manufactured by foam templating method. The morphological properties, compressive properties and fracture toughness of these carbon fibre reinforced epoxy foams are characterised and the reinforcing mechanism and transversely isotropicity are discussed.

5.2 Experimental

5.2.1 Materials

Epoxy resin with $56 \pm 2\%$ biomass content (Greenpoxy 56, $\rho = 1.20 \pm 0.01 \text{ g cm}^{-3}$, $\eta = 2500 \text{ mPa s}$ at 15°C) and amine-based hardener with $58 \pm 3\%$ biomass content (GP 505 V2, $\rho = 0.99 \pm 0.01 \text{ g cm}^{-3}$, $\eta = 1800 \text{ mPa s}$ at 15°C) were purchased from Matrix Composite Materials Company Ltd (Bristol, UK) and used as received. Short carbon

fibres (sCF) in the form of chopped carbon fibre tows (CarbisoTM, 6 mm in length, tow size = 50K, sizing content < 1.5%) were kindly provided by ELG Carbon Fibre Ltd (West Midlands, UK).

5.2.2 Preparation of (short carbon fibre reinforced) epoxy foams

5.2.2.1 Preparation of neat epoxy foams

Neat epoxy foams (sample **0**) were prepared following a previously described procedure [137]. Briefly, 70 g of epoxy resin and 29.4 g of amine-based hardener were added into a 2 L Pyrex glass bowl and mechanically frothed using a handheld mixer (HM 730B, Sainsbury's Supermarket Ltd, London, UK) operating at maximum power output of 200 W for 20 min (**A**) to introduce air bubbles into the mixture. Epoxy resin and hardener mixture frothed for 2.5 min (**B**) was also prepared as previously described. The resulting air-in-resin liquid foams were then transferred into polytetrafluoroethylene coated aluminium mould with dimensions of 100 mm (X) × 100 mm (Y) × 20 mm (Z) and cured at room temperature for 24 h. Epoxy foams produced from the liquid foam templates frothed for 20 min and 2.5 min are herein termed samples **0-A** and **0-B**.

5.2.2.2 Preparation of short carbon fibre reinforced epoxy foams

Short carbon fibre reinforced epoxy foams were also prepared following the previously described procedure. Briefly, 70 g of epoxy resin and 29.4 g of amine-based hardener were added into a 2 L Pyrex glass bowl and mechanically frothed using a handheld mixer operating at maximum power output of 200 W for 20 min. 2.5 wt.-% and 5.0 wt.-%

chopped carbon fibre tows were then added into the air-in-resin liquid foam and further frothed for another 20 s to disperse the chopped carbon fibre tows. A short mixing time of only 20 s was employed as significant carbon fibre entanglement around the two mixing paddles of the hand mixer was observed when longer mixing time was used.

To increase the mixing time of the chopped carbon fibre tows within the air-in-resin liquid foam, a modified mechanical frothing process was adopted. After the initial frothing of the liquid epoxy resin and hardener mixture for 20 min, 2.5 wt.-% and 5.0 wt.-% chopped carbon fibre tows were added into the air-in-resin liquid foam and mixed with only one mixing paddle covered with duct tape for 2 min. This produced a radial flow of the resin-hardener-chopped carbon fibre mixture around the mixing paddle without carbon fibre entanglement.

All the prepared air-in-resin liquid foams containing short carbon fibres were then carefully transferred into polytetrafluoroethylene coated aluminium mould with dimensions of 100 mm (X) $\times$ 100 mm (Y) $\times$ 20 mm (Z) to avoid the disruption of short carbon fibre orientation within the liquid foam. The samples were cured at room temperature for 24 h. Short carbon fibre reinforced epoxy foams produced by mixing the chopped carbon fibre tows for only 20 s are herein designated as sample **1**, and sCF reinforced epoxy foams manufactured by mixing the chopped carbon fibre tows for 2 min are herein designated as sample **2**.

5.2.3 Characterisation of the (sCF reinforced) epoxy foams

5.2.3.1 Density and porosity of the (sCF reinforced) epoxy foams

He pycnometry (Accupyc II 1340, Micromeritics Ltd, Hexton, UK) was used to determine the true density of the pore wall material (ρ_s). Prior to the measurement, the (sCF reinforced) epoxy foams were milled into powder using a jet mill (Picojet 40 AFG, Hosokawa Alpine, Augsburg, Germany) operating at a pressure of 5 bar. The porosity of the (sCF reinforced) epoxy foams (P) was calculated from:

$$P = \left(1 - \frac{\rho_f}{\rho_s}\right) \times 100\% \quad (5.1)$$

where the envelope density of the (sCF reinforced) epoxy foams (ρ_f) was calculated by taking the ratio between the mass and envelope volume of the cut samples.

5.2.3.2 Structure and morphology of the (sCF reinforced) epoxy foams

The internal structure of the fabricated samples was investigated using a scanning electron microscope (SEM) (Hitachi S-3700N, Tokyo, Japan) operating at an accelerating voltage of 5 kV. Prior to SEM, the epoxy foams were cut into rectangular-shaped specimens of 20 mm $\times$ 20 mm $\times$ 10 mm and broken into two halves by hand to reveal their internal structures. The samples were then mounted onto aluminium stubs using carbon tabs and coated with Au (Agar Auto Sputter Coater, Essex, UK) at 40 mA for 1 min. The average pore diameter (D_{pore}) was determined from these SEM images with a population size of 300 pores.

5.2.3.3 Fracture toughness of the (sCF reinforced) epoxy foams

The fracture toughness of the (sCF reinforced) epoxy foams was determined in accordance to ASTM D5045-14 on single edge notched beam (SENB) specimens loaded in 3-point bending mode. The span length used was 80 mm. Prior to the test, the samples were cut into rectangular test specimens with dimensions of 100 mm (l) $\times$ 20 mm (w) $\times$ 10 mm (b). An initial crack of 10 mm was introduced at the centreline of the test specimen such that the initial crack length (a) to width (w) ratio fulfil the requirement of $0.45 \leq (a/w) \leq 0.55$. The initial crack length was created by cutting the first 8 mm with a band-saw and the remaining 2 mm with a sharp scalpel. The precise crack length value was determined from the analysis of the fracture surfaces after the fracture toughness test. The test was conducted using an Instron universal tester (Model 5969, Norwood, USA) equipped with 1 kN load cell. The crosshead displacement speed used was 1 mm min⁻¹. A total of five specimens were tested for each type of sample. The critical stress intensity factor (K_{1c}) was calculated from:

$$K_{1c} = \left(\frac{P_C}{bw^{0.5}} \right) f(a/w) \quad (5.2)$$

where P_C is the load at crack initiation, b is the thickness of the specimen, and $f(a/w)$ is given by:

$$f(a/w) = 6 (a/w)^{0.5} \frac{[1.99 - a/w(1-a/w)(2.15 - 3.93a/w + 2.7(a/w)^2)]}{(1 + 2a/w)(1 - a/w)^{1.5}} \quad (5.3)$$

5.2.3.4 Compressive properties of the (sCF reinforced) epoxy foams

Compression tests were performed on the (sCF reinforced) epoxy foams using an Instron universal tester (Model 5969, Norwood, USA) in accordance to ASTM D1621-16. Test specimens with dimensions of 20 mm × 20 mm × 20 mm were cut and compressed between flat and parallel polished plates. The strain was monitored using a non-contact video extensometer (Imetrum Video Gauge, Bristol, UK). The load cell and crosshead displacement speed used were 50 kN and 2 mm min⁻¹ (equivalent to a strain rate of 0.1 min⁻¹). A total of 5 specimens were tested for each type of sample.

5.3 Results and discussion

5.3.1 Structure and morphology of the (sCF reinforced) epoxy foams

SEM images showing the internal structure and morphology of the fabricated epoxy foams are presented in Figure 5-1. All the fabricated epoxy foams have polydispersed spherical pores with closed-pore structures. This indicates that the air bubbles trapped within the air-in-resin liquid foam (with or without short carbon fibres) were always in equilibrium [154] prior to gelation, as spherically-shaped air bubbles minimise surface tension. Carbon fibre bundles can be observed in sample **1** whilst individualised carbon fibres can be seen in sample **2**. This can be attributed to the differences in the mixing time of chopped carbon fibre tows in the air-in-resin liquid foam. The shorter mixing time of only 20 s led to a homogenous dispersion of the carbon fibre tows in the air-in-

resin liquid foam, but insufficient to individualise the single carbon fibres, leading to the observed carbon fibre bundles in sample **1**.

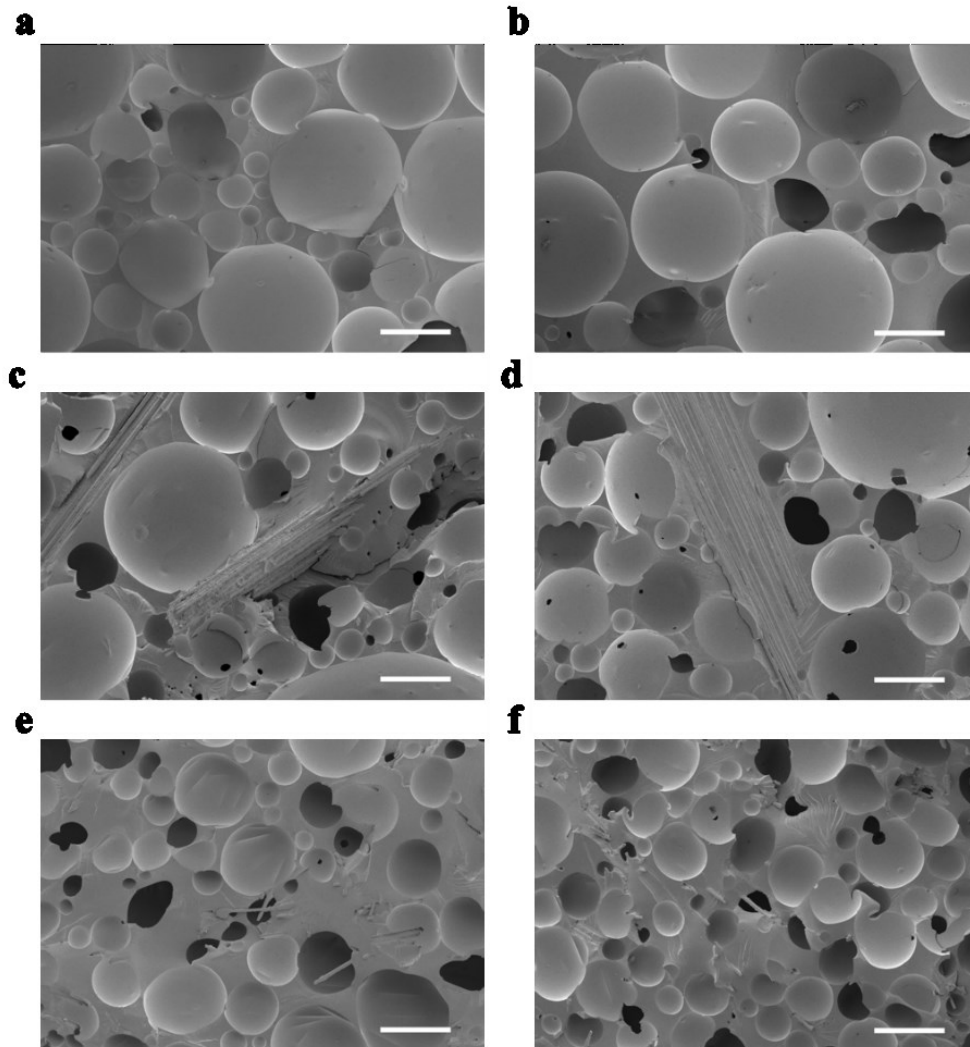


Figure 5-1. Scanning electron micrographs of the (sCF reinforced) epoxy foams. (a) Sample **0-A**, (b) sample **0-B**, (c) sample **1** (2.5 wt.-% sCF reinforced), (d) sample **1** (5.0 wt.-% sCF reinforced), (e) sample **2** (2.5 wt.-% sCF reinforced) and (f) sample **2** (5.0 wt.-% sCF reinforced). The scale bar represented by the solid line is 200 μm .

Increasing the mixing time of chopped carbon fibre tows in the air-in-resin liquid foam to 2 min (sample **2**) aided the individualisation of single carbon fibres from the chopped

carbon fibre tows. The effect of mixing time on the dispersion of carbon fibres in both samples **1** and **2** could also be observed macroscopically (see Figure 5-2). Bundles of carbon fibres could be seen in the cross-section of sample **1** whilst such morphology was not present in sample **2**. Instead, a “marbling” morphology was observed. This “marbling” morphology is characteristic of an eggbeater flow [155, 156], whereby the dispersed phase of a two-immiscible fluid system is stretched and folded by the shear forces generated during mixing. In the case of sample **2**, the high intensity mechanical frothing process and longer mixing time of the added carbon fibre within the air-in-resin liquid foam led to the shearing of the carbon fibre tows, producing striations of carbon fibres characteristic of stretch-and-fold eggbeater flow.

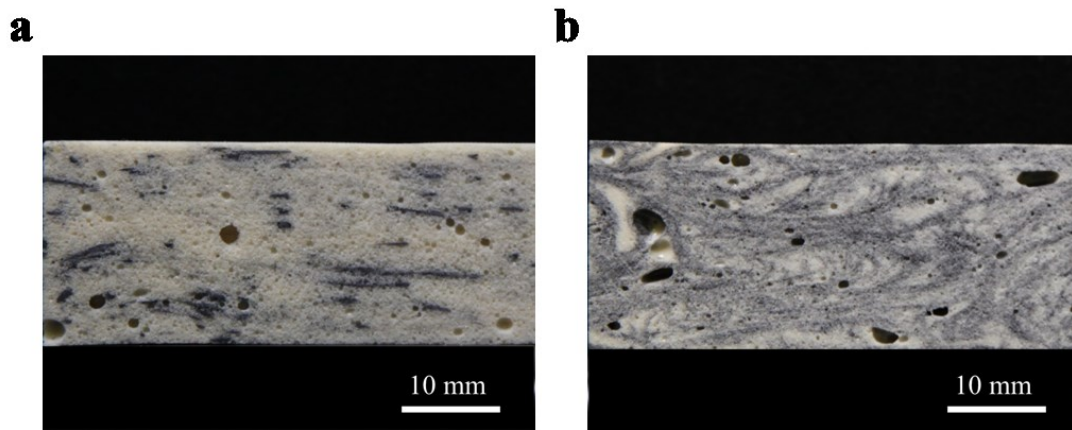


Figure 5-2. Representative cross-sections of (a) sample **1** (2.5 wt.-% sCF reinforced) and (b) sample **2** (2.5 wt.-% sCF reinforced).

The density, porosity and average pore diameter of the (sCF reinforced) epoxy foams are summarised in Table 5-1 and their pore size distributions are shown in Figure 5-3. Sample **0-A**, mechanically frothed for 20 min, possessed an envelope density (ρ_f) of 362

kg m⁻³ and a porosity (P) of 69%, with an average pore diameter (D_{pore}) of 143 μm . Reducing the mechanical frothing time of the liquid epoxy resin and hardener mixture to only 2.5 min (sample **0-B**) led to a decrease in porosity to only 60%. This is also accompanied by an increase in average pore diameter to ~ 200 μm and the broadening of the pore size distribution of sample **0-B** compared to sample **0-A**.

Table 5-1. The true density of the pore wall material (ρ_s), envelope density (ρ_f), porosity (P) and the average pore diameter (D_{pore}) of the (sCF reinforced) epoxy foams.

Sample	ρ_s (kg m ⁻³)	ρ_f (kg m ⁻³)	P (%)	D_{pore} (μm)
0-A	1183 $\pm$ 3	362 $\pm$ 9	69 $\pm$ 1	143 $\pm$ 101
1 (2.5 wt.-% sCF)	1193 $\pm$ 3	366 $\pm$ 11	69 $\pm$ 1	129 $\pm$ 103
1 (5.0 wt.-% sCF)	1200 $\pm$ 2	369 $\pm$ 14	69 $\pm$ 1	124 $\pm$ 76
0-B	1182 $\pm$ 2	461 $\pm$ 8	61 $\pm$ 1	197 $\pm$ 111
2 (2.5 wt.-% sCF)	1191 $\pm$ 3	459 $\pm$ 14	61 $\pm$ 1	95 $\pm$ 42
2 (5.0 wt.-% sCF)	1203 $\pm$ 4	475 $\pm$ 16	60 $\pm$ 1	83 $\pm$ 44

The shorter mechanical frothing time employed to produce sample **0-B** led to insufficient entrainment of air into the air-in-resin liquid foam, as well as insufficient energy input to break up the entrained air bubbles into smaller bubbles. When the added carbon fibre tows were mixed for only 20 s in the air-in-resin liquid foam, the resulting sCF reinforced epoxy foam (sample **1**) were found to possess an envelope density of 366-369 kg m⁻³ and porosity of 69%, similar to that of sample **0-A**. However, increasing the mixing time of the chopped carbon fibre tows in the air-in-resin liquid foam to 2 min (sample **2**) led to a significant increase in envelope density and reduction in porosity to 459-475 kg m⁻³ and $\sim 60\%$. This can be attributed to the disruption of the liquid foam structure as a result

of the longer mixing time employed to disperse the chopped carbon fibre tows in the air-in-resin liquid foam, which is thought to lead to phase separation and the escape of the entrained air bubbles from the air-in-resin liquid foam.

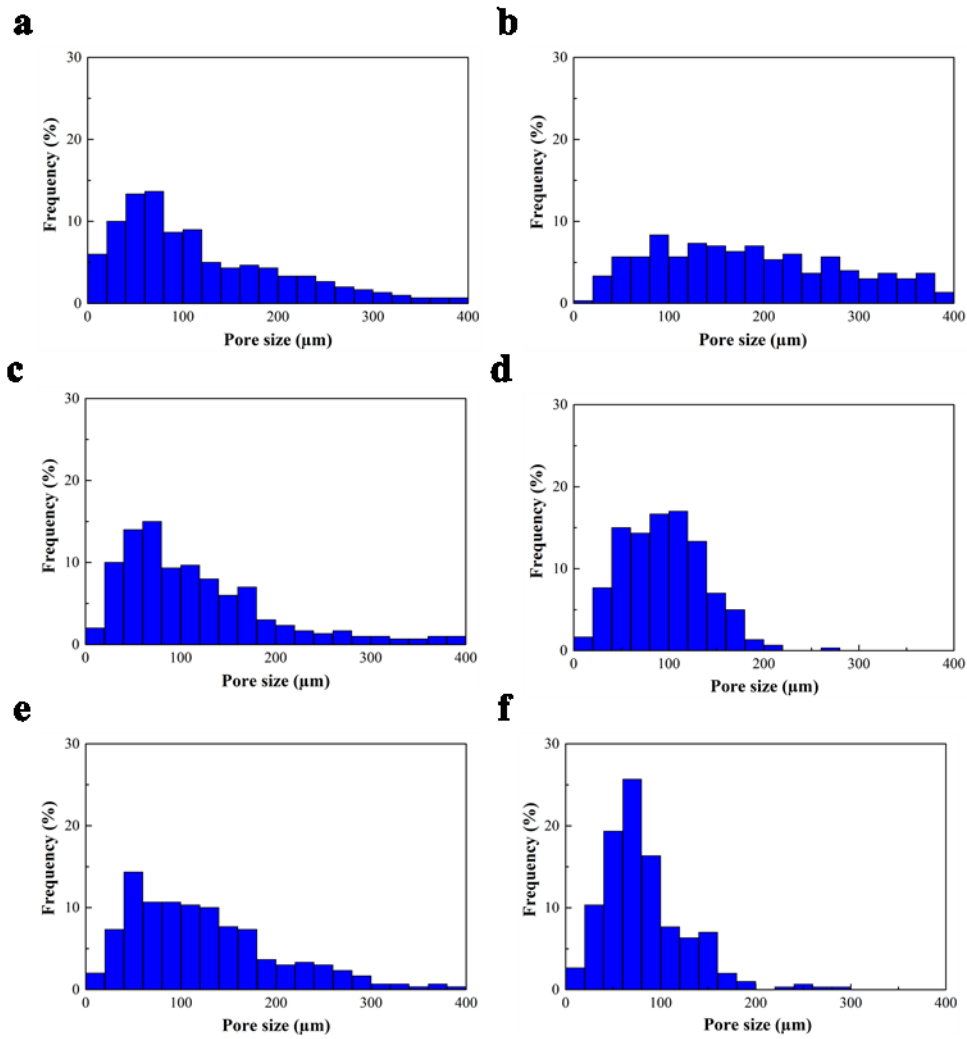


Figure 5-3. Pores size distributions of the (sCF reinforced) epoxy foams. (a) Sample **0-A**, (b) sample **0-B**, (c) sample **1** (2.5 wt.-% sCF reinforced), (d) sample **1** (5.0 wt.-% sCF reinforced), (e) sample **2** (2.5 wt.-% sCF reinforced) and (f) sample **2** (5.0 wt.-% sCF reinforced). The bin size is 20 μm.

In addition to this, the viscosity of the liquid foam increases as mixing of the chopped carbon fibre tows in the air-in-resin liquid foam progresses, due to the viscosifying effect of carbon fibres in a liquid suspension [157]. The increase in viscosity of the liquid foam not only reduces the efficiency of air entrainment during the mixing of chopped carbon fibre tows, but also reduces foam drainage [158], thus reducing the coalescence of air bubbles, which also contributes to the decrease in both the porosity and the average pore diameter, where D_{pore} decreased from 143 μm to $\sim 125 \mu\text{m}$ for sample **1** and $\sim 90 \mu\text{m}$ for sample **2**.

5.3.2 Fracture toughness of the (sCF reinforced) epoxy foams

Figure 5-4 shows the representative load-displacement curves of fracture toughness test specimens loaded in the in-plane and out-of-plane directions. The initial linear part of the load-displacement curves corresponded to an elastic response of the epoxy foams whilst the softening part indicated crack propagation. Neat epoxy foams (samples **0-A** and **0-B**) failed catastrophically, characterised by a single decrease in load to nearly zero after peak load was reached. This is a direct result of the brittleness of the pore wall material in tension, stemming from the highly crosslinked nature of the epoxy network [132]. When sCF was added, both samples **1** and **2** failed in progressive manner, characterised by a sequence of load decrease and increase after peak load until failure.

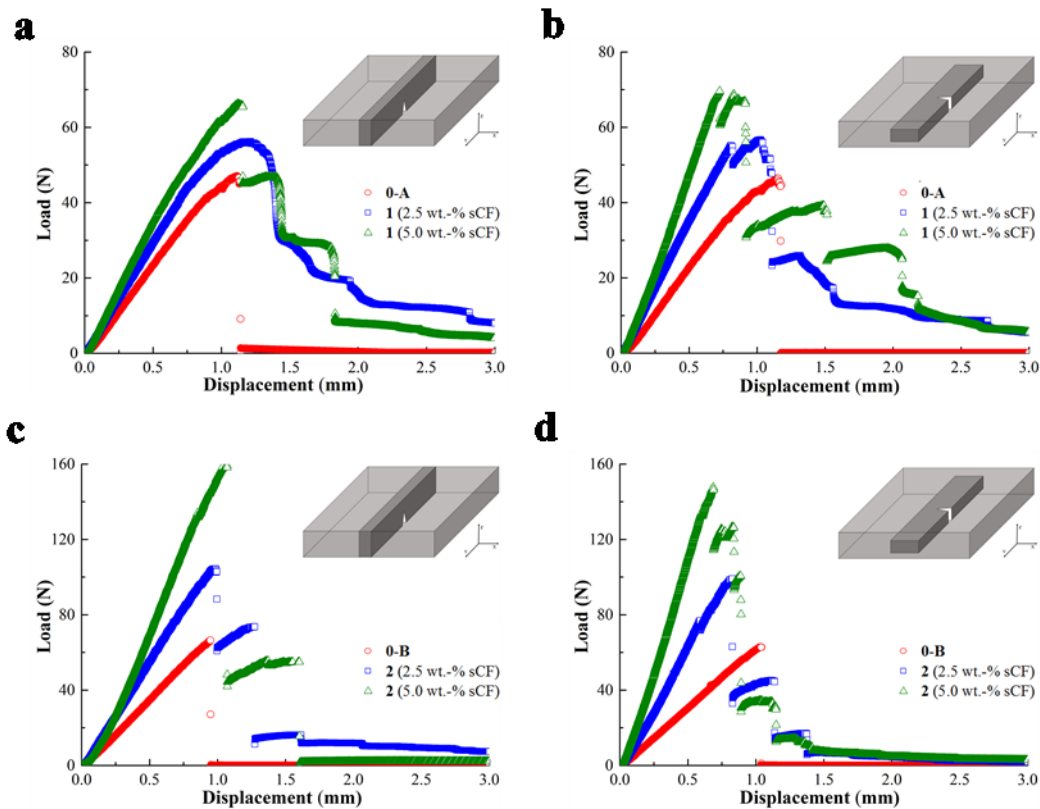


Figure 5-4. Representative load-displacement curves of fracture toughness test. (a) Sample **1** loaded in the out-of-plane direction and (b) sample **1** loaded in the in-plane direction, relative to sample **0-A**; (c) sample **2** loaded in the out-of-plane direction and (d) sample **2** loaded in the in-plane direction, relative to sample **0-B**. The inset diagrams showed preparation of the test specimens (represented by the dark grey) from the original sample (represented by light grey).

Fractographic analysis was conducted on fracture toughness test specimens to investigate the origin of the observed progressive failure. Significant pull-out of carbon fibre bundles can be observed for sample **1** (Figure 5-5(a)) and this is often identified as a toughening mechanism for sCF reinforced polymer composites [159, 160]. Single carbon fibre debonding and pull-out from the matrix material can also be observed for sample **2** (Figure 5-5(c)). Both of these observations imply that when peak load was reached, crack propagates (e.g. a load decrease) until the advancing crack front encounters further resistance in the form of carbon fibre bundles (sample **1**) or regions with high

concentration of individualised carbon fibres (sample **2**). This led to a load increase as additional energy is required to divert the crack, de-bond and/or potentially fracture the carbon fibres. Once the necessary load applied is sufficient to overcome the resistance, the crack continues to propagate, and this is accompanied by another load drop.

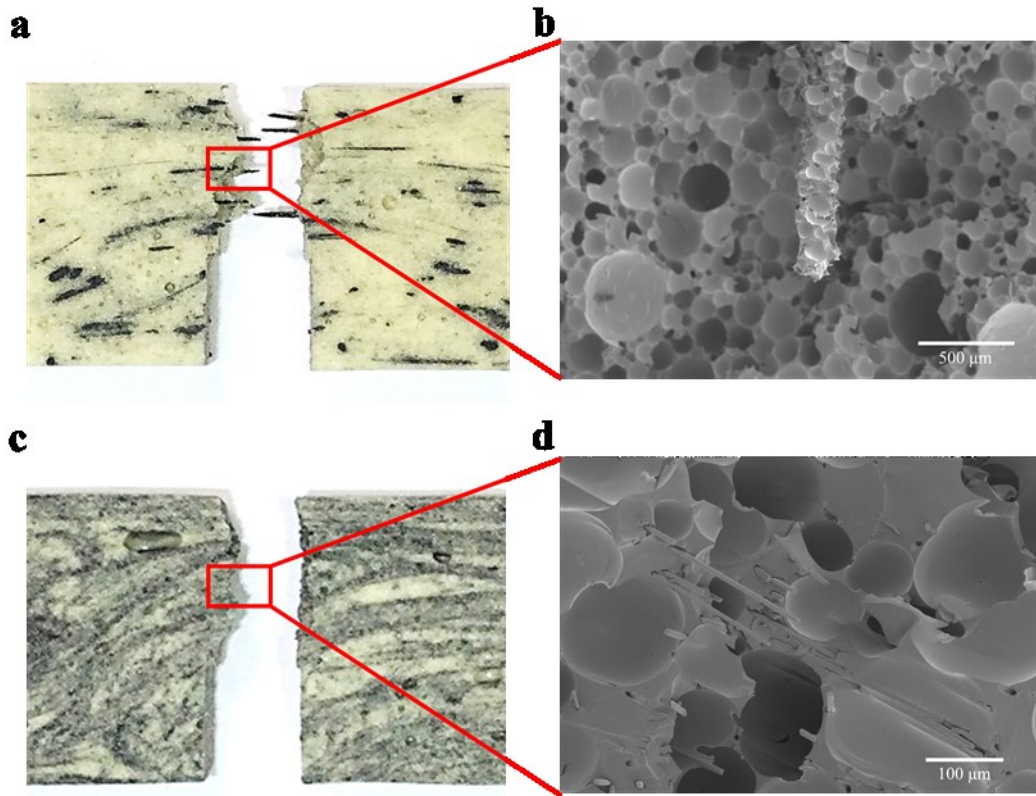


Figure 5-5. Exemplary fracture surfaces of the sCF reinforced epoxy foams after fracture toughness test. (a) & (b) Sample **1** (2.5 wt.-% sCF reinforced) test in out-of-plane direction, and (c) & (d) sample **2** (2.5 wt.-% sCF reinforced) tested in out-of-plane direction.

The critical stress intensity factor (K_{Ic}) of the (sCF reinforced) epoxy foams tested in the in-plane and out-of-plane directions are summarised in Table 5-2. With the addition of 2.5 wt.-% and 5.0 wt.-% of sCF, the K_{Ic} of sample **1** increased by ~30% and ~54%, compared to sample **0-A** with the same porosity of 69%. The increase in the K_{Ic} of

sample **2** is even more pronounced: ~54% and ~113% for 2.5 wt.-% and 5.0-% sCF reinforced epoxy foams, compared to sample **0-B** with similar porosity of ~61%. Since K_{1c} is influenced by both pore size and relative density of a polymer foam [161], normalised critical stress intensity factor ($\tilde{K}_{1c}$) was calculated to ascertain the influence of carbon fibres on the measured fracture toughness of the sCF reinforced epoxy foams (see Table 5-2). It can be seen from this table that the $\tilde{K}_{1c}$ values of sCF reinforced epoxy foams are still consistently higher than the neat epoxy foams. The introduction of carbon fibres increased the tensile strength of the pore wall material, leading to an improvement in the fracture toughness of the sCF reinforced epoxy foams. The higher $\tilde{K}_{1c}$ values of sample **2** compared to sample **1** can be attributed to the more uniform dispersion of the individualised carbon fibres.

Table 5-2. In-plane and out-of-plane critical stress intensity factor (K_{1c}), normalised critical stress intensity factor ($\tilde{K}_{1c}$), compressive modulus (E) and compressive strength (σ) of the (sCF reinforced) epoxy polymers.

Sample	In-plane (X-Y)				Out-of-plane (X-Z)			
	K_{1c} (MPa m ^{0.5})	$\tilde{K}_{1c}^{\dagger}$ (MPa)	E (MPa)	$\sigma^{\ddagger}$ (MPa)	K_{1c} (MPa m ^{0.5})	$\tilde{K}_{1c}^{\dagger}$ (MPa)	E (MPa)	$\sigma^{\ddagger}$ (MPa)
0-A	0.38 ± 0.02	181 ± 6	220 ± 34	6.7 ± 0.3	0.35 ± 0.02	177 ± 6	235 ± 28	6.8 ± 0.3
1 (2.5 wt.-% sCF)	0.46 ± 0.03	241 ± 14	311 ± 33	7.5 ± 0.5	0.45 ± 0.08	246 ± 32	238 ± 33	6.0 ± 0.3
1 (5.0 wt.-% sCF)	0.59 ± 0.06	302 ± 33	347 ± 55	7.4 ± 0.2	0.54 ± 0.06	302 ± 30	214 ± 22	5.5 ± 0.2
0-B	0.54 ± 0.04	161 ± 14	319 ± 52	9.7 ± 0.2	0.54 ± 0.03	156 ± 8	343 ± 42	9.5 ± 0.5
2 (2.5 wt.-% sCF)	0.83 ± 0.06	344 ± 29	588 ± 53	12.0 ± 0.7	0.83 ± 0.16	361 ± 63	351 ± 58	7.2 ± 0.6
2 (5.0 wt.-% sCF)	1.13 ± 0.10	502 ± 38	845 ± 57	14.8 ± 1.6	1.15 ± 0.09	519 ± 59	312 ± 60	7.1 ± 0.7

[†] Normalised critical stress intensity factor, $\tilde{K}_{1c} = \frac{K_{1c}}{\sqrt{D_{\text{pore}}}} \left(\frac{\rho_f}{\rho_s} \right)^{-1.5}$

[‡] The compressive strength is defined as the stress at the yield point (the first point on the stress-strain diagram at which an increase in strain occurs without an increase in stress) if a yield point occurs before 10 % strain or, in the absence of such a yield point, the stress at 10 % strain deformation.

5.3.3 Compressive properties of the (sCF reinforced) epoxy foams

Figure 5-6 shows the representative in-plane and out-of-plane compressive stress-strain curves of the (sCF reinforced) epoxy foams. It can be seen that once maximum compressive stress was reached after the initial elastic response for neat epoxy foams (samples **0-A** and **0-B**), the stress transitioned smoothly into a long plateau (plastic collapse) before densification. For epoxy foams reinforced with short carbon fibres, the evolution of the compressive stress-strain curves is dependent on the loading directions (Figure 5-6 (b) & (d)). When sCF reinforced epoxy foams were compressed in the in-plane direction, a decrease in stress can be observed after maximum stress was reached. This can be attributed to the brittleness of the pore wall material when reinforced by carbon fibres [162, 163], which fractured catastrophically. This is then followed by plastic collapse of the pore wall material. The compressive response of sCF reinforced epoxy foams in the out-of-plane direction (Figure 5-6 (a) & (c)) exhibited a strain-hardening compressive response beyond the initial linear-elastic region. An increase in strain led to an increase in stress after the initial linear elastic response. This suggests an in-plane orientation of the carbon fibres within the sCF reinforced epoxy foams, which increased the resistance towards the in-plane deformation (e.g. polymer foam stretching) of the specimens under out-of-plane loading.

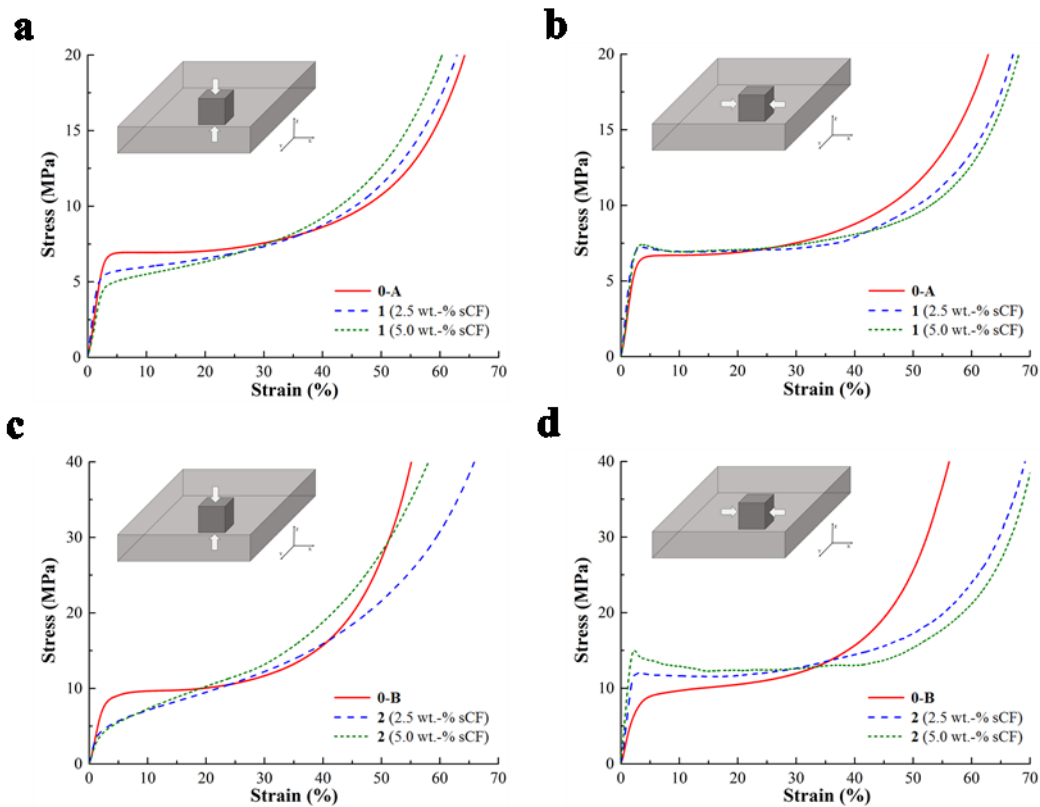


Figure 5-6. Representative compressive stress-strain curves of (a) sample **1** loaded in the out-of-plane direction and (b) sample **1** loaded in the in-plane direction, relative to sample **0-A**, (c) sample **2** loaded in the out-of-plane direction and (d) sample **2** loaded in the in-plane direction, relative to sample **0-B**, respectively. The inset diagrams showed the loading direction of the test specimens (represented by the dark grey) relative to the original samples (represented by light grey).

The observed mechanical anisotropy in the compressive stress-strain curves is also evident in the compressive properties of the (sCF reinforced) epoxy foams (Table 5-2). The compressive modulus and strength of neat epoxy foams were found to be ~230 MPa and ~7 MPa for sample **0-A**, and 330 MPa and ~10 MPa for sample **0-B**, independent of the loading direction. These results are also in good agreement with the fracture toughness of the neat epoxy foams, which is also independent of the loading direction. This is due to the structural and material isotropy of the neat epoxy foams.

When reinforced with carbon fibres, the in-plane compressive modulus and strength of sCF reinforced epoxy foams increased, reaching values of up to 347 MPa and 7.4 MPa for sample **1** reinforced with 5.0 wt.-% sCF, and 845 MPa and 14.8 MPa for sample **2** reinforced with 5.0 wt.-% sCF. The introduction of carbon fibres, on the other hand, did not improve the out-of-plane compressive modulus of the sCF reinforced epoxy foams. The out-of-plane compressive modulus of the sCF reinforced epoxy foams were ~220 MPa for sample **1**, similar to sample **0-A**, and ~330 MPa for sample **2**, similar to sample **0-B**. With the introduction of carbon fibres, the out-of-plane compressive strength of sCF reinforced epoxy foams decreased by up to 20% (from 6.8 MPa to 5.5 MPa) for sample **1** and 25% (from 9.5 MPa to 7.1 MPa) for sample **2**. This is thought to be due to the brittle nature of carbon fibre reinforced pore wall material.

Nevertheless, these results showed the transversely isotropic nature of sCF reinforced epoxy foams produced via foam templating. Since sCF reinforced epoxy foams have isotropic (spherical) pore structures, the observed anisotropy in compressive properties arises from the anisotropy of the pore wall material, i.e. carbon fibre orientation. The high intensity mechanical frothing process generated a radial flow of the liquid foam that distributed the reinforcing carbon fibres preferentially in the in-plane direction, leading to the better mechanical performance in the in-plane direction than the out-of-plane direction. This material anisotropy is similar to that of wood, which is also a porous composite structure, whereby the reinforcing cellulose in the highly crosslinked lignin matrix that made up the pore wall material is predominantly oriented in the longitudinal direction compared to the radial and tangential directions [164].

5.4 Concluding remarks

Short carbon fibre (sCF) reinforced epoxy foams with superior mechanical properties have been successfully fabricated via foam templating method. By optimising the manufacturing process and prolonging the mixing time of the added carbon fibres, single carbon fibres were successfully individualised from the original fibre tows. The pore size was decreased when sCF was introduced to the epoxy foams, and long-time mixing of the carbon fibres also led to a decrease in porosity from ~69% to ~60%, which was due to the disruption and viscosifying effect of the added carbon fibres.

The fracture toughness of the epoxy foams was significantly improved in both in-plane and out-of-plane directions. When 5.0 wt.-% sCF was added and mixed for 20 s, a 55% improvement in critical stress intensity factor (K_{1c}) was observed. When the mixing time was prolonged to 2 min, a 110% increase in K_{1c} was achieved. The toughening mechanisms revealed from the fracture surfaces included pore wall material stiffening, fibre pull-out/breakage and crack deflection.

More significant improvement was observed for the compressive properties of the sCF reinforced epoxy foams. The highest improvement achieved was 165% in compressive modulus and 53% in compressive strength for 5.0 wt.-% sCF reinforced epoxy foams and mixed for 2 min. Anisotropic mechanical properties were observed for sCF reinforced epoxy foams, which were due to the anisotropic fibre orientation (preferentially in the in-plane direction) caused by the radial flow during the mixing process.

Chapter 6 Conclusion and future work

6.1 Conclusion

Foam templating method is a green, simple and versatile manufacturing method. The aim of this thesis is to use foam templating method to develop a new generation of epoxy foams and to widen the potential applications of the foam templated macroporous polymers. The three determined objectives have been successfully achieved.

1) To produce and characterise high porosity foam templated macroporous polymers above the state of the art

The porosity of foam templated macroporous polymers has been increased from 71% to 85% without introducing any blowing agents or stabilisers. This was achieved by applying heat to expand the air bubbles trapped within the liquid foam template prior to gelation of the resin.

2) To enhance the fracture resistance and impact toughness of the foam templated macroporous polymers

The brittleness of the foam templated macroporous polymers has been reduced without sacrificing their mechanical properties. This was achieved by applying hollow elastomeric microspheres. A 15% increase in critical stress intensity factor and 33% increase in Charpy impact strength were observed.

3) To manufacture and characterise short carbon fibre reinforced foam templated macroporous polymers

The mechanical properties of the foam templated macroporous polymers have been significantly improved. The highest compressive properties achieved was $E = 845$ MPa and $\sigma = 14.8$ MPa, representing a 165% and 53% improvement, respectively. The fracture toughness of the foam templated macroporous polymers was also enhanced.

6.2 Future work

6.2.1 Optimising the foam templated macroporous polymers

In this thesis, the porosity, fracture resistance and mechanical performance of the foam templated macroporous polymers have been studied and improved individually. A step further is to consolidate these studies and manufacture foam templated macroporous polymers with all these improved properties. It can be envisaged that macroporous polymers with both high porosities and high mechanical properties are more attractive and competent for structural applications.

The high porosity is achieved by applying heat to the prepared liquid foam templates before the gelation of the resin. This approach is simple and versatile, thus can be feasibly combined with other modification to the liquid foam templates. Also, it has been found that only small content of hollow elastomeric microspheres is needed to reduce the brittleness of the foam templated macroporous polymers, so it is possible to reinforce the

macroporous polymers, i.e. modify the liquid foam templates, with both hollow elastomeric microspheres and short carbon fibres. A viable manufacture process could be first mechanically frothing the epoxy resin and hardener mixture, followed by adding and mixing the hollow elastomeric microspheres and short carbon fibres, then curing the liquid foam template at elevated temperatures before the gelation point of epoxy resin.

6.2.2 Cost analysis on the foam templated macroporous polymers

Cost is one of the most important factors for the consideration of commercialisation of novel materials. The physical and mechanical properties of the foam templated macroporous polymers have been characterised in this thesis, and the results show that they have great potential to be used in many structural applications, such as in sandwich structures for aerospace and automotive applications. For potential commercial exploitation of this novel material, it will be useful to analyse and estimate the costs.

Life-cycle cost analysis (LCCA) can be used, which takes into account all costs related to acquiring raw material, transportation, manufacturing, operation, maintenance and disposal. Instead of providing the initial production cost only, it considers the cost throughout the whole life of the products. Therefore, the analysis results could provide a fair comparison between the novel material and currently available products. In addition, it could also provide some guidance on further optimising the foam templated macroporous polymers to be economically more attractive and cost-effective.

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