Enhancing the fracture resistance and impact toughness of mechanically frothed epoxy foams with hollow elastomeric microspheres

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Abstract

Non-porous elastomeric particles are often employed to improve the toughness of brittle epoxy foams but this results in the decrease in compressive strength and stiffness. Herein, we present a novel strategy utilising hollow elastomeric poly(acrylonitrile-co-methacrylonitrile) microspheres as a toughening agent for epoxy foams. The addition of 0.5 wt.-% hollow microspheres into epoxy foam led to a 15% increase in critical stress intensity factor (K_{1c}) to 0.38 MPa m$^{0.5}$ and 33% increase in Charpy impact strength (a_{cU}) to 1.05 kJ m^{-2}, respectively, compared to unfilled epoxy foam (K_{1c} = 0.33 MPa m$^{0.5}$ and a_{cU} = 0.79 kJ m^{-2}). However, a further increase in the hollow microsphere concentration to 1.0 wt.-% led to microsphere agglomeration, which reduced both K_{1c} and a_{cU} to 0.35 MPa m$^{0.5}$ and 0.93 kJ m^{-2}, respectively. Nevertheless, the added hollow microspheres did not lead to a reduction in the compressive properties of the epoxy foams.

Keywords

Epoxy, macroporous polymers, mechanical properties, toughness and impact resistance.

1. Introduction

Epoxy foams are a family of closed cell high performance macroporous polymers that possess good thermal stability, high chemical and moisture resistance.[1] 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.[2] Epoxy foams are often produced by dispersing hollow microspheres made from either glass[3] or phenolics[4] into the uncured liquid epoxy resin, followed by curing of the resin. These microsphere-filled epoxy foams are more commonly known as syntactic epoxy foams and their porosities are controlled by the concentration of the hollow microspheres introduced into the initial liquid epoxy resin. Epoxy resins can also be foamed using physical[5] or chemical[6] blowing agents to produce epoxy foams.

One major concern when using epoxy foam for various structural applications is its inherent brittleness stemming from the inflexible and highly cross-linked epoxy network.[7] Therefore, 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[8-10] 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.[11] The quasi-static compressive modulus and strength of these rubber particle-filled syntactic epoxy foams, on the other hand, decreased by 50% and 10%, respectively, compared to un-filled syntactic epoxy foams. Similar results were also observed for poly(dimethylsiloxane) (PDMS) particle[12] 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 un-filled syntactic epoxy foams. This is a direct result of using soft and non-porous elastomeric particles, which is necessary to enhance the toughness

of epoxy foams, but at the same time, these elastomeric particles are inherently inferior in compressive properties, which led 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. We propose that hollow elastomeric microspheres will also serve as excellent toughening agent for epoxy foams. Hollow microspheres possess higher specific surface area[1] compared to their non-porous counterparts due to their lower density, an essential energy-absorbing feature to enhance the fracture toughness/resistance of materials via filler-epoxy matrix de-bonding (due to an increase in filler-epoxy matrix interface). In this present study, we report the fracture resistance and Charpy impact toughness enhancement of mechanically frothed epoxy foams filled with lightweight hollow elastomeric microspheres made of poly(acrylonitrile-co-methacrylonitrile). We have previously demonstrated that epoxy foams can be produced using a surfactant- and blowing agent-free foam-templating method,[13, 14] whereby air-in-uncured liquid epoxy foam is first produced using high intensity mechanical frothing, followed by curing of the liquid foam. The air bubbles introduced during the frothing process formed the pores of the resulting macroporous epoxy resin. The porosity of these mechanically frothed macroporous polymers could be controlled by the heat applied during the curing process.[15] Unlike the production of syntactic epoxy foams, high intensity mixing is inherent to the production of the mechanically frothed epoxy foams, which has the added benefit of dispersing the toughening hollow elastomeric microspheres uniformly within the epoxy foams.

Three mechanically frothed epoxy foam formulations, un-filled epoxy foams (**M0**) and epoxy foams filled with 0.5 wt.-% (**M0.5**) and 1.0 wt.-% (**M1**) hollow elastomeric

[1] $\frac{S_P}{S_{NP}} = \frac{\rho_{NP}}{\rho_P}$, where S_P and S_{NP} is the total surface area of porous particles and non-porous particles, respectively, and ρ_P and ρ_{NP} is the density of porous and non-porous particles, respectively.

microspheres, were produced in this work following our previously developed protocol[13, 15] but modified to suit the mechanical frothing of hollow elastomeric microspheres into the air-in-uncured liquid epoxy foam. Briefly, un-filled epoxy foams **M0** were produced by mechanically frothing an epoxy-hardener mixture using a hand mixer operated at a maximum power output of 200 W for 20 min, followed by moulding and curing at room temperature for 24 h. Hollow elastomeric microsphere-filled epoxy foams (**M0.5** and **M1**) were produced by first mechanically frothing an epoxy-hardener mixture for 15 min using a hand mixer operating at its maximum power output of 200 W, followed by the addition of the hollow elastomeric microspheres and mechanically frothed for another 5 min at lower power output of 80 W. The hollow elastomeric microsphere-filled air-in-uncured liquid epoxy foams were then moulded and cured at room temperature for 24 h.

2. Results and discussion

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 g cm^{-3} and 66-68%, respectively, independent of the concentrations of the microsphere 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 Fig. 1. Un-filled epoxy foam **M0** possessed a polydisperse spherical pore structure, characterised by a broad pore size distribution (see Fig. 1a) with an average pore diameter (D_{avg}) of 114 ± 75 μm (see Table 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.

When the mechanically frothed epoxy foams were filled with 0.5 wt.-% (**M0.5**) and 1.0 wt.-% (**M1**) hollow microspheres, the spherical pore morphology was preserved (see Fig. 1b and 1c) but D_{avg} decreased to 70 ± 56 μm and 56 ± 55 μm, respectively (see Table 1). This is

due to the addition of the hollow elastomeric microspheres, which possessed an average microsphere diameter of only 37 ± 17 μm (see Fig. 1d for the pore size distribution of the hollow elastomeric microspheres used in this work). We have estimated the number of hollow elastomeric microspheres added per unit envelope volume of epoxy foam (N_{m}) into **M0.5** and **M1** to be 2533 ± 394 mm^{-3} and 4876 ± 759 mm^{-3}, respectively (see Table 1). This value is significantly higher than the pore density (defined as the number of pores per unit envelope volume of the epoxy foam) of **M0** (see Table 1), resulting in an overall decrease in estimated pore size, as well as narrowing of the pore size distributions of **M0.5** and **M1** (Fig. 1b and c). However, due to the large N_{m} into **M1**, agglomeration of the hollow elastomeric microspheres could also be observed (see Fig. 1c). It should be noted that we did not observe significant agglomeration of hollow elastomeric microspheres in sample **M0.5**.

The facture toughness of the fabricated (hollow elastomeric microsphere-filled) epoxy foams was measured from single-edge notched test specimens with an initial crack length (a) of 10 mm introduced at the centreline of the test specimen loaded in three-point bending mode. Their representative load-displacement curves are shown in Fig. 2a-c. 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 (Fig. 2a), hollow elastomeric microsphere toughened **M0.5** and **M1** exhibited a more progressive failure (Fig. 2b and 2c), indicating that the added microsphere does reduce the brittleness and improve the fracture toughness of the resulting epoxy foams.

The initial critical stress intensity factors ($K_{1\mathrm{c}}$) of samples **M0**, **M0.5** and **M1** are summarised in Table 1. Un-filled epoxy foam **M0** possessed $K_{1\mathrm{c}}$ of 0.33 MPa $m^{0.5}$. When the epoxy foams were filled with 0.5 wt.-% hollow elastomeric microspheres, $K_{1\mathrm{c}}$ increased by 15% to 0.38 MPa $m^{0.5}$ for sample **M0.5**. Similar improvements in (single edge notched) fracture toughness were reported by Benderly et al.[16] but for 10 wt.-% non-porous (carboxy terminated

acrylonitrile butadiene) rubber particle-filled syntactic epoxy foams with a porosity of 50% compared to un-filled syntactic epoxy foam. Pham et al.[8] further reported a (single edge-notched) fracture toughness improvement of only 8% for syntactic epoxy foam filled with 15 wt.-% crumb rubber compared to un-filled syntactic epoxy foam with a porosity of 21%. This signifies the potential of hollow elastomeric microspheres as toughening agent for epoxy foams compared to their non-porous counterpart due to their higher specific surface area. However, a further increase in the concentration of hollow elastomeric microspheres to 1.0 wt.-% (**M1**) led to a decrease in K_{1c} to 0.35 MPa m$^{0.5}$. This decrease 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)[17] and nano-clay particles.[18]

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 mechanically frothed epoxy foams (see Fig. 2d). Textured micro-flow was observed on the fracture surfaces of sample **M0**, indicating a brittle fracture process.[19-21] This is consistent with the load-displacement curve shown in Fig. 2a, 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 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.[22-25]

To further evaluate the resistance of the fabricated (hollow elastomeric microsphere-filled) epoxy foams to crack growth, a plot of K_{1c} as a function of crack opening (Δa) is shown

in Fig. 3a. 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 (on the R-curve of Fig. 2a, this is 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 hollow elastomeric microspheres and more energy is required to propagate the crack.

Charpy impact test was further conducted to investigate the impact toughness of our fabricated (hollow elastomeric microsphere-filled) epoxy foams (see Table 1). 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 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 mechanically frothed 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 **M0.5** and **M1** Charpy impact test specimens[2].

To ascertain whether the added hollow elastomeric microspheres lowered the compressive properties of the mechanically frothed epoxy foams, quasi-static compression test was conducted. The representative compressive stress-strain curves of the fabricated (hollow elastomeric microsphere-filled) epoxy foams are shown in Fig. 2a. 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.[26] Yielding of the foam occurs by plastic deformation of the cell walls,[27, 28] resulting

[2] The fracture surfaces of Charpy impact test specimens can be found in supplementary information.

in an approximately constant plateau stress. At large strains densification occurred, with self contact of the pores and the consequent increase in flow stress. The compressive elastic modulus (E) and strength (σ) of samples **M0**, **M0.5** and **M1** are summarised in Table 1. The values of E and σ range between ~290 MPa and ~8 MPa, respectively, independent of the weight fraction of hollow microspheres added. This confirms our initial hypothesis that the use of hollow elastomeric microspheres as toughnening agent does not reduce the quasi-static compressive stiffness and strength of hollow microsphere-filled epoxy foams (at similar porosity). The added hollow microspheres formed part of the pore structure, instead of reducing the mechanical properties of the pore wall material of the epoxy foams.

3. Concluding remarks

In this work, we have successfully fabricated mechanically frothed epoxy foams with enhanced fracture resistance and impact toughness without sacrificing their quasi-static compressive properties. This was achieved by using hollow elastomeric poly(acrylonitrile-co-methacrylonitrile) 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 g cm^{-3}. The quasi-static compressive modulus and strength of the epoxy foams were measured to be ~290 MPa and ~8 MPa, independent of the concentration of hollow microspheres added, indicating that hollow microspheres do not weaken the epoxy foam structure. 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 microsphere-filled epoxy foams were found to improve over neat and 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 compression properties provides an exciting opportunity to employ high

performance epoxy foams in applications where both toughness and quasi-static compressive properties are equally critical.

Acknowledgements

The authors would like to thank Imperial College London and China Scholarship Council for funding WS. We also greatly acknowledge funding provided by the UK Engineering and Physical Science Research Council (grant number: EP/M012247/1).

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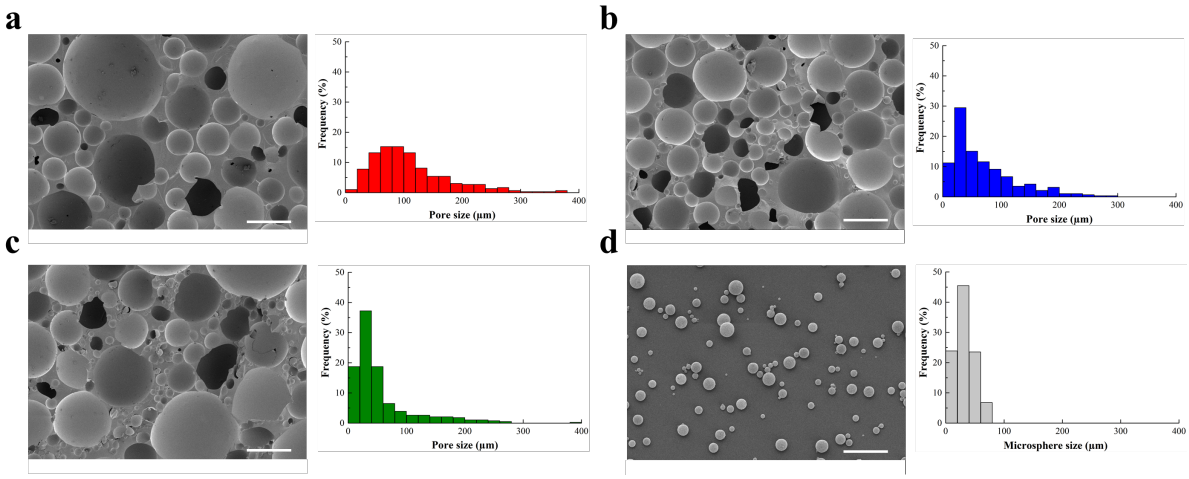


Figure 1. Scanning electron micrographs and pore size distribution of the fabricated samples, as well as the microsphere size distribution of hollow elastomeric microspheres used in this work. (a) Sample **M0** (neat and un-filled epoxy foam), (b) sample **M0.5** (0.5 wt.-% hollow elastomeric microsphere-filled epoxy foam), (c) sample **M1** (1.0 wt.-% hollow elastomeric microsphere-filled epoxy foam) and (d) hollow elastomeric microspheres. The scale bar is 200 µm, and the bin size is 20 µm.

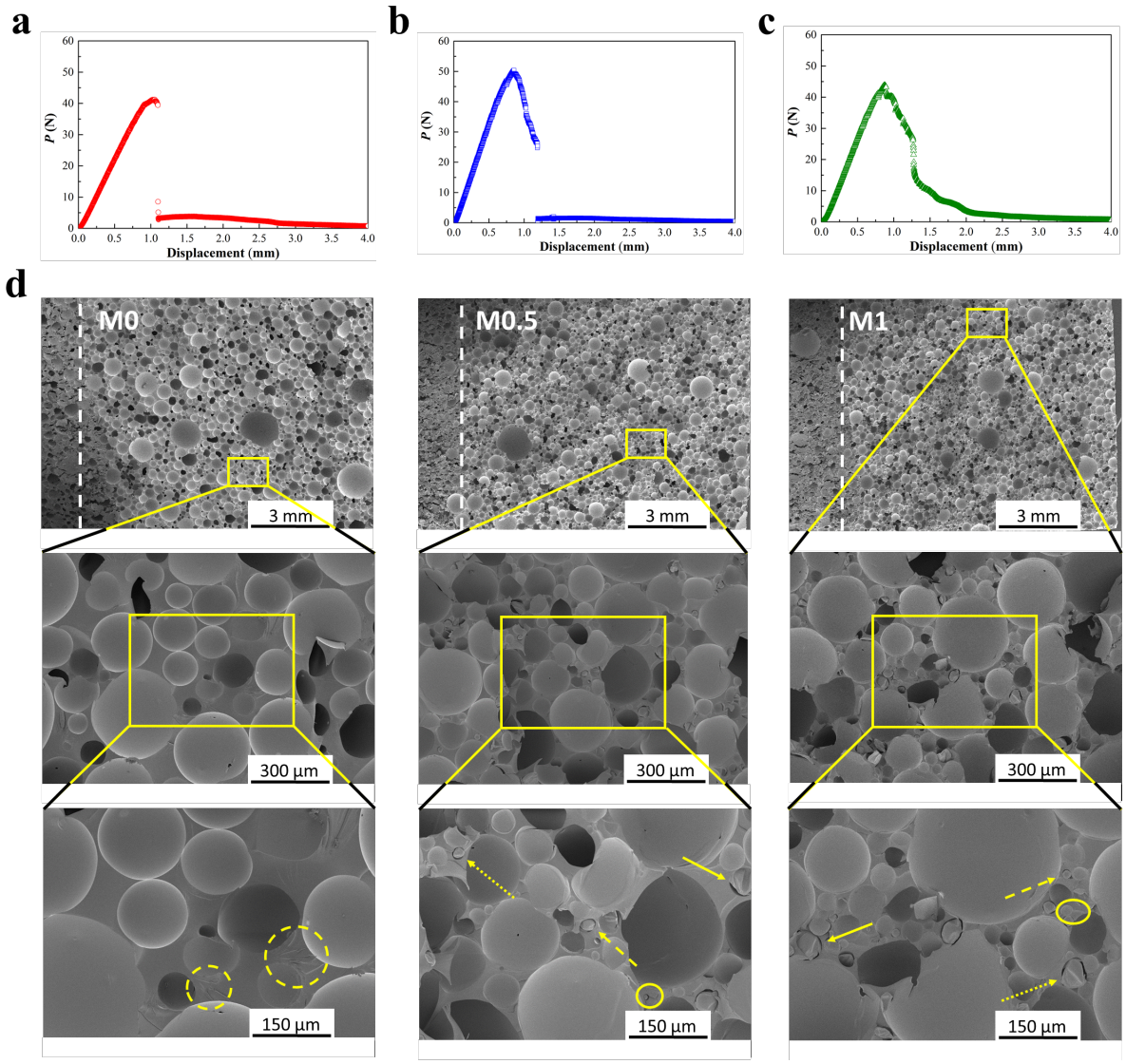


Figure 2. Representative load (P)-displacement curves and fracture surfaces of single edge notched specimens loaded in three-point bending mode. (a) Sample **M0** (neat and un-filled epoxy foam), (b) sample **M0.5** (0.5 wt.-% hollow elastomeric microsphere-filled epoxy foam), (c) sample **M1** (1.0 wt.-% hollow elastomeric microsphere-filled epoxy foam) and (d) fracture surfaces of samples **M0**, **M0.5** and **M1**. 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. Fractured, debonded and deformed microspheres are shown by arrows with solid lines, dash lines and dotted lines, respectively.

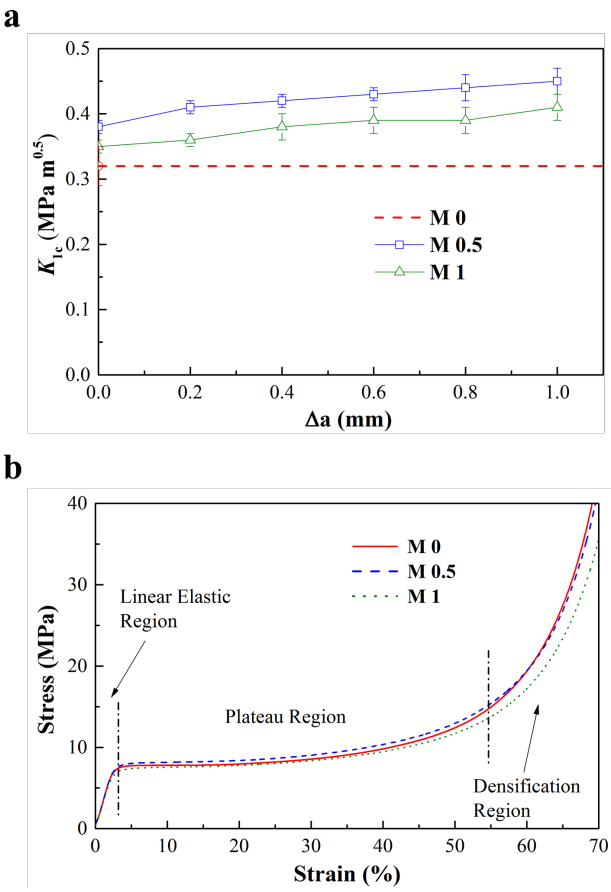
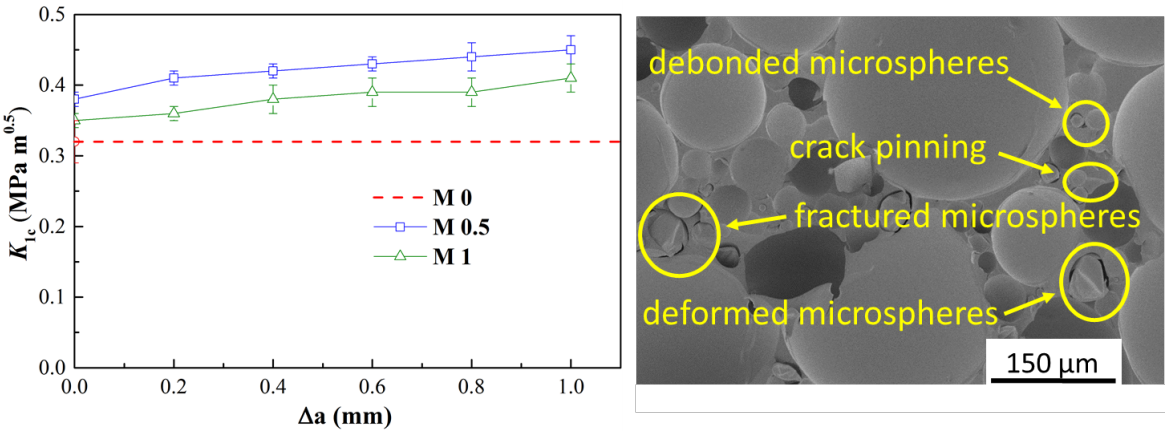


Figure 3. (a) Critical stress intensity factor (K_{1c}) as a function of crack opening (Δa) and (b) representative compressive stress-strain curves of the fabricated (hollow elastomeric microsphere-filled) epoxy foams.

Table 1. Physical and mechanical properties of the fabricated macroporous epoxy resins. P, D_{avg}, N_p, N_m, K_{1c}, a_{cU}, E and σ denote the porosity, average pore diameter, pore density, microsphere density, critical stress intensity factor, Charpy impact strength, compressive modulus and compressive strength, respectively

Sample	P (%)	D_{avg} (μm)	N_p (mm^{-3})	N_m (mm^{-3})	K_{1c} (MPa m$^{0.5}$)	a_{cU} (kJ m^{-2})	E (MPa)	σ (MPa)
M0	68 ± 1	114 ± 75	854 ± 98	0	0.33 ± 0.02	0.79 ± 0.09	290 ± 51	8.0 ± 0.3
M0.5	66 ± 1	70 ± 56	3660 ± 522	2533 ± 394	0.38 ± 0.01	1.05 ± 0.09	290 ± 30	8.1 ± 0.4
M1	67 ± 1	56 ± 55	7402 ± 1116	4876 ± 759	0.35 ± 0.01	0.93 ± 0.04	295 ± 25	7.8 ± 0.3

Graphic Abstract & Table of Contents



Toughening epoxy foam without sacrificing its compressive properties? In this work, we present a method to enhance the fracture resistance and impact toughness of brittle epoxy foam without sacrificing its quasi-static compressive properties using porous elastomeric microspheres. 15% improvement in fracture toughness and 33% increase in Charpy impact strength have been achieved with the failure mode changing from catastrophic to progressive.

Supplementary Information

Enhancing the fracture resistance and impact toughness of mechanically frothed epoxy foams with hollow elastomeric microspheres

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A. Experimental procedure

Materials. Epoxy resin with 56 % biomass content (Greenpoxy 56, ρ = 1.20 ± 0.01 g cm^{-3}, η = 2500 mPa s at 15 °C) and amine-based hardener with 58 % biomass content (GP 505 v2, ρ = 0.99 ± 0.01 g cm^{-3}, η = 1800 mPa s at 15 °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 μm, ρ = 0.03 ± 0.01 g cm^{-3}) was kindly provided by AkzoNobel (Sundsvall, Sweden) and used as the toughening agent for epoxy foams.

Manufacturing of (hollow microsphere-filled) mechanically frothed epoxy foams. Mechanically frothed epoxy foams were prepared using foam-templating method following a previously described procedure[†]. Briefly, 70 g of bio-based 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 of our study, neat and un-filled mechanically frothed epoxy foam (**M0**), the bio-based epoxy resin and amine-based hardener were mechanically frothed for 20 min at maximum power output of 200 W. To produce lightweight hollow microsphere-filled mechanically frothed epoxy foams, the resin-

[†]W. Song, K. Barber, K.-Y. Lee, *Polymer* **2017**, *118*, 97.

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 samples were designated as samples **M0.5** and **M1**, respectively. The (hollow elastomeric microsphere-filled) air-in-uncured liquid epoxy resin foams were 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 × 100 × 25 mm^3 and left to cure at room temperature for 24 h.

Characterisation 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 power 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:

$$P = \left(1 - \frac{\rho_f}{\rho_s}\right) \times 100\% \quad \text{(S1)}$$

The structure and morphology of the (hollow elastomeric microsphere-filled) mechanically frothed 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 their 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_{avg}) 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:

$$N_p = \frac{6P}{\pi {D_{avg}}^3} \quad \text{(S2)}$$

We also define the microphere density within the epoxy foam (N_{m}), defined as the number of the hollow elastomeric microspheres per unit volume of foam:

$$N_{\mathrm{m}} = \frac{6\,\varphi}{\pi\,{D_m}^3} \cdot \frac{\rho_f}{\rho_m} \quad \text{(S3)}$$

where φ is the weight ratio of the added microsphere to the resin and hardener, and D_m and ρ_m is the average diameter and density of the hollow elastomeric microsphere, respectively.

The fracture toughness of the epoxy foams was determined in accordance to ASTM D5045–14 on single edge notched beams (SENB) 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 × 20 × 10 mm^3. An initial crack of ~10 mm was introduced to the rectangular test specimens such that the initial crack length (a) to width (w) ratio fulfil the requirement of $0.45 \leqslant a/w \leqslant 0.55$. The initial crack length was created by cutting the first 8 mm with a band-saw and the last 2 mm with a sharp surgical scalpel. The precise crack length value (a) was determined from analysis of the fracture surfaces after the SENB 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 ($K_{1\mathrm{c}}$) was calculated using:

$$K_{1c} = \left(\frac{P_C}{bw^{0.5}}\right) f(a/w) \quad \text{(S4)}$$

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

$$f(a/w) = 6\,(a/w)^{0.5}\,\frac{[1.99-a/w(1-a/w)(2.15-3.93a/w+2.7(a/w)^2)]}{(1+2a/w)(1-a/w)^{1.5}}\,. \quad \text{(S5)}$$

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 × 10 × 10 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.

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 axial strain in the test specimens. A total of 5 specimens were tested for each sample.

B. SEM images of the fracture surfaces of the samples after Charpy impact test

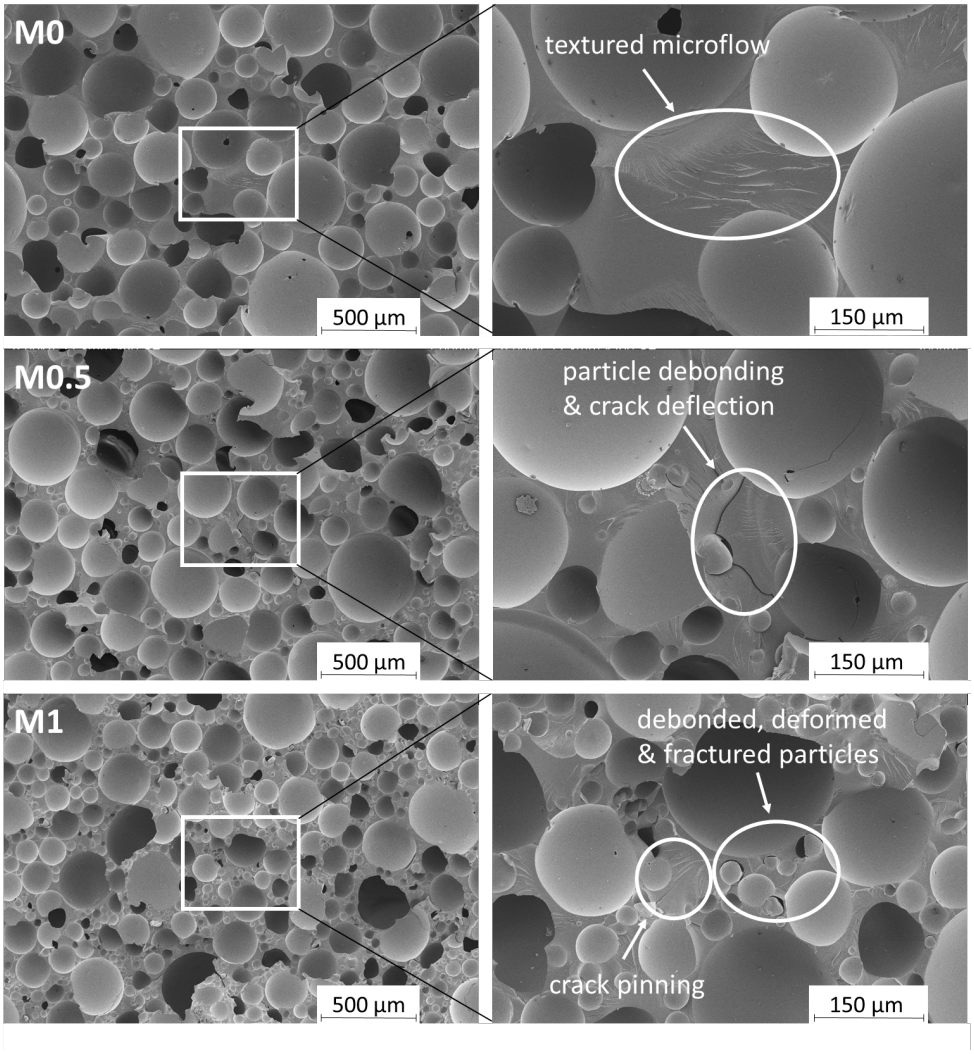


Figure S1. SEM images of the fracture surfaces of the samples after Charpy impact tests.

Figure S1 shows the SEM images of the fracture surfaces after Charpy impact test. In the magnified image of sample **M0**, only some textured microflow can be observed on the epoxy matrix. From the magnified image of sample **M0.5** and sample **M1**, gaps can be seen between some small pores, which indicates debonding of the hollow elastomeric microspheres from the matrix. In addition, some microspheres are deformed and even fractured, which added the toughness of the epoxy foam as well. Crack pinning feature can also be observed, which is due to the impediment of the added microspheres, causing the crack front to deflect and bow out.