Robust synthesis of epoxy resin-filled microcapsules for application to self-healing materials

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One contribution of 15 to a discussion meeting issue 'Catalysis making the world a better place'.

Subject Areas:
materials science

Keywords:
catalysis, microcapsules, self-healing materials, carbon fibre composites

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Mechanically and thermally robust microcapsules containing diglycidyl ether bisphenol A-based epoxy resin and a high-boiling-point organic solvent were synthesized in high yield using *in situ* polymerization of urea and formaldehyde in an oil-in-water emulsion. Microcapsules were characterized in terms of their size and size distribution, shell surface morphology and thermal resistance to the curing cycles of commercially used epoxy polymers. The size distribution of the capsules and characteristics such as shell thickness can be controlled by the specific parameters of microencapsulation, including concentrations of reagents, stirrer speed and sonication. Selected microcapsules, and separated core and shell materials, were analysed using thermogravimetric analysis and differential scanning calorimetry. It is demonstrated that capsules lose minimal 2.5 wt% at temperatures no higher than 120° C. These microcapsules can be applied to self-healing carbon fibre composite structural materials, with preliminary results showing promising performance.

1. Introduction

Microencapsulation of reactive ingredients has attracted interest in a variety of fields, including medicine, agrochemicals, food additives and cosmetics [1–3]. More recently, microencapsulation has been explored in the growing field of self-healing polymers and other

structural materials [4–6]. The active ingredients, including monomers, catalysts and hardeners, are embedded in a host material, ready for release and polymerization, the healing process being typically triggered by a propagating crack that ruptures the microcapsules, releasing the encapsulated materials. Chemical reaction (typically polymerization) or physico-chemical processes lead to bonding of the crack surfaces and restoration of the material's integrity [4–6]. An early example of a capsular self-healing system used dicyclopentadiene (DCPD) as the encapsulated monomer and dispersed particles of Grubbs' catalyst to trigger hardening [7]. In this approach, the released DCPD comes into contact with the catalyst and undergoes ring-opening metathesis polymerization; the poly(urea–formaldehyde) (UF) microcapsules containing the DCPD were prepared using *in situ* polymerization in an oil-in-water emulsion [8]. Using related methodology, chemistries including DCPD/ethylidene-norbornene [9], organic solvents [10,11], epoxy resins [12] and their cross-linkers such as amines [13,14], thiols [15] and glycidyl methacrylate [16] have been successfully encapsulated. Typical capsule shell materials include UF, melamine–UF (UMF) and melamine–formaldehyde (MF), which have proved promising for sequestration of various reactive ingredients [4,5,17,18].

The usual method for microencapsulation using these materials is that liquid core reagents are first dispersed in an aqueous phase containing surfactants/stabilizers and shell-forming monomers. Initially, the shell-forming reagents form a low-molecular-weight pre-polymer, which grows with time and deposits on the interface between the water and oil phases. Polycondensation of urea and formaldehyde continues at the interface and leads to a solid and non-permeable capsule shell. Most of the capsule characteristics (e.g. diameter, wall thickness) can be influenced by controlling the parameters of the emulsification procedure: reaction time, temperature, core-to-shell reagent ratio and stirring speed [19,20].

Here, we report an extensive study on microencapsulation of diglycidyl ether of bisphenol A epoxy resin and organic solvent (ethyl phenylacetate) using *in situ* polymerization in an oil-in-water emulsion. The primary aim of this research was to develop methods by which the exact attributes of microcapsules can be defined, which is necessary in the application of such microcapsules in self-healing structural components. As proof of concept of this application, a flat laminate with embedded microcapsules and dispersed Lewis acid (LA) catalyst ($Sc(OTf)_3$) was manufactured, with the embedded microcapsules and catalyst in the interleave region.

2. Materials and methods

(a) Materials

Ethyl phenylacetate (EPA, $C_6H_5CH_2COOC_2H_5$), urea (NH_2CONH_2), poly(ethylene-*alt*-maleic) anhydride (EMA, M_W = 100 000–500 000, powder), resorcinol (C_6H_4-1,3-$(OH)_2$), formaldehyde (37 wt% in H_2O, CH_2O) and ammonium chloride (NH_4Cl) were purchased from Sigma-Aldrich and used as received. Sodium hydroxide (NaOH) was purchased from Fisher Scientific. Commercial epoxy resin (EPON 828) was purchased from Polysciences Inc. and also used as received. Encapsulation was performed in a round-bottomed glass vessel made in-house, with the following parameters: internal width 75 mm, height 135 mm and curvature depth 15 mm; the vessel was also fitted with a PTFE lid. An overhead stirrer (Caframo Petite Digital Model BDC 250) equipped with a two-bladed axial propeller (35 mm wide) was used for emulsification and mixing.

(b) *In situ* encapsulation of organic solvent and epoxy resin

Poly(UF) microcapsules containing EPON 828–ethyl phenylacetate (table 1) were synthesized via *in situ* polymerization as described in the literature [12]. In a typical procedure, 125 ml of a 1.2 wt% aqueous solution of poly(ethylene-*alt*-maleic) anhydride was placed in the previously defined vessel and 2.50 g urea, 0.250 g resorcinol and 0.250 g ammonium chloride were added and stirred at room temperature until full dissolution. After 10 min, the pH of the aqueous phase

Table 1. Systematic names and designations of microcapsule core materials used in the study. The wt% is measured by weight per cent relative to the organic encapsulated phase assuming that density is equal to 1 g ml^{-1}.

systematic name	EPON 828 (wt%)	EPA (wt%)
E2.5	2.5	97.5
E50	50	50
E75	75	25
E90	90	10

was adjusted by dropwise addition of NaOH (≈0.2 N) from 2.6 to 3.2 and allowed to equilibrate. Stirring speed was increased to the desired rate and 60 ml of a 2.5 wt% solution of epoxy resin (EPON 828) in EPA was dispersed under continued stirring. This emulsion was left at the desired stirring rate (from 800 to 1500 r.p.m.) for a further 10 min and then 6.33 g of aqueous formaldehyde solution was added. In experiments requiring sonication, the tapered 1/8" tip sonication horn of a 750 W ultrasonic homogenizer was immersed in the emulsion, which was sonicated for 3–6 min. The temperature of the system was increased to 55° C. After 4 h, the stirrer was stopped and the microcapsule slurry was left to settle at room temperature for 24 h. Next, capsules were isolated by filtration and rinsed a few times with water and then ethanol. The isolated capsules were dried at 55° C for 24 h. The yield of microcapsules was calculated relative to the mass of used materials.

(c) Size and size distribution analysis

Size and size distribution of microcapsules were analysed by a Zeiss Optical Microscope AXIO Imager.M2 equipped with a video camera AxioCam ICc 1. At least 500 measurements of capsule diameters were taken; for the size distribution, image analysis software (ImageJ) was used.

(d) Surface morphology

Surface morphology analysis was performed with a scanning electron microscope JEOL SEM 5600LV. Dry capsules were placed on the conductive tab and sputter-coated before analysis with a layer of Ag/Pd. Scanning electron microscopy (SEM) was also used to investigate fracture surfaces of delaminated double cantilever beam (DCB) test specimens.

(e) Thermal analysis of microcapsules, and their core and shell materials

Thermal analysis was performed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Mass loss of capsules was recorded under non-isothermal conditions from 25° C to 500° C and during isothermal measurements at different temperatures by a TA Instruments Q500 TGA. Isothermal experiments were performed at 80, 100, 120 and 140° C for 2 h. Dynamic analysis of the capsules and core–shell materials was recorded on a TA Instruments Q200 DSC in a temperature range of 0–250° C.

(f) Composite manufacturing with embedded microcapsules

Flat composite laminates with embedded microcapsules and solid-phase LA were manufactured using carbon/epoxy resin tape (SE 70, Gurit, UK) and adhesive resin film (SA 70, Gurit, UK) using a standard hand lay-up technique. Laminates after lay-up (16 plies (160 × 195 mm)) were placed on an aluminium tool plate, sealed with a vacuum bag and consolidated according to the manufacturer's recommendations at 100° C for 100 min. Microcapsules and $Sc(OTf)_3$ particles were mixed with a resin paste (SA 70, Gurit, UK) at 26 and 2.5 wt%, respectively, and screen-printed onto the middle plane surface during the lay-up. An additional control specimen containing the resin-filled interleave region was manufactured. After curing, composite plates

were removed from the vacuum bag, grit-blasted on their front and trimmed on the edges using a diamond saw. Composite plates were then cut into DCB specimens (20 mm × 175 mm) and piano hinges were bonded to the specimens at the pre-cracked end using Araldite 2014 structural adhesive and left at room temperature until fully cured.

(g) Tests for self-healing

Tests for mode I interlaminar fracture were performed for virgin and healed DCB specimens. A standard test machine (Shimadzu AGX-X) equipped with 1 kN load cell and a video camera was used. Tests were performed in accordance with the ASTM 5528-13 standard method [21]. Specimens were tested in crack opening mode at 3 mm min^{-1} displacement rate, from the release film to the end of the interleave resin region containing microcapsules. After testing, specimens were unloaded, sealed and left at 80° C for 24 h. The healing efficiency (η) was calculated from the ratio of the healed maximum peak load (P_{Healed}) to the virgin maximum peak load (P_{Virgin}):

$$\eta = \frac{P_{\text{Healed}}}{P_{\text{Virgin}}} \times 100\%.$$

3. Results and discussion

(a) Encapsulation of commercial epoxy resins and solvents

UF microcapsules containing epoxy resin–solvent mixtures were synthesized in variable size by *in situ* polymerization in an oil-in-water emulsion (tables 2 and 3). Capsules containing from 2.5 to 90 wt% of the commercial epoxy resin (EPON 828) in ethyl phenylacetate were synthesized by a method adopted from the literature and by a modification of this method (table 4).

(b) Influence of stirring speed/sonication on microcapsule size

Using a literature method [12], the dependence of microcapsule size on epoxy resin concentration in the organic phase was investigated. For all specimens, 60 ml of epoxy resin/solvent containing 2.5, 50, 75 or 90 wt% of epoxy resin was dispersed in 125 ml of water at 800 r.p.m. Organic phases containing 2.5 and 50 wt% of epoxy resin were easily dispersed at this rate and capsules resulted in a wide range of sizes (table 2). At 75 and 90 wt% EPON 828, the high viscosity of these formulations resulted in very poor dispersion at 800 r.p.m.; increasing the stirring rate (to 1000 r.p.m.) was necessary for successful encapsulation.

The dependence of size and size distribution of the microcapsules on stirring rate, sonication and surfactant/stabilizer concentration is reported in table 3. As expected, the size of microcapsules is decreased with increasing stirring speed (figure 1*a*); a representative size distribution at 1100 r.p.m. is given in figure 1*b*. Unfortunately, at higher stirring rates (1200– 1500 r.p.m.) the microcapsules rupture (see entries 9 and 10 in table 3) [16], putting a lower limit of around 100 µm on the size of microcapsules that can be accessed by this method. This is potentially a problem in terms of application to self-healing composites in that it is presumed that smaller diameters will in general have a less detrimental influence on the mechanical performance of the structural material.

To obtain microcapsules with diameters below 100 µm, sonication was required as an alternative homogenization method [22,23]. To ensure full interfacial coverage of newly created droplets, the surfactant/stabilizer (poly(ethylene-*alt*-maleic) anhydride) load was increased to 2.5 wt% relative to the mass of dispersed core materials. After sonication of the emulsion for 3 min at 80% amplitude, the droplet size was decreased sufficiently that microcapsules in the 100 µm range could be prepared at 800 r.p.m. stirring speed, rather than at the 1000 r.p.m. required without sonication. Increasing the surfactant/stabilizer concentration further (table 3, entries 2–4) resulted in even smaller capsules (as low as 4 ± 2 µm), still in acceptable yields. Figure 2 represents a typical size distribution of microcapsules prepared at 5 wt% of surfactant/stabilizer.

Table 2. Encapsulation conditions of EPON 828 at variable concentrations in an oil-in-water emulsion.

EPON 828 in organic phase (wt%)	water phase (ml)	organic phase (ml)	surfactant amount (wt%)[a]	agitation rate (r.p.m.)	mean diameter (µm)
2.5	125	60	1	800	140 ± 80
50	125	60	1	800	200 ± 140
75	125	60	1	1000	170 ± 110
90	125	60	1	1000	190 ± 110

[a]The wt% is measured by weight per cent relative to the organic encapsulated phase assuming that density is equal to 1 g ml^{-1}.

Table 3. Encapsulation conditions of EPON 828 in an oil-in-water emulsion. Reaction volume included 30 ml of organic phase at constant concentration of epoxy resin (10 wt%) to organic solvent dispersed in 62.5 ml of water containing shell-forming monomers (urea, resorcinol and formaldehyde).

no.	pH	agitation rate	amount of surfactant (wt%)[a]	time of sonication (min)	temperature (°C)	yield (%)	mean diameter (µm)
1	3.15	800	2.5	3	55	81.3	100 ± 40
2	3.10	800	3.75	3	55	74.5	60 ± 40
3	3.11	800	5	3	55	66.1	6 ± 3
4	3.09	800	10	5	55	51.0	4 ± 2
5	3.11	800	2.5	0	55	91.6	180 ± 100
6	3.72	900	2.5	0	55	80.5	160 ± 80
7	3.09	1000	2.5	0	55	65.5	100 ± 40
8	3.57	1100	2.5	0	55	41.6	80 ± 80
9	3.8	1200	2.5	0	55	—	—
10	3.6	1500	2.5	0	55	—	—

[a]The wt% is measured by weight per cent relative to the organic encapsulated phase assuming that density is equal to 1 g ml^{-1}.

Table 4. Adopted and modified methods of epoxy resin–solvent encapsulation in an oil-in-water emulsion.

encapsulation method	aqueous phase (ml)	EMA (wt%)[a]	urea (g)	NH_4Cl (g)	resorcinol (g)	formalin (g)
(*a*) literature [12]	125	1	2.50	0.250	0.250	6.33
(*b*) modified	62.5	2.5–10	1.25	0.125	0.125	3.16

[a]The wt% is measured by weight per cent relative to the organic encapsulated phase assuming that density is equal to 1 g ml^{-1}.

(c) Shell wall morphology

Scanning electron micrographs of exemplary microcapsules prepared by adopted and modified methods are presented in figure 3*b* and 3*a*, respectively. Both types of microcapsules contained 75 wt% of the epoxy resin and 25 wt% of ethyl phenylacetate. In both cases, the shell material comprises a thin continuous inner shell (with diameter about 160–200 nm) and a thicker rough exterior wall. It has been reported that the continuous membrane is formed as urea and formaldehyde react in the aqueous phase, resulting in a low-molecular-weight polymer that collapses at the oil/water interface. As the UF reaction progresses, the rough exterior is formed as colloidal poly(UF) particles coalesce, and deposit along the interface [8,19]. As can be seen in figure 3, the modified method in which a higher concentration of surfactant/stabilizer is used

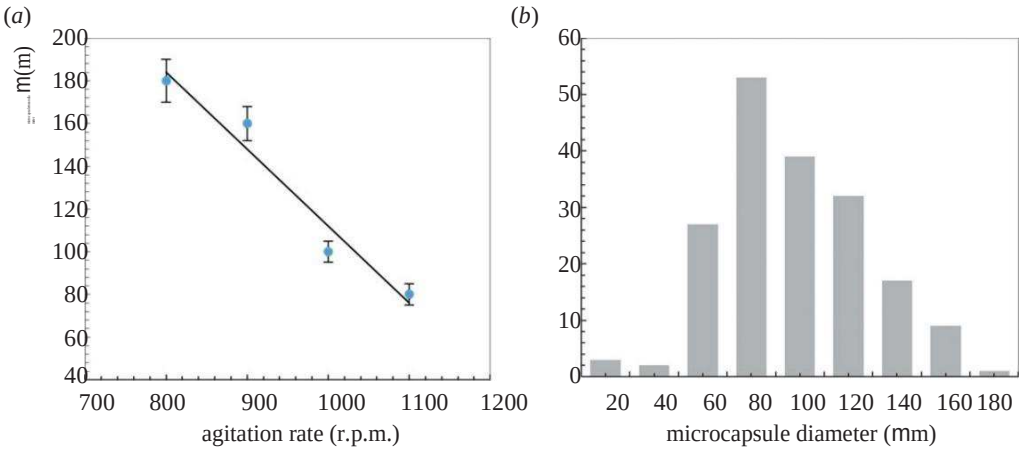

Figure 1. Mean diameter of microcapsules containing 10 wt% of EPON 828: (*a*) diameter of microcapsules as a function of stirring rate and (*b*) representative histogram of microcapsule diameter prepared at 1100 r.p.m. (Online version in colour.)

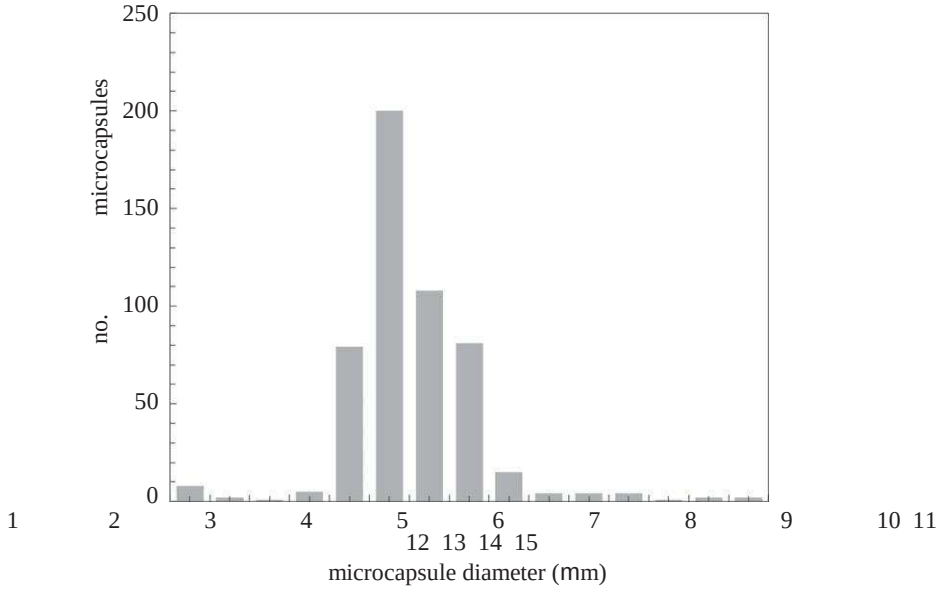

Figure 2. Size distribution of EPON 828–EPA microcapsules prepared at increased surfactant stabilizer concentration (5 wt%) and after sonication.

gives a much more even shell wall morphology, presumably due to the enhanced stabilization of the nascent microcapsules. This enhanced stabilization reduces the amount of small agglomerates that can accrete on the surface of the microcapsules.

(d) Load of shell-forming materials

The mechanical properties of microcapsules are important in their application to self-healing materials, with the requirements to be sufficiently robust to survive structural material manufacture but able to burst after a damage event. It is therefore desirable to be able to systematically change the shell wall thickness, with thicker materials expected to be more robust. To this end, the amount of shell wall-forming materials (urea, NH_4Cl, resorcinol, formaldehyde and the poly(EMA) surfactant/stabilizer) was increased relative to the encapsulated epoxy

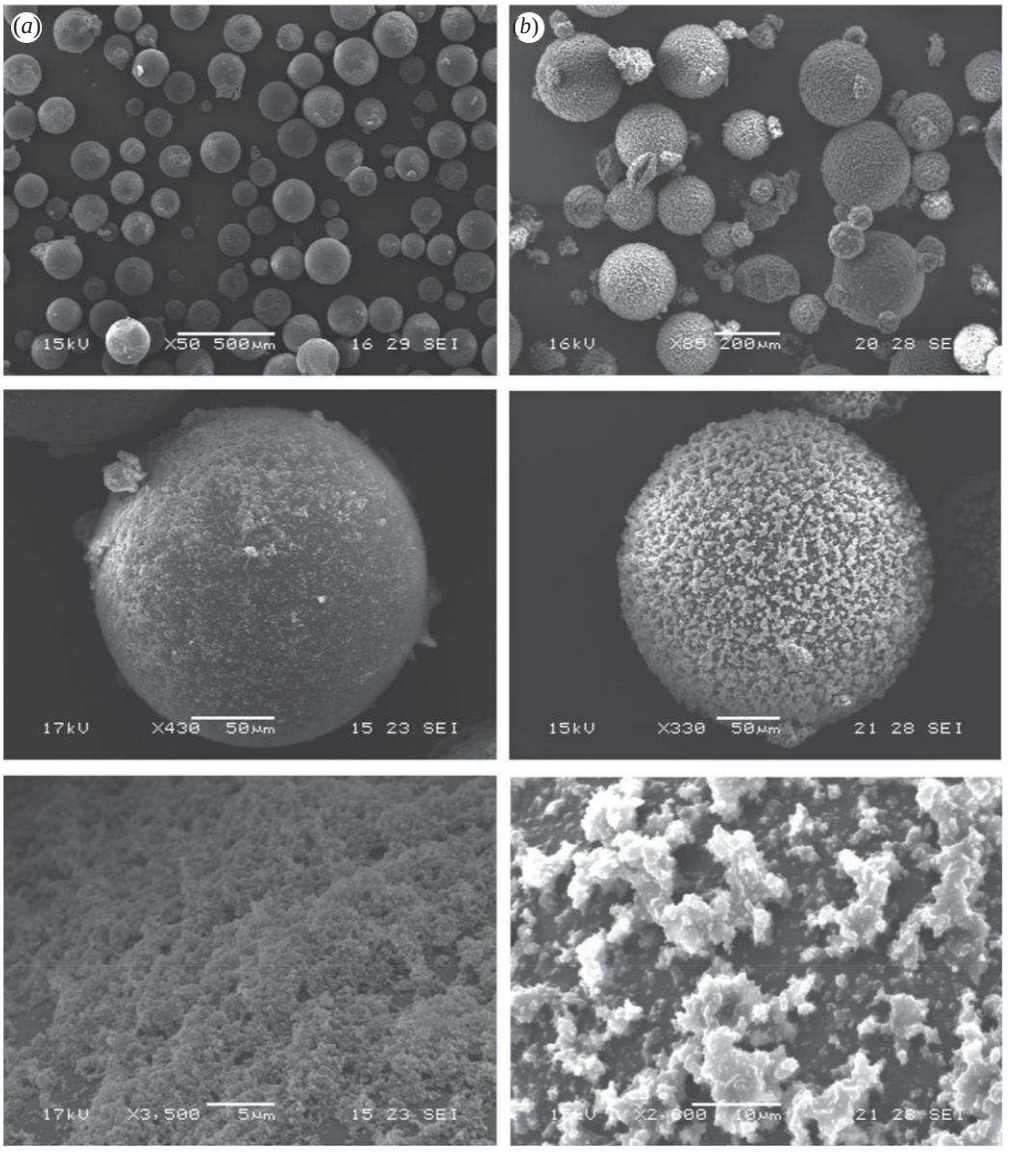

Figure 3. Scanning electron micrographs of (*a*) microcapsules containing 75 wt% of epoxy resin in organic solvent (ethyl phenylacetate) prepared by modified method without application of sonication (tables 3 and 5) and (*b*) microcapsules prepared by method adopted from the literature (table 2, E75) [12].

monomer and aqueous phase, while keeping the ratio between these shell wall-forming materials constant. In total, 150 and 200% increases by weight compared to previous runs were investigated (table 5).

The corresponding SEM micrographs of the resulting samples are presented in figure 4. We observe that increasing the concentration of shell wall-forming materials leads to highly agglomerated microcapsules. This is presumably due to the fast condensation of the pre-polymer prior to deposition at the water–oil interface and is a clear limitation of this method.

(e) Thermal resistance of microcapsules

Experiments to explore the thermal stability of microcapsules were performed for E50 microcapsules (figure 5*a*) using TGA. Microcapsules and separated core/shell materials were

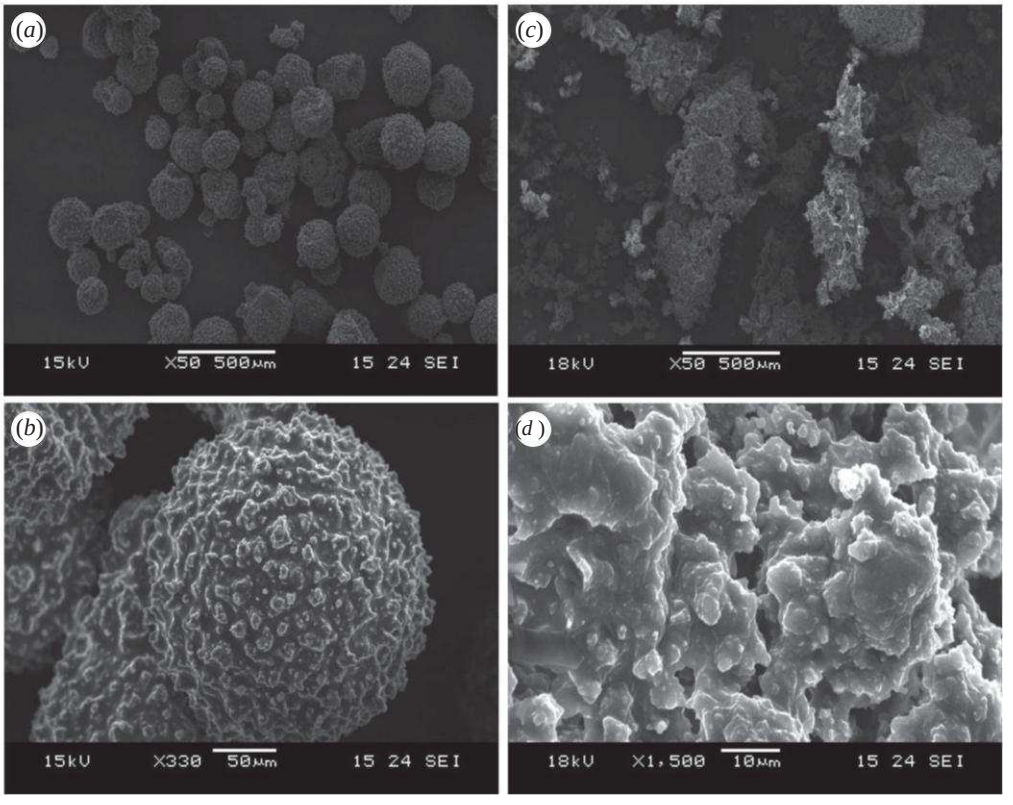

Figure 4. Microcapsules prepared using (*a*,*b*) *in situ* polymerization at 50% and (*c*,*d*) 100% excess of shell-forming monomers (urea, resorcinol and formaldehyde). Reaction was carried out in an oil-in-water emulsion containing 75 wt% of epoxy resin (EPON 828) and 25 wt% of high-boiling-point organic solvent (ethyl phenylacetate) as oil phase.

Table 5. Load of the shell-forming materials used in the study. The encapsulation was carried out as for previous samples at the same conditions of stirring (800 r.p.m.), pH (3.15) and temperature (55°C).

encapsulation method	aqueous phase (ml)	EMA (wt%)[a]	urea (g)	NH_4Cl (g)	resorcinol (g)	formalin (g)
(*a*) standard	62.5	2.5	1.25	0.125	0.125	3.16
(*b*) 150%	62.5	2.5	1.875	0.1875	0.1875	4.74
(*c*) 200%	62.5	2.5	2.5	0.25	0.25	6.32

[a]Weight per cent measured relative to mass of dispersed organic phase (30 ml).

analysed non-isothermally from 25 to 500° C. The first mass loss observed at 170° C is associated with thermal decomposition of the shell polymer, with similar behaviour observed for separated poly(UF) shell wall material. Another onset of mass loss at 210–220° C corresponds to the boiling point of encapsulated ethyl phenylacetate, which continues to 310° C. During continuous heating at high temperatures, the encapsulated epoxy resin partially polymerized, with onset at 360° C. A similar trend is observed for a non-encapsulated core epoxy resin–organic solvent mixture (50% EPON 828 and 50% EPA). To further determine the thermal stability of microcapsules, isothermal experiments were performed at 80, 100, 120 and 140° C for 2 h. The representative mass loss is presented in figure 6*b*. It was observed that microcapsules lose 2.5 wt% of their total mass at 80, 100 and 120° C. This mass loss is associated with the removal of residual water from the shell wall, leading to further cross-linking of the poly(UF). After 2 h at 140° C, an increased mass loss of 6.5% was observed as a result of microcapsule decomposition.

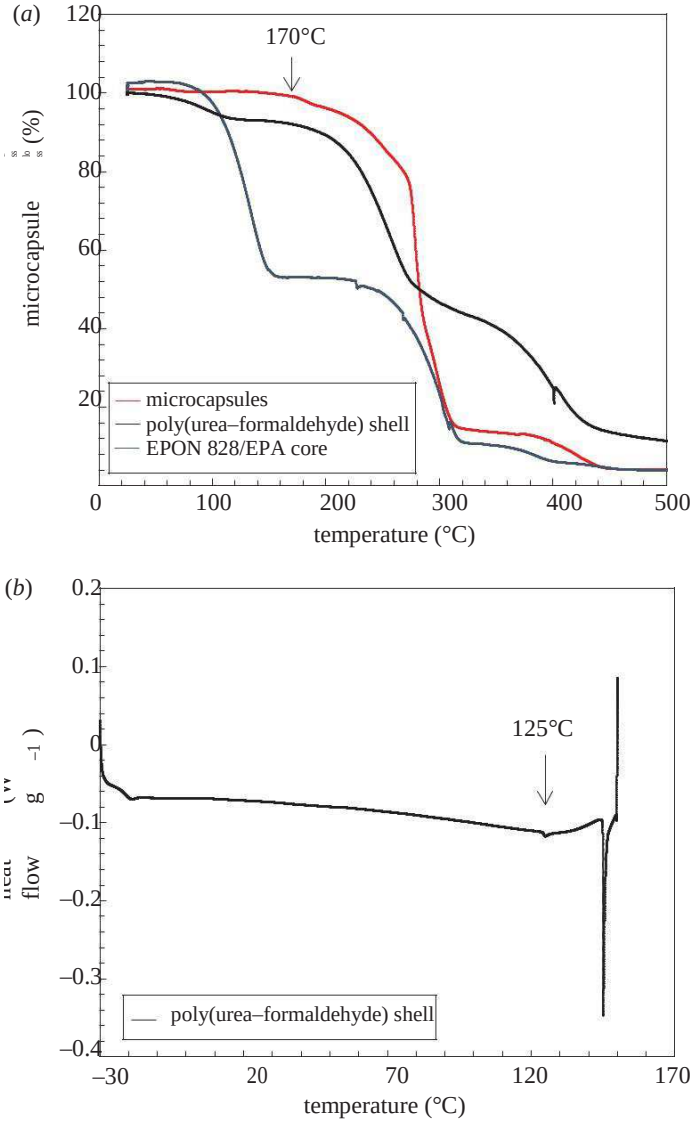

Figure 5. (*a*) Representative TGA for microcapsules containing 50 wt% of commercial epoxy resin and 50 wt% of high-boiling-point solvent (ethyl phenylacetate) and separated core and shell materials. (*b*) Exemplary DSC analysis of separated poly(UF) shell material illustrating its softening point. (Online version in colour.)

DSC was used to determine the thermal behaviour of microcapsules and separated core/shell materials. The glass transition temperature for the separated shell material is 125° C and this is followed by an endotherm with a peak temperature at 145° C (figure 6*a*). This observed glass transition temperature is the upper usage limit of the prepared capsules; beyond this temperature, softening leads to a release of core material. Furthermore, at 237° C we observed an onset of ethyl phenylacetate evaporation combined with homopolymerization of diglycidyl ether of bisphenol A and its thermal decomposition.

(f) Self-healing performance

Preliminary experiments for recovery of fracture properties (mode I) in a carbon fibre reinforced polymer (CFRP) composite were performed for E75 microcapsules. Capsules and the solid

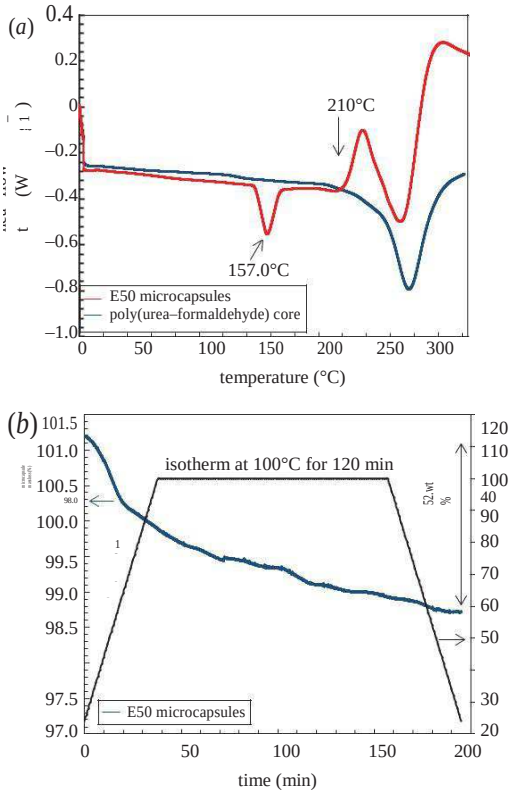

Figure 6. (*a*) DSC curves for microcapsules and separated core materials. (*b*) Representative mass loss of microcapsules during a 2 h isotherm at 100˚ C. (Online version in colour.)

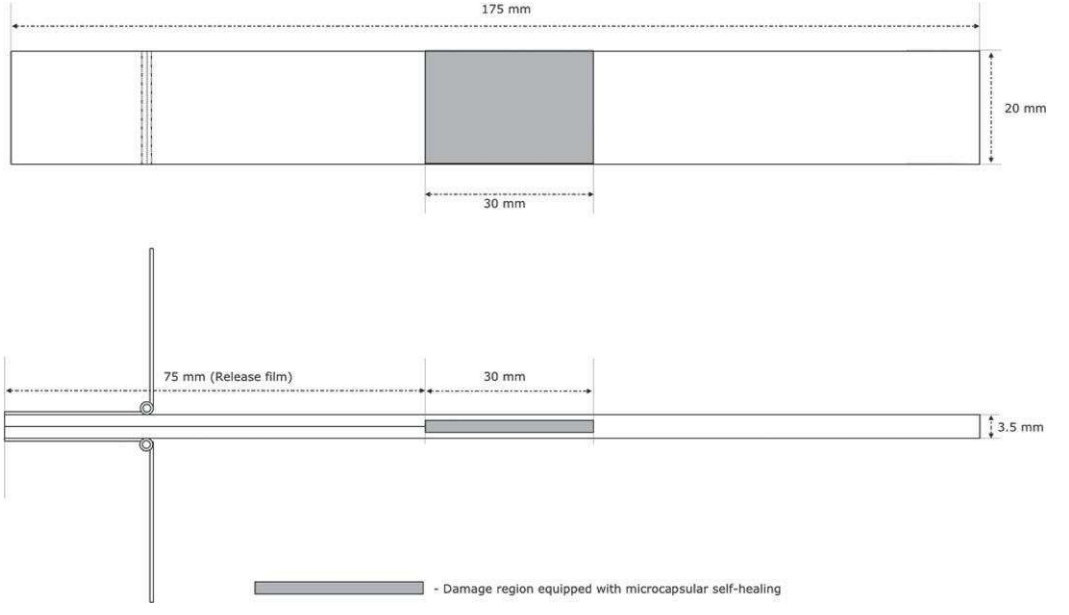

Figure 7. DCB test specimen containing microcapsules in the interleave and solid-phase catalyst in the interleave region. The specimen geometry is adopted from ASTM standard test method D5528-01 [21].

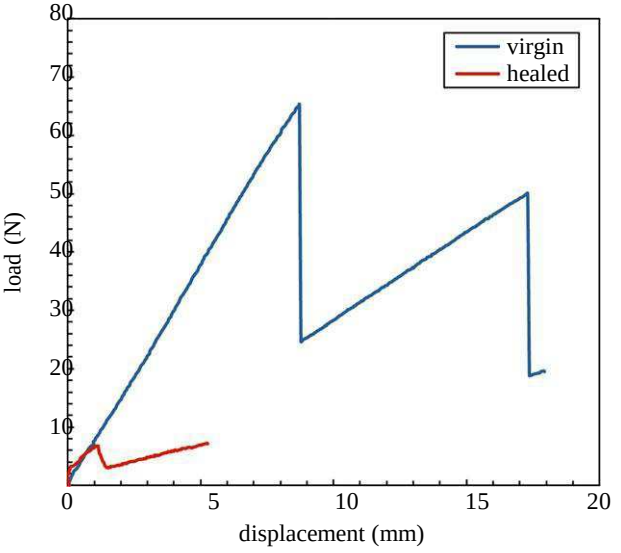

Figure 8. Representative crack arrest for DCB test specimens containing microcapsules and solid-phase LA catalyst in damage region. (Online version in colour.)

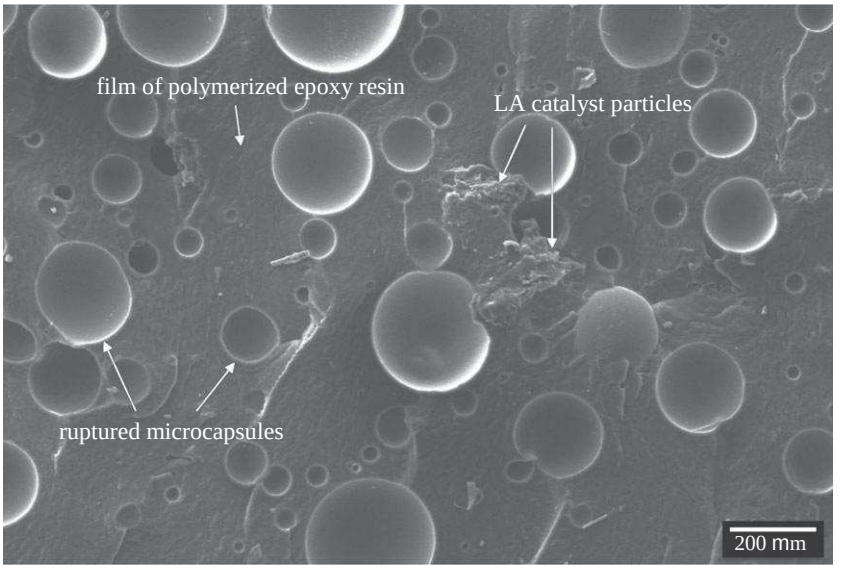

Figure 9. Fracture surface illustrating ruptured microcapsules, particles of embedded LA catalyst particles and thin film of epoxy resin covering the fracture surfaces.

catalyst ($Sc(OTf)_3$) [24] were embedded in a crack propagation region of a unidirectional laminate and tested [21] (figure 7). The presence of a Lewis acid (or Lewis base) catalyst within the structure is crucial for successful polymerization of released epoxy resin. The difference in maximum peak loads recorded on the load–displacement curves (figure 8) for initially fractured specimens and for healed ones was used to quantify self-healing efficiency. A 10% crack arrest was observed for specimens healed at 80° C after 24 h (table 6). This is somewhat lower compared to our previous reports of similar technology [22,24,25] and demonstrates that the test method itself and the manufacturing methods for test specimens are important in fully appreciating the performance of this technology. Crack arrest in this case is associated with cross-linking of released epoxy

Table 6. Designations and load of interleave containing healing chemistries.

designation	wt%[a]	capsule size (μm)	initial load P_{Virgin} (N)	healed load P_{Healed} (N)	η (%)[b]	healing temp. (°C)
control	—	—	81.0 ± 6.4	—	—	80
autonomous	26	170 ± 110	57.2 ± 10.6	5.5 ± 1.5	9.9 ± 3.5	80

[a]Weight of microcapsules calculated according to the mass of epoxy resin used to fill the interleave.

[b]Healing efficiency calculated from the difference in maximum observed load on load–displacement curves for initially fractured and healed DCB specimens.

resin triggered by separately embedded Lewis acid catalyst, indicating that microcapsules are not decomposed during harsh manufacturing conditions of selected epoxy matrix CFRP and that the epoxy resin stored in capsules is in liquid form and is ready for polymerization after release by a propagating crack.

The SEM analysis performed for fracture surfaces revealed ruptured microcapsules, unused $Sc(OTf)_3$ catalyst particles and a thin film of polymerized epoxy resin bridging the fractured surfaces (figure 9). The presence of hollow empty spheres indicated that the poly(UF) shell material is indeed ruptured by the approaching crack.

4. Conclusion

In summary, epoxy resin-filled microcapsules can be reliably synthesized via an oil-in-water microemulsion method. Increased concentrations of surfactant/stabilizer in general are beneficial, allowing for more even microcapsules to be accessed with smaller diameters and at lower stirring rates when used in conjunction with sonication. There are limits to shell wall thickness, since higher concentrations of the necessary reagents lead to unacceptable levels of agglomeration. Thermal stability is limited by the softening temperature of the shell wall polymer. Preliminary application of these materials in self-healing applications shows promising results when used together with Lewis acidic catalysts for the polymerization of the encapsulated epoxy monomer.

Authors' contributions. P.A.B. carried out the laboratory work, obtained SEM micrographs, participated in data analysis, participated in the design of the study and drafted the manuscript. I.P.B. and D.F.W. jointly conceived of the study, coordinated the study and revised the manuscript. All authors gave final approval for publication.

Competing interests. The authors declare no competing interests.

Funding. P.A.B. was funded by the European Union Seventh Framework Programme under FP7-MC-ITN-290308 'SHeMat—Training Network for Self-Healing Materials from Concept to Market'. I.P.B. and D.F.W. are funded by the University of Bristol. The EPSRC UK Catalysis Hub are also thanked for funding.

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