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Robust Synthesis of Epoxy Resin-Filled Poly Urea-Formladehyde Microcapsules for Application to Self-Healing Materials

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Summary

Mechanically and thermally robust microcapsules containing diglycidyl ether of bisphenol A based epoxy resin and a high boiling point organic solvent were synthesised in high yield using *in-situ* polymerisation of urea and formaldehyde in an oil-in-water emulsion. Microcapsules were characterised in terms of their size and size distribution, shell surface morphology and thermal resistance to curing cycles of commercially used epoxy polymers. It is demonstrated that the size distribution of capsules and characteristics such as shell thickness can be influenced by parameters controlling the microencapsulation. Microcapsules small as 6 μm were obtained avoiding potentially damaging emulsification procedure like increased stirring speed. Selected microcapsules and separated core and shell materials were analysed using thermogravimetric analysis (TGA) and differential scanning callorimetry (DSC). Thermal resistance was investigated in order to define their stability to hard temperature conditions of epoxy polymer manufacturing. It is demonstrated that capsules lose minimal 2.5 wt% at temperatures not higher than 120°C. These microcapsules can be applied to the self-healing carbon fibre composite structural materials. The 'proof of concept' studies for recovery of composites fracture properties revealed system stability and activity after composite manufacturing and it's potential in further application.

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]. Liquid active ingredients including monomers, catalysts and hardeners are embedded in a host material, ready for release and polymerisation. The healing process is typically triggered by a propagating crack that ruptures the microcapsules, releasing the encapsulated materials. Chemical reaction (typically polymerisation) or physicochemical processes lead to bonding of the crack surfaces and restoration of material's integrity [4-6]. An early example of a capsular self-healing system was used dicyclopentadiene (DCPD) as the encapsulated monomer and dispersed particles of Grubbs' catalyst to trigger hardening (White *et al*. [7] in 2001). In this approach, the released DCPD comes into contact with the catalyst and undergoes ring-opening metathesis polymerization (ROMP); in this work, poly(urea-formaldehyde) microcapsules containing the DCPD were prepared using *in-situ* polymerisation in an oil-in-water emulsion [8]. Using this methodology, chemistries including Dicyclopentadiene (DCPD)/ethylidene-norbornene (ENB) [9], organic solvents [10,11], epoxy resins [12] and their cross-linkers such as amines [13,14], thiols [15] and glycidyl methacrylate (GMA) [16] were successfully encapsulated. Typical capsule shell materials include urea-formaldehyde (UF), melamine-urea-formaldehyde (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 ingredients are first dispersed in

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a continous aqueous phase containing surfactants/stabilisers 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 water and oil phases. Polycondensation of urea and formaldehyde continues at the interface and leads to a solid and non-permeable capsules shell. Most of the capsules 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 phenyacetate) using the *in-situ* polymerisation 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, necessary in the application of such microcapsules in self-healing structural components. A flat laminate with embedded microcapsules was manufactured with embedded microcapsules in interleave region. Solid phase Lewis Acid catalyst ($Sc(OTf)_3$) was also dispersed to promote crosslinking of released liquid epoxy resin.

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), 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 following parameters; internal width – 75 mm, height 135 mm and curvature depth – 15 mm, vessel was also fitted with a PTFE lid. An overhead stirrer (Caframo Petite Digital Model BDC 250) equipped with two bladed axial propeller (35 mm wide) was used for emulsification and mixing.

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

Poly(urea-formaldehyde) microcapsules containing EPON 828 - ethyl phenylacetate (Table 1) were synthesised *via in-situ* polymerisation as described in 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 of urea, 0.250 g resorcinol and 0.250 g ammonium chloride were added and stirred at room temperature until full dissolution. After 10 minutes, the pH of the aqueous phase 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 – 1500 rpm) for a further 10 minutes and then 6.33 g of aqueous formaldehyde solution was added. In experiments requiring sonication, a tapered 1/8'' tip sonication horn of 750-W ultrasonic homogenizer was immersed in the emulsion, which was sonicated for 3 - 6 minutes. Temperature of the system was increased to 55°C. After 4 hours, the stirrer was stopped and the microcapsules slurry was left to settle at room temperature for 24 hours. Next, capsules were isolated by filtration and rinsed few times with water and then ethanol. The isolated capsules were dried at 55°C for 24 hours. Yield of microcapsules was calculated relatively to mass of used materials.

(c) Size and size distribution analysis

Size and size distribution of microcapsules was analysed by Zeiss Optical Microscope AX10, Imager.M2 equipped with a video camera AxioCam ICc 1. At least 500 measurements of capsules diameters were taken, for the size distribution an image analysis software (ImageJ) was used.

(d) Surface morphology

Surface morphology analysis was performed with a scanning electron microscope JOEL SEM 5600LV. Dry capsules were placed on the conductive tab and sputter coated before analysis with a layer of Ag/Pd. Scanning electron microscopy was also used to investigate fracture surfaces of delaminated double cantilever beam 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 during non-isotherm from 25 to 500°C and isothermal measurements at different temperature by a TA Instruments Q500 TGA. Isothermal experiments were performed at 80, 100, 120 and 140°C for 2 hours. Dynamic analysis of the capsules and core shell materials was recorded on TA Instruments Q200 DSC in a temperatures range of 0 to 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 standard hand lay-up technique. Laminates after lay-up (16 plies (160 mm x 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 minutes. 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. 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 diamond saw. Composite plates were then cut into DCB specimens (20 mm x 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 tests 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 were used. Tests were performed in accordance to the ASTM 5528-01 standard method [25]. Specimens were tested in crack opening mode at 3 mm/min displacement rate, from the release film to the end of interleave resin region containing microcapsules. After testing, specimens were unloaded, sealed and left at 80°C for 24 hours. The healing efficiency was calculated (η) from the ratio of the healed maximum peak load (P_{Healed}) to the virgin maximum peak load (P_{Virgin}).

$$\eta = \frac{P_{Healed}}{P_{Virgin}} \cdot 100\%$$

Results and discussion

(a) Encapsulation of commercial epoxy resins and solvents

Urea-formaldehyde microcapsules containing epoxy resin – solvent mixtures were synthesized in variable size by *in-situ* polymerization in an oil-in-water emulsion (Table 3 and 4). 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 2).

(b) Influence of stirring speed/sonication on microcapsules 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 rpm. Organic phases containing 2.5 and 50 wt% of epoxy resin were easily dispersed at this rate and capsules resulted in wide range of sizes (Table 3). At 75 and 90 wt% EPON 828, the high viscosity of these formulations resulted in very poor dispersion at 800 rpm; increasing stirring rate (to 1000 rpm) 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 4. As expected, the size of microcapsules is decreased with increasing stirring speed (Figure 1a); a representative size distribution at 1100 rpm is given in Figure 1b. Unfortunately, at higher stirring rates (1200 – 1500 rpm) microcapsules rupture (see entries 9 and 10 in Table 4) [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 of the mechanical performance of the structural material.

To obtain microcapsules in diameters below 100 μm, sonication was required as an alternative homogenization method [23]. To ensure full interfacial coverage of new created droplets, 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 minutes at 80% amplitude, the droplet size was decreased sufficiently that microcapsules in the 100 μm range could be prepared at 800 rpm stirring speed, rather than

the 1000 rpm required without sonication. Increasing the surfactant/stabilizer concentration further (Table 4, entries 2-4) resulted in even smaller capsules (as low as 4 ± 2 μm), still in acceptable yields. Figure 2 represents exemplary size distribution of microcapsules prepared at 5 wt% of surfactant/stabilizer.

(c) Shell wall morphology

Scanning electron micrographs of exemplary microcapsules prepared by adopted (right side) and modified (left side) methods are presented in the Figures 3. Both types of microcapsules contained 75% of the epoxy resin and 25wt% of ethyl phenylacetate. In both cases, 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 urea-formaldehyde reaction progresses, the rough exterior is formed as colloidal poly(urea-formaldehyde) 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 gives a much more even shell wall morphology, presumably due to the enhanced stabilization of the nascent microcapsule. This enhanced stabilization reduces the amount of small agglomerates which can accrete on the microcapsule surface.

(d) Load of shell forming materials

The mechanical properties of microcapsules is important in their application to self-healing materials, with a requirement to be sufficiently robust to survive structural material manufacture but being 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, formalin and the poly(EMA) surfactant/stabilizer) was increased relative to the encapsulated epoxy monomer and aqueous phase, whilst keeping the ratio between these shell wall-forming materials constant. 150% and 200% increases by weight compared to previous runs were investigated (Table 5).

The corresponding SEM micrographs of resulted samples are presented in the Figure 4. We observed 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 preformed for E50 microcapsules (see figure 5a) using thermogravimetric analysis (TGA). Microcapsules and separated core/shell materials were analysed non-isothermally from 25 to 500°C. First mass loss observed at 170°C is associated with thermal decomposition of the shell polymer, with similar behaviour observed for separated poly(urea-formaldehyde) shell wall material. Another onset of mass loss was at 210-220°C corresponds to the boiling point of encapsulated ethyl phenyl acetate and continues to 310°C. During continuous heating at high temperatures, the encapsulated epoxy resin partially polymerised with onset at 360°C. A similar trend observation is made 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 hours. The representative mass loss is presented in the Figure 6b. 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 crosslinking of the poly(urea-formaldehyde). After 2 hours at 140°C, an increased mass loss of 6.5% was observed as a result of microcapsule decomposition.

Differential scanning calorimetry (DSC) was used to determine thermal behaviour of microcapsules and separated core/shell materials. The glass transition temperature for the separated shell material is 124.5°C and followed by endotherm with peak temperature at 145.1°C, Figure 6a. 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 homopolymerisation of diglycidyl ether of bisphenol A and its thermal decomposition.

(f) Self-healing performance

A preliminary experiments for recovery of fracture properties (mode I) in a carbon fibre reinforced polymer (CFRP) composite were performed for E 75 microcapsules. Capsules and a solid phase catalyst ($Sc(OTf)_3$) [21] were embedded in a crack propagation region of a unidirectional laminate and tested [25] (Figure 7). The presence of Lewis Acid or Lewis Base catalytic curing agent within structure is crucial for successful polymerisation of released epoxy resin. The difference in maximum peak loads recorded at the load –

displacement curves (figure 8) for initially fractured specimens and for healed was used to quantify self-healing efficiency. A 10% crack arrest was observed for specimens healed at 80°C after 24 hours. This crack arrest is associated with crosslinking of released epoxy resin triggered by separately embedded Lewis Acid catalyst. It indicates 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 polymerisation after release by propagating crack.

The SEM analysis performed for fracture surfaces revealed ruptured microcapsules, not consumed $Sc(OTf)_3$ particles and thin film of polymerised epoxy resin bridging the fractured surfaces, Figure 9. Presence of hollow empty spheres indicated that the poly(urea-formaldehyde) shell material is easily ruptured by approaching crack. The selection of microcapsules shell material and its thickness is crucial in designing of responsive healing system.

Conclusions

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 application shows promising results when used together with Lewis acidic catalysts for the polymerization of the encapsulated epoxy monomer.

Additional Information

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Tables

Table 1 – Systematic names and designations of microcapsules core materials used in the study

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

[1)] Wt % measured by weight percent relatively to organic encapsulated phase assuming that density is equal 1g /mL

Table 2 – Adopted and modified methods of epoxy resin – solvent encapsulation in an oil-in-water emulsion

Encapsulation method	Aqueous phase (mL)	EMA (wt%)[1)]	Urea (*g*)	NH_4Cl (g)	Resorcinol (*g*)	Formalin (*g*)
a) Literature [ref 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

[1)] Wt % measured by weight percent relatively to organic encapsulated phase assuming that density is equal 1g /mL

Table 3 – Encapsulation conditions of EPON 828 at variable concentrations in an oil-in-water emulsion

EPON 828 wt% in organic phase	Water Phase (mL)	Organic Phase	Surfactant Amount (wt%)[1)]	Agitation Rate (rpm)	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

[1)] Wt % measured by weight percent relatively to organic encapsulated phase assuming that density is equal 1g /mL

Table 4 – Encapsulation conditions of EPON 828 in an oil-in-water emulsion

No.	pH	Agitation Rate	Amount of Surfactant (wt%)[1)]	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	-	-

[1)] Wt % measured by weight percent relatively to organic encapsulated phase assuming that density is equal 1g /mL. 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).

Table 5 – Load of the shell forming materials used in the study

Encapsulation method	Aqueous phase (mL)	EMA (wt%)[1)]	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

[1)] Weight percent measured relatively to mass of dispersed organic phase (30 mL).
The encapsulation was carried out as for previous samples at the same conditions of stirring (800 rpm), pH (3.15) and temperature (55°C).

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

Designation	Wt[1)] %	Capsules size (µm)	Initial Load P_{Virgin} (N)	Healed Load P_{Healed} (N)	η (%)[2)]	Healing Temp
Control	-	-	81.0±6.4	-	-	80°C
Autonomous	26	170 ± 110	57.2±10.6	5.5±1.5	9.9±3.5	

[1)] Weight of microcapsules calculated according to the mass of epoxy resin used to fill the interleave
[2)] Healing efficiency calculated from the difference in maximum observed load on load-displacement curves for initially fractured and healed double cantilever specimens.