

ORIGINAL ARTICLE

Microencapsulation of gallium–indium (Ga–In) liquid metal for self-healing applications

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Abstract

Microcapsules containing a liquid metal alloy core of gallium–indium (Ga–In) are prepared via *in situ* urea–formaldehyde (UF) microencapsulation. The capsule size, shape, thermal properties, and shell wall thickness are investigated. We prepare ellipsoidal capsules with major and minor diameter aspect ratios ranging from 1.64 to 1.08 and with major diameters ranging from 245 μm to 3 μm . We observe that as the capsule major diameter decreases, the aspect ratio approaches 1. The thermal properties of the prepared microcapsules are investigated by thermogravimetric (TGA) and differential scanning calorimetry (DSC). Microcapsules are shown to survive incorporation into an epoxy matrix and to trigger via mechanical damage to the cured matrix. Microcapsules containing liquid metal cores may have diverse applications ranging from self-healing to contrast enhancement or the demonstration of mechano-adaptive circuitry.

Keywords

Conductivity restoration, microcapsules, self-healing

History

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Introduction

Microencapsulation enables compartmentalisation and protection of an interior core material from the external environment until release is triggered. Triggered release of the interior core material is induced by external stimuli such as pH change (Esser-Kahn et al., 2010), UV irradiation (Pastine et al., 2009; Broaders et al., 2011), thermal treatment (Chu et al., 2002), or mechanical damage (Brown et al., 2003; Yuan et al., 2007; Blaiszik et al., 2008, 2009). Stimuli-responsive microcapsules have wide applicability (Esser-Kahn et al., 2011), and have been used in applications such as drug delivery, cosmetics, adhesives, food science, and agriculture among many others (Benita, 2006; Ghosh, 2006; Shchukina and Shchukin, 2011). Microencapsulated healing agents have been integral to the development of self-healing materials (Kessler, 2007; Yuan et al., 2008d; Blaiszik et al., 2010). Autonomous repair of crack damage has been achieved in polymers by embedding microcapsules containing polymeric monomer (White et al., 2001; Brown et al., 2002; Kamphaus et al., 2008), poly(dimethyl siloxane) resin and hardener (Cho et al., 2006; Keller et al., 2007, 2008), solvent solution (Caruso et al., 2007, 2008), and epoxy resin and hardener (Yuan et al., 2008a; Jin et al., 2012). In each of these examples, mechanical damage to the material triggers release of healing agent(s), leading to the formation of a healed material in the region of damage. A robust polymeric shell wall is required for capsules to survive polymer processing and remain

stable prior to a damage event. Capsules that meet the requirements for self-healing applications have been prepared by a variety of techniques, including *in situ* reaction of urea and formaldehyde (Brown et al., 2003; Yuan et al., 2006; Cosco et al., 2007; Blaiszik et al., 2008, 2009) or melamine and formaldehyde (Yuan et al., 2008b, 2008c; Liu et al., 2009), interfacial polymerisation of polyurethane prepolymer (Cho et al., 2006), UV polymerisation of acrylates (Xiao et al., 2007, 2009), as well as Pickering techniques (Mookhoek et al., 2008).

More recently, capsule-based approaches have been directed towards restoration of electrical conductivity. By sequestering conductive core materials, restoration of conductivity has been achieved through the formation of conductive charge transfer salts (Odom et al., 2010), deposition of a percolating network of conductive nanoparticles (Caruso et al., 2009), and release of a liquid metal at the site of damage to a microelectronic circuit (Blaiszik et al., 2012). Encapsulation of inorganic conductive materials presents unique challenges. Recent investigations have demonstrated the preparation of nanosized particles via cooling of a liquid metal miniemulsion (Raabe and Hessling, 2010) and micron-sized particles of liquid metal via coating and stabilisation with a variety of self-assembled monolayer ligands and surfactants (Hohman et al., 2011). Here, we report on the encapsulation of eutectic Ga–In metal by *in situ* polymerisation of urea and formaldehyde to produce robust capsules for conductivity restoration applications.

Materials and methods

Microcapsule materials

The liquid metal core materials, gallium (Ga) metal and indium (In) metal (99.9%) shot, were obtained from GalliumSource and Strem Chemicals, respectively. To prevent oxidation, Ga, In, and

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Ga–In alloy were stored in a vacuum desiccator containing a drying agent. Prior to encapsulation, a eutectic alloy of Ga and In (approximately 75 wt% Ga and 25 wt% In) was prepared by mixing the components with a polytetrafluoroethylene (PTFE) stir bar at 55 °C for 2 h.

The microcapsule wall-forming materials, urea (NH₂CONH₂) and ammonium chloride (NH₄Cl), were purchased from Fisher Chemicals (Hampton, NH). Additional wall-forming materials formalin (37% formaldehyde in water) solution and resorcinol (C₆H₄-1,3-(OH)₂) were purchased from Sigma-Aldrich (St Louis, MO). Ethylene–maleic anhydride copolymer (Zemac-400, Zeeland, MI) was kindly provided by Vertellus Chemicals (Indianapolis, IN). As-received EMA powder was mixed overnight with deionised water in a warm bath to obtain a 2.5% (wt/wt) aqueous surfactant solution.

Microencapsulation procedure

Liquid Ga–In alloy was encapsulated via an *in situ* reaction of urea and formaldehyde following the procedure presented in Figure 1. The encapsulation method was adjusted to produce stable capsules less than 10 µm in diameter as indicated by the bracketed text.

For larger capsules prepared via mechanical agitation (bold text in Figure 1), the aqueous encapsulation phase was 20.0 g DI H₂O, 5.00 g ethylene–maleic anhydride copolymer (EMA 2.5% wt/vol), 0.50 g urea, 0.05 g resorcinol, and 0.05 g ammonium chloride. After the solid components were dissolved, the pH was adjusted to 3.50 via addition of 20 wt% NaOH solution. Under continuous agitation, approximately 28.0 g of liquid metal was added, and the combined mixture was stirred on a temperature-controlled hotplate. The temperature was increased via a temperature-controlled hotplate set to a bath target temperature of 55 °C with a ramp rate of 1 °C/min, and held for 4 h. After the

encapsulation was complete, the capsules were washed and decanted six times with 20 ml of DI H₂O and six times with 20 ml of ethanol. Excess ethanol was removed, and the resulting slurry was frozen in liquid nitrogen and lyophilised to obtain a dry capsule powder.

To prepare smaller capsules (<10 µm diameter), sonic agitation was used, the surfactant concentration was increased, and the ammonium chloride concentration was increased (Figure 1 – bracketed text). These changes have been shown in a previous publication to prevent clumping of small diameter capsules and to improve UF shell wall quality (Blaiszik et al., 2008).

Thermal analysis

Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA/DSC 1 (Columbus, OH) under a nitrogen atmosphere at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was performed on a Mettler-Toledo DSC821e (Columbus, OH) under a nitrogen atmosphere, with heat flow (positive exothermal) monitored beginning at 50 °C, descending to –50 °C, and ascending back to 50 °C at a rate of ±5 °C/min.

Imaging and size distribution analysis

SEM imaging and EDS elemental mapping were performed on an FEI/Philips XL30 ESEM-FEG (Hillsboro, OR). Examination of the shell wall exterior was performed on a dried powder of the capsules, and measurements of the shell wall thickness were obtained by fracturing capsules embedded in an epoxy matrix. All SEM samples were sputter coated with gold–palladium to reduce charging of the polymeric shell wall.

Microcapsule size distributions for capsules prepared using mechanical agitation were obtained from optical images of capsules taken using a USAF 1951 calibrated camera (QImaging Micropublisher 3.3, Surrey, BC, Canada). Size distributions for capsules prepared via sonic agitation were obtained using an Accusizer FX particle sizer.

Results

Size distribution

The size of microcapsules was investigated as a function of agitation rate. In most encapsulations reported in the literature, microcapsules are approximately spherical, and the capsule diameter follows a power law relationship with increased shear rate correlated to decreased capsule diameter (Taylor, 1932). Interestingly, Ga–In filled capsules prepared via mechanical agitation were ellipsoidal. For each encapsulation, the major and minor diameters, *a* and *b*, respectively, of the projection of the ellipsoids were recorded. As expected, both characteristic capsule diameters decreased with increased shear rate (Figure 2a). For slower agitation rates, the aspect ratio (*a/b*) was as high as 1.64. However, as the agitation rate was increased, the major and minor diameters decreased, and the aspect ratio also decreased to 1.46. When the shear rate was increased further by sonication, the aspect ratio decreased to 1.08. A linear relationship between the major and the minor diameter was also observed (Figure 2b). No difference in the relationship between major and minor diameters was seen when comparing mechanical and sonic agitation methods. Dickey et al. (2008) investigated the rheological properties of liquid Ga–In and found it to be highly thixotropic with a defined yield stress above which it flows readily. We attribute the ellipsoidal capsule geometry to high surface tension and these complex rheological properties.

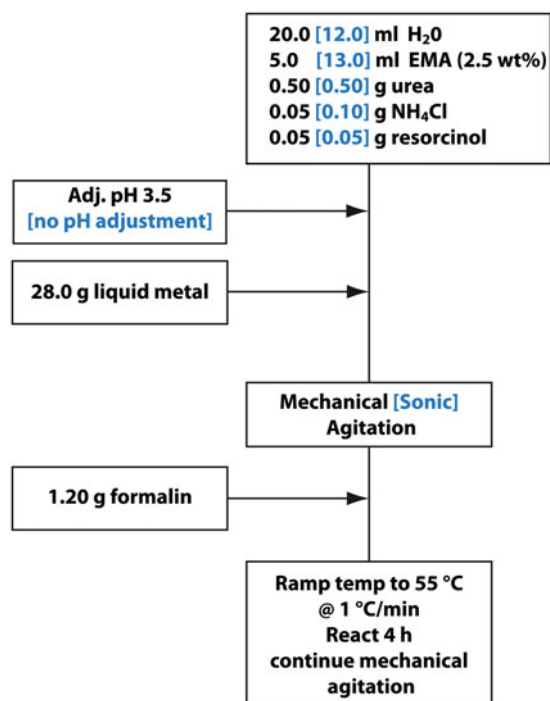


Figure 1. Methods for preparation of UF microcapsules filled with liquid Ga–In metal via *in situ* polymerisation of urea and formaldehyde. The method used to prepare capsules via mechanical agitation is shown in black text. For preparation of smaller capsules (<10 µm) via sonication techniques, the method was adjusted as indicated by the text in brackets (blue).

Surface morphology and shell wall thickness

Representative SEM images of Ga–In microcapsules are shown in Figure 3. Capsules prepared via mechanical agitation (Figure 3a and b) are non-spherical with a wrinkled exterior surface.

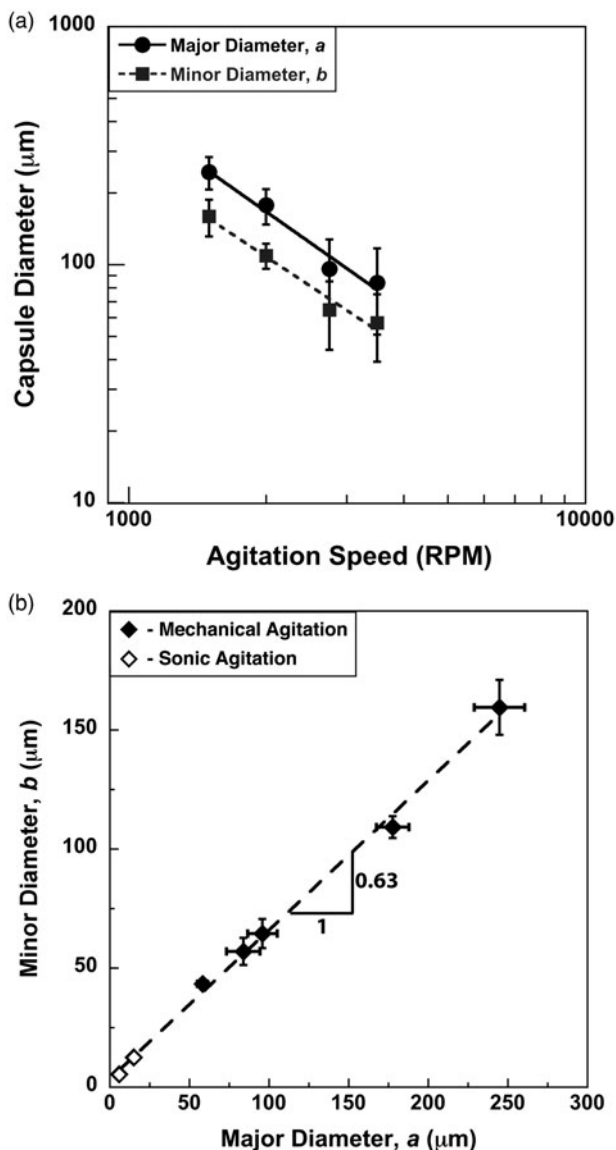
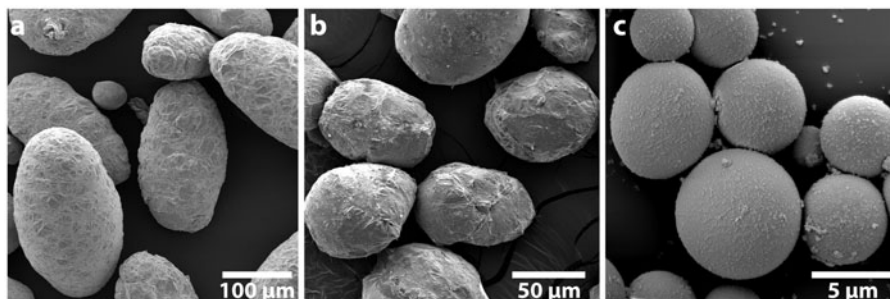


Figure 2. (a) Logarithmic plot of microcapsule mean diameter, major (circles) and minor (squares), measured for capsules prepared at various agitation rates. Vertical error bars represent the standard deviation of the observed mean. (b) Linear relationship between the characteristic major and minor diameters of microcapsules prepared via shear induced by mechanical agitation (diamonds) and ultrasonic agitation (open diamonds).

Figure 3. SEM images of Ga–In filled capsules at varying size scales. Capsules prepared (a) at an agitation rate of 1500 rpm (b) at an agitation rate of 2750 rpm and (c) via sonication.



Capsules prepared via sonication are nearly spherical and have a relatively smooth exterior surface (Figure 3c).

Figure 4 shows higher magnification SEM images of the shell wall. In contrast to previous urea–formaldehyde microcapsules containing organic monomers or solvents (Brown et al., 2003; Blaiszik et al., 2009), the shell wall of the Ga–In microcapsules was notably thinner and was free of a secondary layer of colloidal UF particles. For capsules prepared at 1500 rpm (Figure 4a), the shell wall thickness was 73 ± 14 nm ($n = 17$, where n is the number of measurements). Observation of the shell wall for capsules prepared via sonic agitation was challenging due to the capsule size coupled with the density difference between the capsules and the epoxy matrix. For a small sample size ($n = 4$), the average shell wall thickness was 63 nm, ranging from 57 to 74 nm. Figure 4(b) shows the

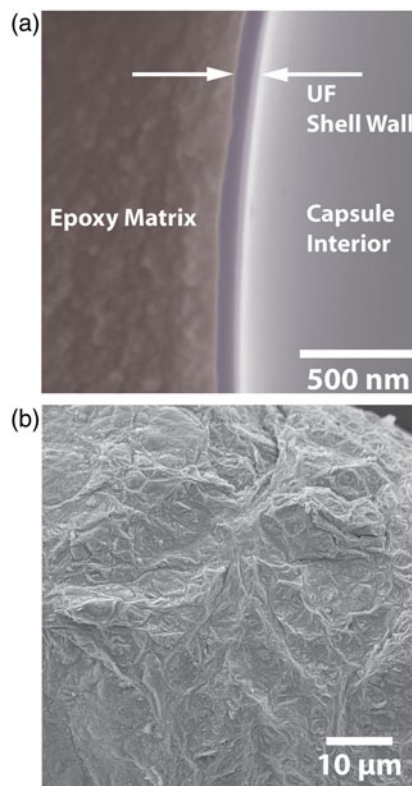


Figure 4. SEM images of Ga–In filled UF microcapsule prepared via mechanical agitation at 1500 rpm. (a) Edge view of the shell wall of the Ga–In filled UF microcapsule after fracture in epoxy matrix. The shell wall is a smooth, thin membrane with a thickness of 73 ± 14 nm. (b) SEM image of the shell wall exterior reveals a wrinkled surface. The Ga–In filled capsules lack the rough exterior shell wall of UF particles typically observed in prior UF encapsulations (Brown et al., 2003; Blaiszik et al., 2009).

wrinkled surface morphology of the shell wall at a higher magnification.

Thermal properties

Thermal stability and core composition are critical characteristics for microcapsule applications. In self-healing, a high core loading is favourable for increasing the amount of healing agent delivered to the site of damage. For Ga–In filled microcapsules, the temperature range for which the metal core is liquid is also an important consideration since the core must flow to the site of damage upon rupture.

The thermal transition behaviour of the capsules was investigated by DSC. The onset of freezing of microencapsulated Ga–In alloy was observed at ca. -2.0°C (Figure 5a). Below this freezing point, the metal in the capsule core is solid and is unlikely to be delivered by mechanical damage. The onset of melting was observed ca. 15.6°C . Above this temperature, the

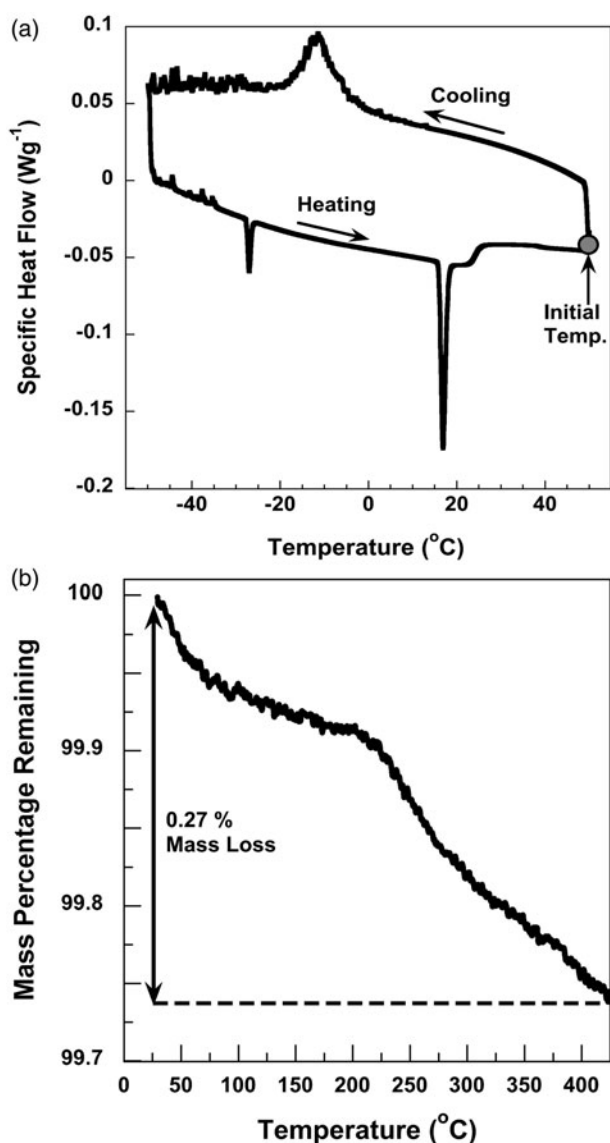


Figure 5. (a) Thermal DSC cycle of Ga–In filled UF capsules with a freezing transition ca. -10°C and a melting transition ca. 16°C . (b) Thermogravimetric analysis of the Ga–In filled UF capsules shows a small mass loss below 100°C attributed to absorbed water and a gradual decrease in mass above 225°C associated with shell wall degradation.

Ga–In alloy is liquid, and the delivery of the Ga–In triggered by mechanical damage is expected.

TGA analysis of the microcapsules (Figure 5b) shows a small mass loss (ca. 0.05%) before 100°C , correlating to absorbed water in the UF shell wall, followed by further mass loss above 225°C attributed to decomposition of the UF shell wall. The remaining mass, greater than 99.7%, is the wt% of the capsule comprised of Ga–In alloy.

Fracture plane elemental analysis

Microcapsules were embedded in the epoxy layer of notched four-point bend fracture specimens and tested following a procedure described previously (Blaiszik et al., 2012). After fracture, samples were analyzed by energy-dispersive X-ray spectroscopy (EDS) to map the release of Ga–In from the microcapsules. As shown in Figure 6, mechanical rupture of the protective UF shell wall triggers release and flow of the Ga–In alloy onto the fracture plane.

Conclusions

A robust method for the preparation of urea–formaldehyde microcapsules with a core of liquid metal (Ga–In alloy) was developed. Following this method, capsules with average major diameters ranging from 3 to $245\ \mu\text{m}$ were prepared and isolated as free-flowing dry powders. The shape of the capsule varied with capsule size ranging from prolate ellipsoidal to nearly spherical for smaller diameters ($<10\ \mu\text{m}$). The shell wall was approximately $73\ \text{nm}$ thick and the exterior surface was free of excess UF particulate debris. The thermal properties of the capsules were investigated, and an onset of melting of the metal core was observed at 15.6°C , consistent with the literature values for the melting point of Ga–In eutectic alloy. Mechanically triggered release of the core material was demonstrated by fracture of a four-point bend specimen containing embedded capsules in a central dielectric epoxy layer. Liquid metal-filled microcapsules have enabled autonomous restoration of conductivity in electronic devices, and they may find utility in the mechanically triggered generation of conductive pathways for adaptive circuits.

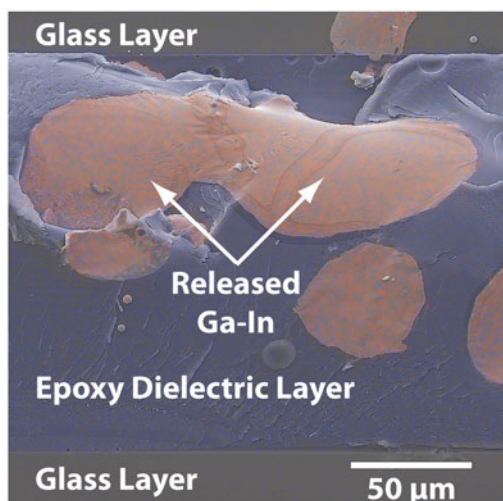


Figure 6. Elemental mapping by EDS of the fracture surface of an epoxy resin verifies release of Ga–In from the capsules upon mechanical damage. The epoxy matrix (purple) mapped via carbon (K_{α}), Ga–In (red) was coloured via combined mapping of Ga (L_{α}) and In (L_{α}) (colour available online).

Declaration of interest

The authors disclose no conflicts of interest. This material is based upon work supported as part of the Center for Electrical Energy Storage-Tailored Interfaces, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number (919 DOE ANL 9F-31921 NS).

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