NEW CAPSULE CHEMISTRIES FOR NANOSCALE SELF-HEALING

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Introduction

Self-healing materials are being developed to improve the lifetime of materials used in various applications including coatings, adhesives, structural components, and even microelectronics. The approach of using microencapsulation for self-healing has been particularly promising with proven success in coatings1 and in bulk epoxy2-5. However, the size of microcapsules limits their use to materials with larger features. In order to apply this approach to materials with smaller features, encapsulation of healing agent on a smaller size-scale must be achieved.

The current scheme for healing using microcapsules consists of a two-part healing system: dicyclopentadiene (DCPD) monomer and Grubbs catalyst. The capsule shells consist of polyureaformaldehyde (PUF). DCPD is first emulsified into an aqueous solution of surfactant using a mixer blade to apply shear force. Urea and formaldehyde react in the aqueous phase to form oligomers. After depositing at the o/w interface, the oligomers further polymerize on the surface of the DCPD droplets. Using this method, capsules can be synthesized with diameters as small as 10 µm in diameter. This size can be reduced further using a higher shear force or by changing the chemical characteristics of the solution.6 In this research, we use sonication to reduce the average capsule diameter to less than 1.5 µm. Ultrahydrophobes have been shown to further reduce the average capsule diameter to 300 nm. However agglomeration is observed in these capsules, limiting their use in bulk material.

A second goal of this work is to modify the surface of these capsules to eliminate agglomeration and improve dispersion in epoxy. It is expected that inorganic shells such as those formed by silica can improve the rigidity of the capsules and open up new opportunities for chemical functionalization. This in turn would limit the surface area of contact, reducing the Van der Waals interactions between the colloids. Together with functionalization, better dispersion of capsules in matrix is expected. Silica has been regrown on many surfaces such as polystyrene colloids and gold nanoparticles.7 Functionalization of the capsules can be accomplished using common sizings found in the composite industry. In this work, Glycidoxypropyltrimethoxysilane (GLYMO) has been used since it has two functionalities: a siloxane bridge to react with the silica surface and an epoxide functionality that matches the monomer functionality of the matrix. The epoxide functionality is expected to improve dispersion in the epoxy resin before curing. During the curing process, it can react with the matrix to improve the bond between the capsules and the matrix. In the future, additional functionalities can be investigated for different matrices.

Experimental

Sub-micron capsule synthesis with silica coating is divided into two steps: polymer capsule synthesis and polymer capsule functionalization. Coating is done within 24 hours of synthesis in order to reduce agglomeration or DCPD loss due to storage.

Polymer Capsule Synthesis. Polymer capsules are synthesized as previously reported.8 Briefly, DCPD, urea, ammonia chloride, and resorcinol were added to a 1.25 wt% solution of ethylene-maleic anhydride and water. This solution is emulsified using a mixing blade at 800 rpm. Further shear forces are created by sonicating the solution for 3 minutes. Formaldehyde is immediately added and the reaction temperature is increased to 55°C. The temperature is held for 4 hours before returning the solution to room temperature. The solution pH is finally adjusted to pH 4.5.

Polymer Capsule Functionalization. Polymer capsules are functionalized utilizing methods described in previously published literature.9, 10 Briefly, capsules are prepared in a DCPD saturated solution of methanol, water and ammonia hydroxide. Tetraethylorthosilicate (TEOS) is slowly added to the solution keeping the concentration of water and ammonia constant. A solution of GLYMO and DCPD saturated methanol is added slowly to functionalize the silica layer with epoxide groups. The coated capsules are vacuum filtered using ethanol to wash the capsules and remove excess water.

Results and Discussion

Using sonication, DCPD was encapsulated in PUF leading to low polydispersity capsules containing a high fill content of DCPD. By using SEM, these capsules were shown to be smooth and non-porous (Figure 1). The capsules were near 1.5 µm in diameter as determined by SEM (Figure 1a). By using ultrahydrophobes, the averaged diameter could be reduced even further to around 300 nm in diameter (Figure 1b). Based on TEM analysis, the capsule wall was 77 nm for the 1.5 µm capsules and 20 nm for the smaller capsules. A detailed description of the synthesis and characterization of these capsules, including a few of the figures shown here can be found in a previous publication work by the authors.11

Figure 1. A SEM image of (a) capsules (1.5 µm) prepared using sonication, and (b) a TEM image of a 300 nm capsule prepared using sonication and an ultrahydrophobe. The contents of the 300 nm capsule have been removed to enable visualization of the shell wall thickness.

TGA, gas chromatography (GC), and elemental analysis were implemented to determine the fill content of DCPD within the capsules. The thermal stability of the capsules was also observed by TGA and a loss of weight corresponding to the boiling point of DCPD was shown near 170°C (Figure 2a). For GC, filled capsules were placed in methylene chloride and the capsule contents were allowed to diffuse across the shell wall over one week. The resulting filtered solution of capsule contents and methylene chloride was analyzed with GC. The resulting peaks were compared to distilled DCPD and methylene chloride to confirm the presence of the monomer (Figure 2b). Finally, elemental analysis was used to obtain a more precise value of fill content. Because PUF contains nitrogen while DCPD does not, an estimated empirical formula for PUF was compared to the CHN analysis of full capsules to show that the capsules contained 78.4 wt% DCPD. Based on the expected geometry and approximated densities of the PUF and DCPD, this is 94% of the potential fill content.

Figure 2. TGA (a) and gas chromatography (b) demonstrate that the 1.5 µm capsules contained DCPD. The capsules are known to be filled with a mixture of both endo- and exo- DCPD. The ratio of the areas under the peaks for endo- and exo-DCPD is similar to the expected concentrations of exo- and endo-DCPD in the capsules.

The capsules were incorporated into an epoxy matrix by first washing them by centrifugation and subsequent redispersion to remove excess reactants. Once washed, they were concentrated and incorporated into epoxy. Because agglomeration occurred during the drying processes, the capsules were incorporated into the epoxy with a small amount of solvent. Images of capsules incorporated in epoxy from their dry and wet forms are depicted in Figure 3. The capsule weight fraction was limited by agglomeration in epoxy when the weight fraction was greater than 3 wt%. Despite this disadvantage,
which limited the weight fraction of capsules below that optical for self-healing, the capsules still improved the mechanical properties of bulk epoxy through toughening mechanisms similar to mechanisms described elsewhere in literature\(^9\). These mechanisms show up as crack tails in microscopy images (Figure 3b).

Higher loadings could be achieved using an inorganic silica coating and surface functionalization. In initial attempts for silica coating, secondary nucleation of small silica particles during the capsule coating reaction was observed. These silica nanoparticles were difficult to separate from the capsules and tended to increase capsule agglomeration. Subsequently, methods were devised to reduce and eliminate this problem. The best results were obtained following a scheme similar to that described by Giesche\(^6\) where the TEOS was added slowly via a syringe pump. This reduced the concentration of TEOS allowing the reaction with the polymer capsule surface to dominate self-nucleation. The surface morphology of the coated capsules was found to be slightly rougher than the polymer capsules. In several samples, this was attributed to the porosity of the shell, and work is under way to reduce the porosity of the silica shell. The shell walls only slightly increased the diameter of the capsules. By analyzing TEM micrographs of microtomed cross-sections of the coated samples, the coating was found to be ~50 nm thick (Figure 4). With the goal of improving dispersion of capsules in epoxy, ligands with an epoxide end group are reacted with the coating surface. The ligand attachment is based on the same siloxane chemistry as the silica regrowth from TEOS. As a result, a solution containing GLYMO is added slowly, via syringe pump, to the reaction mixture obtained after the silica coating process. The GLYMO functionality did not affect the physical characteristics and work is being done to analyze the surface chemistry change. Qualitatively, dispersion of capsules in epoxy is best achieved when using the GLYMO functionality.

The primary advantage to date of the coated capsules is that they can be dried to form a free-flowing powder. In addition, the weight fraction limit due to agglomeration is eliminated. Epoxy functionality was shown to improve dispersion in epoxy, and with this functionality, weight fractions of up to 20 wt% in epoxy could be obtained (Figure 5). Preliminary work has also been done to determine what change, if any, the silica coating has on the thermal and chemical stability of the capsules. No conclusive data has been obtained to date.

New healing test methods have been developed and preliminary tests are indicating self-healing healing capabilities for these capsules. Test methods under investigation include fiber pull-out and four-point bending.

Conclusions

In conclusion, DCPD healing agent has been encapsulated in PUF through surface polymerization in an emulsion. These capsules could subsequently be silica coated in order to form a free-flowing powder of 1.5 µm capsules. The coated capsules could then be incorporated into epoxy at weight fractions up to 20 wt%. Future work is underway to demonstrate the healing capabilities of the capsules.

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References