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As a child, I learned from my father, who is a mechanical engineer, how different machines work and I was captivated by this knowledge. I have always been fascinated by the human body, so when I entered college I wanted to pursue a career in medicine. However, I chose a major—biomedical engineering—that I knew I would love even if I was not accepted into medical school. Biomedical engineering combines my passion for math and science with my fascination of the intricacies of the human body. I decided that I would rather design an implant rather than place one into someone's body.
Age 20, Jessica Berry is studying biomedical engineering and mechanical engineering at the University of Alabama at Birmingham. Upon graduating in 2007, she plans on obtaining a job. After working a few years, she intends on acquiring a master's in biomedical engineering.

Incorporation of Self-Healing Polymers at the Nanoscale

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Abstract

Mechanical failure of a material often occurs due to microcracks within a material; therefore, the extension of selflife of a material by allowing for the retention of mechanical properties is desirable. This study is looking at a way to incorporate nanocapsules into a polymer matrix without clumping. A healing agent is contained within these capsules which polymerizes with a catalyst embedded in the matrix when a crack penetrates the capsule shell wall. The polymerization should cause significant recovery of mechanical properties and extension of the self life of the material. This study is based on a previous study that had obtained healing with microcapsules, and now, through modification, the capsules have been reduced to the nanoscale. The need for reduction is due to the decrease in tensile properties when capsules are added to the matrix. Therefore, the main purpose of the study was to address the issues of the change in properties at the nanoscale (in particular clumping) and to incorporate these nanocapsules into an epoxy matrix with successful dispersion. After the incorporation has been accomplished, fracture and tensile testing are to be performed to compare with the previous larger capsules. The main findings of this study indicate that clumping can be resolved by applying a high shear force when incorporating capsules into epoxy and allowing an agent used to separate the capsules from water to evaporate from the solution so that phase separation between the agent and the epoxy does not occur and cause clumping.

Introduction

Structural polymers are extremely vulnerable to mechanical degradation due to cracks within the matrix of the material which will ultimately cause failure; therefore, it would be advantageous if self-healing in a damaged matrix could occur. The self-healing concept is based on the ability of the body to regenerate through autonomic healing. 1 A procedure has been recently developed that incorporates microcapsules and a catalyst into a polymer matrix to obtain this phenomenon. A healing agent is incorporated into a capsule structure filled with dicyclopentadiene (DCPD), a highly stable monomer with excellent self life, with a shell wall of urea-formaldehyde. Figure 1 illustrates when a crack propagates through the material the healing agent is released from the microcapsules as the crack breaks the shell wall. This healing agent interacts with the Grubbs catalyst to form a polymer through ring-opening metathesis polymerization (ROMP) reaction.[1] Although, self-healing has been achieved with capsules at the microscale, these size capsules have an undesirable effect on the tensile properties of the material. Due to the tensile strength being compromised, the purpose of this experiment was to minimize the size of the capsules to the nanoscale and successfully incorporate (capsules with equal dispersion) these capsules into epoxy. Furthermore, after the successful incorporation of capsules into the network fracture and tensile testing of different weight percent of the nanocapsules will be performed and compared to the previous microcapsules.

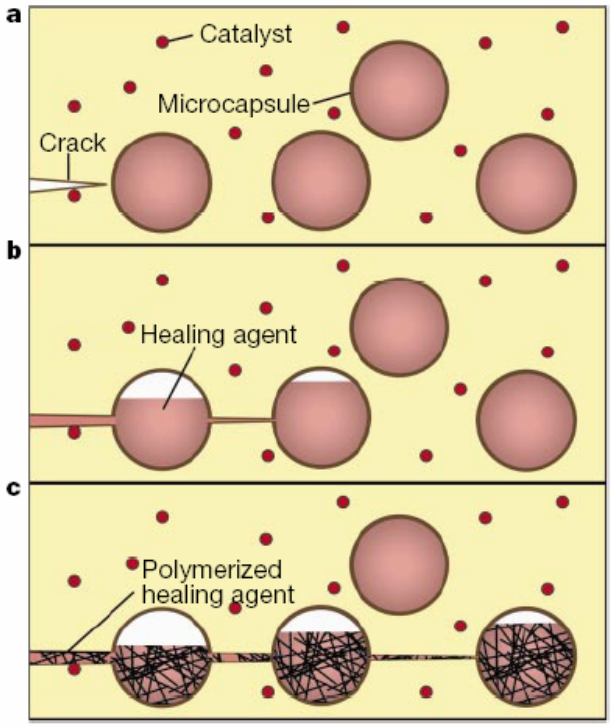


Figure 1: The autonomic healing concept. A microencapsulated healing agent is embedded in a structural composite matrix containing a catalyst capable of polymerizing the healing agent. 1a, Cracks form in the matrix wherever damage occurs; 1b, the crack ruptures the microcapsules, releasing the healing agent into the crack plane through capillary action; 1c**,** the healing agent contacts the catalyst, triggering polymerization that bonds the crack faces closed.[5]

Background

Fracture toughness defined by Kc measures the ability of a material containing a flaw—small pores, inclusions, or micro-cracks—to withstand an applied load. For this experiment, the tapered double-cantilever beam (TDCB) specimen was chosen. (Figure 2) In this type of geometry, the taper allows a constant KI over a range of crack lengths creating crack independency. KI is the rate of change of compliance with crack length.[1] The groove within the specimen ensures that the crack propagates along the centerline of the specimen making an arm break-off less likely to occur creating an inaccurate KIc. As thickness of a specimen increases fracture toughness, Kc, decreases to a constant value. This constant is called the plain strain fracture toughness, KIc, that is normally reported as the property of the material.

A tensile test measures the response of a material to a slowly applied uniaxial force to obtain yield strength, tensile strength, modulus of elasticity, and ductility. The tensile strength of a material is the stress that corresponds to the maximum load in a tensile test. A void within creates a stress concentration which causes failure of the specimen to occur sooner, lowering the tensile strength of the material.

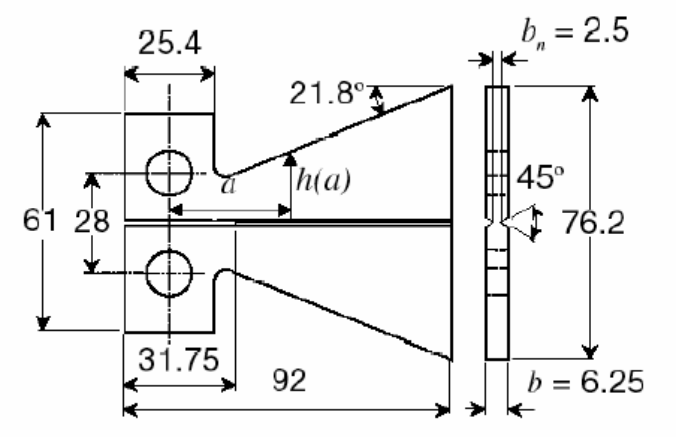


Figure 2: TDCB Fracture Specimen Geometry

When a capsule is incorporated into the epoxy matrix it behaves as an inclusion to lower the tensile strength; however, an increase in fracture toughness does occur. This increase in fracture toughness is due to a crack pinning toughening mechanism. When a crack encounters a capsule, the capsule acts as a solid particle within a composite creating a stress intensity at the location of the capsule which increases the energy required for the crack to propagate. For the self-healing concept to be useful an optimization of the increase in fracture toughness and the decrease in tensile strength must occur. Moreover, this increase in fracture toughness must be sufficiently retained at the location of the healed crack. This ability of the material retention is defined as its healing efficiency, η, which is given by the following: $\eta = K_{Ichealed} / K_{Icvirgin}$.[2]

Approach

A formula to create microcapsules was devised in Beckman Institute at the University of Illinois at Urbana-Champaign under the direction of professors Nancy R. Sottos and Scott R. White. This formula has now been modified by the efforts of graduate student Benjamin Blaiszik to create capsules on the nanoscale, around the order of 1-2 μm.

The basic nanocapsule preparation method is as follows. At room temperature (20-24C), 18.2 ml of deionized water and 6.5 g of 5.0 wt% aqueous solution of EMA copolymer was added to a 50 ml beaker. Next, 0.5 g of urea, 0.1 g of ammonium chloride, and 0.05 g of resorcinol were dissolved in solution. The beaker was suspended in a temperature-controlled water bath on a programmable hotplate with an external temperature probe and agitated at 800 rpm with a digital mixer driving a three-bladed mixing propeller placed just above the bottom of the beaker. During agitation, a drop of octanol was placed in the beaker and then 5.45 g of DCPD was added. Afterwards, the solution was sonicated for 3 minutes at 40% intensity before the addition of 1.2 g of formaldehyde. Tin foil was placed on the beaker and the emulsion was heated at a rate of 1℃/minute to the target temperature of 55℃ for four hours.

Several methods were approached to successfully incorporate these capsules in a matrix of Epon 828 epoxy resin with 12 pph Anacmine DETA curing agent. Direct incorporation into the epoxy was done by first dissolving the volume of capsules in an equal volume of methanol, approximately 30 ml, and then centrifuging for separation of capsules for 30 minutes. These capsules were placed in the Epon 828 and thoroughly mixed with a spatula before degassing for 15 minutes. After the degassing, the 12 pph of DETA was incorporated into the system and degassed again for 15 more minutes. DETA is placed in the solution later because studies have shown that its direct addition deactivates the healing agent.

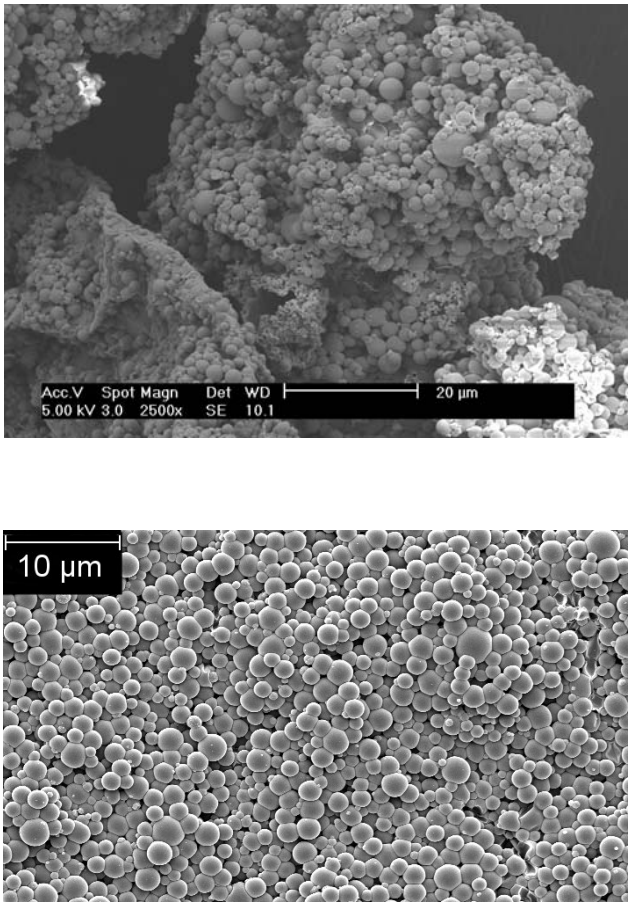


Figure 3: These photos show the clumping that occurred in the nanocapsules at different magnifications.

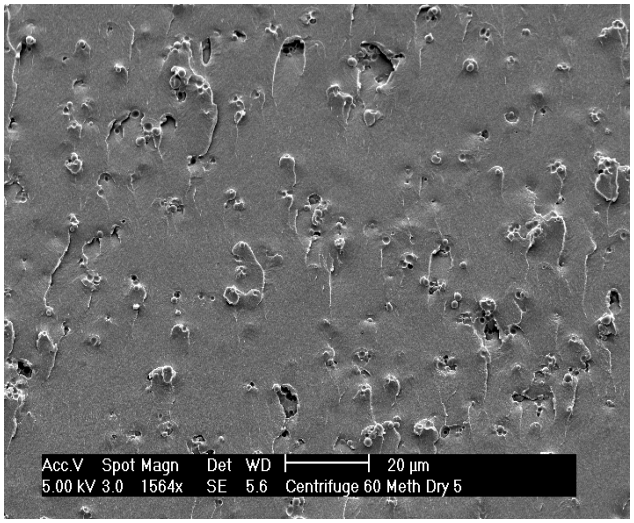
Bullet samples were made from this mixture by placing the composite into a silicone rubber mold and allowing the epoxy to cure for 24 hours at room temperature and then 24 hours at 30°C. These samples were examined by freezing the sample in liquid nitrogen and then cracking the sample with pliers to obtain a fracture surface. The fracture surface was placed on a disc and sputtered with gold- palladium for viewing with a scanning electron microscope (SEM). In addition to the viewing with the SEM, preliminary viewing was performed on an optical microscope to observe clumping issues at a lower level. The standard procedure was also performed without the addition of ammonium chloride to the solution to test the effects of the ionic compound on the attraction of the nanocapsules to each other. This solution was also subjected to sonication by a tapered and bath sonicator before the addition of the DETA. Finally, the standard assay was repeated with the addition of an extra 30 minute cycle on the centrifuge after equal dispersion with methanol, then a redispersion of the separated capsules in methanol and centrifuging for 30 more minutes After this centrifuging, the methanol was allowed to dry for periods of 5 minutes and 10 minutes from the capsule solution in the vial before incorporation into the epoxy and sonication with a tapered sonicator for 5 minutes, after which DETA was added.

Furthermore, the samples were cracked at room temperature and not by freezing in liquid nitrogen.

Once a suitable method has been obtained, then fracture and tensile testing of the different weight percent of capsules can be performed. To perform the fracture testing, a mold of silicone rubber of the TDCB specimen is waxed and a thin rectangular strip of silicone rubber is placed along the center groove of the mold to create a localized sample. The mold is then clamped shut and the polymer created from Epon 828 and 12 pph Anacmine DETA is poured into the mold and allowed to cure for 24 hours at room temperature. Then, the strip from the center is removed and the composite of capsules and epoxy are placed along the central groove and allowed to cure for 24 hours at room temperature and then 24 hours at 30°C. After curing, the samples are removed from the mold and excess epoxy is chiseled away. Furthermore, the holes in the geometry are widened to ensure the specimen can fit in the grips of the test apparatus. The central groove of the specimen is cut with a saw to near the beginning of the taper and a razor blade is placed in this opening and tapped to create a precrack, approximately (range of the length of the precrack?? Between 20-40 mm) in length. The precrack is measured and the specimen is loaded on the testing apparatus with a load cell of 300 lb. to perform the fracture test. In addition, dog bone tensile specimens can be made in a like manner by placing the composite solution of capsules in a silicone rubber mold and allowing it to cure 24 hours at room temperature and 24 hours at 30°C before performing a tensile test.

Results

Direct incorporation into the epoxy matrix did not create capsule dispersion as seen in Figure 3 due to the capsules' attraction towards each other. When the ammonium chloride concentration was decreased, the capsules seem to be less attracted to each other; however, the epoxy did not cure after several days. Sonication of the capsules in the Epon 828 seems to create more dispersion of the capsules, but clumping issues still occurred. Therefore, the methanol drying procedure was instituted to see if there was phase separation between the methanol and epoxy that was causing the capsules to clump. This drying created well-dispersed capsules as seen in Figure 4; however, there is a significantly greater number of debonded capsules than previously seen in the microcapsules.



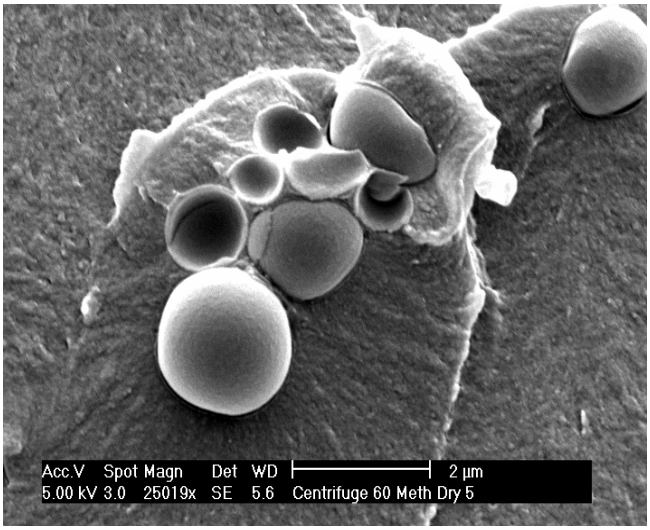


Figure 4: These photos depicted the nanocapsules dispersed in the epoxy matrix at different depths. In the bottom photo it can easily be seen that the nanocapsules do not share a shell wall as previously encountered with clumping, however some of the capsules appear debonded, the capsules that have not ruptured.

Conclusion

At this point, there are still issues with the incorporation of the nanocapsules within the epoxy matrix; however, the issue of clumping has been resolved. Moreover, the issue of debonding can easily be corrected—if due to a surface roughness issue— by the addition of more urea to create a better surface for the epoxy to adhere. The behavior of a particle at the nanoscale level is one of the biggest issues encountered. Once this issue with the debonding of capsules has been resolved, fracture and tensile testing described above can proceed and the results can be compared to the previous microcapsules.

References

(1) Eric Nathaniel Brown. "Fracture and Fatigue of a Self Healing Polymer Composite Material" (Ph.D. diss. University of Illinois at Urbana-Champaign, n.d.).

(2) Brown, E.N. et al. "Fracture Testing of a Self-Healing Polymer Composite," *Experimental Mechanics*; 42, no. 4 (2002): 372-379.