Effect of Microcapsule Size on Tensile Properties of Self-Healing Composites

Joseph H. Lai
Junior in Materials Science and Engineering
University of Michigan-Ann Arbor

Advisors: AE undergraduate assistant Alyssa A. Rzeszutko,
TAM graduate assistant Benjamin J. Blaiszik, and
TAM Prof. Nancy R. Sottos

This project investigates the effect of microcapsule size on the mechanical properties of a self-healing polymer composite. Three different sets of tensile bars were made from an epoxy with each set containing a different size microcapsule at a fixed concentration. Uniaxial tensile tests were performed to determine Young's modulus and ultimate tensile strength. It was found that Young's modulus decreased as microcapsule size increased. No correlation was found between ultimate tensile strength and the microcapsule sizes tested.

Introduction

In all composite materials, the properties of the filler material have a significant effect on the mechanical properties of the overall composite. White et al.[1] have introduced a particle-dispersed polymer composite that has the capability of self-healing upon crack propagation. This composite consists of an epoxy matrix embedded with microcapsules containing a monomer healing agent. Grubbs catalyst is also dispersed throughout the epoxy matrix. Once a crack occurs, the crack propagates along the composite, rupturing the microcapsules and releasing the healing agent. As the healing agent flows along the crack plane, it comes into contact with the Grubbs catalyst and polymerization begins, sealing up the crack. This project analyzes the effect that microcapsule size has on the mechanical properties of the self-healing polymer composite. Composite tensile bar samples were produced containing microcapsules of various sizes at a fixed weight concentration and then mechanically tested for ultimate tensile strength and Young's modulus.

Experimental procedure

Silicon-rubber molds for the tested tensile bars were cast in an aluminum mold using GE Silicones® RTV630 with 630B curing agent. Once six silicon-rubber molds were produced, composite tensile bars were then made using EPON® 828 epoxy resin (diglycidyl ether of bisphenol A, DGEBA) with 12 pph Anacime DETA (diethylenetriamine) curing agent and microcapsules. A set of neat epoxy (no microcapsules) tensile bars were made first by stirring the EPON® 828 epoxy resin with the curing agent until homogeneous and then degassing the mixture for approximately 10 minutes. The longer the mixture is degassed, the more it is free of

air bubbles. However, degassing longer than 10 minutes increases the likelihood of the mixture heating and curing too quickly. The epoxy quickly becomes more viscous or even cures instantaneously. If needed, microcapsules are added at this point and a second degassing is performed for approximately 5–10 minutes. Once degassed, the mixture is then poured at the top of a silicon-rubber mold, which is placed at an angle so as to allow the epoxy to fill the mold without creating any air bubbles. The sample is then placed at room temperature to cure for 24 hours and then in the oven set at 30°C to cure for another 24 hours. Composite tensile bars are produced with the addition of microcapsules stirred into the epoxy mixture after the initial degassing stage.

Microcapsule production is a critical component in researching the effect of microcapsule size on a self-healing composite. Microcapsule production begins with an oil-in-water emulsion, by adding 25 mL of 5 wt% EMA copolymer into 200 mL of deionized water. The addition of EMA lowers the pH level to approximately 2.6. It is crucial that once the EMA is added into the deionized water that the pH falls to between 2.5 and 2.7; otherwise polymerization may not properly occur later on. Once the pH was in the appropriate range, the 3-bladed mixing propeller was lowered to approximately 2/3 from the level of the solution. Microcapsule size is regulated by mixer speed. The log-log graph[2] in Figure 1 displays the relationship of microcapsule diameter size with mixer speed.

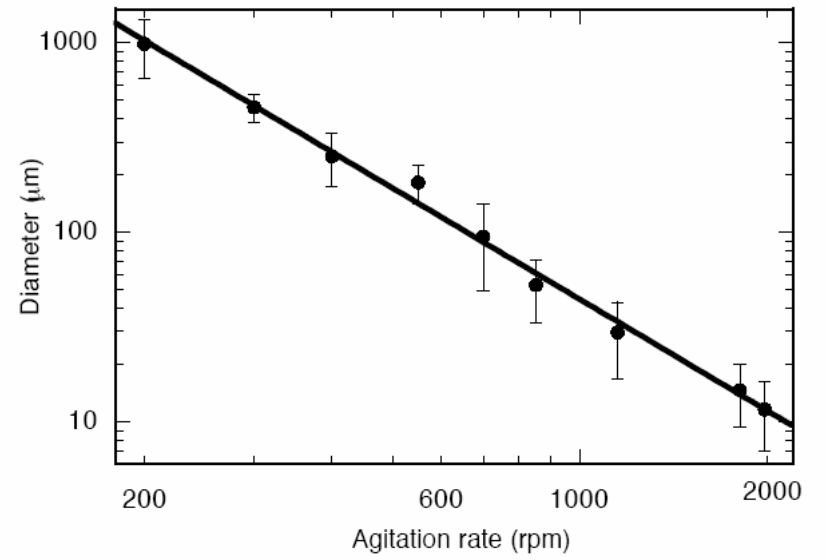

Fig. 1. Average microcapsule diameter as a function of mixing speed.[2]

For 180 μm, the mixing speed was set to 600 rpm; smaller capsules are produced by increasing the mixing speed. In this project, 1000 rpm and 2500 rpm were used to form 60 μm and 20 μm capsules, respectively. These speeds are slightly higher than those suggested by the graph in Fig. 1, but they resulted in a much larger yield of each expected capsule size. At 2500 rpm and at speeds higher than 1500 rpm in general, the mixer has a tendency to vibrate excessively, and to remedy this nuisance, the mixing blade should be raised so that it is just below the surface of the solution. Once the solution is mixing without any excessive vibration, 5 g of urea, 0.5 g ammonium chloride, and 0.5 g resorcinol are added to the solution. The addition of these compounds should not affect the pH level, except for the 5 g of urea, which should raise the pH by a value of 0.1. At this point, this pH should be between 2.6 and 2.8; otherwise an incorrect amount of urea was added. Once the pH level is within the necessary

range, the pH is then increased to 3.5 with drops of sodium hydroxide (NaOH) in order for optimum polymerization of the microcapsule shell wall to occur. Incorrect pH levels throughout the process lead to large yields of urea-formaldehyde debris, unfilled capsules, or even no capsules. Surface bubbles or foam in the solution can result in poor quality microcapsules and so 1 drop of 1-octanol was added to eliminate them. Afterward, 60 mL of dicyclopentadiene (DCPD) healing agent is steadily streamed into the mixture to form an emulsion with EMA. After waiting 10 minutes for the DCPD to stabilize, 12.67 g of 37 wt% aqueous solution of formaldehyde is added into the mixing solution. Last, the mixture is covered and heated to 55°C at a rate of 1°C per minute. After 4 hours of continuous heating and agitation, the urea and formaldehyde have polymerized and the resultant slurry of microcapsules is poured into a coarse frit for drying.

Once frit-dried, the clumps of microcapsules are then dumped in a weigh-boat lined with aluminum foil and dried at room temperature for approximately 24 hours or longer if needed. Clumps of microcapsules are completely dry when they are easily broken up by a slight gust of air. It is absolutely essential for microcapsules to be completely dry prior to sifting; otherwise sifting will result in microcapsule damage or rupture. Once completely dry, microcapsules are sifted for 10 minutes with appropriate sieves stacked up. Finally, microcapsules of the desired size are collected from the appropriate sieve. Each collection is examined under an optical microscope to check for purity of microcapsules. It was found that any more than two 10-minute sifts resulted in a progressively less pure yield of microcapsules, as an increasingly large amount of urea-formaldehyde debris became present with each collection. A size distribution is performed to verify that the capsule sizes are within the expected ranges. By using an optical microscope, an image of the produced capsules is taken, and the diameters are carefully measured out with ImageJ software.[3] Once the diameters of at least 50 microcapsules have been measured out, the data are entered into Microsoft Excel and a histogram plot with a size distribution is generated.

The methods for microcapsule collection, however, led to large quantities of urea-formaldehyde debris, especially for 20 and 60 μm capsules, and had to be modified. With 180 μm capsules, use of the original techniques did result in a pure yield of quality microcapsules (Fig. 2). During sifting, sieves of 350, 250, 180, and 125 μm were used and microcapsules in the 125 μm sieve were collected.

From previous research, the amount of urea-formaldehyde debris present becomes progressively larger as the mixing speed used is increased. This debris is especially present in producing 60 and 20 μm capsules, as can be seen in Figs. 3 and 4.

In an attempt to eliminate some of the debris, acetone was used to rinse the micro-capsules. However, rinsing microcapsules with acetone only allowed DCPD to leak out, leaving behind an empty, deflated urea-formaldehyde shell that can be seen as transparent under a microscope as in Fig. 5. As a refinement of the previous microcapsule extraction techniques, a density separation was performed on the 20 μm capsules by pouring deionized water to the brim of the beaker. Since DCPD is less dense than water, good quality microcapsules filled with DCPD should float in water, while urea-formaldehyde, which is denser than water, should sink to the bottom of the beaker. With DCPD-filled microcapsules separated from unwanted remains of urea-formaldehyde, the top layer of capsules is carefully hand-spooned into another beaker of deionized water to remove further any unwanted urea-formaldehyde particles. The floating layer of quality microcapsules in the second beaker is scooped out and finally dumped into a frit for drying.

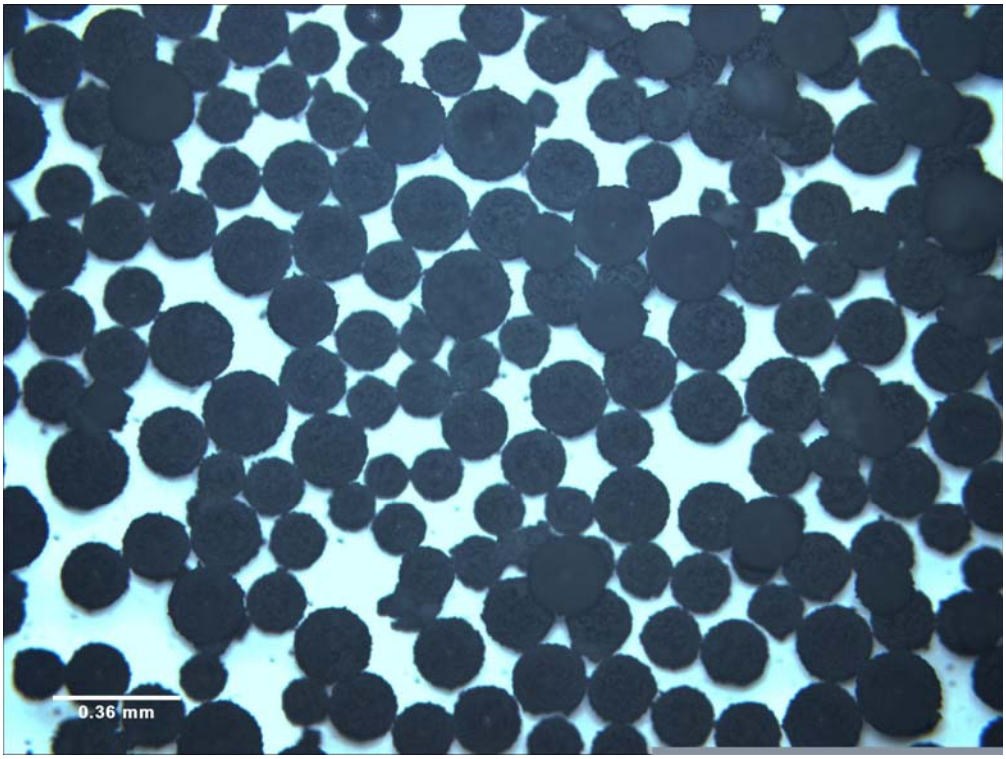

Fig. 2. Microphotograph of 180 µm capsules (5x objective).

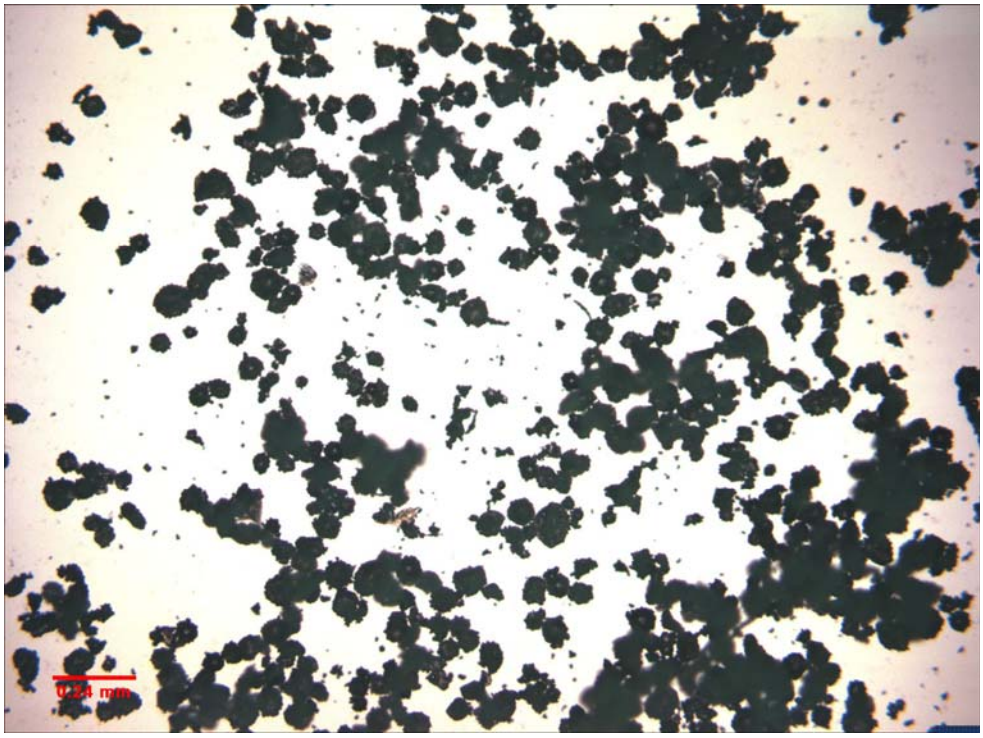

Fig. 3. Microphotograph of 60 µm capsules with UF debris (5x objective).

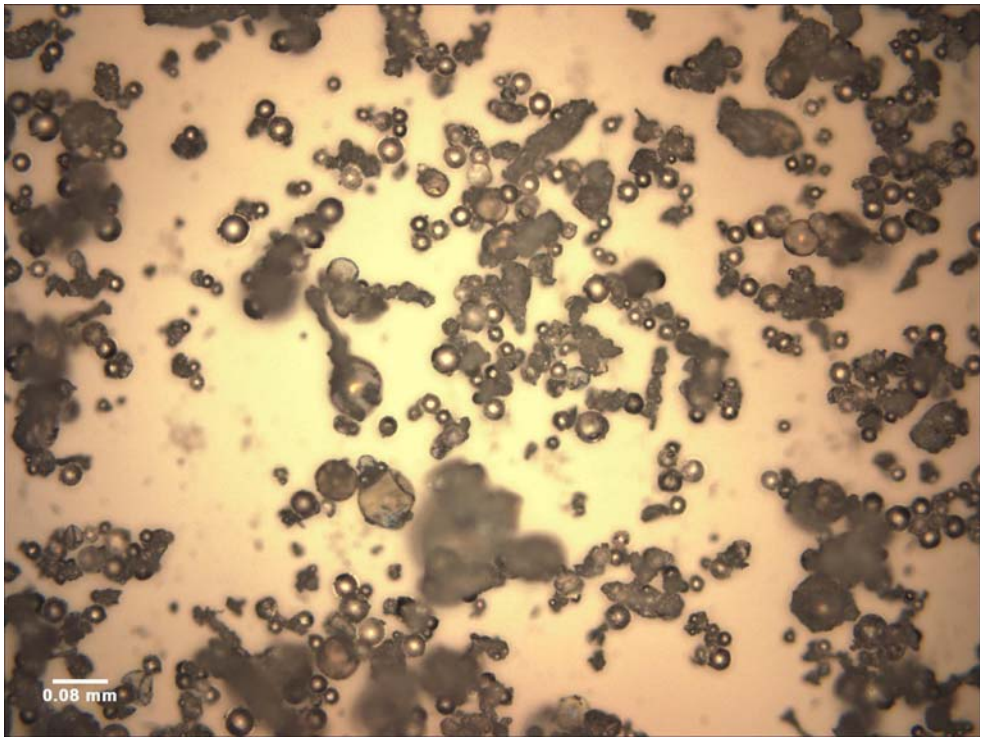

Fig. 4. Microphotograph of 20 µm capsules with UF debris (10x objective).

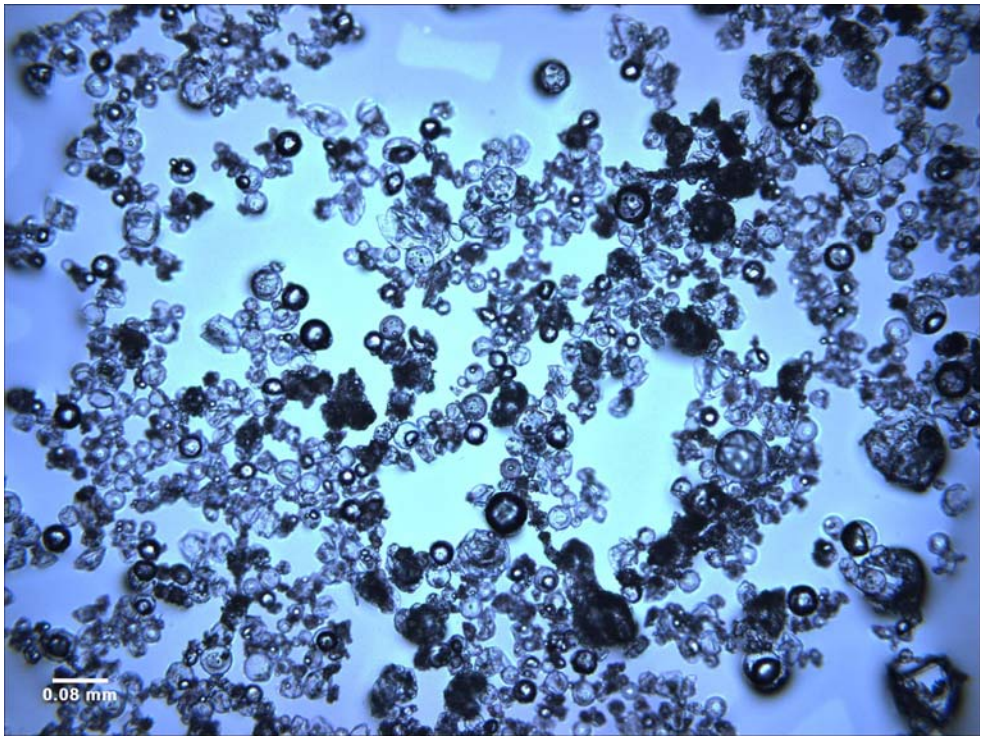

Fig. 5. Microphotograph of 20 µm capsules after acetone rinse (10x objective).

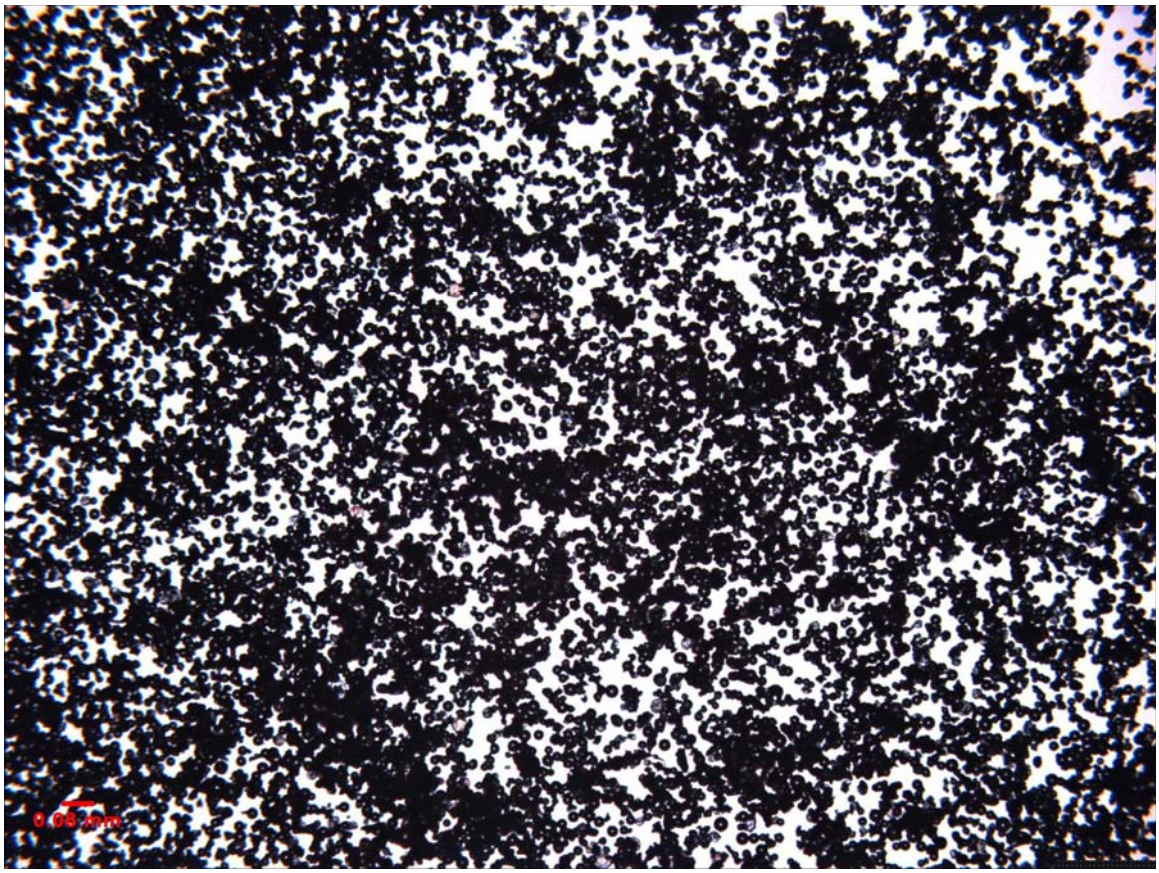

Fig. 6. Microphotograph of purer 20 µm capsules (5x objective). Black clusters are microcapsules lying above one another.

Figure 6 shows a sample of purer microcapsules that were obtained from refining the original techniques of microcapsule extraction. Once frit dried and dried at room temperature, the clumped microcapsules are then sifted for 10 minutes, using a stack of 75 µm, 53 µm, 43 µm, and 38 µm sieves. Since 20 µm capsules are needed in this project, microcapsules in the container beneath the 38 µm sieve were collected. For extraction of 60 µm capsules, a slightly different procedure was used so that a larger and purer yield of microcapsules could be obtained. After 4 hours of continuous agitation and heating, the resulted slurry in the beaker was poured through a stack of 3 sieves: 75, 53, and 45 µm. Rather than immediately separating the different-sized capsules with Ro-Tap as originally done, a wet-sifting technique was performed by rinsing the set of sieves under a running faucet of deionized water, in order to remove better the urea-formaldehyde debris. After continuous washing of microcapsules, the capsules in the 53 µm sieve were rinsed into a beaker and poured onto a filter paper that was dried by a vacuum. The collected microcapsules were then dried at room temperature for approximately 24 hours and then sifted with Ro-Tap for 10 minutes, using sieves of 1 mm, 500 µm, 75 µm, and 53 µm. Once sifted, the improved purity of the microcapsules could immediately be seen as they clearly were more free-flowing than the microcapsules produced with the original techniques. A sample of 60 µm capsules obtained with the refined techniques was examined, and clearly, the microcapsules appeared cleaner and more spherical than before, as can be seen in Fig. 7.

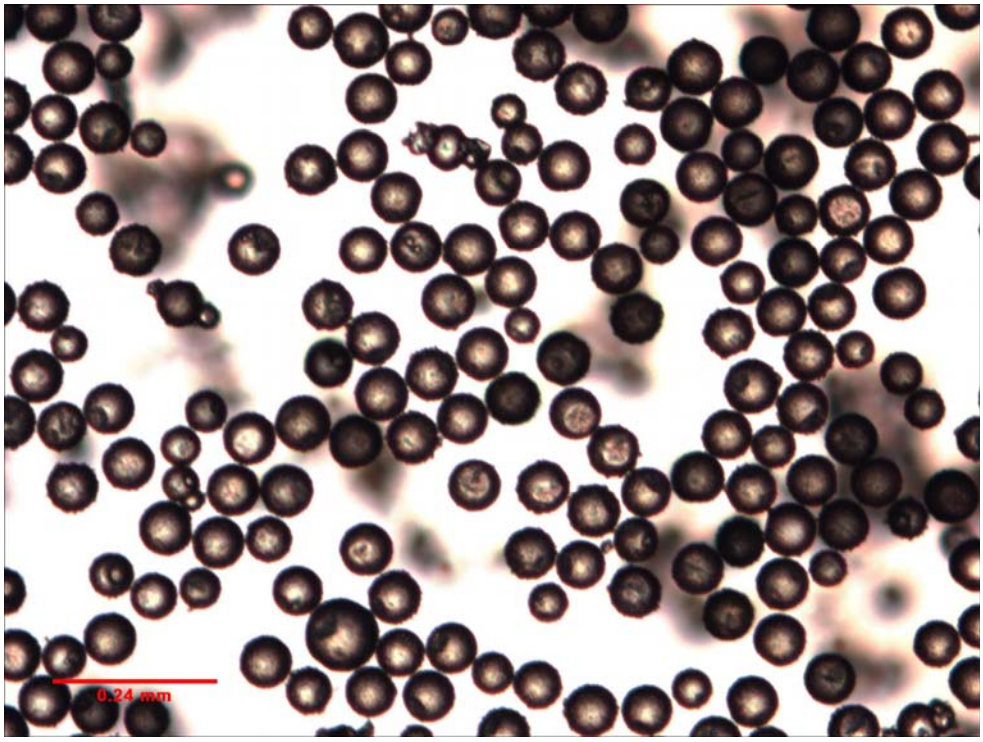

Fig. 7. Microphotograph of purer 60 µm capsules (5x objective). Image appears more magnified than that in Fig. 3 because a new camera with a larger zoom was recently installed.

In making the tensile bar composites, approximately 2–2.5 g of microcapsules were needed for each pair of tensile bars, which would require 12–15 g of microcapsules to be produced for each set of 12 tensile bars. A single batch of 180 µm capsules was able to produce a sufficient yield. However, with 60 µm capsules, 5 batches of microcapsules were necessary just to produce an adequate amount. The 20 µm capsules required 6 batches.

Once an adequate quantity of 180, 20, and 60 µm capsules were produced, tensile bar composites were then fabricated. Preparing the epoxy for making tensile bars should be done one cup at a time to prevent idle epoxy mixtures from curing instantaneously. Each cup represents one batch, which provides enough epoxy for a pair of tensile bars. Degassing more than one cup at a time led to the epoxy curing instantaneously. After the initial degassing stage, microcapsules were added into the epoxy and degassed for another 5 minutes. During this second degassing stage, the epoxy was monitored for signs of boiling, and if it did occur, the degassing process was terminated early. Boiling occurred when the surface of the epoxy started bubbling, rather than foam appearing at the surface of the epoxy; surface foam is indicative of normal degassing. Once degassed, the epoxy–microcapsule mixture was then poured at the top of a silicon-rubber mold that was placed at an angle. The epoxy composite was then given 24 hours to cure at room temperature and another 24 hours to cure in the oven set at 30°C.

The finished tensile bar composites were then individually measured for gage width and length and loaded in the Instron 8500 for mechanical testing. The data that resulted from the tests include strain (%), load (kN), stress (MPa), and time of load (sec).

Results and discussion

The tensile bars in each set were pulled until failure. While a few of the specimens broke in just the gage area as intended, some of the specimens only broke at the pinholes. Most of the specimens that broke in the gage area also broke in one or both of the pinholes. Some of the specimens that broke at the pinholes did not have any bubbles in that region. In the tensile bars that did have bubbles and broke at the pinholes, the crack was observed not to have started from those bubbles, as they were still present after the test. The results for a few of the tensile bars were discarded due to yield of improbable results or improper machine setup of the tensile bars.

During the tests, the data for a few of the tested tensile bars were discarded due to improper loading procedure of the specimen or implausible results. Neat epoxy tensile bars represent microcapsules that are infinitely small. Figure 8 and the associated raw data in Table 1 show that Young's modulus decreases slightly as microcapsule size increases. Therefore, the stiffness of the microcapsule composite increases with decreasing microcapsule size.

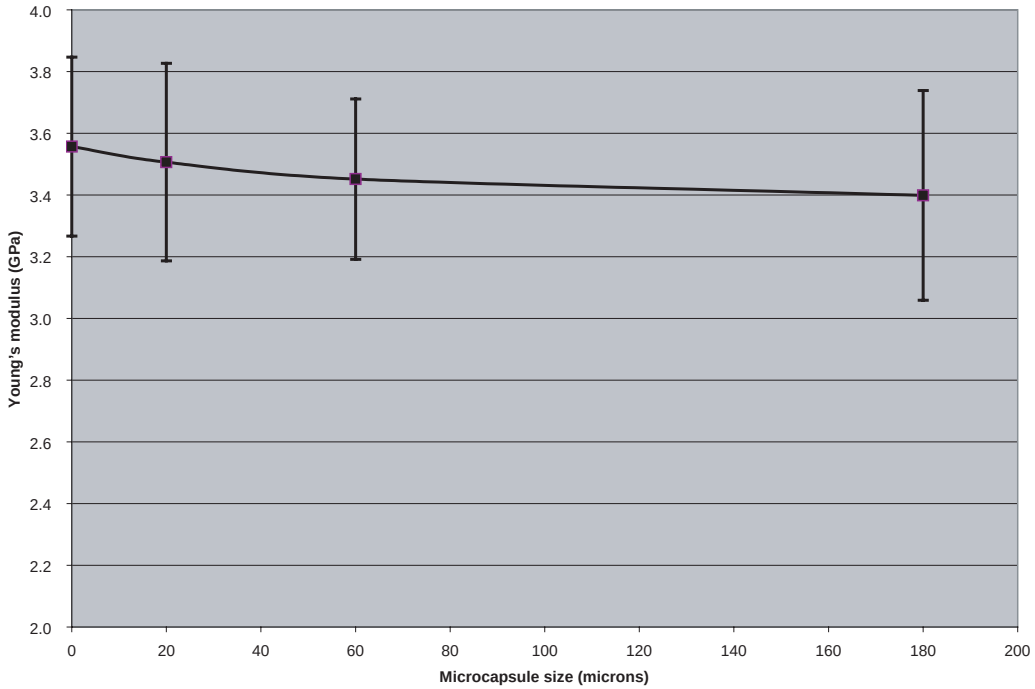

Fig. 8. Young's modulus vs. microcapsule size.

These results reveal that the smaller the capsule size, the more the composite's elastic modulus will approach that of the neat epoxy, that is, an epoxy without any capsules.

The ultimate tensile strength of each bar was also analyzed. Figure 9 and the associated data in Table 2 reveal that, if microcapsules are present, there is no relationship between ultimate tensile strength of the composite and the tested sizes of its embedded microcapsules. However, as Fig. 9 reveals, a steep drop-off in ultimate tensile strength occurs once microcapsules 20 μm and larger are added. Current research is being done on the manufacturing of nanocapsules and whether the ultimate tensile strength will be more similar to that of the neat epoxy.

Bar no.	Young's modulus (GPa)			
	Neat	20 µm	60 µm	180 µm
1	3.98	3.58	3.27	3.01
2	3.60	4.09	3.36	2.95
3	X*	3.05	3.60	3.43
4	3.58	3.93	4.04	3.00
5	3.68	3.27	3.52	X
6	3.78	3.57	3.12	3.28
7	3.31	3.22	3.28	3.92
8	3.52	3.33	3.25	3.69
9	2.95	3.85	3.42	3.24
10	3.91	3.20	X	3.59
11	3.42	3.47	3.69	3.45
12	3.39	3.50	3.42	3.83
Average	3.56	3.51	3.45	3.40
Std dev	0.29	0.32	0.26	0.34

*X denotes discarded results

Table 1. Young's modulus of tested tensile composites.

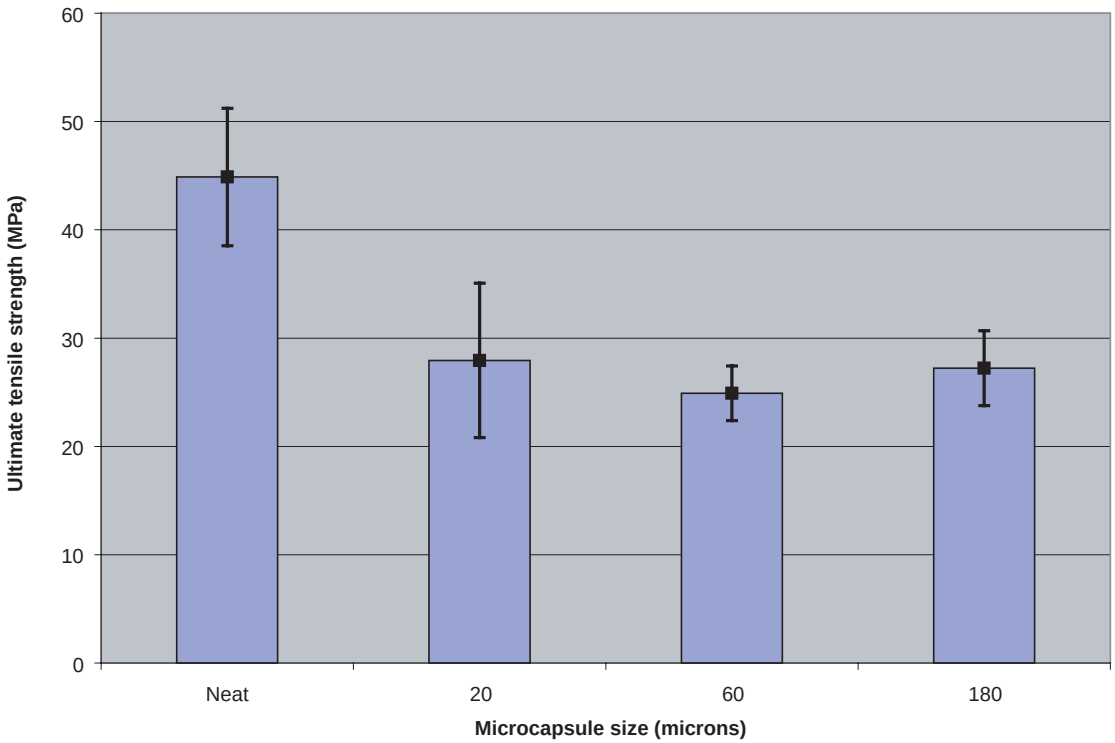

Fig. 9. Ultimate tensile strength vs. microcapsule size.

Bar No.	Ultimate Tensile Strength (MPA)			
	Neat	20 μm	60 μm	180 μm
1	34.0	20.8	26.2	28.8
2	47.3	32.0	21.3	26.6
3	X*	30.8	24.7	28.5
4	51.6	19.7	22.4	25.9
5	39.7	32.0	24.6	X
6	53.1	29.4	26.6	31.0
7	49.1	22.8	27.1	19.4
8	40.6	35.8	27.3	26.4
9	48.4	13.7	20.3	31.1
10	44.0	36.2	X	23.5
11	49.4	34.2	26.7	29.1
12	36.4	28.0	26.9	29.5
Average	44.9	27.9	24.9	27.2
Standard Deviation	6.4	7.1	2.5	3.5
*X denotes discarded test bar or data				

Table 2. Ultimate tensile strength of tested tensile composites.

Summary and conclusions

The effect on Young's modulus and ultimate tensile strength from varying microcapsule size at a fixed concentration was investigated in this project. Microcapsules of sizes 180 μm, 60 μm, and 20 μm were studied. However, original extraction techniques of 60 μm and 20 μm led to an insufficiently low yield of microcapsules and a large yield of urea-formaldehyde debris. The original techniques were refined and a larger quantity of microcapsules with significantly less debris was obtained. Once a purer sample of microcapsules was obtained, a set of 12 tensile bars containing 5 wt% concentration of microcapsules was produced for each microcapsule size. Neat tensile bars (that is, tensile bars containing no capsules) were produced to represent tensile bars containing infinitely small capsules. Uniaxial-tensile tests were performed on the produced tensile bars to reveal information on Young's modulus and ultimate tensile strength. Young's modulus decreased slightly as the size of the microcapsule increased, indicating that the stiffness of the microcapsule composite will increase slightly as microcapsule size is decreased. No correlation was found between ultimate tensile strength and microcapsule sizes greater than 20 μm. A steep drop-off in ultimate tensile strength occurred between the neat epoxy and the rest of the tensile bars, suggesting that smaller-than-20 μm capsules may be required for the ultimate tensile strength to be more similar to that of the neat epoxy.

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