Crack-Shell Interactions in Self-Healing Composites

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1. Introduction

University of Illinois researchers have developed a self-healing composite material, in which minor damage, in the form of cracks, triggers an autonomic healing response [1]. The composite is comprised of an epoxy matrix, a catalyst, and a microcapsulated healing agent (shown in figure 1). Urea-formaldehyde (UF) is used as the shell wall of the microcapsules.

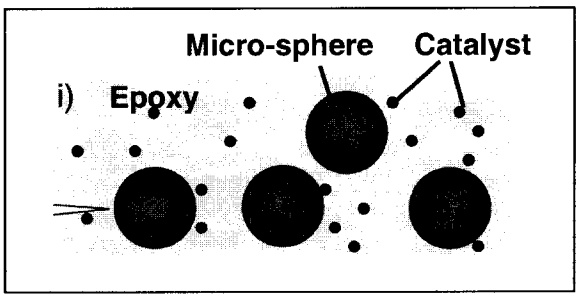


Figure 1. Schematic of self-healing polymer composite.

Figure 2 demonstrates the concept of self-healing. An approaching crack (figure 2i) ruptures a microcapsule (figure 2ii), which spills the healing agent into the crack plane through capillary action [1]. The healing agent reacts with the catalyst and bonds the surfaces of the crack plane (figure 2iii).

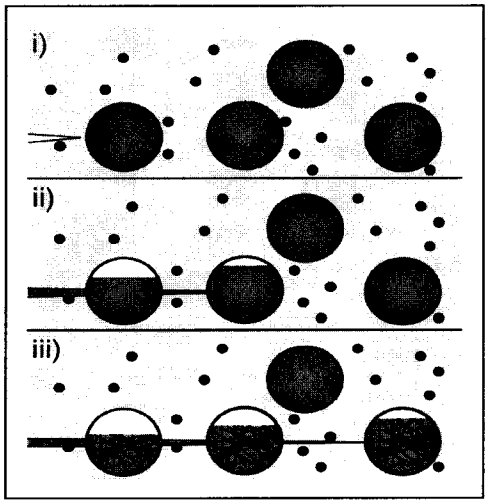


Figure 2. The self-healing concept.

For healing to occur, the capsules must be thin enough so that they rupture when a crack approaches and not so thin that the walls will break during composite processing [1]. This is the basis of our current research, for which we are varying wall properties on a macro scale in order to find an optimal capsule wall. The variables of interest are the wall thickness to sphere diameter ratio, the shell toughness, and the interfacial adhesion

between the spheres and the matrix. The experiment was based on a recent finite element analysis, conducted by Dr. Geubelle's group [2], which analyses the spheres in two dimensional plane strain. An edge-notched specimen with a cylindrical shell, which represents a sphere in two dimensions, was used for the computational analysis.

Figure 3 shows the geometry of the specimen used for this experiment. Since UF is hard to mold, epoxy has been chosen to act as the shell for the experiment. Both materials are brittle and linearly elastic so the epoxy will give a good approximation of the response of the UF. Polymethyl methacrylate (PMMA) substitutes as the matrix because it is easily manufactured and the epoxy will bond to it during curing.

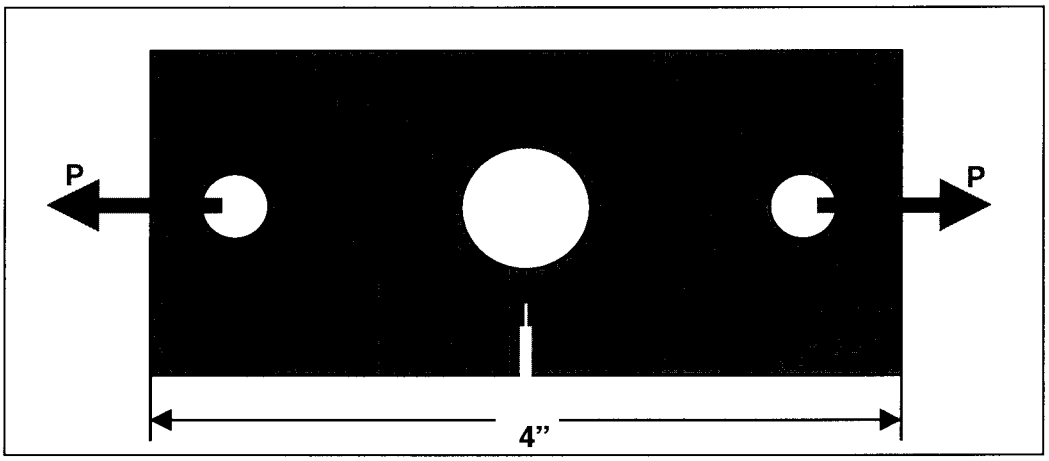


Figure 3. Edge-notched specimen.

Three types of shells were analyzed:

Table 1. Shell types

Type I	Epoxy (EPON 828/DETA)
Type II	Epoxy with 15% flexibilizer (EPON 828/Heloxy 71/DETA)
Type III	Epoxy with 2% release agent (z-6070)

Each type of shell was manufactured into three different wall thickness to shell diameter ratios (t/d_o). Those ratios where quantified as 0.024 (small), 0.050 (medium), and 0.100 (large). All specimens were loaded to failure to determine if a crack would propagate through the shell (Figure 4a) or around the shell (Figure 4b).

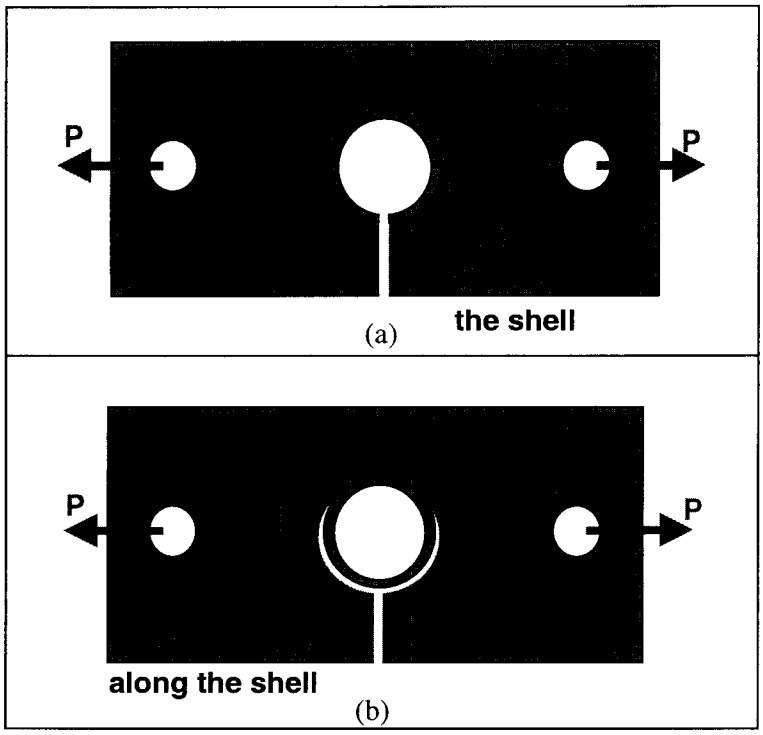


Figure 4. Possible crack path in edge notched specimens.

2. Experimental Procedure

The matrix is cut out of a sheet of PMMA to match the shape shown in Figure 5a. A silicon mold with a thin square base and a cylindrical protrusion is placed into the center hole of the PMMA (Figure 5b). Since the diameter of the silicon cylinder is molded to be smaller than the hole in the PMMA, there is a space between the two where the epoxy shell will be poured. To vary the thickness to diameter ratio of the shell, the diameter of the silicon mold cylinder is left unchanged and the diameter of the hole in the PMMA matrix is varied.

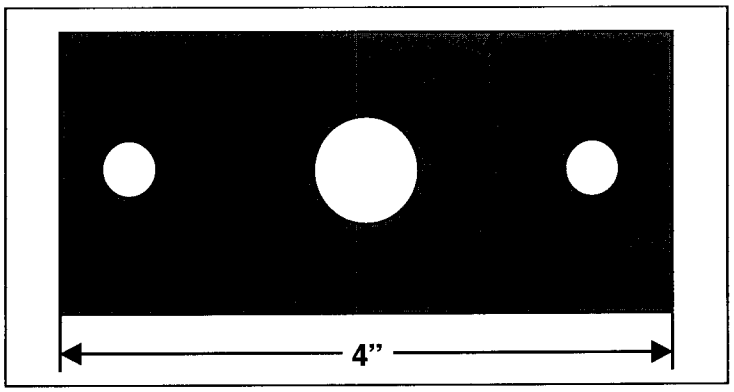


Figure 5a. Sample dimensions.

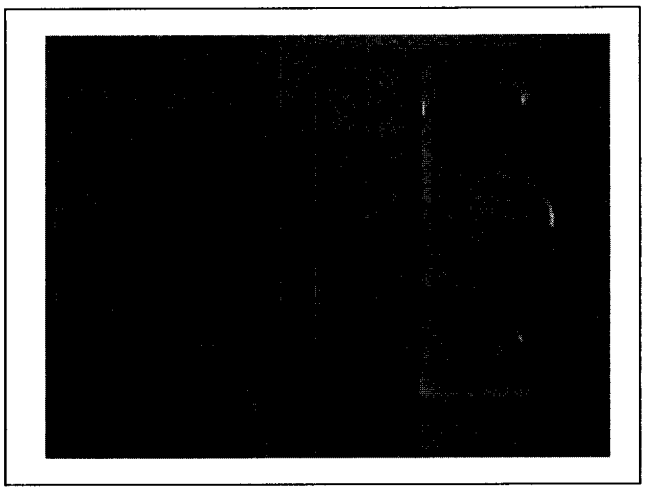


Figure 5b. Photograph showing of silicon rubber mold to create inner epoxy shell.

2.1 Sample Preparation

The silicon molds were cleaned with acetone, then sprayed with release agent dry lubricant (MS-112DF) so that the epoxy will not bond to the silicon. Isopropanol was used to clean the PMMA specimen, and then a light coating of paste wax was applied to the area surrounding the hole so that any excess epoxy on the surface of the specimen could be easily removed after curing.

Before the epoxy can be poured, the top part of the silicon mold's square base must be clamped tightly to the bottom face of the PMMA specimen in order to prevent epoxy leakage. Placing a flat metal brace along the bottom of the silicon mold's base, the mold is clamped to the PMMA specimen with the cylinder protrusion extending completely through the hole (Figure 6). Care must be taken to align the cylinder exactly in the center of the hole in order to produce a shell of constant thickness.

The components for each Type of epoxy being used are measured (see Appendix A), then mixed thoroughly using a wooden tongue depressor. The mixture is then degassed in a vacuum to eliminate any bubbles produced during mixing. Slowly, the epoxy mixture is poured into the space between the silicon cylinder mold and the PMMA hole. Epoxy is cured for twenty-four hours at room temperature and twenty-four hours at 40° C.

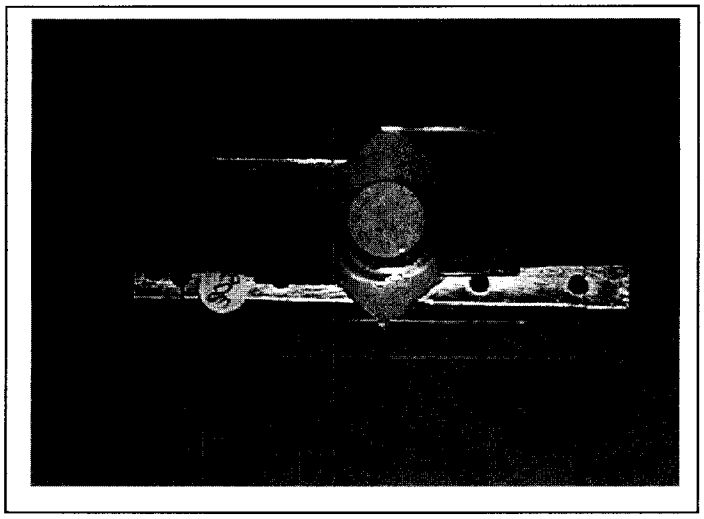
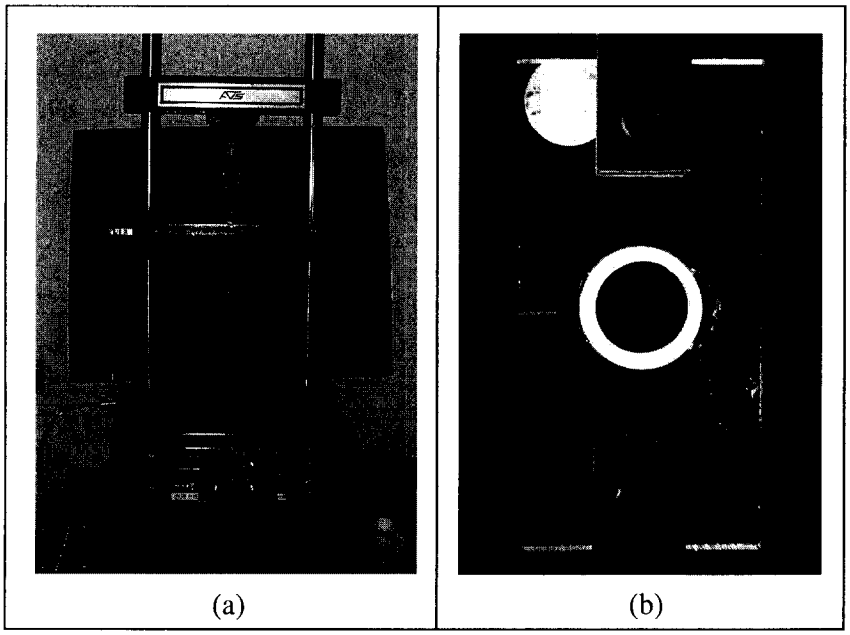


Figure 6. Clamps holding silicon rubber mold in place, while epoxy shell cures.

After the epoxy has cured, the specimen is unclamped and the silicon mold is removed. With the use of a diamond saw, a notch is inserted into the edge of the specimen to represent an approaching crack (seen as the thick white line at the bottom of Figure 3). Then a razor blade is lightly tapped into the notch until a sharp crack tip has formed (seen as the thin line extending from the notch in Figure 3). The specimen is now ready for testing.

2.2 Experimental Testing

Using the load frame seen in Figure 7, the specimens are pin loaded in tension at a strain rate of 0.03 inches per minute. Each specimen is tested to failure to determine the qualitative value of the shell.

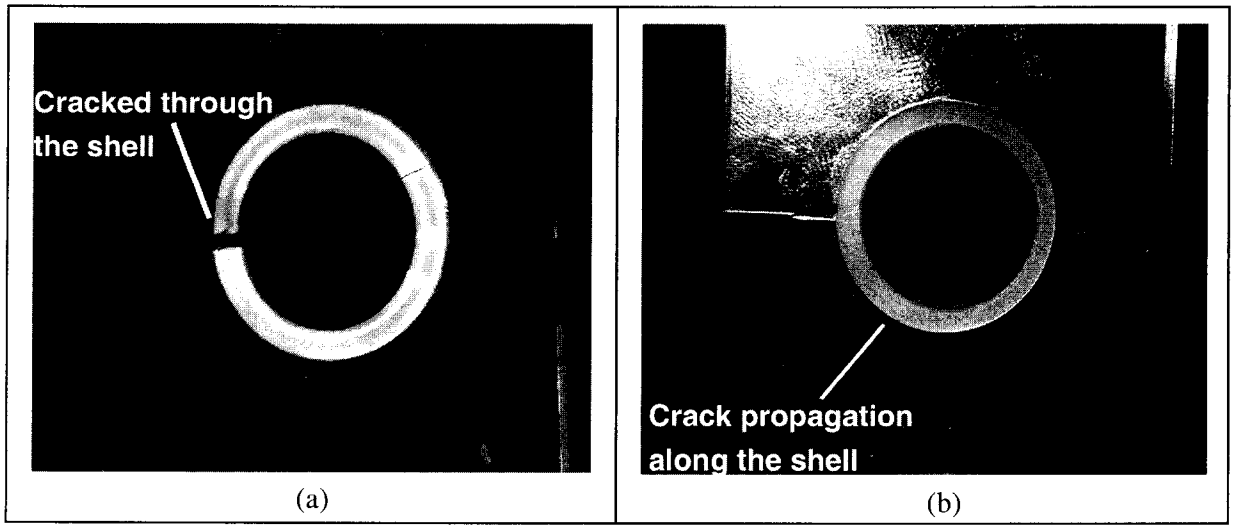


(a) (b)

Figure 7. Photograph of (a) load frame and (b) the specimen in the load frame.

3. Results

We found that the crack propagated through the shells for all thickness to diameter ratios of Type I specimens (Figure 8a). All the other specimens had the crack propagate along the shell (Figure 8b).



(a) (b)

Figure 8. Failed specimen with (a) crack through shell, (b) crack around the shell.

The summary of the data acquired is listed in Table 1 and the complete table of data can be found in Appendix B.

Table 2. Experimental results.

Sample	Type I (Epoxy)	Type II (15% Heloxy 71)	Type III (2% 6070)
Small t/d = 0.024	Cracked Shell	Propagated Along Shell	Propagated Along Shell
Medium t/d = 0.050	Cracked Shell	Propagated Along Shell	Propagated Along Shell
Large t/d = 0.100	Cracked Shell	Propagated Along Shell	Propagated Along Shell

Type II specimens have the addition of the flexiblizer Heloxy 71, which should increase the fracture toughness of the shell. This increase could have caused the crack to deflect around the shell. Compact tension specimens were made and tested to determine the fracture toughness K_{IC} of each Type (see Appendix C).

Table 3. Fracture toughness in $MPa*m^{1/2}$

Specimen	K_{IC}
Type I	1.00
Type II	1.79
Type III	1.3

Type II and Type III have larger fracture toughness values than the PMMA matrix (K_{IC} = 1.10 $MPa*m^{1/2}$) and they both deflect the crack around the shell. But fracture toughness is not the only variable that affects the results. The interfacial adhesion can also play a part in determining where the crack will go.

Type III specimens have the addition of a release agent (z-6070), which should decrease the bond strength at the interface between the epoxy shell and the PMMA matrix. The decrease in bond strength lowers the energy needed for the crack to propagate around the shell. The combination of the increased fracture toughness and the decreased bond strength for Type III specimens, could be the reason that the crack deflected around the shell.

It is possible that the flexibilizer added to the Type II specimens also altered the bond strength between the shell and the matrix. Testing still needs to be done to determine the adhesion effects on each Type of specimen.

4. Future Research Plans

The change in adhesion strength needs to be quantified in order to analyze its affect on the crack-shell interactions. Then the percentages used for the flexiblizer and the release agent can be varied in order to find an optimal shell wall.

Type IV specimens could be made to test the affects of an epoxy with the addition of an adhesion agent. The adhesion agent would increase the bond strength at the interface between the shell and the matrix. This would increase the energy needed for the crack to propagate along the shell.

If possible, we would like to mold UF as the shell and epoxy as the matrix (as is used in the self-healing composites). This will give us more applicable information about the crack-shell interactions in a self-healing composite material.

5. References

[1] White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriram SR, Brown EN, Viswanathan S, Autonomic healing of polymer composites. *Nature*, **Vol. 409**, 794-797 (2001).

[2] Viswanathan, S., Micromechanical Modeling of Self-Healing Polymeric Composites. MS Thesis, Aeronautical and Astronautical Engineering Department., University of Illinois at Urbana-Champaign. (2000)

[3] American Society for Testing and Materials. Standard D5045-91a, Plane-strain fracture toughness and strain energy release rate of plastic materials. Annual Book of ASTM Standards, Philadelphia, ASTM (1991).

Appendix

A. Material contents

1. Epoxy matrix
   The epoxy was prepared using 100 parts EPON 828 epoxide and 12 parts diethylenetriamine (DETA) curing agent.
2. Epoxy matrix with 15% flexibilizer
   The composite was prepared by mixing 100 parts EPON 828 epoxide, 15 parts flexibilizer (Heloxy 71 modifier) and 10.9 parts diethylenetriamine (DETA) curing agent.
3. Epoxy matrix with 2% release agent
   The composite was prepared using 100 parts EPON 828 epoxide, 2 parts release agent (z-6070) and 12 parts DETA.
4. Silicon mold
   The silicon mold is made by mixing 10 parts silicon resin (RTV 630A) with the curing agent RTV 630B. The mold is cured for 24 hours at room temperature and for one hour at 40° C.

B. Complete data sets

Thickness to Diameter Ratio = 0.024 (Small)		
Type I	Result	Strain rate (in/min)
1	Pins pulled out	0.05
2	Cracked shell	0.03
3	Cracked shell	0.03
4	Cracked shell	0.03
5	Cracked shell	0.03
6	Cracked shell	0.03
Type II		
1	Cracked around the shell	0.03
2	Cracked around the shell	0.03
3	Cracked around the shell	0.03
4	Cracked around the shell	0.03
Type III		
1	Cracked around the shell	0.03
2	Cracked around the shell	0.03
3	Cracked around the shell	0.03

Thickness to Diameter Ratio = 0.050 (Medium)		
Type I	Result	Strain rate (in/min)
1	Cracked shell	0.03
2	Cracked shell	0.03
3	Cracked shell	0.03
Type II		
1	Cracked around the shell	0.03
2	Cracked around the shell	0.03
3	Cracked around the shell	0.03
4	Cracked around the shell	0.03
Type III		
1	Cracked around the shell	0.03
2	Cracked around the shell	0.03
3	Cracked around the shell	0.03

Thickness to Diameter Ratio = 0.100 (Large)		
Type I	Result	Strain rate (in/min)
1	Cracked shell	0.03
2	Cracked shell	0.03
3	Cracked shell	0.03
Type II		
1	Cracked around the shell	0.03
2	Cracked around the shell	0.03
Type III		
1	Cracked around the shell	0.03
2	Cracked around the shell	0.03
3	Cracked around the shell	0.03

C. Fracture Toughness

A compact tension specimen was mad for each Type of composite (Figure A). They were loaded in tension to determine the fracture toughness of the material. Fracture toughness can be determined using the following equation:

$$K_{1C} = \frac{Pf\left(\frac{a}{w}\right)}{B\sqrt{w}}$$

Where P is the load at which the specimen fractures, B is the specimen thickness and f is a function of a divided by w. If we say λ=a/w, then the function f(λ) is

$$f(\lambda)=\frac{(2+\lambda)}{(1-\lambda)^{3/2}}\left(0.866+4.64\lambda-13.32\lambda^2+14.72\lambda^3-5.6\lambda^4\right).$$

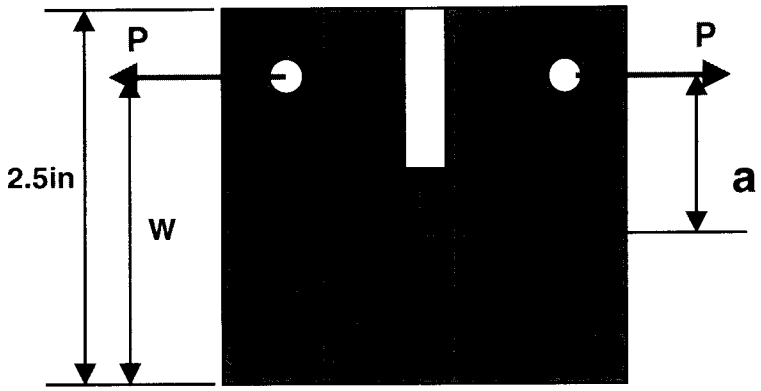


Figure A. Compact Tension Specimen.