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FULL PAPER

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A Self-Healing Poly(Dimethyl Siloxane) Elastomer**

By *Michael W. Keller*, *Scott R. White*, and *Nancy R. Sottos**

Self-healing functionality is imparted to a poly(dimethyl siloxane) (PDMS) elastomer. This new material is produced by the incorporation of a microencapsulated PDMS resin and a microencapsulated crosslinker into the PDMS matrix. A protocol based on the recovery of tear strength is introduced to assess the healing efficiency for these compliant polymers. While most PDMS elastomers possess some ability to re-mend through surface cohesion, the mechanism is generally insufficient to produce significant recovery of initial material strength under ambient conditions. Self-healing PDMS specimens, however, routinely recover between 70–100 % of the original tear strength. Moreover, the addition of microcapsules increases the tear strength of the PDMS. The effect of microcapsule concentration on healing efficiency is also investigated.

1. Introduction

Self-healing polymers and composites that incorporate microencapsulated healing agents exhibit high levels of healing efficiency under both static and dynamic loading conditions.[1–8] Most self-healing research has focused on the autonomic repair of brittle, thermosetting polymers[1–6] and high performance fiber-reinforced epoxy matrix composites.[7–10] These self-healing polymers have low strain-to-failure values, on the order of 2–5 %, and relatively high elastic moduli of 3–4 GPa. In this work, self-healing functionality is imparted to a poly(dimethyl siloxane) (PDMS) elastomer with low modulus and high strain-to-failure behavior.

Elastomers are used in a variety of applications including seals, bladders, and as the matrix for flexible composites, such as tires. While these materials can sustain large deflections with little or no permanent deformation, elastomers can fail through fracture and fatigue processes. These failure modes have been successfully addressed in thermosetting polymers using microcapsule based self-healing. Here we apply the microcapsule self-healing concept to an elastomeric matrix material.

The original self-healing system developed by White et al.[2] contained microencapsulated dicyclopentadiene (DCPD) monomer and a solid phase Grubbs' catalyst embedded in an epoxy matrix. Damage served as the triggering mechanism when an approaching crack ruptured the embedded microcapsules releasing the DCPD into the crack plane through capillary action. Ring-opening metathesis polymerization (ROMP) of the liberated DCPD was initiated by contact with the embedded catalyst, bonding the two crack faces together. The efficiency of crack healing was assessed by the ability of the material to recover fracture toughness (K_{1C}).[2] Healing efficiencies of over 90 % were reported for optimized concentrations of microcapsules and catalyst.[3] In addition to providing an efficient mechanism for self-healing, the presence of DCPD-filled microcapsules significantly increased the inherent fracture toughness of the epoxy resin.[1]

Cho et al. demonstrated self-healing of thermosetting epoxy vinyl esters using a different healing chemistry based on the tin catalyzed polycondensation of silanol functionalized poly(dimethyl siloxane) (PDMS).[4] In their work, a tin catalyst was encapsulated and the functionalized PDMS was phase separated in the matrix. Although lower healing efficiencies were obtained compared to the DCPD and Grubbs' system, this healing system was resistant to deactivation by air, water, or the vinyl ester matrix.

The phase separation healing system in Cho et al.[4] is based on the interaction of two liquid constituents to produce the healing response. This system differs from that of White et al.,[2] which was based on heterogeneous catalysis in which a fluid (the monomeric healing agent) interacts with a solid catalyst particle to initiate the healing reaction. Bond and co-workers[9,10] employ a two part healing chemistry for hollow-fiber

[*] Prof. N. R. Sottos
Department of Materials Science and Engineering
University of Illinois at Urbana-Champaign
1304 W. Green St., Urbana, IL 61801 (USA)
E-mail: n-sottos@uiuc.edu
Prof. N. R. Sottos, M. W. Keller, Prof. S. R. White
The Beckman Institute for Advanced Science and Technology
University of Illinois Urbana-Champaign
405 N. Mathews, Urbana, IL 61801 (USA)
M. W. Keller
Department of Mechanical Science and Engineering
University of Illinois at Urbana-Champaign
1206 W. Green St., Urbana, IL 61801 (USA)
Prof. S. R. White
Department of Aerospace Engineering
University of Illinois at Urbana-Champaign
104 South Wright Street, Urbana, Illinois 61801 USA

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based self-healing composites. The rupture of fluid filled fibers by an approaching crack releases an epoxy resin and hardener into the crack plane to produce healing. This system has the ability to regain a significant portion of the flexural strength of the composite after low speed impact.[10] Both the phase separated and hollow fiber systems have demonstrated that healing chemistry based on the interaction of two fluids can be effective.

We report the development and testing of a low modulus, high strain-to-failure self-healing elastomeric polymer. A stable healing chemistry is achieved by the microencapsulation in poly(urea-formaldehyde) (UF) of the constituent resin and initiator for PDMS in two separate microcapsules. The resin microcapsules contain high-molecular weight vinyl functionalized PDMS and platinum catalyst complexes. Initiator microcapsules contain a PDMS copolymer with active sites that will link to the vinyl functionalized resin via the action of the platinum catalyst. Both types of microcapsules are then embedded in an elastomeric PDMS matrix to produce a self-healing composite material. Damage triggering and healing events occur in an analogous way to the original self-healing epoxy described above. A propagating tear in the PDMS material intersects both resin and initiator microcapsules and ruptures them. The liberated healing fluids then wick onto the tear plane through capillary action and mix. A crosslinking reaction, the same reaction that polymerizes the matrix material, occurs and forms an adhesive polymer layer that rebonds the tear faces. This self-healing material system possesses the unique feature that the healed polymer in the crack plane is the same as the host matrix. A protocol based on the recovery of tear strength is adopted to assess the healing efficiency of the elastic PDMS.

2. Results and Discussion

2.1. Microcapsule Rupture in an Elastomeric Matrix

Microcapsule rupture is critical for self-healing. White et al. utilized an Eshlby-Mura equivalent inclusion model to numerically investigate how an approaching crack interacts with a microcapsule in a linear elastic matrix.[2] The analysis revealed that the crack is drawn to the more compliant capsule. In the current work, we investigate the complex capsule interaction with the nonlinear elastomeric PDMS matrix under tensile loading.

Figure 1 contains a series of images taken of a single microcapsule embedded in a PDMS matrix loaded in tension. The stretch (λ) of the bulk sample is indicated below each microcapsule image. The microcapsule deforms in tandem with the matrix until the bulk stretch reaches $\lambda = 1.50$. As the deformation increases beyond this point, the capsule shell wall begins to fail inside the matrix; this damage is indicated by the white circles in Figure 1. Concurrently, the capsule begins to increase in volume, a process which is similar to void growth. This growth is signaled by the formation of a cavity as the fluid contained in the microcapsule pulls away from the microcapsule wall, indicated by an arrow in Figure 1. Although UF is a brittle material with low strain-to-failure in bulk form, the large strain observed prior to failure in tension is consistent with capsule compression data previously reported.[13] The fluid filled, thin walled (approximately 200 nm thick) microcapsule can sustain significant deformation.

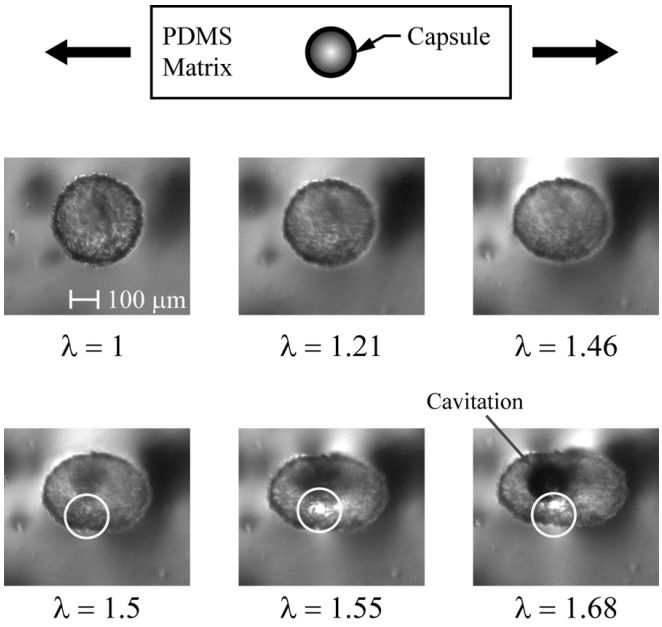

Figure 1. A series of images of a single microcapsule embedded in a PDMS matrix loaded in uniaxial, far-field tension. The schematic at the top of the figure indicates the loading direction.

While the capsules are robust in the highly elastic PDMS matrix, an approaching tear does rupture the capsules. Figure 2a shows scanning electron microscopy (SEM) images of ruptured microcapsules on a failure plane. The capsules in these images contained a volatile solvent rather than a healing fluid. By using capsules containing a solvent, the failure plane could be imaged in SEM without being masked by the healed polymer film or residual healing fluid. The inset images, Figure 2b and

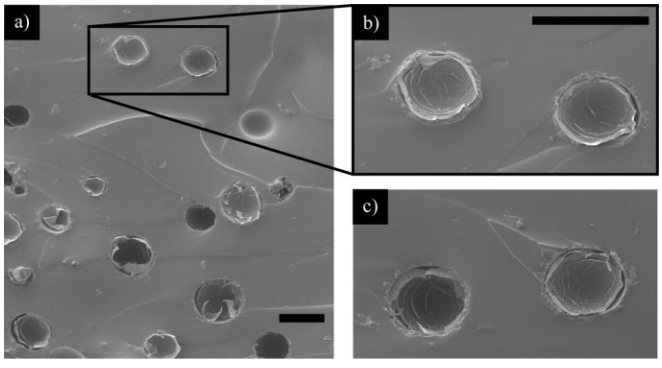

Figure 2. Scanning electron microscopy images of (a) ruptured microcapsules on a PDMS failure surface. Individual capsules highlighted in (b) were imaged on the opposite half of the failure surface in (c). Tear propagation was from right to left in all images. The scale bars represent 100 μm.

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c, are higher magnification micrographs of two ruptured capsules found on the failure plane. The mating facture surface (Fig. 2c) shows shell wall remnants located on the opposite tear surface corresponding to the same region of interest highlighted in Figure 2a, confirming that the capsules were cleaved by a propagating tear.

2.2. Microcapsule Effect on Polymer Properties

The effect of microcapsules on bulk PDMS materials properties, specifically on the tear strength T, was also investigated. The addition of a second, particulate phase is a common method of improving the crack growth resistance of PDMS.[14,15] The trouser tear test was adopted to assess the material performance. In Figure 3, tear strength data are plotted on a log-log scale as a function of increasing microcapsule concentration.

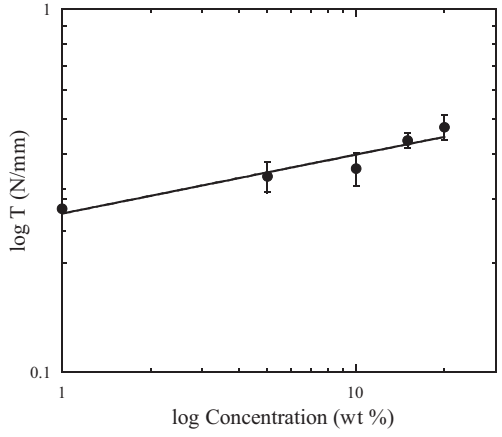

Figure 3. Log-log plot of tear strength against total microcapsule concentration. The line is a power law fit with an exponent of 0.16.

Microcapsule addition has a modest reinforcing effect on the tear strength. The tear energy for 20 wt % microcapsules increased about 25 % over the neat PDMS material. Most importantly, there was no degradation in the tear strength with the addition of capsules.

The toughening effects of the microcapsules are also evident from the morphology of the tear surface. The tear surfaces for a neat PDMS specimen and from a sample with 25 wt % microcapsules are compared in Figure 4. The overall surface features in the microcapsule filled specimen are rougher and the periodic cusps, present on most elastomer tear surfaces,[16] are disrupted. The microcapsule induced morphologies on the tear surface (e.g., tail structures) provide evidence of energy dissipation mechanisms such as crack pinning.

2.3. Evaluation of Self-Healing Performance

Autonomic healing of tear damage was evaluated for four sample types, listed in Table 1. A series of control experiments were carried out with sample types I, II, and III to elucidate the effects of the individual components and delivery on healing performance. Fully in-situ specimens, type IV, contained both initiator and resin microcapsules for the self-healing material.

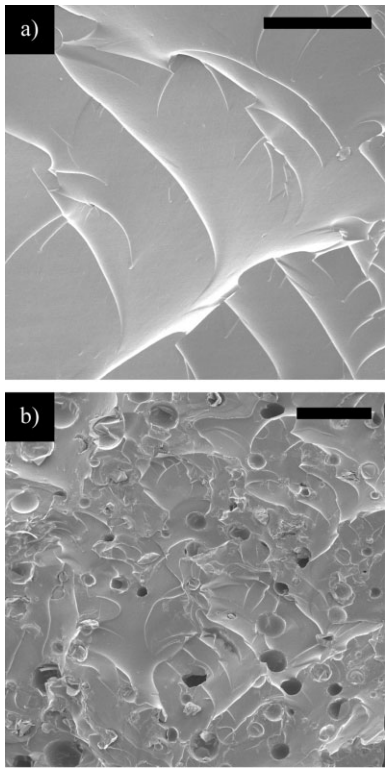

Figure 4. Comparison of tear surfaces for a neat (a) and microcapsule filled (25 wt %) sample (b). Tear propagation is from the bottom of the image upward. The scale bars represent 500 μm.

Table 1. Sample Types and Healing Performance.

Test	Initiator Capsule Concentration	Resin Capsule Concentration	Average Healing Efficiency
I. Neat PDMS	0%	0%	2 [±5]%
II. Reference	0%	0%	57 [±13]%
III. Self-Activated	5%	0%	84 [±24]%
IV. In-situ	5%	5–20%	70–120%

Representative load-displacement data for the virgin and healed tear tests of a fully in-situ specimen (type IV) are shown in Figure 5, where the solid line represents the virgin test and the dashed line represents the healed test. This particular sample contained 10 wt % resin and 5 wt % initiator microcapsules and exhibited 75 % healing efficiency. All samples exhibited unsteady tearing, indicated by the stick-slip behavior, as expected for filled elastomers.[17]

2.4. Control Specimens

The test results of the control specimens, types I, II, and III, are summarized in Table 1, where the numbers in the brackets indicate one standard deviation. Healing efficiencies presented

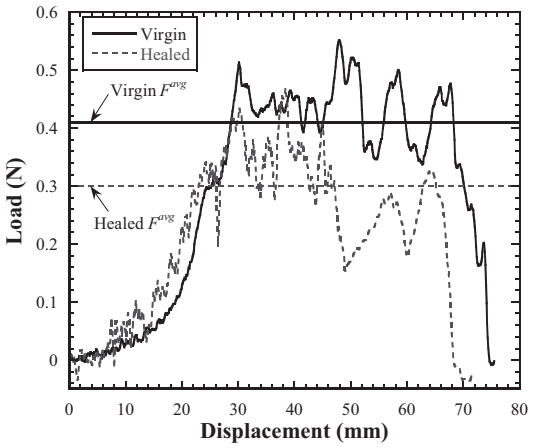

Figure 5. Representative load-displacement data for a virgin and healed test. The horizontal lines represent the average tearing force for a virgin and healed specimen. The healing efficiency for this test was 75 %.

in Table 1 are the average of six specimens. All control tests followed the same protocol as self-healing tests; the samples were tested, stored between microscope slides, and given a 48 hour room temperature healing period.

Type I control specimens (neat PDMS) contained no healing components. These specimens were torn and allowed to "heal" to investigate the contribution of surface cohesion and diffusive bonding to any self-healing response. Only a very small percentage of the virgin tear strength was recovered in these control tests. Type II, neat PDMS reference specimens, were tear tested and then healed manually by injecting 10 μL of premixed PDMS resin and initiator onto the tear surface. On average these specimens recovered 57 % of the virgin tear strength. A third set of self-activated controls (type III) contained 5 wt % initiator microcapsules, but were manually healed by injecting 10 μL of just the PDMS resin only onto the crack plane. The self-activated samples showed increased healing response over that of the reference samples by about 30 %. One source of this increase is likely microcapsule induced roughening of the fracture surface leading to enhanced adhesive bonding.

2.5. Testing of Fully in-situ Specimens

Fully in-situ (type IV) tear tests were conducted in which the concentration of each microcapsule type was varied independently. The concentration of resin capsules was varied from 0 to 20 wt % while holding the initiator capsule concentration constant at 5 wt %. Results of these tests are summarized in Figure 6 where each column represents the average healing efficiency of at least 6 samples. Healing efficiency increases rapidly with increasing resin capsule concentration and by 5 wt % essentially full recovery of the original tear strength is achieved. Initiator capsule concentration was varied from 0 to 7 wt %, while holding the resin capsule concentration constant at 10 wt %. As shown in Figure 7, higher healing efficiencies are achieved with increasing initiator concentration.

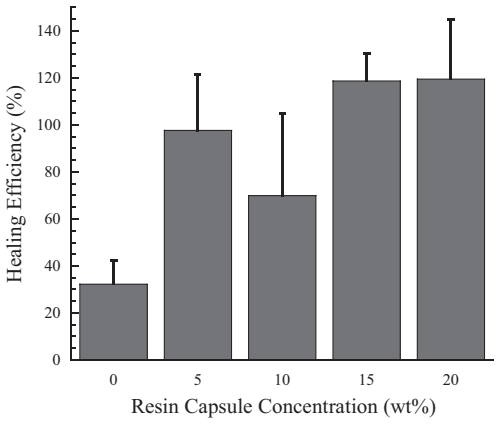

Figure 6. Effect of resin microcapsule concentration on healing efficiency. Initiator microcapsule concentration was 5 wt % in all samples.

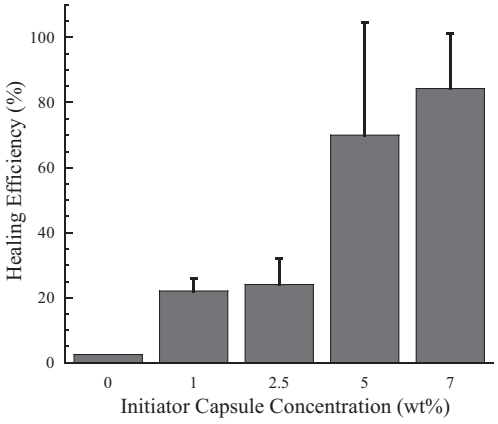

Figure 7. Effect of initiator concentration on healing efficiency. Resin microcapsule concentration was 10 % in all samples.

The healing efficiencies in Figures 6 and 7 that are greater than 100 % are the result of the healed tear deviating from the virgin tear path (Fig. 8). When a tear deviation occurs, the tear may continue to propagate through virgin, undamaged material as occurred in the sample shown in Figure 8, or the tear may eventually return to the virgin (healed) tear path. Each of these possible propagation paths can influence the healing efficiency. If the healing is so complete that the tear does not return to the original tear path, then the healing efficiency can be 100 % or greater as shown in Figures 6 and 7. There is some variabili-

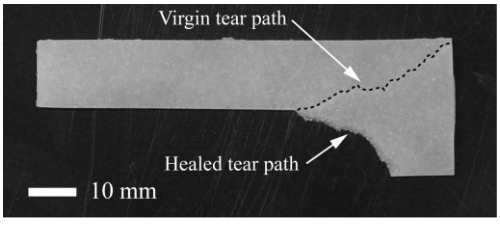

Figure 8. Sample showing a deviated tear. The virgin tear path is highlighted by the dashed line.

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ty in the frequency that a tear path deviation occurs. In Figure 6 the reduction of healing efficiencies between the 5 wt % and 10 wt % was a product of the variability in the occurrence of tear path deviations. The 5 wt % resin group had more tear path deviations than the 10 wt % resin group. The tear path deviation may also be a product of the unique healing chemistry used in this material. Since the healing and matrix chemistry are the same, the close match in material properties of the matrix and bonding layer may allow the healed tear path to deviate into the surrounding virgin matrix rather than following the bond line as in previous self-healing materials.[1–4]

When only initiator capsules were used a measurable healing response was obtained, as shown in Figure 6. This response indicates that the initiator released from the ruptured capsules reacted with excess vinyl functionality in the PDMS matrix. While the crosslinking reaction (Fig. 11) requires active platinum catalyst to occur, the final disposition of the platinum catalyst in a cured PDMS matrix is a topic of some current debate.[18,19] It is possible that active catalyst may still be present in the matrix. This active catalyst, in conjunction with the released initiator, may initiate further crosslinking and produce the observed healing. Specimens containing only resin microcapsules did not produce a healing response beyond that of neat PDMS surface cohesion, see Figure 7 and Table 1, implying that the initiator is mostly consumed during matrix cure.

2.6. Scanning Electron Microscopy of Healed Tear Surfaces

Tear surfaces were imaged using SEM to determine the effectiveness of the microcapsule based healing system in providing adhesive film coverage. The presence of an adhesive bonding layer is difficult to discern when imaging perpendicular to the tear plane (Fig. 4b). A highly structured tear surface, coupled with a lack of contrast between the healing polymer and matrix polymer, both the same material, obscures adhesive film on the tear plane. However when a specimen with a tear deviation is viewed parallel to the tear surface, the adhesive film is more pronounced. Arrows in Figure 9 indicate the adhesive film produced by the rupture of microcapsules and subsequent healing. Figure 9 also reveals that imperfect registrationof the tear surfaces during healing does not preclude a quality healing response. The specimen imaged in Figure 9 had a healing efficiency of 115 %. Adhesive film produced by healing is also apparent in the precut region in front of the tear plane (Fig. 10). The film highlighted in Figure 10 was produced by capsules that were ruptured when the precut was made with a razor blade. Adhesive film in Figure 10 covers 40 % of the area below the start of the tear region (dashed line).

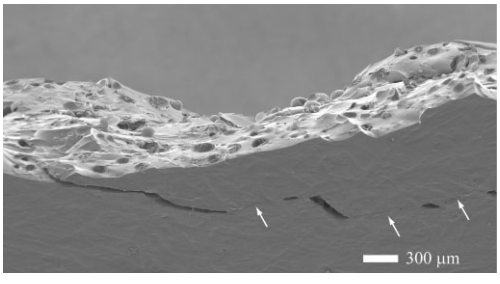

Figure 9. SEM images of a tear surface viewed parallel to the tear plane. The arrows in the image indicate adhesive bonding via self-healing.

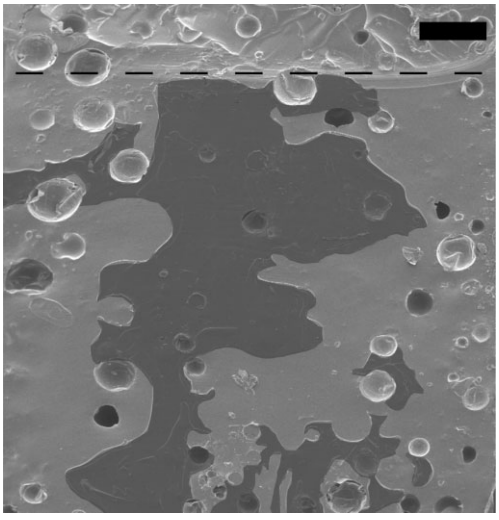

Figure 10. SEM image of the precut zone with the adhesive film generated by ruptured capsules highlighted. The dashed line indicates the beginning of tear zone. The scale bar represents 300 µm.

3. Conclusions

A self-healing elastomer has been developed through the incorporation of a microencapsulated healing chemistry. Two capsule systems are utilized, one containing vinyl terminated poly(dimethyl siloxane) (PDMS) resin and platinum catalyst complexes. The second capsule system contains a PDMS copolymer that crosslinks to the functional PDMS resin via the platinum catalyst. The embedded microcapsules were robust and endured matrix deformations up to 50 % bulk stretch without apparent damage. While the capsules survived a relatively large tensile elastic deformation, the crack propagation during a tear test ruptured the capsules. Tear testing also demonstrated the capability of the self-healing elastomer to routinely recover at least 70 % of the original tear properties. This material is also capable of producing healing efficiencies of 100 % or greater. The addition of microcapsules not only provided an efficient autonomic healing functionality, but also improved the tear resistance of the material. Scanning electron microscopy studies of the tear surfaces indicated that the presence of microcapsules induced a morphological change. The tear surfaces of microcapsule filled specimens were rougher and showed evidence of energy adsorbing mechanisms, such as tails emanating from the trailing edges of ruptured microcapsules.

4. Experimental

Preparation of Self-Healing Samples: A commercially available addition cure PDMS manufactured by Dow Corning under the trade name Sylgard 184™ (Ellsworth Adhesives) is chosen for the elastomeric matrix. This room temperature curable silicone elastomer is a two part system supplied as a high molecular weight vinyl functionalized PDMS resin containing a Pt catalyst and a liquid initiator material containing a hydrosiloxane copolymer. The addition cure PDMS material utilizes a platinum catalyzed hydrosilylation reaction to crosslink the vinyl terminated resin, as shown in Figure 11. In this crosslinking reaction, the vinyl terminated PDMS resin (b) is linked to a functional copolymer, the "initiator," (a) through the action of the platinum catalyst to produce the crosslinked PDMS network (c).

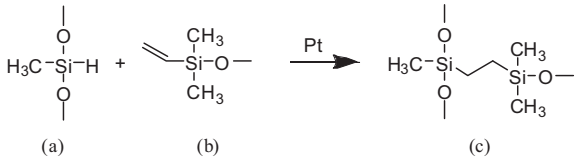

Figure 11. Platinum catalyzed hydrosilylation of vinyl terminated PDMS where (a) is the initiator material, (b) is the vinyl functionalized resin, and (c) is resulting crosslinked network.

The same initiator and resin as used in the PDMS matrix material were encapsulated separately in a poly(urea-formaldehyde) (UF) shell following the in-situ polymerization process described by Brown et al. [11]. Initiator was encapsulated as received, but the resin was diluted with 20 wt % heptane to reduce viscosity. The heptane is mobile and will diffuse out of the microcapsule after a few days at room temperature. Both capsule types had average diameters of 180 μm. A self-healing PDMS sample was prepared by mixing the matrix material in the recommended ratio of 1 part initiator to 10 parts resin and then waiting 4 h before the addition and mixing of the microcapsules.

This precure period was required to increase the viscosity of the matrix material to prevent floating of the buoyant initiator microcapsules. After precure, the resin and initiator capsules were added to the matrix material in the desired concentrations, mechanically mixed, and then poured into an open aluminum mold. The test specimens were cured for 48 h at room temperature and then removed from the mold and prepared for testing.

Tear Testing: Rectangular specimens 25 mm wide, 75 mm long, and between 1 to 2 mm thick were manufactured as described above. A 50 mm precut along the axis of the sample was made with a razor blade just prior to testing (Fig. 12a). Specimens were loaded in tension along the scissored arms of the specimen (Fig. 12c), until a tear propagated through the unslit region (Fig. 12b). The two arms of the specimen were then placed back in contact and secured between two microscope slides. Storing specimens in this fashion helped to ensure good contact between the two tear faces during healing. Specimens were allowed to heal for 48 h at room temperature before subsequent retesting. The precut was then reopened to the original crack length prior to retesting.

Healing efficiency is defined as the recovery of tear strength in the healed specimen compared to the initial virgin test,

$$\eta \equiv \frac{T_{healed}}{T_{virgin}} \tag{1}$$

where T is the tear strength in the virgin and healed states. Tear strength is calculated using the well-known analysis of Rivlin and Thomas for this tear sample [12]

$$T = \frac{2F}{t} \tag{2}$$

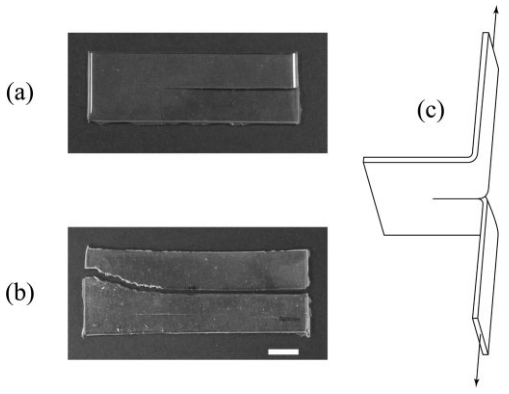

Figure 12. PDMS tear specimens and testing. (a) A virgin specimen prepared for testing and (b) after tear testing. (c) Schematic representation of a tear specimen during a test. The scale bar represents 10 mm.

where F is the force applied to each specimen arm, and t is the thickness of the sample. The force required to propagate the tear is averaged as described in ASTM D624 to give an average tear force for each specimen F_{avg}. Since the sample thickness remains unchanged between the virgin and healed tests the healing efficiency η reduces to the ratio of tearing force for the virgin and healed tests,

$$\eta = \frac{F^{avg}_{healed}}{F^{avg}_{virgin}} \tag{3}$$

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