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Abstract

The autonomic healing ability of an epoxy adhesive containing micro-encapsulated dicyclopentadiene (DCPD) was evaluated. The epoxy resin used was Epon 828 cured with either Versamid 140 or diethylenetriamine (DETA). Variables included total weight percent of micro-capsules (MCs) and catalyst, as well as the catalyst to DCPD ratio. The degree of healing was determined by the fracture toughness before and after 'healing' using double-cantilever beam analysis. It was found that the degree of self-healing was most directly related to the contact area (i.e. crack width) during healing. Temperature also played a significant role. Observed differences between the results of this study and those in literature are discussed.

Contents

Figures

Tables

1. Introduction

In general, healing in polymeric resins can be defined as a means of arresting crack growth and restoring some degree of the virgin material's fracture toughness via the healing process. The original concepts of healing in polymeric systems focused on crack repair and were based largely on solvo-thermal processes.[1] The notion of autonomic repair was advanced primarily by the efforts of Dry et al.[2,3,4] who demonstrated the concept in polymeric resins.[5] Microcapsules (MCs) containing chemicals that would arrest crack growth were encapsulated in the polymeric matrix. The advancing crack would rupture microcapsules in its path and subsequently limit further crack propagation. Recently White et al.[6] demonstrated autonomic healing by incorporating a microencapsulated monomeric liquid into the polymeric matrix. A catalyst was also included in the matrix so that any monomers released due to crack-induced rupture of the microcapsules were crosslinked, thereby arresting crack growth. A single tapered cantilever beam sample was shown to recover 75% of virgin toughness in this system. Similar studies have been performed on composite materials, by incorporating liquid-filled fibers.[7,8]

In this paper, we investigate the autonomic healing of epoxy resins using double cantilever beam analysis. Similar to White's work,[6] microencapsulated DCPD and Grubbs' catalyst were incorporated into the polymeric matrix. The total loading of MCs and catalyst was varied as well as the MC to catalyst ratio.

2. Experimental

Micro-capsule preparation:

All reagents were obtained from Aldrich, Acros, or Fisher Scientific and used as received. Urea-formaldehyde MCs containing liquid DCPD were prepared as follows. 3.50 grams urea, 0.25 gram resorcinol, and 0.25 gram ammonium chloride were dissolved with stirring in 75 milliliter (ml) of water. 50 ml of 5 weight percent (wt%) ethylene maleic anhydride copolymer solution was added and the mixture adjusted to pH of 3.50 using 10 wt% sodium hydroxide solution. The solution was transferred to a 600 ml beaker, and the temperature raised to 50 °C. While stirring at 800 RPM using a 2-blade propeller, 30 ml of DCPD was added. After stirring for 20 minutes, 9.46 g of 37 wt% formaldehyde (stabilized with 10-15 wt% methanol) was added dropwise over 10 minutes. The solution was stirred at temperature for 2 hours after which it was diluted with 200 ml of de-ionized water, the mixing rate reduced to 500 RPM, and then allowed to stir for an additional 4 hours. After cooling, the solution was diluted approximately 1:1 with ethanol and then filtered. The filtrate was washed repeatedly with ethanol followed by a chloroform rinse and then allowed to air dry.

DCB sample preparation:

DCB samples were prepared by placing two aluminum beams (123 mm long x 12.5 mm wide x 5 mm thick) shimmed 4 millimeters apart, into a silicone mold and clamped in place. The internal faces of the beams had been sandblasted, and subsequently ultrasonically cleaned with water and ethanol, to ensure cohesive failure. A hole on either end of the exposed, top beam was used to fill the interstitial volume with epoxy.

Autonomic healing epoxy:

In a typical preparation, the EPON 828 was heated to 71 °C and outgassed under vacuum for 5 minutes. Following outgassing the EPON 828 was reheated to 71 °C. The MCs were sieved through a 250 micron screen to remove clusters prior to use. The MCs and Grubbs catalyst, Bis(tricyclohexylphosphine)benzylidine ruthenium(IV) dichloride (Strem), were thoroughly mixed into the curing agent which was then combined with the warm EPON 828 in the ratio of 100 parts 828 to 52 parts Versamid 140 or 12 parts DETA. The mixture was poured into a syringe and injected into the DCB assembly. The Versamid samples were cured at room temperature for 48 hours, and the DETA samples were cured at room temperature for 24 hours followed by a post-cure heating at 40 °C for 24 hours.

DCB Analysis:

DCB analyses were performed on an Instron 8511 load frame. The samples were saw-cut to enable a knife blade to be inserted between the beams and a sharp crack initiated by impacting the knife blade. The samples were loaded at a ram speed of 0.05 in/min until the crack propagated (until a drop in load was observed) after which the load was released. Multiple measurements were made on each sample by continuing this process until the crack had been propagated through approximately 3/4 of the sample length. The point where each crack stopped was marked on the sample, and this length in conjunction with the load required to drive the crack were used to calculate the toughness. Reported toughness values are the averages of multiple measurements, typically 3-5, excluding the first measurement as it corresponds to the load required to propagate the artificial pre-crack.

Healing was accomplished by releasing the load and allowing the samples to stand at room temperature for at least overnight. Where indicated, samples were clamped prior to standing and/or held at 50 °C, also typically overnight. Determination of the fracture toughness of healed samples was made assuming the same crack lengths from the initial analysis. Reported percent recovery is the post-healing toughness divided by the virgin sample toughness.

3. Results & Discussion

DCPD was successfully microencapsulated in a urea-formaldehyde shell. The size of the microcapsules obtained from this synthesis ranged from 30 to 280 microns, with an average diameter of 97 microns and a median diameter of 90 microns. The particle size distribution as determined from measuring the diameters of 150 MCs from an SEM image is shown in Figure 1. While this may not be statistically significant, it does provide a reference with regard to the effects of particle size and distribution on sample toughness. As very few broken MCs were observed, it is believed that the rinsing and sieving process largely eliminated weak or defective MCs, so that the remaining materials were robust with respect to further processing.

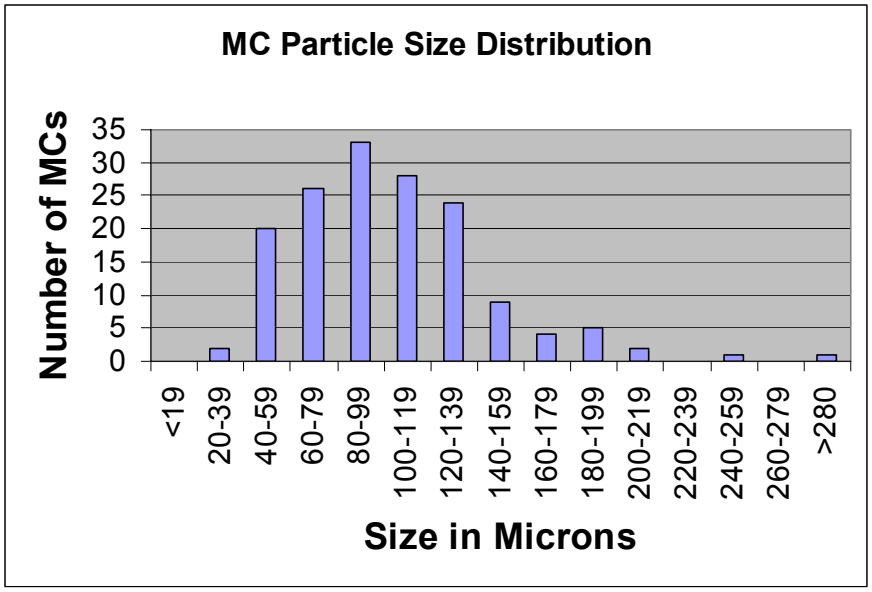


Figure 1. Particle size distribution of DCPD filled microcapsules.

The Grubbs' catalyst dissolved readily in DETA, but appeared to partially re-precipitate when mixed with the EPON resin. The catalyst did not, however, dissolve in the Versamid and a great deal of mixing was required to get it to disperse. Furthermore, the EPON/Versamid system, after adding the catalyst and MCs, was extremely viscous even after reheating to 71 °C. This made it very difficult to fabricate the DCB samples. Because of the combination of poor catalyst dispersion and difficulty in sample preparation, only a limited number of EPON/Versamid samples were prepared.

The DCB fracture toughness (G_c) results of the EPON/Versamid and the EPON/DETA samples are given in Table 1 and Table 2**,** respectively.

Table 1. EPON/Versamid samples.

Experiment #	Description	G_c (J/m^2)
1	Neat epoxy	170
2	Neat epoxy	198
3	Epoxy + 3.75 wt% catalyst	246
4	Epoxy + 3.75 wt% catalyst + 10.00 wt% MCs	253

Table 2. EPON/DETA samples.

Experiment #	Description	G_c (J/m^2)
5	Neat epoxy	183
6	Neat epoxy	202
7	Epoxy + 3.75 wt% catalyst	319
8	Epoxy + 0.625 wt% catalyst + 2.50 wt% MCs	302
9	Epoxy + 1.25 wt% catalyst + 5.00 wt% MCs	359
10	Epoxy + 3.75 wt% catalyst + 15.00 wt% MCs	342

The addition of the catalyst and the MCs increased G_c relative to the neat samples, contrary to observed behavior with hollow microsphere/epoxy composites[9] where fracture toughness did not increase with filler content despite the presence of a crack pinning mechanism. Alternately, with solid silica sphere/epoxy composites,[10] crack pinning and crack tip blunting were observed to increase the fracture toughness with particles ranging from 6 to 30 microns. In this study, there was no indication of either crack pinning or crack tip blunting. An optical micrograph of typical crack propagation through MCs is presented in Figure 2, which is perhaps indicative of good particle-matrix adhesion. Although high particle-matrix adhesion is known to increase the efficiency of crack pinning, the fact that the interior of our particles is more compliant than that of typical filler particles may account for the lack of crack pinning observed, as pointed out by White et al.[6] Since the addition of catalyst without microspheres also increased G_c relative to samples without catalyst, the MCs may not play a role in the observed toughening.

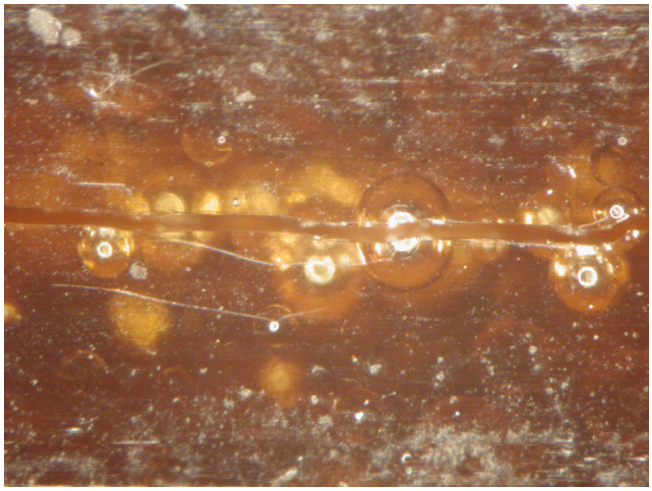


Figure 2. Optical micrograph of typical crack propagation through micro-capsules.

Healing experiments were performed on all the samples in Table 1 and Table 2. Only one, Experiment 4, displayed any recovery of toughness; in this case 44 J/m^2 and hence a 17% recovery. The load-displacement curve from this sample is presented in Figure 3. An examination via optical microscope of the samples that did not heal revealed that the DCPD had re-crystallized on the interior faces of the crack as well as along the sides of the crack (see Figure 4). The melting point of DCPD is nominally 33 °C, which is above the temperature in the laboratory where these experiments were performed. Presumably the stress field in the proximity of the crack tip imparts sufficient energy to convert the monomer to the liquid phase during shell rupture.

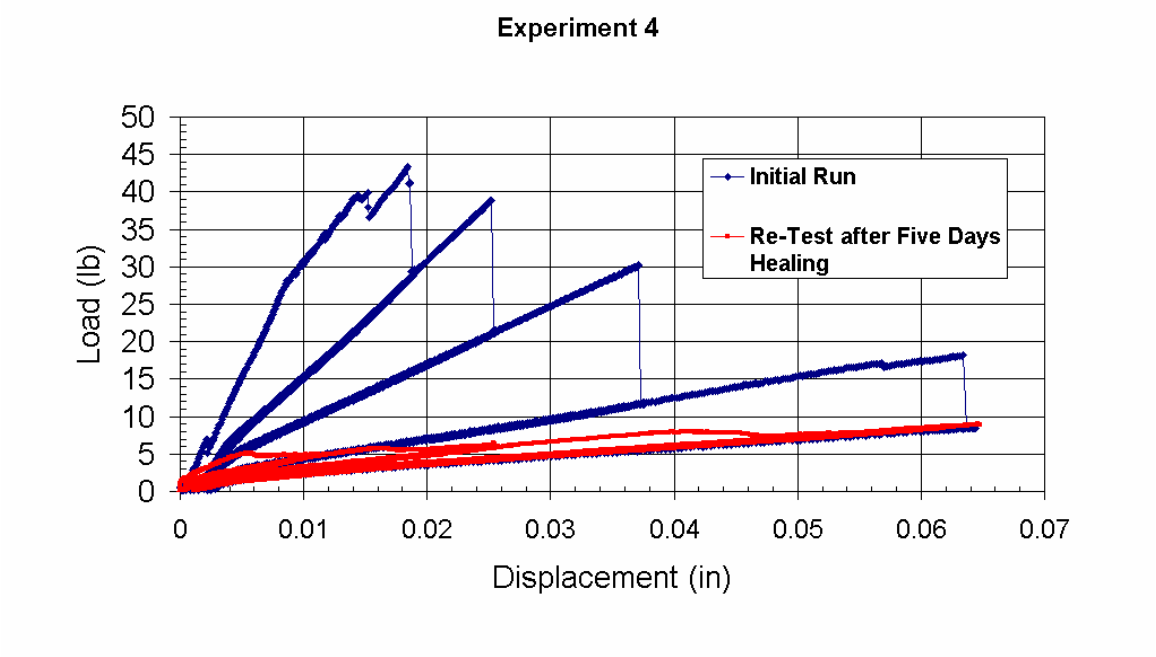


Figure 3. DCB load-displacement curve from Experiment 4.

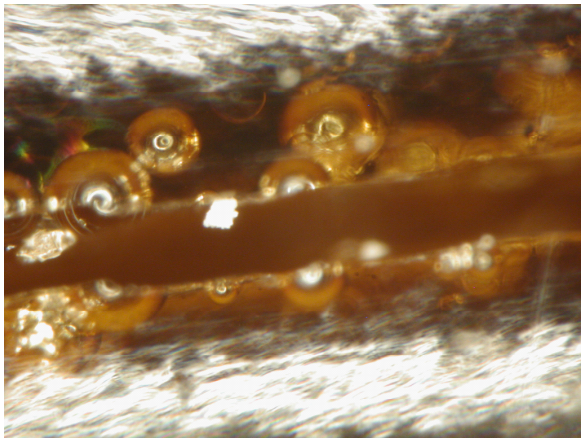
(a)  (b) 

Figure 4. DCB specimen that did not heal, showing that DCBD re-crystallized (a) on the interior faces of the crack and (b) along the sides of the crack.

In an effort to understand these results a series of experiments were performed in which healing was attempted by various combinations of clamping the DCB beams together and holding overnight at 50 °C. Results are given in Table 3. In all cases, examination via optical microscopy revealed similar amounts of MC breakage due to crack propagation.

Table 3. Recovery of DCB samples with clamping and/or elevated temperature.

Experiment #	Description	G_c (J/m^2) Pre/Post healing	% Recovery
11	Neat epoxy Clamped tightly with C-clamp / 50 °C	202 / 0	0
12	Sample from Experiment 10 Clamped tightly with C-clamp / 50 °C	342 / 5	1.5
13	Epoxy + 2.50 wt% catalyst + 10.00 wt% MCs Clamped tightly with C-clamp / 50 °C	270 / 33	12.2
14	Epoxy + 4.20 wt% catalyst + 8.30 wt% MCs Clamped lightly with C-clamp / 50 °C	274 / 0	0
15	Epoxy + 2.50 wt% catalyst + 10.00 wt% MCs No clamping / 50 °C	328 / 0	0

Since the neat epoxy of Experiment 11 did not heal, the healing observed in Experiment 12 must be due to the DCPD, indicating that the re-crystallized DCPD was not (at least, fully) polymerized. The sample from Experiment 10, which had previously been allowed to 'heal' at room temperature (and did not) did however heal due to the subsequently applied temperature and pressure. This, combined with the results of Experiments 13-15, indicate that the lack of healing was due at least in part to insufficient contact between the fracture surfaces rather than solely deactivated/insufficient catalyst, insufficient DCPD, etc.

A possible contributing factor is that the DCPD polymerization at room temperature was limited; the additional energy available at 50 °C allowed frozen, monomeric DCPD to become available for polymerization, as well as providing activation energy to further the degree of cure of the polymerized DCPD.[11] Furthermore, it has been observed that in addition to energy, bulk polymerization of DCPD occurs as a function of catalyst content,[11,12] yet the increased catalyst concentration of Experiment 14 did not yield any toughness recovery.

Hence, the observed behavior is likely due to the methodology of the DCB testing, wherein the crack was propagated over (up to) one half hour prior to allowing the sample to heal. During this time the DCPD flowed over the fracture surface, where it only partially polymerized due to re-freezing and/or insufficient activation energy. When the fracture surfaces are firmly placed back in contact and adequate energy is provided the DCPD cures further and the sample recovers some degree of toughness. This conclusion is also supported by examination of the load-displacement curves between the two samples that displayed the greatest degree of toughness recovery, Experiments 4 (see Figure 3) and 13 (see Figure 5), un-clamped and clamped, respectively. The clamped sample displays 'healing' of the crack all the way to the point of initiation, whereas the unclamped sample has only 'healed' a portion of the crack length. It is not understood, however, why the clamped sample failed catastrophically after reaching a critical load, while the unclamped sample truly seems to have re-bonded, exhibiting crack propagation similar to the neat sample. Though it may also be, at least in part, attributed to differences in the time-scale of DCB measurement. Regardless, the fact that the testing methodology is likely the determining factor in the test results suggests that this technology is also limited in its application; degree of 'healing' is largely a function of the mode and time-scale of crack propagation.

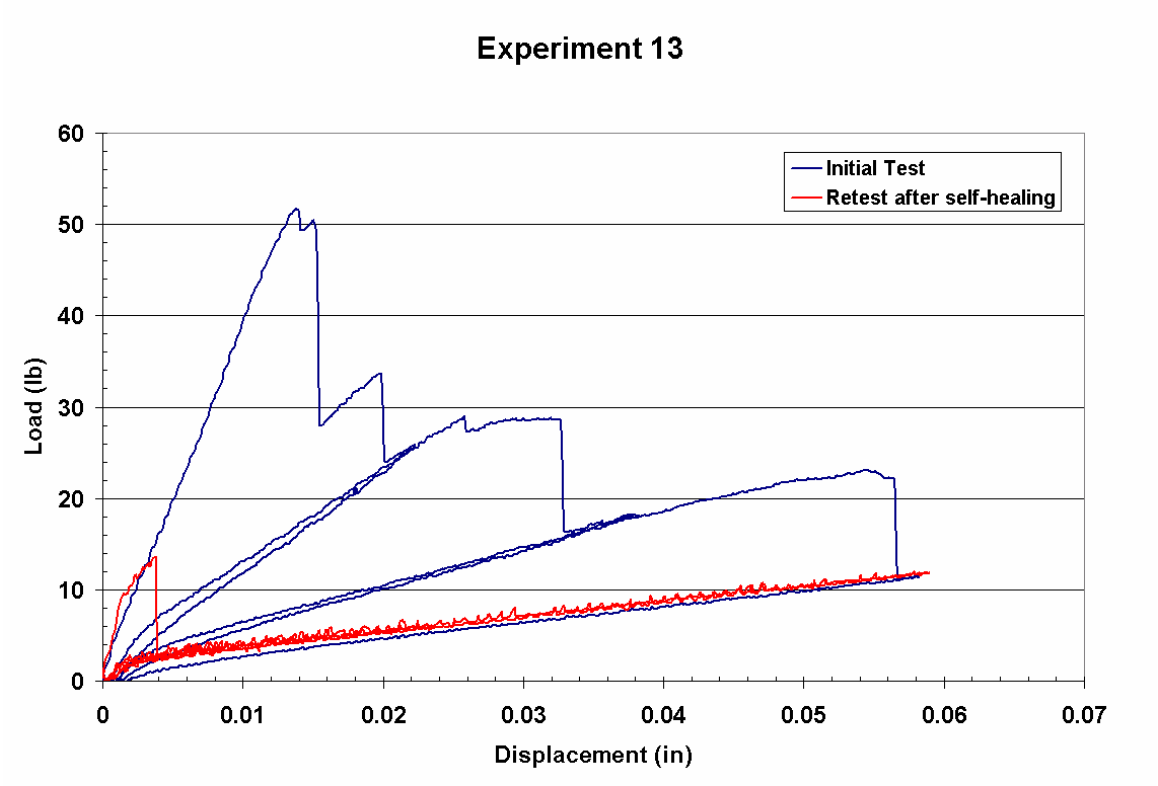


Figure 5. DCB load-displacement curve of Experiment 13.

4. Conclusion

Autonomic healing of epoxy resins can be accomplished by the incorporation of micro-encapsulated crosslinking agents. The ability of a system to 'self-heal' is limited by the mode and time-scale of crack propagation, which also affects the ability of DCPD to act as an effective 'healing' agent.

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