AUTONOMIC HEALING OF POLYMERS AND COMPOSITES

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Summary Inspired by biological systems in which damage triggers an autonomic healing response, structural polymers and polymer matrix composites have been recently developed that possess the ability to *self-heal.* Self-healing is accomplished by incorporating a microencapsulated healing agent and a catalytic chemical trigger within a polymer matrix. When the material is damaged, the microcapsules rupture and release the healing agent into the damaged region through capillary action. As the healing agent contacts the catalyst, polymerization is initiated and the damage is repaired. One promising healing chemistry based on the ring-opening-metathesis-polymerization (ROMP) of dicyclopentadiene and Grubbs' catalyst has yielded static fracture recovery in excess of 90% and greatly extended fatigue life. New healing chemistries and alternate healing approaches are explored with utility in a variety of structural polymer and polymer composite applications.

SELF-HEALING CONCEPT AND MATERIALS

The self-healing concept is shown in Figure 1. A microencapsulated healing agent is embedded along with a catalyst into a polymer matrix. When damage occurs in the polymer a crack propagates through the matrix rupturing the microcapsules in the crack path. The ruptured microcapsules release the healing agent, which is then drawn into the crack through capillary action. Once the healing agent within the crack plane comes into contact with the embedded catalyst, a chemical reaction is triggered and polymerization of the healing agent occurs. The crack faces are then permanently bonded and the strong singularity at the crack tip is relieved.

Fig. 1. Self-healing polymer. A microencapsulated healing agent (tagged with red dye) is released into the fracture plane behind the propagating crack front that dissects the image from left to right. The capsules in front of the crack (top of image) remain unbroken. (E. Brown, Univ. of Illinois, 2001).

A self-healing epoxy was recently developed at the University of Illinois [1-3] based on the ring-opening-metathesis-polymerization (ROMP) of dicyclopentadiene (DCPD) healing agent with a transition metal (Grubbs') catalyst [4]. DCPD was encapsulated in microcapsules with 0.2-micron thick shell made of urea formaldehyde. A small volume fraction of microcapsules was dispersed in an epoxy resin along with Grubbs' catalyst. The embedded microcapsules were shown to rupture in the presence of a crack and release the DCPD monomer into the crack plane. Contact with the embedded Grubbs' catalyst initiated polymerization of the DCPD and rebonded the crack plane. This self-healing epoxy is able to recover over 90% of its virgin fracture toughness [5].

In addition to providing an efficient mechanism for self-healing, the presence of DCPD-filled UF microcapsules also increases the inherent fracture toughness of the epoxy. Under monotonic loading the average maximum toughness with microcapsules is 127% greater than neat epoxy. Fracture of the neat epoxy is brittle, exhibiting a mirror fracture surface. The addition of microcapsules produces a transition of the fracture plane morphology to hackle markings. The increased toughening associated with fluid-filled microcapsules is attributed to increased hackle marking and subsurface microcracking not observed for solid particle fillers [6]. While fracture toughness is an important property for evaluating self-healing performance, fatigue loading is particularly problematic in brittle polymers. The current investigation seeks to apply recent breakthroughs in self-healing technology to repair fatigue cracks in a polymer autonomically.

STATIC FRACTURE RECOVERY AND HEALING KINETICS

The efficiency of crack healing in static fracture is defined based on the ability of a healed sample to recover fracture toughness (K_{Ic}). Fracture toughness is measured for the virgin sample and then the specimen is allowed to heal. The test is repeated after an appropriate period of time for healing and the healed fracture toughness is obtained. The healing efficiency (η) is expressed simply as a ratio of the healed and virgin fracture toghnesses,

$$\eta = \frac{K_{Ic_{healed}}}{K_{Ic_{virgin}}} \quad . \qquad (1)$$

Fracture test results for self-healing epoxy based on ROMP of DCPD are shown in Fig. 2. For these tests, 2.5 wt% of Grubbs' catalyst was combined with EPON 828 epoxy resin (diglycidyl ether of bisphenol-A) and DETA (diethyl triamine) curing agent. To this matrix was added 5 wt% microcapsules containing DCPD monomer. The dashed horizontal line in Fig. 2 shows the average peak load of epoxy control samples with no self-healing capability (no microcapsules). Comparison of the peak load for the control with that of the self-healing epoxy reveals that the addition of the microcapsules significantly toughens the epoxy. The self-healed samples actually recover more than 100% of the critical load for virgin epoxy with no microcapsules.

The time period over which healing takes place depends on a number of factors including environmental temperature, catalyst concentration, dissolution rate, etc. In Fig. 3 the development of static fracture healing efficiency is plotted versus healing time for self-healing epoxy with 2.5%wt Grubbs' catalyst and 10%wt microcapsules. There is an initial dwell period of about 25 minutes during which no appreciable healing can be measured. Thereafter, the healing efficiency increases rapidly before stabilizing at about 55% for this particular formulation. The initial dwell period is believed to be associated with transport of the healing agent to the fracture plane and gelation of the material in the crack. Once gelled, the healing agent begins to support load across the crack plane and a measurable healing efficiency can be identified. Thereafter, the network structure of the healing agent develops exponentially with time as is reflected in data.

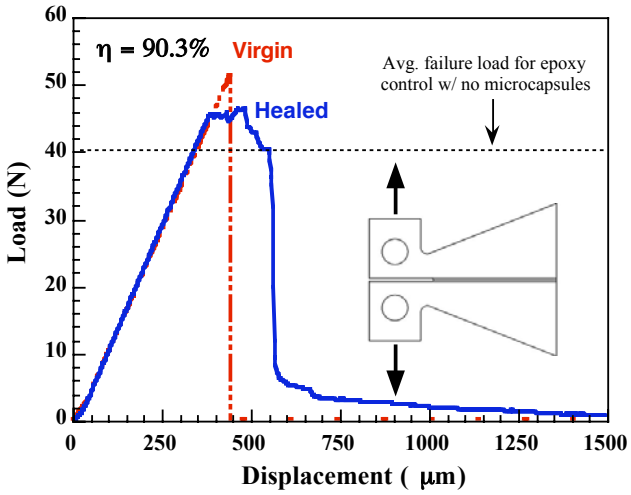

Fig. 2. Load-displacement data for a virgin and healed epoxy fracture toughness specimen [5].

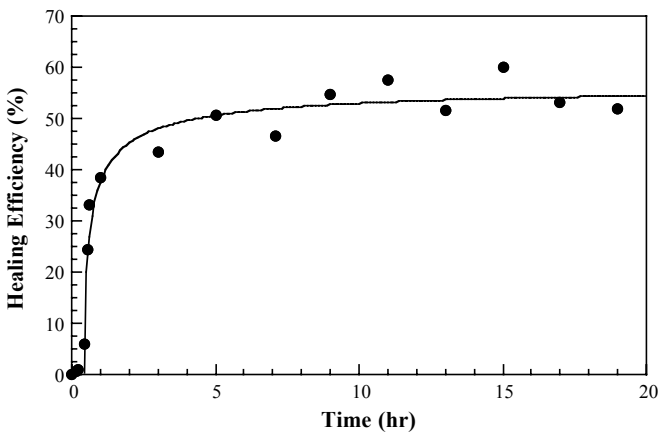

Fig. 3. Development of healing efficiency for a fracture sample with 10 wt % microcapsules and 2.5 wt%. catalyst.

HEALING OF FATIGUE CRACKS

While fracture toughness is an important property for evaluating the performance of self-healing polymers, fatigue loading is the primary cause of structural failures. Preliminary investigations of fatigue crack propagation in self-healing epoxy indicate that significant extension in fatigue life can be obtained. The data in Fig. 4 show the fatigue response for a self-healing epoxy specimen (20%wt microcapsules, 2.5%wt catalyst) in comparison to a control specimen devoid of the catalyst phase. Fatigue crack growth is arrested for about 4 x 105 cycles in the self-healing specimen before it begins to accelerate new the end of the specimen. Overall the fatigue life is extended by a factor of three in this specimen [7].

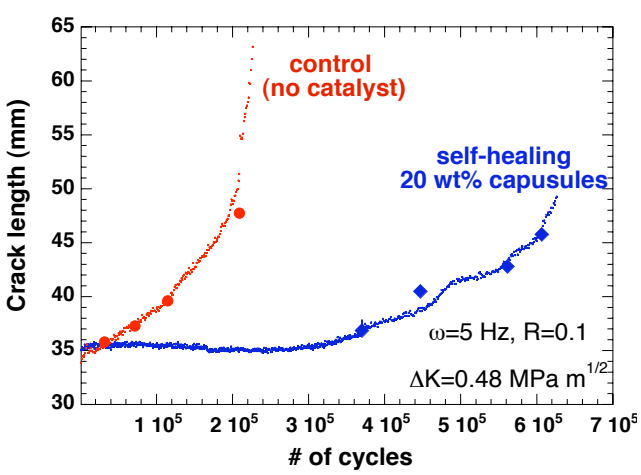

Fig. 4. Crack tip position versus number of cycles to failure for self-healing sample compared to control.

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