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## **Polydimethylsiloxane-Based Self-Healing Materials\*\***

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Self-healing represents a new paradigm for active and responsive materials.<sup>[1]</sup> As first demonstrated by White et al..<sup>[2]</sup> and subsequently in additional publications, [3-6] polymer composites can be engineered to chemically self-heal. However, the chemistry of previous systems possesses inherent shortcomings due to the potential side reactions with the polymer matrix and air. Here we present a new, chemically stable selfhealing materials system based on the tin-catalyzed polycondensation of phase-separated droplets containing hydroxy end-functionalized polydimethylsiloxane (HOPDMS) and polydiethoxysiloxane (PDES). The catalyst, di-n-butyltin dilaurate (DBTL), is contained within polyurethane microcapsules embedded in a vinyl ester matrix and is released when the capsules are broken by mechanical damage. This system possesses a number of important advantages over the previous self-healing methodology, including a) the healing chemistry remains stable in humid or wet environments, b) the chemistry is stable to an elevated temperature (>100 °C), enabling healing in higher-temperature thermoset systems, c) the components are widely available and comparatively low in cost, and d) the concept of phase separation of the healing agent greatly simplifies processing, as the healing agent can now be simply mixed into the polymer matrix.

Although inspired by our previous self-healing methodology, [2] in which the monomeric healing agent was encapsulated and the catalyst was dispersed as particulate throughout an

epoxy matrix, this new system contains a number of distinct differences. The siloxane-based healing agent mixture is *not* encapsulated, rather it is phase-separated in the matrix while the catalyst is encapsulated. The low solubility of siloxane-based polymers enables the HOPDMS-PDES mixture and catalyst-containing microcapsules to be directly blended with the vinyl ester prepolymer, forming a distribution of stable phase-separated droplets and protected catalyst. No reactions take place between the HOPDMS and PDES prior to exposure to the catalyst. When the matrix cracks, a mixture of catalyst released from microcapsules and the healing agent wets the entire crack plane. Addition of an adhesion promoter to the matrix optimizes wetting and bonding of the crack faces. After the healing agent mixture cures, the crack is self-healed (Figs. 1a–c).

The polycondensation of HOPDMS with PDES occurs rap-

The polycondensation of HOPDMS with PDES occurs rapidly at room temperature in the presence of amine and carboxylic acid organotin catalysts.<sup>[7]</sup> Because side reactions are limited, organotin catalysts are highly desirable for curing PDMS-based systems, even in open air.<sup>[7,8]</sup> This stability to

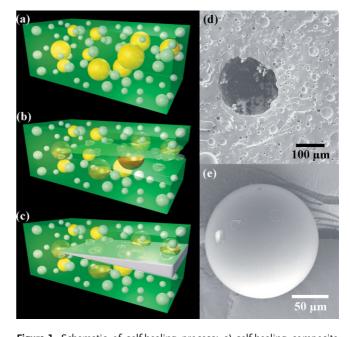


Figure 1. Schematic of self-healing process: a) self-healing composite consisting of microencapsulated catalyst (yellow) and phase-separated healing-agent droplets (white) dispersed in a matrix (green); b) crack propagating into the matrix releasing catalyst and healing agent into the crack plane; c) a crack healed by polymerized PDMS (crack width exaggerated). Scanning electron microscopy (SEM) images of d) the fracture surface, showing an empty microcapsule and voids left by the phase-separated healing agent, and e) a representative microcapsule showing its smooth, uniform surface.

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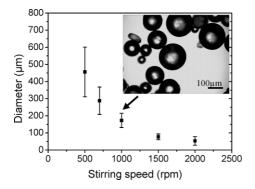
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water and air is of critical importance for practical realization of self-healing and was a prime motivation for this catalyst system.

Prior to testing of the self-healing composite system, several processing variables were investigated. First, elemental analysis was used to confirm the immiscibility of the healing agent in the prepolymer. The vinyl ester prepolymer was vigorously mixed with HOPDMS, PDES, and adhesion promoter, and subsequently placed in a centrifuge to separate the prepolymer and dissolved adhesion promoter from the healing agents. The silicon content of the resulting prepolymer phase was the same as for a control sample consisting of a mixture of prepolymer and adhesion promoter.

The size distribution of the phase-separated droplets in the vinyl ester matrix was determined through scanning electron microscopy (SEM) and optical microscopy. The diameter of the phase-separated droplets after mechanical stirring at 600 rpm ranged from 1 to 20  $\mu m$  (Fig. 1d). The droplet diameter was not a strong function of stirring rate and did not change significantly when samples were stirred between 100 and 2000 rpm.

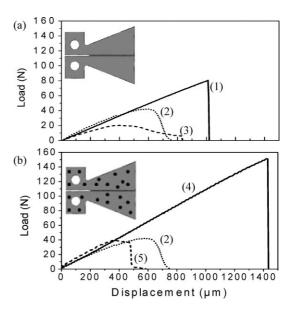
The microcapsules containing the catalyst were formed (prior to embedding in the matrix) through interfacial polymerization [9,10] and consisted of a polyurethane shell surrounding a DBTL–chlorobenzene mixture. The average diameter of these microcapsules was a strong function of stirring rate during the interfacial polymerization process and ranged from 50 to 450  $\mu$ m (Figs. 1e and 2).



**Figure 2.** Diameter of catalyst-containing microcapsules as a function of stirring speed. Inset: optical microscopy image of microcapsules formed at 1000 rpm.

In ex situ tests, mechanically fractured microcapsules effectively cured the PDMS healing agent, while intact microcapsules were not catalytically active, indicating little or no catalyst was present on the exterior of the microcapsules.

The performance of the self-healing composite was assessed via a fracture-test protocol established previously by White and co-workers. This test utilizes a tapered double cantilever beam (TDCB) sample (inset, Fig. 3), which ensures controlled crack growth along the centerline of the brittle specimen and provides a crack-length-independent measure



**Figure 3.** Load–displacement curves of TDCB samples: a) first-fracture sample (1, solid), and injection-healed sample with (2, dotted) and without (3, dashed) adhesion promoter; b) first fracture of sample containing 4 wt% adhesion promoter, 12 wt% PDMS, and 3.6 wt% microcapsules (4, solid) and after self-healing (5, dashed). The injection-healed sample (2, dotted) with adhesion promoter is shown again for comparison.

of fracture toughness for both virgin and healed materials. [11,12] The healing efficiency  $(\eta)$  is calculated as the ratio of the critical fracture loads for the healed and virgin samples.

In situ samples consisting of phase-separated PDMS healing agent and microencapsulated DBTL catalyst dispersed in the cured vinyl ester matrix initially showed low, but nonzero healing after mechanical damage. Post-fracture analysis of these specimens revealed that low  $\eta$  was as a result of poor inherent adhesion of PDMS to the matrix. Failure of these healed specimens was always adhesive between the PDMS healing agent and the vinyl ester matrix surface.

The adhesion promoter, methylacryloxypropyl triethoxysilane, was added to the matrix to improve bond strength. A control experiment was introduced to study the effect of the adhesion promoter on fracture behavior (adhesive versus cohesive failure) without the variables associated with the delivery of phase-separated healing agent and microencapsulated catalyst. Control samples were healed by injecting a solution of premixed healing agent and catalyst into the crack plane of fully fractured samples. As shown in Figure 3a, the addition of adhesion promoter more than doubled the  $\eta$  value of the control samples.

Experiments were then performed on the in situ system with adhesion promoter added. Fracture-test results show that the self-healing system and control samples attain similar values of  $\eta$  (Fig. 3b), indicating that self-healing was equally effective as manually mixing and injecting the PDMS, and bonding the crack closed. A range of healing agent, microcapsule, and adhesion promoter concentrations was investigated (Table 1), with the maximum  $\eta$  value for the in situ healed

**Table 1.** Average maximum load of self-healed vinyl ester. One standard deviation in square brackets.

PDMS	Composition [a]  Adhesion	Microcapsule	Fracture load [N]	Healing efficiency [%]
[wt %]	promoter [wt %]	[wt %]		
8	4	2.4	14 [3]	9 [2]
		5.0	9 [5]	6 [3]
12	2	3.6	14 [2]	9 [1]
	4	3.6	37 [7]	24 [4]
	8	3.6	28 [5]	19 [4]
15	4	2.4	21 [1]	14 [1]
		4.5	37 [3]	24 [3]

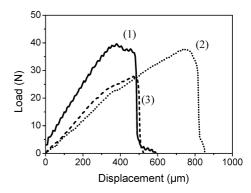
[a] The remainder is vinyl ester.

samples achieved for samples containing 12 wt % PDMS, 4 wt % adhesion promoter, and 3.6 wt % microcapsules.

Also apparent from Figure 3, the critical load to fracture of the virgin, in situ self-healing system (curve 4) is significantly greater than that of the neat vinyl ester matrix used for the control experiments (curve 1). Thus, the inclusion of a phaseseparated healing agent and catalyst microcapsules increases the toughness of the vinyl ester matrix. For the concentrations corresponding to the results in Figure 3b, the increase in mode I fracture toughness is approximately 88 % based on the critical load at fracture. In addition, while both the virgin in situ and control tests exhibit characteristically linear (brittle) fracture behavior, the fracture of healed samples is a nonlinear deformation and failure process, fortuitously absorbing additional energy in the fracture process. The increased fracture toughness of the matrix does, however, lead to lower effective  $\eta$ . Relative to the original vinyl ester matrix, a  $\eta$  value as high as 46 % is achieved.

Although the  $\eta$  values reported in Table 1 are lower than those obtained by White et al. for a self-healing epoxy based on Grubbs catalyst and an encapsulated dicyclopentadiene healing agent, this new PDMS-based materials system still holds great promise. Low  $\eta$  values are to be expected given that the PDMS has significantly lower stiffness and fracture toughness than the matrix material. In many applications, however, simply filling or sealing the crack from harsh environments is as important as recovering full fracture strength in the test protocol. For example, the PDMS-based healing system has potential for healing surface cracks or scratches in protective coatings used in corrosive environments.

Healing under real-world conditions, for example, in the presence of water, is considerably more complex than in the laboratory frame. The effect of water on self-healing was examined by a simple experiment in which a TDCB sample was fractured, immersed in water prior to bringing the two sides together, and then healed under water. This sample was compared to samples healed in air under high (>90 %) and low (10 %) relative humidity (RH). The fracture load of the sample healed under water decreased only  $\sim 25$  % with respect to the other samples (Fig. 4), even though the system has not yet been optimized for healing under water.



**Figure 4.** Load–displacement curves of TDCB samples containing 4 wt% adhesion promoter, 12 wt% PDMS, and 3.6 wt% microcapsules healed in air at low RH (1, solid), in air at high RH (2, dotted), and immersed in water (3, dashed).

Self-healing has the potential to extend the lifetime and increase the reliability of thermosetting polymers used in a wide variety of applications ranging from microelectronics to aerospace. The materials system presented in this paper greatly extends the capability of self-healing polymers by introducing a new, environmentally stable healing chemistry and demonstrating the concept of phase-separating healing agents in a structural polymer matrix. Phase separation of the healing agent is an approach that may be applicable to a broad class of new healing chemistries for structural polymers, and stability to water and air significantly increases the probability that self-healing could be extended to coatings and thin films in harsh environments.

## Experimental

Microcapsule Synthesis: The urethane prepolymer was synthesized through the reaction of toluene 2,4-diisocyanate (TDI, Aldrich, 22.0 g, melting point, mp = 19.5-21.5 °C) and 1,4-butanediol (5.0 g) in cyclohexanone (142 g, boiling point, bp<sub>760</sub>=155.6 °C) at 80 °C for 24 h. The solution of TDI and cyclohexanone was first mixed and allowed to react under mechanical stirring in a round-bottomed flask. 1,4-butanediol was then added at 5 mLmin<sup>-1</sup> using a syringe pump while stirring. To avoid formation of a gel during microencapsulation, the molar ratio of TDI to 1,4-butandediol was kept below 2.3. The cyclohexanone was evaporated under vacuum at 100 °C. The synthesized urethane prepolymer had excess isocyanate functional groups, which could be reacted to form a higher-molecular-weight polymer through the use of a chain extender. The amount of chain extender added was determined by titration of the isocyanate functional group in urethane prepolymer following ASTM D2572-97. To form the tincatalyst-containing urethane microcapsules, the urethane prepolymer (3.0 g) and DBTL (Gelest, 1 g) were dissolved in 32 g chlorobenzene and added to 28.8 g of a water solution containing 15 wt % gum arabic (Aldrich, suspending agent). After the mixture was stirred for 30 min at 70 °C, 30 wt % (relative to the urethane prepolymer) of ethylene glycol (chain extender) was added into the solution at 5 mL min<sup>-1</sup>. Spherical microcapsules containing dissolved DBTL in chlorobenzene with smooth surfaces were obtained after 2 h at 70 °C with mechanical stirring at 1000 rpm.

Vinyl Ester Matrix Polymerization and TDCB Sample Formation: The specific self-healing polymer composite described in this paper consisted of phase-separated liquid droplets of the PDMS-based heal-

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ing agent and DBTL-catalyst-containing microcapsules dispersed in a mixture of vinyl ester (DOW DERAKANE 510A-40) and adhesion promoter. The vinyl ester was cured using benzoylperoxide (BPO) and dimethylaniline (DMA) as the initiator and activator, respectively. 1 wt % BPO was dissolved in the prepolymer. After the BPO was completely dissolved, the mixture of HOPDMS and PDES was added into the prepolymer with mechanical stirring, followed by degassing under vacuum. The microcapsules containing DBTL were then mixed with the degassed solution and 0.1 wt % DMA, followed by a final degassing. This mixture was poured into a closed silicone rubber mold and cured for 24 h at room temperature. The sample was then cured at 50 °C for another 24 h.

Fracture Testing and Healing Efficiency: After preparation of TDCB specimens, a sharp pre-crack was created by gently tapping a razor blade into the molded starter notch in the samples. All fracture specimens were tested under displacement control, using pin loading and a 5  $\mu$ m s<sup>-1</sup> displacement rate. Samples were tested to failure, measuring compliance and peak load. Samples were unloaded, allowing the crack faces to come back into contact, and healed in this state for 24 h at 50 °C. Using the protocol established by White and co-workers [2,3], healing efficiency ( $\eta$ ) was calculated as

$$\eta = \frac{P_{\text{C}_{\text{bested}}}}{P_{\text{C}_{\text{virsin}}}} \tag{1}$$

where  $P_{c_{\text{brealted}}}$  is the critical fracture load of the healed specimen and  $P_{c_{\text{trigin}}}$  is the critical fracture load of the virgin specimen. The healing efficiency and standard deviation were calculated from a minimum of five fracture tests (Table 1).

Healing under Water: The preparation and first fracture of TDCB samples tested under humid and wet states were performed by the same methods as for the dry state. A set of fractured TDCB samples were immersed into a water bath for  $\sim 30 \, \mathrm{s}$  and reassembled in air without drying the samples. The reassembled samples were submerged back into the water bath, which was then placed into an oven

for 24 h at 50 °C. Another set of fractured TDCB samples were reattached in air and separately healed in the same oven for 24 h at 50 °C to determine the effect of healing under high humidity. The healed specimens were tested to failure following the standard procedure.

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