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Room-Temperature Polydimethylsiloxane-Based Self-Healing Polymers

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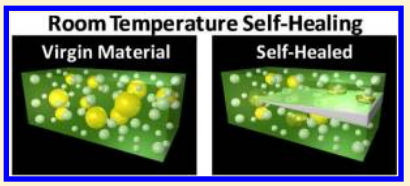
ABSTRACT: Polymers that respond in a productive fashion to their environment are under active development as they offer significant advantages over traditional materials. For example, polymers with the ability to self-heal and recover a significant fraction of their initial properties after being subjected to a damage event are of significant interest. Here we study the effect of healing agent viscosity and catalyst activity on self-healing at and near room temperature. The viscosity of the PDMS healing agent was varied from 14 to 40 000 cP, and the tin-based catalysts di-*n*-butyltin dilaurate, dimethyl-dineodacanoate tin, di-n-butyl bis(2-ethylenehexanoate), tin II oleate, and tetrakis(acetoxydibutyl tinoxy)silane were studied. Both vinyl ester and epoxy matrices were investigated. By optimizing the viscosity of the PDMS healing agent and the catalytic activity, as well as selection of the appropriate adhesion promoter, a PDMS-based self-healing system which healed at room temperature was obtained.



KEYWORDS: *self-healing, PDMS, epoxy, phase separation, room temperature, viscosity, catalytic activity, tin catalyst, microcapsules*

INTRODUCTION

Unlike conventional synthetic polymers, living organisms can self-repair damage without external input at or near room temperature. Self-healing synthetic materials which replicate some of the healing functionalities of living systems, and thus offer the potential to extend material lifetimes and increase material reliability for a variety of applications, are now being developed. In the majority of these cases, self-healing of mechanically generated cracks has been demonstrated;[1−21] however, materials which evolve in a productive fashion prior to failure are now even being investigated.[22] The approach of White et al., in which encapsulated monomeric healing agents are released by a damage event, and then cured by a dispersed catalyst has proven particularly effective.[1−6] Recently we designed a new environmentally stable self-healing system based on polydimethylsiloxane (PDMS) chemistry and phase-separated (rather than encapsulated) healing agents in polymer matrices.[10] From a processing standpoint, the use of phase separation rather than encapsulation of healing agents presents a number of advantages; however, such an approach requires the PDMS prepolymer to be chemically compatible with the matrix, and thus we also explored systems in which the PDMS prepolymer was encapsulated.[11]

In our prior work, effective self-healing was only observed after heating to 50 °C,[10] and thus, a more reactive prepolymer-catalyst system is needed for room-temperature self-healing. A popular room temperature PDMS curing chemistry is platinum-catalyzed hydrosilylation;[23] however, this approach is generally not appropriate for self-healing because many chemicals found in common thermosets inhibit the Pt catalyzed cure. Here we report self-healing at room temperature through the use of highly active organotin catalysts and PDMS healing agents with optimized viscosities. It is interesting to note that the viscosity of most PDMS-based polymers is only weakly dependent on temperature.[24]

EXPERIMENTAL SECTION

Catalyst Containing Microcapsules. The urethane prepolymer was synthesized via a reaction between 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_{760} = 155.6 °C) at 80 °C for 24 h. The solution containing TDI and cyclohexanone was mixed and allowed to react with mechanical stirring in a round-bottomed flask. 1,4-Butanediol was then added at 5 mL/min using a syringe pump while stirring. To avoid formation of a gel during microencapsulation, the molar ratio of TDI to 1,4-butanediol was kept below 2.3. The cyclohexanone was evaporated under vacuum at 100 °C. The synthesized urethane prepolymer contained excess isocyanate functional groups, which could react to form a higher-molecular-weight polymer through the use of a chain extender. The quantity of chain extender added was determined by titration of the isocyanate functional group in the urethane prepolymer following ASTM D2572-97. To form the tin catalyst-containing urethane microcapsules, the urethane prepolymer (3.0 g) and 1 g of tin catalyst dissolved in 32 g

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chlorobenzene was added to 28.8 g of a water solution containing 15 wt % gum arabic (Aldrich, suspending agent). The tin catalysts studied were di-*n*-butyltin dilaurate (DBTL), dimethyl-dineodacanoate tin (DMDN-Sn), di-n-butyl bis(2-ethylenehexanoate) (DBBE-Sn), and tin II oleate, all obtained from Gelest, and tetrakis(acetoxydibutyl tinoxy)silane (TKAS). The TKAS synthesis is outlined in the following, and TKAS was dissolved at 2 wt % in chlorobenzene rather than the 3 wt % of the other catalysts. After the catalyst containing mixture was mechanically stirred at 1000 rpm for 30 min at 70 °C, 30 wt % (relative to the urethane prepolymer) ethylene glycol (chain extender) was added to the solution at a rate of 5 mL/min with stirring (same rate). Spherical microcapsules with smooth surfaces containing the tin catalyst dissolved in chlorobenzene were obtained after 2 h at 70 °C.

Synthesis of TKAS Catalyst. A 0.1 mol portion of di-n-butyltin diacetate and 0.025 mol of tetraethylsilicate were mixed in a round-bottom flask. The mixture was heated to 150 °C while stirring under anhydrous conditions. The reaction byproduct, ethyl acetate, was distilled off at atmospheric pressure. The ethyl acetate started to condense at 130 °C and was significantly removed by distillation after 15 min at 150 °C. The solution was cooled in an ice bath, and the purified TKAS was harvested by filtration. The TKAS final product formed wax-like spherulites that were soluble in solvents, including petroleum ether, cyclohexane, ethyl acetate, dichloroethane, carbon tetrachloride, acetone, and chlorobenzene. A 1 g portion of the crude TKAS was dissolved in 10 mL of chlorobenzene with stirring at 80 °C. The solution was cooled in an ice bath and filtered using a sintered glass filter, capturing the purified TKAS.

PDMS Healing Agent-Containing Microcapsule Synthesis. PDMS-containing urea-formaldehyde microcapsules were formed via interfacial polymerization following the method of White et al.[1] The various hydroxyl end-functionalized polydimethylsiloxane (HOPDMS) and polydiethoxysiloxane (PDES) compounds used to make the healing agent were obtained from Gelest. The physical properties of these compounds, including viscosity, were taken from the Gelest data sheets. Viscosity data was obtained at room temperature. The following HOPDMS compounds were studied: DMS-S27, DMS-S32, DMS-S35, DMS-S42, and DMS-S45. The PDES was PSI-021. A PDMS healing agent formed using the lower molecular weight S27 can be directly encapsulated by urea-formaldehyde microencapsulation, but high molecular weight PDMS samples (formed using S32, S35, S42, and S45) were diluted to 20 wt % concentration with n-heptane before encapsulation. Urea (5.0 g), followed by resorcinol (0.5 g) and ammonium chloride (0.5 g), were dissolved in water (200 mL) in a 600 mL beaker. A 2.5 wt % solution of ethylene maleic anhydride copolymer (50 mL) was added to the reaction mixture, and the pH of the reaction mixture was adjusted to 3.5. The reaction mixture was agitated at 700 rpm, and to the stirred solution was added 60 mL of a mixture of HOPDMS (58 mL) (or diluted HOPDMS) and PDES (2 mL) achieving an average droplet size of 120 μm. A 37% formaldehyde (12.67g) solution was added to the agitated emulsion, and the temperature was raised to 55 °C and maintained for 4 h. After 4 h, the reaction mixture was cooled to room temperature, and the microcapsules were separated.

Self-Healing Polymer Based on Phase Separated PDMS. One class of self-healing polymer composites examined in this study consisted of 12 wt % phase-separated liquid droplets of the PDMS-based healing agent, 3.6 wt % catalyst-containing microcapsules, and 4 wt % adhesion promoter, methylacryloxy propyl triethoxy silane (MAPTS, $C_{13}H_{26}O_5Si$) dispersed in a vinyl ester (DOW Derakane 510A-40). The HOPDMS and PDES were mixed in a ratio of 29:1. The following Gelest HOPDMS compounds were studied: DMS-S12, DMS-S15, DMS-S27, DMS-S32, DMS-S35, DMS-S42, and DMS-S45. The vinyl ester was cured using benzoylperoxide (BPO) and dimethylaniline (DMA) as the initiator and activator, respectively. A 1 wt % BPO sample was dissolved in the prepolymer. After the BPO was completely dissolved, the mixture of HOPDMS and PDES was added to the prepolymer with mechanical stirring, followed by degassing under vacuum. The microcapsules containing a catalyst were then mixed with the degassed solution and 0.1 wt % DMA, followed by a final degassing step. This mixture was poured into a closed silicone rubber mold and cured for 24 h at room temperature (20 °C). The sample was then cured at 50 °C for another 24 h.

Self-Healing Polymer Based on Microencapsulated PDMS. The other class of self-healing polymer composite in this study consisted of the microencapsulated PDMS healing agent and catalyst containing microcapsules dispersed in a mixture of epoxy (EPON 828, Shell Chemical Inc.) and adhesion promoter, (3-trimethoxysilylpropyl)dimethylene triamine (TESDMTA, $C_{10}H_{27}N_3O_3Si$). Epoxy matrix was mixed with 12 phr (parts per hundred resin) diethylenetriamine (DETA, Shell Chemical Inc.) using mechanical stirring, followed by degassing under vacuum. The PDMS containing microcapsules and catalyst containing microcapsules were then mixed with the degassed solution with mechanical stirring, followed by final degassing step. Unless otherwise specified, samples contained 3 wt % catalyst-containing microcapsules and 14 wt % PDMS-containing microcapsules. This mixture was poured into a closed silicone rubber mold and cured for 24 h at room temperature (20 °C) and at 30 °C for another 24 h.

Fracture Testing and Healing Efficiency. After preparation of TDCB (tapered double cantilever beam) specimens described previously,[1] a sharp precrack 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 μm/s displacement rate. Samples were tested to failure, and the compliance and peak load were measured. Samples were unloaded, allowing the crack faces to come back into contact, and were healed in this state for 24 h with heating at 50 °C, 30 °C, or room temperature. The healing data was calculated from the average of a minimum of five fracture tests, each on a different sample.

RESULTS AND DISCUSSION

Phase Separated Healing Agent System. Introduction of a phase-separated healing agent into a polymer matrix is a very simple approach for healing agent introduction, but it requires a high degree of immiscibility between the healing agent and the matrix material. To verify immiscibility, the vinyl ester prepolymer was vigorously mixed with HOPDMS, PDES, and an adhesion promoter, and then centrifuged to separate the phase-separated healing agents from the prepolymer and dissolved adhesion promoter (Table 1). By elemental analysis,

Table 1. Elemental Analysis of Matrix (A), Healing Agent Mixture (B), and Matrix after Removal of Phase Separated Components (C)

	A [Derakane 510A-40, MAPTS]		B [HOPDMS + PDES]		C [A + B after removal of phase separated material]	
element	trial 1[a]	trial 2[b]	trial 1[a]	trial 2[b]	trial 1[a]	trial 2[b]
C	62.44	62.83	32.38	32.21	60.21	59.28
H	5.52	5.60	8.10	8.19	5.51	5.33
N	0.44	0.27	0.19	0.42	0.30	0.19
Si	ND	0.138	23.92	24.85	ND	0.166

[a]Elemental analysis based on Si[28]. [b]Elemental analysis based on Si[29].

the silicon content of the resulting prepolymer after centrifugal removal of the phase separated healing agents (Table 1, column C) was nearly identical to a control sample consisting of a mixture of the prepolymer and the adhesion promoter which had not been exposed to the healing agent (Table 1, column A), indicating nearly complete immiscibility. Table 1, column B, gives the elemental analysis of the PDMS healing agent mixture. The use of phase-separated reagents that induce healing upon structural damage provides a number of advantages, in particular its simplicity; however, if the polymer matrix had

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contained a significant volume fraction of dissolved healing agent, the mechanical properties of the matrix may have been impacted.

a. Effect of Healing Agent Viscosity on Low Temperature Healing. Lower viscosity epoxy resins tend to cure at lower temperatures than high viscosity resins,[23] and the same may be true for the PDMS system. We thus investigated lower viscosity healing agents as a route to low temperature self-healing. In the bulk, the PDMS polycondensation chemistry proceeds at room temperature; however, self-healing was not significantly observed at room temperature, perhaps due to incomplete mixing of the PDMS prepolymer and catalyst (DBTL) in the crack plane (Table 2). The average maximum loads from monotonic fracture testing of control and *in situ* TDCB samples containing a PDMS healing agent (S45) with a viscosity of 50 000 cP are summarized in Table 2. The control sample consisted of an epoxy vinyl ester matrix with a 4 wt % adhesion promoter, whereas the *in situ* sample was composed of matrix, 4 wt % adhesion promoter, 12 wt % phase separated PDMS, and 3.6 wt % DBTL containing microcapsules. Adhesion promoter (MAPTS) was added to the matrix to improve the bond strength between the healing agent and the matrix. Control samples were healed by injecting a solution containing a premixed healing agent and DBTL in chlorobenzene into the crack planes of fully fractured samples. As shown in Table 2, the efficiency of healing decreased significantly as the healing temperature decreased (and this was particularly true for the *in situ* system).

Table 2. Average Maximum Load of Control and *in Situ* Samples as a Function of Healing Temperature for Self-Healing Vinyl Ester with Phase-Separated S45-Based PDMS Healing Agent

	av maximum load (*N*) [standard deviation]	
healing temp (°C)	control sample	*in situ* sample
RT (20)	21 [1]	5 [3]
30	30 [5]	17 [13]
50	41 [4]	37 [7]

If the viscosity of the PDMS precursor is reduced to increase the reaction rate, it may translate to better healing efficiencies at low temperatures. Two low viscosity commercially available PDMS healing agents were tested: S42 and S35 from Gelest with viscosities of 18 000 cP and 35 000 cP, respectively. One concern was if the lower viscosity PDMS would phase separate from the matrix material. By SEM, it was observed that both healing agents phase-separate from the matrix (Figure 1). The average size of the S35 phase-separated droplets was smaller than the S42 droplets (Table 3). In fracture tests after healing at 30 °C (Table 4), the lower viscosity PDMS healing agent displayed better healing efficiency than the higher viscosity agent.

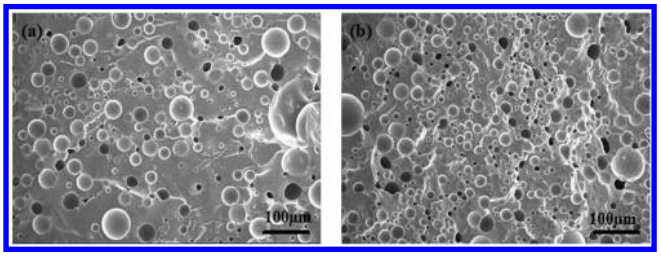

Figure 1. SEM images of fracture surface of the epoxy vinyl ester composite containing phase-separated PDMS healing materials: (a) S42 (viscosity 14 000 cP) and (b) S35 (viscosity 4000 cP).

Table 3. Diameter of the Phase-Separated PDMS Droplets as a Function of the Viscosity and Molecular Weight of PDMS Healing Agent

PDMS	viscosity (cP)	molecular weight (g/mol)	droplet diameter (μm) av [standard deviation]
S42	18 000	77 000	15.9 [10.2]
S35	3500	49 000	9.8 [4.8]

Table 4. Maximum Load of Self-Healed Samples Using Various Viscosity PDMS Healing Agents, and Healing Agent Physical Properties

				maximum load after healing (N)	
PDMS	viscosity (cP)	MW (g/mol)	% hydroxyl group (OH)	RT	30 °C
S12	16−32	400−700	4.5−7.5	no healing	no healing
S15	45−85	2000−3500	0.9−1.2	no healing	no healing
S27	700−800	18 000	0.2	16	21
S32	2000	36 000	0.09	15	29
S35	3500	49 000	0.07	17	29
S42	18 000	77 000	0.04	10	15
S45	50 000	110 000	0.03	5	17

Comparison between the healing efficiency of the phase-separated PDMS healing agents shows that the healing efficiency and viscosity were closely related. The viscosity was optimized for low-temperature healing by performing TDCB fracture toughness tests and comparing the maximum load of the self-healed samples with the TDCB geometry as a function of the PDMS healing agent viscosity (Table 4). The healing properties of the self-healing composite improved upon reduction of the healing agent viscosity, with an optimum viscosity range 2000−3500 cP. The PDMS healing agents with a molecular weight of less than 4000 Da ($\ll$1000 cP) did not heal because the healing agent was not adequately dispersed into the matrix (these PDMS healing agents did not remain dispersed in the matrix and formed an immiscible liquid layer on top of the matrix after matrix polymerization). It should be noted that the maximum load supported by the samples optimized for low temperature self-healing was always less than the healing efficiency of the conventional samples healed at 50 °C (Table 2), and so optimization of the catalyst is also needed.

b. Effect of Catalyst Activity. To further enhance low temperature self-healing, a number of commercially available organotin catalysts were tested. We hypothesize that a combination of low viscosity healing agents and a more effective catalyst should yield better low-temperature PDMS-based self-healing. The organotin catalyst used for the work above, DBTL, features long ligand chains (Figure 2a) attached to the tin atom. Shah reported enhanced catalytic activity using organotin catalysts with shorter ligand chains (Figure 2b,c).[25] Longer ester and alkyl groups bonded to the tin atoms decreased the catalytic activity, but the catalytic activity decrease saturates above 32 total carbon atoms.[25] It is also

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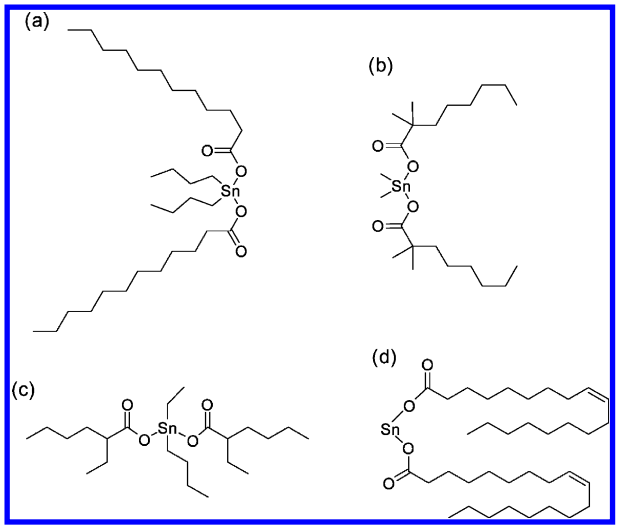

Figure 2. Catalyst chemical structures: (a) DBTL, (b) DMDN-Sn, (c) DBBE-Sn, and (d) tin(II) oleate.

possible that tin(II) rather than tin(IV) catalysts may yield a more effective catalyst (Figure 2d).[26] Although the reaction mechanism is not well understood, it has been suggested that the catalytic activity depends primarily on steric and electronic effects.[25,26]

Along with our previously published synthesis of DBTL containing microcapsules,[10] we also successfully synthesized microcapsules (Figure 3) containing the three organotin

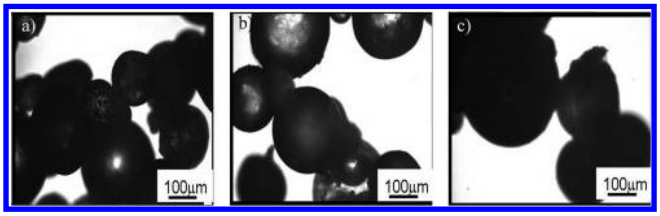

Figure 3. Optical microscope images of microcapsules containing various organotin catalysts: (a) DMDN-Sn, (b) DBBE-Sn, (c) tin(II) oleate.

catalysts shown in Figure 2b–d. DMDN-Sn features a shorter alkyl chain, and DBBE-Sn features a shorter ester chain than the original catalyst. Tin(II) oleate is a Sn^{2+} catalyst, and the others are Sn^{4+} catalysts. The room temperature healing efficiency of epoxy vinyl ester systems containing these catalyst-containing microcapsules and various low-viscosity PDMS was evaluated.

The healing performance of different catalysts was measured using monotonic tests with TDCB samples. Table 5 shows the monotonic test results using a low molecular weight PDMS (based on S35) and the various catalyst-containing microcapsules. The test results showed that the healing efficiency increased with the use of more active catalysts at low temperatures. The maximum fracture load observed for a single sample using the DMDN-Sn catalyst was 20 N when healed at room temperature and 30 N when healed at 30 °C, close to the load obtained using the injected control sample test. PDMS is not intrinsically a tough material, and thus, all PDMS healed samples failed at loads significantly lower than the virgin fraction of the epoxy samples.

Dual Microcapsule Self-healing System. The previously discussed self-healing systems were based on microencapsulated catalysts and phase-separated PDMS liquid droplets in an epoxy vinyl ester matrix. Although single microcapsule self-healing systems containing a phase separated healing agent have some processing benefits, dual microcapsule self-healing systems composed of PDMS-containing microcapsules and catalyst-containing microcapsules can be applied much more generally, as interactions between the uncured matrix polymer and the healing agents can largely be ignored as we showed in our earlier work on dual microcapsule self-healing coatings.[11] For example, an epoxy based on an amine curing agent is not compatible with the phase separation approach.

Table 5. TDCB Fracture Load of Virgin (One Sample for Each Temperature) and Self-Healed Samples Healed at 20 and 30 °C Formed Using Various Catalysts[a]

	fracture load of healed specimen, av maximum load (N) [1 standard deviation]	
catalyst	RT (20 °C)	30 °C
virgin fracture	152	143
DBTL	5 [3]	17 [13]
DMDN-Sn	14 [7]	26 [0.2]
DBBE-Sn	17 [0.6]	26 [4]
tin II oleate	9 [3]	7 [3]

[a]The virgin sample contained PDMS (S35) and DMDN-Sn catalyst-containing microcapsules. All samples contained adhesion promoter.

A dual microcapsule self-healing system was prepared by synthesizing PDMS-containing microcapsules, and using them in conjunction with the catalyst containing microcapsules. PDMS-containing microcapsules were synthesized with a urea-formaldehyde-based shell[1] as noted in the Experimental Section. The size of the PDMS-containing microcapsules was controlled by the mechanical stirring speed.[27] Both the PDMS-containing and tin catalyst-containing microcapsules were dispersed into the matrix along with, in some cases, an adhesion promoter (TESDMTA).

The healing properties of the dual microcapsule self-healing system were investigated using a fracture test with the TDCB sample geometry.[1] First, the effects of healing agent and catalyst mass fractions on self-healing were investigated. These samples did not contain an adhesion promoter. Not surprisingly, the maximum load of the healed samples increased as the quantity of healing agent increased (Figure 4). The concentration of

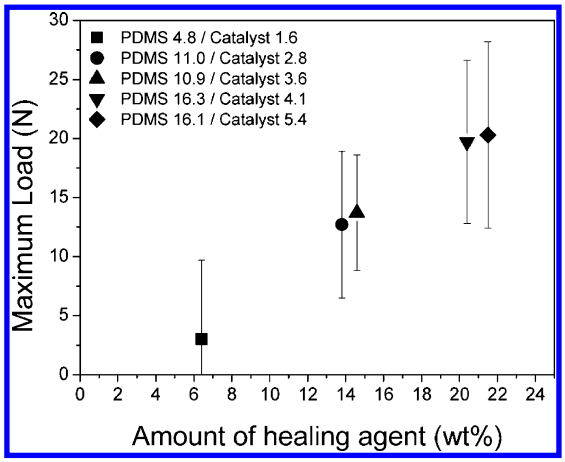

Figure 4. Maximum load of healed TDCB specimens as a function of the quantity of PDMS- and catalyst-containing microcapsules. Samples were healed at 50 °C.

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catalyst-containing microcapsules was held proportional to the concentration of the PDMS-containing microcapsules. Slight changes in the quantity of catalyst-containing microcapsules did not greatly change the healing properties. The highest average maximum load of the sample healed at 50 °C was 20 N, which was 17 N lower than that of the single microcapsule self-healing system. The primary reason for the lower strength appears to be the lack of adhesion promoter in the matrix.

The adhesion promoter improves the adhesion strength between the epoxy matrix and the PDMS healing material. The previously used adhesion promoter (MAPTS) for the epoxy vinyl ester system contained vinyl groups that reacted with the vinyl ester matrix and ethoxy silane groups that reacted with the PDMS healing agent. This adhesion promoter would not be effective in epoxy systems because the vinyl groups do not react with the epoxy matrix. Thus, a new adhesion promoter, TESDMTA, which contained amine groups that reacted with the epoxy matrix and methoxy groups that reacted with the hydroxyl groups of PDMS was used. The healing properties of the TDCB samples containing TESDMTA were confirmed by manually injecting a healing agent into the crack plane. The maximum load of the samples without the TESDMTA was 25 N. When MAPTS was used as an adhesion promoter, the maximum load was only slightly higher, but with TESDMTA, the maximum load increased to 50 N (Figure 5). TESDMTA

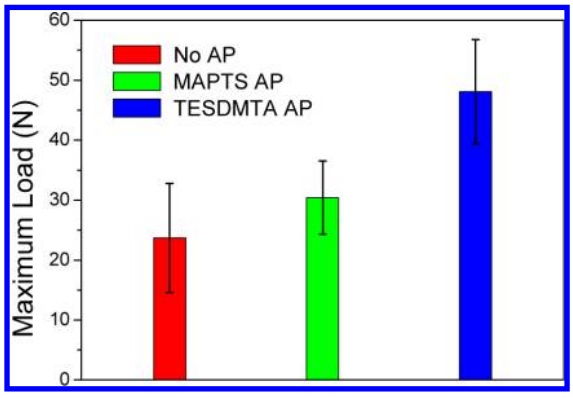

Figure 5. Maximum loads of the TDCB specimens manually healed by injecting PDMS healing agent with and without adhesion promoters (AP). Samples healed at 50 °C.

was then tested in the dual microcapsule self-healing system with *in situ* samples. Figure 6 shows that TESDMTA optimized for the epoxy matrix improved the adhesion strength, and the maximum load of the healed in situ sample exceeded 30 N.

Low-Temperature Dual-Capsule Self-Healing. Room temperature self-healing was already demonstrated for the single capsule system by reducing the viscosity of the PDMS healing agent and proper selection of the organotin catalyst. However, the efficiency for the dual capsule system, even near room temperature (30 °C), was still significantly below (Figure 6, 9.6 N ± 1.8 N) that of elevated temperatures (Figure 6, 22.0 N ± 11.1 N), and thus, a new catalyst, TKAS ($Si[OSn(n\text{-}C_4H_9)_2OOCCH_3]_4$), was investigated. TKAS has the advantage over the alkyl ester tin catalysts shown in Figure 2, in that it does not need to come in contact with moisture for activation (important in environments, such as deep within a sample, where water is not present). Upon contact with moisture, the alkyl ester tin catalysts are converted to the catalytically active alkyl hydroxyl tin which reacts with alkyl alkoxy silanes to form

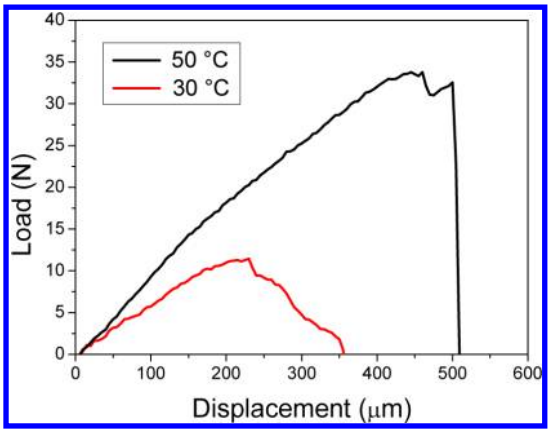

Figure 6. Monotonic fracture test results of the dual microcapsule self-healing polymer (TDCB geometry) healed at 30 and 50 °C. The self-healing composite was composed of epoxy with an amine curing agent, 3 wt % TESDMTA adhesion promoter, 14 wt % PDMS (S32, viscosity 1600 cP) containing microcapsules, and 3 wt % DMDN-Sn catalyst-containing microcapsules.

a compound containing a Sn−O−Si linkage which catalyzes the forming of the highly polymerized PDMS, something not necessary for TKAS.[28] The TKAS catalyst was synthesized as described in a U.S. patent.[29] The next step was to micro-encapsulate the TKAS catalyst as described in Experimental Section. Figure 7 shows a representative optical micrograph of the TKAS catalyst containing polyurethane microcapsules.

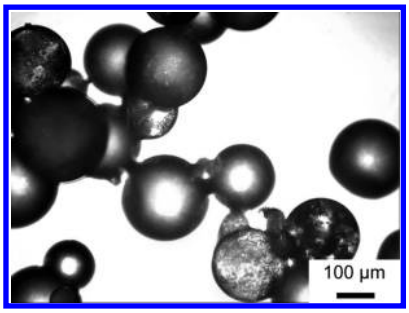

Figure 7. Optical micrograph of TKAS catalyst-containing microcapsules.

The healing performance of a dual-microcapsule self-healing polymer composite containing TKAS catalyst-containing microcapsules was investigated. Figure 8 shows the monotonic test results for the dual-microcapsule self-healing polymer containing TKAS catalyst-containing microcapsules healed at room temperature and 30 °C. The average maximum load of the healed samples improved significantly upon addition of the TKAS catalyst-containing microcapsules compared to the previous catalysts (Table 5), and the room-temperature healing properties were comparable (18.4 N ± 10.6 N) to those measured with healing at 30 °C (19.7 N ± 7.5 N).

The healing properties for the TKAS system at 50 °C were compared with the best single-microcapsule system. The single-microcapsule system (TKAS catalyst containing microcapsules and DMS-S32-based healing agent) yielded only a slightly higher maximum load after healing (35.1 N ± 5.8 N) than that observed for the TKAS catalyst and DMS-S32-based healing agent dual-capsule system (33.0 N ± 4.2 N). Using TKAS, slightly better healing did occur at 50 °C than at lower

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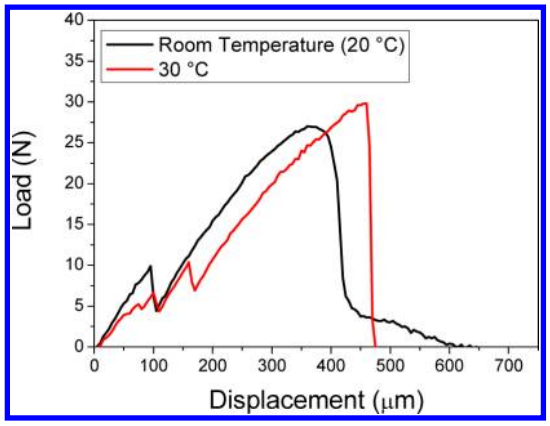

Figure 8. Results from the monotonic fracture tests with the TDCB geometry for virgin samples and fractured samples healed at room temperature and 30 °C using the TKAS catalyst. The self-healing composites were composed of epoxy and an amine curing agent, 3 wt % TESDMTA adhesion promoter, 14 wt % PDMS-containing (S32, viscosity 1600 cP) microcapsules, and 3 wt % TKAS catalyst-containing microcapsules.

temperatures (Figure 8), although it appears TKAS is a particularly effective catalyst for lower temperature applications.

■ CONCLUSIONS

Here we demonstrated the effect of healing agent viscosity and catalyst activity on self-healing at and near room temperature. By optimizing the viscosity of the PDMS healing agent and the catalytic activity, as well as selection of the appropriate adhesion promoter, both single and dual capsule PDMS-based self-healing systems which operate at room temperature were obtained. Lowering the viscosity alone was not sufficient for room temperature self-healing, and thus an active catalyst was synthesized. The dual microcapsule self-healing system was compared with a single microcapsule self-healing system. Although the healing properties of the dual microcapsule self-healing system were slightly lower than those of the single microcapsule self-healing system, the dual microcapsule system may have significant benefits for general matrix applications. The self-healing system composed of a PDMS healing agent with optimum viscosity and the TKAS catalyst-containing microcapsules was very effective in self-healing at room temperature.

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Notes

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