ACS APPLIED MATERIALS & INTERFACES

RESEARCH ARTICLE

www.acsami.org

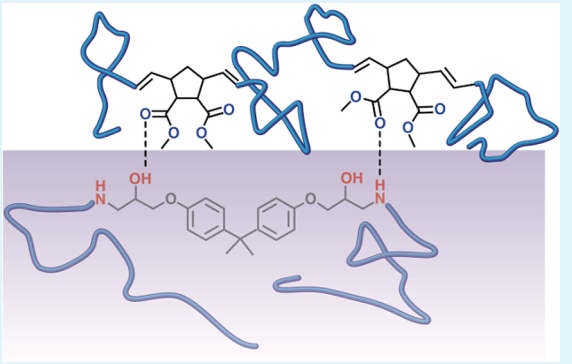
Adhesion Promotion via Noncovalent Interactions in Self-Healing Polymers

Gerald O. Wilson,[†,‡] Mary M. Caruso,[‡,§] Stuart R. Schelkopf,[§] Nancy R. Sottos,[†,‡] Scott R. White,[‡,⊥] and Jeffrey S. Moore*[,†,‡,§]

[†]Department of Materials Science and Engineering, [‡]Beckman Institute, [§]Department of Chemistry, and [⊥]Department of Aerospace Engineering, University of Illinois at Urbana−Champaign

Supporting Information

ABSTRACT: Dimethylnorbornene ester (DNE) is successfully used as a noncovalent adhesion promoter. DNE was confirmed to copolymerize with dicyclopentadiene (DCPD) to yield a copolymer with better adhesion to an EPON 828 epoxy matrix relative to poly(DCPD) alone. The mechanical properties of the copolymer were comparable to that of poly(DCPD) alone. An optimized blend of the monomers was encapsulated using a urea-formaldehyde microencapsulation procedure and the resulting capsules were used for in situ self-healing experiments. Improved healing efficiency was observed for samples containing the DCPD/DNE capsules under conditions in which the monomers were efficiently polymerized.



KEYWORDS: noncovalent interactions, self-healing polymers, adhesion, ring-opening metathesis polymerization, microencapsulation, fracture testing

INTRODUCTION

The efficiency of damage repair in self-healing polymers based on ring-opening metathesis polymerization (ROMP),[1−12] depends on the strength of the poly(DCPD)-matrix interface. Failure of this interface during fracture is typically due to a combination of adhesive and cohesive mechanisms.[13] Better healing efficiency of these systems requires improving the adhesion of the poly(DCPD) to the fracture surface of the matrix without compromising the cohesive strength of the poly(DCPD). Cho and coworkers have successfully demonstrated the use of an adhesion promoter to improve adhesion in a self-healing polymer by chemically bonding the polymerized healing agent to the matrix.[14] Cho's PDMS-based self-healing system incorporated methylacryloxypropyl triethoxysilane, which contains an acrylic functional group for copolymerization with the vinyl ester matrix and an ethoxy silane group for copolymerization with the hydroxyl end-functionalized polydimethylsiloxane. The presence of the adhesion promoter resulted in greater than 100% improvement of the healing efficiency in both reference and *in* situ tests. A similar observation was made when (3-trimethoxysilylpropyl) dimethylenetriamine was incorporated into an epoxy-based self-healing coating system.[15] This system contained a silyl ether group for reaction with PDMS-based self-healing chemistry and amine groups for reacting with epoxy

In this paper, we investigate the feasibility of using noncovalent adhesion promotion to improve the performance of ROMP-based self-healing systems. Instead of synthesizing a specific adhesion promoter capable of covalently bonding to the matrix resin and the polymerized healing agent for each new matrix and healing agent combination, we sought a more universal design. Specifically, we tested the use of a comonomer capable of copolymerization with DCPD that can also noncovalently bond to the matrix. When microcapsules containing a mixture of DCPD and the comonomer (cohealing agent) are ruptured, the mixture is released into the crack plane where it comes in contact and reacts with a catalyst embedded in the matrix thus initiating ROMP. Assuming the mechanical properties of the resulting polymer are not significantly compromised by presence of the comonomer, noncovalent interactions across the polymerized healing agent-matrix interface should improve adhesion at the crack plane and hence the healing efficiency of the system (Figure 1). This hypothesis is consistent with previous reports in which polymer additives commonly referred to as compatibilizers have been used to reinforce the interfaces between immiscible polymers, similarly improving the adhesive strength.[16,17]

The swelling of thermoset polymers by various solvents is well-documented.[18,19] Once released into the crack plane, therefore, it is likely that DCPD monomer penetrates the network of thermoset matrices such as epoxies. Upon contact with the catalyst exposed in the crack plane, polymerization is initiated, linking up DCPD molecules present on the surface of the crack plane and those now present within the thermoset network. The result is the formation of interpenetrated networks which should strengthen

Received: May 10, 2011
Accepted: July 5, 2011
Published: July 05, 2011

dx.doi.org/10.1021/am200584z | *ACS Appl. Mater. Interfaces* 2011, 3, 3072–3077

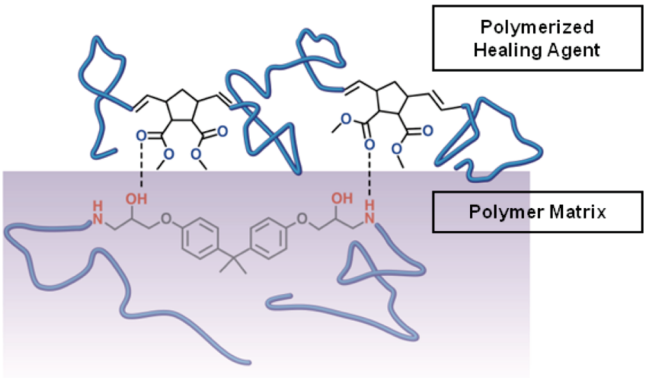


Figure 1. Schematic concept of noncovalent adhesion promotion in a self-healing system. The polymer formed in the crack plane contains hydrogen-bond-donating groups that interact with hydrogen-bond-accepting groups present in the epoxy matrix.

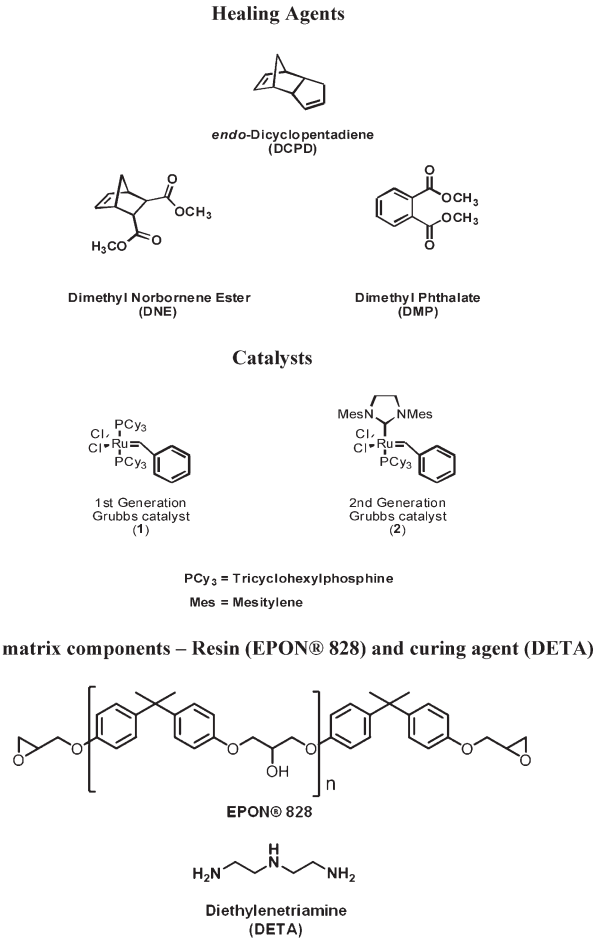
the poly(DCPD)-matrix interface. In addition to greater adhesive strength because of entangled polymer networks, we hypothesize that the presence of greater noncovalent interactions between the healing agent and the matrix will lead to improved overall adhesive strength and self-healing performance. An important advantage to the use of ROMP chemistry for self-healing is that its functional group compatibility makes it possible to design a system which includes hydrogen bonding donor and acceptor sites.

To test these ideas, we compared the effect of two different cohealing agents on the self-healing performance of poly(DCPD). Dimethylnorbornene ester (DNE) was selected as a cohealing agent because it contains a norbornene group for copolymerization with DCPD and ester groups for noncovalent bonding with an epoxy matrix (Chart 1). Dimethylphthalate (DMP) is structurally similar to DNE because it contains ester groups capable of noncovalent bonding with an epoxy matrix. However, DMP has no norbornene group capable of copolymerization with DCPD. Comparison of self-healing efficiency for DNE and DMP allows us to isolate the effect of copolymerization on healing performance.

EXPERIMENTAL SECTION

First- and second-generation Grubbs' catalysts (**1** and **2** respectively, Chart 1) were obtained from Sigma-Aldrich and freeze-dried before use.[20] Dicyclopentadiene (DCPD) was obtained from Acros Organics and dimethylphthalate (DMP) was obtained from Sigma-Aldrich. Both DCPD and DMP were degassed (consecutive freeze−pump−thaw cycles) before use. Dimethylnorbornene ester (DNE) was synthesized by slight modification of a procedure reported elsewhere.[21] The resin EPON 828 was obtained from Miller-Stephenson Chemical Company and the curing agent diethylenetriamine (DETA) was obtained from Air Products and Chemicals Inc. (both resin and curing agent are depicted in Chart 1). DSC experiments were performed on a Mettler-Toledo DSC 821^e instrument connected to a computer equipped with STAR^e (version 6.0) evaluation software. TGA experiments were performed on a Mettler-Toledo TGA 4400 instrument connected to the same computer equipped with the STAR^e evaluation software. Gas chromatography (GC) was performed on a Hewlett-Packard 5890 Series II gas chromatograph with a 530 μm internal diameter capillary and flame ionization detector. Environmental scanning electron microscopy (ESEM) images were taken using a Philips XL30 ESEM-FEG instrument using samples that had been sputter-coated with gold−palladium.

Chart 1



Synthesis of DNE. A mixture of *endo*bicyclo[2.2.1] hept-5-ene-2,3-dicarboxylic anhydride (32.8 g) and *p*-toluenesulfonic acid (0.50 g) was dissolved in methanol (60 mL) and refluxed for 10 h. The solution was cooled, excess methanol was removed under vacuum, and then washed with 95% ether, water, saturated $NaHCO_3$ (2x), and saturated NaCl. The product was distilled at 0.25 mmHg and 80 °C as a clear oil (19.03 g, 54.7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 (t, 2H, J = 1.6, vinyl), 3.52 (s/m, 6H, methyl), 3.20 (dd, 2H, J = 1.2, 0.4, next to C═O), 3.07 (m, 2H, J = 1.6, 1.2), 1.38 (m, 1H, bridgehead), 1.24 (m, 1H, bridgehead). ^{13}C NMR (500 MHz, $CDCl_3$) δ 173.18, 153.13, 51.76, 48.90, 48.25, 46.45. MS (CI) Exp. 210.16 Obs. [M^+ + 1] 211.1 $C_{11}H_{14}O_4$.

DSC Experiments. Samples for the DSC experiments were prepared by adding 0.25 wt % of either first- or second-generation Grubbs' catalyst to DCPD, DNE, or DMP. The monomers and catalyst were quickly and thoroughly mixed and approximately 10 mg was transferred to the DSC instrument. The sample was then heated from 25 to 300 °C at a rate of 10 °C/min (10 K/min) under a N_2 atmosphere.

TGA Experiments. TGA experiments on DCPD and DCPD/DNE microcapsules were performed by adding approximately 5 mg of the microcapsule sample to the TGA instrument and heating the sample from 25 to 650 °C at a rate of 10 °C/min (10 K/min) under a N_2 atmosphere.

GC Experiments. Four separate GC experiments were performed. For the first three experiments, the sample reagents DCPD, DNE or DCPD containing 10 wt % DNE were diluted using methylene chloride and approximately 1 μL of the resulting mixture was injected into the GC instrument. For the fourth experiment, DCPD/DNE microcapsules were crushed in a vial, extracted with methylene chloride and filtered.

Approximately 1 μL of the filtrate was injected into the GC instrument. For all experiments, the temperature was linearly ramped from 25 to 200 °C at a rate of 20 °C/min (20 K/min).

Determination of T_g. The T_g for poly(DCPD) prepared with either first- or second-generation Grubbs' catalyst (0.25 wt %) and containing varying concentrations of DNE and DMP was obtained through DSC temperature sweep experiments in which samples containing DCPD, catalyst and either DNE or DMP in the appropriate concentration were heated from 25 to 300 °C at 10 °C/min (10 K/min), cooled, and then reheated from 25 to 300 °C at the same rate. The T_g was calculated as the midpoint temperature of the second order transition in specific heat during the reheating segment using the STAR^e evaluation software.

Lap-Shear Experiments. Epoxy substrates prepared from EPON 828 and DETA were cast in the desired geometry (Supporting Information, Figure S2) in silicon molds. The desired area of overlap was carefully marked on each sample. The appropriate healing agent mixture (0.03 mL, 0.25 wt % catalyst) was carefully injected into the space in the overlap. The two halves of the sample were then held in place by binder clips as shown in Figure S3 (see the Supporting Information) for 24 h. The sample was then fixed on a load frame with two wedge grips (see Figure S4 in the Supporting Information) and loaded in tension under displacement control at a rate of 20 μm/s until failure.

Fracture Experiments. Reference test samples were prepared by mixing EPON 828 epoxy resin with DETA (12 phr) and casting the mixture into the long-groove tapered double cantilever beam (TDCB) geometry in silicon molds (see the Supporting Information, Figure S5). Testing followed the protocol established by Brown and co-workers.[2] After using a razor blade to initiate a precrack, the specimens were then pin loaded and tested under displacement control at a rate of 5 μm/s. Once completely fractured, the appropriate healing agent mixture (10 μL, 0.25 wt % catalyst) was injected into the crack plane and the two halves of each specimen were brought back in contact and left to heal for 24 h at room temperature before retesting to failure.

Table 1. Thermal Behavior for ROMP of DCPD and DNE by Catalysts 1 and 2

catalyst	monomer	heat of reaction (J/g)	onset T (°C)	T_g (°C)
1	DCPD	265	36	162
1	DNE	47	43	118
2	DCPD	368	52	156
2	DNE	235	49	148

In situ self-healing samples were prepared and tested similarly except that instead of injecting a healing agent mixture, the catalyst and microcapsules containing either DCPD or a blend of DCPD and DNE were mixed into the resin mixture and cast to form the TDCB specimen. These samples were fractured as described above and the two halves were brought back in contact and allowed to heal at a specified temperature without manual injection of any additional healing agent.

RESULTS AND DISCUSSION

The most successful ROMP-based self-healing systems utilized catalyst **1**. However, catalyst **2** has demonstrated greater activity, particularly for a variety of sterically demanding and electron-deficient olefins.[22,23] Consistent with this observation, we have also previously demonstrated that while **1** was incapable of polymerizing a blend of DCPD and the more sterically encumbered 5-norbornene-2-carboxylic acid (NCA), the same blend was successfully polymerized by **2**.[10] Taking these observations into consideration, the reactivity of DNE with both **1** and **2** was compared with that of DCPD.

Healing Agent Reactivity with Catalysts. The reactivities of DCPD and DNE with catalysts **1** and **2** were compared by DSC experiments in which 0.25 wt % of catalyst was mixed into separate samples of each of the two monomers and the resulting

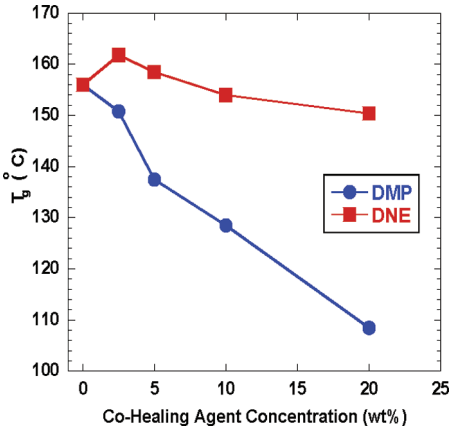


Figure 2. Glass-transition temperature (T_g) as a function of the amount of cohealing agent added to DCPD.

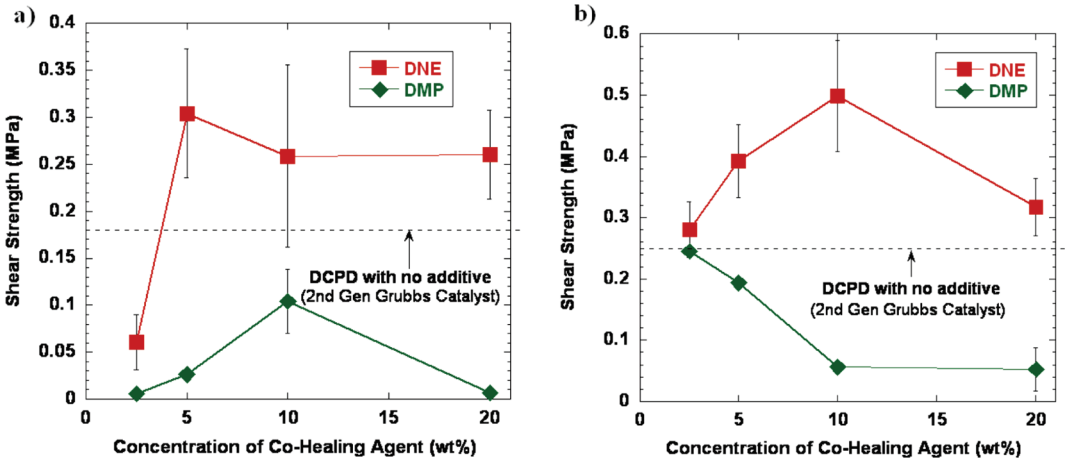


Figure 3. Shear strength of lap joints as a function of the concentration of cohealing agent (DNE or DMP) added to DCPD (Each data point represents the average of shear strength data for at least 4 samples and the error bars represent 1 standard deviation). (a) Data obtained at RT. (b) Data obtained at 50 °C.

samples were heated from 25 to 300 °C at a rate of 10 °C/min. The results are summarized in the Supporting Information (Figure S1). Several important observations were made from this experiment. As expected, both catalysts successfully initiated ROMP of DCPD as denoted by the significant exotherms observed for both generations of Grubbs' catalyst, but the onset temperature was higher with **2** than with **1**. More importantly, the exotherm for the ROMP of DNE with **1** was almost negligible compared to that observed with **2** and a large endotherm corresponding to the boiling of residual monomer was observed for the ROMP of DNE with **1**, but not with **2**. Furthermore, the T_g of the polymer resulting from ROMP with **1** is significantly lower than that resulting from ROMP with **2** (Table 1).

Consistent with previous results,[10] it was concluded that catalyst **1** is not active enough to polymerize DNE to any appreciable extent. Moreover the use of catalyst **2** in bulk ROMP of DCPD led to a decrease in initial ROMP rates. A decrease in initial ROMP rates has the ultimate effect of a lower healing efficiency as loss of monomer due to evaporation or absorption of the healing agent into the matrix depletes the amount of healing agent present in the crack plane. Usually, these losses occur at a much slower rate relative to polymerization, but for **2**, monomer loss and polymerization are likely to be competitive. It is important to note therefore that although the use of **2** allows us to evaluate the effect of the use of a cohealing agent on adhesion and eventual self-healing performance, the complexities due to slower polymerization result in a lower baseline of performance relative to previous examples of self-healing systems utilizing **1**.

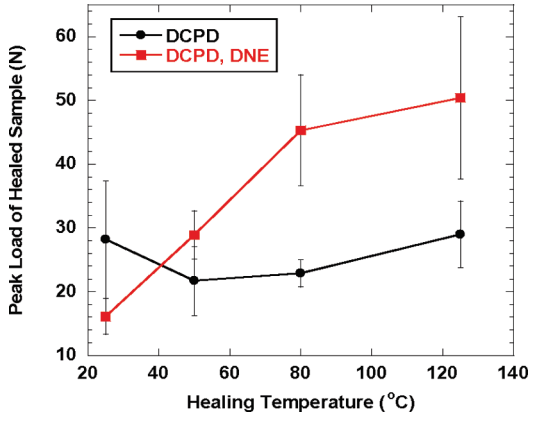


Figure 4. Peak load of healed reference test samples as a function of healing temperature.

Effect of Additive Concentration on ROMP Kinetics and T_g. Having established the ability of **2** to polymerize both DCPD and DNE, we determined the effect of the concentration of either DNE or DMP on the copolymerization with DCPD. For both DNE and DMP, the effect on the onset temperature of ROMP was marginal as it was observed to decrease from 52 to 49 °C for both DNE and DMP. This observation suggests that initial ROMP kinetics were not adversely affected by either additive. The glass-transition temperatures of polymerized samples however, showed that although the addition of DMP resulted in the significant decrease in T_g expected from the incorporation of a plasticizer, the addition of DNE resulted first in an increase in T_g at 5 wt % and a moderate decrease as the concentration of DNE was increased to 20 wt % (Figure 2). The increase in T_g with small amounts of DNE is likely due to an initial improvement in cross-link density of the final polymer. The higher cross-link density is a result of increased reaction kinetics with lower concentrations of DNE relative to DCPD (Table 1, onset temperature for ROMP with catalyst 2). At higher concentrations of DNE, steric effects are more dominant in the final polymer, leading to lower T_g.

Effect of Co-Healing Agent Concentration on Adhesion. Lap-shear experiments were used to evaluate the effect of DNE as an additive for improving adhesion. At RT (approximately 22 °C), the addition of 2.5 wt % DNE was observed to decrease adhesion relative to DCPD alone. This observation is possibly due to negative effects of plasticization from unreacted DNE relative to any positive gains due to adhesion promotion. The greatest adhesion promotion occurred at 5 wt %, although performances recorded at 10 and 20 wt % were significantly higher than results obtained with DCPD alone, presumably because of domination of noncovalent adhesion promotion over plasticization (Figure 3a). In general, the addition of DMP was deleterious to the adhesive performance of DCPD. The adhesion appeared to be concentration dependent, but all adhesion performance data of DMP were inferior to the results obtained with DCPD alone.

Similar lap-shear experiments were performed on samples polymerized at elevated temperature (50 °C) to minimize plasticization due to sluggish ROMP initiation rates observed with **2** at RT. At 50 °C, which is closer to the onset temperature of ROMP of DCPD (52 °C) and DNE (49 °C), improvement in adhesion was observed at 2.5 wt % DNE and increased by almost 100% at an optimal concentration of 10 wt % DNE. On the contrary, but not unexpectedly, adhesion performance was observed to decrease rapidly with the addition of DMP (Figure 3b). Analysis of the fracture surfaces showed more cohesive failure for samples utilizing

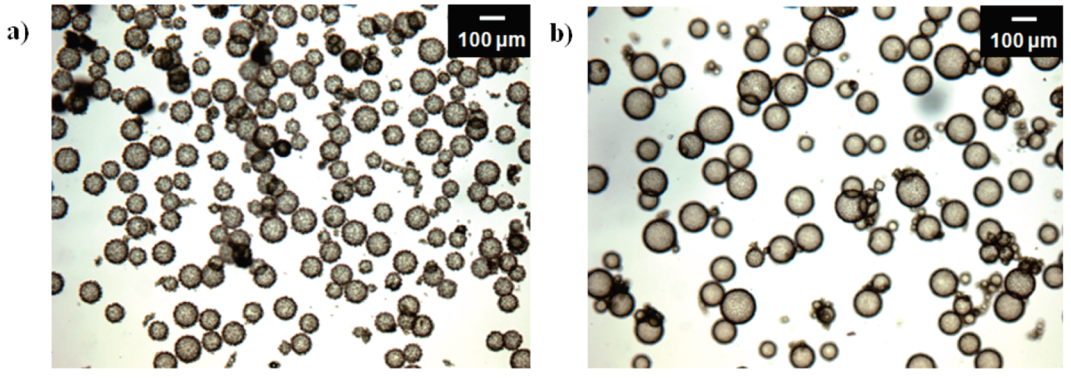


Figure 5. Representative batches of (a) urea-formaldehyde microcapsules containing DCPD and (b) urea-formaldehyde microcapsules containing DCPD and 10 wt % DNE.

the DCPD/DNE healing agent blend, whereas DCPD and DCPD/DMP healing agents exhibited more adhesive and mixed mode failures. Furthermore, the amount of healing agent retained on the fracture surface for DCPD/DNE was significantly greater than DCPD/DMP (see Figure S6 in the Supporting Information).

Reference TDCB Experiments. Reference tests were performed to compare the self-healing potential of a mixture of DCPD and 10 wt % DNE (optimized healing agent combination in lap-shear experiments) to DCPD alone. The peak fracture loads for samples manually healed by injecting a mixture of DCPD and catalyst **2**, showed almost no dependence on temperature as all loads recorded were approximately between 22 and 28 N (Figure 4). This observation is likely due to an inadequate concentration of catalyst needed to convert all DCPD available to poly(DCPD). Peak fracture loads for samples healed with the DCPD/DNE mixture and catalyst **2** showed a strong dependence on temperature with the highest peak fracture recorded for samples healed at 120 °C. This result represents an improvement of greater than 200% over the results obtained at RT and almost 70% improvement over results obtained with DCPD alone at the same temperature. For samples healed at room temperature, reference test results obtained with the DCPD/DNE healing agent mixture were inferior to the results obtained with DCPD alone. As the healing temperature increased, initiation rates and overall degree of conversion increased, leading to better monomer conversion and polymer with improved mechanical properties.

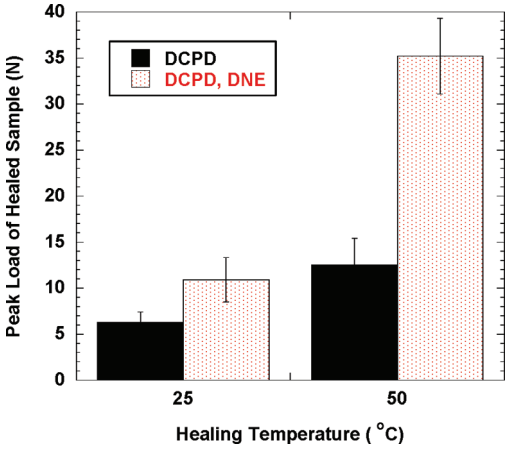


Figure 6. Peak load of healed in situ samples as a function of healing temperature.

At the highest peak fracture load observed for the DCPD/DNE mixture, the cohealing agent mixture outperformed DCPD alone by almost 80%. The improvement in adhesion and mechanical properties due to copolymerization with a ROMP comonomer is consistent with similar observations made for the copolymerization of DCPD with 5-norbornene-2-carboxylic acid or 5-ethylidene-2-norbornene.[10] The cohealing agent improves adhesion and self-healing performance by first serving as a solvent to dissociate the more slowly reacting cyclopentene olefin of DCPD in favor of the more reactive norbornene olefin and then reacting to form a copolymer with improved adhesion to the matrix.

Preparation and Testing of In situ Samples. An important consideration in the selection of healing agents for self-healing applications is compartmentalization, which often takes the form of microencapsulation. Healing agents must be sufficiently hydrophobic for facile encapsulation, another factor considered for the selection of DNE as cohealing agent. A mixture of DCPD and DNE (10 wt %) was encapsulated using a procedure optimized by Brown et al.[24] The resulting capsules are compared to capsules containing DCPD only in Figure 5. The microcapsule composition was evaluated by gas chromatography (GC). The GC traces for all experiments performed are included in the Supporting Information. The GC trace for core material extracted from the DCPD/DNE microcapsules exhibited peaks for both DCPD and DNE confirming the presence of both monomers in the microcapsules. The resulting microcapsules were also evaluated by thermogravimetric analysis (TGA) and exhibited slightly improved thermal stability relative to microcapsules containing DCPD alone most likely due to boiling point elevation because of the presence of DNE in the mixture (see the Supporting Information).

To evaluate the self-healing performance of the DCPD/DNE healing agent mixture, we prepared two sets of TDCB samples. Both sets contained 1 wt % catalyst **2**; one set had 10 wt % DCPD/DNE microcapsules while the second set contained microcapsules of DCPD alone. Both sets of samples were fractured, realigned and allowed to heal for 24 h at 25 °C or at 50 °C. A comparison of the performance of both sets of data is shown in Figure 6. The DCPD/DNE mixture outperformed DCPD alone both at 25 °C and much more significantly at 50 °C. Although the self-healing performance of the DCPD/DNE healing agent combination using catalyst **2** is less impressive than previously reported results for systems utilizing DCPD alone and catalyst **1**, the performance discrepancy is due to slower initiation kinetics of ROMP with catalyst **2**. At elevated temperatures when slower ROMP rates are no longer an issue, improved self-healing performance is observed because of the use of DNE as a cohealing agent.

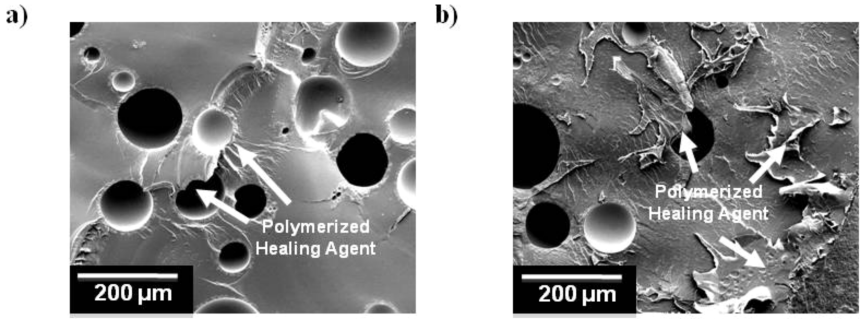


Figure 7. (a) TDCB fracture plane for sample containing DCPD/DNE capsules healed at 25 °C. Less polymerized healing agent is observed on the surface. (b) Similar fracture plane but samples were healed at 50 °C. Polymerized healing agent observed on the fracture plane is identified by the arrows. Scale bars for both images measure 200 μm.

Representative fracture surfaces comparing samples healed at 25 °C to those healed at 50 °C show significantly more polymerized healing agent on the surface of the samples healed at 50 °C (Figure 7). This observation confirms the need for rapid initiation kinetics to maximize adhesion promotion due to the presence of a cohealing agent.

CONCLUSIONS

We have demonstrated the feasibility of using a noncovalent adhesion promoter for improved self-healing performance. By using DMP as a control, we were able to demonstrate the need for copolymerization of the adhesion promoter with the healing agent. In standard adhesion evaluation tests such as lap-shear experiments, and more standard self-healing performance evaluation tests such as TDCB fracture testing the DNE cohealing agent showed significant improvement under conditions in which the monomers were efficiently polymerized. The combination of DCPD and the cohealing agent DNE was successfully encapsulated and the resulting microcapsules were used in self-healing experiments that demonstrated superior self-healing performance relative to DCPD alone. These results add a new consideration in the design of self-healing systems and suggest the possible widespread use of noncovalent adhesion promoters, broadening the scope of tools that can be used for improving healing efficiencies in self-healing polymers.

ASSOCIATED CONTENT

Supporting Information. Fracture and lap-shear test sample images and dimensions, ESEM images showing surfaces of lap-shear samples, DSC data, GC data and TGA data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: jsmoore@illinois.edu.

ACKNOWLEDGMENT

This work was supported by the Air Force Office of Scientific Research (MURI Grant FA9550-05-1-0346) and the Department of Defense (National Defense Science and Engineering Graduate Fellowship). ESEM images were acquired in the Beckman Institute Microscopy Suite.

REFERENCES

(1) White, S. R.; Sottos, N. R.; Guebelle, P. R.; Moore, J. S.; Kessler, M. R.; Sriram, S. R.; Brown, E. N.; Viswanathan, S. *Nature* **2001**, *409*, 794–797.
(2) Brown, E. N.; White, S. R.; Sottos, N. R. *Exp. Mech.* **2002**, *42*, 372–379.
(3) Brown, E. N.; White, S. R.; Sottos, N. R. *Compos. Sci. Technol.* **2005**, *65*, 2466–2473.
(4) Brown, E. N.; White, S. R.; Sottos, N. R. *Compos. Sci. Technol.* **2005**, *65*, 2474–2480.
(5) Rule, J. D.; Brown, E. N.; Sottos, N. R.; White, S. R.; Moore, J. S. *Adv. Mater.* **2005**, *17*, 205–208.
(6) Mauldin, T. C.; Rule, J. D.; Sottos, N. R.; White, S. R.; Moore, J. S. *J. R. Soc. Interface* **2007**, *4*, 389–393.
(7) Jones, A. S.; Rule, J. D.; Moore, J. S.; Sottos, N. R.; White, S. R. *J. R. Soc. Interface* **2007**, *4*, 395–403.
(8) Rule, J. D.; Sottos, N. R.; White, S. R. *Polymer* **2007**, *48*, 3520–3529.
(9) Wilson, G. O.; Moore, J. S; White, S. R.; Sottos, N. R.; Andersson, H. M. *Adv. Funct. Mater.* **2008**, *18*, 44–52.
(10) Wilson, G. O.; Caruso, M. M.; Reimer, N. T.; White, S. R.; Sottos, N. R.; Moore, J. S. *Chem. Mater.* **2008**, *20*, 3288–3297.
(11) Blaiszik, B. J.; Sottos, N. R.; White, S. R. *Compos. Sci. Technol.* **2008**, *68*, 978–986.
(12) Patel, A. J.; Sottos, N. R.; Wetzel, E. D.; White, S. R. *Composites A* **2010**, *41*, 360–368.
(13) Brown, E. N. Ph.D. Thesis, University of Illinois, Urbana, IL, 2002.
(14) Cho, S. H.; Andersson, H. M.; White, S. R.; Sottos, N. R.; Braun, P. V. *Adv. Mater.* **2006**, *18*, 997–1000.
(15) Cho, S.; White, S. R.; Braun, P. V. *Adv. Mater.* **2009**, *21*, 645–649.
(16) Kramer, E. J.; Norton, L. J.; Dai, C. A.; Sha, Y.; Hui, C. Y. *Faraday Discuss.* **1994**, *98*, 31–46.
(17) Sha, Y.; Hui, C. Y.; Kramer, E. J.; Hahn, S. F.; Berglund, C. A. *Macromolecules* **1996**, *29*, 4728–4736.
(18) Allred, R. E.; Hall, N. H. *Polym. Eng. Sci.* **1979**, *19*, 907–909.
(19) Vanlandingham, M. R.; Eduljee, R. F.; Gillespie, J. W. *J. Appl. Polym. Sci.* **1999**, *71*, 787–798.
(20) Jones, A. S.; Rule, J. D.; Moore, J. S.; White, S. R.; Sottos, N. R. *Chem. Mater.* **2006**, *18*, 1312–1317.
(21) Morgan, M. S.; Tipson, R. S.; Lowy, A.; Baldwin, W. E. *J. Am. Chem. Soc.* **1944**, *66*, 404–407.
(22) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4035–4037.
(23) Love, J. A.; Sanford, M. S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 10103–10109.
(24) Brown, E. N.; Kessler, M. R.; Sottos, N. R.; White, S. R. *J. Microencapsulation* **2003**, *20*, 719–730.