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# Thermally Stable Autonomic Healing in Epoxy using a Dual-Microcapsule System

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High-performance thermosetting structural polymers and composites are increasingly used in consumer products when high strength and stiffness, low weight, and environmental stability are required. The intrinsic brittleness and flaw sensitivity of these materials make them susceptible to failure by the accumulation of fatigue damage until a critical flaw size is exceeded.[1] In nature, biological systems invoke self-repair strategies to mitigate failure. Similarly, synthetic self-healing polymers and composites utilize inherent material resources to repair damage whenever and wherever it occurs during the lifetime of the material.[2,3] Nearly all reported synthetic self-healing strategies either require significant external energy for the repair, or are limited to modest temperatures for autonomic functionality.[3,4] Since many high-performance thermosetting polymers are cured at elevated temperature (ca. 121–177 °C), a successful self-healing system requires overcoming a paradoxical technical requirement. For autonomous healing at room temperature the required healing chemistry must be thermodynamically favorable with a kinetic pathway that only becomes viable upon damage. In practice, the kinetic "switch" is realized through physical isolation of reactants (e.g. dual capsules of reactants A and B) whose contents mix when damage occurs. As thermal energy is increased during elevated temperature curing of the matrix, the kinetic stability approaches thermal limits, and increases the risk of premature reaction of the healing chemistry, undesirable side reactions, or degradation of the catalytic reactants. The ideal healing chemistry is one that is robust, cost-effective, environmentally stable, and provides superior mechanical healing performance. Curing above 120 °C for several hours dictates that the self-healing system must possess excellent thermal stability. While the vast majority of prior work on capsule-based self-healing systems has focused on polymers that are cured at a maximum temperature < 45 °C,[5–8] self-healing of higher temperature cured epoxies has been attempted, albeit with moderate success. Mangun et al. demonstrated a dual-capsule poly(dimethylsiloxane) healing chemistry with ca. 52% healing efficiency in an epoxy matrix post-cured at 100 °C for 1 h.[9] More recently, Jin et al. reported a dual-capsule amine-epoxy healing chemistry with 91% efficiency in a room temperature cured epoxy, but post-curing at 121 °C for 8 h reduced the healing efficiency to 40%.[10] Here, we report for the first time a dual-capsule healing chemistry that satisfies the rigorous demands for high-performance polymers cured at elevated temperature.

Our approach is predicated on the isolation of epoxy and amine reactants in separate polymeric microcapsules with excellent thermal stability. Epoxy resin capsules (123 ± 34 μm) were produced by in situ polymerization a polyurethane (PU) – poly(urea-formaldehyde) (UF) double-shell wall following a previously established protocol[11] around a core of bisphenol-A epoxy resin diluted with a low viscosity reactive diluent (o-cresyl glycidyl ether), as shown in **Figure 1**a. Amine capsules (111 ± 3 μm) were prepared following a method[10] of vacuum infiltration of polyoxypropylenetriamine (POPTA) into polymeric hollow microcapsules (Figure 1b). Hollow microcapsules were first synthesized by forming a UF shell wall around entrapped air bubbles in an aqueous solution. Upon air-drying and sieving, hollow capsules were then immersed in a liquid amine for vacuum infiltration in a cylindrical vacuum jar. After several hours under vacuum, microcapsules that settled to the bottom were filled with amine and removed by filtering and used without rinsing.

POPTA (440 Da) is a trifunctional primary amine curing agent (Figure 1b) which has moderate reactivity at room temperature and was selected after extensive screening of potential amines that satisfy the necessary stability and processing requirements. Thermogravimetric analysis (TGA) shows good thermal stability of amine capsules to well above 200 °C (Figure 1d). Both neat POPTA and amine capsules show nearly identical weight loss traces. The diluted epoxy resin is a low viscosity (5–7 poise at 25 °C) system consisting of bisphenol-A epoxy resin (377 Da) diluted with 26% o-cresyl glycidyl ether (CGE) (164 Da) which shows a step transition in the TGA trace (Figure 1d) indicating early loss of the reactive diluent upon thermal exposure (Figure 1a).

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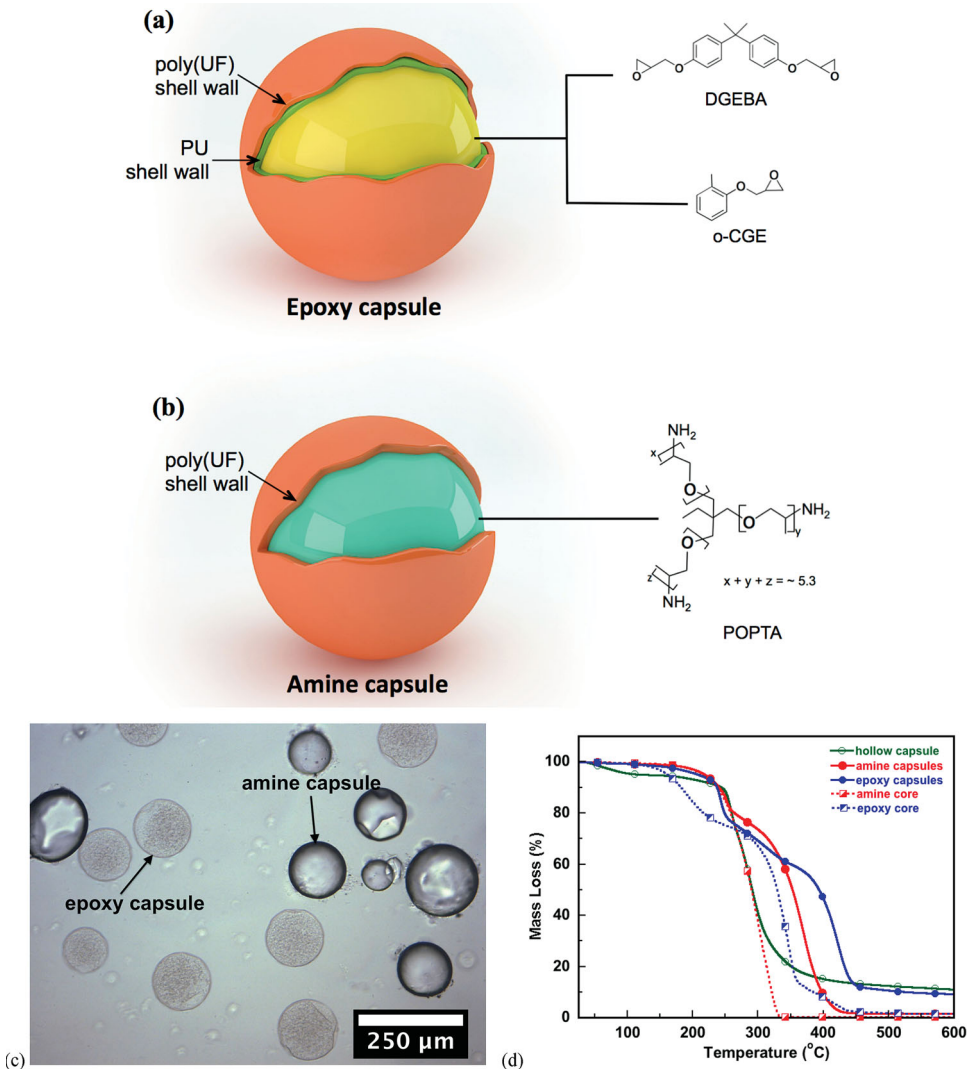


**Figure 1.** Epoxy-amine dual-capsule healing system. (a) Epoxy capsules consist of a polyurethane – poly(urea-formaldehyde) double shell wall and a DGEBA/o-CGE core. (b) Amine capsules contain a poly(urea-formaldehyde) shell wall and a POPTA core. (c) Optical micrograph showing both epoxy and amine microcapsules dispersed in an uncured epoxy matrix. (d) TGA traces of microcapsules and their corresponding core contents (as-received).

A high-performance epoxy matrix system, Araldite/Aradur 8615 (Huntsman Advanced Materials), was used as the matrix material in this study. A glass transition temperature ($T_g$) as high as 212 °C can be obtained by appropriate elevated temperature curing conditions (**Table 1**).

Given the importance of the stoichiometry, we initially investigated the healing performance of fracture specimens (cured at various temperatures) in which the ratio of epoxy to amine capsules was varied while holding the total capsule concentration constant at 10 wt%. The healing efficiency is defined as the ratio of healed to virgin fracture toughness.[12] For specimens cured at 50 °C for 6 h followed by 121 °C for 6 h, the highest average healing efficiency (89 ± 13%) was obtained at an equal mass ratio of amine:epoxy capsules (5:5) as shown in **Figure 2**a.

**Table 1.** Summary of glass transition temperatures of Araldite/Aradur 8615 epoxy cured at various conditions. All samples were pre-cured overnight at room temperature

| Cure Cycle | Cure conditions | Curing degree (%) | $T_g$ of neat epoxy (°C) | $T_g$ of epoxy with capsules (°C)[a] |
|---|---|---|---|---|
| A | 50 °C (6 h) + 121 °C (6 h) | 100 | 152 | 152 |
| B | 50 °C (6 h) + 150 °C (6 h) | 100 | 187 | 189 |
| C | 50 °C (6 h) + 121°C (2 h) + 177 °C (3 h) | 100 | 212 | 213 |

[a]All samples contained 5 wt% amine capsules and 5 wt% epoxy capsules.



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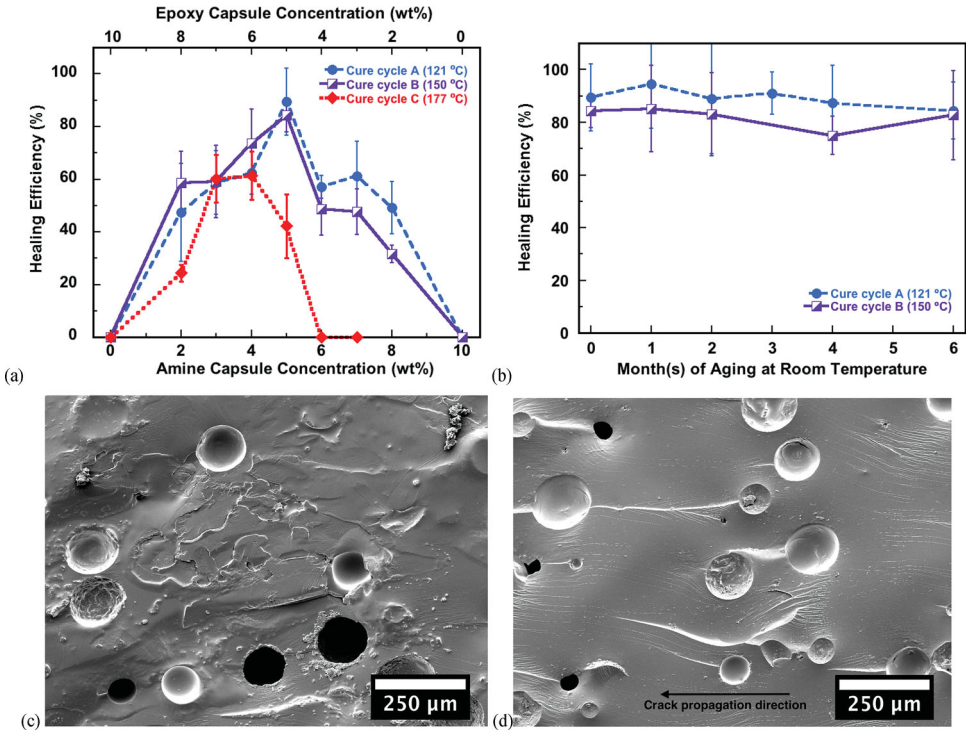


**Figure 2.** Characterization of healing performance. (a) Effect of amine:epoxy capsule weight ratio at a constant 10 wt% total capsule concentration for specimens cured at elevated temperatures. (b) Long-term stability of self-healing samples containing 5 wt% amine capsules and 5 wt% epoxy capsules cured using cure cycle A and B (121 °C and 150 °C, respectively), then exposed to ambient conditions for various times before fracture testing. (see Supporting Information, Tables S1-S3 for all testing data). SEM images of (c) fracture surface revealed after self-healed fracture test and (d) fracture surface rinsed with ethanol immediately after virgin fracture to remove healing agents and prevent polymerization. Both SEM images are from specimens containing 5 wt% amine capsules and 5 wt% epoxy capsules cured using cure cycle A.

The required healing time to reach optimal healing was concurrently determined to be 2 days at room temperature and this healing time was used for all subsequent experiments (see Supporting Information, Figure S1). Because the mean diameters of both capsule types were similar, the volumetric ratio of healing agents is roughly the same as the capsule weight ratio. The true stoichiometric ratio for our healing chemistry is 4.3:10, indicating a preferential loss of core materials from amine capsules during specimen preparation and curing.

To further investigate the loss of core materials from microcapsules during various heat treatments, we mixed both capsule types with the matrix epoxy and placed the sample between two glass slides mounted on a heated stage under a microscope. Optical microscopy reveals an index of refraction mismatch when core material diffuses out of the capsule into the surrounding epoxy matrix creating a void within the capsule (**Figure 3**a). In general, voids formed and enlarged due to diffusion of core materials for both types of capsules as the curing temperature and time increased. Amine capsules began losing core material after 6 h exposure at 50 °C. The volume loss of amine core quickly increased from 1.3% to 6.9% after the first 2 hours at 121 °C and then increased steadily to 7.8% after 6 hours exposure (Figure 3a). Most importantly, ca. 92.2% of the amine core contents were preserved after 6 h exposure to 121 °C curing conditions, a dramatic improvement from previous dual capsule amine-epoxy healing system, in which the majority of the amine reactant was lost after post-cure at elevated temperature.[10] For epoxy capsules, no detectable loss of core materials occurred at 50 °C, possibly due to the larger molecular weight of the core materials and the double shell wall capsule providing better thermal stability. Exposure to 121 °C for 6 h led to ca. 6.3% loss of the epoxy core contents, as shown in Figure 3a. In all cases, the loss of the core material is driven both by thermal and chemical diffusion processes such that TGA stability alone is insufficient to establish viability of the healing system.

The healed fracture plane of a self-healing specimen was inspected using scanning electron microscopy (SEM). The fracture plane reveals significant texture of healed material (as shown in Figure 2c), indicative of in situ formation of polymerized healing agents and excellent bond strength to the host epoxy matrix. In stark contrast, the unhealed fracture surface (Figure 2d) with healing materials rinsed away using ethanol immediately after fracture reveals a relatively smooth surface and remnants of ruptured microcapsules. Most importantly, the autonomic reaction of healing agents at the crack plane leads to the ca. 90% recovery of virgin fracture toughness of epoxy cured at elevated temperature (121 °C, 6 h) with a $T_g$ of ca. 152 °C, a significant advancement from previous self-healing polymers.

The healing performance for samples cured at even higher temperatures was also examined, and these results are included in Figure 2a. For samples cured at 150 °C, the highest average

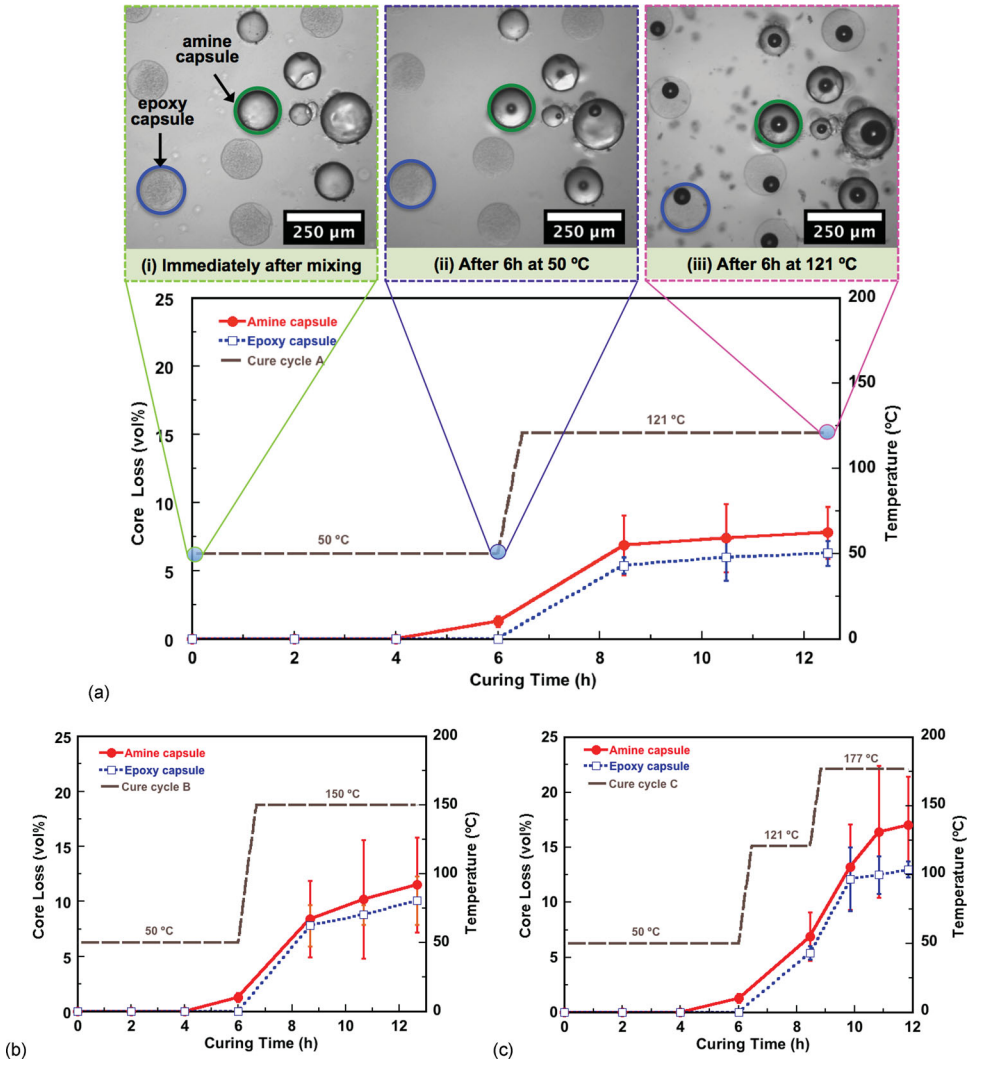


**Figure 3.** Characterization of core content loss as a function of curing time for amine and epoxy capsules. (a) Cure cycle A. Optical images showing the corresponding evolution of capsule core loss in epoxy matrix during curing, from left to right: (i) immediately after mixing, (ii) after the first hold at 50 °C for 6 h, and (iii) at the end of cure cycle A. (b) Cure cycle B. (c) Cure cycle C.

healing efficiency (84 ± 7%) was obtained at a mass ratio of 5:5 for amine:epoxy capsules, the same as those cured at 121 °C. The healing efficiency for samples cured 177 °C peaked at 61 ± 9% for a mass ratio of 4:6, and then vanished beyond 5:5 mass ratio. Higher exposure temperature caused more loss of core contents for both types of capsules (Figure 3b and c). These results indicate that both the temperature and time of exposure significantly affect the diffusion of the core contents for both types of capsules. The loss of core material from the amine capsules leads to incomplete crosslinking and low degree of cure. The complete lack of healing for samples cured at 177 °C with concentrations below 6 wt% amine capsules strongly supports this argument. The loss of core material from the epoxy capsules is likely biased towards the reactive diluent first, which leads to increased viscosity of the epoxy resin and poor mixing of reactants in the crack plane. As a result, healing efficiency decreased as the curing temperature increased. Nevertheless, in all cases the addition of microcapsules did not lower $T_g$ (Table 1), an important thermal property for high performance structural composites.

In separate experiments, neat epoxy specimens (Control I) cured at 121 °C were healed by injection of ca. 0.8 μL premixed epoxy and amine reactants at the stoichiometric ratio. This quantity of healing agent is approximately equivalent to the total volume of healing agent released after fracture from 10 wt% capsules with an average diameter of 120 μm.[13] An average healing efficiency of 153 ± 7% was measured although substantial crack deviation from the virgin fracture path occurred,[6,7] confirming the exceptional mechanical performance of this healing system. Two other controls were evaluated in which 10 wt% epoxy capsules were used (Control II) or 10 wt% amine capsules (Control III). No healing occurred for either case, confirming that the recovery of fracture toughness for self-healing specimens is due to the in situ autonomous reaction of epoxy and amine reactants released from their respective capsules.



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The long-term stability of this self-healing system at ambient conditions was also investigated. Self-healing specimens containing 5 wt% amine capsules and 5 wt% epoxy capsules were manufactured and cured at 121 °C or 150 °C and then aged at ambient conditions for up to six months before testing. The fracture test results plotted in Figure 2b show little change in healing efficiency after aging for six months, indicating excellent stability of the healing system within a fully cured epoxy matrix under ambient conditions. These results are a significant advancement from previous self-healing studies for solvent-based healing,[7,8] in which healing efficiency decreased significantly after one month and vanished after eight months due to lack of residual functional groups in the epoxy matrix.[14]

The demonstration of a high $T_g$ structural epoxy that autonomically heals at room temperature represents a significant advancement for the field of self-healing materials. By matching the healing chemistry to the host epoxy matrix, excellent mechanical recovery is obtained in a high-$T_g$ structural polymer. Our dual-capsule approach is generic and offers a platform for exploring new healing chemistries. The vacuum infiltration of hollow capsules is a simple approach to the encapsulation of highly reactive core materials (e.g. amine curing agents). Beyond the immediate target of self-healing, environmentally stable dual capsule systems can enable other functionalities in polymers and composites such as damage assessment, environmental sensing, and corrosion protection and mitigation.

## Experimental Section

*Materials*: Epoxy resins EPON 828 (diglycidyl ether of bisphenol-A) and EPON 813 (diluted version of EPON 828) as well as amine curing agents diethylenetriamine (DETA, EPIKURE 3223) and polyoxypropylenetriamine (EPIKURE 3233) were purchased from Miller-Stephenson (Houston, TX) and used as-received. An elevated temperature cured epoxy system (Araldite/Aradur 8615) was received from Huntsman Advanced Materials. Urea, triethanolamine, formic acid, and Formalin (37% formaldehyde in water) were obtained from Sigma-Aldrich (Saint Louis, MO). Ethylene-maleic anhydride (EMA) copolymer (Zema-400) powder with average $M_w$ = 400 kDa was received from Zeeland Chemicals and used in a 2.5 wt% deionized water solution.

*Synthesis of Microcapsules*: EPON 813 is diluted EPON 828 epoxy resin containing 26% o-cresyl glycidyl ether (CGE) with a low viscosity (5–7 poise at 25 °C). Epoxy microcapsules were synthesized by polymerization of polyurethane (PU) – poly(urea-formaldehyde) (UF) double shell wall following the procedure described by Caruso et al.[11] with an agitation rate of 800 RPM. Capsules were filtered and rinsed two to three times using ethanol and then sieved between 125–180 μm, yielding an average diameter of 123 ± 34 μm. Amine microcapsules (average diameter: 111 ± 37 μm) were prepared by infiltrating EPIKURE 3233 into polymeric hollow capsules, following an established method.[10]

*Healing Performance Evaluation*: Localized short groove TDCB fracture specimens were used to evaluate the healing performance.[13] To prepare TDCB specimens, EPON 828 and 12 pph diethylenetriamine (DETA) were mixed, degassed to remove trapped air, and poured into silicone rubber molds (with silicone rubber inserts) to cure overnight. The silicone rubber inserts were then removed and Araldite/Aradur 8615 (100:50 by weight) mixed with or without capsules was poured into the insert and allowed to cure overnight at room temperature then cured at elevated temperatures (see Supporting Information for more details on TDCB testing).

*Characterization of Microcapsules*: Capsule size distributions were obtained from multiple optical images taken with a Leica DMR optical microscope interfaced with ImageJ software (version 1.45). At least 200 separate microcapsule diameters were measured to obtain the size distribution. A field emission environmental scanning electronic microscope (SEM) (Philips XL30 ESEM-FEG) was used to image the fracture surfaces of specimens and microcapsules under high magnification. Fracture surfaces of interest were sputter-coated with ca. 30 nm thick layer of gold-palladium before imaging. Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA851® under nitrogen flow and a heating rate of 10 °C/min.

*Measurement of Glass Transition Temperature*: The glass transition temperature ($T_g$) of Araldite/Aradur 8615 can vary depending on curing conditions. Glass transition temperatures were measured using dynamic mechanical analysis (DMA) following ASTM standard D5023–07. Rectangular specimens (29.0 × 4.0 × 2.0 mm) were tested in three-point bending (25 mm span) in a DMA (TA Instrument RSA III). The temperature of the sample was increased from 20 °C to 255 °C at a rate of 5 °C $min^{-1}$. The $T_g$ was measured based on the peak in the tangent of the phase angle.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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