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# A self-healing biomaterial based on free-radical polymerization

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**Abstract:** Self-healing chemistry used for damage repair have not previously been demonstrated for free-radical polymerization pathways. However, this chemistry is important for addition polymers such as poly(methyl methacrylate) used in bone cement and epoxy vinyl ester used in dental resins. Self-healing biomaterials offer the potential for safer and longer lasting implants and restoratives by slowing or arresting crack damage. In the free-radical self-healing system reported here, the three components required for polymerization (free-radical peroxide initiator, tertiary amine activator, and vinyl acrylate monomers) are compartmentalized into two separate microcapsules—one containing the peroxide initiator, and the other containing both monomer and activator. Crack damage ruptures the capsules so that the three components mix and react to form a new polymer that effectively rebonds the crack and restores approximately 75% of the original fracture toughness. Optimal healing is obtained by a systematic evaluation of the effect of monomer, initiator, and activator concentration on healing performance. © 2013 Wiley Periodicals, Inc. J Biomed Mater Res Part A: 102A: 3024–3032, 2014.

**Key Words:** self-healing, radical polymerization, microencapsulation, simulated body fluid, epoxy vinyl ester

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## INTRODUCTION

Mechanical damage to bulk polymers typically begins as a microcrack, potentially leading to failure of the material in the absence of a method to inhibit crack growth. In living systems, damage automatically initiates a healing response, and this function has been emulated by synthetic self-healing systems.[1] Self-healing polymers are engineered with the unique ability to extend the lifetime of materials by repairing damage using various chemical mechanisms that are triggered by crack formation.[2] There have been very few reports on extending this self-healing concept to biomaterials[3–5] or on using a radical-based self-healing chemistry.[6] Herein, we present a two-part system based on free-radical self-healing chemistry for use in biomaterials such as bone cement or dental resins.

In the United States alone, there are on average 200,000 total hip replacements and 400,000 knee replacement surgeries performed annually, and these numbers are expected to more than double within the next 20 years.[7] Not only do these surgeries affect a large population, but patients typically undergo revision surgeries about every 10 years, mainly due to dislocation and loosening of the initial prosthesis from the bone.[8] The polymeric material used to anchor metal prostheses to contiguous bone is an acrylic resin-based bone cement formulation.[9] This two-part poly (methyl methacrylate) (PMMA) bone cement has emerged as one of the most widely used biomaterials in revision surgeries and knee/hip replacements since its development by Charnley in 1960.[9] The components of this formulation include cross-linked PMMA beads, a liquid methyl methacrylate (MMA) monomer polymerized by free-radical conditions with a peroxide initiator and a tertiary amine activator.[10,11] The liquid and solid components are mixed together just before use in surgery at which time the MMA monomer polymerizes *in vivo*.

The long-term stability of bone cement has been a major concern because of the brittleness and poor wear resistance of the polymeric matrix. Secondary fillers such as carbon nanotubes,[12] silver particles,[13] or dispersed copolymers such as polyethylene[14] have been used to reduce the brittle

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nature of the cement and increase the fracture toughness. The development of self-healing polymers in the past decade[1,15,16] presents an opportunity for extending the lifetime of bone cements. One group recently demonstrated self-healing capability in PMMA bone cement containing dicyclopentadiene monomer-filled microcapsules and Grubbs' catalyst particles.[3] However, the toxicity and cost of the metathesis catalyst are likely to discourage the use of this self-healing chemistry in a practical biomaterial application. More recently, the tissue adhesive, 2-octylcyanoacrylate was successfully encapsulated,[5] and these microcapsules could be incorporated into future self-healing biomaterials, resulting in a catalyst-free system.

We report an alternative chemistry based on the reaction between acrylate monomers, a peroxide initiator, and a tertiary amine activator. Evaluations of various peroxide initiators and tertiary amine activators were conducted to identify benzoyl peroxide (BPO) as the ideal initiator based on its stoichiometric concentration, reactivity, and thermal stability.[17] In this work, we present a self-healing system where all of the reaction components have been compartmentalized in microcapsules and the microcapsules embedded in a polymer matrix. The objectives were to maximize healing efficiency by forming a polymer via free-radical initiation at a kinetically favorable rate at ambient and *in vivo* temperatures.

## EXPERIMENTAL SECTION

### Materials

Benzoyl peroxide (BPO, Sigma-Aldrich), and 4,4'-methylene bis(*N,N*-dimethylaniline) (MBDMA, Acros Chemical) were ground into a fine powder before use behind a blast shield due to its shock sensitivity. Ethyl phenylacetate (EPA), phenyl acetate (PA), dichloromethane (DCM), dimethylaniline (DMA), trimethylolpropane triacrylate (TMPTA), trimethylolpropane ethoxylate triacrylate (TMPET), bisphenol A ethoxylate diacrylate (Bis-EMA), urea, ammonium chloride ($NH_4Cl$), resorcinol, and formaldehyde solution (formalin, 37 wt/vol %) were purchased from Sigma–Aldrich and used as received. Ethylene-maleic anhydride (EMA) copolymer (Zemac®-400) powder with an average molecular weight of 400 kDa was graciously donated by Vertellus and used as a 2.5 wt % aqueous solution. The Derakane 510A-40 Epoxy Vinyl Ester (EVE) resin was generously donated by Ashland Chemicals and used as received.

### Instrumentation

Absorption spectra were recorded from 200 to 800 nm with a background scan of PA and EPA using a Shimadzu UV-Visible Spectrophotometer, model number UV-1601PC. Approximately 25 mg DCM-washed microcapsules were ruptured in a mortar and pestle, and 2.5 mL solvent (either PA or EPA) was added. The capsule/solvent mixture was added to a 5 mL syringe then filtered through a 0.45 μm syringe filter into a quartz cuvette for UV analysis. Healed EVE fracture surfaces were imaged by scanning electron microscopy (SEM, Philips XL30 ESEM-FEG instrument with a 5 kV electron source) after sputter-coating with a gold-palladium source.

### Thermal analysis

Dynamic and isothermal differential scanning calorimetry (DSC) experiments were performed on a Mettler-Toledo DSC821$^e$. All DSC experiments were performed in 40 μL aluminum crucibles. Average sample sizes were 5–10 mg. Dynamic experiments were performed under nitrogen atmosphere from 25 to 300°C at a rate of 10°C/min. For experiments with capsule mixtures, samples of 25 mg total were ruptured between glass slides and were transferred quickly to DSC pans, crimped, and loaded into the instrument. Isothermal DSC experiments were performed at 25°C for 120 min. Samples tested contained monomer mixtures of TMPET:Bis-EMA at various ratios, with BPO (1 wt %) and DMA (0.1 wt %). In foil-covered 20 mL scintillation vials, BPO was first added to the monomer mixtures and vortexed for 1 min; DMA was then added to this solution via pipette immediately before loading the sample into the DSC. The degree of monomer conversion ($\alpha_t$) was determined from isothermal experiments as a function of time using the following equation:

$$\alpha_t = 100\,\frac{Q_t}{Q_T} \tag{1}$$

where $Q_t$ is the reaction heat at time $t$, and $Q_T$ is the total heat of polymerization (calculated from dynamic experiments). To determine the thermal stability of the microcapsules, thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA851$^e$ instrument calibrated by indium, aluminum, and zinc standards. The mass loss was recorded during a heating cycle over the temperature range of 25–650°C at a constant rate of 10°C/min in an atmosphere of $N_2$. For each experiment, ~2–5 mg of sample was accurately weighed (±0.02 mg) into an alumina crucible.

### Microcapsule preparation

Microencapsulation was carried out following standard procedures[18] to produce a urea-formaldehyde (UF) polymer shell encapsulating the intended core material. Initiator capsules containing BPO in PA were prepared at 450 RPM.[17] For monomer/activator microcapsules, it is important to keep solutions in a dark environment (foil-covered vials) as much as possible to prevent light-induced polymerization. In foil-covered 100 mL glass containers, 0.3 g MBDMA (0.5 wt % of total solution) was first weighed and dissolved in 12.1 g EPA (20 wt % of total solution), then 36 g TMPET and 12 g Bis-EMA were weighed and added to the container in this order. The solutions were sonicated for 40 min before encapsulation. Stock solutions of monomers/activator were also prepared in smaller volumes at a variety of monomer ratios and used for thermal analysis and reference testing, as described below. UF microcapsules[18] of the monomers were prepared at 400 RPM with a slight modification to the original procedure. The amount of wall-forming materials was reduced by half, while the 60 mL of core material remained constant.[19] Additionally, the reaction vessel (600-mL beaker) was covered entirely in foil during the encapsulation.

### Sample preparation and testing

Epoxy vinyl ester (EVE) long-groove TDCB samples[20] for reference tests were prepared by mixing 1 wt % BPO into the Derakane 510A-40 resin at 1500 RPM for 5 min, followed by the addition of 0.1 wt % DMA.[21,22] The mixture was then poured into silicone molds and allowed to cure at RT for 24 h. After fracturing the specimens on a load frame under displacement control at a rate of 5 μm/s, monomer mixtures of TMPET:Bis-EMA and BPO in PA at a 5:1 ratio (by weight) were injected into the crack plane via micropipette (25 μL for each TDCB sample). The samples were clipped at the top and bottom of the specimens, and allowed to heal at various temperatures (RT, 37°C, 50°C) in a MicroClimate® Environmental Chamber (Cincinnati Sub-Zero Products) at 40% relative humidity for 24 h before retesting to failure. Four to six samples were tested for each data entry. For short-groove[23] *in situ* EVE samples, the central insert section of the sample was prepared with the same matrix materials and procedure as above (EVE, BPO, and DMA) and the appropriate amount of microcapsules (0–15 wt %) were mixed in the resin and poured into PDMS molds. The samples were allowed to cure at RT for an additional 24 h after which they were precracked and pin-loaded at a rate of 5 μm/s under displacement control on a load frame until the crack propagated to the end of the 25 mm groove. The samples were removed from the load frame and allowed to heal at RT for 24 h. For the healing time study, samples were left at RT for the following time periods: 14 min, 30 min, 2, 4, 9, 18, 24, and 48 h. The samples were then re-tested and healing efficiencies were measured. Healing efficiency (η) is defined as the ratio between the healed and the virgin fracture toughness,[20] which for the TDCB geometry reduces to:

$$\eta = K_{IC}^{\text{healed}} / K_{IC}^{\text{virgin}} = P_C^{\text{healed}} / P_C^{\text{virgin}} \tag{2}$$

where $K_{IC}$ is the fracture toughness and $P_C$ is the critical fracture load of each sample.

### Simulated body fluid experiments

Using published procedures,[24] 1 L of simulated body fluid (SBF) was prepared in a 2 L flask that was charged with all the dry salts and large stir bar. The amounts and concentrations of the salts used are reported in Supporting Information Table S3. Then, 1 L MilliQ water was added to the flask, and the solution was covered and stirred overnight with slight heat (35°C) until the solids had dissolved. Concentrated HCl was added via pipette until the pH of the solution was 7.25 (2–3 drops). Then, 500 mL were added to an empty plastic pipette tip container and equilibrated at 37°C, 40% relative humidity in the MicroClimate® environmental chamber for 5 h before adding the fracture specimens. Five *in situ* short-groove TDCB EVE samples with 5 wt % capsules (monomer/activator and BPO at a 5:1 ratio by mass) were prepared as described above and fractured with a razor blade and immediately submerged into the SBF in the environmental chamber. The pipette tip box cover was slid into place to prevent evaporation of the SBF. An identical set of five *in situ* TDCB samples were prepared, fractured, and placed to heal in the environmental chamber at 37°C (not in the SBF) to serve as the control specimens for this experiment.

## RESULTS AND DISCUSSION

### Preparation of initiator and monomer/activator capsules

Free-radical initiators have been encapsulated in the past and other groups have demonstrated the stability of these capsules.[25,26] The suitability of five peroxide initiators for a free-radical initiated self-healing system was previously evaluated in our laboratory, and it was reported that BPO and lauroyl peroxide (LPO) had the lowest onset polymerization temperatures for an EVE resin.[17] Although BPO and LPO are well-studied peroxide initiators for free-radical conditions,[27,28] BPO emerged as the best performing initiator across the range of evaluation criteria most pertinent to self-healing (including thermal stability and polymerization kinetics). To facilitate encapsulation and delivery of this free-radical initiator, a maximum of 9.9 wt % of BPO was dissolved into the solvent phenyl acetate (PA) and encapsulated in a UF shell wall at 450 RPM to yield capsules with an average diameter of 106 ± 24 μm [Fig. 1(a)]. TGA scans of capsules stored at room temperature up to 3 months showed no significant mass loss when compared to an initial scan of the synthesized microcapsules (Supporting Information). Further characterization included comparison of UV-visible scans from the core solution of ruptured microcapsules to core solution samples taken before encapsulation (Supporting Information), and the presence of BPO was confirmed by the absorption peak observed at 290 nm.

For the activator component of the self-healing free-radical system, the encapsulation of dimethylaniline (DMA) was attempted with an interfacial polymerization reaction to make polyurethane shell wall capsules.[22] Although the initial stability of these capsules was reasonable, it was found that the core liquid permeated the shell wall over time. Instead, an alternative tertiary amine, 4,4′-methylene-bis(*N*,*N*-dimethylaniline) or MBDMA, was encapsulated. This solid phase activator also demonstrated a lower onset temperature of polymerization than DMA when used as 0.1 wt % of an EVE resin mixture.[18] To determine the maximum concentration that could be encapsulated, MBDMA was dissolved in ethyl phenylacetate (EPA) from 0.2–1 g in a total volume of 60 mL solvent. Optical images of the resulting capsules are included in the Supporting Information. EPA is a nontoxic solvent used in food additives.[29] When encapsulations were attempted at concentrations greater than 1 g MBDMA in 60 mL EPA, no capsules formed presumably due to inhibition of the UF shell wall reaction.

Because vinyl monomers and tertiary amine activators are unreactive on their own, these components were combined in one microcapsule, referred to as the monomer/

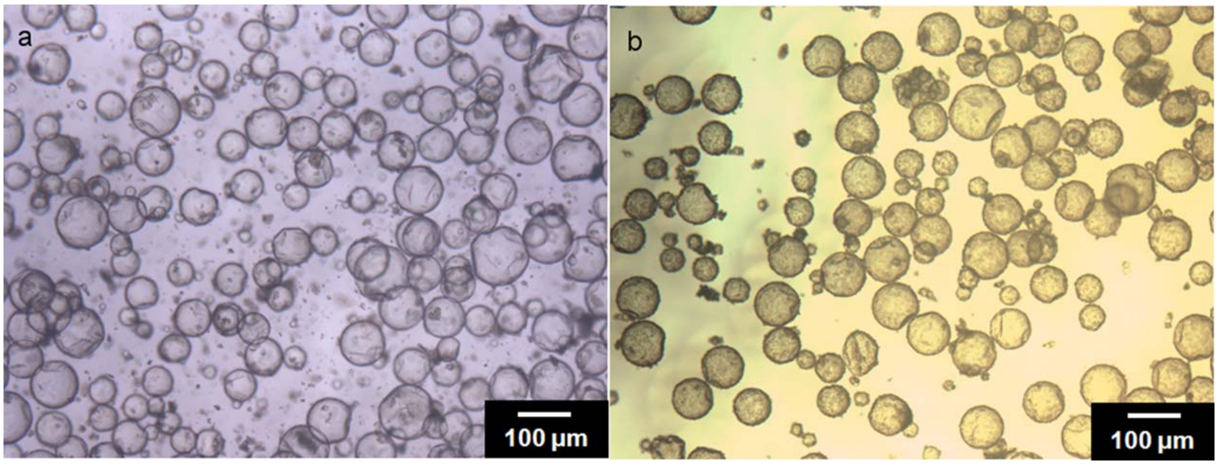


**FIGURE 1**. Optical micrographs of capsules containing core solutions of (a) BPO in PA and (b) monomer mixture with amine activator in EPA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

activator (M/A) capsules. Chemical structures of the capsule components are shown in Figure 2. These capsules were prepared by first dissolving the solid MBDMA activator into EPA and then sonicating this mixture with a combination of multifunctional vinyl monomers [trimethylolpropane triacrylate (TMPTA) or trimethylolpropane ethoxylate triacrylate (TMPET), and bisphenol A ethoxylate diacrylate (Bis-EMA)]. These monomers were selected because of their structural similarity to monomers used in dental resins and other biomaterials.[30] The solution generated was successfully encapsulated at a stir rate of 400 RPM. Optical images of these M/A capsules are shown in Figure 1(b) and the average diameters were $130 \pm 30$ μm. These capsules were characterized by TGA and UV-visible spectroscopy to confirm the core components in the same manner as the initiator capsules (Supporting Information). With the capsules produced, an optimal ratio of M/A to initiator capsules was needed. An initial range of activator/initiator ratios had been reported[17] and established a starting point for these studies. The optimal ratio from a qualitative screening experiment was found to be 5:1 M/A capsules to BPO capsules and the following experiments used this ratio throughout.

### Optimization of monomer/activator capsules

EVE resin was chosen as the matrix for the self-healing experiments due to its use in dental composites[22] as a free-radical cured matrix, as well as serving at the matrix for other demonstrated self-healing systems in our laboratory.[21,31] Additionally, the acrylic functional groups are similar to those present in monomers used in orthopedic implants making EVE a suitable candidate for these studies. Short-groove tapered-double-cantilever beam (TDCB) samples[23] were prepared with 1 wt % BPO and 0.1 wt % DMA in EVE and cured for 24 h at RT (chemical structures of the EVE resin are shown in Fig. 3). The central, insert region of the sample was composed of the same resin mixed with 10 wt % capsules and cured at RT for another 24 h. Two different trifunctional monomers (TMPTA and TMPET)[32] were

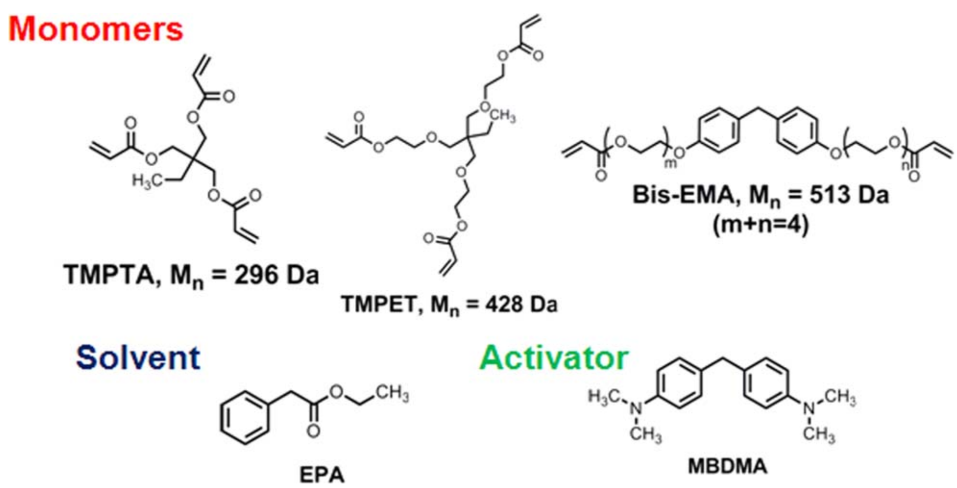


**FIGURE 2**. Chemical structures of components in the core mixture of monomer/activator microcapsules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

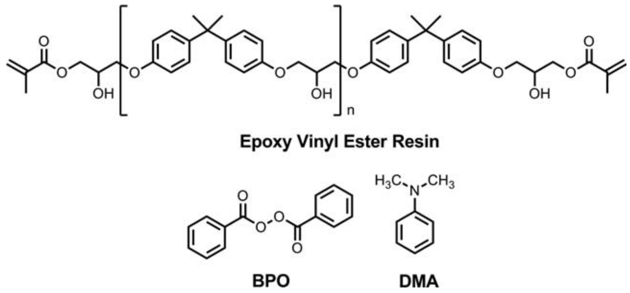


**FIGURE 3.** Chemical structures of epoxy vinyl ester matrix components.

analyzed for healing performance. A series of tests were performed in which the amount of MBDMA in the capsules core was systematically varied from 0.2 to 1.7 wt % in capsules of TMPET/Bis-EMA or TMPTA/Bis-EMA. In all experiments, a ratio of 5:1 M/A to BPO capsules was used. The *in situ* healing results are shown in Figure 4(a). When TMPTA was used with Bis-EMA, the highest reported healing efficiency was $\eta = 0.46$ at 0.7 wt % MBDMA in the M/A capsule core. TMPET has a higher molecular weight than TMPTA and produces a more robust polymer, which was evidenced by higher healing efficiencies at all concentrations tested. When this monomer was used with Bis-EMA, the highest healing efficiency was $\eta = 0.69$ at a concentration of 0.5% MBDMA in the M/A capsule core. Since TMPET consistently reported higher healing efficiencies, it was used instead of TMPTA in further studies.

To determine the optimal solvent concentration, a separate series of tests were performed in which the amount of solvent was varied from 2 to 20 mL or 3 to 33% of the core solutions. For these tests, the total volume of core material (60 mL), the monomer ratio (3:1 TMPET:Bis-EMA),

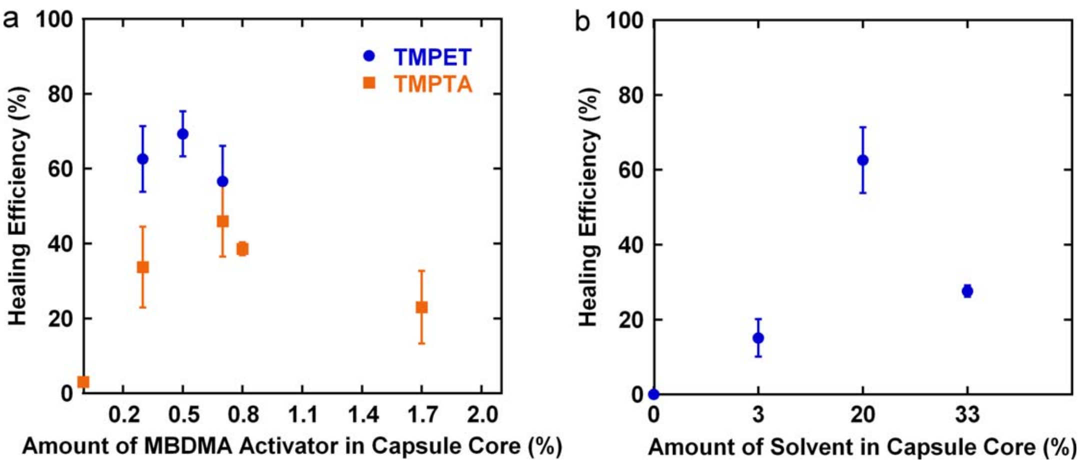


**FIGURE 4.** Self-healing performance as a function of (a) MBDMA activator and (b) solvent in the microcapsule core material (relative % to other core components). The error bars represent one standard deviation based on 4–5 samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

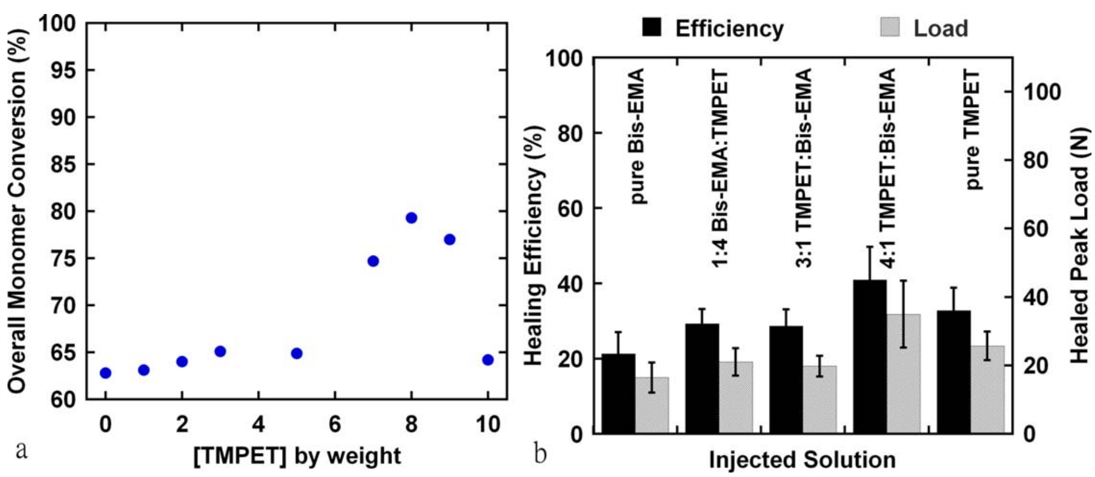


**FIGURE 5.** Effect of TMPET concentration on system performance. (a) Overall monomer conversion (%) as measured by DSC for various TMPET:Bis-EMA monomer mixtures. (b) Healing performance at RT (25°C) from reference tests in which 25 μL of the healing solution (as indicated) together with 9.9% BPO in PA was injected into the crack plane, then clamped and allowed to heal for 24 h. Error bars indicated standard deviation for 4–6 samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

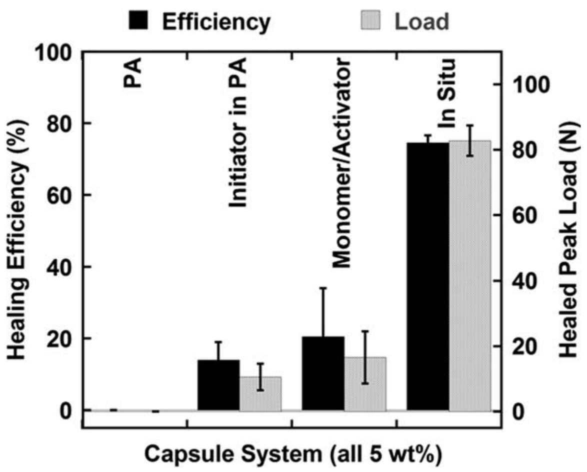


**FIGURE 6**. Summary of self-healing performance at room temperature for BPO initiator capsules, TMPET/Bis-EMA and MBDMA capsules (monomer/activator), and M/A + initiator (in situ) capsule systems. The error bars represent one standard deviation based on 4–5 short-groove *in situ* TDCB samples with 5 wt % capsule loadings.

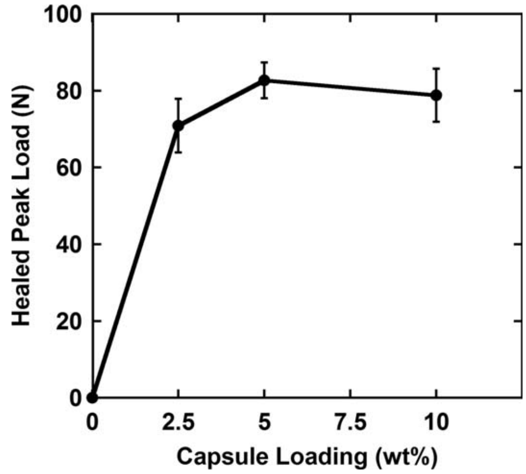


**FIGURE 8**. Healing performance for M/A capsules with BPO in PA capsules at a 5:1 ratio. The error bars represent one standard deviation based on 3–5 short-groove *in situ* TDCB samples and healing was reported at room temperature 24 h after the initial virgin fracture event.

and the amount of amine (0.5% MBDMA) were all kept constant [Fig. 4(b)]. For the results reported in Figure 4(b), the highest healing efficiency is obtained when capsules containing 20% (12 mL) EPA solvent were used ($\eta = 0.63$), whereas a lower healing performance was observed with less or more solvent (3% EPA, $\eta = 0.15$ and 33% EPA, $\eta = 0.28$).

The ratio of the TMPET and Bis-EMA monomers used to this point was determined to be 3:1 from preliminary experiments. However, for this modified system, we sought to determine if this was the optimal ratio between TMPET and Bis-EMA, and evaluated the kinetics of polymerization with DSC and reference fracture tests. Different ratios of TMPET:Bis-EMA were cured with 1 wt % BPO and 0.1 wt

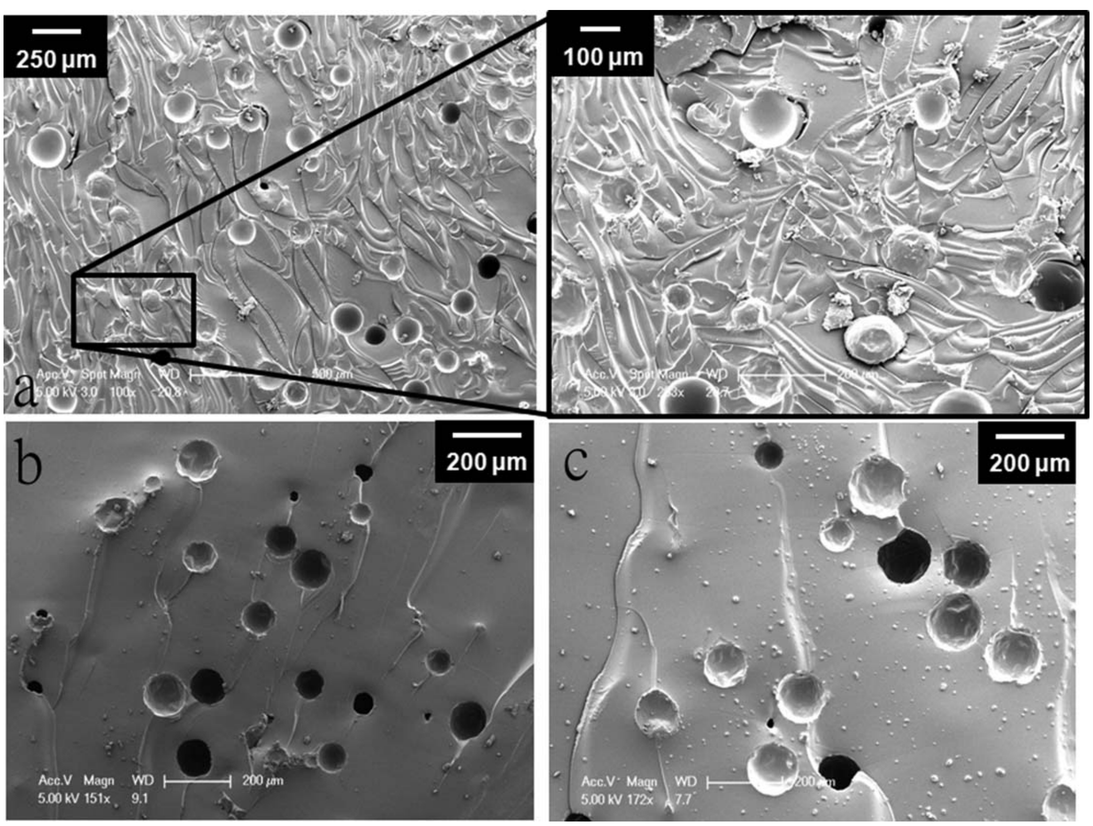


**FIGURE 7**. SEM images of healed fracture planes for (a) self-healing two capsule system (10 wt % capsule loadings), (b) BPO in PA capsules only, and (c) M/A capsules only.

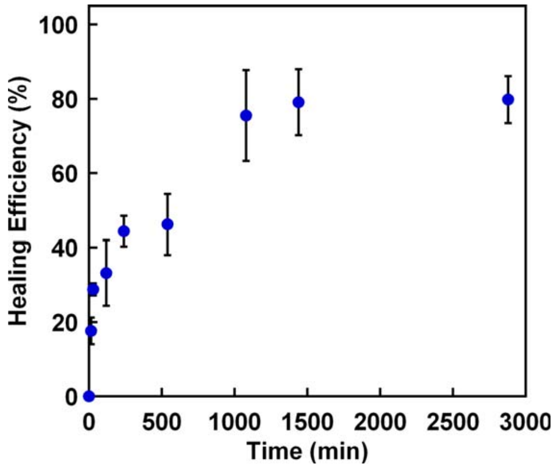


**FIGURE 9**. Kinetics of self-healing for TDCB specimens with 5 wt % capsule loading of BPO initiator and monomer/activator capsules at time intervals after initial fracture has occurred. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

% DMA and compared to previously reported experimented results.[22] Polymerization was monitored for 2 h by isothermal DSC at room temperature for each ratio and compared to the total heat of reaction from dynamic experiments at the same ratio. As reported in Figure 5(a), overall monomer conversion increased as the amount of TMPET (a trifunctional acrylate) increased relative to Bis-EMA (a bifunctional acrylate. The highest percent conversion (79%) was obtained for the 4:1 TMPET:Bis-EMA mixture, and this ratio also gave the lowest onset temperature (46°C) during dynamic DSC experiments. Similar results were observed for fracture and healing tests of reference test specimens healed with different monomer mixtures [Fig. 5(b)]. For these experiments, various M/A solutions were prepared with a consistent amount of amine and solvent—0.5% MBDMA and 20% EPA—and then added at a 5:1 ratio to 9.9 wt % BPO in PA solution. The prepared healing solution was then injected into the crack plane of fractured samples composed of neat EVE (no capsules), clamped together, and allowed to

**TABLE I. Summary of Self-healing Test Results for Specimens Containing 5% Capsules (5:1 Ratio of Monomer to Initiator Capsules**

| Healing Temperature (°C) | Healed Peak Load (N) | Healing Efficiency (%) | # of Samples |
|---|---|---|---|
| 25 | $82.7 \pm 4.6$ | $74.6 \pm 2.0$ | 3 |
| 37 | $70 \pm 6.4$ | $58.9 \pm 6.4$ | 5 |
| 37 (in SBF)[a] | $76.8 \pm 15.7$ | $64.4 \pm 13.2$ | 10 |

[a]SBF = simulated body fluid solution at pH 7.25.

heal at RT for 24 h. The highest healing efficiency (40%) was obtained for the 4:1 TMPET:Bis-EMA case. In contrast, the lowest efficiency was observed for pure Bis-EMA (no TMPET), which corresponded to the lowest observed monomer conversion by DSC.

Attempts to synthesize capsules with the 4:1 TMPET:-Bis-EMA ratio were ultimately unsuccessful through multiple experimental conditions. Evidence that the viscosity of the 4:1 mixture was too high or was interfering with the encapsulation chemistry focused our efforts on the 3:1 ratio of TMPET:Bis-EMA, which had given high monomer conversion percentages in the kinetics study. This ratio of the monomer was successfully encapsulated, and the resulting microcapsules were dry and free-flowing. For all subsequent self-healing studies, capsules containing a 3:1 ratio of the TMPET:Bis-EMA monomers was used.

**Self-healing performance**

Self-healing was assessed by repeated fracture of TDCB specimens with no external intervention during healing. Fracture specimens contained 5 wt % capsules in EVE matrix in a 5:1 ratio of M/A capsules (75% 3:1 TMPET:Bis-EMA, 0.5% MBDMA, 20% EPA) to BPO. A summary of test results is reported in Figure 6 together with various control systems. Healing efficiencies at RT are reported for samples tested 24 h after the initial fracture event. Very little healing was observed for samples containing only initiator capsules, whereas about 20% healing efficiency

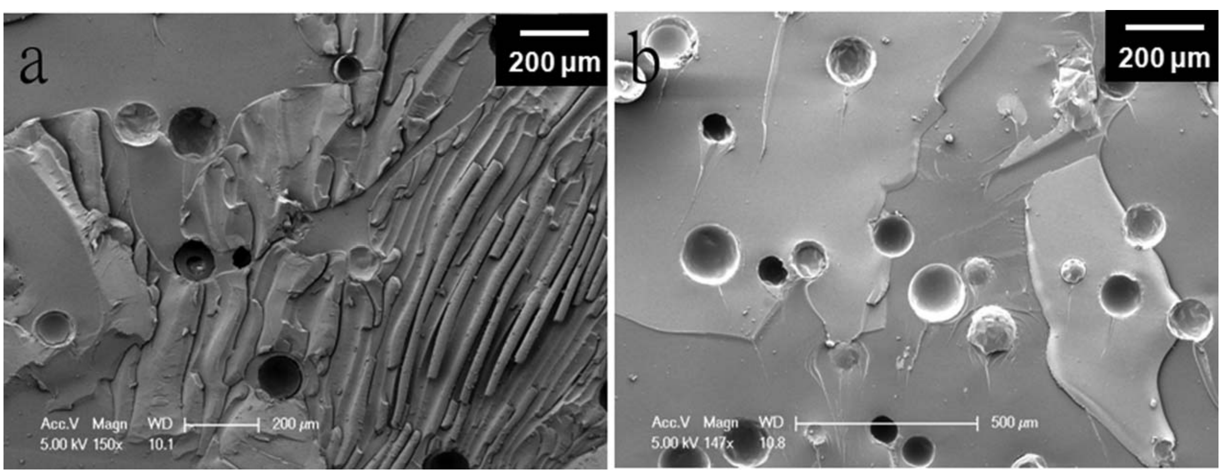


**FIGURE 10**. SEM images of healed fracture surfaces after healing at 37°C in the environmental chamber at 40% relative humidity (a) immersed in the SBF and (b) not immersed.

($\eta = 0.20$) was noted for specimens with M/A capsules only. Some healing occurs from the released M/A solution with residual BPO solid particles within the EVE matrix. When compared to the other control systems, the self-healing system having both capsules exhibits significantly greater healing efficiency. SEM imaging of fracture surfaces reveals clear evidence of *in situ* generation of a polymer film on the crack plane during healing [Fig. 7(a)]. In stark contrast, no evidence of a polymer film could be detected for control specimens [Fig. 7(b,c)].

The relationship between capsule loading and healing efficiency was systematically explored and the best result was observed from healing with a 5 wt % capsule loading (Fig. 8). Additionally, the kinetics of self-healing was evaluated for specimens containing 5 wt % capsules (Fig. 9).[15,33,34] Within 14 min of the initial virgin fracture event, about 20% fracture toughness recovery was observed and full healing was achieved by about 24 h.

### SBF environment

We analyzed the self-healing of samples in a SBF environment[24] to demonstrate feasibility as a self-healing biomaterial. SBF was prepared following previously reported procedures at a pH 7.25[24] and equilibrated at 37°C in an environmental chamber. One set of TDCB samples containing 5 wt % capsules was prepared and immersed in the SBF immediately following the virgin fracture event. Another set of identical samples were prepared and exposed to the same temperature and humidity conditions, but not immersed in the SBF to serve as a control. After 24 h, the samples were dried and fracture tested at RT. The results are shown in Table I. Within error, the samples in and out of the SBF were comparable in their healing performance. By examining the fracture surfaces of healing specimens for each set, a different morphology of polymer film was present on the samples immersed in the SBF (Fig. 10). However, exposure to SBF does not degrade the self-healing chemical reaction and high healing efficiency was obtained.

## CONCLUSIONS

A two-capsule system was demonstrated self-healing biomaterials based on free-radical polymerization. One capsule contains a peroxide initiator in solution, while the other capsule contains two acrylate monomers and a tertiary amine in solvent. All reaction components were systematically optimized to achieve high healing efficiency (75%) at room temperature in an EVE matrix. Healing was studied as a function of time, temperature, and in a SBF environment. The possible applications for this system have not been fully explored, and could be expanded for use in dental resins and acrylic-based orthopedic cements, as the chemistry used is based on polymerization of acrylate-containing monomers.

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