

Physical Characterization of a Self-Healing Dental Restorative Material

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ABSTRACT: The objectives of this study were to determine the efficacy of self-healing a highly filled composite and to investigate the physical properties of a model dental compound formulated to autonomously heal cracks. A visible light cured model resin consisting of TEGMA : UDMA : BisGMA (1 : 1 : 1) at 45% w/w with silane 0.7 μ glass was formulated with a self-healing system consisting of encapsulated dicyclopentadiene and Grubbs' catalyst. The base resin was also formulated and characterized with the microcapsules alone, Grubbs' catalyst alone, and no healing additives. Fracture toughness (K_{Ic}) was assessed using single edge notch specimens in three-point bend ($n = 12$). Data was analyzed with ANOVA/Tukey's at $p \leq 0.05$. DMA was

performed from -140 to 250°C at $2^\circ/\text{min}$ and 1 Hz. Storage and loss modulus, T_g and $\tan \delta$, was recorded for each material. The self-healing material was loaded to failure, was left to sit for 7 days and then loaded a second time to failure to determine healing in the material. These specimens had a $K_{Ic} = 0.69 \pm 0.072$ for a 57% average recovery rate of the original fracture toughness. The fracture toughness of the self-healing material was statistically similar to the control. The modulus decreased in the composites with encapsulated dicyclopentadiene. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 428–434, 2010

Key words: composites; dental polymers

INTRODUCTION

Despite numerous preventive oral health strategies, dental caries remains a significant oral health problem. More than 50% of children aged 6–8 will have dental caries and over 80% of adolescents over age 17 will have experienced the disease.¹ Caries is also seen in adults both as a primary disease and as recurrent disease in already treated teeth. Advances in diagnosis and treatment have led to noninvasive remineralizing techniques to treat caries. However, mechanical removal of diseased hard tissue and restoration and replacement of enamel and dentin is still the most widely used clinical strategy for treating primary caries, restoring function to the tooth, and also blocking further decay. In addition, nearly 50% of newly placed restorations are replacements of failed restorations.^{2–6} Clearly, restorative materials are a key component of treating this widespread disease.

The selection of a restorative material has significantly changed in recent years. Although dental amalgam is still considered a cost effective material, there is a growing demand for tooth colored alternatives that will provide the same clinical longevity that is enjoyed by dental amalgam. The use of composite resins has grown significantly internationally as a material of choice for replacing amalgam as a restorative material for posterior restorations.^{5,6} This demand is partially consumer driven by preference for esthetic materials and the concerns regarding the mercury content of amalgam.⁷ It is also driven by dentists recognizing the promise of resin-based bonded materials in preserving and even supporting tooth structure. Numerous studies have suggested that bonding the restoration to the remaining tooth structure decreases fracture of multi-surface permanent molar restorations.^{8–11} Unfortunately, modern composite resins have not yet achieved the level of mechanical properties found in dental amalgam. This has led to shorter clinical service and narrower clinical indications for composite resin materials compared to amalgam.

Manhart's¹² thorough review of the clinical literature from 1990 to 2003 reported a mean annual failure rate of 2.2% with a range of 0–9% for direct composite restorations. Fracture of composite resins is cited by numerous clinical investigators as the second most common reason for restoration

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replacement.³⁻⁶ Burke reports that more than 25% of composite resin replacements are driven by some form of fracture.² Fracture failures are typically described as either bulk or marginal fractures. The most frequently cited reason for restoration replacement is recurrent decay around or adjacent to an existing restoration. It is likely that fracture at the margin can lead to a clinical environment at the interface between a restoration and the tooth that collects dental plaque and thus promotes decay. Therefore, improving the fracture resistance of a dental restorative might not only reduce failures due to fracture but also recurrent caries as well.

Numerous strategies have been used in the drive to develop resin based materials with greater mechanical properties and thus better resistance to fracture failure. Some have focused on the resin continuous phase by maximizing conversion and crosslinking.¹³ Most initiatives have targeted manipulation of the discontinuous (filler) phase of the composite resin. Optimizing filler size and increasing filler loading, improving filler bonding to the resin matrix, using fiber fillers and nano sized fillers have all been the strategies that have realized modest physical property improvement.¹⁴ Nano structured materials may represent a viable strategy for generating a dental restorative with superior physical properties. These materials have the advantage of significantly changing the bulk properties of a material by making small changes in the constituent building blocks of the material.¹⁵

Contemporary understanding of fracture fatigue principles define a three-staged fracture process.¹⁶ The first is crack initiation, followed by slow crack growth, then fast fracture. The last phase is very short and thus the useful fracture resistance of a material is accounted for in the first two phases. In the case of a dental composite resin, subsurface porosities or micro-cracks, filler particles, crazes, or surface heterogeneities can all be the nucleation locations for crack initiation. Water exposure can also accelerate slow crack growth by degrading the filler-matrix interface and by swelling the matrix resins.¹⁷⁻¹⁹

Dispersed fillers can in theory blunt crack propagation and disperse the energy of slow crack propagation.²⁰ However, the dynamic environment of the oral cavity with cyclic loading and moisture and other solvent attack can clearly overwhelm the intrinsic ability of conventional materials to resist crack growth that leads to catastrophic material failure.

The early efforts of self healing by Dry and Li concentrated on structural composites.^{21,22} An encapsulated liquid repair system that consisted of brittle wall containers was mixed into a structural material. The containers were fractured during impact allowing a liquid repair resin to flow into the area of damage where it was then cured. The importance of their

work was demonstrating that structural concrete with stored repair materials did not weaken the bulk physical properties of the material. Dry demonstrated the concept for repairing cracks in polymer matrices using glass capillary tubes.²³ Pang has described a "bleeding composite" where an ultraviolet fluorescent dye was used to visualize penetration of a healing agent in to cracks induced into a structural polymer while restoring mechanical strength to the material.²⁴

Investigations of microcapsule filled polymers have used different terms such as hollow spheres, hollow particles, and bubbles. A main example in the literature reports the behavior of glass microcapsules in polymer systems.²⁴ Similar to the concrete work, a degradation of the properties was not observed. For example, an epoxy system with a 10% volume fraction of glass microcapsules demonstrated a 127% increase in fracture toughness.²⁵⁻²⁷ However, transferring these specific approaches into a practical dental restorative would be limited by the lack of compatibility of hollow glass tubes as a filler component in a dental restorative material. These fractured reservoirs would potentially be highly damaging to opposing teeth.

White²⁸⁻³¹ has introduced a novel polymeric filler as an approach for a bio-mimetic self healing polymer system. In his model epoxy system, dicyclopentadiene was encapsulated in urea-formaldehyde microcapsules. These were dispersed in the matrix along with a catalyst based on a metathesis polymerization reaction. As a propagating crack ruptures the microsphere, the dicyclopentadiene healing agent is released, filling the flaw and becoming exposed to the catalyst. Contact with the catalyst phase initiates polymerization and the healing agent rebuilds structural integrity across the crack plane. Upon optimization, the new structural epoxy formulated by the team at Illinois was able to recover more than 90% of its initial fracture toughness.²⁹

In this article, we explored the efficacy of the aforementioned approach in a model dental composite. The dental composite system provides a unique challenge using this approach in that it is highly filled with glass filler. This system is also an acrylic based system, as opposed to an epoxy based system, thereby determining the efficacy of the olefin metathesis chemistry in a different chemical environment. Additionally, we performed dynamic mechanical analysis on the system incorporating the various healing agents in the composite to determine how these types of fillers affected the mechanical properties of the composite. Although there are issues associated with biocompatibility and esthetics with this specific chemical system for use as a dental material, successful demonstration of self healing in this model should lead to an increased effort in a chemical approach suitable for the oral environment.

EXPERIMENTAL

Materials

The following dental monomers used as the continuous phase in the composites: bisphenol-A-glycidyl dimethacrylate (bisGMA), triethyleneglycol dimethacrylate (TEGDMA), and urethane dimethacrylate (UDMA) were used as received from Esstech. The photoinitiator system was camphorquinone and ethyl-4-dimethylaminobenzoate both from Sigma-Aldrich. The filler used was silanated barium borosilicate glass with a mean particle size of 0.7μ also provided by Esstech Inc. (Essington, PA). Dicyclopentadiene was purchased from Aldrich and was purified by filtration and vacuum distillation prior to microencapsulation. Encapsulation of the dicyclopentadiene was performed by an acid catalyzed *in situ* polymerization of formaldehyde and urea following a published procedure.³² The following chemicals used in the encapsulation were purchased from Aldrich and were used as received: urea, formaldehyde, ammonium chloride, and resorcinol. The ethylene maleic anhydride copolymer was purchased from Zeeland Chemicals. Grubbs' catalyst was purchased from Aldrich and used as received.

Preparation of composites

For the control composite, resin matrix (45% wt fraction) consisted of Bis-GMA/UDMA/TEGDMA mixtures (1 : 1 : 1 wt/wt/wt). The monomers were mixed first for 2 min at 3000 rpm in a Flacktek (Landrum, SC) DAC 150 Speedmixer. The silanated glass (55% wt fraction) was mixed in three equal parts with the resin using the Speedmixer for three 2 min intervals at 3000 rpm. The photoinitiator system which consisted of camphorquinone (0.5 wt %) and ethyl-4-dimethylaminobenzoate (0.5 wt %) was added last and mixed for 2 min at 3000 rpm. In the composites containing the self healing fillers, the Grubbs' catalyst and dicyclopentadiene spheres were added after the glass, but before the photoinitiator system. We found this to lead to more consistent results, perhaps due to minimizing an interaction between the dimethylaminobenzoate and the Grubbs' catalyst. These fillers replaced the weight fraction of the resin phase, keeping 55% silanated glass constant between each run. The self healing fillers were also mixed at 3000 rpm for 2 min after the addition of the glass filler.

Fracture toughness measurements

For fracture toughness measurements, specimen with correct geometry for the single-edge notched method were prepared (Fig. 1) by filling a stainless steel mold ($2.5 \text{ mm} \times 5 \text{ mm} \times 20 \text{ mm}$) with unpolymerized material, taking care to minimize entrapped

air. The lower surface of the mold was overlaid with a glass slide covered with a Mylar sheet to avoid adhesion with the unpolymerized material. The completed assembly was irradiated by using a Spectrum 800 curing light at 600 mW/cm^2 . Specimens were light cured in appropriate molds in five overlapping steps for 30 s on both sides of the specimen. Then, the mold was dismantled and the composite was carefully removed by unscrewing the stainless steel mold. Specimens were stored in water at 37°C for 24 h before testing. Ten to twelve specimen bars were prepared for each composite. The single-edge notched specimens were tested at a loading rate of 0.5 mm/min on a universal testing machine from the Instron (Norwood, MA) using a maximum load cell capacity of 250 N.

Dynamic mechanical analysis

For DMA tests, bar specimens were prepared by filling a stainless steel mold ($2 \text{ mm} \times 2 \text{ mm} \times 40 \text{ mm}$) with unpolymerized material, taking care to minimize entrapped air. The lower surface of the mold was overlaid with a glass slide covered with a Mylar sheet to avoid adhesion with the unpolymerized material. The completed assembly was irradiated by using a Spectrum 800 curing light at 600 mW/cm^2 . Specimens were light cured in appropriate molds in five overlapping steps for 30 s on both sides of the specimen. Then, the mold was dismantled and the composite was carefully removed by unscrewing the stainless steel mold. Specimens were stored in water at 37°C for 24 h before testing. Three specimen bars were prepared for each composite. DMA tests were performed on a Diamond dynamic mechanical analyzer (Perkin-Elmer, Waltham, MA) using a dual-cantilever clamp. A frequency of 1 Hz was applied at the temperature range of -140 to 240°C at a heating rate of 2°C/min . Storage modulus (E'), loss modulus (E''), and tangent delta were plotted against temperature over this period. DMA measurements were taken on samples that were not damaged. These experiments were performed to determine how the fillers affected the modulus values of these composites.

RESULTS AND DISCUSSION

Initial efforts on this project focused on the replication of White's self healing approach in a dental composite. The dental composite presented several different challenges from the original work of White in neat epoxy resins. The major difference between the epoxy resin and the dental composite is that the dental composite is highly filled with glass. For example, it was unclear if the presence of 55% (w/w) glass filler would statistically prevent the healing agent containing microcapsules from

being distributed in an effective manner that would allow efficient healing. Other challenges included the new chemical environment for the Grubbs' catalyst and whether this olefin metathesis catalyst would remain stable in the presence of the various functional groups associated with the dental monomers and initiator system. Another concern about the incorporation of White's approach for a dental composite was whether liquid filled microcapsules would also toughen a dental composite comparably to an epoxy resin.

Brown and coworkers²⁹ determined the important variables for efficient healing and increased fracture toughness in a model epoxy resin. They found that the optimum healing efficiency was attained with catalyst loadings greater than 2.5% (in a range of 0–4 wt %). In terms of microcapsule loading, virgin fracture toughness increased with loading up to 15 wt % of this component. It was found that although microcapsule size had a direct influence on the volume of healing agent released into the crack plane, healing efficiency was not limited by microcapsule size. However, fracture toughness of the composite and the healed material improved with decreasing size of the microcapsule. Maximum healing efficiency of 90% was obtained within 10 h of the fracture event under the optimized formulations in this study of this epoxy system. We used the work of Brown as a guide to our formulations to show the efficacy of autonomic healing in a dental composite. We used 2 wt % of Grubbs' catalyst that had an average size of 200–400 nm and 5 wt % of microcapsules that had an average size of 50 μm for the preparation of the dental composites. It was not our intention to optimize this approach for demonstrating autonomic healing in a dental composite as we were concerned with the biocompatibility of the Grubbs' catalyst and dicyclopentadiene.

The dental resin matrix we used was a mixture of bisphenol A glycidyl dimethacrylate, urethane dime-

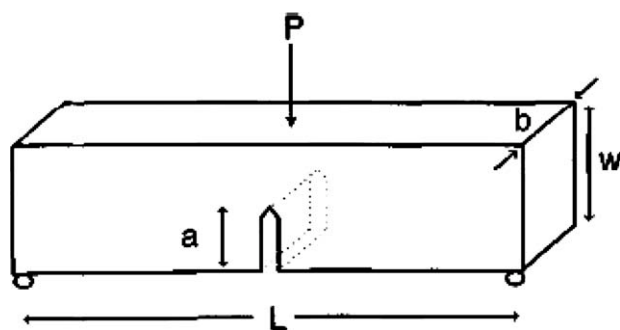


Figure 1 Specimen geometry for the determination of fracture toughness by the single-edge notched method. $K_{Ic} = [3PLa^{1/2}/2bw^2] \times f(a/w)$, where $w = 5$ mm; $b = 2.5$ mm; $a = 2.5$ mm; $L = 20$ mm; and $f(a/w) = 1.93 - 3.07(a/w) + 14.53(a/w)^2 - 25.11(a/w)^3 + 25.80(a/w)^4$.

TABLE I
The Average K_{Ic} Values of Different Formulations

| Glass filler percent | Dicyclopentadiene microcapsules (wt %) | Grubbs' catalyst (wt %) | K_{Ic} ($\text{MPa} \times \text{m}^{1/2}$) |
|----------------------|--|-------------------------|---|
| 55 | | | 1.21 ± 0.09 |
| 55 | 5 | | 1.30 ± 0.07 |
| 55 | | 2 | 1.53 ± 0.17 |
| 55 | 5 | 2 | 1.10 ± 0.06 |

The control formulation did not include any of the healing chemistry. The other formulations contained both of the healing agents together and individually. The data reported is the average of three sets of 10–12 samples each.

thacrylate, and triethyleneglycol dimethacrylate. The system was initiated using ethyl-4-(dimethylamino)-benzoate and camphorquinone and was filled with silanated glass. The method used to determine fracture toughness of these composites was the single-edge notched method. Figure 1 shows the sample geometry used in this method. The samples were prepared in the mold using the following dimensions ($w = 5$ mm, $b = 2.5$ mm, $a = 2.5$ mm, $L = 20$ mm).³³

Table I listed below shows the average K_{Ic} values of different formulations. The control formulation did not include any of the healing chemistry. The other formulations contained both of the healing agents together and individually. The data reported is the average of three sets of 10–12 samples each. The single-edge notched specimens were tested at a loading rate of 0.5 mm/min on a universal testing machine from the Instron. The control dental composite, filled only with glass, had an average K_{Ic} value of $1.21 \text{ MPa} \times \text{m}^{1/2}$. When 5 wt % of the resin matrix was replaced with dicyclopentadiene filled microcapsules with an average size of 50 μm , the average K_{Ic} value was $1.30 \text{ MPa} \times \text{m}^{1/2}$. When 2 wt % of the resin matrix was replaced with Grubbs' catalyst, the K_{Ic} of the composite was $1.53 \text{ MPa} \times \text{m}^{1/2}$. Finally, when 7 wt % of the resin matrix was replaced with 5 wt % dicyclopentadiene microcapsules and 2 wt % Grubbs' catalyst, the K_{Ic} was $1.10 \text{ MPa} \times \text{m}^{1/2}$. The wt % and size of the dicyclopentadiene filled microcapsules and weight percent of Grubbs' catalyst used were based on what was optimal for the epoxy systems. Although the fracture toughness was slightly weakened in these composites, these systems were not optimized as it was not the goal of this preliminary research.

The efficacy of self-healing in the model dental composite was obtained by fracture toughness testing of single-edge notched specimens. The virgin fracture toughness was measured by the critical load, applied in a direction parallel to the notch, required to propagate a crack from the notch along

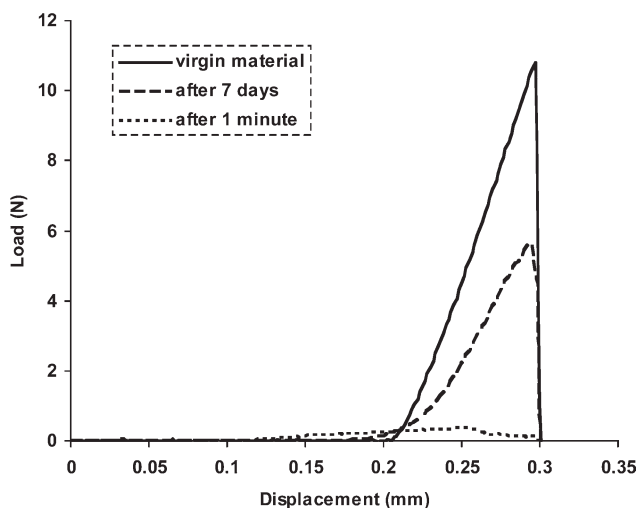


Figure 2 Load displacement curves of model dental compound with self-healing composition.

the mid-plane and fail the specimen (Fig. 2). On occasion, a sample completely broke in to two pieces. These samples were discarded and not included in the study. After the load was eliminated, the crack was permitted to heal at room temperature without external interference. Control and self-healing composites were prepared, where the following control specimens were produced: (1) dental composite containing neither Grubbs' catalyst nor dicyclopentadiene containing microcapsules; (2) dental composite with Grubbs' catalyst but no dicyclopentadiene containing microcapsules; and (3) dental composite with dicyclopentadiene containing microcapsules and no Grubbs' catalyst. Fracture toughness measurements were performed on samples with both of the self-healing fillers and the three controls after 1 min and 7 days. A representative load-displacement curve for a virgin self-healing composite sample is plotted in Figure 2. Load-displacement curves that were allowed to heal for 1 min and 7 days are also plotted in Figure 2. The results in Figure 2 demonstrate recovery of about 65% of the virgin fracture load for that sample. The sample that was allowed to heal for 1 min did not appear to be able to bear a significant load. This is likely due to the fact that the maximum load capacity of the cell was 250 N. Therefore, the small load that the sample was capable of bearing was too small to detect. The average K_{IC} for the self healed samples was $0.69 \text{ MPa} \times \text{m}^{1/2}$ with a standard deviation of 0.072. This correlates to 57% recovery of the virgin materials' fracture toughness. In great contrast, all three types of control samples showed no healing and were unable to carry any load upon reloading.

Dynamic mechanical analysis of the composites was performed to determine the effect of adding the self healing fillers on some of the physical properties

TABLE II
The Average E' , E'' , and $\tan \delta$ Values of Different Formulations

| Sample | $E' \times 10^9$ (Pa) | $E'' \times 10^8$ (Pa) | T_g ($^{\circ}\text{C}$) | $\tan \delta$ |
|--------------------|-----------------------|------------------------|------------------------------|---------------|
| Control | 6.7 ± 0.2 | 3.5 ± 0.1 | 137 | 0.2342 |
| Capsules | 5.1 ± 0.3 | 3.1 ± 0.2 | 125 | 0.2493 |
| Grubbs' | 7.7 ± 0.1 | 4.2 ± 0.1 | 131 | 0.2289 |
| Capsules + Grubbs' | 4.1 ± 0.4 | 2.5 ± 0.3 | 126 | 0.2460 |

The control formulation did not include any of the healing chemistry. The other formulations contained both of the healing agents together and individually.

of the modified dental restorative material. Table II reports the storage modulus (E'), loss modulus (E''), glass transition temperature (T_g), and $\tan \delta$ values for the four sets of composites at 37°C at a frequency of 1 Hz. The E' is a sign of elastic behavior and describes the capacity of the composite to store elastic energy associated with recoverable elastic deformation. The plot of the E' versus temperature for the four sets of samples is shown in Figure 3. The E'' , which is associated with unrecoverable viscous loss, specifies the capacity of the composite to dissipate mechanical energy through conversion into heat by molecular motion. The loss tangent, $\tan \delta$, is the ratio E''/E' . The plot of the $\tan \delta$ as a function of temperature for the four sets of samples is shown in Figure 4. The T_g is reported as the peak of $\tan \delta$.

Whereas the fracture toughness measurements of the set of four samples did not statistically show a decrease in the mechanical properties of the model

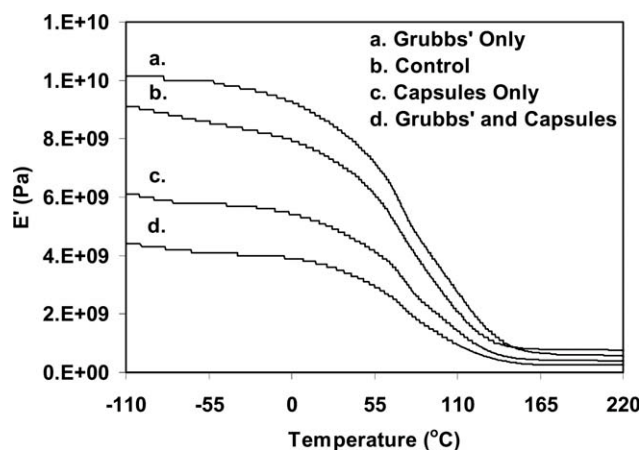


Figure 3 E' scans from dynamic mechanical analysis thermograms of a representative series of composites that were synthesized with different formulations. Scan a represents the formulation with 2 wt % of Grubbs' catalyst, scan b represents the model composite with no healing additives, scan c represents the formulation with 5 wt % of the microcapsules, and scan d represents the formulation with both 2 wt % Grubbs' catalyst and 5 wt % microcapsules.

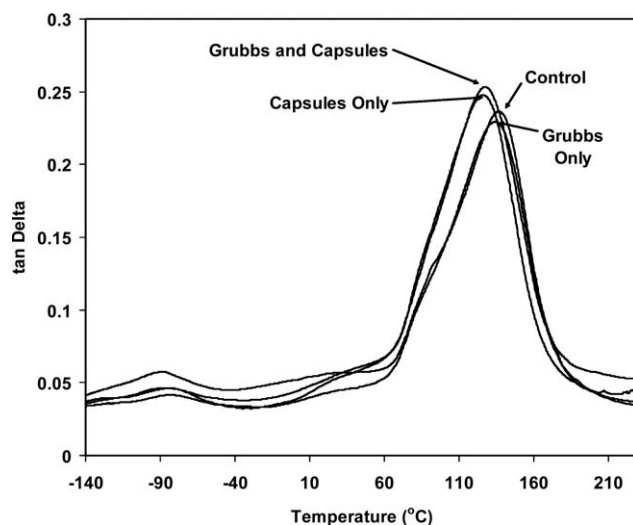


Figure 4 Tan δ scans from dynamic mechanical analysis thermograms of a representative series of composites that were synthesized with different formulations. These formulations include (a) one with 2 wt % of Grubbs' catalyst, (b) one with no healing additives, (c) one with 5 wt % of the microcapsules, and (d) one with both 2 wt % Grubbs' catalyst and 5 wt % microcapsules.

composites, the addition of 5 wt % microcapsules decreased the E' of the composite containing the microcapsules only and the microcapsules combined with the Grubbs' catalyst. This phenomenon could be due to the lack of interaction in terms of bonding between the microcapsules and the continuous phase. Since the fracture toughness did not decrease by the addition of the microcapsules, the microcapsules did not likely interfere with crack propagation in the composite. Although there is a decrease in the crosslink density of the overall composite by replacing a small percent of the resin with microcapsules, we do not believe that is the primary source of the decrease in modulus. The fact that we decreased the resin component in effect increases the ratio of glass filler to the resin phase. It has been shown that an increase in glass filler relative to the resin phase increases the modulus of a composite. The fact that the corresponding increase is not seen, and actually a decrease in modulus is observed we feel that the decrease in modulus is primarily due to the fact that the additional phase is not part of the continuous network. This hypothesis could be supported by looking at similar systems where large particles have been incorporated into the system. Epoxy systems toughened by large rubber particles in which the filler is compatible with the continuous phase tend to show an increase in modulus with increased amounts of rubber filler.^{26,34–36} However, epoxy systems filled with poly(dimethylsiloxane) particles which are incompatible with the continuous phase show a decrease in the modulus of the composite with increased amounts of filler.³⁷

Incorporation of the Grubbs' catalyst resulted in similar results when comparing the fracture toughness to the modulus measurements. This might be explained by the fact that the Grubbs' catalyst particles are significantly smaller than the microcapsules. Whereas the microcapsules were on average 50 μm , the Grubbs' catalyst fillers were on the order of a few hundred nanometers.

CONCLUSIONS

The objective of this study was to investigate the physical properties of a model dental compound formulated to autonomously heal cracks. A visible light cured model resin consisting of TEGMA : UDMA : BisGMA (1 : 1 : 1) at 45% w/w with silane 0.7 μ glass was formulated with a self-healing system consisting of encapsulated dicyclopentadiene spheres and Grubbs' metathesis catalyst. Fracture toughness (K_{Ic}) was assessed using single edge notch specimens. Dynamic mechanical analysis was performed from -140 to 250°C at $2^\circ/\text{min}$ and 1 Hz. Storage and loss modulus, glass transition temperature, and tangent of delta was recorded for each material. The self-healing material was loaded to failure, was left to sit for 7 days and was then loaded a second time to failure to determine healing in the material. These specimens had a K_{Ic} of 0.69 ± 0.072 for a 57% average recovery rate of the original fracture toughness. The fracture toughness of the self healing material was statistically similar ($p > 0.05$) to the control. These results suggest that despite the highly filled nature of dental composites, these materials can recover mechanical properties by the incorporation of embedded monomers and catalyst. Our future efforts will focus on approaches that focus on the incorporation of chemistry that address the issues of biocompatibility and esthetics.

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