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Stress Relaxation of Trithiocarbonate-Dimethacrylate-based Dental Composites

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Abstract

Objectives—To reduce polymerization-induced shrinkage stress while maintaining mechanical properties, reversible addition-fragmentation chain transfer (RAFT)-capable functional groups were incorporated into a photopolymerizable dimethacrylate-based dental composite. We hypothesize that the incorporation of trithiocarbonate-based RAFT functional groups into conventional dimethacrylate dental resins will reduce polymerization stress.

Methods—A trithiocarbonate dimethacrylate (TTCDMA) monomer, capable of undergoing radical-mediated RAFT, is mixed with 70 wt% BisGMA (bisphenylglycidyl dimethacrylate) and compared to a conventional dental resin comprised of TEGDMA (triethylene glycol dimethacrylate) and 70 wt% BisGMA. The shrinkage stress and methacrylate conversion were simultaneously measured during polymerization. The fracture toughness and elastic modulus were measured to evaluate the effect of the TTCDMA monomer on the mechanical properties. All the materials used herein were evaluated as a composite, including 75 wt% silica fillers. ANOVA (CI 95%) was conducted to assess the differences between the means.

Results—The TTCDMA composite exhibited a 65% stress reduction compared with TEGDMA-BisGMA though the reaction rate was slower than the conventional dental composite, owing to the additional RAFT reaction. The fracture toughness and elastic modulus of the TTCDMA-based composite were not significantly different than in the TEGDMA-based composite, while the T_g was decreased by 30°C to 155±2°C.

Significance—Despite only replacing the reactive-diluent, significant and dramatic stress reduction was observed while maintaining the elastic modulus and fracture toughness. This new RAFT-capable monomer shows great promise to replace the reactive diluent in BisGMA-based dental materials. Formulation optimization and further exploration of other RAFT-capable functional groups will provide further stress reduction in dental materials.

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Keywords

restorative material; low stress; polymer networks; trithio carbonate; addition-fragmentation chain transfer; photopolymerization

INTRODUCTION

Polymer-based composites have been vastly improved over the past few decades; however, volume shrinkage and the associated stress that evolve during curing remain a critical drawback, as they lead to microcracking, microleakage, and secondary caries [1]. During the polymerization of dimethacrylate-based resins, which represent the primary polymerizable component of dental composites, a large stress arises due to the nature of the monomer-polymer densification process. Once the resin undergoes a transition from a liquid-like to a solid-like material (i.e., sol-to-gel transition), the shrinkage stress begins to build throughout the remainder of the polymerization due to the decreasing of molecular spacing. Methacrylate-based polymerizations are particularly susceptible to stress development owing to both the low gel-point conversion [2] as well as the large amount of volume shrinkage per double bond that occurs [3].

There have been several approaches to reduce stress[4] that utilize different polymerizable functional groups and/or different polymerization mechanisms to reduce the volume shrinkage and/or delay the gel point, including thiol-ene [5–6] and thiol-yne reactions[7–8], polymerization-induced phase separation [9], and ring-opening polymerizations.[10–11] We have previously reported the incorporation of a reversible covalent bond, which undergoes addition-fragmentation chain transfer (AFCT – e.g., see Figure 1A), into a polymerizable material that leads to significant stress reduction.[12–14]. The AFCT functional groups facilitate stress relaxation throughout the polymerization by undergoing a bond breaking and reforming exactly the same chemical structure before the bond breaking with leading to rearrangement of network strands; [12–14] thus, this approach is focused on stress dissipation rather than reducing volume shrinkage. The allyl sulfide AFCT functional group was incorporated in both thiol-ene [12] and thiol-yne reactions [15] to yield significant polymerization stress reduction. Unfortunately, the effect is reduced in non-thiol containing resins, such as methacrylates, since the complete reversibility of the allyl sulfide AFCT mechanism requires the presence of thiyl radicals (See Figure 1(A)). While allyl sulfide incorporation into a methacrylate-based system does lead to reduced stress, the effect is significantly diminished with increasing methacrylate content [16]. The presence of the carbon-centered radical in methacrylate homopolymerizations leads to irreversible AFCT of the allyl sulfide group (See Figure 1(B)).

The trithiocarbonate functional group is frequently used as a reversible addition-fragmentation chain transfer (RAFT) agent to synthesize polymers having low polydispersity [17]. Unlike the allyl sulfide functional group, the trithiocarbonate functional group is capable of fully reversible AFCT when reacting with a carbon-centered radical, such as those present in a methacrylate polymerization (Figure 1(C)). We hypothesize that the incorporation of a trithiocarbonate-based dimethacrylate monomer will significantly lower the polymerization stress in a conventional dental resin compared with an otherwise similar dimethacrylate monomer formulation. Here, the effect of adding a trithiocarbonate dimethacrylate monomer to reduce stress was evaluated by replacing the reactive diluent, TEGDMA, within a conventional BisGMA-TEGDMA (bisphenylglycidyl dimethacrylate/triethylene glycol dimethacrylate) dental composite. In addition, fracture toughness and elastic modulus were measured to compare the mechanical properties. All experiments were performed on the formulated composite, which includes 75 wt% silica fillers.

MATERIALS & METHODS

Materials

The monomers and photoinitiator used in this study are shown in Figure 2. S,S'-bis[α,α' -dimethyl- α'' -(acetyloxy)ethyl 2-methyl-2-propenoate]-trithiocarbonate (TTCDMA, Trithio carbonate dimethacrylate) was synthesized from S,S'-bis(α,α' -dimethyl- α'' -acetyl chloride)-trithiocarbonate and 2-hydroxyethyl methacrylate (HEMA) following the procedure in the literature [18]. The crude oil was purified by dissolving it in a 9:1 hexanes:ethyl acetate mixture and subsequently filtering the insoluble impurities. Column chromatography was performed using an 8:2 hexanes/ethyl acetate solution. S,S'-bis(α,α' -dimethyl- α'' -acetyl chloride)-trithiocarbonate product was made by the chlorination of the S,S'-bis(α,α' -dimethyl- α'' -acetic acid)-trithiocarbonate with thionyl chloride [18]. S,S'-bis(α,α' -dimethyl- α'' -acetic acid)-trithiocarbonate was prepared according to a previously published procedure [19]. Bisphenylglycidyl dimethacrylate (BisGMA, provided by Esstech) and triethylene glycol dimethacrylate (TEGDMA, provided by Esstech) were used as received. Resins were composed of 70 wt.% BisGMA and 30wt.% of either TEGDMA or TTCDMA. A phosphine oxide, phenyl bis(2,4,6-trimethyl benzoyl) (BAPO, BASF Corp.), was utilized at 1.5 wt% in the resins as a visible light-active photoinitiator. 75 wt.% of barium glass filler (0.4 μ m, Schott(Elmsford, NY)), no surface treated) was used to comprise the composite.

Methods

Composite samples (2mm thickness) were irradiated at 70 mW/cm² intensity with 400–500 nm light (Acticure 4000) for 20 minutes to observe the conversion of the methacrylate functional group during polymerization. The methacrylate conversion was determined by monitoring the infrared absorption peak centered at 6166 cm⁻¹ (C=C-H stretching, overtone) using Fourier transform infrared (FTIR) spectroscopy (Nicolet 750). Specimens for fracture toughness test were prepared by photocuring composites at the same irradiation condition with the IR experiments in a cuboid mold (5.5 mm length * 25 mm width * 2.5 mm thickness) having a razor blade (2 mm length * 0.2 mm width * 2.5 mm thickness) which is positioned in the top-center of the mold by vertically across the cuboid to form the initial crack in the test specimen. After the specimens are separated from the mold, the specimen surface was ground with sandpaper to create uniform dimension and remove defects. Fracture toughness was measured by using a Mechanical Test System (MTS, The 858 Mini Bionix II Test System) using a 3-point bending test procedure (the force was applied from the opposite side of the initial crack of the specimen, specimen dimension; 25 mm length * 2.5 mm width * 5.5 mm thickness) with 20mm span and 1mm/minute rate. The elastic moduli (E') and glass transition temperature (T_g) of the polymerized samples were determined by dynamic mechanical analysis (DMA) (TA Instruments Q800). DMA experiments were performed at a strain and frequency of 0.1% and 1 Hz, respectively, and scanning the temperature twice at ramp rate of 2 °C/minute. The T_g was assigned as the temperature at the tan delta peak maximum [20–21] of the second heating scan. This methodology does not measure the T_g of the as cured sample due to changes in conversion that occur during the first thermal scan. Rather, the measurement is indicative of the maximum T_g achieved under these conditions. [22–23] Specimens used for DMA experiments were prepared by sandwiching the uncured composite in a rectangular mold (2 mm gap) and irradiating under the same conditions used for the FTIR experiments. The shrinkage stress was monitored using tensometry (Paffenbarger Research Center, American Dental Association Health Foundation)[6, 24], which was equipped with optical fibers which enable simultaneous monitoring of the reaction progression via FTIR spectroscopy. Uncured composite was injected between two glass rods which are positioned in a 9 cm beam length of the stainless steel beam. Samples were covered with a plastic sheath to

prevent oxygen inhibition of the methacrylate during polymerization. ANOVA (CI 95%) was conducted to determine differences between the means for all the reported results.

RESULTS

Fracture toughness and DMA measurements of the BisGMA-TEGDMA and BisGMA-TTCDMA composites are presented in Figure 3. The elastic modulus of the TTCDMA-based composite is slightly lower than for the TEGDMA-based composite over the temperature range from 10°C to 100°C. As the glass transition of the TTCDMA-based composite is lower than the TEGDMA-based composite, the TTCDMA-based composite also exhibits an elastic modulus decreases at correspondingly lower temperatures. The average fracture toughness value of the as-cured TTCDMA sample was higher than but not statistically different from the TEGDMA control at the 95% confidence level (Figure 3A).

The reaction kinetics for the BisGMA-TEGDMA and BisGMA-TTCDMA composites were monitored for 20 minutes during irradiation (Figure 4). The methacrylate conversion in the TTCDMA-based composite was lower initially; however, the final conversion was the same as the TEGDMA-based control system. The shrinkage stress evolution of the TTCDMA-based composite is slower than that of the TEGDMA-based composite. While both composites exhibited similar final conversion values, the final shrinkage stress of the TTCDMA-based system was 65% lower than the stress level of the TEGDMA-based composite (Figure 5A).

DISCUSSION

The TTCDMA monomer was designed to have a similar molecular structure with TEGDMA, targeting its use as a reactive diluent to replace TEGDMA while simultaneously adding RAFT capability to promote stress relaxation. Since the RAFT reaction is favorable when the leaving radical group is stable, the TTCDMA core, which replaces ethylene glycol, was designed to have a dimethyl substituted carbon adjacent to the trithiocarbonate; therefore, the carbon-sulfur fragmentation product (Figure 1C) generates a more stable tertiary carbon radical.[19] However, the molecular weight of TTCDMA is significantly larger than TEGDMA and thus the crosslink density of the network is slightly reduced at an equivalent conversion. Nevertheless, while the incorporation of the TTCDMA decreases the T_g compared with the control composite, its utilization does not affect the fracture toughness of the material (Figure 3A). More importantly, the TTCDMA-based composite, despite containing only 30% of monomers with the RAFT core, exhibits a much lower stress as compared with the TEGDMA-based composite (Figure 5A). Reduced polymerization rate can lower the final conversion; however, here, the TTCDMA-based composite exhibited an equivalent methacrylate conversion relative to the TEGDMA-based composite.

As shown in Figure 5B, the origin of the stress is also significantly different in these two systems due to the AFCT mechanism. In conventional dimethacrylate polymerizations, the stress begins to rise at very low conversions; however, the stress in the TTCDMA-based composite begins to rise only after nearly 40 % conversion of methacrylate groups. This behavior is in stark contrast to the TEGDMA-based composite where the stress begins to increase before 10 % methacrylate conversion. It is clear that the incorporation of a RAFT-capable functional group, particularly one such as the trithiocarbonate that is capable of multiple reversible reactions with a methacrylate radical, into a dimethacrylate polymerization, even in low amounts, dramatically alters the stress evolution behavior in these systems. This outcome represents a new paradigm to consider in methacrylate-based dental restorative materials for preserving overall network mechanics while reducing stress levels.

CONCLUSION

BisGMA-TEGDMA and trithiocarbonate-containing BisGMA-TTCDMA-based composites were investigated to demonstrate stress relaxation via RAFT. The trithiocarbonate functional group was implemented to successfully induce RAFT which led to network rearrangement. Ultimately, the inclusion of this mechanism resulted in a 65 % stress reduction as compared to the standard BisGMA-TEGDMA composite. Fracture toughness of the TTCDMA-based composite was slightly higher though not significantly different from the TEGDMA-based composite even though the TTCDMA-based composite has dramatically reduced stress. In summary, the RAFT mechanism for stress relaxation via the inclusion of trithiocarbonates and similar RAFT moieties has potential for replacing conventional dimethacrylate materials with nearly identical mechanical properties but stress levels that are a fraction of current composites.

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Figure 1.

(A) Schematic of the allyl sulfide AFCT mechanism in the presence of a thiyl radical which results in a symmetrical chemical structure that promotes reversibility. (B) Schematic of the allyl sulfide AFCT mechanism in the presence of a carbon-centered radical which results in an asymmetrical chemical structure and irreversibility. (C) Schematic of the RAFT mechanism of a trithiocarbonate in the presence of a carbon-centered radical which results in a symmetrical chemical structure and complete reversibility.

Figure 2.

Materials used: (1) BisGMA (2) TEGDMA (3) TTCDMA (4) BAPO

Figure 3.

(A) Fracture toughness, (B) Elastic modulus, and (C) tangent δ of BisGMA-TEGDMA 70/30 wt% (●) and BisGMA-TTCDMA 70/30 wt% (□) composites. Composites containing 1.5 wt% BAPO, 75wt% of silica filler were prepared by irradiation using a 400–500 nm wavelength filter at an intensity of 70 mW/cm².

Figure 4. Reaction behavior of the methacrylate group in BisGMA-TEGDMA 70/30 wt% (●) and BisGMA-TTCDMA 70/30 wt% (□) composites. Resins contain 1.5wt% BAPO and were cured using 400–500nm light at 70 mW/cm².

Figure 5.

Polymerization shrinkage stress versus (A) time and (B) methacrylate conversion for BisGMA-TEGDMA 70/30 wt% (●) and BisGMA-TTCDMA 70/30 wt% (□) composites. Composites shown here contain 1.5 wt% BAPO and 75wt% silica filler, and were irradiated at 70 mW/cm² using 400–500 nm light.

Table 1

Summary of the methacrylate conversion, stress, T_g , elastic modulus (E'), and fracture toughness for BisGMA-TEGDMA 70/30 wt% and BisGMA-TTCDMA 70/30 wt% composites. The composite is formulated with 75wt% filler and 25wt% resin. Resins includes 1.5 wt% of BAP0 as a visible light initiator and are exposed to 400–500nm light at 70mW/cm² for 20 minutes.

Systems	Methacrylate conversion	Stress [MPa]	T_g [°C]	E' at 25°C before heating [GPa]	Fracture Toughness [MPa·m ^{0.5}]
BisGMA-TEGDMA	0.67 ± 0.003 ^a	1.7 ± 0.04 ^a	184 ± 1 ^a	16 ± 3 ^a	1.18 ± 0.09 ^a
BisGMA-TTCDMA	0.68 ± 0.02 ^a	0.6 ± 0.02 ^b	155 ± 2 ^b	14 ± 2 ^a	1.24 ± 0.09 ^a

In each of the experiments, values followed by the same letter in the same column are not significantly different using an ANOVA test with a 95% confidence level.