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Investigation of thiol-ene and thiol-ene–methacrylate based resins as dental restorative materials

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ABSTRACT

Objectives. The objective of this work was to evaluate thiol-norbornene and thiol-ene–methacrylate systems as the resin phase of dental restorative materials and demonstrate their superior performance as compared to dimethacrylate materials.

Methods. Polymerization kinetics and overall functional group conversions were determined by Fourier transform infrared spectroscopy (FTIR). Flexural strength and modulus were determined with a 3-point flexural test. Polymerization-induced shrinkage stress was measured with a tensometer.

Results. Thiol-ene polymer systems were demonstrated to exhibit advantageous properties for dental restorative materials in regards to rapid curing kinetics, high conversion, and low shrinkage and stress. However, both the thiol-norbornene and thiol-allyl ether systems studied here exhibit significant reductions in flexural strength and modulus relative to BisGMA/TEGDMA. By utilizing the thiol-ene component as the reactive diluent in dimethacrylate systems, high flexural modulus and strength are achieved while dramatically reducing the polymerization shrinkage stress. The methacrylate–thiol-allyl ether and methacrylate–thiol-norbornene systems both exhibited equivalent flexural modulus (2.1 ± 0.1 GPa) and slightly reduced flexural strength (95 ± 1 and 101 ± 3 MPa, respectively) relative to BisGMA/TEGDMA (flexural modulus; 2.2 + 0.1 GPa and flexural strength; 112 ± 3 MPa). Both the methacrylate–thiol-allyl ether and methacrylate–thiol-norbornene systems exhibited dramatic reductions in shrinkage stress (1.1 ± 0.1 and 1.1 ± 0.2 MPa, respectively) relative to BisGMA/TEGDMA (2.6 ± 0.2 MPa).

Significance. The improved polymerization kinetics and overall functional group conversion, coupled with reductions in shrinkage stress while maintaining equivalent flexural modulus, result in a superior overall dental restorative material as compared to traditional bulk dimethacrylate resins.

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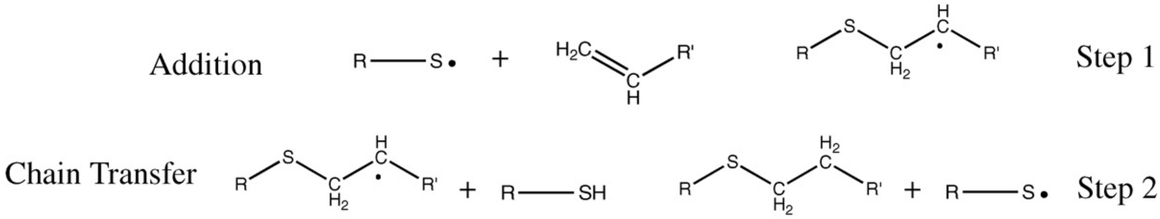
1. Introduction

Resin-based composites are currently utilized as an alternative to dental amalgams for repairing tooth defects. The resin component of these composites is composed primarily of either an aromatic or urethane dimethacrylate, typically 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane (BisGMA) or urethane dimethacrylate (UDMA). Due to the high viscosity of these materials, a diluent is added to increase conversion and manipulate the consistency of the composite paste. The most commonly utilized diluent is triethylene glycol dimethacrylate (TEGDMA). Arguably, the most significant drawback of polymer-based materials is shrinkage and shrinkage stress that arise during polymerization [1–3]. Upon curing, composite systems undergo from 2% to 4% volumetric shrinkage, resulting in stresses that arise between the composite and the tooth of as much as 130 kg/cm^2 [4]. Bonding between the composite and tooth is negatively impacted by these shrinkage stresses and can lead to marginal gaps through which saliva and bacteria can penetrate into the tooth structure, leading to marginal staining, if not secondary cavity formation [5,6].

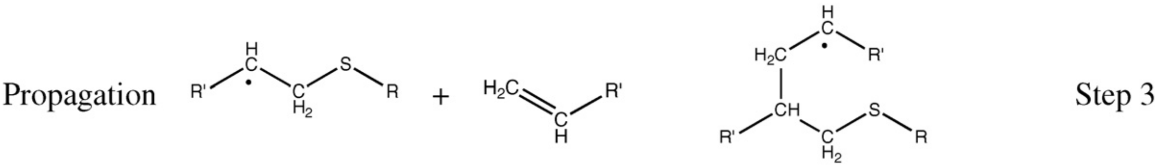
In addition to undergoing polymerization shrinkage, most polymer composites exhibit relatively low double bond conversion upon curing. Multifunctional monomers used for dental restorations typically exhibit final double bond conversion of 50–75% [7–9]. Furthermore, researchers have found at least 6% residual monomer in BisGMA/TEGDMA resin systems after curing [10], which can be heightened by cyclization [11] or lower conversion. This unreacted monomer is extractable and may leach into the body where various fates are possible. Even though the dentin layer below a restoration has been found to reduce the amount of monomer that diffuses to the pulp space [12], concern still remains about both local and systemic sensitization and allergic reactions some patients exhibit to residual monomer [13,14].

In this work, thiol-ene-based polymer systems are evaluated as alternatives to purely methacrylate-based resins. Thiol-enes differ fundamentally from methacrylate systems in that they polymerize via radical-mediated step-growth reactions between multifunctional thiol and vinyl monomers rather than a chain-growth process [15,16]. Initiation occurs via typical photoinitiators, such as excitation of diaryl ketones followed by hydrogen abstraction (most commonly benzophenone) and by direct cleavage initiators such as dimethoxyphenyl acetophenone (DMPA) [15,17] or without any initiators at all [15,18]. Camphorquinone and an amine accelerator, as is commonly utilized in dental materials, can also be utilized to initiate polymerization. Radical termination occurs via bimolecular radical–radical recombinations [19,20].

In cases where the ene monomer is not homopolymerizable, the polymerization proceeds by a step-growth addition mechanism via sequential propagation of a thiyl radical through an ene functional group followed by chain transfer to the thiol, which regenerates the thiyl radical [15,16,18,21,22]. This successive propagation/chain transfer mechanism is the basis for the traditional thiol-ene step-growth mechanism and is presented in the scheme below:



An additional level of complexity is involved in the polymerization mechanism due to additional propagation steps that occur when a ternary thiol-ene (e.g., methacrylate–thiol-ene) polymerization is considered [18,23,24]. The propagation mechanism for these types of thiol-ene systems includes a carbon radical propagation step (step 3) in addition to the thiyl radical propagation and chain transfer steps (steps 1 and 2). A ternary system therefore exhibits a combination of both step-growth and chain-growth polymerization mechanisms, depending on the composition and the relative kinetics for each step in the reaction.



The step-growth mechanism of thiol-ene polymerizations leads to several unique polymerization properties that make them advantageous for use as dental restorative materials. Owing to the slower build up of molecular weight associated with the step-growth mechanism, the viscosity of the reacting media does not significantly increase until high conversion, enabling rapid polymerizations to a higher final conversion, which can dramatically reduce the amount of residual extractable monomer in the material. This outcome results in uniform consumption of low molecular weight species, and a more homogeneous, crosslinked polymer is formed. Thiol-ene polymerizations are not significantly inhibited by oxygen and therefore do not exhibit an uncured tacky layer at surfaces exposed to ambient conditions [15,18]. Most