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Thiol-ene functionalized siloxanes for use as elastomeric dental impression materials

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ABSTRACT

Objectives. Thiol- and allyl-functionalized siloxane oligomers are synthesized and evaluated for use as a radical-mediated, rapid set elastomeric dental impression material. Thiol-ene siloxane formulations are crosslinked using a redox-initiated polymerization scheme, and the mechanical properties of the thiol-ene network are manipulated through the incorporation of varying degrees of plasticizer and kaolin filler. Formulations with medium and light body consistencies are further evaluated for their ability to accurately replicate features on both the gross and microscopic levels. We hypothesize that thiol-ene functionalized siloxane systems will exhibit faster setting times and greater detail reproduction than commercially available polyvinylsiloxane (PVS) materials of comparable consistencies.

Methods. Thiol-ene functionalized siloxane mixtures formulated with varying levels of redox initiators, plasticizer, and kaolin filler are made and evaluated for their polymerization speed (FTIR), consistency (ISO4823.9.2), and surface energy (goniometer). Feature replication is evaluated quantitatively by SEM. The T_g , storage modulus, and creep behavior are determined by DMA.

Results. Increasing redox initiation rate increases the polymerization rate but at high levels also limits working time. Combining 0.86 wt% oxidizing agent with up to 5 wt% plasticizer gave a working time of 3 min and a setting time of 2 min. The selected medium and light body thiol-ene formulations also achieved greater qualitative detail reproduction than the commercial material and reproduced micrometer patterns with 98% accuracy.

Significance. Improving detail reproduction and setting speed is a primary focus of dental impression material design and synthesis. Radical-mediated polymerizations, particularly thiol-ene reactions, are recognized for their speed, reduced shrinkage, and 'click' nature.

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1. Introduction

Synthetic elastomeric impression materials are widely used in clinical dentistry to obtain negative replicas of hard and soft intraoral tissues from which positive gypsum casts can

be prepared. Since the casts serve as templates for the fabrication of dentures, crowns, and various orthodontic appliances, precise and transferable detail reproduction is demanded of the impression. To achieve a high degree of detail reproducibility, the impression material must possess sufficient hydrophilicity to coat moist oral surfaces and

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adequate fluidity to surround small features [1]. Furthermore, the impression material should be biocompatible, have reasonable working and setting times, resist permanent deformation upon removal from the mouth, and maintain dimensional stability after setting for multiple casts to be poured [2].

Toward these objectives, four classes of synthetic elastomeric dental impression materials are currently available: polysulfide, condensation silicone, addition silicone, and polyether. Although most impression materials on the market today are recognized for providing acceptable detail reproduction [3], they remain limited by their long setting times and susceptibility to dimensional instabilities [4,5]. Average setting times range from 6 min (addition silicon) to 13 min (polysulfide), with each second within the mouth serving as a source of motion-induced distortion by the patient [2]. Moreover, each class of impression material has the potential to diminish in accuracy over time. Polysulfide and condensation silicones release liquid by-products as they set, while the addition silicones (or polyvinyl siloxanes, PVS) release gas by-products. Consequently, polysulfide and condensation silicone impressions may shrink upon evaporation of water or ethanol, respectively [6,7]. Meanwhile, casts poured from PVS impressions may contain pits or voids if adequate time is not provided between full set and positive rendition [8]. Lastly, the hydrophilic nature of the polyether class of materials makes the impressions subject to swelling through absorption of moisture from the surrounding environment [9].

Clearly, the setting mechanisms employed by the current classes of materials do not offer an optimal route for a quick-setting, dimensionally stable material. Free radical-mediated polymerizations, on the other hand, are known to occur rapidly while remaining amenable to various modes of initiation including light, heat, and chemical processes [10]. Of particular interest for an impression material application is the radical-mediated thiol-ene polymerization. The thiol-ene 'click' reaction is well documented in the literature as proceeding at rapid rates while remaining uninhibited by oxygen, releasing no by-products, and requiring no solvents to attain quantitative conversions [11,12]. Moreover, the thiol-ene reaction mechanism proceeds through a series of alternating propagation and chain transfer events prior to termination that makes the reaction a step growth rather than a chain growth process (Fig. 1) [13]. As a result, networks formed via thiol-ene reactions exhibit delayed gelation and are quite homogenous. The delay in gelation is of particular importance for an impression material application since the preservation of the liquid state will allow the working time to be extended without compromising the reaction rate. Furthermore, the limited bond capacity of sulfur leads to less volumetric shrinkage in the thiol-ene polymerization than would be seen in a comparable vinyl-based system, such as that seen in the PVS class of materials [14].

While these advantages of thiol-ene reactions have led to a significant increase in its implementation and the general reference to it as one of the most prominent of the click reactions, there are some drawbacks to the thiol-ene reaction under some circumstances as well, all of which were circumvented here by a careful selection of monomers and conditions. Odor is often cited as a significant potential issue with any thiol-containing resin; however, here, the use of

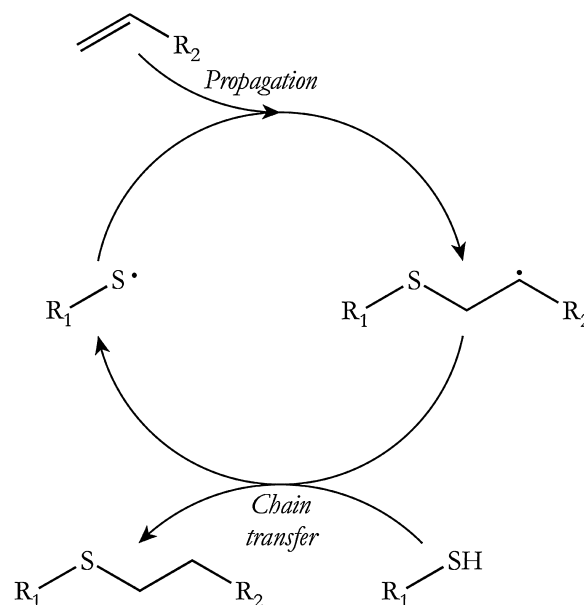


Fig. 1 – Schematic of the thiol-ene reaction mechanism. The thiol-ene polymerization proceeds through a cyclic step growth mechanism consisting of alternating propagation/chain transfer steps following initiation and prior to termination. The reaction mechanism assumes ideal conditions in which the alternating steps proceed at the same overall rate and homopolymerization of the ene is minimized.

higher molecular weight, purified monomers eliminates the low molecular weight impurities and compounds that cause the odor. Careful selection of the ene is also necessary to eliminate the homopolymerization reaction as has been done here. Further, others have noted that the thiol-ene reaction is not well-suited for polymer-polymer conjugation and other reactions that involve dilute concentrations of functional groups, particularly when large concentrations of photoinitiator are used [15]. Under these dilute functional group conditions, side reactions such as chain transfer to oxygen and radical-radical termination that are unimportant in bulk polymerizations such as those used here become relatively much more important.

Thiol-ene chemistry could potentially be incorporated into a wide range of monomer species; however, impression materials must be elastomeric at room temperature with adequate strength to resist tearing when removed from the mouth or significantly compressing under the weight of casting agents. Consequently, siloxanes are a fitting material selection for implementation with a thiol-ene-based setting/polymerization reaction given their noted flexibility, mechanical integrity, and biocompatibility [16]. Siloxanes are also highly amenable to functionalization, and multifunctional polymers can be readily synthesized through the condensation of pendant $-Cl$, $-OH$, or $-OR$ groups by a variety of catalytic species [17]. Hence, the primary objective of this study is to evaluate the use of thiol- and ene-functionalized siloxanes as a viable alternative to current impression materials. Specifically, a single thiol-ene functionalized siloxane

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