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Kinetics and mechanics of photo-polymerized triazole-containing thermosetting composites *via* the copper(I)-catalyzed azide-alkyne cycloaddition

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ABSTRACT

Objective. Several features necessary for polymer composite materials in practical applications such as dental restorative materials were investigated in photo-curable CuAAC (copper(I)-catalyzed azide-alkyne cycloaddition) thermosetting resin-based composites with varying filler loadings and compared to a conventional BisGMA/TEGDMA based composite.

Methods. Tri-functional alkyne and di-functional azide monomers were synthesized for CuAAC resins and incorporated with alkyne-functionalized glass microfillers for CuAAC composites. Polymerization kinetics, *in situ* temperature change, and shrinkage stress were monitored simultaneously with a tensometer coupled with FTIR spectroscopy and a data-logging thermocouple. The glass transition temperature was analyzed by dynamic mechanical analysis. Flexural modulus/strength and flexural toughness were characterized in three-point bending on a universal testing machine.

Results. The photo-CuAAC polymerization of composites containing between 0 and 60 wt% microfiller achieved ~99% conversion with a dramatic reduction in the maximum heat of reaction (~20 °C decrease) for the 60 wt% filled CuAAC composites as compared with the unfilled CuAAC resin. CuAAC composites with 60 wt% microfiller generated more than twice lower shrinkage stress of 0.43 ± 0.01 MPa, equivalent flexural modulus of 6.1 ± 0.7 GPa, equivalent flexural strength of 107 ± 9 MPa, and more than 10 times higher energy absorption of 10 ± 1 $\mathrm{MJ\,m^{-3}}$ when strained to 11% relative to BisGMA-based composites at equivalent filler loadings.

Significance. Mechanically robust and highly tough, photo-polymerized CuAAC composites with reduced shrinkage stress and a modest reaction exotherm were generated and resulted in essentially complete conversion.

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1. Introduction

Conventional resin-based dental restorative composites are formulated predominantly from inorganic fillers dispersed in matrices comprised of BisGMA or other related dimethacrylate-based monomer mixtures. These composites are esthetically appealing, mechanically stiff, and biocompatible thermosetting materials with rapid photo-curing kinetics upon incident visible light activation [1–3]. Typically, a high volume fraction of inorganic silica/glass fillers is used in combination with the resin in dental composites, for instance, 30–65 v/v% or 40–80 wt/wt% of 0.4–1.0 μm fillers/resins [4]. The roles of the filler involve enhanced mechanical performance including properties such as hardness, strength, and wear resistance, along with improved biocompatibility and moisture resistance [3,5] as well as reduced thermal expansion coefficient and polymerization-induced volumetric shrinkage that leads to significant stress [6]. However, extensive filler loading in resin-based composites can hinder photopolymerization kinetics due to light scattering and also influence handling properties due to the substantial increase in initial viscosity of the uncured composite paste as compared to the unfilled resin [7]. Therefore, the influence of filler types, shapes, sizes, concentrations, and functionalization on kinetics, mechanics, rheology, biocompatibility, and handling properties of resin-based composites has been investigated widely in the search for a more durable and practical dental restorative composite material [1,8–12].

Different classifications of inorganic fillers include metal oxides (*e.g.*: silica, aluminum oxide, titanium dioxide), alkaline silicate glass, bioactive or biomimetic fillers (*e.g.*: hydroxyapatite), and organic-inorganic hybrids [7]. Silicon dioxides are often utilized in resin-based dental composites [11] due to their mechanical performance along with reduced water-sorption and solubility [7]. Chemical functionalization of the filler that leads to covalent interactions between the filler particles and the polymer matrix after polymerization improves mechanical performance and hydrophobicity of composites as well as handling properties of the uncured pastes [1,13,14]. Silane derivatives with reactive functional groups, *e.g.*, methacrylates, are used as coupling agents to chemically modify the surface of inorganic particles, enhance particle dispersion, and promote interfacial bonding between the resin and filler *via* copolymerization [1,14]. In addition to bulk silica particles, mesoporous silica nanofillers have also been utilized where their porous structure facilitates mechanical interlocking with the polymerizable resin phase [15,16]. In contrast to micro-sized fillers (0.1–5 μm) with maximum particle loadings of 70 vol% or 85 wt%, nano-sized fillers (5–100 nm) are more restricted with respect to the maximum loading levels in photo-curable dental composites due to particle aggregation, viscosity increase, and light scattering associated with the significant increase in specific surface area of the particles [3,11,16,17]. As a consequence, nano-filled composites typically have reduced mechanical performance while enabling other positive attributes related to reduced opacity and improved polishability, hardness and wear resistance [11]. Alternatively, hybrid fillers consisting of both micro- and nano-sized particles are often employed in resin-based composites with enhanced packing fraction and surface smoothness [4].

Despite significant advances in filler development, failure of practical resin-based dental composites have been associated with high polymerization shrinkage stress [6], brittleness [18], monomer toxicity, and extractables [19] as well as the formation of biofilms [20]. These issues, which shorten the service lifetime of composite restoratives, arise in part due to the nature of chain-growth polymerization associated with the conventional curing of methacrylate-based composites [2]. The free-radical photopolymerization of BisGMA-based dimethacrylates generates highly crosslinked, glassy networks that are structurally heterogeneous and highly brittle [18], while also being prone to hydrolytic and enzymatic degradation in moist environments due to the presence of ester functionalities in the monomer structures [10]. In addition, the low gel point conversion that occurs in a chain-growth polymerization of dimethacrylate resins necessitates that significant polymerization-induced shrinkage stress will arise while the relatively low conversion at which vitrification occurs limits the maximum conversion and may lead to significant amount of residual monomer [6,21]. The shrinkage and stress development can lead to micro-cracks, adhesive failures, and secondary caries [22]. Over the past decade, alternative chemistries/mechanisms to minimize or eliminate the detrimental characteristics associated with traditional methacrylate-based dental resins have been explored. Ring-opening polymerizations utilizing epoxy, silorane, or cyclopropyl functional groups in resins as well as on nanofillers generated low volumetric shrinkage [23–26], and step-growth polymerization of thiol-ene or CuAAC (copper(I)-catalyzed azide-alkyne cycloaddition) resins achieved reduced polymerization shrinkage stress *via* delayed gelation [27–29]. In addition, hybrid polymerizations of ternary systems including chain-growth polymerization of methacrylates with step-growth polymerization of thiol-ene/thiol-yne, produced interpenetrating polymer networks (IPNs) with a dramatic reduction in shrinkage stress [30–32]. Further, incorporation of allyl sulfide or trithiocarbonate functionalities in dimethacrylate-based or other polymerized networks effectively lowered polymerization shrinkage stress *via* addition-fragmentation chain transfer [33–36].

Previously, we introduced the photo-initiated copper(I)-catalyzed azide-alkyne cycloaddition (photo-CuAAC) polymerization [37,38] (Scheme 1) as a means to prepare a glassy thermoset with significantly reduced polymerization shrinkage stress at complete conversion while simultaneously maintaining improved mechanical performance [29]. The preeminent benefits of the photo-CuAAC polymers over conventional BisGMA-based dimethacrylate polymers lie not only in the nature of the step-growth polymerization and the associated delayed gel point conversion, which contributes to reduced shrinkage stress [29], but also on the formation of rigid triazole linkages as a product that significantly enhance the overall mechanical behavior [38–40]. Furthermore, owing to the "click" chemistry of a highly orthogonal CuAAC reaction without forming a byproduct [41,42], the kinetics and mechanics of the CuAAC resin-based crosslinked photopolymers have been explored with varying monomer structures, photoinitiators, copper salts, and/or