Dental Restorative Materials Based on Thiol-Michael Photopolymerization

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Abstract

Step-growth thiol-Michael photopolymerizable resins, constituting an alternative chemistry to the current methacrylate-based chain-growth polymerizations, were developed and evaluated for use as dental restorative materials. The beneficial features inherent to anion-mediated thiol-Michael polymerizations were explored, such as rapid photocuring, low stress generation, ester content tunability, and improved mechanical performance in a moist environment. An ester-free tetrafunctional thiol and a ultraviolet-sensitive photobase generator were implemented to facilitate thiol-Michael photopolymerization. Thiol-Michael resins of varied ester content were fabricated under suitable light activation. Polymerization kinetics and shrinkage stress were determined with Fourier-transform infrared spectroscopy coupled with tensometery measurements. Thermomechanical properties of new materials were evaluated by dynamic mechanical analysis and in 3-point bending stress-strain experiments. Photopolymerization kinetics, polymerization shrinkage stress, glass transition temperature, flexural modulus, flexural toughness, and water sorption/solubility were compared between different thiol-Michael systems and the BisGMA/TEGDMA control. Furthermore, the mechanical performance of 2 thiol-Michael composites and a control composite were compared before and after extensive conditioning in water. All photobase-catalyzed thiol-Michael polymerization matrices achieved >90% conversion with a dramatic reduction in shrinkage stress as compared with the unfilled dimethacrylate control. One prototype of ester-free thiol-Michael formulations had significantly better water uptake properties than the BisGMA/TEGDMA control system. Although exhibiting relatively lower Young's modulus and glass transition temperatures, highly uniform thiol-Michael materials achieved much higher toughness than the BisGMA/TEGDMA control. Moreover, low-ester thiol-Michael composite systems show stable mechanical performance even after extensive water treatment. Although further resin/curing methodology optimization is required, the photopolymerized thiol-Michael prototype resins can now be recognized as promising candidates for implementation in composite dental restorative materials.

Keywords: polymer, click chemistry, methacrylate, composite resin, light-curing of dental resins, dental leakage

Introduction

Composite dental restoratives are currently based on the radical-mediated crosslinking polymerization of multifunctional methacrylate monomers (Ferracane 2011). Conveniently initiated by visible light exposure, methacrylate-based composites are fast cured in situ, resulting in mechanically robust aesthetic materials with good biocompatibility. However, they are restricted by the nature of chain-growth polymerizations, and several negative effects associated with the methacrylate systems cannot be entirely overcome (Moszner and Salz 2001; Cramer et al. 2011). These include limited reactive group conversion (Dewaele et al. 2006), significant shrinkage stress (Braga et al. 2005), and moisture absorption (Sideridou et al. 2004). Additionally, the presence of moisture and ester functionality in the methacrylate network enables enzymatic and hydrolytic degradation, with an associated reduction in long-term mechanical performance (Sideridou et al. 2003). Many efforts have been undertaken to resolve the omnipresent concerns inherent to methacrylates. These include soft-start curing (Yap et al. 2001), optimization of handling and processing

(Shah and Stansbury 2006), alternative polymerization methods (Hamano et al. 2012), and monomer innovations (Khatri et al. 2003). However, the problems with methacrylates are fundamentally related to the polymerization mechanism, the monomer structures used, or both. Therefore, all the potential disadvantages of methacrylate-based systems indicate that alternate chemistries will eventually be required for new generations of dental restorative materials.

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In the past 2 decades, several polymerization reactions, as an alternative to methacrylate chain-growth reactions, have gained attention in dental resin development. Nonmethacrylate monomers cured via different mechanisms were considered, such as ring-opening step-growth polymerization of oxiranes and spiroorthocarbonates (Eick et al. 2002), and a significant amount of work has been dedicated to the development of various step-growth thiol-ene dental resins (Boulden et al. 2011). Inherent to the polymerization mechanism, step-growth thiol-ene polymerizations have many advantages as compared with highly brittle methacrylates, including rapid kinetics, high functional group conversions, and a generation of uniform and tough network polymers (Burujeny et al. 2017). In the quest for improving overall resin stability and, by that, extending the service times of dental composites, other formulations having no or significantly reduced interchain ester content have been proposed. For example, photoinitiated copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) step-growth polymerization has been proposed as another chemistry able to produce low-shrinkage dental resin composites with enhanced overall mechanical performance owing to the in situ formation of rigid triazole links (Song et al. 2016). In another recent example, ether-based distyrenyl monomers or hydrolytically stable acrylamides were incorporated into methacrylate dental resins with the goal to enhance the long-term performance and durability of dental resin systems (Gonzalez-Bonet et al. 2015; Pfeifer and Ferracane 2017).

Herein, we developed and propose for the first time photoinitiated thiol-Michael polymerization as an alternative chemistry for designing durable dental resin composites, as compared with the conventional dimethacrylate-based system—that is, 2,2-bis[p-(3-methacryloxy-2-hydroxypropoxy) phenyl]propane (BisGMA) and triethylene glycol dimethacrylate (TEGDMA)—cured under the same conditions. As a member of the "click" reaction family (Kolb et al. 2001), the thiol-Michael reaction is well known for its high functional group conversions, simplicity, and effectiveness, which positively differentiate it from other techniques in applications such as surface modification (Adzima and Bowman 2012), microparticle and nanoparticle synthesis (Wang et al. 2015), and polymer network construction (Chatani, Wang, et al. 2014). Thiol-Michael polymerizations differ fundamentally from the prevalent dental systems, wherein the polymerization follows the anion-mediated step-growth reaction route between thiol and electron-deficient vinyl monomers rather than being radical mediated (Appendix Fig. 1; Chan et al. 2010).

Limited by available photoinitiation methodologies, silicon-based ester-free thiol-Michael glasses were recently constructed with triethylamine or (2,2,6,6-tetramethylpiperidin-1-yl)oxyl by thermal initiation and shown to outperform ester-based analogue materials for enhanced hydrolytic resistance and improved strength and toughness (Podgorski, Becka, Chatani, et al. 2015). Moreover, with the recent progress in the designing of photobase generators (Sarker et al. 2001), spatial and temporal control of the photoinitiated thiol-Michael reaction has achieved improvements in photoreaction efficiency (Xi et al. 2014), visible wavelength sensitivity (Zhang et al. 2016), and

reaction orthogonality (Chatani, Gong, et al. 2014). Therefore, with these new tools, we investigated the photoinitiated thiol-Michael polymerization based on ester-containing and ester-free monomer systems. Photopolymerization kinetics, thermomechanical performance (glass transition temperature, Young's modulus, flexural strength, and toughness), shrinkage stress development, and water sorption tests were performed on the photocured thiol-Michael resins and composites. The materials' characteristics as dental restoratives were evaluated by performing pairwise comparisons with a conventional BisGMA/ TEGDMA (70:30) dimethacrylate control.

Materials and Methods

Materials

Pentaerythritol tetra(3-mercaptopropionate) (PETMP), divinyl sulfone (DVS), and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were purchased from Sigma-Aldrich. Tris(2-hydroxyethyl)isocyanurate triacrylate (SR368) was purchased from Sartomer. The BisGMA/TEGDMA comonomer mixture was used as donated from ESSTECH. The silane thiol (SiTSH) and functionalized fillers were synthesized according to previously reported procedures (Podgorski, Becka, Claudino, et al. 2015b). The synthetic procedure and photolytic decomposition pathway of 2-(2-nitrophenyl)-propyloxycarbonyl-1,1,3,3-tetramethyl-guanidine (NPPOC-TMG) were described in a recent report (Zhang et al. 2016). The structures of the thiol and vinyl functionalized monomers are depicted in Figure 1.

Resin Preparation

A 1:1 molar ratio of thiol:vinyl functional groups in any analyzed monomer mixture containing 0.5 or 2 wt% of NPPOC-TMG was prepared. These resins were mixed in the presence of dichloromethane to form a homogenous mixture, and dichloromethane was removed in vacuo. For the control sample, 0.5 wt% DMPA was added to a BisGMA/TEGDMA comonomer mixture. For the composite resins, functionalized silica microfillers (d ~ 0.4 μm) and resins were blended in a speedmixer (DAC 150 FVZ; FlackTek) for 10 min to ensure uniform formulation at 50/50 resin/filler wt% ratios. All resins and composites were cured with 100 mW/cm^2 of 320- to 390-nm light for material property characterization except in kinetic studies, where the curing was also performed with 60 mW/cm^2 of 365-nm light to investigate the effects of curing conditions on reaction kinetics and shrinkage stress.

Fourier Transform Infrared Spectroscopy

Polymerization kinetics and shrinkage stress measurements were monitored in situ with a Fourier-transform infrared spectroscopy instrument (Nicolet 6700) coupled with a tensometer. Irradiation was performed from the bottom of the glass rod with a light guide connected to a mercury lamp (Acticure 4000; EXFO) with a 365- or 320- to 390-nm bandgap filter. The light intensity transmitted through the glass rod was kept at 60 to
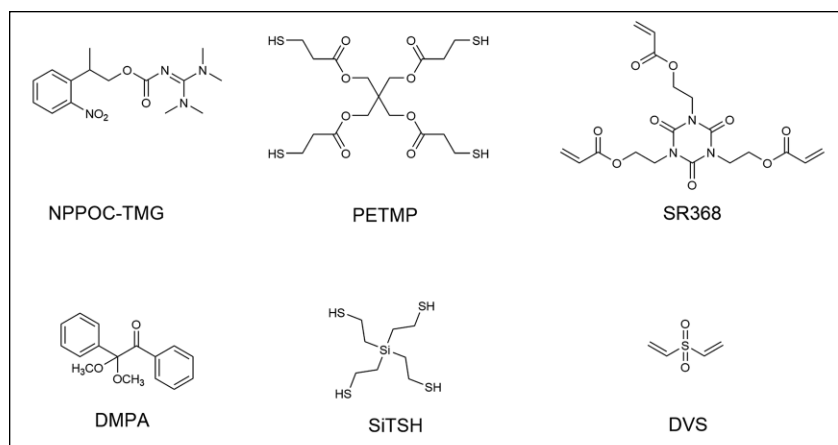
Figure 1. Thiol and vinyl functionalized monomers, photobase generator NPPOC-TMG, and radical initiator (DMPA) utilized in this study. DMPA, 2,2-dimethoxy-2-phenylacetophenone; DVS, divinyl sulfone; NPPOC-TMG, 2-(2-nitrophenyl)-propyloxycarbonyl-1,1,3,3-tetramethylguanidine; PETMP, pentaerythritol tetra(3-mercaptopropionate); SR368, tris(2-hydroxyethyl)isocyanurate triacrylate; SiTSH, silane thiol.

100 mW/cm^2, as measured by a radiometer (Model 100; Demetron Research Corp.). Samples were irradiated for 10 min until the monitored group absorption peak no longer decreased. The final resin conversions were calculated per the absorbance peak area of the vinyl functional group, around 6,160 cm^{-1} in the near-infrared spectrum.

Polymerization Shrinkage Stress Measurement

In situ polymerization shrinkage stress measurements were performed with a tensometer (American Dental Association Health Foundation). Samples were placed between 2 silanized glass rods (6 mm in diameter, 1 mm in thickness) and sealed with a polytetrafluoroethylene sleeve. The shrinkage stress was monitored for 5 min after the light source was switched off to obtain the final shrinkage stress at ambient temperature. The total measurement time was 15 min.

Water Sorption Test

Rectangular samples (2 × 4 × 25 mm) were used for composite water sorption tests, which were also designed to examine the potential hydrolytic degradation of the resin due only to water rather than any enzymatic, acidic, or basic cleavage. The samples were placed in deionized water at 37 °C, and the changes in their dry masses were recorded every 24 h. The water was exchanged 3 times within the initial 3 mo and twice more after that. To investigate the deleterious effects in a humid environment, dynamic mechanical analysis (DMA) and flexural tests were performed for composite samples before and after extended water conditioning.

Dynamic Mechanical Analysis

Mechanical performance (modulus and glass transition temperature) of the dental resins in this study was characterized with DMA Q800 (TA Instruments) in multifrequency strain mode with a sinusoidal stress of 1-Hz frequency and a heating rate of 3 °C·min^{-1}. The glass transition temperature was determined as the peak of the tan delta curve. The sample dimensions were 0.25 × 5 × 25 mm and 2 × 4 × 25 mm for unfilled polymers and composites, respectively.

Three-Point Bending Flexural Test

Flexural strength, Young's modulus, and toughness were measured via a 3-point bending test (MTS 858 Mini Bionix II) with a strain rate of 1 mm·min^{-1} and a span of 20 mm. Rectangular samples sized 2 × 2 × 25 mm and 2 × 4 × 25 mm were used for unfilled polymers and composites, respectively. Flexural modulus was determined from the slope between 0.5% and 1% strain. Flexural strength, σ, was calculated as $3FL/2BH^2$, where F is the maximum load and $L, H,$ and B are the sample dimensions.

Results and Discussion

In the present study, 4 thiol-Michael compositions of varied ester content were investigated for potential use as dental restorative resins. The thiol-Michael compositions were stoichiometric combinations of 2 multifunctional thiols and 2 vinyls mixed in one-to-one functional group ratios. As the thiol reactant, 2 tetrathiols were used—namely, a commercial ester-based PETMP and a synthetic ester-free SiTSH. As the electron-deficient vinyls, a triazonetrione-based triacrylate (SR368) and DVS were chosen (Fig. 1). Vinyl sulfone, although a potentially toxic compound, has a history of being used in biological applications, and its thiol-Michael peptide-infused hydrogel materials were shown to support cell viability (Zustiak and Leach 2010). Furthermore, the DVS monomer used here is only a representative of vinyl sulfone monomers to demonstrate the feasibility of this approach. Any future issues with toxicity are readily addressed by forming oligomers based on thiol-Michael reactions of vinyl sulfones and thiols that could be used to increase monomer molecular mass and eliminate DVS from the mixture. The dimethacrylate composition formulated from BisGMA (70 wt%) and TEGDMA (30 wt%) was used in all comparisons. All composition mixtures and their viscosities are listed in Appendix Table 1. The broad range of variations in relatively low viscosities of the thiol-Michael resin systems would suggest a convenient adjustment of the inorganic filler loadings in composite mixtures to further tune the handling characteristics and also to prevent any filler sedimentation.

Although using visible light for the curing of dental resins is the only acceptable method in current clinical dental practice, the

thiol-Michael resins employed here are initiated with an ultraviolet (UV)–sensitive photobase, which is relatively insensitive to visible light. Despite recent progress in the synthesis of visible light–responsive photobases (Suyama et al. 2006; Suyama and Shirai 2009), they still somewhat lack in efficiency in the bulk cure of relatively opaque silica filled systems. It is worth noting that there is no expectation that the curing methodology (i.e., whether visible or UV light is used) will affect the performance of the material, as previously demonstrated (Lovell et al. 2001). Because of its synthetic simplicity, good solubility, and high photobase efficiency after exposure (Xi et al. 2013), the NPPOC-TMG photobase was selected for this study.

Initial kinetic experiments were performed on unfilled resins cured with UV light of either 365 nm/60 mW/cm^2 for the photobase load of 2 wt% or 320 to 390 nm/100 mW/cm^2 for 0.5 wt% NPPOC-TMG, respectively. Simultaneously, with the infrared real-time conversion assessment, shrinkage stress experiments were performed. The conversion-time profiles for the thiol-Michael resins as well as the BisGMA/TEGDMA control are included in Figure 2. Figure 2a depicts kinetic plots for resins cured with lower-intensity light (60 mW/cm^2), whereas Figure 2b illustrates 2 selected thiol-Michael systems and the control irradiated with 100-mW/cm^2 light of broader UV-spectrum light (320 to 390 nm). At higher light intensities, each composition is fast-cured to reach maximum conversion in about 3 to 6 s of irradiation, and the differences in the reaction rates are negligible.

There are, however, significant differences in the conversions attained. As expected, the dimethacrylate control achieved the lowest conversion regardless of the curing conditions. Due to the advantage of delayed gelation in a step-growth system, the final conversions of the thiol-Michael polymerizations are all higher than BisGMA/TEGDMA. Vitrification in the dimethacrylate polymerization dramatically limits the mobility of all reactive species at elevated conversions, which leads to an undesired low conversion. Contrarily, for the thiol-Michael polymers, vitrification does not occur until much higher conversions, resulting in preserving the reactive species mobility and enabling conversions >90% to be reached. Additionally, the nature of this step-growth process implies minimal amounts of unreacted and thus leachable monomers, especially at close-to-complete conversions as compared with the dimethacrylate control, operating according to a chain-growth mechanism (Stansbury and Dickens 2001). For example, if we assume equal reactivity of the 2 functional groups, then at 90% vinyl sulfone conversion, only 1% of the DVS would be left unreacted and be potentially extractable; at 95% conversion, this drops to 0.25% extractable. Appendix Table 2 summarizes the
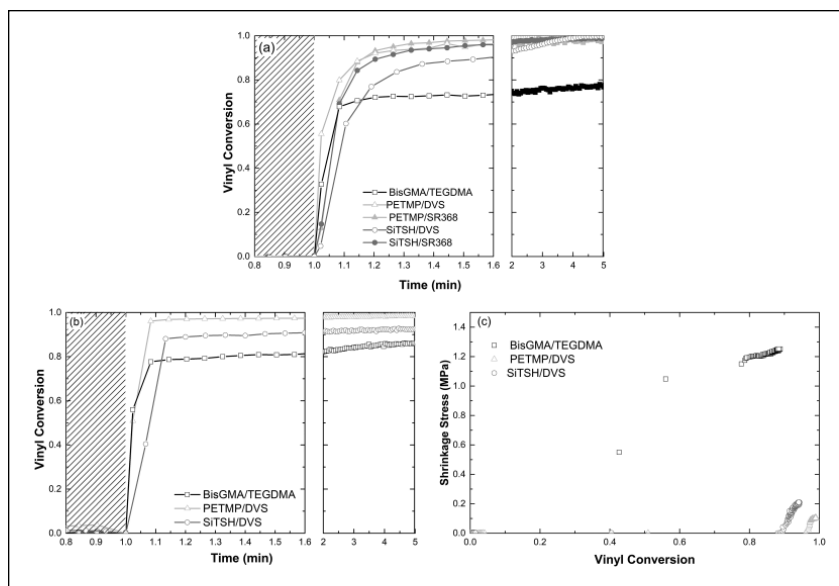

Figure 2. Polymerization kinetics and shrinkage stress measurements for thiol-Michael resins and BisGMA/TEGDMA control systems. Vinyl conversions versus time for resins cured with ultraviolet (UV) light (365 nm) of (**a**) 60-mW/cm^2 intensity and (**b**) 100-mW/cm^2 intensity with a 320- to 390-nm filter. (**c**) Shrinkage stress evaluation as a function of double-bond conversion for thiol-Michael and BisGMA/TEGDMA resins cured with UV light of 100-mW/cm^2 intensity with a 320- to 390-nm filter. Each mixture was stabilized in the dark for 1 min and then irradiated for 10 min at ambient temperature. BisGMA/TEGDMA, 2,2-bis[p-(3-methacryloxy-2-hydroxypropoxy) phenyl]propane / triethylene glycol dimethacrylate; DVS, divinyl sulfone; NPPOC-TMG, 2-(2-nitrophenyl)-propyloxycarbonyl-1,1,3,3-tetramethylguanidine; PETMP, pentaerythritol tetra(3-mercaptopropionate); SR368, tris(2-hydroxyethyl)isocyanurate triacrylate; SiTSH, silane thiol.

final functional group conversions after 10-min irradiation as well as the shrinkage stress data.

Figure 2c presents the shrinkage stress versus conversion plots for PETMP/DVS, SiTSH/DVS, and BisGMA/TEGDMA. In earlier reports, step-growth systems were shown to exhibit reduced polymerization shrinkage stress as compared with chain-growth crosslinking polymerizations of dimethacrylates. As a step-growth process, the thiol-Michael polymerization is expected to have an improved capability for accommodating the shrinkage without leading to stress; therefore, a lower amount of internal stresses are generated during curing (Podgorski et al. 2014). Indeed, the analysis of the photocured thiol-Michael resins revealed very low shrinkage stress development at higher functional group conversions relative to the dimethacrylate control (Fig. 2c, Appendix Table 2). Similar to other reports, where step-growth polymerizations such as thiol-ene and CuAAC showed significant reductions in shrinkage stress (Podgorski, Becka, Claudino, et al. 2015a; Song et al. 2016) as compared with chain-growth radical polymerizations such as BisGMA/TEGDMA, the step-growth mechanism delays gelation in the thiol-Michael systems, which facilitates high final conversion as well as less postgel shrinkage and lower final shrinkage stress.

Conventional methacrylate-based dental materials contain molar concentrations of ester moieties that are susceptible to extraction, hydrolytic cleavage, and enzymatic degradation by esterases. Moisture absorption into these composites thus negatively affects mechanical properties such as modulus and

Table 1. Mechanical Performance Results for Thiol-Michael and BisGMA/TEGDMA Systems.

Resin System	T_g, °C	Young's Modulus, GPa	Flexural Strength, MPa	Toughness, J·m⁻³
BisGMA/TEGDMA	169 (10)	3.1 (1.3)	66 (25)	1.2 (0.8)
PETMP/DVS	47 (2)	0.63 (0.2)	24 (6)	1.8 (0.5)
PETMP/SR368	53 (1)	0.03 (0.02)	4.3 (1.9)	0.31 (0.16)
SiTSH/DVS	79 (3)	1.9 (0.1)	66 (2)	5.1 (0.6)
SiTSH/SR368	53 (2)	0.20 (0.01)	6.0 (1.5)	0.49 (0.09)

Systems were cured with 2 wt% NPPOC-TMG and 100 mW/cm² of 320 to 390 nm at ambient temperature. Values are presented as mean (SD). Samples for water absorption were postcured in 70 °C overnight. See Appendix Figure 3 for the dynamic mechanical analysis plots for thiol-Michael systems.
BisGMA/TEGDMA, 2,2-bis[p-(3-methacryloxy-2-hydroxypropoxy) phenyl]propane / triethylene glycol dimethacrylate; DVS, divinyl sulfone; NPPOC-TMG, 2-(2-nitrophenyl)-propyloxycarbonyl-1,1,3,3-tetramethylguanidine; PETMP, pentaerythritol tetra(3-mercaptopropionate); SiTSH, silane thiol; SR368, tris(2-hydroxyethyl)isocyanurate triacrylate; T_g, glass transition temperature.

Table 2. Effects of Extended Moisture Absorption on Mechanical Performance for Thiol-Michael and BisGMA/TEGDMA Composite Systems.

Condition: Resin System	Young's Modulus, GPa	Flexural Strength, MPa	Toughness, J·m⁻³
Before water conditioning			
BisGMA/TEGDMA	7.4 (0.3)	57 (11)	0.91 (0.28)
PETMP/DVS	2.3 (0.3)	24 (2)	4.0 (0.7)
SiTSH/DVS	4.5 (0.7)	41 (6)	1.4 (0.4)
After 22 mo of water sorption			
BisGMA/TEGDMA	4.2 (0.3)	21 (5)	0.19 (0.1)
PETMP/DVS	0.28 (0.05)	9.1 (1.2)	0.98 (0.39)
SiTSH/DVS	4.3 (0.2)	45 (3)	1.0 (0.4)

With 50 wt% functionalized silica filler composites cured with 2 wt% NPPOC-TMG and 100 mW/cm² of 320-390 nm at ambient temperature. Values are presented as mean (SD).
BisGMA/TEGDMA, 2,2-bis[p-(3-methacryloxy-2-hydroxypropoxy) phenyl]propane / triethylene glycol dimethacrylate; DVS, divinyl sulfone; NPPOC-TMG, 2-(2-nitrophenyl)-propyloxycarbonyl-1,1,3,3-tetramethylguanidine; PETMP, pentaerythritol tetra(3-mercaptopropionate); SiTSH, silane thiol; SR368, tris(2-hydroxyethyl)isocyanurate triacrylate.

strength due to plasticization (McCabe and Rusby 2004). Moreover, when some of the network crosslinks are degraded through the hydrolytic or enzymatic ester cleavage processes, it decreases the crosslinking density and further weakens the overall composite. It is therefore important to consider water uptake studies for any dental composite. The water sorption results for unfilled thiol-Michael resin systems are shown in Appendix Table 3. Furthermore, 3 selected composite systems were tested for water sorption over an extended amount of time (Fig. 3).

According to the accepted standard, a polymerized dental polymer can swell by no more than 5 wt% in 7 d at body temperature (Sideridou et al. 2004). The actual extent of swelling would depend on multiple factors, such as the composition, functional group conversions achieved (light intensities, initiator content), the hydrophilic/hydrophobic characters of monomers used, filler loadings, exposure time, and sample geometry (Rahim et al. 2012). The standard gives a good estimate of a material's performance, given that it is just the initial swelling that can affect the mechanical properties. However, if the composite reaches an equilibrium swelling or degrades over a period longer than just 7 d, the mechanical properties would be expected to further deteriorate over an extended time. As seen in Figure 3, after 4 mo of water exposure, the dimethacrylate material swells by >5 wt% and has not stopped swelling.

Generally, in composite dental restoratives, equilibrium swelling will be achieved only at very extended times due to the slow diffusion and uptake of water into these very glassy matrices in which the mobility of even small molecules is severely limited. This behavior implies that over longer exposure times, other deleterious effects may be taking place and, therefore, more property changes would be expected. However, the ester-free composition absorbs only 2 wt% of water, quickly reaching equilibrium, whereas the BisGMA/TEGDMA composite exhibits a continuous increase. Interestingly, after the initial mass increase, the PETMP/DVS system—the most loosely crosslinked and highly hydrophilic—begins to lose a small amount of mass, likely associated with extraction of small amounts of unreacted material. However, the most important consequences of prolonged exposure to moist conditions are the changes that arise in the material properties discussed here.

Basic mechanical properties of thiol-Michael and BisGMA/TEGDMA resins—including glass transition temperature, Young's modulus, flexural strength, and toughness—are summarized in Table 1. Thiol-Michael unfilled samples had a glass transition temperature from 40 °C to 79 °C. Due to the silica core and relatively low molecular mass, the presence of SiTSH greatly improved the glass transition temperature of the thiol-Michael resins.

By properly designing the thiol-Michael systems, our approach was to improve the mechanical properties through elimination of the flexible ester-containing moieties and

simultaneously introduce secondary interactions via sulfone groups as an auxiliary reinforcement mechanism to counteract the lower covalent crosslink density. The rigid backbone structure of the BisGMA monomer enhances the mechanical properties of BisGMA/TEGDMA, leading to higher Young's modulus and flexural strength. However, the brittleness of this material, caused by its heterogeneous nature and high crosslink density, results in lower toughness than what is observed in thiol-Michael systems. Importantly, all SiTSH-containing mixtures resulted in tough glasses when polymerized at ambient conditions. Even though the initial values of strength and modulus are lower for the thiol-Michael materials, we predict that these values would improve in glass-filled composites and, above all, after conditioning in a humid environment. To test this hypothesis, the mechanical properties were analyzed in composite samples before and after extended water conditioning. The relevant results are summarized in Table 2.

From the tabulated data, it is evident that although the unfilled SiTSH/DVS sample exhibited almost 3-times lower Young's modulus than the unfilled BisGMA/TEGDMA, the conditioned composites are basically equivalent in terms of glassy modulus results. After 2 y of uninterrupted water exposure, the dimethacrylate control suffered a >40% drop in modulus, >60% drop in flexural strength, and close to 80% drop in toughness. However, conditioned for the same amount of time, the thiol-vinyl sulfone composite remained practically unaffected in terms of modulus, strength, and toughness. These results point to an extraordinary stability of an ester-free thiol-vinyl sulfone composite in a moist environment.

Conclusion

In summary, we demonstrated that thiol-Michael resin systems, particularly those incorporating ester-free monomers, have the potential for creating high-modulus tough glasses that are stable for extended times in a moist environment. The new step-growth resins can be filled with silica particles and photocured to yield composite materials of low shrinkage stress, high conversions, and improved resistance to moist environments. These attributes make them promising candidates for new dental materials development based on alternative chemistries that dissent from the use of methacrylate esters. Although this study attempted to show the broad feasibility and potential benefits of the thiol-Michael resins and composites, the thiol-Michael reactions require more research to improve the clinical suitability of numerous aspects of the resin formulations, fillers, and photobase initiators. This initial study demonstrates crucial features of thiol-Michael, particularly thiol-vinyl sulfone crosslinking systems, that dovetail toward mutually recognized new development directions that will likely define the future of dental composite materials.

Author Contributions

S. Huang, X. Zhang, contributed to conception, design, data acquisition, analysis, and interpretation, drafted and critically revised the manuscript; M. Podgórski, c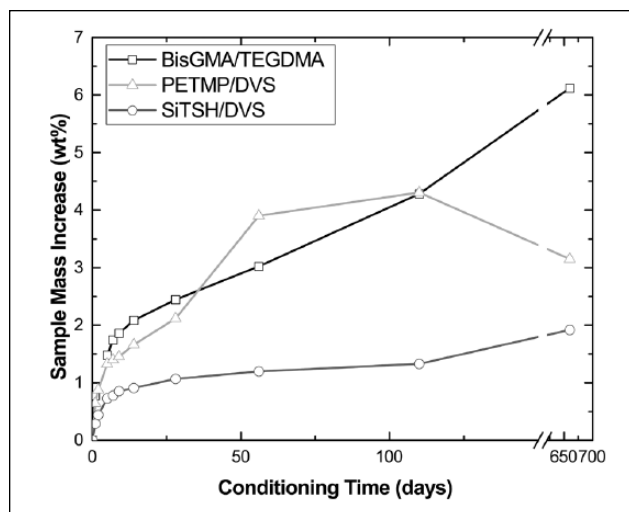ontributed to conception, design, data analysis, and interpretation, drafted and critically revised the manuscript; J. Sinha, contributed to conception, design, data acquisition, analysis, and interpretation, critically revised the manuscript; M. Claudino, contributed to design and data acquisition, critically revised the manuscript; J.R. Stansbury, C.N. Bowman, contributed to conception, design, data analysis, and interpretation, critically revised the manuscript. All authors gave final approval and agree to be accountable for all aspects of the work.

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Figure 3. Composite mass increase with conditioning time. The resins were filled with 50 wt% silica microparticles (d ~ 0.4 μm), cured with 300-mW/cm^2 light (320 to 390 nm) for 2 min on each side, and then placed in deionized water at 37 °C. Their mass was monitored over the course of 22 mo. Significantly lower water sorption of the SiTSH/DVS composite (around 2 wt%) versus the methacrylate-based material (>6 wt%) is evident. An ester-based PETMP/DVS system initially swells to around 4 wt% due to its low crosslinking density and increased affinity to water; then, a mass drop is observed owing to possible hydrolytic degradation. BisGMA/TEGDMA, 2,2-bis[p-(3-methacryloxy-2-hydroxypropoxy) phenyl]propane / triethylene glycol dimethacrylate; DVS, divinyl sulfone; PETMP, pentaerythritol tetra(3-mercaptopropionate); SiTSH, silane thiol.

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