Published in final edited form as:

Dent Mater. 2012 November ; 28(11): 1113–1119. doi:10.1016/j.dental.2012.06.012.

Novel Dental Restorative Materials having Low Polymerization Shrinkage Stress via Stress Relaxation by Addition-Fragmentation Chain Transfer

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Abstract

Objectives—To produce a reduced stress dental restorative material while simultaneously maintaining excellent mechanical properties, we have incorporated an allyl sulfide functional group into norbornene-methacrylate comonomer resins. We hypothesize that the addition-fragmentation chain transfer (AFCT) enabled by the presence of the allyl sulfide relieves stress in these methacrylate-based systems while retaining excellent mechanical properties owing to the high glass transition temperature of norbornene-containing resins.

Methods—An allyl sulfide-containing dinorbornene was stoichiometrically formulated with a ring-containing allyl sulfide-possessing methacrylate. To evaluate the stress relaxation effect as a function of the allyl sulfide concentration, a propyl sulfide-based dinorbornene, not capable of addition-fragmentation, was also formulated with the methacrylate monomer. Shrinkage stress, the glass transition temperature and the elastic modulus were all measured. The composite flexural strength and modulus were also measured. ANOVA (CI 95%) was conducted to determine differences between the means.

Results—Increasing the allyl sulfide content in the resin dramatically reduces the final stress in the norbornene-methacrylate systems. Both norbornene-methacrylate resins demonstrated almost zero stress (more than 96% stress reduction) compared with the conventional BisGMA/TEGDMA 70/30 wt% control. Mechanical properties of the allyl sulfide-based dental composites were improved to the point of being statistically indistinguishable from the control BisGMA-TEGDMA by changing the molar ratio between the methacrylate and norbornene functionalities.

Significance—The allyl sulfide-containing norbornene-methacrylate networks possessed super-ambient T_g , and demonstrated significantly lower shrinkage stress when compared with the

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control (BisGMA/TEGDMA 70 to 30 wt%). Although additional development remains, these low stress materials exhibit excellent mechanical properties which are appropriate for use as dental restorative materials.

Keywords

restorative material; low stress; polymer networks; allyl sulfide; addition-fragmentation chain transfer; photopolymerization

INTRODUCTION

Modern dental restorative materials have favored photoactivated polymer-based composites over the more traditional mercury-based amalgams due to several advantages including on-demand and rapid curing as well as the formation of a material that possesses an aesthetically desirable natural tooth color. Unfortunately, the volume shrinkage which occurs during photopolymerization results in a stress that has the potential to cause adhesive failure, initiate microleakage and cause recurrent caries[1]. Polymerization stress in commercial dimethacrylate-based composites is especially problematic due to the early gelation exhibited in chain-growth polymerizations [2-3]. Many researchers have attempted to mitigate this stress by minimizing volume shrinkage via novel polymerization schemes[4], such as thiol-ene polymerizations [5-6] [7-8], ring-opening polymerizations [9] [10], and polymerization-induced phase separation [11]. In the present work, we utilize addition-fragmentation chain transfer (AFCT) [12] to create adaptable polymer networks[13] with radical-mediated bond rearrangement that occurs throughout the polymerization, leading to stress relaxation and the formation of a low stress material.

Addition-fragmentation chain transfer (AFCT) enables the relaxation of polymerization shrinkage-induced stress within a forming polymer network by promoting the rearrangement of the network connectivity without any associated reduction in the crosslink density or the mechanical properties of the ultimate materials [13-15] [16]. In previous studies, the presence of the allyl sulfide functional group was shown to reduce the final stress in thiol-ene [14] and thiol-yne [16] resins via AFCT. The AFCT mechanism is a non-degradative process of recurring chain scission and recombination which enables the network to maintain its chemical and mechanical properties before and after AFCT is activated. In the previous thiol-ene and thiol-yne studies, the thiyl radical would react with the allyl sulfide bond to induce AFCT, while simultaneously regenerating a thiyl radical and thereby inducing a cascade of reactions (Figure 1(A)).

The incorporation of the AFCT mechanism into a methacrylate-based resin was recently performed by formulating a bisphenyl-a-dimethacrylate monomer with thiol-ene monomers that contained allyl sulfide moieties[15]. A dramatic reduction in stress was observed upon increasing the allyl sulfide-containing thiol-ene fraction of the resin; however, this reduction was accompanied by reduced mechanical properties (i.e., glass transition temperature and modulus were significantly reduced). Nevertheless, this work demonstrated that allyl sulfide-mediated AFCT was capable of reducing the stress in glassy, methacrylate-based materials.

In an effort to produce a low stress material while also achieving mechanical properties appropriate for a dental restorative, we have incorporated an allyl sulfide functional group into a norbornene-methacrylate monomer system. We hypothesize that AFCT mediated by the allyl sulfide would relieve stress in this methacrylate-based system while retaining the desirable mechanical properties associated with the bulky molecular structure of the norbornene which increases the glass transition temperature of the ultimate resin and

composite. The desired curing behavior of the resin was achieved by using 470nm wavelength light in combination with Ge-based photoinitiators. The mechanical properties and shrinkage stress of these systems were evaluated and compared with a control formulation comprised of 70/30 wt% BisGMA/TEGDMA. The flexural strength and modulus as well as the glass transition temperature of the composites were examined, with the composites containing 75 wt% glass filler.

MATERIALS & METHODS

Materials

The materials used in this study are shown in Figure 2. 2-Methylene-propane-1,3-di(norbornene sulfide) (MDNS) was designed and synthesized to form a polymer network that simultaneously achieves a high glass transition temperature associated with the norbornene groups and lower stress through AFCT of the allyl sulfide. As a negative control, 2-methyl-propane-1,3-di(norbornene sulfide) (MeDNS), which is analogous to MDNS though not capable of undergoing AFCT, was also synthesized. MDNS and MeDNS were synthesized from 5-bromomethyl norbornene with 3-mercapto-2-(mercaptomethyl)-1-propene and 1,3-dimercapto-2-methylpropane, respectively, according to the method described in the literature [14]. A waxy/hazy solid (MDNS) and viscous/colorless liquid (MeDNS) were received after purification. To synthesize 5-bromomethyl norbornene, a reaction of 1,3-dicyclopentadiene (16g, 0.12mol, ACROS) with allyl bromide (35g, 0.29mol, Sigma Aldrich) was performed in a pressure vessel heated at 170 °C for 12 hours [17]. It was distilled at 175 °C at 1 atmosphere pressure prior to use. Additionally, 2-(methacryloyloxyethyl) 7-methylene-1,5-dithiocane-3-yl phthalate (PAS, phthalate allyl sulfide, synthesized by 3M [18]) was also evaluated. This monomer has the stress-relieving benefits of an allyl sulfide moiety (in the ring) as well as the enhanced crosslinking density associated with the methacrylate chain-growth mechanism. Bisphenylglycidyl dimethacrylate (BisGMA, provided by Esstech) and triethylene glycol dimethacrylate (TEGDMA, provided by Esstech) were used as received. A Ge-based photoinitiator (Dibenzoyl diethyl germane, synthesized) and phosphine oxide, phenyl bis(2,4,6-trimethyl benzoyl) (BAPO, Ciba Specialty Chemicals), visible light-active photoinitiator, were utilized at 3 wt%. The Ge-based photoinitiator (Dibenzoyl diethyl germane, synthesized) was prepared by a synthesis from diethyldi(2-phenyl-1,3-dithian-2-yl)germane (8.27g, 15.9 mmol, synthesized[19]), CaCO₃ (25g, 247.4 mmol, Sigma Aldrich), and iodine (48.3g, 190.3 mmol, Fisher Chemical) following a procedure in the literature [19]. A surface treated microparticle silica filler (size range: 0.01 to 3.6 μm, average size 0.6 μm) was obtained from 3M. Composites were prepared by mixing 75 wt% of silica filler and 25 wt% of resin which includes 3 wt% of photoinitiator in a Flacktek at 30 rpm for 2 minutes. While many of the composites include sulfur-containing compounds, there is no noticeably distinct odor that emanates from these composites beyond that of conventional methacrylate composites.

Methods

The vinyl functional group conversion in each resin was determined using Fourier transform infrared (FTIR) spectroscopy (Nicolet 750) during photopolymerization. Samples (50μm thickness) were irradiated for 5 minutes at 10 mW/cm² intensity by one of two visible-light dental lamps (G-light equipped with a 470 nm band-pass filter (GC America Inc.) and 430 nm dental LED light (MODEL 5560 ALZ, 3M)). The conversions of the methacrylate, norbornene, and allyl sulfide were determined by monitoring infrared absorption peaks centered at 3105 cm⁻¹ (C=C-H stretching), 3058 cm⁻¹ (C=C-H stretching), and 3077 cm⁻¹ (C=C-H stretching), respectively. Gaussian fitting was used to deconvolute the peak areas as the methacrylate peak is overlapped with the norbornene and allyl sulfide peaks.[14-15]

The shrinkage stress was monitored using tensometry (Paffenbarger Research Center, American Dental Association Health Foundation)[6, 20] during the photopolymerization of each resin or composite. A tensometer utilizes the cantilever beam deflection theory to evaluate how much the beam deflects for a given stress level. In this study, three different beam configurations were necessary to measure the model and control resins due to the limitations of each beam configuration in regards to accurate measurement of the stress level. Since the targeted resin possesses a stress level that is insufficient to deflect the lower compliance beam (stiffer) beam which was used for the control resin, a more deflective beam configuration had to be used to measure stress for the model resins. To adjust compliance for the model system with the same beam type, a shorter beam length was utilized, which was previously reported to lead to increased measured stress levels as the beam length decreases[20]. Therefore, the stress value of the model resin, which was obtained with the shorter beam configuration, would be expected to be even lower if it could be measured accurately at the same length and compliance as the control. Therefore, the difference between the model and control systems are even larger than that which is reported here, and what is reported here represents a conservative estimate of the difference between the sample and control. The experiments were performed by irradiating samples (6 mm in diameter and 1 mm thick) for 5 minutes at 10 mW/cm² intensity using the G-light dental lamp (equipped with a 470 nm filter).

The elastic modulus (E') and glass transition temperature (T_g) of the polymerized samples were determined by dynamic mechanical analysis (DMA) (TA Instruments Q800). Rectangular samples (length*width*thickness : ~8mm*5mm*1mm) were prepared by sandwiching the material between 2 glass slides with 1mm thickness spacers and cured under identical irradiation conditions to those used in the tensometer experiments. Experiments were performed at a strain and frequency of 0.1% and 1 Hz, respectively, and scanning the temperature twice at a ramp rate of 1 °C/minute. The T_g was assigned as the temperature at the tan delta peak maximum [21-22] of the second scan. Flexural strength and modulus were measured by using a Mechanical Test System (MTS, The 858 Mini Bionix II Test System) using a 3-point bending test procedure with 20mm span and 1mm/minute rate. For these tests, 2mm samples were prepared by the same method as described for the DMA sample preparation. All experiments were repeated three times. ANOVA (CI 95%) was conducted to determine statistically significant differences between the means for all the reported results at the 95% confidence level.

RESULTS

Methacrylate conversions for samples formulated with a 1:2 molar ratio of MDNS to PAS (i.e., a 1:1 norbornene to methacrylate functional group ratio due to the two norbornenes per MDNS molecule), which contains 3wt% of either a Ge-based photoinitiator (dibenzoyldiethylgermane) or BAPO (phosphine oxide, phenyl bis(2,4,6-trimethyl benzoyl)), are shown as a function of time in Figure 3(A). Additionally, we examined the effect of the irradiation wavelength, using either 470 or 430 nm light, on the curing kinetics. Formulating the resin with BAPO resulted in a slow reaction rate using either 470 nm or 430 nm light owing to the low absorption of BAPO at these wavelengths. In contrast, the Ge-based photoinitiator, which absorbs light in the 470 nm region, yields an enhanced reaction rate due to the greater photon absorption rate.

A resin containing MeDNS, a propyl sulfide-containing analog monomer, is also evaluated as a negative control relative to the resin containing MDNS. The propyl sulfide has a nearly identical structure, functionality, polymerization capability and molecular volume as the allyl sulfide but is incapable of undergoing AFCT. The polymerization rate of the propyl sulfide-containing system is faster than for the allyl sulfide-containing system due to AFCT

of the allyl sulfide, as noted previously [14-16]. The norbornene conversion of the resins examined here demonstrates similar reaction trends as the methacrylate conversion, but with a lower final conversion (~40%). As expected with the AFCT mechanism, the allyl sulfide conversion is less than 6% for all systems, indicating that radical addition to the allyl sulfide primarily proceeds through the desired AFCT mechanism rather than through a variety of other undesirable reactions that would lead to consumption of the allyl sulfide functional group.

Shrinkage stress during polymerization was measured using 470nm light with the Ge-based initiator for BisGMA-TEGDMA 70/30 wt%, MDNS-PAS, and MeDNS-PAS resins (Figure 4(A)). Both MDNS-PAS and MeDNS-PAS systems demonstrated 96% and 92% reduced stress, respectively, compared with the conventional BisGMA-TEGDMA 70/30 wt% resin. Since both of the allyl sulfide-containing norbornene-methacrylate resins possess such a low stress level, different compliance configurations were necessary to measure these low stress values. The MDNS-containing resin exhibits a 50% lower final stress when compared with the MeDNS-containing resin as the concentration of the allyl sulfide moiety is increased in the MDNS resin. Selected mechanical properties of the polymerized resins and composites (i.e., resins filled with silica) are shown in Table 2. As the stress is reduced in the norbornene-methacrylate system, mechanical properties such as the elastic modulus and glass transition temperature are also reduced when compared with the BisGMA-TEGDMA control system. However, as the methacrylate ratio was increased (1:1 to 1:2 or 1:4 norbornene:methacrylate ratio), the flexural strength and modulus exhibited significant improvement (Figure 4(C)) while maintaining the stress level significantly lower than in the BisGMA/TEGDMA composite (Figure 4(B)).

In Table 1, the norbornene conversions for all the materials demonstrate similar reaction behavior with the methacrylate, but the final conversion is lower than the methacrylate functional group. Recognizing the inability of the norbornene group to homopolymerize, to improve the final conversion of the norbornene functional group, the relative methacrylate amount was increased in the MDNS-PAS resin. The conversion of these resins, which includes a resin with a 1:8 molar ratio of MDNS to PAS (1:4 of norbornene to methacrylate functional group ratio) is shown in Figure 3(B). The ultimate norbornene conversion increases with increasing methacrylate content in each of these systems.

DISCUSSION

The total curing time for the material must be sufficiently short to be considered practical for dental applications. Classically, the photopolymerization rate is proportional to the square root of the initiation rate, which depends on the photoinitiator concentration and its effective absorption of the incident irradiation [23]. The Ge-based initiator has a relatively high light absorption at 470nm in comparison with BAPO [19]. The effect of light absorption is clearly observed in the large differences in reaction rates between resins using the Ge-based initiator versus BAPO (Figure 3(A)). The faster reaction rate observed in the propyl sulfide-containing system (MeDNS-PAS) compared with the allyl sulfide-based system (MDNS-PAS) owes to the higher concentration of the AFCT capable allyl sulfide functional groups (Figure 3). While both resins contain allyl sulfide functional groups resulting from the PAS monomer, the MDNS-PAS system also has an allyl sulfide in the MDNS monomer. The presence of the allyl sulfides reduces the reaction rate through sequestration of some of the radicals in the AFCT process as illustrated in Figure 1(B) and (C).

Polymerization shrinkage stress is the superposition of stress stored during network formation and dissipated by flow and, in the case of AFCT capable materials, network rearrangement. MeDNS has a similar molecular structure to MDNS; however, the allyl

sulfide is replaced with propyl sulfide to eliminate any possible AFCT in this monomer. The final network structure, as represented primarily by the crosslink density, of both materials is similar since chain propagation through the allyl sulfide group is limited. As demonstrated in Figure 4(A), incorporation of the allyl sulfide functionality provides an excellent mechanism for stress relaxation via network rearrangement, as observed in the reduced polymerization shrinkage stress in the MDNS-PAS system containing a larger amount of the allyl sulfide functional group.

Both the MDNS-PAS and MeDNS-PAS resins demonstrated excellent stress reduction (more than 96%) as compared to the conventional BisGMA/TEGDMA 70/30 wt% resin (Figure 4(A)). The lower stress is due to at least two effects. AFCT through the allyl sulfide moieties relaxes stress during polymerization by network rearrangement. Additionally, the nature of the ring-opening reaction of the allyl sulfide-containing ring in PAS also reduces volume shrinkage and the corresponding stress. While there are other minor effects, the very low stress, which is dramatically different from the BisGMA/TEGDMA control, necessitating the use of a higher compliance cantilever to measure the stress, indicates that the synergistic combination of AFCT and ring opening are the likely reasons for the reduced shrinkage stress observed in the norbornene-PAS system.

The mechanical properties of the filled composite, varying the ratio of norbornene to methacrylate, are shown in Figure 4(C) and Table 2. The flexural strength and modulus of the MDNS-PAS composite in 1:1 norbornene to methacrylate functional group ratio were lower than those of the BisGMA/TEGDMA-based composite (Figure 4(C)). Further enhancement of the mechanical properties is achieved simply by, for example, the incorporation of other crosslinking agents or the adjustment of the norbornene to methacrylate ratio. The reduced mechanical properties most likely result from the low norbornene conversion, which is attributed to poor copolymerization with the methacrylate and the inability of the norbornene to homopolymerize. As the ratio of norbornene to methacrylate functional groups is 1 to 1, homopolymerization of the methacrylate produces a stoichiometric imbalance, significantly effecting the copolymerization and final norbornene conversion. Increasing the methacrylate ratio improved the norbornene conversion by increasing the likelihood of reaction between the norbornene and a carbon-centered radical. Using excess methacrylate also improved the flexural modulus and strength while yielding only a slightly increased level of polymerization stress.

CONCLUSIONS

Incorporation of AFCT of allyl sulfide and ring-opening polymerization mechanisms in a norbornene-methacrylate monomer resin demonstrated almost zero shrinkage stress (more than 96% stress reduction) compared with a conventional BisGMA/TEGDMA 70/30 wt% resin. Increasing the amount of the allyl sulfide-containing species in the resin formulation reduces the final stress as shown in the MDNS-PAS system which is reduced by as much as 50% compared with the MeDNS-PAS system. The mechanical properties of the allyl sulfide-based dental resins were improved (i.e. flexural modulus: from 6.3 GPa to 14.5 GPa) by changing the molar ratio of the methacrylate and norbornene functional groups while increasing the shrinkage stress level only minimally. Although more development remains such as improving the polymerization rate and evaluating moisture uptake and shelf stability, these low stress resins exhibit excellent mechanical properties and stress development and hold significant promise as dental restorative materials.

Acknowledgments

This investigation was supported by NIDCR 2 R01 DE-010959-11 from the National Institutes of Health and NSF 0933828.

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Figure 1.

(A) Schematic of the allyl sulfide AFCT mechanism in the presence of a thiyl radical which results in bond rearrangement but regeneration of the identical chemical structure. (B) Schematic of the allyl sulfide AFCT mechanism in the presence of a carbon-centered radical which results in an asymmetric chemical structure. (C) Schematic of the AFCT mechanism in the presence of a carbon-centered radical which results in a symmetric but AFCT-incapable structure.

Figure 2.
Materials used: (1) MDNS (2) MeDNS (3) PAS (4) Dibenzoyldiethylgermane (5) BAPO (6) Bis-GMA (7) TEGDMA

Figure 3.

(A) Reaction behavior of the methacrylate functional group using 470 nm light with dibenzoyldiethylgermane (square), 470 nm light with BAPO (circle), and 430 nm light with BAPO (triangle) versus time for allyl sulfide-containing MDNS-PAS (open symbols) and propyl sulfide-containing MeDNS-PAS (closed symbols) resins. Resins were formed from a 1:1 norbornene:methacrylate molar ratio. (B) Norbornene conversion versus methacrylate conversion of 1:1 (square) and 1:4 (circle) norbornene:methacrylate molar ratio in MDNS-PAS resins which contain 3 wt% dibenzoyldiethylgermane, irradiated at 10 mW/cm² using 470 nm light.

Figure 4.

(A) Polymerization shrinkage stress versus time of BisGMA-TEGDMA 70/30 wt% resin (square), MDNS-PAS resin (1:1 norbornene to methacrylate) (triangle), and MDNS-PAS resin (1:1 norbornene to methacrylate) (circle). Different compliance beams were necessary. (See the methods section) (B) Polymerization shrinkage stress versus time of MDNS-PAS composites as the ratio of norbornene to methacrylate changes from 1:1 (triangle) to 1:4 (circle). (C) Flexural modulus and flexural strength of BisGMA-TEGDMA 70/30 wt%, MDNS-PAS (1:1 norbornene to methacrylate), and MDNS-PAS (1:4 norbornene to methacrylate) composites. Composites include 75 wt% silica filler and 25 wt% resins. Resins include 3 wt% dibenzoyldiethylgermane. Samples were irradiated at 10 mW/cm² using 470 nm light.

Table 1

Final conversion of resin systems.

Resin System (Norbornene:Methacrylate)	Irradiation wavelength/photoinitiator (wt%)	Functional group conversions [%]		
		Methacrylate	Norbornene	Allyl sulfide
MeDNS_PAS (1:1)	470nm/Ge-based PI (3wt%)	100 (1)	25 (2)	5 (1)
MDNS_PAS (1:1)		97 (1)	23 (2)	2 (1)
MDNS_PAS (1:4)		71 (1)	41 (1)	4 (1)
MeDNS_PAS (1:1)	470nm/BAPO (3wt%)	83 (1)	9 (1)	4 (1)
MDNS_PAS (1:1)		60 (1)	5 (1)	3 (1)
MeDNS_PAS (1:1)	430nm/BAPO (3wt%)	98 (1)	11 (1)	6 (1)
MDNS_PAS (1:1)		83 (1)	9 (1)	2 (1)

Table 2

Summary of T_g , Elastic modulus (E'), Flexural strength, and Flexural modulus of unfilled resins and filled dental composites. The composite is formulated with 75wt% silica filler and 25wt% resin. Resins include 3 wt% dibenzoyldiethylgermane. Samples were irradiated with 10 mW/cm² of 470 nm light. Different beam configurations were used in the stress measurements. 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.

Systems (Norbornene : Methacrylate)	Stress [KPa]	Compliance of the tensometer [$\mu\text{m}/\text{N}$]	T_g [$^{\circ}\text{C}$]	E' at 0°C [GPa]	E' at 25°C Before heating [GPa]	Flexural modulus [GPa]	Flexural strength [MPa]
Resin MeDNS_PAS (1:1)	250 (10) ^a	270	70	1.7	1.4	-	-
Resin MDNS_PAS (1:1)	130 (10) ^b	270	55	2.2	1.0	-	-
Resin BisGMA_TEGDMA 70/30 wt% *	2900 (100) ^c	2	160	3.5	1.8	-	-
Composite MDNS_PAS (1:1)	370 (30) ^d	29	65	13	9.8	6.3 (0.5) ^a	53 (2) ^a
Composite MDNS_PAS (1:2)	400 (10) ^d	29	90	14	13.4	13.5 (1) ^b	92 (10) ^b
Composite MDNS_PAS (1:4)	420 (30) ^d	29	110	13	12.9	14.5 (0.3) ^b	87 (4) ^b
Composite BisGMA_TEGMA 70/30 wt%	640 (20) ^e	29	210	13	12.5	15.3 (1) ^b	118 (10) ^c