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Using hyperbranched oligomer functionalized glass fillers to reduce shrinkage stress

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Abstract

Objective—Fillers are widely utilized to enhance the mechanical properties of polymer resins. However, polymerization stress has the potential to increase due to the higher elastic modulus achieved upon filler addition. Here, we demonstrate a hyperbranched oligomer functionalized glass filler UV curable resin composite which is able to reduce the shrinkage stress without sacrificing mechanical properties.

Methods—A 16-functional alkene-terminated hyperbranched oligomer is synthesized by thiol-acrylate and thiol-yne reactions and the product structure is analyzed by ¹H-NMR, mass spectroscopy, and gel permeation chromatography. Surface functionalization of the glass filler is measured by thermogravimetric analysis. Reaction kinetics, mechanical properties and shrinkage stress are studied via Fourier transform infrared spectroscopy, dynamic mechanical analysis and a tensometer, respectively.

Results—Silica nanoparticles are functionalized with a flexible 16-functional alkene-terminated hyperbranched oligomer which is synthesized by multistage thiol-ene/yne reactions. 93% of the particle surface was covered by this oligomer and an interfacial layer ranging from 0.7 – 4.5 nm thickness is generated. A composite system with these functionalized silica nanoparticles incorporated into the thiol-yne-methacrylate resin demonstrates 30% reduction of shrinkage stress (from 0.9 MPa to 0.6 MPa) without sacrificing the modulus (3100 ± 300 MPa) or glass transition temperature (62 ± 3 °C). Moreover, the shrinkage stress of the composite system builds up at much later stages of the polymerization as compared to the control system.

Significance—Due to the capability of reducing shrinkage stress without sacrificing mechanical properties, this composite system will be a great candidate for dental composite applications.

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Keywords

Thiol-yne-methacrylate; Hyperbranched oligomer functionalized glass fillers; Shrinkage stress

1. Introduction

Inorganic fillers are widely incorporated into photocurable resins to increase the mechanical properties, particularly the modulus and hardness, while reducing the overall shrinkage through a reduction in the volume fraction of resin. These inorganic fillers are often functionalized with reactive organic groups so that the filler and the polymer matrix are integrated by covalent bonds between the phases to achieve enhanced reinforcement.[1]

Polymerization induced shrinkage and shrinkage stress are unavoidably generated during polymerization due to the formation of a higher density polymer and gelation of the polymer network. In filled systems, the shrinkage is reduced by reducing the volume fraction of the resin;[2] however, the overall shrinkage stress in some cases may increase due to the higher modulus associated with the composites where this general behavior is predicted by Hooke's law.[3] Under these conditions, stress is generated throughout the resin and often concentrated at the resin-filler interface. The stress accumulates at the resin/filler interface because the filler is the lowest compliance portion of the composite.[4] Moreover, during the exothermic radical polymerization, a significant difference in the temperature and thermal expansion arises between the polymer matrix and the inorganic filler, resulting in further stress accumulation at the resin/filler interface.[5] Many studies have focused on modifying the resin systems as a means to reduce shrinkage stress.[2] In contrast, there are fewer methods that have been investigated for modifying the filler/resin interface as a means to reduce the shrinkage stress. In one collection of work, Shah and Stansbury reported that shrinkage stress can be reduced by functionalizing the filler with polymer brushes that serve as an interfacial layer which mitigates stress development.[6,7]

In recent years, dendrimers and hyperbranched polymers have been reported as additional components in polymer resin systems that reduce shrinkage or shrinkage stress when compared with other similar molecular weight molecules. It has been reported that mixtures of dendrimers and epoxy composites reduced polymerization shrinkage stress based on the different reactivities of the dendrimer and the resin systems[8] and that the mixture of the hyper-branched polymers and dental resin systems reduces the volumetric shrinkage.[9] With this potential to reduce shrinkage or shrinkage stress, it is interesting to explore the use of a hyperbranched polymer as an interfacial layer between the filler and resin in the composite system. In this paper, a flexible hyperbranched molecular structure is designed and immobilized on the glass filler. Using the hyperbranched oligomer as an interfacial layer provides higher compliance and enough mobility between the polymer matrix and the inorganic fillers to reduce the shrinkage stress. Moreover, the highly available functional groups on the surface of the hyperbranched oligomer may also improve the efficiency of the covalent bounding and subsequent integration of the glass filler into the resin.

'Click reactions' have more recently been utilized to synthesize dendrimers due to their high selectivity, high yield, no by-products and insensitivity to water and air.[10] In particular, various thiol-X click reactions have been utilized to control molecular architecture as synthetic routes for dendrimer synthesis [11,12] because of their advantages of high conversion, solvent free formulation, UV initiated reactions and limited oxygen inhibition. [10] Different types of thioether [13] and double bond terminated dendrimers [14] have been synthesized, and it has been reported that a combination of two click reactions, Cu(I)-catalyzed alkyne-azide cycloadditions (CuAAC) and thiol-ene reactions, was used to

synthesize a 6-generation dendrimer in a single day.[15] Thiol-yne reactions have also been employed in dendrimer synthesis,[16] and a sixteen-functional alcohol or acid functionalized oligomer was synthesized from a tetrayne and an AB₂ molecule via a one-step reaction.[17]

2. Experimental

2.1. Materials

Propargyl acrylate, triethylamine (TEA), thioglycerol, *N,N*-dimethylformamide (DMF), 4-pentenoic anhydride, anhydrous tetrahydrofuran (THF), pyridine, 4-(dimethylamino)pyridine (DMAP), trans-indole acrylic acid (IAA), and sodium citrate monobasic were purchased from Sigma-Aldrich. Dichloromethane (DCM), ethyl ether, hexane, ethyl acetate, sodium bicarbonate, sodium chloride and anhydrous sodium sulfate were purchased from Fisher. 2,2'-dimethoxy-2-phenylacetophenone (Irgacure 651) was donated by BASF Co. Pentaerythritol tetra(3-mercaptopropionate) (PETMP) and ethoxylated bisphenol A dimethacrylate (EO/phenol 1.5) (EBPADMA) were donated by Evans Chemetics and Esstech Inc., respectively. 1,6-heptadiyne (HDY) was purchased from Aldrich.

2.2. Methods

Here, a 16-alkene-terminated hyperbranched oligomer was synthesized via a combination of thiol-acrylate and thiol-yne reactions as shown in Scheme 1. First, a tetrathiol core was reacted with propargyl acrylate via a thiol-acrylate Michael addition using triethylamine as the catalyst to obtain a tetrayne molecule [18], which was further reacted with thioglycerol via a thiol-yne click reaction initiated by a UV photoinitiator, Irgacure 651.[17] Subsequently, a condensation reaction of alcohol and anhydride was carried out to obtain a 16 alkene functional hyperbranched oligomer.[14] Subsequently, this hyperbranched alkene oligomer is immobilized to the thiol functionalized glass filler via a UV photoinitiated thiol-ene reaction. The hyperbranched oligomer functionalized glass filler was incorporated into a thiol-yne-methacrylate ternary resin system, which has been reported as a resin system with high modulus and glass transition temperature that achieves low shrinkage stress.[19] The reaction kinetics, mechanical properties and shrinkage stress of this composites system were studied.

2.2.1. Synthesis of 4-functional alkyne molecule (compound I)—PETMP (4.88 g, 10 mmol) was dissolved in 120 mL DCM in a one-neck round flask and TEA (0.28 mL, 2 mmol) was added. 4.4 equivalents (to PETMP) of propargyl acrylate (4.84 g, 44 mmol) were dissolved in 60 mL DCM and added dropwise to the flask by an addition funnel. The reaction was left overnight with stirring. Then, the reaction mixture was washed by saturated sodium citrate monobasic, saturated sodium bicarbonate and brine (3 × 200 mL each). The organic layer was dried over anhydrous sodium sulfate, filtered and then concentrated. A clear viscous liquid (14 g, 15 mmol, 75% yield) was obtained. ¹H NMR (300 MHz, CDCl₃, δ (ppm)): δ 4.67 (8H), δ 4.12 (8H), δ 2.80 – 2.73 (16H), δ 2.65 – 2.57 (16H), δ 2.48 (4H).

2.2.2 Synthesis of 16 functional alcohol-terminated oligomer (compound II)—The 4-functional alkyne (compound I) (14 g, 15 mmol) was dissolved in 40 mL DMF in a single-neck round bottom flask and mixed with thioglycerol (13.7 g, 127 mmol, 5% excess) and DMPA (1.35 g, 5 mmol, 5 wt%). The flask was vacuumed and purged by nitrogen with stirring. The sample was irradiated by a UV light source (Acticure, EFOS, Mississauga, Ontario, Canada) passing through a 320–500 nm filter at 10 mW/cm² for 4 hours. After rotavapping the DMF, the viscous material was precipitated by ethyl ether five times and dried overnight. A yellow viscous liquid (17 g, 9.5 mmol, 63% yield) was obtained. ¹H

NMR (300 MHz, DMSO-*d*₆, δ (ppm)): δ 4.84 – 4.75 (8H), δ 4.60 – 4.54 (8H), δ 4.31 – 4.05 (16H), δ 3.60 – 3.51 (8H), δ 3.21 – 3.13 (4H).

2.2.3. Synthesis of 16 hyperbranched alkene-terminated oligomer (compound III)—The 16-functional alcohol (compound II) (4.73 g, 2.6 mmol) was dissolved in 150 mL anhydrous THF in a single-neck round bottom flask and purged with argon. This liquid was transferred to a three-neck flask with molecular sieves. 0.15 equivalents (relative to the alcohol functional group) of DMAP (0.77 g, 6 mmol), 3 equivalents of anhydrous pyridine (10 g, 126 mmol) and 3 equivalents of 4-pentenoic anhydride (23 g, 126 mmol) were added to the flask with stirring. The reaction was left overnight, quenched by water, and then diluted by DCM and filtered. The reaction mixture was then washed by water (5 $\times$ 300 mL), saturated sodium bicarbonate and brine (3 $\times$ 200 mL each). The organic layer was dried over anhydrous sodium sulfate, filtered and then concentrated. A clear viscous liquid (4.7 g, 1.5 mmol, 57% yield) was obtained. ¹H NMR (300 MHz, CDCl₃, δ (ppm)): δ 5.90 – 5.72 (16.5H), δ 5.20 – 4.95 (41.8H), δ 4.46 – 4.05 (32H), δ 3.19 – 3.03 (3.7H), δ 2.95 – 2.49 (55.4H), δ 2.49 – 2.28 (67.6H).

The final hyperbranched oligomer product contained 70% 16-alkene terminated hyperbranched oligomer, 19% coupling by-products and 11% small molecule impurities as synthesized via thiol-acrylate Michael addition and thiol-yne click reactions. The oligomer structure is determined by ¹H-NMR, mass spectrum (MALDI and HPCL/MS) and gel permeation chromatography (GPC). Via the thiol-ene radical coupling reaction, 93% of the particle surface is covered by the hyperbranched oligomer and an interfacial layer with 0.7 – 4.5 nm thickness is generated. More detailed discussions are given in Supplementary Materials Fig. 5 – 11.

2.2.4. Synthesis of thiol functionalized glass filler—Silica nanoparticles OX50 (5 g) were added to 100 mL cyclohexane with stirring until well dispersed in a single-neck round bottom flask. n-propylamine (0.1 g) was added to the mixture with stirring for 15 minutes. (3-mercaptopropyl)trimethoxysilane (0.5 g) was added to the mixture and reacted for 30 minutes at room temperature followed by increasing the temperature to 60 °C to react for another 30 minutes. The solvent was removed at 60 °C and the powder was heated 90 °C for 1 hour by a rotary evaporator. The powder was then dried at 80 °C in a vacuum oven overnight.

2.2.5. Reactive immobilization of the hyperbranched oligomer to the glass filler—The 16 alkene-terminated hyperbranched molecule (compound III) (0.5 g) and Irgacure 651 (0.05 g) were dissolved in 10 mL DMC. Silica nanoparticles OX50 (1 g) were added to the mixture with stirring until well dispersed. Then, the mixture was reacted under 320 – 500 nm UV light at 15 mW/cm² for 2 hours. The particles were isolated by centrifuge and washed by DCM 3 times, then finally dried in a vacuum oven at 35 °C overnight.

2.3. Characterization

2.3.1. Hyperbranched Oligomer Characterization—A 300 MHz NMR spectrometer (Bruker 300 UltraShield) was used to obtain ¹H spectra. The chemical shifts are referenced to CHCl₃ 7.25 ppm and DMSO 2.5 ppm. MALDI-TOF (positive mode) was used to determine the molecular weight of the product. 200 mg product was dissolved in 1:1 methanol/DCM and IAA was used as the matrix. Gel permeation chromatography (GPC) (Viscotek 3580) was performed in tetrahydrofuran (THF) with three detectors (refractive index, light scattering and viscometer) used to evaluate the sample.

2.3.2. Particle Characterization—Thermogravimetric analysis (TGA) (Pyris 7, Perkin Elmer) was utilized to determine the weight loss from functionalized silica particles as a means for determining the degree of functionalization on the particles. The weight change of a 10 mg sample as a function of temperature was evaluated with temperature ramping from 50 – 850 °C at 10 °C/min under a nitrogen flow of 20 mL/min.

2.3.3. Composite Characterization—The functionalized filler was incorporated into a thiol-yne-methacrylate ternary resin (PETMP:HDY:EBPADMA=2:1:2.7) which was previously developed and evaluated.[19] For each specimen, at least three replicates were evaluated. The one-way analysis of variance (ANOVA) method was used to analyze conversion, glass transition temperature, elastic modulus and shrinkage stress values at $P < 0.05$ ($n=3$). Pairwise comparisons were analyzed by Student-Newman-Keuls pairwise comparisons

Fourier transform infrared spectroscopy (FTIR) (Magna 750, series II, Nicolet Instrument Corp., Madison, WI) combined with a UV-light source (Acticure, EFOS, Mississauga, Ontario, Canada) was utilized to measure the real time conversion during curing. Composite samples were cured with 365 nm light at 10 mW/cm² in the FTIR chamber. Mid-IR was employed to study the reaction kinetics with ~10 µm thick samples between NaCl plates. The conversion of the alkyne functional groups was determined by monitoring the C-H stretch at 3288 cm⁻¹, the thiol functional groups were monitored via the S-H stretch at 2570 cm⁻¹, and the methacrylate functional group conversion was determined by measuring the C=C vibration absorption at 1637 cm⁻¹. To couple with various mechanical property measurements, near-IR was utilized to evaluate functional group conversions in polymerizations of 1 mm thick samples polymerized between glass slides. The alkyne and methacrylate conversions were monitored by the C-H vibration peak at 6505 cm⁻¹ and the C=C vibration peak at 6163 cm⁻¹, respectively.

A dynamic mechanical analyzer DMA Q800 (TA Instruments) was utilized to measure the glass transition temperatures and moduli of samples with 1 × 2 × 10 mm rectangular dimensions. Multi-frequency strain mode was utilized by applying a sinusoidal stress of 1 Hz frequency with the temperature ramping from -40 to 160 °C at 3 °C/minute. The T_g was determined as the maximum of the tan delta curve. The modulus values at ambient temperature and well into the rubbery state were measured at 25 °C and at 50 °C above the glass transition temperature, respectively. The specimens were stored for approximately one week following polymerization prior to the elastic modulus measurement.

A cantilever mode tensometer (American Dental Association Health Foundation) combined with a UV-light source (Acticure, EFOS, Mississauga, Ontario, Canada) and the simultaneous implementation of FTIR via optical fibers (Magna 750, series II, Nicolet Instrument Corp., Madison, WI) were utilized to measure the shrinkage stress and conversion during polymerization by 15 minutes. The samples were disk shapes with 6 mm diameter and 1 mm thickness. An aluminum beam with 3.6 µm/N compliance was chosen to enable the stress measurement of all the test and control formulations.

3. Results

In Fig. 1, the polymerization kinetics were evaluated for four different samples: (1) resin without filler, (2) with 20% thiol functionalized filler, (3) 20% hyperbranched oligomer functionalized filler and (4) 20% thiol functionalized filler with additional hyperbranched oligomers added to the bulk resin. Thus, in sample 3 the oligomers are immobilized on the filler by covalent bonding while in sample 4 an equivalent amount of functional oligomer is added into the bulk resin by physically mixing the components rather than coupling the

oligomer to the interface. The reaction rates of the samples with fillers are all slightly faster than the control resin without filler due to the increased viscosity of the filled systems. Only minor differences are observed in the reaction rates among all three composite systems. Though having different reaction rates at the early stage of the reaction, these four systems all reach similar final methacrylate and thiol conversions after 15 minutes of irradiation (MA = 91 ± 1 % and thiol = 53 ± 1 %) without statistical difference shown in Table 1. The final conversion of the alkyne group in all three filler systems is 74 ± 2 %, and in the control resin system it is 64 ± 4 %.

The moduli of all three filled systems are obviously higher than the control resin at both ambient temperature and in the rubbery state as shown in Fig. 2 (a) and Table 1 and statistically significant differences were shown among these values. Compared with the glassy modulus of the control resin (2200 ± 200 MPa) at ambient temperature, those of the thiol functionalized filler, hyperbranched oligomer functionalized filler, and the thiol functionalized filler with additional hyperbranched oligomer are 3100 ± 300 , 3100 ± 300 and 2800 ± 200 MPa, respectively, resulting from the reinforcement of the inorganic filler. The rubbery moduli of all three filled systems achieve a value near 40 MPa, significantly higher than the control resin in the absence of filler (22 ± 1 MPa). The T_g of the thiol functionalized filler, hyperbranched oligomer functionalized filler, and the thiol functionalized filler with additional hyperbranched oligomer are 64 ± 4 , 64 ± 4 and 66 ± 1 °C, respectively, and slightly higher than the non-filled system (58 ± 3 °C), which exhibit a slightly broader glass transition window though no statistically significant difference has been shown among the T_g values.

In the filled systems, the volumetric shrinkage is reduced due to the reduction of the resin fraction which, by itself, would reduce the shrinkage stress. However, the higher modulus of the filled system is expected to lead to an increase in the shrinkage stress. Demonstrating a balance of these two factors, Table 1 shows similar shrinkage stress values (0.9 ± 0.1 MPa) for the resin without filler and the resin containing only 20 wt% thiol functionalized filler. Interestingly, both hyperbranched oligomer functionalized filler and thiol functionalized filler with additional hyperbranched oligomer show a much lower shrinkage stress (0.6 ± 0.1 MPa) indicating that the incorporation of a functional hyperbranched oligomer into filled systems is able to reduce the shrinkage stress significantly. Fig. 3 demonstrates that the shrinkage stress builds up with the methacrylate conversion. The resin without filler, resin with thiol functionalized filler, and hyperbranched oligomer functionalized filler all reach nearly the same methacrylate conversion and the thiol functionalized filler with additional hyperbranched oligomer reaches a slightly higher conversion, indicating the shrinkage stress of the systems with hyperbranched oligomer are reduced by 30% without sacrificing conversion or mechanical properties. Moreover, these systems with the hyperbranched oligomer develop the stress at a late curing stage (~70% MA conversion).

4. Discussion

This 16 functional alkene-terminated hyperbranched molecule was covalently immobilized to the thiol functionalized OX50 silica nanoparticles by the thiol-ene click reaction initiated by 320 – 500 nm UV light irradiation and the photoinitiator Irgacure 651 (Scheme 2). The TGA result in Fig. 10 in Supplementary Materials shows that 1.7 and 5.3 % initial weight losses were found from thiol and oligomer-functionalized particles, respectively. Based on the weight loss, there are 1.3 thiols per nm^2 , which is estimated as approximately a monolayer; and there are 0.14 hyperbranched oligomers per nm^2 indicating that each hyperbranched oligomer reacts with approximately 9 thiol groups, leaving approximately 0.8 free alkene functional groups per nm^2 on the interfacial layer. Moreover, Chemdraw 3D predicts a tetrahedral shape with the cross-sectional area of approximately 6.5 nm^2 for the

hyperbranched oligomer at its lowest energy. Compared with a spherical OX50 particle having a diameter of 40 nm, if the surface of the particles is fully packed with tetrahedral molecules, theoretically there are approximately 0.15 oligomeric molecules per nm², and the experimental result of 0.14 molecules per nm² would represent 93% coverage. Furthermore, when attaching to the particle surface, the tetrahedral molecules are likely to assume a different, non-equilibrium shape. Thus, the maximum thickness of the interfacial layer would be ~4.5 nm for the tetrahedral shape and the minimum thickness of ~0.7 nm is estimated for dense packing, assuming the density of the grafted organic layer is 1.1 g/mol. The thickness of the interfacial layer may also change during polymerization of the composite resin in response to the shrinkage and interfacial stress.

When the fillers are added to the resin, the reaction rates of the composites are faster than the pure resin system. This outcome arises because the termination rate is reduced by increasing viscosity, resulting in a faster overall reaction rate in the filled systems. The reduced termination rate in filled systems also leads to the higher final conversion of the alkyne group as shown in Table 1. Moreover, the reaction rates of the composites with thiol functionalized particles are slightly higher than that of the system with the hyperbranched oligomer functionalized particles due to the different functional group concentration and mobility in the interfacial layer. However, since the amount of the functional groups on the particle surface is very small compared with the functional group concentration in the bulk, only minor differences are observed.

Even though, T_g and modulus are increased comparing with non-filled system, there are very subtle difference between the filled systems. The higher final conversion of the system containing the thiol functionalized particles with free oligomer causes slightly higher T_g (see Table 1 near IR conversion); however, a thiol functionalized particle has fewer reactive sites at the surface compared with the oligomer functionalized particle, thus, particles might loosely incorporate with the resin and slightly lower the elastic modulus. The elastic modulus values in Table 1 are lower than the commercial composites because only 20% filler is added to the samples compared with more than 70% in commercial composites. In addition to the expected increase in modulus of the composites, for oligomers covalently coupled to the particle interface as compared to those free in solution, the geometry of these distinct species is expected to be much different. We hypothesize the reason for reducing the shrinkage stress in both filled systems with hyperbranched oligomers is that the hyperbranched oligomer provides additional mobility and capability to relax the network to relieve the shrinkage stress.

5. Conclusions

OX50 silica nanoparticles were functionalized by a flexible 16 functional alkene-terminated hyperbranched oligomer which was synthesized by various step-wise thiol-ene/yne reactions. 93% of the particle surface is covered by the hyperbranched oligomer and an interfacial layer ranging from 0.7 – 4.5 nm thickness is generated. A composite system with this filler incorporated into a thiol-yne-methacrylate resin was designed and evaluated. Compared with the control systems, this composite system is able to reduce the shrinkage stress by 30% (from 0.9 MPa to 0.6 MPa) while maintaining equivalent modulus and glass transition temperature. Moreover, the shrinkage stress of this composite builds up at a much later stage in the polymerization. These interesting phenomena are observed in both composite systems with (1) immobilized hyperbranched oligomer and (2) in a physical mixture of the oligomer, resin and filler.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1. Real time conversions for the methacrylate (open symbols) and thiol (filled symbols) functional groups in the thiol-yne-methacrylate ternary resin without filler ($\square$), resin with 20 wt% thiol functionalized filler (∇), hyperbranched oligomer functionalized filler ($\circ$) and thiol functionalized filler with physically mixed hyper branched oligomer (Δ). The systems were initiated with 1.0 wt% Irgacure 184 and cured by 365nm light at 10mW/cm². The triplet results are listed in Table 1.

Fig. 2.

(a) Storage Modulus and (b) $\tan \delta$ vs. temperature for the thiol-yne-methacrylate ternary resin without filler (— · — · —), resin with 20 wt% thiol functionalized filler (— — —), hyper branched oligomer functionalized filler (· · ·) and thiol functionalized filler with additional hyper branched oligomer (—). The systems were initiated with 1.0 wt% Irgacure 184 and cured by 365nm light at 10mW/cm². The curves are the average of triplet replicates listed in Table 1.

Fig. 3. Shrinkage stress vs. methacrylate conversion of the thiol-yne-methacrylate ternary resin (1) without filler, (2) resin with 20 wt% thiol functionalized filler, (3) hyperbranched oligomer functionalized filler and (4) thiol functionalized filler with additional hyperbranched oligomer. The systems were initiated with 1.0 wt% Irgacure 184 and cured by 365nm light at 10mW/cm². The triplet results are listed in Table 1.

Scheme 1.
Synthesis scheme for making the 16 functional alkene-terminated hyperbranched oligomer.

Scheme 2.

Generalized synthesis scheme for the a) thiol functionalized silica particles and b) hyperbranched oligomer functionalized silica particles.

Table 1

Mechanical properties and shrinkage stress values of the thiol-yne-methacrylate resin with 20% fillers. The systems were initiated with 1.0 wt% Irigacure 184 and cured by 365nm light at 10mW/cm².

	MA conversion	Mid IR SH conversion	Yne conversion	Near IR MA conversion	E' (MPa)	T _g (°C)	Stress (MPa)
No filler	0.91(0.01) ^a	0.54(0.01) ^a	0.64(0.04) ^a	0.91(0.01) ^{a,b}	2200(200) ^a	58(3) ^a	0.9(0.1) ^a
Thiol functionalized filler	0.91(0.01) ^a	0.54(0.01) ^a	0.74(0.01) ^b	0.94(0.03) ^{a,b}	3100(300) ^b	64(4) ^a	0.9(0.1) ^a
Hyperbranched oligomer functionalized filler	0.91(0.02) ^a	0.52(0.01) ^a	0.72(0.01) ^b	0.89(0.01) ^a	3100(300) ^b	64(4) ^a	0.6(0.2) ^b
Thiol functionalized filler physically mixing hyperbranched oligomer	0.90(0.01) ^a	0.54(0.01) ^a	0.75(0.02) ^b	0.96(0.04) ^b	2800(200) ^b	66(1) ^a	0.6(0.1) ^b

letters within each column designate statistically significant groups based on one-way ANOVA at P<0.05 (n=3) using Student-Newman-Keuls pairwise comparisons