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Application of an Addition-Fragmentation-Chain Transfer Monomer in Di(meth)acrylate Network Formation to Reduce Polymerization Shrinkage Stress

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Abstract

A new addition-fragmentation chain transfer (AFT) capable moiety was incorporated into a dimethacrylate monomer that participated readily in network formation by copolymerizing with multifunctional methacrylates or acrylates. The process of AFT occurred simultaneously with photopolymerization of the AFT monomer (AFM) and other (meth)acrylate monomers leading to polymer stress relaxation via network reconfiguration. At low loading levels of the AFM, a significant reduction in shrinkage stress, especially for acrylate monomers, was observed with nominal effects on conversion. At higher loading levels of the AFM, the photopolymerization reaction kinetics and final double bond conversion were significantly lowered along with a delay in the gel-point conversion. Electron paramagnetic resonance studies during polymerization revealed the presence of a distinct radical species that was present in proportional quantities to the AFM content in the system. The lifetime and the character of the persistent radicals were altered due to the presence of the distinctive radical, in turn affecting the polymerization kinetics. With polymerization conducted at higher irradiance, the differential conversion between the control resin and samples with moderate AFM content was minimal, especially for the methacrylate-based formulations.

Introduction

Radical initiated photopolymerization reactions offer significant advantages such as user defined spatial and temporal control as well as rapid curing and low energy demand. Applications including coatings, adhesives, dental materials, tissue engineering and 3D printing extensively use photopolymerizations. Radical-mediated photopolymerizations are used primarily with vinyl monomers such as (meth)acrylates and thiol-ene compositions but are also applied to an ever growing variety of other systems.^{1–4} One common problem that accompanies bulk polymerization of monomers like methacrylates and acrylates is the volumetric shrinkage associated with the conversion of monomer to polymer.⁵ When shrinkage is restricted by enforced adhesion to a substrate of limited compliance during polymerization, these restrictions lead to the development of stresses within the polymer that correspond with modulus evolution and produce a variety of defects and failure modes.^{6–11} Consideration of polymerization-induced stress development is especially significant in films and coatings¹², additive manufacturing^{13,14} and biomaterials.¹⁵ For example, in dental restorative materials, the photopolymerization reaction is used to produce a high modulus

restorative material where the reaction takes place in a tooth to which the particulate-filled composite is simultaneously adhesively bonded, often on all but one surface. The stresses generated due to photopolymerization, which easily rise to the megapascal level^{8,16}, can be transferred to the tooth and can lead to failure of the restorative, the interface or even cause damage in the tooth.^{17–20} In coatings and other layered structures such as those developed in additive manufacturing, polymerization shrinkage stresses lead to delamination at the layer-layer interface and warping of the overall device structure. Clearly, in each of these applications, it is desirable to mitigate the development of stresses and limit their impact on the final device performance.

As such, a significant amount of research has been directed toward control of polymerization shrinkage and the associated shrinkage stress. One way to reduce shrinkage is by a reduction in reactive group concentration in the monomer, which can be achieved by the design of higher weight monomers²¹, or by formulation with reactive oligomeric species²² or through the addition of prepolymeric nanogel additives.^{23,24} Polymerization-induced phase separation has also been used to reduce shrinkage and shrinkage stress as has the development of step growth photopolymerization reactions. In particular, the thiol-ene reaction has been explored extensively due to its step growth molecular weight evolution which introduces inherently lower overall shrinkage and allows for delayed gelation that further reduces the shrinkage stress.^{25,26}

In thermosetting polymers, the developing network structure is locked in place as it forms during curing. This “freezing” of the network promotes the characteristic lack of moldability associated with thermoset polymers and does not allow for relief of stress that progressively accumulates throughout the post-gel polymerization process. These stresses thus remain locked into the network. To alleviate the effect of the immobile network, a more recent approach toward reducing shrinkage stress utilizes covalent adaptable networks (CANs).²⁷ As the name suggests, the networks are constructed via covalent bonds that are dynamic and enable the network structure to “adapt” when subjected to specific stimuli. Once a stimulus is applied, the covalent bonds in the network dynamically break, relax and rearrange to form new bonds, in the process releasing the stress that has been built up during the formation of the network. In the case where the bond exchange process is induced by light exposure, the process has been termed “photoplasticity” as it enables an otherwise elastic material to exhibit plastic-like behavior as it relaxes.^{28,29} Uniquely, the end result remains a covalently crosslinked network that has the same crosslink density and mechanical properties as a comparable nonadaptive network but with lower shrinkage stress. The network formation and reorganization processes are either independent or interrelated with either simultaneous or sequential activation possible, depending on the specific mechanisms used for the polymerization and dynamic covalent chemistry.²⁷

CANs that involve reversible crosslinking reactions are an integral part of the network structure such network connections can be broken and reformed, leading to rearrangement to a lower energy state with each revision step.²⁷ There are two primary ways of achieving this behavior – in one case some or all of the bonds are broken upon application of a stimulus and then reformed upon removal of the stimulus. This approach results in a reduction of the intermediate and final crosslink density of the network depending on the conditions used,

such as the temperature and the equilibrium between the undissociated and dissociated states. An example of this type of *reversible addition* mechanism is observed in reversible Diels Alder reactions where the Diels-Alder adduct can be broken upon heating and then reformed upon cooling, which has been used successfully to create healable materials.³⁰ The other way to achieve the reversible rearrangement is to have continuous and *reversible exchange* of covalent bonds upon application of a stimulus. Examples of this include transesterification reactions^{31,32} and reactions involving a reversible addition-fragmentation mechanism.^{29,33–35} The kinetics of bond exchange determine the speed at which the reversible covalent interchange takes place and since the number of bonds before and after the exchange remains essentially the same, the network crosslink density remains unaltered.

Reversible bond exchange as a CANs mechanism has been used widely in recent times to help alleviate stress during polymerization. Addition-fragmentation chain transfer (AFCT) exchange type of reactions fall in the class of the reversible bond exchange mechanism. Examples of AFCT reactions that have been used to help alleviate shrinkage stress include the use of allyl sulfide groups in thiol-ene and thiol-yne polymerizations and using trithiocarbonates in methacrylate polymerizations.^{36–38} More recently, β -allyl sulfone monomers with various vinyl activating groups have been used as chain transfer agents to reduce shrinkage stress while increasing toughness.⁴

The study presented here focused on a novel addition-fragmentation-chain transfer monomer, henceforth called AFM (Figure 1), that in addition to terminal methacrylate reactive groups has a complementary internal double bond with a β -quaternary carbon center. The distinguishing feature is that the addition of a free radical species to the internal vinyl group can then proceed to a degradative radical rearrangement (fragmentation) to yield an α -carbonyl tertiary radical and another internal unsaturated ester. The current work uses the AFM as an additive in model (meth)acrylate comonomer mixtures to study its effect on photopolymerization kinetics and shrinkage stress development as a function of AFM concentration. To probe the underlying mechanisms at work with this structure, this work is extended to include use of the AFM precursor that is capable of addition fragmentation but lacks the terminal methacrylate groups necessary for crosslink formation. The hypothesis to be tested is that even small amounts of AFM in a copolymerization result in significant reductions in shrinkage stress without significant compromise to the mechanical properties of the network. Mechanistic investigations are done using electron paramagnetic resonance (EPR) spectroscopy to determine the type and persistence of specific radical structures that may exist upon addition of the AFM in typical (meth)acrylate photopolymerizations.

Materials and Methods

Materials

All the samples used in this study were formulated and generously donated by 3M (St. Paul, MN) and used as received. Two model comonomer mixtures were examined in this study. The first was composed of bisphenol A diglycidyl ether dimethacrylate (BisGMA) and triethylene glycol dimethacrylate (TEGDMA) premixed in weight ratio 70:30 to which various amounts (0, 2.5, 5, 10 and 20 wt%) of the addition-fragmentation-chain transfer monomer (AFM) were added. The second consisted of the analogous bisphenol A diglycidyl

ether diacrylate (BisGA) and triethylene glycol diacrylate (TEGDA) also premixed in 70:30 weight ratio and modified with various amounts (0, 2.5, 5, 10 and 20 wt%) of AFM. Each of these mixtures had 0.28 wt% camphorquinone, 1.1 wt% ethyl 4-dimethylaminobenzoate, 0.3 wt% diphenyl iodonium hexafluorophosphate as a visible light initiating system along with 0.05 wt% 2,6-di-tert-butyl-p-cresol (BHT) as an inhibitor. The neat AFM and the precursor to the AFM (AFM-precursor) without the methacrylate end groups were also acquired.

Syntheses of the AFM and AFM-precursor were performed at 3M according to previously reported procedures.³⁹ Briefly, the AFM-precursor was obtained by distillation of a methyl methacrylate oligomer mixture following previous literature⁴⁰, that was further hydrolyzed by using 4M aqueous potassium hydroxide solution at 90 °C. The resulting mixture was acidified using HCl to a pH = 1 and the white precipitate was filtered and washed with water to yield diacid as white solid.⁴¹ AFM-1 was obtained via the triphenyl antimony catalyzed ring opening of glycidyl methacrylate with diacid at 100 °C. The AFM-1 was isolated as a clear, pale yellow viscous liquid.³⁹ The structure and purity of the AFM and AFM-precursor were confirmed with NMR.

AFM-precursor—¹H NMR (400 MHz, CDCl₃) δ 6.23 (d, 1H), 5.54 (m, 1H), 3.75 (s, 3H), 3.66 (s, 3H), 2.63 (d, 2H), 1.18 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 177.6, 168.0, 137.5, 128.0, 51.9, 43.0, 41.2, 25.0.

AFM—¹H NMR (400 MHz, CDCl₃) δ 6.30 – 6.08 (m, 3H), 5.63 (m, 3H), 4.48 – 4.06 (m, 8H), 3.82 (m, 1H), 3.08 – 2.42 (m, 4H), 2.03 – 1.85 (m, 6H), 1.26 – 1.15 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 177.1, 167.4, 167.4, 167.3, 136.8, 135.8, 128.9, 126.4, 73.0, 68.1, 68.0, 66.0, 65.6, 65.3, 62.5, 61.4, 42.8, 41.8, 25.1, 24.9, 18.3.

Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier Transform Infrared Spectroscopy (Nicolet 6700 FT-IR, Thermo Scientific) in near infrared (NIR) mode was used to monitor the overall double bond peak area and provide real-time conversion during photopolymerization. The =CH₂ absorption peak at 6165 cm⁻¹ was monitored to track the real-time polymerization. Measurements were taken at a wavenumber resolution of 4 cm⁻¹ with 32 scans per spectrum being acquired for static scans before and after polymerization and 2 scans per spectrum for real-time measurements, which provides an acquisition rate of 2 spectra/s.

Shrinkage Stress measurement

Dynamic photopolymerization shrinkage stress was measured using a tensometer, which is a cantilever-based instrument (American Dental Assoc. Health Foundation). The principle involves measurement of the deflection in a beam due to the force generated by a polymerizing material. Briefly, a sample (1 mm thickness) is placed between two cylindrical quartz rods (6 mm diameter) that are positioned coaxially and whose ends have been polished and treated with a methacrylate functional silane (Fusion, George Taub Products). The bottom rod is fixed while the top one is attached to a steel beam that is anchored at one end while the other end is free to move, acting as a single cantilever. A visible light LED curing (IQ2, Dentsply, output wavelength ~ 450–475 nm) was positioned below the bottom

rod and the tip of the light guide is exactly beneath the rod. Upon irradiation, light is transmitted along the quartz rod to the sample and as the sample polymerizes, it deflects the top beam as it shrinks due to adhesion with the silane-coated quartz rods. The deflection of the beam is determined by a LVDT (Linear Variable Differential Transformer). The tensometer is calibrated to convert the change in voltage measured by the LVDT to a force measurement and this can consequently be converted to a stress value by considering the cross-sectional area of the sample. The shrinkage stress measurement is done real-time along with photopolymerization and simultaneous determination of the double bond-conversion via aligned NIR fiber optic cables (1 mm diameter).⁷

For the stress measurements, the tensometer and NIR data collection were started together with irradiation commencing after 30 s. The exposure extended for 30 s with stress and conversion continuously monitored for 20 min. Before testing, the curing light irradiance exiting the quartz rod was measured with an appropriate visible light radiometer (Demetron). For these shrinkage stress measurements, irradiance reaching the samples was determined to be about 200 mW/cm².

Photorheology

A rheometer (ARES, TA Instruments) was used to determine the crossover point between storage and loss moduli during polymerization. This crossover point can be taken to estimate the gel point conversion of the sample where an infinite polymer network develops in the material. The rheometer was modified to function as a photorheometer, allowing for polymerization of the sample with light while simultaneously using NIR fiber optics to monitor real time conversion⁴². The rheometer was used in a parallel plate configuration with samples being placed between two quartz plates (20 mm diameter, sample thickness = 0.5 mm). The sample was oscillated at a frequency of 10 Hz and at 50% strain using automatic strain adjustment mode to prevent the rheometer from overloading during the experiment. NIR fiber optics were used in the same configuration as in the tensometer to collect real time kinetic data during polymerization. An Acticure 4000 (EXFO) with a 400–500 nm filter was used as the light source at an incident light intensity of 2 mW/cm².

Dynamic Mechanical Analysis (DMA)

A QA 800 DMA (TA Instruments) was used to measure storage and loss moduli and tan delta of polymer samples. Specimens (rectangular bars with dimensions 4×1×25 mm) were prepared by curing the monomer mixtures between glass slides using a high-pressure mercury arc lamp (Acticure 4000, EXFO) and using a 400–500 nm filter. Specimens were irradiated on both the sides at 100 mW/cm² for 10 min per side. Specimens were cooled to –50 °C inside the DMA and heated at a rate of 3 °C/min up to 200 °C. This heating cycle was performed two times for the BisGMA/TEGDMA series of materials and three times for the BisGA/TEGDA series of materials.

Electron Paramagnetic Resonance (EPR)

Detection of radicals generated during polymerization was conducted using a Bruker Elexsys E 500 EPR spectrometer equipped with a Super High Sensitivity Resonator (SHQE cavity). The samples were injected in thin walled quartz EPR tubes (2 mm diameter,

Wilmaad-LabGlass, NJ) and inserted into the EPR chamber. An EXFO Acticure lamp was used for irradiation (400–500 nm filter, 2 mW/cm² at sample) with the light guide attached to a fixture on the EPR in front of the sample chamber. The EPR chamber had slits cut out on the face that allowed the light to pass through to be able to carry out photopolymerization. Exposure to the curing light was either continuous throughout the EPR data collection interval or it was intentionally interrupted while extended EPR monitoring was continued. Real-time NIR conversion measurement could not be coupled with the EPR so analogous samples were removed from the EPR to determine the degree of conversion under various photocuring conditions and intervals. Relative radical concentrations were determined by performing double integration on the acquired spectra that had intensity on the Y-axis and field strength on the X-axis as the independent variables.

Results and Discussion

Scheme 1 shows the addition of a radical to the internal vinyl of the AFM and its subsequent fragmentation. The fragmented radical species that is generated can further initiate polymerization or more addition-fragmentation steps to form a polymer that has a methacrylate terminated radical. This polymer radical can again add with the AFM and regenerate the α -carbonyl tertiary radical and also a polymer that can further fragment and add monomers. This process of forming and breaking covalent bonds while the overall network is being generated can go on repeatedly and this process leads to the reduction of shrinkage stress during polymerization as the reshuffling of covalent bonds inevitability leads to the stress relief. The AFM has methacrylate functional groups on each end and hence is readily integrated into a network containing (meth)acrylate monomers. In a normal thermoset network containing multifunctional (meth)acrylates, once the covalent bonds are formed (Figure 2a) the network is essentially “unchangeable” and the bonds remain fixed. Addition of the AFM into such a network enables the bond exchange within the network (Figure 2b), rendering it dynamic. Thus, upon photopolymerization and network formation, the AFM becomes a part of the network and also fragments and adds monomer, both in the free state as well as while it is part of the network. This breaking and reforming of covalent bonds as the network is being formed enables flow and ultimately stress relief.

Kinetics and Shrinkage Stress measurements

The addition-fragmentation monomer (AFM) is a dimethacrylate that was added in various proportions to two different free radically photocurable resins. Formulation of the AFM with either acrylate (BisGA/TEGDA) or methacrylate (BisGMA/TEGDMA) resins was done in order to analyze the effect of the AFM on the bulk photopolymerization kinetics and shrinkage stress development in systems with different kinetic behavior and propagating radical character. Simultaneous measurement of dynamic shrinkage stress and overall double bond conversion allows for accurate indexing of the shrinkage stress development as a function of double bond conversion, which eliminates the effect of differences in reaction kinetics and conversion as anticipated here regarding the (meth)acrylate resins. Efforts were made to differentiate the internal and terminal vinyl group absorbances using both NIR and mid-IR spectroscopic analysis techniques. Unfortunately, these reactive functional groups were not resolvable and so the reaction kinetic data and degree of conversion values reported

here are based on the averaged overall vinyl group concentrations. The double bond conversion is defined as the change in the total vinyl group concentration with respect to the total initial vinyl group concentration at the start of the photopolymerization experiment, including both the terminal methacrylate moieties as well as the relatively small amount of internal double bonds from any AFM. Initial discussion here is focused on just the effects of the AFM on photopolymerization kinetics and limiting degree of conversion achieved.

The photopolymerization kinetic profiles for the BisGMA/TEGDMA system with progressive incorporation of the AFM (Figure 3a) demonstrate a gradual reduction in the final conversion along with a steady decrease in the reaction rate (Table S1). The unmodified BisGMA/TEGDMA control resin provides the expected vitrification-limited ambient-temperature photopolymerization accompanied by a modest degree of post-cure promoted by trapped radical species within the glassy polymer network.^{43,44} For samples with the AFM, there is a reduction in the polymerization rate and the samples appear to reach a conversion plateau without necessarily encountering vitrification limitations at high loadings of the AFM. This behavior indicates that either the reactive groups or the radicals are less mobile or more stable and are not able to efficiently propagate polymerization. While only slowed moderately with 5 wt% or less AFM, the reaction rate decelerates significantly beyond 5 wt% addition of the AFM, which indicates greater stability/slower reinitiation for AFM-based radical species compared with common methacrylate propagating radical centers. This behavior is expected as reaction with the AFM double bond leads to the formation of a somewhat more stable radical intermediate, and the lowering of the rate is consistent with what is observed in linear polymers formed with RAFT polymerizations. For the BisGA/TEGDA acrylate samples, the effect of AFM on the photopolymerization reaction kinetics is even more pronounced (Figure 3b). At 2.5 wt% AFM addition, there is minimal change in final double bond conversion or reaction rate from the control without AFM. At the 2.5 wt% loading, this corresponds to the internal vinyl group in the AFM comonomer contributing approximately 1% of the overall reactive groups to the resin. With addition of 5 wt% or more of AFM to the acrylate-functional monomers, the reaction rate and final double bond conversion are both dramatically reduced. Particularly in the acrylate resin with AFM, conversion plateaus as soon as the light is switched off with very little post-cure occurring, which indicates a lack of active radicals capable of transient continuation of the polymerization. The differential behavior in the acrylate resin as compared with the methacrylate is likely associated with the different double bond reactivities in these two systems. While an acrylic radical is less stable than a methacrylic radical, the acrylate double bond is actually somewhat less reactive than its methacrylate counterpart to most radicals, and the polymerization rate of the acrylate may be reduced by the addition of a methacrylate compound⁴⁵. As such, once reaction with the AFM moiety occurs, reinitiation in the acrylate system is significantly slower than in the methacrylate resin, thus leading to the more dramatic rate suppression observed here. It should be noted that the AFM is a dimethacrylate. The reaction rates in acrylate-methacrylate copolymerizations depend on the reactivity ratios. Studies of copolymerization of acrylates and methacrylates have reported the reactivity ratio to be greater than 1 and the methacrylates tend to start polymerizing before the acrylates⁴⁵. So due to the AFM being a dimethacrylate, it is possible that it is preferentially integrated into the early-stage network instead of following a statistical

distribution of acrylates and methacrylates. At the same time the AFM-based radicals sequester the acrylate propagating radicals and once these are part of the network and hence immobile, the reaction rate should start reducing and also the final conversion should be limited.

Real-time shrinkage stress development is shown in Figure 4. In conventional di(meth)acrylate polymerizations, stress development evolves as the integrated product of the constrained post-gel shrinkage and elastic modulus with minimal potential for stress relaxation⁷. While polymerization shrinkage was not measured here, we make the assumption that the overall free shrinkage as a function of conversion is effectively equivalent with or without the presence of the AFM. For the BisGMA/TEGDMA-based samples, the reduction in the final shrinkage stress follows the same trend as the reduction in final double bond conversion. The reduction in stress, however, is more than proportional to any reduction in conversion. This behavior can be due to two contributing factors – 1) the bond rearrangement due to the addition-fragmentation chain transfer process produces direct stress relief and 2) the reduction in conversion implies that the modulus of the sample is lower and as shrinkage stress is coupled to the modulus, this behavior also may lead to lower shrinkage stress. As with the kinetic measurements, the reduction in shrinkage stress for the BisGA/TEGDA system is more drastic with the addition of the AFM. At 2.5 wt% AFM addition, a 25% decrease in shrinkage stress is achieved with similar levels of conversion, while at 5 wt% AFM addition, there is a more than 50% reduction in shrinkage stress. With higher AFM content, the shrinkage stress remains close to zero as might be expected in connection with the very limited final conversion attained with these higher AFM-content formulations.

To ascertain that the labile double bond in the AFM is responsible for the addition fragmentation and reduction in stress, a sample composed of BisGA/TEGDA with 10 wt% AFM was compared with the same resin modified with 10 wt% added TEGDMA. Both AFM and TEGDMA are dimethacrylates; however, the TEGDMA obviously lacks the internal double bond and access to the addition-fragmentation mechanism. The sample containing TEGDMA demonstrates faster kinetics and reaches a higher double bond conversion and shrinkage stress as compared to the sample containing the AFM (Figure 5). The values that this sample achieves are much closer to the neat BisGA/TEGDA, showing that the kinetics and shrinkage stress are not affected unless the AFM is present.

Photorheology

The AFM alleviates the shrinkage stress by continuous rearrangement of the covalent bonds throughout the polymerization, which is expected to provide a degree of controlled chain growth and a significant effect on the gel-point conversion due to the delay in the development of a long range network that otherwise develops very early in chain-growth polymerizations.^{46,47} Photorheology measurements can be used to determine the crossover point between G' and G'' , which is a reasonable approximation of the gel point during polymerization.^{48,49} The relatively slow data sampling rate for the rheometer necessitated a lower irradiance level to have sufficient time to obtain an accurate crossover conversion. Figure 6 shows the results for the two systems with the conversion at the crossover point for

each sample provided in Table S2. The control resin gels almost immediately after starting the irradiation with the crossover occurring at less than 1% conversion. As the amount of added AFM increases, the gel point conversion increases. For the same amount of AFM, the BisGMA/TEGDMA samples gel more quickly and at slightly lower conversion than the corresponding BisGA/TEGDA samples. Both the storage and loss moduli develop at a slower rate compared to the control resin with the addition of increasing amounts of the AFM; particularly for the BisGA/TEGDA materials.

Dynamic mechanical analysis measurements

Dynamic mechanical analysis (DMA) was performed to study the network properties of the photocured materials. For the BisGMA/TEGDMA resin formulations, the first scan in the DMA reveals two peaks for all the samples (Figure 7a). Ambient temperature photocuring for chain growth polymerizations leads to structurally heterogeneous networks in which there are domains that range from dense, glassy states to regions with more mobility. This behavior leads to a very broad glass transition as evidenced in the tan delta plot. The lower temperature peaks in the first heating are considered to reflect the network that is formed in the ambient photopolymerization with a thermal transition that spans $> 100^{\circ}\text{C}$. The second higher temperature peak is created during the thermal analysis process and represents the densified network produced as residual radical species and reactive sites achieve sufficient mobility to undergo further polymerization. Figure 7b shows the tan delta curves for the second heating cycle in the DMA where the discrete low temperature peak no longer appears. Glass transition temperatures, taken as the tan delta maxima, are reduced with increasing amounts of AFM. The extended photocuring protocol used to prepare the DMA test specimens provided higher initial conversion but with identical ranking as compared to the dynamic conversion results (Figure 3). The initial conversion and thermally enhanced conversion values obtained at the end of second heating scans in the DMA are listed in Table S3. There is a consistent increase of about 15°C in the post-cure conversion regardless of the AFM content in these BisGMA/TEGDMA resins samples. The trend to lower glass transition temperature with added AFM follows the trend in the limiting conversion. Figure 7c shows the storage modulus as a function of temperature (second heating scan only here). At or below ambient temperature, there is no significant difference in the modulus values between the different samples. The rubbery region shows a monotonic reduction in crosslink density with increasing AFM content. This outcome can also be attributed to the reduction in final conversion associated with the addition of the AFM.

Figure 8a shows first scan in the DMA for the BisGA/TEGDA series. The more uniform first heating plots for the acrylate resin samples indicate much more limited post-cure during this first cycle as compared with the methacrylate-based resins. There is a progressive decrease in the glass transition temperature as the amount of the AFM increases, which corresponds to the progressive decrease in conversion prior to DMA testing. For this series, three heating scans were performed as the samples continued curing even after two heating scans. Figure 8b represents the tan delta curve for the 3rd heating scan in the DMA. The control sample with no AFM has a single peak with the glass transition temperature around 100°C . Samples with 2.5% and 5 wt% AFM exhibit single tan delta peaks with a similar glass transition temperature. The samples with 10 wt% and 20 wt% AFM show a broad

shoulder at lower temperatures in addition to a major peak at 100 °C. The broadening of the transition at high AFM loading indicates an increase in the structural heterogeneity with the presence of a significant amount of persistent, more mobile regions within the network even after repeated heating. The initial lower conversion of the samples with high AFM content could lead to more quenching of residual radical centers as compared to the samples with low or no AFM content; however, as shown in Table S3, there is also a significant progressive increase in the conversion rise associated with the thermal post-curing as the AFM content is increased. The storage modulus plot in Figure 9c shows that the 20 wt% AFM sample has a lower rubbery modulus as well as lower limiting conversion as compared to the other samples.

Electron Paramagnetic Resonance Measurements

The polymerization process in multifunctional (meth)acrylates can lead to long-lived radicals that can be detected using electron paramagnetic resonance (EPR) spectroscopy.⁴³ The polymerization proceeds through various stages. The initial pre-gel state typically involves low viscosity with polymeric chains able to move via translational diffusion, favoring bimolecular termination⁴⁴. The propagating radicals are generally at low concentration at this early stage and may be not easily detectable by EPR. Once the gel point is reached and the matrix viscosity increases, translational diffusion is suppressed, reducing the termination rate. Autoacceleration is typically noticed with the corresponding increase in the concentration of the propagating radicals. At this stage, the radicals are easily detected by EPR. The system finally reaches a vitrification point where mobility is extremely limited, trapping a high proportion of radicals in the network. EPR spectra were collected while conducting real-time photopolymerization of AFM and non-AFM containing formulations. These experiments were done to detect changes in the EPR spectra during each stage of the polymerization for the control resins and those with added AFM.

Figures S5 and S6 show the development of EPR spectra for BisGMA/TEGDMA, BisGMA/TEGDMA + 20% AFM, BisGA/TEGDA and BisGA/TEGDA + 20% AFM, respectively. In the BisGMA/TEGDMA spectra (Figure S5a) at very early stages of polymerization, the line shape looks different than the succeeding spectra. It can be seen that the spectrum develops into a 9-line spectrum, that is characteristic of methacrylate polymerization. The spectra are noisy initially due to low radical concentrations but become sharper as polymerization proceeds and the radical concentration increases. The 9-line spectrum obtained during methacrylate polymerization has been the subject of much research. It is considered to be an overlaid 5+4 line spectra. The propagating chain-end radical in methacrylate polymerization (Figure 9a) is found to be the dominant species during polymerization and has been simulated to reveal an EPR spectrum that is similar to the one observed in this work.⁴⁴ The propagating radical has three β -methyl group protons and two β -methylene group protons that lead to the observed spectrum. Upon addition of 20 wt% AFM to the BisGMA/TEGDMA, there is significant change in the line shape seen in the EPR spectra (Figure S5b). The initial spectrum in the low viscosity regime is noisy and appears similar to the initial spectrum for the BisGMA/TEGDMA sample. However, the evolving and final spectra differ considerably from that with no AFM present (Figure S5a), which is indicative of a distinctive radical species associated with the AFM.

Figure S6a shows the EPR spectrum progression for the BisGA/TEGDA system. The final spectrum at the end of the polymerization resembles the EPR spectra for acrylates reported in the literature. This particular spectrum has been attributed to more stable mid-chain radical structures, which are obtained by hydrogen abstraction from the propagating radical (Figure 9b).

When the AFM is added to this mixture, the final spectrum is now different than the acrylate control resin polymerization (Figure S6b). This result indicates that the final radical structure and composition are very different than the one obtained at the end of a purely acrylate polymerization. It should be noted that under similar irradiation conditions, the 20 wt% AFM sample reaches much lower conversion as compared to the pure acrylate polymerization and so the final spectra (Figure S6b) is obtained at significantly different double bond conversion level compared to the BisGA/TEGDA spectrum (S6a). It is possible that the spectrum can change more once the conversion is increased to a greater extent.

Figure 10 shows the collected series of final EPR spectra for the BisGMA/TEGDMA/AFM photopolymers. It is clear that with the addition of the AFM, certain peaks emerge and then decline as others build. The change in the heights of the peaks point to the change in radical concentration. EPR measurements were done on the AFM homopolymer and overlaying its spectrum with that of BisGMA/TEGDMA with 20% AFM (Figure 11) shows that in the vitrified state, they are indeed very similar. The radical structure predicted to result from the polymerization of the AFM as depicted in Scheme 1 is shown in Figure 12.

Figure 13 shows the series of end-stage EPR spectra of the BisGA/TEGDA series with increasing amounts of AFM. It can be seen that the peaks at 3500 and 3550 Gauss shift as the amount of AFM increases. Newer peaks also start appearing at 3545 Gauss. The final spectrum of the BisGA/TEGDA/20%-AFM now seems to tend towards the spectrum of the AFM (Figure 10).

The similarities in the EPR spectra of both the methacrylate and the acrylate series upon the addition of significant amounts of the AFM as compared to the EPR spectrum of the AFM homopolymer strongly suggest the presence of persistent radicals as proposed from the AFM fragmentation (Figure 11). The kinetics and shrinkage stress results are all explained by delving deeper into the mechanism of the AFM during polymerization. Scheme 1 and Figure 2 show the possible operating mechanism of the AFM. Upon irradiation, a free radical species, which could be from the photoinitiator or a propagating radical, can add to the AFM that then fragments to form an α -carbonyl tertiary radical and an unsaturated ester closed-shell product. The radical that is generated can further initiate polymerization to form a polymer that has a methacrylate terminated radical. This polymer radical can again add with the AFM and regenerate the α -carbonyl tertiary radical and also a polymer that can further fragment and add monomers. This process of forming and breaking covalent bonds while the overall network is being generated can occur repeatedly with cumulative stress relief associated with each bond breaking process.

There are two main reasons for the shrinkage stress reduction. The constant rearrangement of the network due to the addition-fragmentation and chain transfer processes during

polymerization contribute to the slower development of shrinkage stress. The other contributing factor for lowering the shrinkage stress is the reduction in reaction rate due to the addition fragmentation chain transfer mechanism. It has been reported that reduction in polymerization rate allows for the network to reduce shrinkage stress by flow as there is more time and higher conversion achieved before the gel point is reached.¹⁰ In addition-fragmentation-chain-transfer, there are different processes such as addition to monomer, fragmentation and addition to propagating radical going on and depending on the rates of the corresponding processes, the rate of conversion of the double bond can vary. In the current study, the α -carbonyl tertiary radical that is generated is a stable radical and can have a long lifetime. As seen in Figure 2, this radical can potentially add to monomer or reversibly go back to the starting monomer and fragment again. Depending on the kinetic parameters, if these steps are slow compared to the monomer addition, the AFM can act as a radical reservoir, effectively slowing down the overall conversion and also potentially limiting the final double bond conversion. This behavior is seen in the kinetic plots (Figure 3) where increasing amounts of AFM slow down the reaction rate and reduce the final double bond conversion. EPR data (Figures S5 and S6) also gives evidence to the radical reservoir phenomenon as the final spectrum of the monomer mixture upon polymerization more closely resembles that generated by the AFM alone as significant amounts of the AFM are added to the monomer mixture.

The effect of the AFM on radical decay was studied from the EPR time series experiments for all the samples at different conversion levels. Initial kinetic studies were performed in the FT-IR to mirror the irradiation conditions that the EPR samples would be subjected to and irradiation times were determined to reach specific levels of conversion. Samples in the EPR were then subjected to the same irradiation conditions and the spectra followed over time. Relative radical concentrations were calculated by performing double integration on the spectra at specific points in time during the measurement, with the field strength (Gauss) as the independent variable on the x-axis and the intensity counts on the y-axis as the dependent variable. Since all the EPR measurements were performed under the same conditions, the radical concentrations that were calculated for the different experiments can be considered relative to each other. Real-time evolution and decay of radical concentrations is in the supplementary information and the data is summarized in Table 2. The final conversion range for all the samples ranged from low (< 1%) to high (final limiting conversion at the end of 60 min of irradiation) and moderate (approximately midway between 0% and the high conversion points). Samples in each of these ranges are listed together for the methacrylate and acrylate series, respectively.

For the methacrylate series taken to high conversion, the radical concentration at the end of the 60 min irradiation period reduces with increasing amounts of the AFM, with a reduction in radical production rate. At this stage, all the materials are glassy and there is a very slow reduction in the radical concentration over a 12 h period as evident from the decay plot (Figure S7). For the moderate conversion levels, there is a reverse trend in terms of the radical concentration at the end of the irradiation period (Figure S8). The concentration of radicals increases as the AFM amount increases. It should be noted that since the reaction rate is slowed with addition of increasing amounts of the AFM, irradiation was continued correspondingly for increasingly longer periods of time to be able to reach similar values of

final conversion. The decay of the radicals is faster than that at the high levels of conversion. The radicals are still highly immobile and unable to terminate rapidly. For the low conversion measurements (<1%), the radical concentration is very low and there is no specific trend for the amount of radicals produced and their decay rates, which are all relatively rapid. EPR spectra at low levels of radical concentration are very noisy, and the decay rate is faster as compared to the spectral acquisition rate, resulting in significant uncertainty (Figure S9). It is, however, safe to claim that there are no persistent radicals after a few minutes of turning off the curing light at such a low level of conversion.

For the acrylate series taken to high conversion, the concentration of radicals drops significantly with the addition of increasing amounts of the AFM. The peak radical concentration is also lower and the radical decay rate is faster compared to the corresponding methacrylate high conversion series. An interesting trend is observed in the initial part of the real-time radical decay plot when the AFM is added. There is an increase in radical concentration in the initial few minutes of the cure but then the radical concentration dips and reduces steadily before increasing again to reach a maximum value until the light is turned off with further radical decay (Figure S10). This indicates the disappearance of one radical species and the subsequent increase in concentration of another radical species. For the moderate level conversion, the samples with the AFM are irradiated for much longer times as compared to the sample without AFM to be able to reach the appropriate level of conversion. The sample without AFM has the lowest radical concentration and decays rapidly as the light is turned off. The samples with AFM reach slightly higher levels of radical concentration but start decaying even as the light is on (Figure S11). The radicals in the low conversion batch decay rapidly as soon as the light is turned off. As noted, at this low level of conversion, the spectra are extremely noisy and the radical concentrations are less certain (Figure S12). However, the decay in radical population even as the light remains on points to a rapid termination mechanism that is reflected in the rapid slowing down of kinetics in the acrylate series with the addition of increasing amounts of the AFM.

Conclusions

The addition fragmentation monomer utilized in the di(meth)acrylate networks serves as a useful and potent additive to reduce shrinkage stress in polymerizing networks. The gel point of the networks was increased and shrinkage stress was reduced to a significant extent with introduction of increasing amounts of the AFM. Addition of the AFM does result in reduction of the polymerization rate and final double bond conversion due to production of radical species with increased stability in both the acrylate and methacrylate networks. The reduction in conversion at low amounts of AFM addition and under higher irradiance conditions is minor while the corresponding reduction in stress is significant. The effect on kinetics and stress reduction is much more pronounced in acrylate polymerization as compared to methacrylate polymerization. EPR analysis helped to elucidate the changes in transient and persistent radical species during and following network formation due to the AFM.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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BisGMA(X = CH₃)/BisGA(X = H) TEGDMA(X = CH₃)/TEGDA(X = H)

AFM-precursor

AFM

Figure 1.
Structures of model monomers used in the study.

Figure 2.

Network rearrangement upon photopolymerization in AFM-based networks – (a) Normal thermoset network lacking AFM functionality forms a network that has fixed linkages and (b) Network with AFM functionality that can rearrange by breaking and reforming bonds

Figure 3. Double bond conversion as a function of time for (a) BisGMA/TEGDMA and (b) BisGA/TEGDA series. Photocuring conditions: laminated 6×1 mm disc specimens exposed for 30 s at an incident irradiation intensity of 200 mW/cm^2 commencing at $t = 30$ s.

Figure 4. Shrinkage stress development as a function of time for (a) BisGMA/TEGDMA and (b) BisGA/TEGDA series. Irradiation intensity – 200 mW/cm² for 30 s. Light was started at 30 s after start of run.

Figure 5.

Comparison of the effect of AFM and TEGDMA addition to BisGA/TEGDA (a) Shrinkage stress and (b) Double bond conversion. Irradiation intensity – 200 mW/cm² for 30 s. Light was started at 30 s after start of run. Sample dimensions – 6 mm diameter disc with 1 mm thickness

Figure 6. Storage and loss moduli as a function of time for (a) BisGMA/TEGDMA and (b) BisGA/TEGDA series. The gel point conversion is estimated from the crossover between the storage and loss moduli. Irradiation intensity – 2 mW/cm² for 30 s. Light was started at 30 s after start of the run. Sample dimensions – 20 mm diameter disc with 0.5 mm thickness

Figure 7. Dynamic mechanical analysis of the BisGMA/TEGDMA series. Tan delta for (a) 1st heating scan and (b) 2nd heating scan; (c) Storage modulus at 2nd heating scan.

Figure 8. Dynamic mechanical analysis of BisGA/TEGDA series. Tan delta for (a) 1st heating scan and (b) 3rd heating scan; (c) Storage modulus at 3rd heating scan.

Figure 9.
Propagating radical in (a) methacrylate polymerization and (b) acrylate polymerization

Figure 10.

Final EPR spectra for BisGMA/TEGDMA series. Each spectrum is taken at the end of the polymerization run for each corresponding sample.

Figure 11.
EPR spectra of AFM (red) and BisGMA/TEGDMA with 20% AFM (black).

Figure 12.
Proposed radical structure generated from the fragmentation reaction of the AFM.

Figure 13. Final EPR spectra for BisGA/TEGDA series. Each spectrum is taken at the end of polymerization run for each corresponding sample.

Scheme 1.
Mechanism of addition-fragmentation of AFM upon addition of a radical species ($R^\cdot$)

Total radical concentration as a function of low, moderate and high levels of double bond conversion. Samples were cured (400–500 nm at 2 mW/cm²) varying amounts of time to reach specific conversion levels and then the light switched off to allow for radical decay. Each EPR scan was about 45 s long and a 1000 scans were collected for each measurement. Radical concentrations were obtained by double integration of the corresponding EPR spectra and are reported in arbitrary and scalable units. The time to decay to half the highest radical concentration was estimated from the data.

Table 1

BisGMA/TEGDMA series						
Conversion level	AFM wt %	Time of Irradiation	Approximate Conversion (%)	Highest Radical Concentration (arbitrary units)	Decay Half-life	Final Stable Radical Concentration (arbitrary units)
Low	0	15s	1–2	20	190s	0
	2.5	20s	1–2	20	250s	0
	5	25s	1–2	20	130s	0
	10	25s	1–2	10	150s	0
	20	30s	1–2	20	75s	0
Moderate	0	35s	40	210	N/A	130
	2.5	70s	40	450	N/A	300
	5	90s	40	640	N/A	530
	10	120s	40	600	940s	200
	20	150s	40	1170	12380s	510
High	0	60min	65	4560	N/A	4230
	2.5	60min	60	3550	N/A	3400
	5	60min	60	3360	N/A	3210
	10	60min	60	2870	N/A	2750
	20	60min	55	2780	N/A	2630
BisGA/TEGDA series						
Low	0	30s	1–2	30	60s	0
	2.5	45s	1–2	50	160s	0
	5	45s	1–2	60	110s	0

BisGMA/TEGDMA series						
Conversion level	AFM wt %	Time of Irradiation	Approximate Conversion (%)	Highest Radical Concentration (arbitrary units)	Decay Half-life	Final Stable Radical Concentration (arbitrary units)
Moderate	10	45s	1–2	70	90s	0
	20	60s	1–2	80	115s	0
	0	45s	35	30	95s	0
	2.5	15min	25	100	515s	0
	5	25min	25	120	690s	0
High	10	30min	15	80	1230s	0
	20	40min	5	100	1495s	0
	0	60min	75	710	N/A	370
	2.5	60min	65	340	N/A	170
	5	60min	55	310	N/A	160
	10	60min	30	190	460s	10
	20	60min	15	110	1145s	0