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A Study of Shrinkage Stress Reduction and Mechanical Properties of Nanogel-Modified Resin Systems

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Abstract

A series of nanogel compositions were prepared from urethane dimethacrylate (UDMA) and isobornyl methacrylate (IBMA) in the presence of a thiol chain transfer agent. The linear oligomer of IBMA was synthesized by a similar solution polymerization technique. The nanogels were prepared with different crosslinker concentrations to achieve varied branching densities and molecular weights. The prepolymers were dispersed in triethylene glycol dimethacrylate at loading levels ranging from 10 wt% to 50 wt%. Photopolymerization reaction kinetics of all prepolymer modified systems were enhanced relative to the nanogel-free control during early stage polymerization while limiting conversion was similar for most samples. Volumetric polymerization shrinkage was reduced proportionally with the prepolymer content while the corresponding decrease in polymerization stress was potentially greater than an additive linear behavior. Flexural strength for inert linear polymer-modified systems decreased significantly with the increase in the prepolymer content; however, with an increase in the crosslinker concentration within the nanogel additives, and an increase in the concentration of residual pendant reactive sites, flexural strength was maintained or improved regardless of the nanogel loading level. This demonstrates that covalent attachment rather than just physical entanglement with the polymer matrix is important for effective polymer mechanical reinforcement by nanogel additives. Reactive nanogel additives can be considered as a practical, generic means to achieve substantial reductions in polymerization shrinkage and shrinkage stress in common polymers.

INTRODUCTION

Volumetric shrinkage and shrinkage stress generated during the polymerization process remain as critical problems for a wide array of polymeric materials applications, particularly for vinyl-based glassy networks formed by a chain-growth mechanism that involves early gelation¹⁻². During polymerization, shrinkage stress starts to build after the gel point when the system cannot dissipate stress by flow and particularly during vitrification where stress increases precipitously in conjunction with the rise in modulus in the glassy state. Various strategies have been applied to reduce shrinkage stress including the development of new

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monomers or modification of curing procedures. Epoxy and other monomers that undergo ring-opening polymerization have shown significantly reduced volumetric shrinkage and varied results in terms of stress development³⁻⁴. In addition, the polymerization mechanism can be altered to overcome early gelation and onset of vitrification for chain-growth radical polymerization. For example, thiol-ene or thiol-yne systems undergo an alternating step-growth/chain-transfer mechanism that has been shown to predictably delay gelation and vitrification thereby reducing stress⁵⁻⁷. An allyl sulfide-based material has also been used to relax polymerization stress by an addition-fragmentation mechanism during network formation⁸⁻⁹. Polymerization-induced phase separation has also been studied with the formation of structurally and compositionally discrete regimes during the polymerization process as a method to control polymerization shrinkage and stress¹⁰⁻¹². In addition, nanofiller particles¹³ that involve the creation of nanocavitation¹⁴ have shown interesting results to achieve desired stress reduction behavior. Modifications of the photocuring process have also been reported as a means to reduce stress development¹⁵⁻¹⁷.

Nanogels are internally cyclized and branched polymeric particles¹⁸, which have drawn substantial attention as drug delivery¹⁹⁻²⁰, tissue engineering²¹ and photonic materials²² due to their versatile structures, large number of chain ends and the ability to incorporate stimuli-responsive functionalities. Solution²³⁻²⁴ or emulsion²⁵ polymerization of a monomer and a crosslinker are typically applied for a one-step synthesis of nanogels. Nanogels can be added to monomer matrix to provide stable, transparent solution of swollen, dispersed or overlapping particles. During polymerization, this allows for physical entanglement and potential chemical crosslinking between nanogel structures and the resin network, which can help reinforce the mechanical properties of the final network²⁶⁻²⁷. A preliminary study compared the effects of reactive and nonreactive nanogel additives in triethylene glycol dimethacrylate on polymerization reaction kinetics as well as shrinkage and shrinkage stress²⁸. This work also included an assessment of final polymer mechanical properties as well as the potential for incorporation of secondary inorganic filler for composite applications. For the nonreactive nanogel, polymer flexural strength dropped significantly at moderate to high loading levels (>20 wt% nanogel contents), while the reactive nanogels, which had methacrylate functional groups located at chain ends, maintained high flexural strength. Additional studies concerned with how various nanogel additive structures influence polymerization shrinkage and stress development as well as mechanical properties and kinetics would be helpful to better understand the critical factors that determine the final polymeric properties and therefore, serve as a guide to solve specific application problems.

In the current study, a series of nanogels with different molecular weights and branching densities have been synthesized from isobornyl methacrylate (IBMA) and urethane dimethacrylate [1,6-bis(methacryloxy-2-ethylcarbonyl)-2,4,4-trimethylhexane] (UDMA). UDMA is a very reactive dimethacrylate monomer that generates strong polymeric networks. IBMA provides a very high glass transition temperature and hydrophobic character to the copolymer. Formulations were prepared by dispersing each prepolymer into a dimethacrylate monomer and then various properties were evaluated including rheology, photopolymerization kinetics, polymerization shrinkage, shrinkage stress, flexural strength, flexural modulus and T_g of the cured samples at different nanogel loading concentrations.

EXPERIMENTAL

Materials

Isobornyl methacrylate (IBMA), 2-mercaptoethanol (ME), azobisisobutyronitrile (AIBN), triethylene glycol dimethacrylate (TEGDMA), hexanes (>98.5%), methanol, methyl ethyl ketone (MEK) and toluene (99.8%) were obtained from Sigma-Aldrich (Milwaukee, WI). 2,2-Dimethoxy-2-phenylacetophenone (DMPA) was purchased from BASF (Ciba-Geigy

Co., Hawthorne, NY). Monomer structures are shown as Figure 1. UDMA was obtained from Esstech (Essington, PA). The inhibitor was removed from IBMA by treatment with activated basic alumina (Brockman I, Sigma-Aldrich). All other materials were used as received.

Synthesis of PIBMA oligomer and nanogels

For the IBMA oligomer (PIBMA) synthesis, the monomer was mixed with ME (15 mol% relative to IBMA) as chain transfer agent. AIBN as the free radical thermal initiator was added at 1 mol% based on the IBMA content and the mixture was diluted 1:1 with toluene. The solution was heated in an oil bath for 2 h at 80 °C under a nitrogen atmosphere with a circulated water condenser in place.

For nanogel syntheses, UDMA and IBMA were mixed at 10:90, 30:70 or 50:50 molar ratios and ME (15 mol% relative to monomers) was added to avoid macrogelation as well as to assist in control of the nanogel molecular weight. AIBN was added at 1 mol% relative to the monomer content. A four-fold excess of toluene relative to monomer was added to the 10:90 and 30:70 IBMA and UDMA molar combinations, while a six-fold excess of MEK was added to the 50:50 molar ratio of IBMA and UDMA since the latter composition was prone to macrogelation. The solutions were thermally polymerized as described for PIBMA. The resulting nanogel products are designated as N19, N37 and N55, respectively, according to the UDMA and IBMA comonomer molar ratio.

After the reaction, all of which reached greater than 60 % conversion as analyzed by mid-IR spectroscopy, the relative ratio of the two comonomers in each nanogel sample was confirmed by ¹H NMR characterization to be similar to the feed ratios used. The clear nanogel solutions were added dropwise to a 10-fold excess of methanol (for PIBMA and N19) or hexanes (for N37 and N55), which resulted in the precipitation of the polymeric materials. The precipitate was isolated by decanting and the residual solvent was removed under high vacuum. ¹H NMR characterization of the resulting nanogels demonstrated copolymer compositions similar to that of the monomer feed ratios.

Nanogel Structural Analysis

Triple-detection gel permeation chromatography (GPC; Viscotek, Westborough, MA) with differential refractive index (RI, Viscotek VE 3580), viscosity and light scattering detectors (Viscotek 270 dual detector) was employed for the analysis of linear polymer and nanogel molecular weight, polydispersity index (PDI) and average hydrodynamic radius (R_h). A mixture of tetrahydrofuran (THF) and acetone (90:10 volume ratio) was used as eluent with a flow rate of 1 mL/min at 35 °C in a series of four columns spanning molecular weight of 10^4 – 10^7 calibrated with a 65 kDa poly(methyl methacrylate) standard. Proton nuclear magnetic resonance (¹H NMR; Bruker Avance-III 300, NMR lab, University of Colorado) was used to aid nanogel structural determination in deuterated chloroform with spectra obtained from 64 scans. All data was analyzed with MestRenova 5.3.2 software.

Mixture of Resin with PIBMA or Nanogels

PIBMA and nanogels were added to TEGDMA in mass ratios of 10 % to 50 % in 10 % increments. Unfilled TEGDMA was used as the control. DMPA (0.5 wt%, relative to resin) was added to each sample. Samples were mechanically agitated until all prepolymers were fully dispersed to give optically clear monomer solutions.

Rheology Test

A rheometer (TA ARES) was used to measure the viscosity of nanogel-modified resins with 20 mm diameter parallel plates at 20 °C. Zero shear viscosity data were determined from shear rate sweeps. Three replicates were conducted for each system.

Volumetric Polymerization Shrinkage

A non-contact linear variable differential transducer-based linometer (Academic Center for Dentistry Amsterdam, The Netherlands) was used for real-time volumetric shrinkage testing. The detailed procedure is described in prior literature²⁹. All specimens (n = 3) with a cylindrical geometry (3 mm diameter and 1 mm thickness) were irradiated under 365 (± 10) nm UV light at 10 mW/cm² irradiant intensity with limiting shrinkage data reported at the end of the 10 min illumination interval.

Shrinkage Stress Measurement

A cantilever beam-based tensometer (Paffenbarger Research Center, American Dental Association Foundation, Gaithersburg, MD) was utilized for the measurement of dynamic shrinkage stress. Instrument details and operation methods are provided in other publications³⁰⁻³¹. Each material (cylindrical shape with 6 mm diameter and 1.5 mm thickness, n = 3) was evaluated continuously during irradiation with 365 (± 10) nm UV light at intensity of 10 mW/cm² for 15 min.

Photopolymerization Kinetics

During the stress evaluation, near-infrared spectroscopy was simultaneously incorporated during the photopolymerization process to measure the reaction kinetics profile. The detailed experimental procedure has been reported previously³¹. The peak area of the first overtone absorbance of the methacrylate =CH₂ group at 6165 cm⁻¹ was followed throughout the polymerization process³². Three replicates were carried out for each system.

Flexural Strength Test

A universal testing machine (Mini-Bionix II, MTS, Eden Prairie, MN) was applied for gathering mechanical property data (under room temperature). Sample specimens (n = 3) with dimensions of 15 × 2 × 2 mm were photopolymerized under 365 (± 10) nm UV light irradiation with 5 mW/cm² intensity for 16 min. Flexural modulus and strength were determined in three-point bending on a 10 mm span at a crosshead speed of 1 mm/min.

Dynamic Mechanic Analysis (DMA) Testing

A DMA (Perkin Elmer 8000, Waltham, MA, USA) was applied to measure the T_g of different prepolymers by sandwiching 10 mg of polymer powder in a thin aluminum pocket, which was then subjected to single cantilever cyclic displacement of 50 μm at 1 Hz in air. Specimens of PIBMA (n = 3), N19 (n = 3), N37 (n = 2) and N55 (n = 1) were heated to 180 °C with tan δ data collected as the sample was cooled to 25 °C at 2 °C/min. Single batch materials of each polymer were used for the DMA analyses.

A separate DMA (TA Q800) was applied for the measurement of the tan δ profiles of nanogel-modified TEGDMA polymeric systems. Samples (n = 3) with a dimension of 25 × 2 × 1 mm were prepared under the same curing condition as the flexural strength test except that they additionally underwent post-cure conditioning at 160 °C overnight in an oven to reach a high conversion (>98 %). A strain and frequency of 0.02 % and 1 Hz, respectively, was applied in tension to the samples during a temperature scan from 0 °C to 220 °C at 2 °C/min. The tan δ peaks were deconvoluted using the Gaussian–Lorentzian function of PeakFit software (Systat Software Inc.).

RESULTS AND DISCUSSION

Nanogel Characterization

GPC analysis of nanogels N19, N37 and N55 together with the PIBMA oligomer demonstrate the much higher molecular weight and broader molecular weight distributions of the nanogel materials compared with linear PIBMA (Figure 2). Specific data about weight average molecular weight (M_w), polydispersity index (PDI) and hydrodynamic radius (R_h) are listed in Table 1. The consistency of GPC results for replicate runs as well as the transparency of the solvent or monomer dispersed nanogel materials indicates these are discrete, single macromolecular nanoparticles rather than aggregated structures. For the PIBMA synthesis, 15 mol% of mercaptoethanol as a chain transfer agent (CTA) limited the molecular weight to approximately 20 repeat units on average. As the 10, 30 and 50 mol% UDMA is added, this corresponds to 2, 6 and 10 potential branch points per chain, respectively, assuming similar degrees of polymerization. With the increase of crosslinker concentration, the M_w correspondingly increased due to the formation of branched, interconnected and cyclized multi-chain structures. The PDI for the PIBMA sample is low for a free radically initiated polymerization but this can be explained by the high CTA concentration that significantly restricts biradical termination. The nanogels are higher in PDI than the linear polymer analog due to normal distributions of chain number within nanogels, intraparticle cyclization reactions and various interparticle reactions. However, the nanogel PDI values are still relatively low for highly branched, multi-chain polymeric structures. The solvent swollen particle size based on low/right angle light scattering in the GPC analysis (in THF/acetone) shows that R_h increased with the crosslinker concentration for N19 and N37, because of the significantly increased M_w , but not in a proportional manner since an increase in the branching density at a given molecular weight will tend to reduce the R_h due to internal densification. This also explains why the most highly branched N55 nanogel, which presents the highest molecular weight, has a lower R_h compared with N19 and N37. Also to be considered is that while the greater solvent concentration used in the N55 synthesis, could be expected to produce a more expanded nanogel structure, the use of MEK in place of toluene also undoubtedly affects nanogel structure. But since MEK was determined to be a better solvent than toluene for the more polar N55, its more compact structure relative to its higher molecular weight is most likely due to the significantly higher internal crosslink density rather than any solvent effects.

The DMA data applied to prepolymer T_g (Table 1) demonstrate that with the increase of crosslinker concentration in the nanogel, T_g dropped from 144 °C for PIBMA to 75 °C for N55. This progressive decrease in T_g with increasing UDMA content is likely due to the previously mentioned increase in flexible crosslinker units and pendant groups within the nanogel that leads to increased molecular mobility and less ability to form densely packed structures than linear PIBMA.

From proton NMR analysis (Figure 3) following nanogel precipitation, residual C=C double bonds from pendant UDMA groups have chemical shifts at 6.2 and 5.6 ppm, and the broad peaks from 2.8 to 3.5 ppm are from the methylene protons adjacent to –NH– groups in UDMA. Since all residual C=C double bonds in the nanogels are from UDMA (verified by comparison with PIBMA ^1H NMR spectrum), by integration of peak areas for the vinyl and methylene protons, there are 2.5 %, 21 % and 33 % pendant UDMA units with unreacted methacrylate groups for N19, N37 and N55. In other words, the ratio of overall residual double bond group concentration is 1:25:66 for N19, N37 and N55, respectively.

Viscosity Test

Rheology measurements in uncured TEGDMA were applied to gather the viscosity data (Figure 4). With the addition of nanogels at different loading levels, viscosity increased significantly from 0.006 Pa·s for the TEGDMA control to more than 100 Pa·s for 50 wt% modified materials. N19 and N37 modified systems have very similar viscosity as a function of loading probably because of the similar R_h values of the nanogels. In the moderate loading range (20 - 40 % loading levels), where nanogel particles are approaching or modestly exceeding the percolation threshold in the monomer, the N55 nanogel produces a lower viscosity than the other nanogels due to its smaller R_h . At the 50 % prepolymer concentration, where interparticle or entangled chain interactions are dominant, the solution viscosity results converge. The viscosity effect of N55 is similar to that of PIBMA despite the dramatic difference in prepolymer molecular weight.

Volumetric Shrinkage Tests

Dimensional change during polymerization is due to reduced distance between covalently attached monomer units relative to free monomer as well as the limited mobility of polymer chains that permit higher packing densities. Bulk volumetric change is decreased by addition of prepolymerized nanogels into the system due to the displacement of reactive monomer and the relatively rigid nanogel structures compared with the matrix polymer network formed under ambient conditions. N37 and N55 were chosen to analyze the volumetric shrinkage at various weight percentages. Since the nanogel bulk densities are expected to be similar to that of the final TEGDMA homopolymer²⁸, the weight and volume fractions are not substantially different. At limiting conversion, the unfilled TEGDMA resin produced a volumetric shrinkage value of 10.1 % (Figure 5). By the addition of 10 wt% of either of these nanogels, the shrinkage was reduced by approximately 10 %. With the incorporation of additional nanogel, shrinkage decreased in a more or less linear manner with respect to the nanogel content. The slightly greater shrinkage reduction, 46.6 vol% compared with 41.4 vol% for N37 and N55, respectively, at the 50 wt% nanogel loading level could be due to a somewhat higher bulk density of the more highly branched nanogel, which would reduce its relative volume fraction or it could also be associated with the higher residual pendant methacrylate concentration in the N55 nanogel.

Mechanical Properties Evaluation

Flexural strength measurements for 0 - 50 wt% of PIBMA, N19, N37 and N55 systems are shown in Table 2. All cured samples were optically clear, which indicates no polymerization-induced phase separation or nanogel aggregation was associated with the curing process. The flexural strength, which is obtained in three-point bending mode, involves both tensile and compressive components in the stress field. The control system had a flexural strength of 77 MPa and by adding 10 wt% PIBMA into the resin, the flexural strength was maintained or even improved. However, when 20 – 50 wt% of PIBMA was added, the flexural strength reduced dramatically to about 10 MPa for the highest prepolymer content. A similar trend is observed with the N19-modified resin system in which the flexural strength shows an obvious decrease when 20 wt% or more of the nanogel is introduced into the resin; although, the extent of the mechanical strength decrease is less than that associated with the PIBMA additive. Flexural strength for the N37 materials systems was effectively constant until 40 wt% of the nanogel was added to the resin. Most notably, the N55-modified resin series produced a uniform flexural strength regardless of the prepolymer content. The flexural modulus was maintained or improved with the linear prepolymer additive as well as with all the nanogels at all concentrations. The nanogels with high branching densities appear better suited to maintain flexural strength at a high loading level even though these nanogels present a lower bulk T_g compared to those with lower UDMA contents. This is most likely because nanogels made with a high crosslinker

concentration had more unreacted functional groups within their structure and those residual double bonds react with the resin to form covalent crosslink points. Moreover, higher branching densities can also be expected to contribute to higher degrees of hydrogen bonding and entanglement/physical crosslinking between the nanogels and resin matrix. These types of interactions, whether in the form of continuous or discontinuous domain structure are apparently necessary to maintain the mechanical strength integrity of the overall polymer network. Alternatively, linear polymers and nanogels prepared with low crosslinker concentrations have relatively limited physical entanglement potential with the matrix polymer network because of the short individual chains involved here. They are also depleted in residual double bonds to serve as chemical attachment points to the matrix. It should also be noted that the degree of conversion was independently established for the mechanical strength specimens and that the limiting conversion values are in quite good agreement with the results obtained during the stress measurements, which indicates that these interrelated properties are being compared for self-consistent materials.

DMA was also employed to characterize the $\tan \delta$ curves for the control and prepolymer-modified, fully polymerized (thermally post-cured) systems at various additive concentrations. For the control system, a broad $\tan \delta$ peak (T_g at 162.9 ± 3.3 °C) was observed, which indicates a very heterogeneous polymer in terms of structural crosslink density variations within the TEGDMA homopolymer network. The bulk N19 nanogel has a T_g at 121.5 ± 2.9 °C. When N19 was introduced at 10 wt%, an additional peak was observed at 140.0 °C (Figure 6), which represents the N19-modified regions within the TEGDMA matrix. With the increase of N19 content, the peak increased in intensity and became narrower as the prepolymer-modified region expanded. Similar $\tan \delta$ behavior is revealed for other prepolymer-modified systems in that by addition of prepolymer, a separate peak, which gradually becomes dominant, with a T_g intermediate to that of the bulk nanogel and the TEGDMA homopolymer control. T_g values of these prepolymer hybrid phases are 157.5, 129.9 and 129.5 °C, for PIBMA, N37 and N55 (Figure 6) systems, respectively, obtained from the highest loading concentration profile. With increasing prepolymer branching densities, the differential between the bulk prepolymer T_g and that of the hybrid regimes within the TEGDMA matrix expanded. This T_g differential of more than 50 °C observed for the N55-modified polymer is most likely due to the relatively large concentration of pendent reactive methacrylate groups in this nanogel, since its higher branching density would be expected to decrease the content of infiltrated TEGDMA within the hybrid polymer structure. By deconvolution of the multiphase $\tan \delta$ profiles, the prepolymer-modified regions and the TEGDMA homopolymer could be isolated for these systems. With the increase of nanogel concentration, an increase of $\tan \delta$ values was observed and TEGDMA phase disappeared completely, as demonstrated by a good single peak fit, at the 50 % of loading level for all of the nanogel-modified polymers. This indicates that the high level of nanogel loading, the bulk matrix is no longer present and the TEGDMA-swollen nanogel particles contribute a densely packed, continuous secondary network within the final polymer. While not examined here, significantly higher nanogel loading levels can be achieved since the globular, short chain-based nanogels can form overlapping, interdigitated structures.

Kinetics and Shrinkage Stress Tests

From Figure 7 and Table 3, the unmodified TEGDMA control reached about 82 % conversion after 15 min of irradiation. The initial rate of polymerization (R_p) for TEGDMA, as characteristic for low viscosity, network-forming monomers, shows the typical early stage auto-acceleration with a rate maximum that occurs at approximately 46 % conversion. The addition of the linear PIBMA prepolymer produced a modest, progressive decrease in the maximum reaction rate as well as a significant reduction in the conversion at the onset of

vitrification. Beyond the 20 wt% loading level, there was also a modest reduction in the limiting conversion achieved using the PIBMA prepolymer additive. With the nanogel additives, the final conversion reached values from 76-84 % and the more highly branched N37 and N55 materials tended to promote better retention if not an enhancement in the limiting conversion results. The positive effect of prepolymer on the polymerization rate is significantly greater for the nanogel additives, even at the very high loading levels, compared with the results with the linear PIBMA additive. When the nanogels are incorporated into the resin at relatively low loading levels, two phases are imposed – the bulk TEGDMA and the nanogel structures infiltrated by TEGDMA monomer. The interior and interfacial regions of the nanogel phase presents a higher viscosity environment, particularly with the more highly branched nanogels, than the pure monomer. Therefore, when the polymerization reaction is initiated, depending on the amount of nanogel added, varying proportions of monomer will be in the more mobility-restricted state and the overall auto-acceleration behavior would also vary accordingly. At the 50 wt% nanogel loading level, there is no bulk TEGDMA present due to near contact or overlap of the monomer-swollen nanogel regions, which has been confirmed by the DMA results. The photoinitiator is assumed to be uniformly dispersed between the nanogel and bulk monomer. The reasons why the N55-modified materials reach higher conversion than the other additive composites are probably due to (1) N55 nanogels have more unreacted double bonds (C=C) in the structure which enhance R_p and lead to a higher final conversion than other systems; and (2) the N55 nanogel has the lowest prepolymer T_g (Table 1) and the mobility for N55 systems is greater to allow higher conversion by delaying vitrification compared to other systems with the same prepolymer concentration.

Shrinkage stress generation during polymerization is a critical problem for glassy crosslinked polymeric materials. The baseline stress value of ambient temperature photocured TEGDMA samples was about 5 MPa. By adding different percentages of PIBMA or nanogels, the final stress was reduced a little more than linearly additive fashion compared to the control system. For example, at a uniform loading of 30 wt% of the different prepolymer additives, stress values were decreased by 42 %, 45 %, 34 % and 29 % for PIBMA, N19, N37 and N55 as compared with the control system. The reason why PIBMA and N19 systems reduced stress more than proportionally to their concentration is most likely because these materials reached a significantly lower conversion, which would be expected to correlate with a lower elastic modulus, than the control while N37 and N55 all reached the similar or higher final conversion. The stress values are very sensitive to the final conversion because stress rises more rapidly with conversion after vitrification³¹. For loading levels up to 50 %, shrinkage stress was reduced by more than half for all of these systems. Shrinkage stress is correlated with volumetric shrinkage and the modulus of the final polymeric material with both these properties dependent on conversion. From the previous section, volumetric shrinkage values of those systems are more or less linearly related to the loading percentage of prepolymer. The elastic moduli of PIBMA and N19 systems are lower compared to the control system and decrease with the increase of loading ratio. Meanwhile, all N37 and N55 systems have comparable elastic moduli with the control system. This indicates that shrinkage stress reduction is derived mainly from the decrease of volumetric shrinkage for the N37 and N55 systems. Moreover, to achieve excellent mechanical strength along with significant stress reduction, reactive nanogels appear to be the appropriate choice.

CONCLUSION

Three nanogels with different branching densities together with a linear oligomer were synthesized and then mixed with a dimethacrylate resin at various concentrations. The volumetric shrinkage and shrinkage stress can be reduced at least in proportion to the

concentration of prepolymer used. Mechanical strength of the final polymers decreased dramatically with increasing concentrations of PIBMA or N19, while there was no reduction in strength or modulus for the N55-modified polymer up to the 50 % loading limit examined here. Viscosity increased significantly with the increase in the prepolymer concentration, and this leads to more prominent autoacceleration of the reaction kinetics for materials containing the more highly branched nanogel additives, particularly at high loading levels that maximize the proportion of nanogel-infiltrated monomer. It was found that all of the nanogel additives provided densely packed secondary network structure at about the 50 % loading level.

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Research Highlights

1. Several nanogels were synthesized with different crosslinking densities and residual double bond concentration;
2. With nanogel presents in a resin system, reaction rate can be reinforced and a similar final conversion;
3. Mechanical properties can be maintained at a high level with control for the nanogel with highest crosslinking density;
4. Nanogels can reduce shrinkage and stress during network formation in a proportional manner;
5. Nanogel swelling behavior can be calculated from Tan δ profiles.

Figure 1. Molecular structures for methacrylate monomers and schematic interpretation of nanogels with different branching densities.

Figure 2.
GPC – RI traces for PIBMA, N19, N37 and N55 prepolymers.

Figure 3.
 ^1H NMR spectra for N19, N37 and N55.

Figure 4. Viscosity data for PIBMA, N19, N37 and N55 prepolymer in TEGDMA at various loading levels from 0 to 50 wt%. Note: error bars are included but are generally smaller than the symbols.

Figure 5. Volumetric shrinkage results for N37 and N55 nanogel systems at 0 - 50 wt% addition values.

Figure 6.

Tan δ behaviors for the N19 and N55 modified systems at different loading levels as a function of temperature from 0 °C to 220 °C with $f=1$ Hz and a scan rate of 2 °C/min. Samples were preheated to 160 °C for overnight to prevent continued thermal polymerization during the DMA testing.

Figure 7. Photopolymerization kinetics profiles for control as well as PIBMA, N19, N37, and N55 nanogel-modified systems at 0 - 50 wt% addition values in the early stage of polymerization. All composites were irradiated with $365 (\pm 10)$ nm UV light at an intensity of 10 mW/cm^2 starting at 0.5 min with 0.5 wt% DMPA (relative to TEGDMA) as photoinitiator.

Table 1

GPC and DMA characterization of PIBMA, N19, N37 and N55 prepolymers

	Mw (Da)	PDI	R_h (nm)	T_g (°C)*
PIBMA	4.3E+03	1.09	1.17	143.8 ± 5.3
N19	1.7E+04	2.43	4.14	121.5 ± 2.9
N37	6.6E+04	2.64	5.71	94.9
N55	1.2E+05	2.62	4.00	74.7

* Replicate runs using this method were found to give variations of ± 5 °C and the T_g for a powdered poly(methyl methacrylate) standard (122 kDa) was 108 ± 1 °C (n=3).

Table 2

Flexural strength test for PIBMA, N19, N37 and N55 modified systems

Composite Formula	Prepolymer in Resin (wt%)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Final Conversion (%)
Control	0	76.8 ± 9.5	1.95 ± 0.27	82.2 ± 2.5
PIBMA/TEGDMA	10	89.3 ± 4.7	2.42 ± 0.10	82.4 ± 1.0
	20	33.9 ± 5.3	2.58 ± 0.07	79.8 ± 5.6
	30	15.9 ± 5.4	2.61 ± 0.11	79.8 ± 1.8
	40	13.2 ± 6.2	2.53 ± 0.10	82.0 ± 3.5
	50	9.1 ± 1.3	2.37 ± 0.33	69.1 ± 1.7
N19/TEGDMA	10	75.1 ± 15.5	2.05 ± 0.48	82.3 ± 1.9
	20	47.6 ± 2.0	1.98 ± 0.07	82.5 ± 1.5
	30	31.8 ± 8.3	2.47 ± 0.34	78.1 ± 2.9
	40	24.5 ± 12.2	2.71 ± 0.51	86.8 ± 0.2
	50	10.9 ± 0.9	2.96 ± 0.27	72.0 ± 1.3
N37/TEGDMA	10	82.3 ± 11.4	2.10 ± 0.25	81.8 ± 0.5
	20	81.3 ± 10.9	2.14 ± 0.16	81.8 ± 0.9
	30	83.2 ± 7.0	2.28 ± 0.36	81.2 ± 0.3
	40	60.3 ± 6.7	2.39 ± 0.24	80.8 ± 0.9
	50	29.9 ± 7.7	3.17 ± 0.12	72.4 ± 2.1
N55/TEGDMA	10	78.7 ± 8.1	1.82 ± 0.06	81.8 ± 0.2
	20	75.9 ± 5.7	1.85 ± 0.04	81.7 ± 0.6
	30	91.2 ± 2.3	2.37 ± 0.04	81.6 ± 0.6
	40	88.7 ± 1.6	2.30 ± 0.12	81.5 ± 2.0
	50	81.1 ± 28.5	2.41 ± 0.12	80.2 ± 1.8

Table 3

Stress, final conversion, maximum rate of polymerization (R_p^{max}) and relating conversion values for prepolymer modified composite systems

Composite Formula	Wt% of Prepolymer in Resin	Final Conversion (%)	Final Stress (MPa)	R_p^{max} (%*s ⁻¹)	Conversion at R_p^{max} (%)
Control	0	82.1 ± 2.3	4.98 ± 0.38	15.6 ± 1.1	46.4 ± 3.9
PIBMA/TEGDMA	10	83.5 ± 0.3	4.84 ± 0.23	12.6 ± 0.3	47.7 ± 7.0
	20	82.6 ± 0.7	3.68 ± 0.07	8.3 ± 0.5	36.4 ± 0.7
	30	78.3 ± 0.2	2.88 ± 0.15	7.2 ± 0.7	38.3 ± 1.9
	40	78.3 ± 2.6	2.61 ± 0.17	6.3 ± 0.4	29.2 ± 7.6
	50	76.5 ± 1.4	2.35 ± 0.07	8.0 ± 0.3	35.6 ± 2.4
N19/TEGDMA	10	81.0 ± 3.2	4.70 ± 0.05	10.7 ± 1.6	45.1 ± 0.8
	20	82.7 ± 1.8	3.39 ± 0.01	8.7 ± 0.3	35.8 ± 1.9
	30	79.1 ± 1.9	2.75 ± 0.20	9.2 ± 1.5	42.4 ± 9.5
	40	79.8 ± 0.1	2.48 ± 0.27	11.3 ± 0.2	42.3 ± 3.7
	50	75.6 ± 2.0	2.36 ± 0.12	13.4 ± 1.3	35.3 ± 3.8
N37/TEGDMA	10	83.0 ± 1.5	4.76 ± 0.19	15.0 ± 1.4	45.0 ± 1.2
	20	83.6 ± 0.4	4.00 ± 0.09	12.8 ± 1.7	49.5 ± 2.9
	30	83.5 ± 1.0	3.27 ± 0.30	18.9 ± 0.5	52.9 ± 3.2
	40	80.1 ± 1.8	2.62 ± 0.16	19.0 ± 1.5	50.4 ± 1.9
	50	79.9 ± 0.4	2.40 ± 0.19	18.6 ± 0.4	45.4 ± 0.2
N55/TEGDMA	10	83.2 ± 2.1	4.84 ± 0.29	16.5 ± 0.8	45.6 ± 1.9
	20	84.2 ± 0.2	4.30 ± 0.05	17.4 ± 0.2	49.0 ± 3.8
	30	84.4 ± 0.9	3.53 ± 0.24	23.5 ± 0.8	55.6 ± 2.3
	40	83.9 ± 0.2	2.72 ± 0.44	25.3 ± 1.1	49.0 ± 2.5
	50	78.9 ± 0.5	2.02 ± 0.03	22.7 ± 0.9	40.1 ± 3.8