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Effect of the addition of thiourethane oligomers on the sol–gel composition of BisGMA/TEGDMA polymer networks

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ABSTRACT

Objectives. Thiourethane oligomers have been shown to increase the fracture toughness and reduce the polymerization stress of methacrylate-based materials. However, network formation has not been elucidated in these materials yet. The aim of this study was to evaluate how the addition of a thiourethane oligomer (TU) influences the sol/gel composition and network structure of methacrylate-based materials using dynamic mechanical analysis and extraction methods.

Materials and methods. BisGMA/TEGDMA at systematically varied mass ratios (20/80 to 80/20 wt%) were mixed with pre-polymerized thiourethane oligomers at 0 (control) or 20 wt%, synthesized by combining pentaerythritol tetra-3-mercaptopropionate with dicyclohexylmethane 4,4′-Diisocyanate, at 1:2 isocyanate:thiol. 0.1 wt% of 2,2-Dimethoxy-2-phenylacetophenone was added as the photoinitiator and 0.3 wt% of 2,6-di-*tert*-butyl-4-methylphenol was added as a free radical inhibitor. Disk specimens (0.8 × 10 mm in diameter, n = 3) were photoactivated at 270 mW/ (320–500 nm) for 1 min. The degree of conversion (DC) was measured in near-IR ($\tilde{6}165\ \text{cm}^{-1}$). Specimens were immersed in two different solvents (water for 7 days or dicholoromethane for 48 h). Water sorption (WS) and solubility (SL) were obtained according to ISO 4049. The leachates for both solutions were analyzed with ^{1}H-NMR (400 MHz, $CDCL_3$). Bar specimens (1 × 3 × 25 mm, photocured and then post-processed at 180 °C for 8 h to DC > 95%) were subjected to dynamic mechanical analysis (−30 to 230 °C) to obtain glass transition temperature (Tg), tan delta curves and crosslinking density (ν). Data was analyzed with two-way ANOVA/Tukey's test (95%).

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Results. In general, the presence of TU increased the overall conversion. The WS was similar for all groups, but the SL decreased by 2-fold with the addition of the TU oligomer for all compositions, except BisGMA/TEGDMA 80/20. The BisGMA concentration of the leachates increased with increasing BisGMA in the initial mixture, and with the presence of thiourethane. This compositional drift of the gel with the presence of TU was attributed to the preferential dissolution of TEGDMA into the TU network. Tg and ν decreased with the addition of TU, as expected. The addition of TU produced more homogeneous networks, as evidenced by narrower breadth of the tan delta curve.

Conclusion. The addition of TU affected the composition of the sol/gel in crosslinked networks, which were more homogeneous and presented 2-fold less potentially toxic leachates than the methacrylate controls.

Clinical significance. The addition of TU may produce less cytotoxic materials based on the increased conversion and reduced amount of unreacted extractables from its network after water storage.

1. Introduction

Typical resin composites used in dental restorative applications are composed of a mixture of dimethacrylate monomers with inorganic fillers [1]. The most common dimethacrylate used in such materials is Bisphenol A diglycidyl ether dimethacrylate (BisGMA), combined with lower viscosity diluent monomers to improve the degree of conversion, inorganic filler content in the composite and also reduce leachable components [2]. The most common diluent is triethylene glycol dimethacrylate (TEGDMA), but urethane dimethacrylate (UDMA) and ethoxylated bisphenol- A dimethacrylate (BisEMA) are also commonly used. The co-polymerization of these methacrylates is complex, and the relative participation of each monomer in different phases of the reaction (pre-gel, autoacceleration and vitrification) depends on the diffusional capabilities of each monomer, as well as on the reactivity of its vinyl bonds [3]. One study has demonstrated that BisGMA participates in the gel formation early in conversion, but as polymerization progresses, the composition of the gel becomes richer in TEGDMA [4]. In fact, by analyzing the sol phase (unreacted monomers) at various stages of polymerization, the increased contribution of TEGDMA to the polymer network in co-polymerizations with BisGMA has been demonstrated, pointing to a compositional drift during polymerization reactions [4,5]. It is expected that the inclusion of additional monomers or oligomers will alter this balance, and therefore, any proposed modifications in the composition must also evaluate and take into account the possible compositional shifts during polymerization.

Recently, additives based on thiourethane oligomers have been proposed as modifiers in highly filled dental composites, with several advantages including significantly increased fracture toughness and decreased polymerization stress [6]. These additives are synthesized by combining excess multifunctional thiols with diisocyanates, forming a network loosely crosslinked by thiourethane bonds, which are thought to facilitate crack arrest, increase abrasion resistance and tear strength, aided by stable and strong intermolecular hydrogen bonds [7]. In the case of thiourethane oligomers, pendant thiols impart chain-transfer capability to the polymerizing methacrylate networks, delaying gelation/vitrification and thus reducing polymerization stress while at the same time increasing the limiting conversion [6]. Due to their effects on network formation, it is reasonable to assume that the addition of thiourethanes may affect the compositional drift in dimethacrylate co-polymerizations.

Since the compositional drift directly affects the resulting network, final conversion and the type and concentration of monomers that can potentially be extracted from the polymer while in service, this study aimed at investigating the sol/gel composition of systematically varied BisGMA/TEGDMA networks modified by the addition of thiourethane oligomers. Extractions were conducted in water or organic solvents, and the composition of the extracts was evaluated using nuclear magnetic resonance. Water was used to conform to ISO 4049 (water sorption and solubility tests - [8]) and dichloromethane was used as the organic solvent capable of extracting the quasi-totality of unreacted monomers (sol portion) from polymerized specimens [4]. In addition, the resulting network was characterized with dynamic mechanical analysis, to obtain glass transition temperature and degree of crosslinking. The hypotheses to be tested were that composites formulated with TU will increase degree of conversion, and affect the amount and composition of the leachates.

2. Material and methods

2.1. Composite formulation

All reagents were purchased from Sigma–Aldrich (Milwaukee, WI, USA) and used without further purification. The commercial monomers used to prepare the composites were all obtained from ESSTECH (Essington, PA, USA). The thiourethane oligomer used in this study was synthesized as previously described [6] by combining pentaerythritol tetra-3-mercaptopropionate (PETMP) with dicyclohexylmethane 4,4′-Diisocyanate (HMDI) at a 1:2 molar ratio of isocyanate:thiol to avoid gelation and allow for pendant thiols. This produces a loosely crosslinked oligomer, with average molecular weight of 5 kDa and average pendant thiol concentration of 58 mM/g, as demonstrated in a previous study [6]. BisGMA/TEGDMA was used as the organic resin matrix, mixed at 20/80, 40/60, 50/50, 60/40 and 80/20 mass ratios. Thiourethanes were added at 0 (control) or 20 wt%, since this concentration was previously demonstrated to produces increased conversion and fracture toughness and reduced polymerization stress [6]. 0.1 wt% of 2,2-Dimethoxy-2-phenylacetophenone (DMPA) was added as a single component photoinitiator and 0.3 wt% of 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added as a freeradical inhibitor.

2.2. *Curing conditions and degree of conversion*

Disk specimens (10 mm diameter and 0.8 mm thickness n = 10), were made using a rubber mold sandwiched between glass slides, and photocured with a mercury arc lamp (320–500 nm at 270 mW/cm^2) for 1 min. The irradiance was recorded at the surface of the specimen, which was kept at a distance of 7 cm from the tip of the light guide to minimize the effects of heat generation and to ensure uniform curing. The irradiance was checked daily with a power meter, and the light emission spectrum was characterized using the MARC resin calibrator (BlueLight analytics, Halifax, Nova Scotia, Canada). The degree of conversion (DC - %) was measured in near-IR using the vinyl overtone peak at 6165 cm^{-1}, with 32 scans per spectrum at 4 cm^{-1} resolution [9].

The DC was calculated based on the ratio of the vinyl peak before (npol) and after (pol) photoactivation as follows:

$$DC = \left(1 - \frac{pol}{npol}\right) \times 100$$

All specimens were stored dry for 24 h after photoactivation and individual masses were recorded (m1) prior to being stored in the two extraction solvents (water or dichloromethane), as described below.

2.3. *Water sorption and solubility and extraction with an organic solvent*

Half of the disks were stored in water (5 mL) for 7 days at room temperature. Excess water was then removed with absorbent paper and the mass (m2) was subsequently recorded. The discs were then dried to constant mass (m3) in a vacuum desiccator. Water sorption (Wsp) and solubility (Wsl) ($\mu g/mm^3$) were calculated based on standard ISO 4049 [8], according to the equation, where V_0 is the volume of the specimen ($2\pi r^2 h$):

$$Wsp = (m2 - m1)/Vo$$

$$Wsl = (m3 - m1)/Vo$$

The remaining half of the specimens were stored in dichloromethane (CH_2Cl_2, 5 mL) for 48 h, and the weighing procedure described above was repeated to obtain the amount of mass extracted with the organic solvent.

The leachatesin the storage solutions were lyophilized and re-suspended in deuterated chloroform for ^{1}H-NMR analysis (400 MHz, $CDCL_3$). Relative concentrations of BisGMA and TEGDMA in solution were calculated based on the signals for the different methyl protons in the ^{1}H-NMR spectra, as shown in the representative spectrum in Fig. 1. In summary, BisGMA contains two types of methyl groups: at 1.93 and 1.61 ppm, respectively, each with a relative integration of 6 protons (12 methyl protons total). TEGDMA contains one type of methyl group at 1.93 ppm, with a relative integration of 6 protons. In a mixture of the two monomers, the 1.93 ppm peak corresponds to the sum of protons of each molecule, but the 1.61 ppm peak contains only the BisGMA protons. Therefore, the molar percentage of BisGMA in each extracted mixture was calculated as follows:

$$BisGMA\,\% = \frac{integration\ of\ 1.61\,ppm}{integration\ of\ 1.93\,ppm} \times 100$$

2.4. *Dynamic mechanical analysis (DMA)*

Bar specimens measuring 1 × 3 × 25 mm were produced following the same curing protocol described for the water sorption and solubility specimens. The specimens were thermally post-cured at 180 °C (above the expected glass transition temperature of the materials) for 8 h prior to testing. This was done to avoid additional curing during DMA testing. Dynamic mechanical analysis (Q800, TA Instruments, New Castle, DE, USA) was performed in tension mode at constant amplitude of 5 μm with 1% strain rate at a frequency of 1 Hz. A temperature sweep was conducted from −30 to 230 °C, at a heating rate of 3 °C/min. Storage modulus (E'), loss modulus (E") and tan delta values were recorded during the heating cycle and plotted as a function of temperature. The glass transition temperature (Tg) was defined as the peak maximum of the tan delta curve. Network heterogeneity was estimated using the breadth of the tan delta curve, from which the width at half height was calculated. The crosslinking density was calculated from the rubbery plateau of the E′ curve [10], using the equation

$$E = 3\nu dRT$$

where E is the elastic modulus at the rubbery plateau (in MPa), ν is the concentration of active strands (crosslinking density in mol/kg), d is the density (kg/m^3,), R is the gas constant (8.314472 J/(mol·K) and T is the temperature (K).

2.5. *Statistical analysis*

Sample sizes were based in previous studies or followed ISO recommendations, and were confirmed to provide power of 90% or better. The data were tested for normal distribution (Anderson–Darling) and homoscedasticity (Levene's test), followed by parametric statistical tests. A two-way analysis of variance (ANOVA) was performed and multiple comparisons were made using Tukey's test (95%). All analyses were carried out using statistical package Sigma Plot version 13.1 (Systat Software Inc.).

3. Results

The results for degree of conversion for the disc specimens prior to storage in water for all materials (with and without TU) are shown in Fig. 2. Both factors and the interaction were significant ($p < 0.001$). For the materials not containing TU, the lowest conversion values were observed for the 50/50

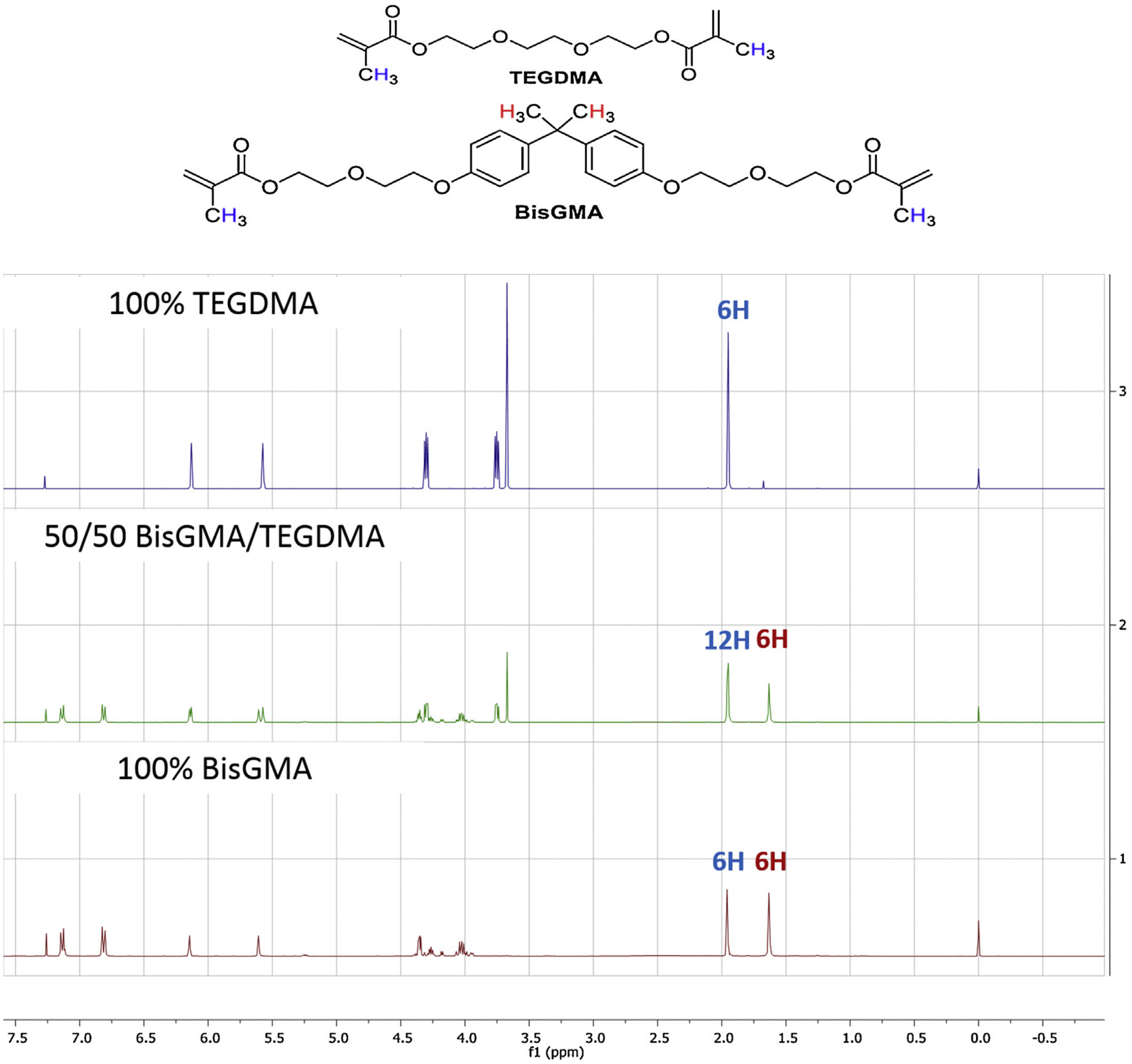

Fig. 1 – ^{1}HNMR spectra for BisGMA, TEGDMA and BisGMA/TEGDMA 50/50 mixtures, highlighting the methyl proton region used to calculate the relative concentration of each monomer in the extracted products after storage in water or dichloromethane.

and 60/40 BisGMA/TEGDMA groups, statistically similar to the 20/80 group. For the TU-containing materials, there was no statistical difference among the different TEGDMA concentrations. The presence of TU led to statistically higher conversion for all groups, except BisGMA/TEGDMA 80/20.

The results for water sorption and solubility are shown in Fig. 3. For water sorption, the monomer composition was significant ($p = 0.007$) but the presence of TU and the interaction were not ($p = 0.572$ and $p = 0.087$, respectively). For solubility in water, neither the factors nor the interaction were significant ($p = 0.001$ for all). The results for mass loss after storage in dichloromethane and water (same as the water solubility results shown in Fig. 3, but with adjusted Y scale) are shown in Fig. 4. For mass loss after storage in dichloromethane, the factor “monomer composition” and the interaction were significant ($p = 0.001$) while the factor “TU concentration” was not ($p = 0.058$). The mass loss with the organic solvent was much greater than that observed with water. The sol extracted increased with the concentration of BisGMA in the mixture for materials both with and without TU. TU-containing groups showed a significant increase in the amount of mass extracted for 40/60, 60/40 and 80/20 BisGMA/TEGDMA groups, and a decrease in the mass extracted for 50/50 BisGMA/TEGDMA groups in relation to the materials without TU. The 20/80 BisGMA/TEGDMA composition showed statistically similar mass loss for materials, regardless of the presence of TU.

Fig. 5 shows the sol composition after extraction for materials with or without TU in the original monomer mixtures. For this test, no statistical analysis was performed, since the leachates of each of the 5 specimens stored in water or dichloromethane were combined, and only one qualitative ^{1}H-NMR spectra were obtained for each group. For the leachates extracted with water, there was no detectable presence of BisGMA in the leachates, meaning that 100% of what was extracted was made up of TEGDMA monomers. For the dichloromethane extractions, both BisGMA and TEGDMA were

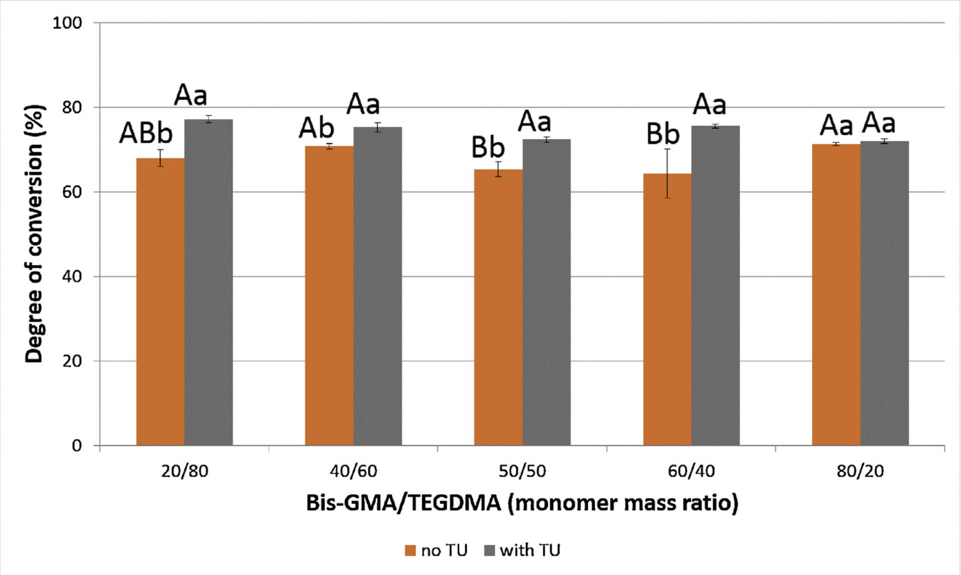

Fig. 2 – Degree of conversion (%) as a function of Bis-GMA/TEGDMA mass ratio. Upper case letters refer to comparisons within TU or non-TU containing groups, and lower case letters refer to comparisons within each BisGMA/TEGDMA ratio.

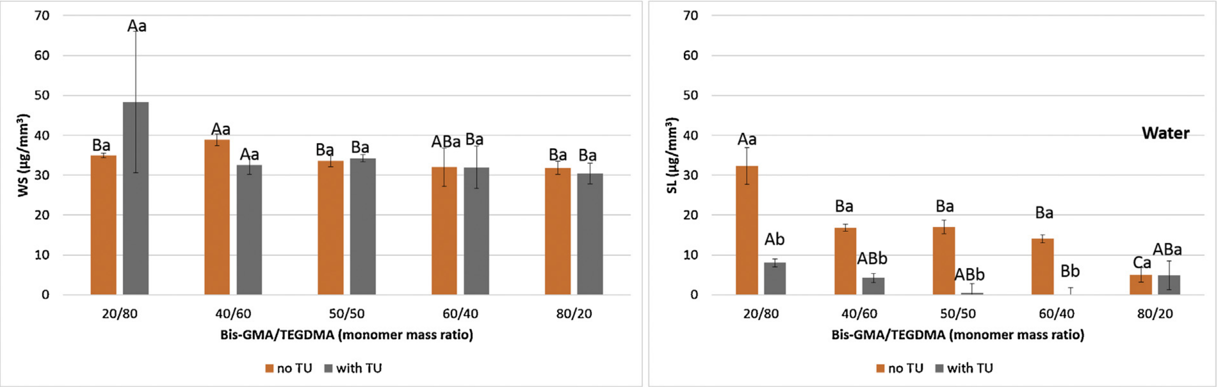

Fig. 3 – Water sorption and solubility (µg/mm^3) as a function of Bis-GMA/TEGDMA mass ratio. Upper case letters refer to comparisons within TU or non-TU containing groups, and lower case letters refer to comparisons within each BisGMA/TEGDMA ratio.

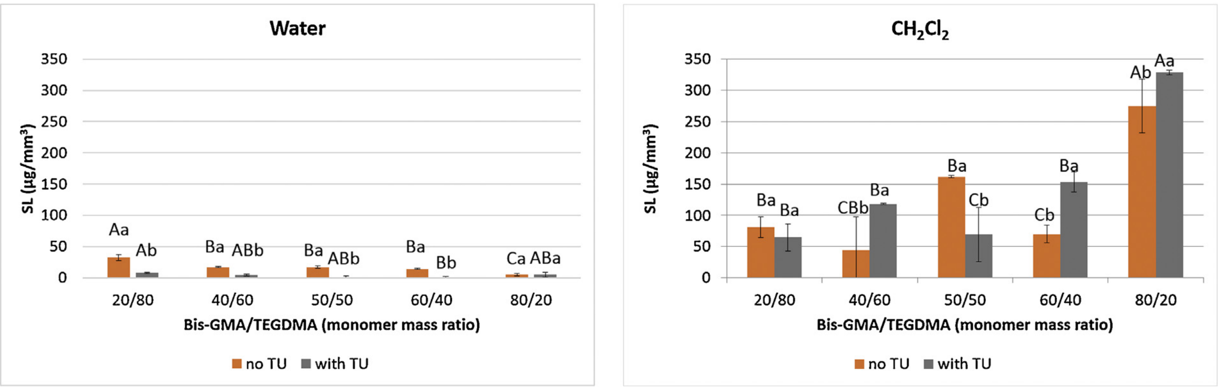

Fig. 4 – Solubility (or final mass extracted - µg/mm^3) after storage in water or dichloromethane as a function of Bis-GMA/TEGDMA mass ratio. Upper case letters refer to comparisons within TU or non-TU containing groups, and lower case letters refer to comparisons within each BisGMA/TEGDMA ratio.

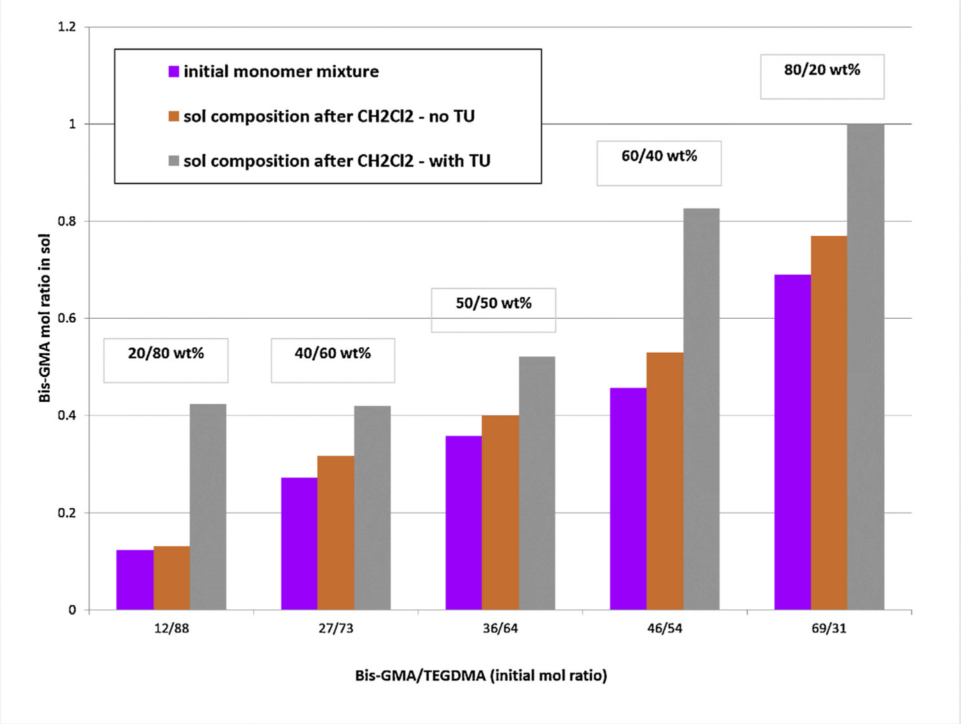

Fig. 5 – Composition of the sol after extraction in dichloromethane for the different BisGMA/TEGDMA ratios with or without addition of thiourethanes. The composition is shown in mols in the graph axis, and in weight in the insert boxes. The left-most bars on the data set refer to the initial molar concentration of BisGMA in the monomer mixture, and the subsequent bars show the composition of the sol (extracted from the disks).

detected. The molar concentration of the BisGMA in the sol increased as the initial BisGMA concentration increased. Except for the 20/80 BisGMA/TEGDMA group, the concentration of BisGMA in the sol was higher than the initial concentration for all groups. The presence of TU led to even higher BisGMA concentrations in the sol.

Fig. 6 shows the dynamic mechanical analysis results. All specimens showed conversion greater than 95% (without TU) or greater than 99% (with TU) after post-curing and prior to DMA testing. Two-way ANOVA indicated that the monomer composition and the interaction were not significant ($p = 0.393$ and $p = 0.248$, respectively), while the presence of TU was significant ($p = 0.001$), with all TU-containing materials presenting higher conversion even at those levels. For glass transition temperature (Tg), the factors and the interaction were significant ($p = 0.001$). For the materials not containing TU, there was no statistical difference among the different BisGMA/TEGDMA compositions. For the TU-containing materials, the 20/80 BisGMA/TEGDMA group presented Tg statistically higher than the other groups. Except for 20/80 BisGMA/TEGDMA, all TU-containing materials showed lower Tg values compared to the non TU-containing counterpart. For crosslinking density (ν), the factors and the interaction were significant ($p = 0.001$). For materials without TU, the highest ν values were observed for 40/60 and 50/50 BisGMA/TEGDMA groups, which were statistically higher than the rest. The TU-containing materials led to consistently lower crosslinking density, and all values within that group were statistically similar to each other. For width at half height of tan delta peak (WHH, indirect measure of polymer heterogeneity), the TU concentration and the interaction were significant ($p = 0.001$ and $p = 0.014$, respectively) while the monomer composition was not ($p = 0.145$). All materials without TU were statistically similar to each other, and all materials with TU were statistically similar to each other. The addition of TU led to statistically lower WHH for all BisGMA/TEGDMA compositions.

4. Discussion

The BisGMA/TEGDMA monomers were used as models in this study to identify any potential effect of the addition of thiourethanes on the sol/gel composition of methacrylate networks. In general terms, the gel portion of the material contains the monomer units that are involved in the actual network, either as crosslinks, or otherwise part of polymeric chains, and includes partially reacted multifunctional monomers [3]. Conversely, the sol represents the portion that can be extracted, and includes unreacted monomers and small oligomers [4]. The leachates (sol) of fully cured specimens were analyzed with nuclear magnetic resonance and the relative BisGMA/TEGDMA composition of the sol was compared to the initial composition of the monomer mixtures, with or without the addition of thiourethanes. The selection of BisGMA/TEGDMA was based on the fact that these are commonly used monomers to formulate dental composites, which have been extensively characterized in the literature [11]. The participation of BisGMA in network formation has

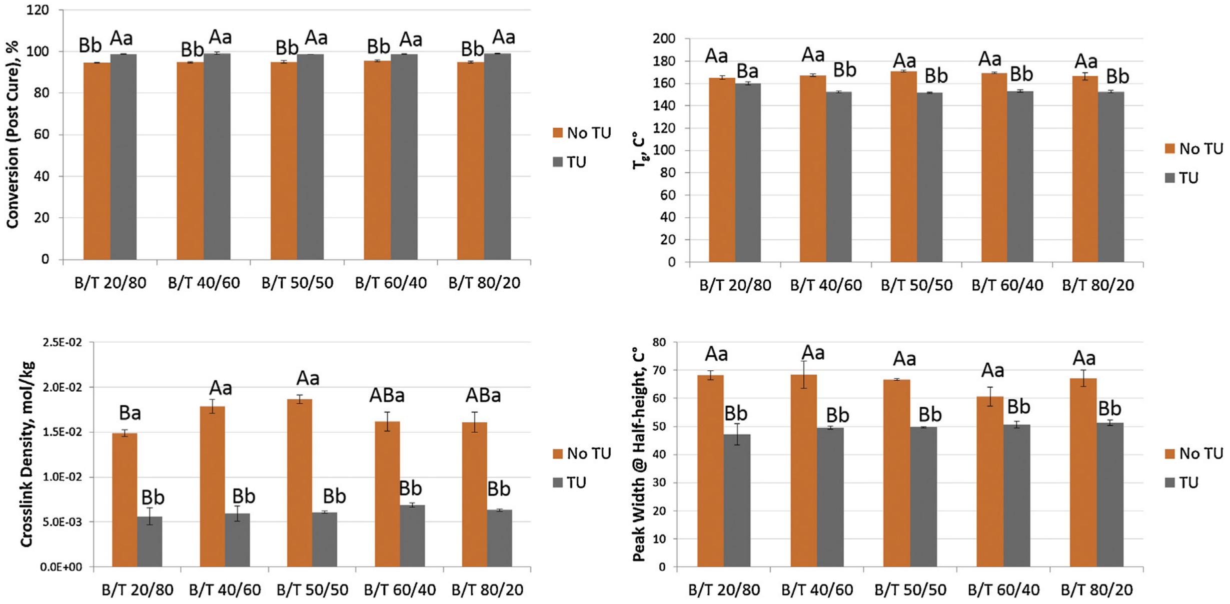

Fig. 6 – Results for the dynamic mechanical analysis (−30 to 230 °C) of all groups tested. From top left, clockwise: degree of conversion of the tested specimens after heat treatment in the oven and prior to DMA testing; glass transition temperature (Tg); breadth of tan delta curve (reported as the width at half height); and crosslinking density calculated from the rubbery plateau of the storage modulus). Upper case letters refer to comparisons within TU or non-TU containing groups, and lower case letters refer to comparisons within each BisGMA/TEGDMA ratio.

been demonstrated to be predominant at the early stages of conversion, while TEGDMA contributes at the later stages in conversion [4]. The addition of any compounds to this mixture is expected to alter the balance of reactivity of the dimethacrylate components [12], and in this particular study, this was hypothesized to affect the amount and composition of the sol/gel in crosslinked networks. Thiourethane oligomers were selected for this study due to recent reports in the literature demonstrating their ability to significantly improve dimethacrylate networks, specifically the ones used in dental cements and composites [6,13]. These oligomers take advantage of thio-carbamate bonds to increase fracture toughness, and of chain-transfer reactions afforded by the pendant thiols to delay gelation and vitrification, and ultimately reduce polymerization stress and increase limiting conversion [6,7]. However, the effect of the addition of these chain-transfer compounds on the sol/gel composition of dimethacrylate networks had not been investigated to date.

The conversion was greater than 65% for all groups tested, and, in general, the presence of TU increased the overall values by about 10% on average, as previously demonstrated [6,14]. This increase in conversion has been attributed to delayed gelation/vitrification of the network via chain-transfer reactions afforded by the pendant thiols from the thiourethane within the polymerizing methacrylate network [7,15]. Chain-transfer is a chain-breaking mechanism [16,17], expected to decrease the crosslinking density, as was indeed confirmed in this study and will be discussed in more detail later. The increase in conversion was not sufficient to influence the water sorption of the materials containing TU, regardless of the BisGMA/TEGDMA composition. However, the solubility in water was severely diminished by the presence of TU for every BisGMA/TEGDMA ratio, except for 80/20. This decrease can be explained by two overlapping factors. (1) The increase in conversion is expected to decrease the amount of unreacted monomers available to be extracted [18]; (2) The addition of a high molecular weight oligomer to the network hampers diffusion of molecules out of the material. For the 20/80 BisGMA/TEGDMA composition, the solubility decreased by over 70%, from 32 to 9 μm/mm^3, which was a statistically significant difference. For other groups, the reduction in solubility brought by the presence of TU in the composition varied from 75 to 99%. BisGMA/TEGDMA 80/20 was the only group where the presence of TU did not affect the solubility, which is likely due to the same reason that the conversion did not increase: at that composition, the increase in viscosity given by the BisGMA-predominant composition combined with a viscous oligomer might have created limitations to diffusion of polymerizing species, in turn leading to less homogeneous network formation, ultimately facilitating the leaching of components. This was not corroborated by the tan delta width at half-height results, however, as will be explored in more detail later. It is noteworthy that for the 50/50 and 60/40 BisGMA/TEGDMA compositions virtually no leachates were present after immersion in water when the TU was included in the composition. Finally, the analysis of ^{1}H-NMR spectra revealed that, for the groups where leachates were detected, the composition of the sol contained only trace amounts of BisGMA, with TEGDMA being by far the predominant species. This was true even for the compositions where BisGMA was the main component, suggesting that the extraction solvent used (water) was not capable of extracting any potentially unreacted BisGMA due to its large molecular weight and relatively lower hydrophilicity (log P = 5.09) compared to TEGDMA (log P = 1.42) [19]. In fact, the overall solubility decreased with the increase in BisGMA concentration in the initial composition. This agrees with previously reported data showing that the amount of the more hydrophobic BisGMA is dramatically underestimated with the use of aqueous extraction solutions [18].

It is important to highlight, therefore, that the amount of leachates extracted by immersion in pure water does not correspond to the total sol composition of the material [4]. For that reason, a separate series of extractions was conducted using dichloromethane as a strong organic solvent. While the extraction in water more closely approximates the clinical scenario, the extraction in dichloromethane allows us to analyze the quasi-totality of the sol composition, or a worst-case scenario. The amount of sol extracted from the polymerized discs increased by one order of magnitude with the use of dichloromethane compared to water. Importantly, this increase was more pronounced for the groups containing higher concentrations of BisGMA, in contrast with what was observed in the water immersions. This shows that the dichloromethane was indeed able to extract even the most hydrophobic, highest molecular weight species in the sol. In this case, the ^{1}H-NMR analysis showed that the initial composition and the presence of TU significantly influenced the composition of the sol. For all materials, as the mol ratio of BisGMA increased in the initial monomer mixture, the overall BisGMA concentration on the sol increased, as expected. Also the BisGMA/TEGDMA ratio also increased for the higher initial BisGMA concentrations — for example, in the BisGMA/TEGDMA 80/20 weight ratio, the mol ratio of the initial mixture is 69/31 (based on molecular weights of 512 and 286 g/mol for BisGMA and TEGDMA, respectively), whereas the mol ratio of BisGMA/TEGDMA in the sol was 77/23. This demonstrates that the participation of TEGDMA in the gel was greater than BisGMA, which is explained by TEGDMA's greater flexibility as well as lower viscosity. This compositional drift at limiting conversions has been previously demonstrated for dimethacrylate networks [4].

Interestingly, for the materials containing TU, the participation of BisGMA in the sol is even more pronounced. This is true for all compositions, with increased participation in the sol ranging from 28 to 70 mol% in relation to the initial composition. For example, in the case of BisGMA/TEGDMA 80/20 weight ratio (mol ratio of 69/31 in the initial monomer mixture), the concentration of BisGMA in the sol when TU is present increases to close to 100 mol%, a 31% increase in relation to the initial composition (69 mol%). This shows that in the TU-containing materials, TEGDMA has a much greater participation in the gel. Possible explanations for this finding are the lower viscosity and greater hydrophilic character of TEGDMA, which likely facilitate its solvation into the hydrogen bonding-rich TU oligomer "pre-network". It is then possible that most of the TEGDMA is entrapped within the TU oligomer, possibly also forming shorter chains with reduced crosslinking, and creating BisGMA-rich regions elsewhere in the polymer. This also partially explains the increased overall solubility of the TU-containing materials in dichloromethane, since greater heterogeneity and shorter chains facilitate molecular diffusion and extraction of unreacted monomers and other low molecular weight species.

Dynamic mechanical analysis was used in this study to elucidate network structure. Post-photoactivation heat treatment was used to ensure that the maximum conversion was achieved before the specimens were subjected to the temperature sweep required by the test, without causing further polymerization. This is required to obtain accurate measurements of the glass transition temperature (Tg), elastic modulus and tan delta curves [10]. Due to the increased level of conversion, these networks are not exactly the same as the ones discussed in the extraction studies, which would have warranted the use of thermal stabilizers, such as iniferters [20], not used here. The use of iniferter-containing materials and partial cure specimens will be the subject of future investigations. With those caveats, and using specimens with conversion levels greater than 98% for all materials, no statistical differences were found in terms of Tg among the materials without TU, regardless of the BisGMA concentration. This was not expected, since at the same conversion, the higher monomeric Tg of BisGMA (−10 °C compared to −80 °C for TEGDMA) [21], given by strong hydrogen bonding and rigidity of the BPA core [22], was anticipated to increase the polymeric Tg. The explanation is likely a combination of the crosslinking density and the polymeric heterogeneity, estimated in this study by the breadth of tan delta peak [23] and quantified as the peak width at half-height — the wider the peak, the more heterogeneous the material [10]. In general, the compositions with the lowest crosslinking density were also the ones with the broadest tan delta peaks (less homogeneous), which are both related to polymer packing and free volume distribution. In the case of the 20/80 BisGMA/TEGDMA compositions, the lower crosslinking density/greater heterogeneity is explained by the high tendency to cyclization presented by TEGDMA [23]. On the other side of the spectrum, as already explained, the 80/20 BisGMA/TEGDMA composition presents much greater diffusion limitations due to BisGMA's viscosity and lack of flexibility [3]. When TU was added to the mixtures, the Tg, the crosslinking density and the breadth of tan delta decreased, regardless of the initial BisGMA/TEGDMA composition. The decrease in Tg was expected and is previously reported [6], and is based on the inclusion of a lower Tg "pre-network" in the mixture. The Tg of the TU used in this study is −5 °C. The only group where the addition of TU did not lead to a statistically significant reduction in Tg was the 20/80 BisGMA/TEGDMA composition. In that particular case, the low Tg of the TU was likely counteracted by the increase in initial viscosity. The low viscosity of TEGDMA-rich systems leads to predominance of termination-controlled reactions and cyclization early in conversion, thus decreasing the overall conversion [24]. That way, by increasing the initial viscosity beyond a certain threshold, the addition of TU acted synergistically and increased the overall conversion of the system, partially counteracting the effect of its low Tg on the overall Tg of the network. The decrease in crosslinking density was expected also, since the chain-transfer reactions afforded by the pendant thiols in the TU backbone are chain-breaking [16], as already mentioned. Previous reports have demonstrated, however, that this does not affect other mechanical properties, which actually increase with the presence of TU, for reasons beyond the scope of this present study [6,13,14]. Those same chain-breaking reactions, however, have been shown to produce more homogeneous polymer networks [7], as was indeed shown here. All TU-containing groups presented narrower tan delta peaks, for all compositions. Again, the 20/80 BisGMA/TEGDMA was the composition to benefit the most from the addition of TU in obtaining more homogeneous networks, also likely due to the increased conversion and decreased degree of cyclization, as already discussed.

5. Conclusion

In conclusion, this study demonstrated that the presence of thiourethane additives affects network formation and ultimately the composition of the sol/gel in dimethacrylate networks. The presence of thiourethanes favored the contribution of TEGDMA to the overall network formation, as evidenced by the increase in BisGMA concentrations after extraction with dichloromethane.

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REFERENCES

[1] Fugolin APP, Pfeifer CS. New resins for dental composites. J Dent Res 2017;96:1085–91.
[2] Pfeifer CS. Polymer-based direct filling materials. Dent Clin North Am 2017;61:733–50.
[3] Anseth KS, Wang CM, Bowman CN. Reaction behaviour and kinetic constants for photopolymerizations of multi(meth)acrylate monomers. Polymer 1994;35:3243–50.
[4] Stansbury JW, Dickens SH. Network formation and compositional drift during photo-initiated copolymerization of dimethacrylate monomers. Polymer 2001;42:6363–9.
[5] Pfeifer CS, Shelton ZR, Braga RR, Windmoller D, MacHado JC, Stansbury JW. Characterization of dimethacrylate polymeric networks: a study of the crosslinked structure formed by monomers used in dental composites. Eur Polym J 2011;47:162–70.
[6] Bacchi A, Dobson A, Ferracane JL, Consani R, Pfeifer CS. Thio-urethanes improve properties of dual-cured composite cements. J Dent Res 2014;93:1320–5.
[7] Senyurt AF, Wei H, Hoyle CE, Piland SG, Gould TE. Ternary thiol– ene/acrylate photopolymers: effect of acrylate structure on mechanical properties. Macromolecules 2007;40:4901–9.
[8] 4049 I. Dentistry — polymer-based filling, restorative and luting materials. International Standards Organization; 2000.
[9] Stansbury JW, Dickens SH. Determination of double bond conversion in dental resins by near infrared spectroscopy. Dent Mater 2001;17:71–9.
[10] Dean KM, Cook WD, Lin MY. Small angle neutron scattering and dynamic mechanical thermal analysis of dimethacrylate/epoxy IPNs. Eur Polym J 2006;42:2872–87.
[11] Asmussen E, Peutzfeldt A. Influence of UEDMA, BisGMA and TEGDMA on selected mechanical properties of experimental resin composites. Dent Mater 1998;14:51–6.
[12] Elliott JE, Anseth JW, Bowman CN. Kinetic modeling of the effect of solvent concentration on primary cyclization during polymerization of multifunctional monomers. Chem Eng Sci 2001;56:3173–84.
[13] Bacchi A, Nelson M, Pfeifer CS. Characterization of methacrylate-based composites containing thio-urethane oligomers. Dent Mater 2016;32:233–9.
[14] Faria-e-Silva AL, dos Santos A, Girotto EM, Pfeifer CS. Impact of thiourethane filler surface functionalization on composite properties. J Appl Polym Sci 2019:136.
[15] Pfeifer CS, Wilson ND, Shelton ZR, Stansbury JW. Delayed gelation through chain-transfer reactions: mechanism for stress reduction in methacrylate networks. Polymer 2011;52:3295–303.
[16] Berchtold KA, Lovell LG, Nie J, Haciolu B, Bowman CN. The significance of chain length dependent termination in cross-linking polymerizations. Polymer 2001;42:4925–9.
[17] Berchtold KA, Lovestead TM, Bowman CN. Coupling chain length dependent and reaction diffusion controlled termination in the free radical polymerization of multivinyl (meth)acrylates. Macromolecules 2002;35:7968–75.
[18] Ferracane JL, Condon JR. Rate of elution of leachable components from composite. Dent Mater 1990;6:282–7.
[19] Abedin F, Roughton B, Spencer P, Ye Q, Camarda K. Computational molecular design of water compatible dentin adhesive system. Comput Aided Chem Eng 2015:2081–6.
[20] Lamb JR, Qin KP, Johnson JA. Visible-light-mediated, additive-free, and open-to-air controlled radical polymerization of acrylates and acrylamides. Polym Chem 2019;10:1585–90.
[21] Stansbury JW. Dimethacrylate network formation and polymer property evolution as determined by the selection of monomers and curing conditions. Dent Mater 2012;28:13–22.
[22] Lemon MT, Jones MS, Stansbury JW. Hydrogen bonding interactions in methacrylate monomers and polymers. J Biomed Mater Res A 2007;83:734–46.
[23] Elliott JE, Lovell LG, Bowman CN. Primary cyclization in the polymerization of bis-GMA and TEGDMA: a modeling approach to understanding the cure of dental resins. Dent Mater 2001;17:221–9.
[24] Odian G. Principles of polymerization; 2004.