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Rheological and mechanical properties and interfacial stress development of composite cements modified with thio-urethane oligomers

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Abstract

Objectives—Thio-urethane oligomers have been shown to reduce stress and increase toughness in highly filled composite materials. This study evaluated the influence of thio-urethane backbone structure on rheological and mechanical properties of resin cements modified with a fixed concentration of the oligomers.

Methods—Thio-urethane oligomers (TU) were synthesized by combining thiols - pentaerythritol tetra-3-mercaptopropionate (PETMP) or trimethylol-tris-3-mercaptopropionate (TMP) - with isocyanates - 1,6-Hexanediol-diisocyanate (HDDI) (aliphatic) or 1,3-bis(1-isocyanato-1-methylethyl)benzene (BDI) (aromatic) or dicyclohexylmethane 4,4'-Diisocyanate (HMDI) (cyclic), at 1:2 isocyanate:thiol, leaving pendant thiols. 20 wt% TU were added to BisGMA-UDMA-TEGDMA (5:3:2). 60 wt% silanated inorganic fillers were added. Near-IR was used to follow methacrylate conversion and rate of polymerization ($R_{p_{max}}$). Mechanical properties were evaluated in three-point bending (ISO 4049) for flexural strength/modulus (FS/FM, and toughness), and notched specimens (ASTM Standard E399-90) for fracture toughness (K_{IC}). PS was measured on the Bioman. Viscosity (V) and gel-points (defined as the crossover between storage and loss shear moduli (G'/G'')) were obtained with rheometry. Glass transition temperature (T_g), cross-link density and homogeneity of the network were obtained with dynamic mechanical analysis. Film-thickness was evaluated according to ISO 4049.

Results—DC and mechanical properties increased and $R_{p_{max}}$ and PS decreased with the addition of TUs. Gelation (G'/G'') was delayed and DC at G'/G'' increased in TU groups. T_g and cross-link density dropped in TU groups, while oligomers led to more homogenous networks. An increase in

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Conflict of interest

The authors declare no conflict of interest.

V was observed, with no effect on film-thickness. Significant reductions in PS were achieved at the same time conversion and mechanical properties increased.

Significance—The addition of thio-urethane oligomers proved successful in improving several key properties of resin cements, without disrupting the procedures dentists use to polymerize the material. This approach has potential to be translated to commercial materials very readily.

Keywords

resin cements; thio-urethane oligomers; polymerization stress; mechanical strength; rheological properties; dynamic mechanical analysis

1. Introduction

Composite cements are extensively used in adhesive dentistry because of their ability to chemically bond to the restorative material and, in some cases, also to the tooth structure. They are very useful in a plethora of clinical applications, such as veneers, onlays, inlays, crowns, fixed partial bridges and intra-canal posts [1]. The adhesive bonding of materials with composite cements promotes higher bond strength and lower solubility in the oral environment than other luting agents. Higher mechanical properties of composite cements are also important to extend the stability of the bonding interface constantly subjected to tensile, compressive and oblique loads, as well as to strengthen the restorative material [2].

The vast majority of contemporary composite cements is methacrylate-based, which achieve vitrification at very early stages of polymerization. This, allied with the volumetric shrinkage intrinsic to the polymerization process, leads to the development of polymerization stress in the bulk of the material and bonding interfaces. Current commercially available composite cements have shown volumetric shrinkage ranging from 1.7 to 5.3% [3].

For years, studies have focused on increasing the mechanical properties and reducing the polymerization stress of methacrylate-based materials. Oligomers based on thiol-ene “click-reactions” have been suggested to increase degree of conversion, mechanical properties and homogeneity of methacrylate networks [4]. Previous work conducted in our group has presented encouraging proof of concept results in regards to the use of thio-urethane oligomers to improve properties of composite cements, with increase in degree of conversion, general mechanical properties and reduction in shrinkage and stress of polymerization [5, 6]. The general mechanism for improved conversion and decreased polymerization stress stems from the chain-transfer reactions of the thiol functionalities pending from the thio-urethane oligomer, which delay gelation, as previously described for small molecule thiols [4]. The increase in toughness and fracture toughness is a well-known advantage of the thio-urethane bond [4]. One additional advantage of using these oligomers in dental materials applications is that the inclusion of the thio-urethanes does not require any change in the basic curing chemistry or clinical procedures the dentist uses to polymerize the materials.

Therefore, the objectives of this study were to expand on previously reported work and synthesize thiol-terminated thio-urethane oligomers with different backbone structures and to assess the properties of methacrylate-based composite cements modified with such oligomers. The oligomer concentration was kept at 20 wt% as this was previously determined to be the best compromise between stress reduction and improvement in mechanical properties. The hypotheses of this study were that the use of thio-urethanes would improve general mechanical properties, increase the degree of conversion, and reduce polymerization stress of composite cements.

2. Materials and Methods

2.1 Materials composition

The experimental composite cement formulated for the study (BUT) was composed of Bis-phenol A diglycidyl dimethacrylate (Bis-GMA; Esstech, Essington, PA, USA), urethane dimethacrylate (UDMA; Esstech) and tri-ethylene glycol dimethacrylate (TEGDMA; Esstech) in a 50:30:20 mass ratio. Photoinitiators were added to the monomers as follows: 0.6 wt% of a tertiary amine (EDMAB - ethyl 4-dimethylaminobenzoate; Avocado, Heysham, England), 0.2 wt% of di-camphoroquinone (Polysciences Inc., Warrington, PA, USA), and 0.5 wt% inhibitor (BHT - 2,6-di-tert-butyl-4-methylphenol; SigmaAldrich, St. Louis, MO, USA).

Six oligomers were synthesized in solution in the presence of catalytic amounts of triethylamine. Multi-functional thiols - pentaerythritol tetra-3-mercaptopropionate (PETMP) or trimethylol-tris-3-mercaptopropionate (TMP) – were combined with di-functional isocyanates - 1,6-Hexanediol-diisocyanate (HDDI) (aliphatic) or 1,3-bis(1-isocyanato-1-methylethyl)benzene (BDI) (aromatic) or Dicyclohexylmethane 4,4'-Diisocyanate (HMDI) (cyclic) in 4 × volume of dichloromethane (very diluted solution). In addition, the isocyanate:thiol ratio was kept at 1:2 (by mol) to avoid gelation of the oligomer during reaction, according to the Flory-Stockmeyer theory [7], leaving pendant thiols. Oligomers were purified by precipitation in hexanes and rotaevaporation, and then characterized by ¹H-NMR and mid-IR spectroscopy [5]. The disappearance of the isocyanate peak at 2270 cm⁻¹ and the appearance of resonance signals at 3.70 ppm were used as evidence for completion of isocyanate reaction and thio-urethane bond formation, respectively [8]. The thiol group (SH) concentration for each oligomer was determined using a titration method with Ellman's reagent well established in the literature [9]. Thio-urethane oligomers were added to the methacrylate organic phase in proportion of 20 wt%, as defined in our previous investigation [6]. The final oligomer product presented as a viscous liquid at room temperature, and was completely miscible with methacrylate monomers.

Filler was introduced at 60 wt% (Barium glass 0.7 μm, density 3.0 g/ml, refractive index 1.553 - V117 4107, Esstech), with the aid of a mechanical mixer (DAC 150 Speed mixer, Flacktek, Landrum, SC, USA) for 5 min at 2400 rpm. All procedures were carried out under yellow lights.

2.2 Photopolymerization reaction kinetics and degree of conversion

The degree of conversion (DC) was obtained using near-infrared (NIR) spectroscopy in specimens of 10 mm in diameter and 0.8 mm thick laminated between two glass slides. The methacrylate =CH₂ absorption at 6165 cm⁻¹ [10] was recorded before and after 60 s of irradiation at 700 mW/cm² (Bluephase, Ivoclar vivadent, Lichtenstein) with the light source in direct contact with the glass slide mold. Real-time monitoring of the polymerization kinetics was carried out in specimens of the same size at 2 scans per spectrum with 4 cm⁻¹ resolution, which provides a greater than 2 Hz data acquisition rate. Kinetic data was collected continuously for 5 min. Samples (*n*=5) were irradiated for 60 s at an incident irradiance of 550 mW/cm². The light attenuation in this case was due to a distance of 2 cm separating the tip of the light guide and the surface of the specimen.

2.3 Flexural strength, elastic modulus and toughness

The 3-point bending method was used to access the flexural strength. Tests were carried out with a universal test machine (Q-test, MTS, Eden Prairie, WI) at a cross-head speed of 0.5 mm min⁻¹. The bar specimens were prepared in dimensions of 2 mm × 2 mm × 25 mm according to ISO 4049 [11]. The specimens (*n*=10) were fabricated between glass slides and photopolymerized with three overlapping 60 s exposures at 700 mW/cm². Specimens were stored dry for one week in dark containers at room temperature. The flexural strength (FS) in MPa was then calculated as:

$$FS (\sigma) = \frac{3Fl}{2bh^2}$$

where *F* stands for load at fracture (*N*), *l* is the span length (20 mm), and *b* and *h* are the width and thickness of the specimens in mm, respectively.

The elastic modulus was determined from the slope of the initial linear part of stress-strain curve.

$$E = \frac{Fl^3}{4bh^3d}$$

F = the load at some point on the linear region of the stress-strain curve

d = the slack compensated deflection at load *F*

l, *b*, and *h* are as defined above

Toughness was calculated in MPa from the integration of the stress × strain curve using software (Origin 9.1, OriginLab Corporation, Northampton, MA, USA).

2.4 Polymerization stress

The Bioman apparatus [12] was used to access the polymerization stress in real time. This system consists of a cantilever load cell whose extremity contains a 5-mm diameter, 0.5-mm

tall steel rod. The surface of the rod was treated with a thin layer of Metal primer (Z-prime plus, Bisco, Schaumburg, IL, USA). The opposite surface was a rigid fused silica glass plate of 3 mm thickness, treated with a thin layer of silane ceramic primer (3M ESPE, St. Paul, MN, USA). The cement ($n=5$) was then inserted into the 0.5-mm gap between the upper rod and the lower glass slide and shaped into a cylinder, providing a C-factor of 4. The specimens were photoactivated through the glass during 60 s at an incident irradiance of 700 mW/cm² (Bluephase 2) and the stress followed for 500 s. The load signal from the cantilever cell was amplified and acquired by a computer.

2.5 Fracture toughness

The method utilized to determine fracture toughness (K_{IC}) was based on the evaluation of pre-cracked specimens under fatigue in linear-elastic, plane-strain conditions [13]. Single-edge notch beam (SENB) specimens were fabricated according to ASTM Standard E399-90 [13] in a 5 mm × 2 mm × 25 mm split steel mold with a razor blade providing a 2.5 mm notch in the middle of the specimens. The cement was photoactivated during 60 s at an incidence of 700 mW/cm². The bending fracture test was performed using a universal test machine (Q-test) at a cross-head speed of 0.5 mm min⁻¹ and K_{IC} was calculated according the following equation:

$$K_{IC} = \frac{3PL}{2BW^{3/2}} \left\{ 1.93 \left(\frac{a}{W} \right)^{1/2} - 3.07 \left(\frac{a}{W} \right)^{3/2} + 14.53 \left(\frac{a}{W} \right)^{5/2} - 25.11 \left(\frac{a}{W} \right)^{7/2} + 25.8 \left(\frac{a}{W} \right)^{9/2} \right\}$$

where P is load at fracture (N), L the length, W the width, B the thickness, and a is the notch length (all in mm) [14].

2.6 Viscosity and film-thickness

Viscosity was measured in a cone-plate rheometer (ARES, TA Instruments, New Castle, DE, USA). Approximately 1 g of each material was placed between 20-mm diameter plates and tested at 1 Hz with a gap of 0.3 mm ($n=3$).

Film thickness was determined according to ISO 4049 [11]; 200 mg of freshly mixed cement was sandwiched between mylar sheets (50 × 50 mm). A 150-N load was applied to an area of 200 mm² for 300 sec. The material was photoactivated for 60 sec using the LED light source used in the previous experiments (BluePhase 2, 700 mW/cm²). The film of cement ($n = 3$) was peeled off the mylar sheet and measured with a digital caliper to 0.01 mm.

2.7 Gelation profiles and comparison with polymerization kinetics

Samples of selected formulations were sandwiched between two 20 mm parallel quartz disc plates, attached to a rheometer (DHR-1, TA Instruments, New Castle, DE, USA) and tested in shear at a frequency of 10 Hz with 0.01% strain (ensuring that the test was carried out within the linear viscoelastic regime), while being photopolymerized at 70 mW/cm² with a UV curing light irradiation during 300 s. The irradiance was kept low to allow the recording of the crossover between G' (storage modulus) and G'' (loss modulus), used to indirectly estimate the time to gel point [15]. The final storage modulus was recorded after 500 s.

Polymerization reaction kinetics was followed by near infra-red spectroscopy as previously described by using the same light intensity (70 mW/cm²) and sample thickness (300 µm) to obtain the degree of conversion at the same time to gel point obtained in the rheometer.

2.8 Glass transition temperature, storage modulus, cross-link density and network heterogeneity

A DMA instrument was used with the temperature scan established over the range of −50 °C to 250 °C with a ramping rate of 3 °C per min in tension mode [16]. Samples ($n = 3$, 15 mm × 3 mm × 1 mm) were irradiated at 700 mW/cm² during 60 s (Bluephase 2), stored for one week in dark containers at room temperature and at the final kept at 170 °C for 15 h. This protocol was performed to ensure the maximum achievable degree of conversion and prevent any further polymerization from occurring during the heating cycle required for the dynamic mechanical testing. The peak value of tan delta curve was used to define the glass transition temperature (T_g) [17]. The loss and storage moduli were recorded as a function of temperature [16]. The heterogeneity of the polymer network was defined by the width at half-height of the tan delta curve [18]. Crosslink density was calculated by mean of the storage modulus in the rubbery plateau [19], applying the following equation:

$$v = \frac{E'}{3dRT}$$

where v is the crosslink density (mol/kg), E' is storage modulus (MPa), d is the density (g/ml), R is the gas constant (8.314472 J/mol K) and T is temperature (K).

2.9 Statistical analysis

Statistical analysis was carried out using one-way ANOVA. Multiple comparisons were done using Tukey's test. All tests were carried out at a global level of significance of 95%.

3. Results

3.1 Photopolymerization reaction kinetics and degree of conversion

Degree of conversion (Table 1) significantly increased in all thio-urethane groups either immediately or after 72 h post light curing. Oligomer-formulated groups led to an increase in degree of conversion of up to 9% immediately and after 72 h (with TMP-AL oligomer). The experimental thio-urethane groups presented similar conversion values.

The maximum rate of polymerization ($R_{p_{max}}$, Table 1) had a statistically significant reduction in all cements composed by oligomers. $R_{p_{max}}$ decreased from 9.26 %·s^{−1} in the control group to a range of 2.20–2.60 %·s^{−1} in thio-urethane groups, with a reduction of up to 77% (caused by PETMP-AL and PETMP-CC oligomers). Figure 1 represents the kinetic profiles for all groups. Not only is the maximum rate of polymerization ($R_{p_{max}}$) lower than the control, but the rate of deceleration is also lower, as evidenced by the $R_{p_{max}} \times DC$ curves (Figure 1).

3.2 Flexural strength, elastic modulus, toughness and fracture toughness

All thio-urethane groups showed significant higher flexural strength (FS – Table 2) than control. Cements composed by TMP-AR and TMP-CC showed the highest FS values with a raise of 57% and 54%, respectively, in regard to control, being also statistical significant higher than TMP-AL.

The elastic modulus (E – Table 2) was significantly improved by the formulation of cements with thio-urethane oligomers in regards to control (except for TMP-AL). The cement composed by TMP AR version of oligomer showed the highest E values with an increase of 48% in MPa value in relation to the control.

Toughness (T – Table 2) also had a significant increase in all thio-urethane groups in regards to the control. The PETMP-AL version of oligomer led to the overall highest T values, 105% higher than the control, and also statistically greater than the cements composed by TMP-AL and TMP-AR oligomers.

All thio-urethane groups led to a significant increase in fracture toughness (K_{IC} – Table 2) irrespective of oligomer type. K_{IC} increased by up to 38%, from 1.94 MPa.m^{1/2} for the control group to 2.69 MPa.m^{1/2} for the TMP-AR oligomer.

3.3 Polymerization stress, gelation profiles and final shear storage modulus (G', rheometry) and comparison with polymerization kinetics

Polymerization stress (Table 3, Figure 2) has shown a significant reduction in cements composed with thio-urethane oligomers in regard to the control for all groups. The lowest stress value was presented by PETMP-AR, 77% lower than the control and also significantly higher than other oligomer groups (except for PETMP-AL).

The time to gel point (estimated at the crossover of storage/loss shear moduli, G'/G'' - Table 3) has shown significant increase in all TU groups in comparison to control, with PETMP-AL showing the statistical highest values among them. The PETMP-AR version of oligomer was also statistically greater than other TU groups.

A significant increase in degree of conversion at the same time to G'/G'' obtained in the rheometer was observed in the separate IR experiments for all TU groups in regards to the control (Table 3). The TEPMP-AR version has shown statistically greater degree of conversion at G'/G'' than all other groups.

TU oligomers were able to increase the final shear storage modulus (G') measured from the rheometer (except for PETMP-AR and PETMP-CC) (Table 3).

3.4 Glass transition temperature, storage modulus at the rubbery plateau (E'), cross-link density and heterogeneity of network (dynamic mechanical analysis)

The glass transition temperature (T_g – Table 4) showed a significant reduction in all thio-urethane groups compared to the control. PETMP-AL and PETMP-AR have shown the statistically lowest values among the oligomer-based groups.

Storage modulus at the rubbery plateau (E') has also shown a significant reduction in all thio-urethane groups in comparison to control, which led to statistically lower values of crosslinking density in those groups (Table 4).

More homogenous networks were observed for all thio-urethane groups in comparison to control, as evidenced by the lower width at half-height values for the modified groups (Table 4). Among the oligomer groups, PETMP-AR and TMP-CC presented the greatest homogeneity, significant different only from PETMP-CC.

3.5 Viscosity and film-thickness

All thio-urethane groups presented significant increase in viscosity compared to the control (Table 5). TMP-CC presented the overall highest value, statistically different from all other groups. TMP-AL showed statistically lower viscosity among the oligomers. The clinically relevant parameter of film-thickness (Table 5), however, was statistically similar for all cements evaluated in the study.

4. Discussion

The benefits of formulating resin cements containing thio-urethane oligomers were assessed in this study. The use of such oligomers has shown a significant improvement of the general properties of cements, especially the increase of degree of conversion and mechanical properties and the reduction of polymerization stress, confirming the hypotheses of the study. All types of thio-urethane oligomers provided a significant increase in degree of conversion compared to the control, while results were similar among oligomer-modified groups. Degree of conversion increased by up to 9% in TU groups immediately after light curing, as well as after 72 h (with TMP-AL oligomer). The polymerization reaction kinetics has shown a significant reduction in maximum rate of polymerization of up to 77% with the addition of the oligomer, from $9.26 \text{ \%} \cdot \text{s}^{-1}$ in the control group to a range of $2.20\text{--}2.60 \text{ \%} \cdot \text{s}^{-1}$ in thio-urethane groups. The deceleration rate was also observed to be significantly slower for all thio-urethane-containing cements. Those kinetic features are due to chain-transfer reactions between the thiol and the vinyl group, which are chain-breaking [20]. This means that the point at which diffusion limitations start to hamper polymerization is delayed to much higher conversion values, resulting in a higher conversion overall [20]. In fact, the polymerization of thiol-enes and thiol-methacrylates has been described to progress through a radically-assisted step-growth mechanism [21, 22], in which stiffness development in the network is also delayed to higher conversion values. This has been considered important to reduce polymerization stress [6], as well as to increase the material's mechanical properties [23], as will be discussed later.

Mechanical properties are of great interest in case of resin cements as they are directly related to long-term success of restorations. In indirect restorations, it is imperative that the thin cement layer is able to withstand constant tensile, oblique and compressive stresses in the clinical situation. The elastic modulus has been pointed as important for the strengthening of the restoration, mainly in the case of brittle materials such as ceramics [2]. K_{IC} has been considered of even greater importance for resin cements because micro defects are common into the structure of composite materials after their clinical application [24].

One previous report has associated the increase of toughness and K_{IC} with the improvement in μ TBS of indirect restorations [5]. Mechanical properties obtained from three-point bending tests have shown a significant improvement with the formulation of resin cements based on thio-urethane oligomers. Flexural strength (FS) improved in all TU groups in relation to the control with an increase of up to 57% (with TPM-AR). The elastic modulus (E) significantly improved in thio-urethane groups compared to the control (except for TMP-AL). TUs led to an increase of up to 48% in modulus (with TMP-AR version of oligomer). Toughness (T) also presented a significant increase in all thio-urethane groups in regards to the control. The addition of oligomers led to up to 105% higher toughness values than control (PETMP-AL version). All thio-urethane groups led to significant increases in fracture toughness (K_{IC}), of up to 38% (with TMP-AR oligomer). The increase in the abovementioned mechanical properties can be partially explained by the 9% higher degree of conversion achieved in TU-based cements. However, this relatively modest increase in degree of conversion alone cannot explain the more significant improvement in mechanical properties, especially toughness and fracture toughness. Previous work has demonstrated the greater network homogeneity achieved with such oligomers, which along with the greater flexibility of the thio-urethane and thiol-methacrylate networks formed [25, 26], also helps explain the increased amount of energy necessary to fracture bars in flexure. Moreover, the lower overall rate of polymerization and slower rates of deceleration (Figure 1) may also have contributed to increased mechanical properties, according to the results of previous studies [23]. In the case of K_{IC} , it is possible that lower residual tensile stresses built up in the bulk of the material, and especially around the inorganic filler particles, has contributed to the improvement in mechanical properties [27]. It can be speculated that the presence of the thio-urethane oligomers led to lower stress intensity as the crack tip reaches the filler particle, which in turn, led to a positive effect on fracture toughness [23, 28].

Dynamic mechanical analysis revealed a significant reduction in glass transition temperature (T_g) for all thio-urethane-based materials. PETMP-AL and PETMP-AR presented the statistically lowest values among all groups. T_g is dependent on the microstructure of the polymer network, so a slight reduction in T_g was expected based on the flexibility provided by the thio-urethane and thiol-methacrylate polymers when compared to neat methacrylate, as previously reported [26]. The decrease in T_g can also be explained by the decrease in crosslinking density observed for materials containing the oligomer, as calculated from the storage modulus at the rubbery plateau. The decrease in crosslinking density was somewhat surprising, given the fact that the oligomers presented a significant concentration of thiol functionalities available to react and, therefore, form multiple crosslinks through the oligomer. One possible explanation is that part of the methacrylate network is replaced by a loosely crosslinked oligomer. The breadth of the tan delta peak ($^{\circ}\text{C}$) allows for the measurement of the degree of heterogeneity of a polymer network (the larger the width at half-height of tan delta peak, the more heterogeneous the polymer). This study has shown that all thio-urethane-based cements present a significant more homogenous network when compared to the control group, which also helps explain the increase in all mechanical properties in spite of the slight decrease in T_g and crosslinking density.

Polymerization stress was significantly reduced in all TU groups in comparison to the control (Table 3). The lowest stress value was observed with PETMP-AR which was also

statistically significant to other oligomer groups (except for PETMP-AL). A previous study with oligomer-based materials has demonstrated a reduction in volumetric shrinkage with the addition of thio-urethane oligomers [6]. This reduction was expected based on the pre-polymerized character of oligomer which decreases the concentration of methacrylate double-bonds per unit volume of the material [29]. However, previous work from our laboratory demonstrated, with the relatively low amount of thio-urethane (only 6 wt% of the total mass of composite), that the somewhat modest reduction in shrinkage alone does not account for the reduction in stress. Other evidence that helps explain the reduction in stress are the lower maximum rate of polymerization and the slower deceleration rate (Figure 1) observed in TU materials, which point to delayed gelation/vitrification [30]. This can be inferred from the results from the rheometer experiments. While the DMA provides insight into the network of polymers at their limiting conversions, the rheometer allows us to follow the development of network stiffness in real-time with polymerization. Ideally, these experiments are coupled with near-IR conversion measurements [30]. In this study, the conversion of specimens of similar thickness polymerized with similar irradiance and final dose was followed separately, and the time to reach the crossover between storage and loss modulus in shear was used to estimate the conversion at which the crossover took place. The chain-transfer reactions from the pendant thiols on the thio-urethane backbone to the surrounding methacrylate matrix delayed gelation (G'/G'') to a higher degree of conversion in all TU-based materials (more markedly for PETMP-AL and PETMP-AR, the highest among the oligomer groups), avoiding early-stage diffusion limitations to polymerization, delaying stress development [30, 31], and ultimately reducing overall polymerization stress [16, 32]. In addition, the final shear storage modulus obtained from rheometer has shown a significant increase in cements composed by selected groups of oligomers (except for PETMP-AL and PETMP-CC). As already discussed, this can be partially explained by the increase in conversion and more homogeneous network formed for the thio-urethane-modified materials. It is important to note that, due to the nature of the rheometer evaluation and inherent methodology limitations, lower irradiance (70 mW/cm^2) was used to allow for the recording of the G'/G'' crossover. We also acknowledge that, ideally, all these experiments should have been conducted under nitrogen purge to avoid border effects caused by oxygen inhibition that likely super-estimated the time to gelation [30]. However, thiol-based materials are known to be less prone to oxygen inhibition [21]. Considering that all groups were ran under the same conditions, the time to gelation must have been more super-estimated for the pure methacrylate groups compared to the thio-urethane modified groups. Therefore, if not precise in terms of absolute values, the results of the present study provided an accurate ranking of all groups, in spite of the likelihood of under-estimation of the differences in time to gelation between neat and thio-urethane modified networks. In addition, the rankings observed in this study agree with previously reported data where those shortcomings in methodology were not present [30].

The rheometer was also used to measure the resin cement viscosity. All thio-urethane-containing cements have shown a significant increase in rheological properties in comparison to the control group. The statistically highest value was presented by TMP-CC version. The viscosity increase in TU-based materials is expected based on the high molecular weight and potential for hydrogen bonding with the addition of such oligomers. In

dental clinical applications, excessively low viscosity cements have been reported to cause concerns when flow into the subgingival sulcus is observed, since it may cause inflammation and long-term complications if not correctly removed. At the same time, the cement viscosity must not affect the adaptation of the restoration. Therefore, film-thickness was determined according to standard method [11]. In this study, in spite of the increased viscosity of TU cements, no increase in film thickness was observed, with all experimental groups presenting values similar to the control. Moreover, all TU groups presented a film-thickness lower than 50 μm , which is defined as the maximum accepted according to ISO 4049 [11].

5. Conclusion

The use of thio-urethane oligomers to formulate resin cements has shown to increase the degree of conversion and general mechanical properties, while significantly reducing the maximum rate of polymerization and the polymerization stress. Oligomers were also able to increase the network homogeneity, with slight reduction in glass transition temperature and cross-link density. Gel point was delayed to higher degrees of conversion. Viscosity significantly increased with the use of thio-urethanes without compromising film-thickness. All the improvements provided by the thio-urethane oligomers do not require modifications in the traditional clinical procedures to use resin cements, which facilitates the translation to a commercial product.

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Statement of Significance

The formulation of composite cements based on thio-urethane oligomers provides:

1. Increase in Degree of conversion and reduction in $R_{p_{max}}$
2. Delay in gelation and reduction in polymerization stress
3. Increase in mechanical properties
4. More homogenous networks

Figure 1.

Degree of conversion as a function of the rate of polymerization for the control and thio-urethane-based groups (PET – tetrafunctional thiol; TMP – trifunctional thiol; AR – aromatic isocyanate; AL – aliphatic isocyanate; CC – cyclic isocyanate). Materials were photoactivated with 550 mW/cm² for 60 s, while vinyl conversion was followed in real time for 5 min.

Figure 2.

Polymerization stress in respect of the time for thio-urethane groups in comparison to control (PET – tetrafunctional thiol; TMP – trifunctional thiol; AR – aromatic isocyanate; AL – aliphatic isocyanate; CC – cyclic isocyanate). Materials were photoactivated with 700 mW/cm² for 60 s, while polymerization stress development was followed in real time for 10 min.

Table 1

Mean and standard deviation for Degree of conversion (DC) and maximum rate of polymerization ($R_{p_{max}}$) for all cements. Values followed by the same superscript within the same test are statistically similar ($\alpha=5\%$).

	DC (%)		$R_{p_{max}}$ (%.s ⁻¹)
	Immediate	After 72 h	
Control	63.5(0.72)b	72.1(1.01)b	9.26(0.25)b
PETMP-AL	68.7(0.35)a	77.2(0.30)a	2.20(0.17)a
PETMP-AR	66.7(0.63)a	76.2(1.84)a	2.23(0.05)a
PETMP-CC	67.5(1.76)a	76.5(0.66)a	2.20(0.20)a
TMP-AL	69.2(0.47)a	78.2(1.45)a	2.60(0.00)a
TMP-AR	68.6(0.51)a	78.1(0.47)a	2.50(0.10)a
TMP-CC	69.1(1.47)a	76.3(0.45)a	2.56(0.15)a
<i>p-value</i>	<i>0.000</i>	<i>0.000</i>	<i>0.000</i>

Table 2

Mean and standard deviation for flexural strength (FS), elastic modulus (E), toughness (T) and fracture toughness (K_{IC}) for all cements. Values followed by the same superscript within the same test are statistically similar ($\alpha=5\%$).

	FS (MPa)	E (GPa)	T (J/m³)	K_{IC} (MPa.m^{1/2})
Control	106.8(10.6)c	4.00(0.26)c	0.89(0.18)c	1.94(0.21)b
PETMP-AL	152.7(19.4)ab	5.18(0.56)ab	1.83(0.23)a	2.58(0.35)a
PETMP-AR	155.2(19.1)ab	5.16(0.54)ab	1.67(0.29)ab	2.48(0.15)a
PETMP-CC	160.1(17.7)ab	5.74(0.58)ab	1.60(0.23)ab	2.64(0.24)a
TMP-AL	141.5(15.8)b	5.07(0.32)bc	1.43(0.23)b	2.63(0.29)a
TMP-AR	167.4(16.5)a	5.93(0.48)a	1.39(0.28)b	2.69(0.14)a
TMP-CC	164.4(23.7)a	5.84(0.48)ab	1.63(0.33)ab	2.56(0.12)a
<i>p-value</i>	<i>0.000</i>	<i>0.000</i>	<i>0.000</i>	<i>0.000</i>

Table 3

Mean and standard deviation for polymerization stress, gelation profiles (G'/G'' and final storage modulus) and degree of conversion at time to G'/G'' . Values followed by the same superscript within the same test are statistically similar ($\alpha=5\%$).

	Polymerization stress (MPa)	Time to G'/G'' (s)	DC at the same time to G'/G'' (%)	Final storage modulus (G' , MPa)
Control	13.5(0.65)a	36.6(1.1)d	3.7(0.35)d	4.59(0.08)c
PETMP-AL	4.63(0.44)cd	135.6(9.6)b	13.0(2.75)b	4.40(0.33)c
PETMP-AR	3.15(0.48)d	187.6(10.2)a	22.5(2.80)a	7.05(0.76)ab
PETMP-CC	5.83(0.07)bc	103.3(4.0)c	6.16(0.61)c	5.34(0.79)bc
TMP-AL	6.86(1.08)b	109.6(3.7)c	10.6(1.78)b	7.00(0.71)ab
TMP-AR	5.97(0.32)bc	101.6(12.0)c	12.9(1.32)b	7.93(0.71)a
TMP-CC	5.43(1.18)bc	106.6(1.5)c	14.1(1.60)b	7.11(0.72)ab
<i>p-value</i>	<i>0.000</i>	<i>0.000</i>	<i>0.000</i>	<i>0.000</i>

Table 4

Mean and standard deviation for glass transition temperature, storage modulus at rubbery plateau, cross-link density and heterogeneity of network. Values followed by the same superscript within the same test are statistically similar ($\alpha=5\%$).

	Tg (°C)	Storage modulus at the rubbery plateau (MPa)	Cross-link density (mol/kg)	Width at half-height of tan delta peak (°C)
Control	180.3(1.1)a	505.0(53.0)a	0.0237 (0.0021)a	50.5(2.29)a
PETMP-AL	137.6(2.5)c	344.6(26.3)bc	0.0170 (0.0012)bc	36.8(2.75)bc
PETMP-AR	137.0(3.0)c	259.3(34.0)c	0.0145 (0.0009)c	34.7(1.95)c
PETMP-CC	150.3(2.5)b	354.3(23.8)b	0.0182 (0.0011)b	42.7(1.04)b
TMP-AL	153.3(0.5)b	344.3(9.0)bc	0.0171 (0.0005)bc	41.0(2.64)bc
TMP-AR	147.3(3.0)b	292.0(18.1)bc	0.0158 (0.0011)bc	36.3(3.32)bc
TMP-CC	152.3(3.2)b	364.0(36.6)b	0.0173 (0.0007)bc	34.9(1.00)c
<i>p-value</i>	<i>0.000</i>	<i>0.000</i>	<i>0.000</i>	<i>0.000</i>

Table 5

Mean and standard deviation for viscosity and film-thickness achieved by all resin cements. Values followed by the same superscript within the same test are statistically similar ($\alpha=5\%$).

	Viscosity (log Pa.s)	Film-thickness (μm)
Control	1.05E+02 (7.47E+00)d	43.6 (2.5)a
PETMP-AL	4.97E+02 (2.28E+01)bc	41.6 (2.1)a
PETMP-AR	5.49E+02 (2.80E+01)b	42.3 (3.8)a
PETMP-CC	5.64E+02 (6.82E+01)b	43.0 (2.0)a
TMP-AL	4.61E+02 (4.40E+01)c	42.6 (4.2)a
TMP-AR	5.56E+02 (5.32E+00)b	43.6 (2.3)a
TMP-CC	6.66E+02 (3.68E+01)a	43.3 (2.1)a
<i>p-value</i>	<i>0.000</i>	<i>0.970</i>