



# Influence of the organic matrix composition on the polymerization behavior and bulk properties of resin composites containing thiourethane-functionalized fillers

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## ABSTRACT

**Objectives:** The incorporation of thiourethane-based oligomeric additives into resin composite formulations leads to improvement in mechanical properties and reduction in polymerization stress, but may increase viscosity. The objective of this study was to functionalize filler particle surfaces with thiourethane silane molecules and determine the impact of the inorganic filler loading and surface treatment on the behavior of experimental resin composites with systematically-varied organic matrices.

**Methods:** Thiourethane oligomer was synthesized *de novo*, and grafted to the surface of 0.7 μm barium glass. BisGMA and TEGDMA (BT) were combined (at 30:70, 50:50 or 70:30 wt%) to 50 or 75 wt% of methacrylate (MA-Sil – control) or thiourethane-silanized (TU-Sil) particles. Composites were made polymerizable by the addition of 0.2 wt% BAPO and 0.05 wt% BHT was added as inhibitor. A mercury arc lamp (320–500 nm) at 800 mW/cm<sup>2</sup> was used for all curing procedures. Kinetics of polymerization was assessed by near-IR spectroscopy in real time. Polymerization stress was determined with a cantilever system in real time (Bioman). Flexural modulus and strength were determined in 3-point bending (25 × 2 × 2 mm). Water sorption and solubility and film thickness were tested according to ISO 4049. Polymeric network characteristics were analyzed by dynamic mechanical analysis (DMA). Data was analyzed with two-way ANOVA/Tukey's test (95%).

**Results:** Viscosity increased with the increase in BisGMA and/or filler amounts. Overall, TU-Sil containing composites showed delayed vitrification and higher final DC. Filler concentration did not affect DC neither flexural strength. DC decreased with increasing BisGMA content. Polymerization stress reduced and flexural modulus increased for higher filler content, especially for formulations containing TU-Sil particles. The water stability was positively affected by the increase in amount of BisGMA and inorganic filler particles. In terms of polymeric network, the addition of TU-Sil particles increased the T<sub>g</sub> and decreased the E' and cross-link density.

**Conclusions:** With the exception of flexural modulus, all tested properties were significantly impacted by the matrix viscosity and/or the addition of TU-Sil filler particles. In general, the use of thiourethane oligomers as a silane coupling agent was able to reinforce the materials and reduce the polymerization stress without negatively affecting the viscosity of the system.

## 1. Introduction

Manufacturers place great importance on the rheological properties of commercial resin composites, because the viscosity may strongly influence many aspects of their handling characteristics, i.e. ease of placement, ability to shape, adaptation to the dental substrate, stickiness, and slumping resistance [1]. The viscosity of the organic matrix also directly affects the amount of inorganic filler that can be added. In

addition, the viscosity plays an even more complex role on a molecular level, and affects the onset of diffusional limitations to polymerization, which in turn affect the final conversion and potentially the degree of crosslinking of the material [2]. Combined, all of these factors influence mechanical properties, esthetic characteristics, biocompatibility, and the overall stability of the dental restoration.

The viscosity of the composite paste is determined by the composition of the organic matrix and the relative amount of inorganic fillers.

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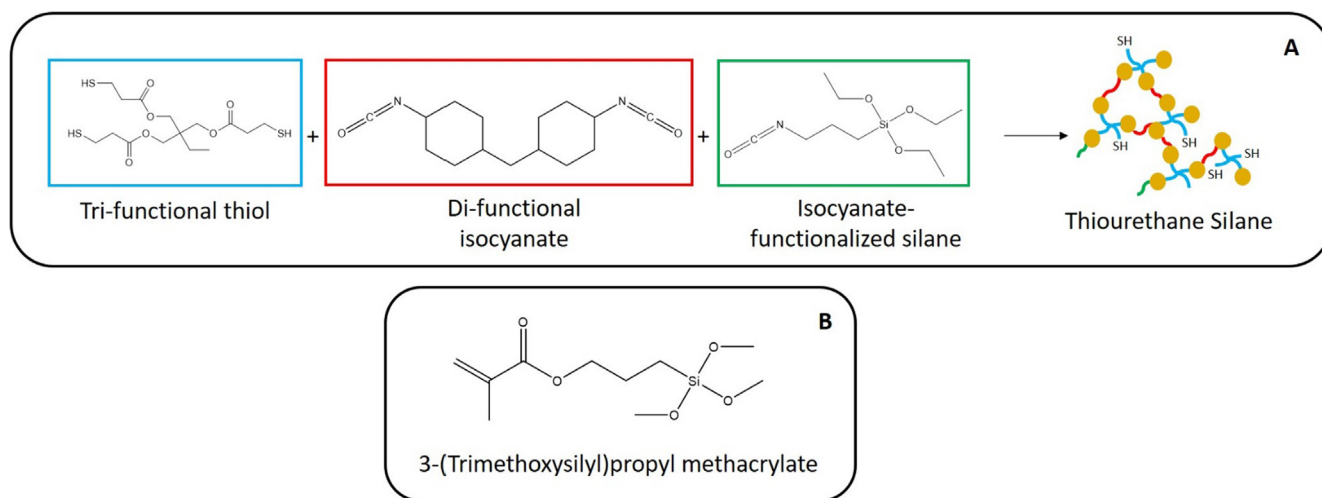
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**Fig. 1.** (A) Schematic representation of the thiourethane silane synthesized by the reaction of a trifunctional thiol, a di-functional isocyanate, and an isocyanate-functionalized triethoxy silane. The final product bears pendant thiols (-SH) to undergo chain transfer reaction with the methacrylate organic matrix, and pendant ethoxy silanes to graft to the inorganic filler particle surface (represented in green). The molecular weight is approximately 5 kDa [20]. (B) Chemical structure of the commercially-sourced 3-(Trimethoxysilyl)propyl methacrylate used on methacrylate-silanized filler particles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The most common approach to adjust the viscosity of the organic matrix is to combine monomers of different viscosities, which are influenced by their molecular weight and strength of their secondary intermolecular interactions [3]. It has been shown that the combination of bisphenol A-glycidyl methacrylate (BisGMA) with triethyleneglycol dimethacrylate (TEGDMA) at mass ratios varying from 50 to 75% provides increased reactivity, overall conversion and mechanical properties [3–5]. BisGMA is a high viscosity monomer ( $> 1000$  Pa s) bearing a rigid aromatic core, with  $MW = 512$  g mol<sup>-1</sup> and strong hydrogen bonding donor potential provided by two hydroxyl groups per molecule. TEGDMA is a flexible, low viscosity (0.05 Pa s) aliphatic diluent monomer with  $MW = 286$  g mol<sup>-1</sup>, and limited hydrogen bonding acceptor potential [5]. The final viscosity is determined by the amount of the inorganic filler incorporated into the organic matrix, i.e. increasing the filler fraction from 40 vol% to 60 vol% may lead to more than one order of magnitude increase in viscosity (from 100 to 1000 Pa s) [6], and the size and dispersion of filler particles into the matrix [1].

Clinical evidence shows that dental composite restorations have shorter service lives than desirable, often being replaced due to secondary caries [7,8]. Even though commercial low-shrink/low-stress materials have not shown better performance than conventional materials [9], *in vitro* evidence suggests that the stress generated during the polymerization reaction, and the consequent gaps formed at the composite/tooth interface [10], might increase bacterial colonization and demineralization at the tooth-restoration interface [11]. Therefore, the incorporation of stress-reducing additives into the resin composite formulations has been suggested as an attempt to overcome this issue. The broad field of additives includes nanotubes, whiskers, POSS (polyhedral oligomeric silsesquioxanes), nanogels, PPF (pre-polymerized fillers), thiol-ene [12] and thiourethane oligomers [13–15]. An important consideration related to the incorporation of such additives into the resin composite formulation is the increased viscosity [16,17]. For example, while the addition of thiourethane oligomers to the monomer matrix produced composites with enhanced cure and fracture toughness and reduced contraction stress, the viscosity of the resin matrix was increased substantially [16]. This led to investigations into producing materials with the benefits of the thiourethane, but without affecting flow and handling properties.

Recently, the use of toughening, stress-reducing thiourethane oligomers as a surface modifier grafted onto the surface of inorganic fillers

has been proposed [18,19], and one study showed that the addition of 50 wt% of thiourethane-functionalized filler particles (TU-Sil) into an organic matrix composed by BisGMA, UDMA and TEGDMA (50:30:20, respectively) led to 15–33% polymerization stress reduction and up to 1.5 fold increase in fracture toughness, without significantly affecting the viscosity [19]. In order to take advantage of the addition of these stress-reducing/reinforcing agents, while still producing mixtures containing high volume fractions of inorganic fillers, it is crucial to evaluate the impact the different filler treatments have on the viscosity of the material when associated with organic matrices of different initial viscosities. With this in mind, the present study aimed at functionalizing filler particles with oligomeric thiourethanes and determining the impact of the inorganic filler content and organic matrix viscosity on polymerization kinetics, mechanical properties, polymerization stress, film thickness, water stability, and polymer network characteristics by dynamic mechanical analysis. The tested hypotheses were: (1) the addition of TU-Sil filler particles will decrease the polymerization stress without compromising kinetics of polymerization, mechanical properties, viscosity and network formation, and (2) more viscous systems will present lower rates of polymerization, degree of conversion and polymerization stress.

## 2. Materials & methods

### 2.1. Synthesis of thiourethane and functionalization of barium particles

The thiourethane synthesis has been previously described [19]. Briefly, a trifunctional thiol (trimethylol-tris-3-mercaptopropionate, TMP), difunctional isocyanate (1-isocyanato-4-[(4-isocyanatocyclohexyl) methyl] cyclohexane, DHDI), and a trimethoxy silane – (3-(triethoxysilyl)propyl isocyanate) were combined at 2.5:1:1 mol% in solution. The solvent for the reaction was methylene chloride and trimethylamine was used as catalyst. The oligomer was purified by precipitation in hexanes and roto-evaporation. The oligomer characterization was carried out with mid-IR (by the disappearance of the isocyanate peak at 2270 cm<sup>-1</sup>) and NMR spectroscopy (resonance signals at 3.70 ppm) (Fig. 1).

For the thiourethane filler particles functionalization procedure, the oligomer was mixed in an ethanol:millipore water solution (80:20 vol %, respectively) acidified by glacial acetic acid (pH ~ 4.5). The thiourethane was added at 2 wt% of the ethanol:water solution. Neat

barium (0.7  $\mu\text{m}$  ultrafine, Schott Dental Glass, Landshut, Germany) was incorporated into the solution and kept under magnetic agitation for 24 h, filtered, washed in hexanes, and dried for 4 days at 37 °C. Filler silanization efficiency was checked using thermogravimetric analysis (Discovery TGA55, TA Instruments – Waters LLC, New Castle, DE). Approximately 15 mg of filler was placed in a high temperature platinum pan and subjected to a heat ramp (50–850 °C, 10 °C/min) and the mass loss was recorded over time.

## 2.2. Resin composite preparation

The organic matrix of the experimental resin composites consisted of BisGMA (Bisphenol A diglycidyl dimethacrylate) and TEGDMA (triethylene glycol dimethacrylate) (BT) combined at 30:70, 50:50 or 70:30 wt%. The inorganic content was based on thiourethane-functionalized filler particles (Tu-Sil – described above) or its commercially methacrylate-silanized analogous version (MA-Sil – 0.7  $\mu\text{m}$  Ultrafine, Schott Dental Glass, Landshut, Germany) incorporated in 50 or 75 wt%, totalizing 12 experimental groups. The formulations were made polymerizable by the addition of 0.2 wt% BAPO (Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide) and 0.05 wt% of BHT (2,6-di-tert-butyl-4-methylphenol) was incorporated as inhibitor.

All photocuring procedures were performed with a mercury arc lamp (EXFO Acticure 4000 UV Cure; Mississauga, Ontario, Canada) filtered to 320–500 nm and delivering 800 mW/cm<sup>2</sup> directly to the surface of the specimen, already accounting for light loss through the different test set ups. The irradiance of the arc lamp was characterized daily prior to starting the experiments using a power meter based on a thermopile system (Moletron, Portland, OR, USA). The wavelength distribution was characterized with a bench-top UV-Vis apparatus (USB2000, Ocean Optics, Largo, FL, USA).

## 2.3. Polymerization kinetics

Three disks (rubber molds of 10 mm diameter and 0.8 mm thickness), laminated between two glass slides, were photoactivated and the polymerization kinetics was recorded in real-time for 300 s with near-infrared spectroscopy (2 scans per spectrum with 4 cm<sup>-1</sup> resolution; Nicolet 6700 FTIR Spectrometer, Thermo Electron Corporation, Waltham, MA, USA –) in real-time during the photopolymerization (300 s, 4.2 cm distance between the light guide and glass slide surface, delivering 800 mW/cm<sup>2</sup> as measured at the specimen surface). The area corresponding to the methacrylate double bond overtone at 6165 cm<sup>-1</sup> was followed to calculate the degree of conversion and the polymerization rate was obtained from the first derivative of the conversion versus time curve (n = 3).

## 2.4. Water sorption and solubility

The same discs used to follow polymerization kinetics were subject to water sorption and solubility, according to ISO 4049. The initial mass (M1) was measured before incubation in 5 ml of millipore water, the mass after 7-day water storage water incubation (M2), and the final mass (M3) after the sample mass was stabilized under dry storage in a desiccator connected to the house vacuum. Water sorption (WS) and solubility (SL) in  $\mu\text{g}/\text{mm}^3$  were calculated according to equations (1) and (2), respectively:

$$WS = \frac{M2 - M3}{V} \times 1000 \quad (1)$$

$$SL = \frac{M1 - M3}{V} \times 1000 \quad (2)$$

where V is the volume of the disc specimen (in mm<sup>3</sup>).

## 2.5. Polymerization stress

Polymerization stress (PS) was tested in real-time for 300 s during the photopolymerization (800 mW/cm<sup>2</sup>) on disk-shaped samples (5 mm diameter  $\times$  1 mm thick) in a single cantilever device “Biomax” [21]. In brief, the system consists of a vertical piston placed perpendicular to the load cell axis and opposite to a fused silica glass plate maintaining a 1-mm gap between them, in which the uncured sample is loaded. In order to avoid sample debonding during the photopolymerization, the piston surface was treated with a metal primer (Z-Prime Plus, Bisco Inc, Schaumburg, IL, USA) and the glass surface with silane (Ceramic Primer, 3M Oral Care, St. Paul, MN, USA) (n = 5).

## 2.6. Flexural Strength, elastic modulus and toughness

Flexural Strength (FS), Flexural Modulus (FE) and Toughness (G<sub>IC</sub>) were assessed by three-point bending test according to ISO 4049. Rectangular bars (2.0  $\times$  2.0  $\times$  25.0 mm) were produced in metal molds placed between two glass slides and polymerized for 120 s bottom and surface samples, at a distance of 7 cm between the light guide tip and the glass slide delivering 800 mW/cm<sup>2</sup>. This distance created a light spot size sufficient to cover the entire surface of the specimen, avoiding multiple expositions and uncontrolled overlapping. Bars were stored in dry conditions for 24 at room temperature (n = 10). Specimens were tested at 0.5 mm/min cross-head speed with 20 mm distance between supports. FS (MPa) and FE modulus (GPa) were calculated according to the following equations:

$$FS = \frac{L \times D^3}{4 \times w \times h^3 \times d} \times 10^{-3} \quad (3)$$

$$FE = \frac{3LD^3}{2wdh^3} \quad (4)$$

where L is the maximum load (N), D the span between the supports (mm), w the specimen width (mm), h the specimen height (mm), and d the deflection corresponding to L (mm).

Toughness was calculated as the area under stress-strain curve up to the fracture load.

## 2.7. Viscosity and film thickness

The viscosity of the organic matrices were assessed by a cone-plate rheometer (ARES, TA Instruments, New Castle, DE, USA). Approximately 1 g of each resin was placed between 20-mm diameter plates and tested at 1 Hz with a gap of 0.3 mm (n = 3).

The viscosity of the composites was assessed by film thickness (FT). Sample preparation was performed according to ISO Specification 4049 and as described previously in the literature [22]. Briefly, the 0.2 g of the uncured composites was sandwiched between two Mylar strips and pressed between two glass slabs statically loaded with 2 kg. After 60 s, the load was removed and the samples photocured for 60 s at 800 mW/cm<sup>2</sup>. The thickness of the resin composite films were measured using a digital caliper at three different locations for each sample and the average of the measurements was considered as the sample final thickness (n = 3).

## 2.8. Dynamic mechanical analysis

Glass transition temperature (T<sub>g</sub>), storage modulus (E'), and polymer cross-link density were assessed on sample beams (15 mm long  $\times$  3 mm wide  $\times$  1 mm thick) irradiated for 120 s at 800 mW/cm<sup>2</sup>. In order to maximize the degree of conversion and prevent any further polymerization during the test, the bars were submitted to a heat treatment at 170 °C for 15 h. While that produces networks that are different than the ones produced in the other test set ups, this test was included to provide insight on the rank order of materials in terms of

network structure. The bars were tested using a DMA Instrument (DMA Q800, TA Instruments, New Castle, United States), in tension mode with the temperature varying from  $-50\text{ }^{\circ}\text{C}$  to  $250\text{ }^{\circ}\text{C}$ , and ramping rate of  $3\text{ }^{\circ}\text{C}/\text{min}$ . The  $T_g$  was recorded as the peak value of the tan delta curve and storage modulus ( $E'$ ) as a function of temperature. For the calculation of the cross-link density ( $\nu$ ), the mean of the  $E'$  in the rubbery plateau was entered into Eq. (5):

$$\nu = \frac{E'}{3dRT} \quad (5)$$

where  $\nu$  is the cross-link density (mol/kg),  $E'$  is the storage modulus (MPa),  $d$  is the density (g/ml),  $R$  is the gas constant ( $8.314472\text{ J/mol K}$ ), and  $T$  is the temperature (K).

## 2.9. Statistical analysis

Data were analyzed for normality (Anderson-Darling) and homocedasticity (Bartlett/Levene), then subjected to ANOVA. Three way ANOVA (organic matrix composition with three levels, filler loading (%) with two levels, and filler surface treatment with two levels) was used to determine which factors and interactions were significant. Subsequently, averages were contrasted by Tukey's test ( $\alpha = 0.05$ ).

## 3. Results

The results of the three-way ANOVA for all tested variables and their interactions are shown in Table 1. Except for the mechanical properties in flexure, the triple interaction was not significant for any of the variables.

Kinetics of polymerization results are presented in Table 2. In terms of final DC, in general, resin composites containing TU-Sil filler particles reached higher values (ranging from 69.6 to 81.7%) than MA-Sil systems (ranging from 65.3 to 73.6%), regardless of the filler concentration (with just a few exceptions). The filler loading did not influence conversion within the same filler surface treatment and organic matrix composition, except in two cases (TU-SIL at 30:70 and 70:30) where DC was higher with higher filler load. In general, BT 70:30 showed lower values of conversion (in all cases except for TU-SIL), whereas BT 30:70 and 50:50 had similar final conversion, regardless of the filler loading and surface treatment. BT 30:70 formulations had the lowest  $RP_{MAX}$  values ( $p < 0.0001$ ), though there were no differences for the three resins with MA-Sil at 50% filler load. When comparing the different filler loadings, the highest values were attained by compositions containing 75% filler (BT 50:50 MA-Sil/ TU-Sil and BT 70:30 TU-Sil – 18.7, 21.6, and 18.4%  $s^{-1}$ , respectively). The polymerization rate as a function of the degree of conversion curves show slow deceleration

rates, with a quasi-plateau in rate between 10 and 30% conversion for all of the BT 30:70 formulations and in BT 50:50 75% TU-Sil resin composite (Fig. 2). In relation to DC at  $RP_{MAX}$ , in general, the highest values were attained for BT 30:70, with BT 70:30 having the lowest conversions though not significantly different than BT50:50.

The results for WS (water sorption) and SL (solubility) are presented in Fig. 3. The WS values ranged between  $33.42 \pm 1.59$  and  $15.38 \pm 0.92\text{ }\mu\text{g}/\text{mm}^3$  and SL between  $7.43 \pm 0.92$  and  $2.65 \pm 0.92\text{ }\mu\text{g}/\text{mm}^3$ . In general, the WS and SL values decreased with increases in BisGMA and filler loading. In addition, although there is no significant difference, there is a trend for formulations containing TU-Sil particles to show lower values of WS and SL than MA-Sil-based resin composites. There was no correlation between final degree of conversion and SL ( $R^2 = 0.137$ ) or WS ( $R^2 = 0.001$ ).

Polymerization stress as a function of time curves are depicted in Fig. 4A and the average/standard deviation values in Fig. 4B. In general, composites with higher BisGMA concentration (BT 70:30) showed reduced PS in relation to BT 30:70 and 50:50 (significantly for 50% MA-SIL and 75% MA-Sil). Additionally, half of the composites with higher filler concentration had lower values of polymerization stress (exceptions were BT 30:70 MA-Sil, BT 70:30 MA-Sil, and BT 30:70 TU-Sil. The addition of 75 wt% TU-Sil inorganic particles resulted in significantly lower PS results in comparison to the MA-Sil analogous formulations for BT 30:70 and 50:50 formulations (reduction of 28 and 26%, respectively). Regarding the viscosities for the resins only, all groups were statistically different ( $p < 0.001$ ), with values of in  $0.04 \pm 0.01$ ,  $0.17 \pm 0.01$ , and  $1.17 \pm 0.02\text{ Pa s}$  for BT 30:70, 50:50 and 70:30, respectively.

Film thickness (FT) values ranged between  $2.47 \pm 0.03$  and  $0.15 \pm 0.07\text{ mm}$  (Fig. 4C). The FT increased significantly with the filler loading and BisGMA content ( $p < 0.0001$ ). The highest values were obtained for BT 70:30 75% TU-Sil ( $2.47 \pm 0.03\text{ mm}$ ), followed by BT 70:30 75% MA-Sil ( $1.6 \pm 0.07\text{ mm}$ ), BT 50:50 75% TU-Sil ( $0.94 \pm 0.09\text{ mm}$ ), and 50:50 75% MA-Sil ( $0.6 \pm 0.03\text{ mm}$ ), and the TU-Sil versions produced thicker film than the MA-Sil versions.

The mechanical properties results are shown in Fig. 5. In terms of FS (flexural strength), there is significant difference only between BT 30:70 75% TU-Sil/ BT 50:50 50% TU-Sil / BT 50:50 75% MA-Sil ( $121.0 \pm 14.9$ ,  $123.2 \pm 14.8$  and  $127.5 \pm 11.9\text{ MPa}$ , respectively) and BT 50:50 50% MA-Sil / BT 70:30 50% MA-Sil ( $89.8 \pm 14.9$  and  $86.7 \pm 11.8\text{ MPa}$ , respectively). All other groups showed intermediate results.  $E$  (flexural modulus) was significantly affected by the filler particle percentage. All resin composites filled at 75 wt% showed higher values than their analogous versions filled at 50 wt% ( $p < 0.05$ ). In terms of  $G_{IC}$ , in general, systems containing 50% TU-Sil showed the highest values followed by 50% MA-Sil compositions

**Table 1**

Three-way ANOVA for all experiments in the present study. The factors were organic matrix (3 levels: BT 30:70, 50:50 and 70:30), percentage of filler particles (2 levels: 50 and 75 wt%), and filler particle surface functionalization (2 levels: MA-Sil and TU-Sil). The significance level was  $\alpha = 0.05$ . Non-significant interactions are highlighted in bold. Tests.

		Organic Matrix	Filler %	Filler Treatment	Organic Matrix * Filler %	Organic Matrix * Filler Treatment	Filler % * Filler Treatment	Organic Matrix * Filler % * Filler Treatment
3-way ANOVA	$RP_{MAX}$	< 0.0001	< 0.0001	0.0077	< 0.0001	0.0084	< 0.0001	<b>0.6270</b>
	DC@	< 0.0001	<b>0.6965</b>	0.0131	<b>0.9780</b>	0.0414	<b>0.3907</b>	<b>0.9595</b>
	$RP_{MAX}$							
	Final DC	< 0.0001	0.0002	< 0.0001	0.0108	<b>0.1535</b>	< 0.0001	<b>0.1283</b>
	FS	0.0015	0.0003	0.0049	<b>0.4691</b>	<b>0.1514</b>	0.0282	0.0017
	FE	< 0.0001	< 0.0001	<b>0.9859</b>	0.0067	0.0052	0.0010	< 0.0001
	$G_{IC}$	< 0.0001	< 0.0001	0.0022	<b>0.0933</b>	<b>0.2227</b>	<b>0.0597</b>	<b>0.8284</b>
	WS	< 0.0001	< 0.0001	0.0192	<b>0.4764</b>	0.0090	<b>0.5907</b>	<b>0.9549</b>
	SL	<b>0.1291</b>	0.0022	0.0426	<b>0.2046</b>	<b>0.1637</b>	<b>0.2121</b>	<b>0.1907</b>
	PS	< 0.0001	< 0.0001	< 0.0001	0.0003	0.0337	0.0220	<b>0.4332</b>
	FT	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001
	$T_g$	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001
	$E'$	< 0.0001	0.0136	<b>0.0540</b>	< 0.0001	< 0.0001	0.0001	< 0.0001
$\nu$	< 0.0001	0.0051	0.0353	< 0.0001	< 0.0001	0.0001	< 0.0001	

**Table 2**

Average and standard deviation of maximum rate of polymerization, degree of conversion at maximum rate of polymerization and final conversion for all tested formulations. Values followed by different letters within the same variable indicate statistically significant differences ( $\alpha = 0.05$ ).

BisGMA:TEGDMA (wt%)	Methacrylate or thiourethane functionalized filler content (wt%)			
	50%		75%	
	MA-Sil	TU-Sil	MA-Sil	TU-Sil
Maximum rate of polymerization – $RP_{max}$ (% $s^{-1}$ )				
30:70	9.5 (2.1) bc	6.1 (0.6) c	5.5 (0.3) c	9.1 (1.9) bc
50:50	13.2 (2.7) b	11.2 (0.6) b	18.7 (0.3) a	21.6 (0.3) a
70:30	9.6 (1.9) bc	11.7 (1.9) b	11.8 (2.3) b	18.4 (2.3) a
Degree of conversion at maximum rate of polymerization – $Dc$ at – $RP_{max}$ (%)				
30:70	19.6 (1.2) abc	26.2 (3.9) ab	19.5 (2.1) abc	27.9 (5.6) a
50:50	15.2 (3.0) c	16.6 (4.8) bc	14.9 (2.2) c	17.7 (4.5) abc
70:30	13.1 (3.3) c	11.5 (2.1) c	11.8 (2.9) c	13.2 (4.2) c
Final degree of conversion (%)				
30:70	73.5 (1.3) cd	75.4 (0.6) bc	71.6 (1.6) de	81.7 (0.3) a
50:50	73.6 (0.7) cd	78.7 (1.8) ab	70.7 (0.9) de	81.5 (1.4) a
70:30	67.0 (0.2) fg	69.6 (1.2) ef	65.3 (0.8) g	78.0 (2.5) ab

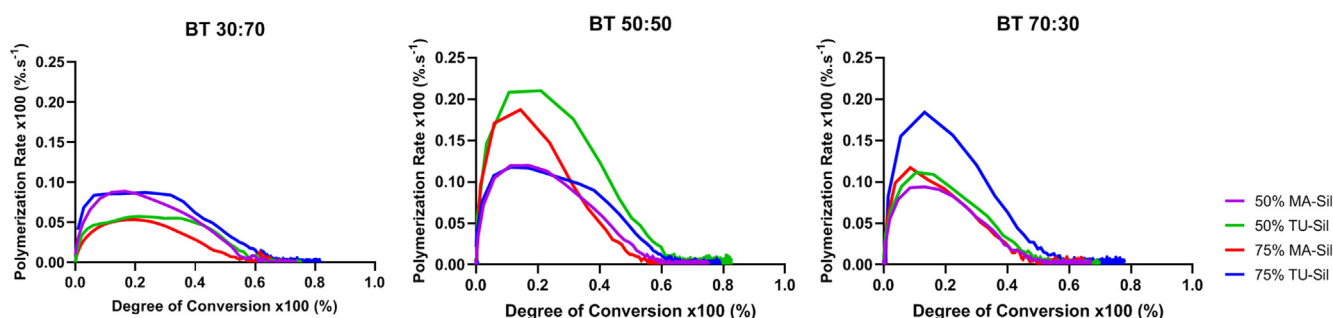


Fig. 2. Rate of polymerization (% $s^{-1}$ ) as a function of degree of conversion (%) for BisGMA:TEGDMA-based resin composites filled with 0.7  $\mu m$  MA-Sil or TU-Sil particles. The polymerization reaction was followed in real time for 300 s as the dental composites were photopolymerized at 800  $mW/cm^2$ .

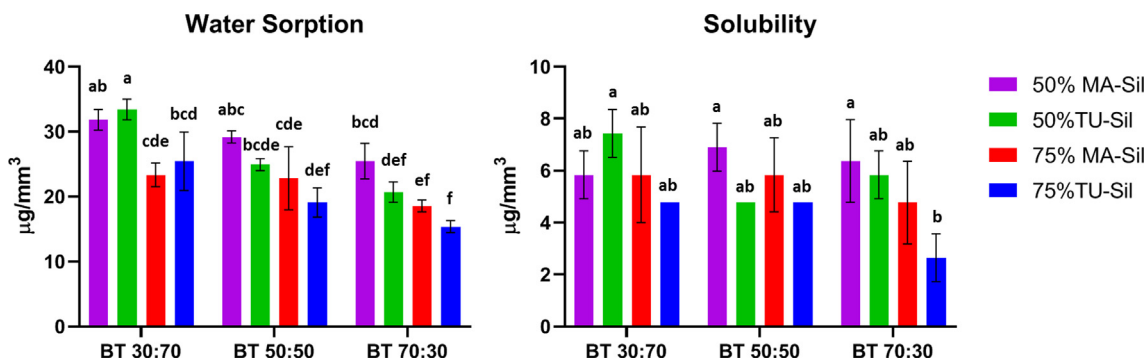


Fig. 3. Water Sorption (WS) and Solubility (SL) results after 7-day water incubation for all tested experimental resin composites. Different letters indicate statistically significant differences among the groups ( $\alpha = 0.05$ ).

(averaged  $2.11 \pm 0.79$  and  $1.40 \pm 0.41$  MPa, respectively). In addition,  $G_{IC}$  increased as filler percentage and BisGMA ratio decreased. Overall, organic matrix and particle surface functionalization did not affect FS, E or  $G_{IC}$ .

Dynamic mechanical analysis results are reported in Table 3. The samples containing 75 wt% MA-Sil in BT 30:70 and 50:50 matrices did not survive the test, which made it impossible to analyze the data. Glass transition temperature ( $T_g$ ) results ranged from  $176.5 \pm 3.2$  °C to  $158.6 \pm 1.4$  °C, with higher values for systems containing TU-silanized fillers, especially in 50 wt% formulations.  $E'$  at rubbery plateau was used to calculate the degree of crosslinking ( $\nu$ ), which decreased as the BisGMA ratios increase for the 50%-filled composites. BT 70:30 75% MA-Sil presented the highest crosslinking density ( $0.13 \pm 0.02$  mol/kg). The TGA results showed weight loss of 12.6% for TU-Sil and 4.2% for the commercial MA-Sil.

#### 4. Discussion

The last 10 years have been marked by the extensive development of the resin composite organic matrix, including monomers and additives aimed at controlling the polymerization stress and to further the reinforcing effect provided by the inorganic filler [15,17,20], with the ultimate goal to increase the lifespan of the dental restorations. In the case of the incorporation of additives, a recurrent concern is that these compounds may result in a significant increase in viscosity due to inter-particle interactions [17,20]. It is widely known that the initial viscosity of a polymerizing medium affects kinetics of polymerization, and may lead to premature gelation, leading to lower final degrees of conversion [2]. In addition, higher initial viscosity in the organic matrix also precludes the incorporation of larger amounts of inorganic filler particles. One solution for this issue is the incorporation of additives as a

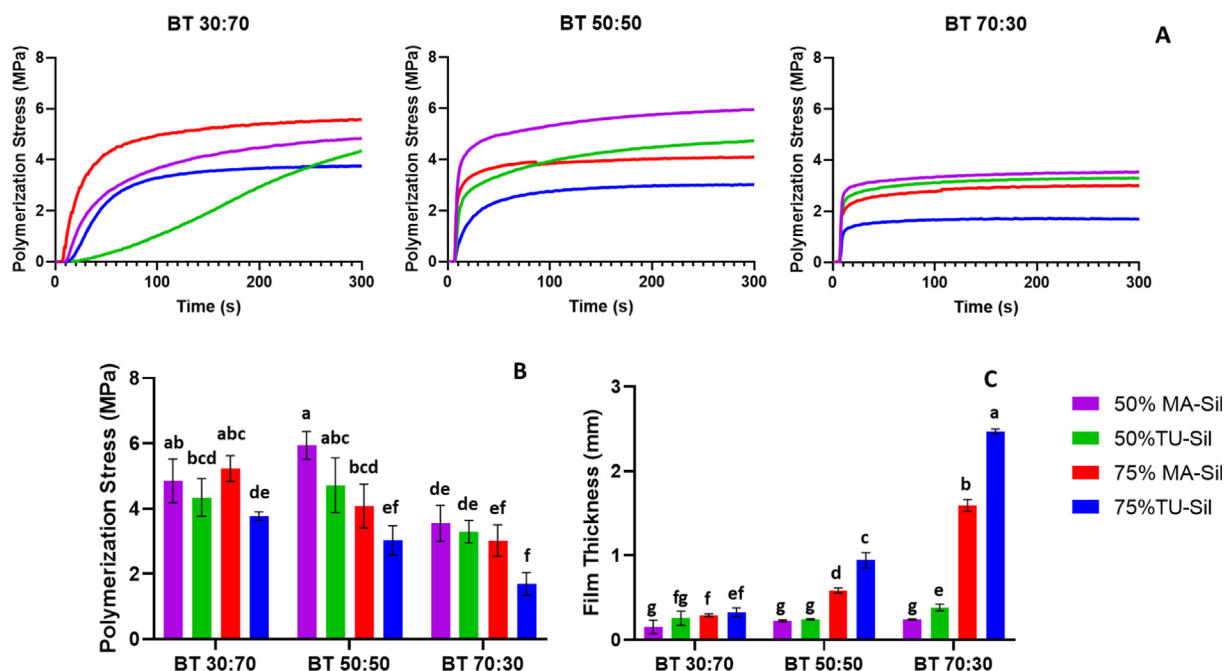


Fig. 4. (A) Polymerization stress (MPa) plotted as a functional of time (seconds) for all formulations grouped by the ratio between BisGMA:TEGDMA. (B) Final polymerization stress (MPa) after 5 min of photoactivation at 800 mW/cm<sup>2</sup>. (C) Film thickness (mm) measured in samples of 0.2 g kept under 2 kg static load for 60 s for all experimental groups. Different letters indicate statistically significant differences among the groups ( $\alpha = 0.05$ ).

surface treatment of the filler particles, though this, until now, had not been investigated using a systematic approach in terms of the organic matrix composition [19,23].

In general, the presence of TU-functionalized fillers did not affect the maximum rate of polymerization (with one exception, explored in detail later), nor the degree of conversion at  $RP_{MAX}$ . The final degree of conversion was higher for four out of six formulations containing TU compared with the MA-functionalized counterparts. The effect of the different organic matrix compositions was much more marked. Systems with higher BisGMA concentration (BT 50:50 and BT 70:30) showed faster polymerization rates (higher  $RP_{MAX}$ ) than BT 30:70, the less viscous system. Right at the beginning of the reaction, the high mobility of the system allows for the propagation constant ( $k_p$ ) to increase, which leads to the formation of high molecular weight species. As a result, the system becomes less reactive due to diffusional limitations, especially of these high molecular weight species. Eventually, the diffusional limitations start to inhibit termination ( $k_t$ ), which leads to autoacceleration (increase in  $k_p$ ) up to the rate maximum [2]. In formulations with low initial viscosity, autoacceleration happens at much lower values of conversion. Therefore, the values of  $RP_{MAX}$  never increase significantly, and at the same time the termination events also decrease, since it is increasingly unlikely for termination by combination and/or disproportionation to take place in this reaction medium

[24]. This explains the quasi-plateau observed for the rate of polymerization as a function of degree of conversion for BT 30:70 (Fig. 1), which indicates that the system was able to maintain enough mobility to continue propagation at a low rate, leading to higher degree of conversion values at  $RP_{MAX}$ . After that point, vitrification started to develop, with the increase in viscosity limiting propagation, which also becomes diffusion-controlled. The reaction then starts to decelerate. In addition to the decrease in viscosity, TEGDMA's flexible backbone and lack of strong intermolecular interactions, in contrast to BisGMA, makes its network less sterically hindered, which also stimulates macro-radical segmental movement for a longer period of time [25]. Finally, TEGDMA also has a tendency for cyclization, which contributes to overall conversion, but not to network development and stiffening of the material [26]. In summary, the addition of higher amounts of TEGDMA into the formulations shifts the diffusion control of propagation, delaying its onset to higher conversions [25], as denoted by the  $DC@RP_{MAX}$  values found here. It is important to highlight, however, that in spite of the tendency of TEGDMA to cyclize, this did not affect the crosslinking density nor the  $T_g$  of the materials (Table 3). High levels of cyclization have been shown to markedly reduce cross-linking density and glass transition temperature [26–28], but our results demonstrate that at the concentrations used here, TEGDMA did not jeopardize network formation. This is evidenced by the DMA results, as already mentioned, as

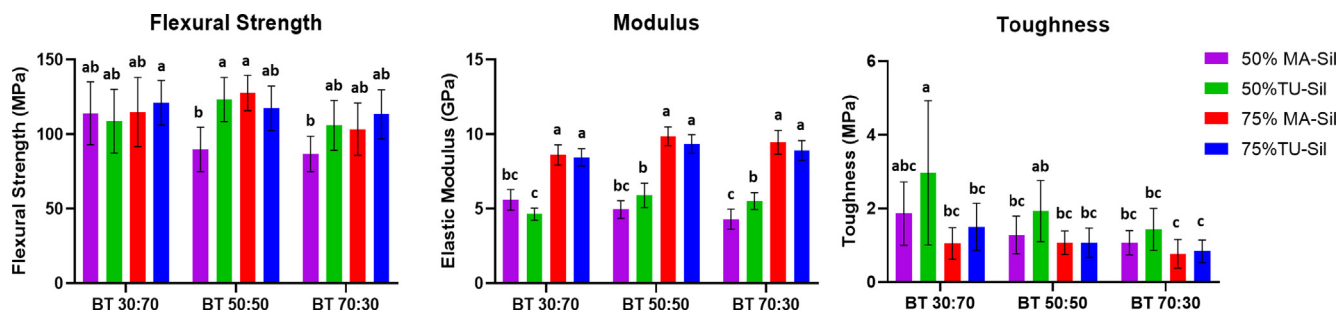


Fig. 5. Flexural Strength (MPa), Elastic Modulus (GPa) and Toughness (MPa) for all resin composites tested in three-point bending after 48 h dry storage. Different letters indicate statistically significant differences ( $\alpha = 0.05$ ).

**Table 3**

Average and standard deviation for glass transition temperature ( $T_g$  - °C), storage modulus at the rubbery plateau ( $E'$ , GPa), and crosslinking density ( $\nu$  - mol/kg) results for all formulations obtained from dynamic mechanical analysis test. Values followed by the same letter within the same variable indicate statistical similarity ( $\alpha = 0.05$ ).

BisGMA:TEGDMA (wt%)	Methacrylate or thiourethane functionalized filler content (wt%)			
	50%		75%	
	MA-Sil	TU-Sil	MA-Sil	TU-Sil
$T_g$ (°C)				
30:70	165.3 (0.8) bc	174.4 (1.9) ab	NA	158.6 (1.4) c
50:50	163.4 (2.0) c	174.3 (10.7) abc	NA	169.2 (1.2) abc
70:30	159.3 (1.3) c	176.5 (3.2) a	169.0 (0.6) abc	167.5 (2.0) abc
$E'$ at the rubbery plateau (GPa)				
30:70	711.6 (1 1 1) b	628.5 (59.0) bc	NA	788.1 (77.8) b
50:50	602.0 (1 0 0) bc	432.6 (68.9) c	NA	749.6 (87.1) b
70:30	356.9 (60.0) c	349.4 (32.4) c	1476.2 (277.6) a	615.9 (40.2) bc
Cross-link density ( $\nu$ ) (mol/kg)				
30:70	0.0597 (0.0093) bc	0.0563 (0.0055) bc	NA	0.0732 (0.0070) b
50:50	0.0553 (0.0094) bc	0.0386 (0.0052) c	NA	0.0679 (0.0080) b
70:30	0.0331 (0.0055) c	0.0311 (0.0028) c	0.1339 (0.025) a	0.0561 (0.0039) bc

well as by the flexural strength/flexural modulus results. It is important to highlight that the presence of the thiourethane may have contributed to prevent TEGDMA cyclization, via possible hydrogen bonding of the -SH group in TU with the hydrogen-bond acceptor glycol units in TEGDMA. Finally, it is important to note that the DMA results are obtained in materials with higher conversion overall, achieved after post-cure heat treatment. While it is absolutely acknowledged that this does not directly correlate with the data obtained with the other tests, it does provide ranking and comparison among the materials tested.

The formulations based on BT 70:30 showed, in general, the lowest values of DC at  $RP_{MAX}$ . The high concentration of BisGMA was indeed expected to make the reaction environment more hindered, which in turn led to early autoacceleration of the polymerization reaction [25]. The high initial and increasing viscosity of the reaction environment also led to limited final DC for this composition [25]. A plateau was also identified in the polymerization kinetics profile of the BT 50:50 75% TU-Sil group. This can be explained by the chain-transfer ability of the pendant thiols with vinyl groups, leading to delayed gelation/vitrification and allowing for increased degree of conversion before the reaction becomes diffusion-limited. This also explains the increased final DC presented by all groups containing 75 wt% TU-Sil filler particles [20]. Interestingly, even in the highly hindered BT 70:30 matrix system, the addition of 75 wt% TU-Sil increased the final DC by nearly 13% in relation to its analogous MA-Sil version (final DC = 78.0 and 65.3%, respectively). This indicates that the chain-transfer reactions at this higher overall TU concentration delayed the development of diffusion limitations at a level sufficient to overcome the effect of the initial viscosity, ultimately leading to higher final double bond conversion. This reinforces the crucial role played by the chain-transfer events in delaying the point in conversion at which the limitation to the mobility of the reacting species hampers polymerization, which allows for not only higher final DC, but also for reduced polymerization stress generation [29].

The same samples used in the kinetics of polymerization test were subjected to water incubation in order to check water sorption and solubility of the experimental resin composites. In general, the increase in BisGMA and increase in TEGDMA ratios made the composites less susceptible to absorb water. The LogP (octanol-water partition coefficient) of the organic matrices BT 30:70, 50:50 and 70:30 are 2.521, 3.255 and 3.989, respectively. Since higher values of LogP are associated with lower values of water sorption [30], it was expected that the decrease in the concentration of the hydrophilic TEGDMA and increase in the hydrophobic BisGMA would make the organic matrices more hydrophobic (higher LogP) and, ultimately, less water absorbing. Additionally, in general, 75%-filled composites showed lower numeric

values of WS and SL, which is expected based on the reduced volume of organic matrix. In terms of filler surface treatment, resin composites containing TU-Sil particles showed lower numeric values of WS and SL, which may be associated with the hydrophobicity of the thiourethane oligomer used to functionalize the filler particles in comparison to the hydrophilic 3-(Trimethoxysilyl)propyl methacrylate. Likewise, in respect to SL, no marked differences were observed among the tested formulations, irrespective of organic matrix or filler surface compositions.

The filler concentration impacted the stress development, as expected. On one hand, the greater filler content reduces volumetric shrinkage, but on the other hand, it increases modulus (stiffness) of the material [31]. This was indeed observed in this study, and these factors have shown complex interactions with each other and with the degree of conversion [32]. As for the role of the organic matrix, in general, the composites with higher BisGMA content (BT 70:30) showed lower stress values, which is probably correlated to both the lower shrinkage expected to be obtained with the higher molecular weight BisGMA (not measured here) and the reduced values of final DC imposed by the hindered reaction environment due to the restriction mobility of the large and stiff BisGMA molecular structure [2]. At the 75 wt% filler loading level, TU-Sil-functionalized particles led to 28% and 34% lower stress compared to the MA-Sil counterparts in BT 30:70 and 50:50 organic matrices, respectively. This effect has been shown in previous studies in methacrylate-based systems containing thiourethanes either as oligomer or as surface filler particle functionalizing agent [15,18,19]. When the thiourethane oligomer is added to the organic matrix, the reduction in polymerization stress is mainly related to the chain-transfer reactions, which are responsible for delaying the gelation and vitrification and possibly contributing to stress relaxation. TU also leads to the formation of a more homogenous polymer network, possibly limiting the development of internal stress, especially after the diffusion limitation occurs [29]. In the case when the TU is used as a filler particle coating, a few possible reasons for stress reduction/relief include: (1) reduced volumetric shrinkage owing to the high molecular weight TU; (2) reduction in the energy of propagating cracks/stress due to the low  $T_g$  of the oligomer and flexibility of the thiocarbamate bonds located at the matrix-particle interface; (3) multi-functional, brush-like structure of the oligomer, providing sites for stress transfer at the interface; (4) possible stress relaxation via dynamic bond formation; (5) uncoated areas on the surface of TU-Sil particles acting as defect sites, and finally; (6) greater filler dispersion [33]. In summary, we hypothesize that the same delayed gelation/vitrification demonstrated for the additives in the matrix is likely at play here, but the fact that this is now localized at high-stress the matrix-filler interface potentiates the

overall stress reduction, even at an overall lower TU concentration.

It is important to highlight that the stress reduction provided by the TU-containing materials was achieved while increasing conversion, and at no expense to the stiffness. In fact, the flexural modulus, strength and toughness results for some TU-SIL-containing formulations were the highest recorded. Thiol-containing networks tend to be more homogeneous, in part due to chain-transfer events, and in the specific case of thiol-isocyanates, the high flexibility and toughness of the covalent thiocarbamate bonds can also contribute to improved properties [34]. In tandem with the improved filler particle-organic matrix interaction due to the multifunctional groups available on the thiourethane oligomer, all of these may have enhanced the mechanical behavior. The addition of higher amounts of inorganic particles did not significantly impact the flexural strength but increased the flexural modulus results and decreased the toughness. In the range of filler loading variation studied here, other investigations have demonstrated either no change or even a slight decrease in flexural strength with larger amounts of nanosilica and micro barium silicate [35]. This demonstrates that there is a threshold for each particle system in which the flexural strength is positively impacted by the incorporation of higher amounts of inorganic content, and above which hydrodynamic effects (clustering, jamming and percolating) may actually jeopardize properties [35,36]. The increase in modulus with the increased filler loading was expected, as previously shown by many others [31,37,38]. The decrease in toughness in compositions containing higher filler content and BisGMA ratio was also expected since both factors increase the brittleness of the systems, which leads to catastrophic failure with little elastic deformation. On the other hand, TEGDMA acts as a flexible crosslinking agent [39].

Dynamic mechanical analysis was conducted to gain deeper insight into the network formation and possibly explain the results for properties in bending and polymerization stress. As already noted, it is acknowledged that either set of properties (obtained by DMA or bend bars) are assessed in distinct polymer networks due to the thermal treatment prior to the DMA test – this is a limitation of the method, but still provides useful ranking among the materials. No correlation analysis was attempted between the two sets of data. For BT 30:70 or 50:50 filled with 75% MA-Sil particles, the samples did not survive the test. This was due to brittleness in the samples after the thermal treatment applied before the DMA test. This is not completely unexpected since the methacrylate silane forms rigid covalent bonds with the organic matrix. The high content of TEGDMA, presumably with more heterogeneous polymer networks due to microgel formation, is also likely a contributor to the brittleness of the samples. All TU-Sil samples survived, even the ones containing high concentrations of TEGDMA. This is explained by the greater toughness of TU-containing materials as has been reported for formulations in which the oligomer was added directly to the monomer matrix [20]. It is interesting to note that the increased toughness was also observed when the TU was added as a filler surface functionality. The only statistical differences when comparing analogous methacrylate- and TU-containing pairs was observed for BT 70:30 loaded at 50 wt%. In this case, the lower conversion observed for the higher BisGMA concentrations highlighted the toughening effect of the TU. In other words, the addition of TU may be a good alternative to reinforce materials under sub-optimal polymerization conditions. The  $E'$  at rubbery plateau was used to calculate the degree of cross-linking of the network above the  $T_g$  and below the melting temperature. The lack of statistical difference among the groups filled at 50 wt% was not expected, but may be related to the post-processing procedures (samples were kept at 170 °C for 15 h) performed in order to achieve the highest final DC and prevent any further conversion during the heating cycle of the test. In fact, a possible decrease in crosslinking density was expected with the addition of TU [40], which is explained by the chain-breaking nature of the chain-transfer reactions of thiol to vinyl [41]. This is actually demonstrated in the 75 wt% filler groups. The composition containing MA-Sil (BT 70:30 – the only group that

survived the test) showed an approximately 2.5 times greater cross-link density in comparison with the analogous TU-Sil group. No clear trends were identified concerning the effect of monomer composition on crosslinking density, which is due to the fact that competing events are occurring simultaneously. It is also likely that the differences that may have existed prior to the thermal treatment were eliminated by the thermal treatment conducted prior to the DMA test. For example, the addition of BisGMA increases the modulus due to its backbone rigidity but also contributes to lower conversion. TEGDMA contributes to network heterogeneity due to its tendency to cyclization, which reduces properties in flexure and crosslinking, but also makes chain slippage more difficult, which can potentially increase  $T_g$  [42].  $T_g$  values ranged from 159 to 177 °C, with numerically greater values for TU-containing materials.

Finally, a clinically-relevant concern is the viscosity (or final handling characteristics) of the material. In this study, film thickness measurements were used as a proxy for viscosity [22]. As expected, the film thickness increased with higher BisGMA concentration and filler loading. Moreover, a clear trend was observed between increase in film thickness and decrease in generated stress, which further reinforces the crucial role played by the initial viscosity on the polymerization reaction.

## 5. Conclusion

The resin composite viscosity played a key role in the kinetics of polymerization, water sorption and solubility, polymerization stress and mechanical properties but not on the polymer network formation assessed by dynamic mechanical analysis test. Despite the reduction in crosslinking density observed with the addition of thiourethane surface-modified filler particles, the mechanical properties were either enhanced or not impacted, and the polymerization stress generation was markedly decreased.

## CRedit authorship contribution statement

**Ana Paula Fugolin:** Methodology, Writing - original draft, Formal analysis, Supervision, Visualization. **Ana Rosa Costa:** Investigation, Data curation, Formal analysis. **Emilie Kono:** Investigation, Data curation. **Eleanor Quirk:** Investigation, Data curation. **Jack L. Ferracane:** Writing - review & editing. **Carmem S. Pfeifer:** Conceptualization, Methodology, Resources, Project administration, Funding acquisition, Writing - review & editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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