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# Effect of thiourethane filler surface functionalization on stress, conversion and mechanical properties of restorative dental composites

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## ABSTRACT

**Objectives.** This study evaluated the efficacy of a thiourethane(TU)-modified silane agent in improving properties in filled composites.

**Methods.** The TU-silane agent was synthesized by combining 1,3-bis(1-isocyanato-1-methylethyl)benzene and 3-(triethoxysilyl)propyl isocyanate with trimethylol-tris-3-mercaptopropionate (TMP), at 1:2 isocyanate:thiol, leaving pendant thiol and alkoxy silane groups. Barium glass fillers (1 μm average particle size) were functionalized with 5 wt% TU-silane in an acidic ethanol solution. Commercially available 3-(trimethoxysilyl)propyl methacrylate (MA-silane) and (3-mercaptopropyl)trimethoxysilane (SH-silane), as well as no silane treatment (NO-silane), were used as controls. Composites were made with BisGMA-UDMA-TEGDMA (5:3:2), camphorquinone/ethyl-4-dimethylaminobenzoate (0.2/0.8 wt%) and di-tert-butyl hydroxytoluene (0.3 wt%) and 70 wt% silanated inorganic fillers. Polymerization stress (PS) was measured using a cantilever beam apparatus (Bioman). Methacrylate conversion (DC) and rate of polymerization (RP) during photoactivation (800 mW/cm<sup>2</sup>) were followed in real-time with near-IR. Flexural strength/modulus (FS/FM) were evaluated in three-point bending with 2 × 2 × 25 mm. Statistical analysis: 2-way ANOVA/Tukey's test (α = 5%).

**Results.** DC, Rp<sub>max</sub> and E were similar for all groups tested. FS was similar for the TU- and MA-silane, which were statistically higher than the untreated and SH-silane groups. Stress

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reductions in relation to the MA-silane were observed for all groups, but statistically more markedly for the TU-silane material. This is likely due to stress relaxation and/or toughening provided at the filler interface by the oligomeric TU structure.

*Significance.* TU-silane oligomers favorably modified conventional dimethacrylate networks with minimal disruption to existing curing chemistry, in filled composites. For the same conversion values, stress reductions of up to 50% were observed, without compromise to mechanical properties or handling characteristics.

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## 1. Introduction

Despite the low annual failure rates (1–3%) observed for composite restorations in posterior teeth, with most failures observed being related to secondary caries and fractures of the tooth structure or restorative materials, on average, restorations last about 10 years in service [1–3]. Secondary caries is significantly affected by risk factors associated to the patients [4–6], but the presence of defects at the restoration margins can increase the likelihood of bacterial recolonization and reestablishment of the disease in the region [7–9]. Further, the fact that the composite undergoes polymerization, and consequently shrinkage, confined by the cavity walls leads to the transfer of stresses to the bonded interface, which in turn favor the development of marginal defects [10–12], as well as cracks on the tooth structure [12,13]. Therefore, clinical strategies and material developments have been attempted with the goal of minimizing the deleterious effects associated with polymerization shrinkage of resin-based materials [11,12].

The main modifications in the organic matrix of composites in the last years focused on developing low-shrinking monomers, either via lower molar shrinkage coefficients, as is the case in the epoxide-based material that polymerizes via a ring-opening mechanism (i.e., silorane monomers), or via higher molecular weight monomers, or via the addition of pre-polymerized additives [11,14,15]. This was done with the assumption that reduction in polymerization shrinkage would necessarily lead to reduced polymerization stress and, in turn, better restoration longevity [10]. Clinical studies have demonstrated that this is not always the case [5,10]. In this context, thiourethane oligomers have been proposed as an alternative stress reducing additive, allying the higher molecular weight of the oligomer with thiol chemistry, which affords lower stress through delayed gelation and vitrification [16–19]. The rationale is that the thiol functional groups work as chain transfer agents to promote a radically assisted step-growth polymerization of methacrylates [18,19]. In fact, several prior studies demonstrated the effectiveness of the addition of thiourethane oligomers on polymerization stress reduction and depth of polymerization increase, which in turn relates to the high refractive index of these oligomers [20–23].

However, it has also been demonstrated that the effect of thiourethane depends on its concentration, and that the addition of this oligomer to resin matrix is somewhat limited due to viscosity concerns [18,19]. Higher concentrations of thiourethane increase the resin viscosity, complicating the addition of fillers and compromising the handling char-

acteristics of composite. One possible solution to improve the distribution of such oligomers within the composite is to tether them to the filler particles. Other studies have demonstrated that polymer brush functionalization may improve wetting of silicon-containing surfaces, and actually improve their interaction with relatively hydrophobic monomers [24,25]. In the case of particle–particle interactions, which are of interest to the composite application, it is known that the functionalization of the filler surface greatly influences particle packing [26].

Therefore, the present study aimed to investigate the effect of filler silanization with a thiourethane oligomer on polymerization kinetics, mechanical properties and polymerization stress of filled methacrylate-based dental composites, as compared to fillers silanized with a conventional methacrylate silane. The null hypothesis was that the silane type does not affect the outcomes evaluated.

## 2. Material and methods

### 2.1. Experimental design

This study was designed as a single factor evaluation of the type/presence of silane in five levels. Non-silanized fillers were treated with methacrylate, thiol or thiourethane silanes, while filler silanized by manufacturer using a methacrylate silane and filler without any surface treatment (non-silanized) were used as positive and negative controls, respectively. The variable responses were polymerization kinetics and stress; flexural strength and elastic modulus of composites assessed by 3-point bending test.

### 2.2. Synthesis of thiourethane

Except where noted, all reagents used in this study were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. The thiourethane silane was synthesized using trimethylolpropane tris(3-mercaptopropionate) (TMP), 1,3-bis(1-isocyanato-1-methylethyl) benzene (BDI) and 3-(triethoxysilyl)propyl isocyanate, at 2.5:1:1 mol ratios. Reagents were mixed in a 100 mL round-bottom flask containing 50 mL dichloromethane, under magnetic stirring at room temperature, using nitrogen gas as the reaction atmosphere for 30 min. After this time, three drops of triethylamine were added, followed by additional magnetically stirring over an ice bath for 24 h. Reaction completion was confirmed by the

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