DENTAL MATERIALS 32 (2016) 978–986

Available online at www.sciencedirect.com

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journal homepage: www.intl.elsevierhealth.com/journals/dema

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

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ARTICLE INFO

Article history:
Received 4 December 2015
Received in revised form
28 January 2016
Accepted 11 May 2016

Keywords:
Resin cements
Thio-urethane oligomers
Polymerization stress
Mechanical strength
Rheological properties
Dynamic mechanical analysis

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-diissocyante (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 let to more homogenous networks. An increase in 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.

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http://dx.doi.org/10.1016/j.dental.2016.05.003
0109-5641/

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 DL-camphoroquinone (Polysciences Inc., Warrington, PA, USA), and 0.5 wt% inhibitor (BHT – 2,6-di-tert-butyl-4-methylphenol; Sigma–Aldrich, 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-diissocyante (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–Stockmayer theory [7], leaving pendant thiols. Oligomers were purified by precipitation in hexanes and rotaevaporation, and then characterized by ^{1}H 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 $=CH_2$ absorption at 6165 cm^{-1} [10] was recorded before and after 60 s of irradiation at 700 mW/cm^2 (Bluephase, Ivoclar Vivadent, Liechtenstein) 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