



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

Thio-urethane oligomers improve the properties of light-cured resin cements

Ataís Bacchi^{a,b}, Rafael L. Consani^a, Gedalias C. Martim^c, Carmem S. Pfeifer^{d,*}

^a Piracicaba Dental School, Campinas State University, Prosthodontics and Periodontics, Av. Limeira, 901, Piracicaba, BR 13414-903, Brazil

^b Meridional Faculty – IMED, School of Dentistry, Prosthodontics and Dental Materials, Av. Senador Pinheiro, 304, Passo Fundo, RS 99070-220, Brazil

^c Maringa State University, Department of Chemistry, Av. Colombo 5790, Maringa, PR 87020-900, Brazil

^d Oregon Health and Science University, Biomaterials and Biomechanics, 611 SW Campus Dr, rm 501, Portland, OR 97239, USA

ARTICLE INFO

Article history:

Received 21 June 2014

Received in revised form

6 November 2014

Accepted 10 February 2015

Keywords:

Resin cements

Thio-urethane oligomers

Polymerization stress

Mechanical resistance

ABSTRACT

Thio-urethanes were synthesized by combining 1,6-hexanediol-diisocyanate (aliphatic) with pentaerythritol tetra-3-mercaptopropionate (PETMP) or 1,3-bis(1-isocyanato-1-methylethyl)benzene (aromatic) with trimethylol-tris-3-mercaptopropionate (TMP), at 1:2 isocyanate:thiol, leaving pendant thiols. Oligomers were added at 10–30 phr to BisGMA-UDMA-TEGDMA (5:3:2, BUT). 25 wt% silanated inorganic fillers were added. Commercial cement (Relyx Veneer, 3M-ESPE) was also evaluated with 10–20 phr of aromatic oligomer. Near-IR was used to follow methacrylate conversion (DC) 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}). Polymerization stress (PS) was measured on the Bioman. Volumetric shrinkage (VS, %) was measured with the bonded disk technique. Results were analyzed with ANOVA/Tukey's test ($\alpha = 5\%$).

In general terms, for BUT cements, conversion and mechanical properties in flexure increased for selected groups with the addition of thio-urethane oligomers. The aromatic versions resulted in greater FS/FM than aliphatic. Fracture toughness increased by two-fold in the experimental groups (from $1.17 \pm 0.36 \text{ MPa m}^{1/2}$ to around $3.23 \pm 0.22 \text{ MPa m}^{1/2}$). $R_{p_{max}}$ decreased with the addition of thio-urethanes, though the vitrification point was not statistically different from the control. VS and PS decreased with both oligomers. For the commercial cement, 20 phr of oligomer increased DC, vitrification, reduced $R_{p_{max}}$ and also significantly increased K_{IC} , and reduced PS and FM.

Thio-urethane oligomers were shown to favorably modify conventional dimethacrylate networks. Significant reductions in polymerization stress were achieved at the same time conversion and fracture toughness increased.

© 2015 Academy of Dental Materials. Published by Elsevier Ltd. All rights reserved.

* Corresponding author. Tel.: +1 503 494 3288; fax: +1 503 494 8260.

E-mail address: pfeiferc@ohsu.edu (C.S. Pfeifer).

<http://dx.doi.org/10.1016/j.dental.2015.02.008>

0109-5641/© 2015 Academy of Dental Materials. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Bonded indirect restorations play a major role in contemporary dentistry [1]. Resin cements have become popular clinically because of their ability to bond both to the tooth structure and to the restoration [2]. Examples of their clinical applications include adhesion of ceramic fragments, crowns, bridges, and intra-canal posts. Due to the necessary (and sometimes excessive) taper on tooth preparations, and to constant incidence of tensile, compressive and oblique loads, resin cements must have high mechanical properties, as well as resistance to dissolution and strong bond to structures [2–4].

Conventional resin cements are based on methacrylate monomers which undergo vitrification at early stages of polymerization [5], increasing the strain/stress at the bonded interface and in the bulk of the material structure [6]. This condition increases the risk of gap formation at the interface of cementation, which may lead to an increase of the material solubility, microleakage and staining, ultimately compromising the longevity of treatment [7]. Based on the confined geometry in which the cement is applied, current operative techniques available are not efficient in avoiding the development of strain/stress during the indirect restoration placement and, therefore, the solution to minimize stress generation needs to be based on improvements made directly to the material [8].

The use of thiol-enes has been proposed in dental composites, with successful results as stress reducing agents. The step growth nature of the thiol-ene and thiol-methacrylate polymerizations, given by chain-transfer reactions of the thiol to the ene/vinyl, leads to more homogeneous network formation and ultimately increased conversion in comparison to the pure methacrylate counterparts [9,10] and for selected compositions, improvements in flexural strength, depth of cure and water solubility have also been reported [9,11]. However, concerns over the somewhat compromised mechanical properties and the stability (shelf-life) of the fully formulated composite materials have delayed the commercial translation of thiol-ene-based materials [9,12]. Another concern that applies to small molecule thiols is the foul odor associated with the material.

As an alternative to conventional thiol-enes or thiol-methacrylates, others have proposed the use of thio-urethane networks in applications where mechanical properties in general, but more specifically toughness and resistance to impact, are desirable [13,14]. Some studies have demonstrated the more homogeneous nature of thio-urethane networks compared to the simple urethane counterparts, as well as the increased toughness values [13,14]. In those studies, thiols are combined with isocyanates *in situ*, in a reaction catalyzed by a base. Currently, these are two-part systems (at least until compounds such as photo-base generators are readily accessible – [15], not suitable for dental composite applications. However, previous studies have demonstrated it to be possible to synthesize high molecular weight pre-polymerized thio-urethane oligomers to be later added to a secondary monomer matrix, polymerizable through a radical mechanism [16]. When the oligomer is designed to have pendant thiols from the backbone, chain-transfer reactions to the

surrounding methacrylate matrix result in delayed gelation and vitrification and, as consequence, reduction in polymerization stress [16]. Due to the high molecular weight, reductions in the volumetric shrinkage are also expected, as well as the elimination of the odor concerns. Importantly, thiol-terminated thio-urethanes are capable of forming a more homogeneous network with the methacrylate, and also increase final conversion [17].

Therefore, the objectives of this study were to synthesize thiol-terminated thio-urethane oligomers with different backbone structures and to assess the properties of methacrylate-based resin cements modified with the oligomers. The hypotheses of this study were that the use of thio-urethanes would (I) increase the degree of conversion, (II) improve the material mechanical properties and (III) reduce the volumetric shrinkage/polymerization stress.

2. Materials and methods

2.1. Experimental materials composition

The experimental resin 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 matrix 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).

Oligomers were synthesized in solution (methylene chloride) by combining 1,6-hexanediol-diisocyanate (HDDI) (aliphatic) with pentaerythritol tetra-3-mercaptopropionate (PETMP) or 1,3-bis(1-isocyanato-1-methylethyl)benzene (BDI) (aromatic) with trimethylol-tris-3-mercaptopropionate (TMP), at 1:2 isocyanate:thiol molar ratio, leaving pendant thiols. Triethylamine was used as a base in catalytic amounts. Oligomers were purified by precipitation in hexanes and rotavapouration, and then characterized by ¹H-NMR and mid-IR spectroscopy [18]. 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 [19]. Thio-urethane oligomers were added to the methacrylate organic matrix in proportions of 0 (control), 10, 20 and 30 parts per hundred resin, phr (which corresponds to 9.1 wt%, 16.7 wt% and 27.7 wt%, respectively).

Filler was introduced at 25 wt% (15% OX-50 – 0.04 μm; 85% 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.

One commercial light-cured cement (RelyX Veneer, 3M Espe, St. Paul, USA – lot N521803; Ref 7614A1, A1/light yellow shade) composed by BisGMA/TEGDMA and 66 wt% zirconia/silica filler was modified by addition of 10 phr and 20 phr of aromatic oligomer to the organic matrix (or 9.1 wt% and

Download English Version:

<https://daneshyari.com/en/article/1420682>

Download Persian Version:

<https://daneshyari.com/article/1420682>

[Daneshyari.com](https://daneshyari.com)