Impact of thio-urethane additive and filler type on light-transmission and depth of polymerization of dental composites

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ABSTRACT

Objective. This study evaluated the effects of filler type and the addition of thio-urethane oligomers on light-transmission, polymerization kinetics and depth of cure of resin composites.

Methods. BisGMA:UDMA:TEGMA (5:3:2 wt%) were mixed with 0 (control) or 20 wt% thio-urethane. Fillers with various sizes and refractive indices were included and refractive index (RI) measured. Unfilled resins were used as controls. The RIs of materials were measured before and after polymerization. The irradiance reaching the bottom of 3-mm thick specimens was measured during the polymerization. Degree of conversion to a depth of 5 mm was mapped. An optical bench was used to simultaneously follow conversion and light transmission.

Results. The addition of thio-urethane increased the RI for all composites. As expected, RI also increased with conversion for all materials. The one exception was for the material filled with OX-50, in which the RI of the composite decreased with conversion. In this case, the irradiance at the bottom of the 3 mm specimen was also the lowest among all groups. The addition of thio-urethanes had only minimal effect on light transmission within a filler type, but led to increased conversion in depth for all groups. The filler type itself had a greater effect on light transmission, and that correlated well with the degree of conversion.

Significance. The effect of the thio-urethane addition on degree of conversion in depth was dependent on filler type. The additive can be tailored to improve the RI match with the filler to optimize light transmission in dental composites.

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1. Introduction

The vast majority of posterior restorations is performed using direct resin composites, with an annual failure rate of around 2%, resulting in cumulative survival values of as high as 60% after 20 years follow-up [1]. The expansion in use of composites to restore posterior teeth is mainly due to a significant improvement in wear behavior and general mechanical properties, which allowed this material to be applied in high load bearing zones [2]. However, there are still many drawbacks that prevent composite restorations from surviving longer than an

average of 10 years [4], failing mainly due to secondary caries and fracture [1–4]. One drawback is the the polymerization stress that develops at the interface [5], as well as the comparatively lower fracture toughness of these materials in relation to metal- and ceramic-based restorations [6]. Importantly, the mechanical properties are directly correlated to the degree of conversion, which in turn depends on sufficient amount of light reaching all areas of the restoration [7,8]. For that reason, manufacturers recommend curing the composite in increments no thicker than 2 mm. An additional reason to place the composite in increments is to decrease the C-factor within each increment, which in theory would reduce polymerization stress [5]. This incremental requirement makes the placement of composite restorations extremely time-consuming, especially in large preparations, and is also the source of significant variation among clinicians.

Recently, the use of bulk-fill composites has increased among clinicians, with increments up to 4-mm being usually recommended, reportedly without compromise to the polymerization of composite or changes to the stress development compared with the traditional incremental technique [9,10]. Those materials are specially formulated with higher concentration of or more efficient photoinitiator systems, and/or with reduced filler content [11]. Previous studies have indeed demonstrated that the effectiveness of bulk-fill composites in promoting curing in depth is material-dependent [10]. For those materials, the changes in formulation do not include the monomer systems [for the most part], and the increased translucency is commonly achieved changing the filler size and/or pigments. Then, the influence of the refractive index mismatch between the lower RI organic and higher RI inorganic phases is not addressed. The greater the mismatch, the more light scattering takes place, and according to Monte Carlo theory, the lesser the light penetration through the depth of the material [12]. For several composites, this mismatch is more marked at the beginning of the polymerization reaction, and tends to decrease as conversion increases because the RI of the organic matrix increases as the process progresses [13]. One strategy, therefore, to minimize light scattering and consequently increase photon penetration depth is to have the refractive indices of both phases [organic and inorganic] be as close as possible at the beginning of the polymerization [14]. Since the refractive index of the filler is generally higher than the organic matrix, the use of compounds with higher refractive index in the organic matrix can be advocated. Some moieties, such as aromatic rings, urethane linkages and thiols, are known to increase the refractive index of organic compounds [15].

Thio-urethane oligomers, recently proposed as additives in resin composites, can be tailored to present several features that increase refractive index. These oligomers have been shown to produce networks with significantly improved fracture toughness and reduced polymerization stress, while at the same time achieving high conversion using the same procedures clinicians use to polymerize composites in practice [16–19]. The additional potential to minimize the mismatch with the inorganic filler phase in dental composites has not been investigated thus far. Therefore, this study proposes to investigate the influence of thio-urethane additives on the refractive index, polymerization kinetics, light transmission

and depth of cure of resin composites as a function of filler type. The null hypothesis is that the thio-urethanes will now affect any of these parameters.

2. Material and methods

2.1. Composite formulations

BisGMA (Bis-phenol A diglycidyl dimethacrylate), UDMA (urethane dimethacrylate), and TEGDMA (tri-ethylene glycol dimethacrylate), all from Esstech (Essington, PA, USA), were mixed in 50/30/20 wt% ratio. Thio-urethane oligomer was synthesized in solution (methylene chloride) by combining 1,3-bis(1-isocyanato-1-methylethyl) benzene with trimethylol-tris-3-mercaptopropionate, at 1:2 isocyanate:thiol molar ratio, leaving pendant thiols. The reaction was catalyzed by addition of Triethylamine and the thio-urethane was purified by precipitation in hexanes and rotaevaporation. The thio-urethane synthesized was added to the monomer mixture at a concentration of 20 wt% to produce the experimental matrix. No thio-urethane containing materials were used as the control. The photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) was added to 0.1 wt%, and 0.5 wt% of BHT (2,6-di-*tert*-butyl-4-methylphenol) was used as the inhibitor. Photoinitiator and inhibitor were obtained from SigmaAldrich (St. Louis, MO, USA). For each matrix, four composites were formulated varying the type of filler (Table 1), while neat resin was used as control. Fillers with average particle sizes of 0.05, 0.08 and 0.11 μm and refractive index of 1.54 (higher than the initial refractive index of the organic matrix) were added at 40 wt%. 0.05 μm average particle size colloidal silica (OX50), with refractive index of 1.45 (lower than the initial refractive index of the organic matrix) was added at 20 wt% due to excessive viscosity increase. This last material was only used for comparison with the neat resin in the statistical analysis.

2.2. Refractive index

The unpolymerized materials were placed over the horizontal main prism of an Abbe-type refractometer (Ningbo Gamry Optical Instrument Co., Shanghai, China) with refractive index scale ranging from 1300 to 1700, and precision of 0.0003. Polymer films were built between two polyester strips, photoactivated with a mercury arc lamp (Acticure 4000, Electro-Optical Engineering Inc., Montreal, Canada) for 5 min at 320 mW/cm^2 (320–500 nm). 1-Bromonaphthalene was used as a high refractive index interfacial contact agent to allow the refractive index reading of polymer films. Refractive index readings were obtained at room temperature at triplicate. For the isolated fillers, the refractive index values provided by the manufacturers were used.

2.3. Light-transmission through 3 mm specimens (measured with UV–vis spectrophotometer)

Unpolymerized materials were inserted into silicon molds (3.0 mm of diameter, 3.0 mm of depth) between two polyester strips and then, placed over the top surface sensor of a