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Investigation on the use of triphenyl bismuth as radiopacifier for (di)methacrylate dental adhesives

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ABSTRACT

In this study the suitability of using the organometallic compound triphenyl bismuth (TPB) as a radiopacifier for dental adhesive resins was investigated. A model photocurable (di)methacrylate co-monomer was loaded with 0 (control), 5%, 10%, 15%, 20%, or 30% mass fraction of TPB. Viscosity of the monomer was assessed using an oscillatory viscometer. Polymer radiopacity was investigated using a phosphor plate digital system. Other fundamental polymer properties evaluated were: translucency parameter by spectrophotometry, degree of C=C conversion by infrared spectroscopy, flexural strength/modulus and work-of-fracture in 3-point bending mode, water/ethanol sorption and solubility, and shear bond strength to dentin. Data were analyzed using one-way ANOVA (homoscedastic data) or ANOVA on Ranks (heteroscedastic data) followed by Student-Newman–Keuls' test (5%). The phenyl rings of TPB were identified by peaks in the 700–800-cm^{-1} infrared area. Incorporation of $\geq$ 20% of TPB affected the co-monomer viscosity. Linear increase in radiopacity was associated with the increase in TPB concentration, although no significant differences were detected between 20% and 30%. Addition of TPB did not affect monomer conversion or dentin bond strength. Flexural properties were generally lower for materials with $\geq$ 10% of TPB. Polymer translucency was affected by TPB incorporation above 10%. Ethanol/water sorption was lower in TPB-containing materials, while solubility was higher. TPB may be a suitable agent to render dental adhesives radiopaque, although methods to improve the polymer strength might be necessary.

1. Introduction

Dental adhesives are usually comprised of a solvated or non-solvated (di)methacrylate co-monomer that polymerizes under visible light irradiation. The structure of the co-polymer is inherently radiolucent due to the low density of the resin monomers, which consist of molecular structures containing light elements as carbon, hydrogen and oxygen. The radiolucency of dental adhesives is a significant clinical concern as it might lead to the formation of radiolucent areas under composite restorations [1,2]. These areas may be radiographically misinterpreted as a process of secondary caries development or presence of an unfilled area at the restorative interface, ultimately resulting in the unnecessary replacement of restorations [3].

Unlike resin composites and other biomedical materials, radiopacity of adhesives cannot be achieved by incorporation of insoluble heavy metal salts or glasses [4,5] because this approach would render the materials too viscous, interfering with their flowability, infiltration into tooth structures, and bonding performance. It has been reported that an organometallic compound, triphenyl bismuth (TPB, Fig. 1), may be a suitable radiopacifier for polymethyl methacrylate-based bone cements [6] without adversely affecting the polymerization kinetics and mechanical properties [7]. TPB is a whitish, odorless powder that is relatively hydrophobic and non-polar. Cytotoxicity tests have shown lower toxicity for TPB compared with methacrylates [8].

TPB could be considered an alternative radiopacifier to highly polar inorganic particles because it is miscible with many polymers, and also does not complex or deactivate the amine co-initiator used associated with the photosensitizer camphorquinone [9–11]. Therefore, the aim of this study was to investigate the suitability of using TPB as radiopacifier for a model (di)methacrylate-based dental adhesive resin. The hypothesis tested was that TPB would provide radiopacity without interfering with other material properties.

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2. Materials and methods

2.1. Preparation of the model adhesive co-monomer

A model co-monomer was formulated based on a 2:1:1 mass ratio of the monomers 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane (Bis-GMA—Evonik, Essen, Germany), triethyleneglycol dimethacrylate (Esstech Inc., Essington, PA, USA), and 2-hydroxyethyl methacrylate (Sigma-Aldrich, St. Louis, MO, USA). To render the co-monomer photocurable, 1 mol% of the photosensitizer camphorquinone (Esstech) and 2 mol% of the co-initiator ethyl 4-dimethylamino benzoate (Sigma-Aldrich) were incorporated. TPB powder was added at mass fractions of 0 (control), 5%, 10%, 15%, 20%, or 30%. The temperature of the co-monomer was elevated to 60 °C and TPB incorporated by sonication and manual mixing. Fourier transform infrared (FTIR) spectra of the control and TPB-modified (di)methacrylate co-monomers are shown in Fig. 2. All photoactivation procedures were carried out using a light-emitting diode curing unit (Radii; SDI, Bayswater, Victoria, Australia) with an irradiance of 800 mW/cm².

2.2. Monomer viscosity

Viscosity measurements of the uncured materials were performed using an oscillatory digital viscometer (LVDV-II+Pro; Brookfield, Middleboro, MA, USA). A standard 10 mL volume of each material was dispensed in the equipment operating under the following settings: temperature of 25 °C, speed of 50 rpm, shear rate of 66 Hz, and run time of 60 s. Four specimens were tested for each material.

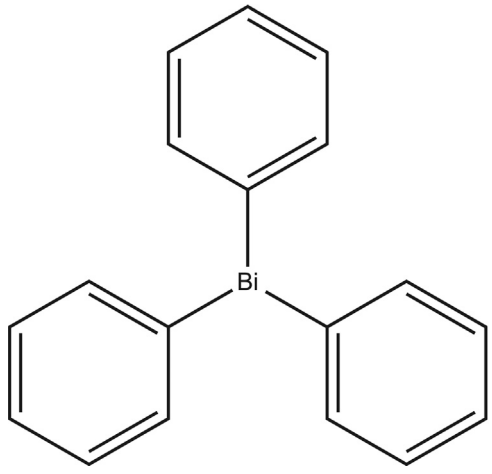

Fig. 1. Molecular structure of the radiopacity additive triphenyl bismuth (MW=440.29).

2.3. Radiopacity

Radiographic images of five cylindrical specimens (diameter 7 mm, thickness 1 mm) per adhesive were obtained with a phosphor plate digital system (VistaScan; Dürr, Bietigheim-Bissingen, Germany) operating at 70 kV and 8 mA, using 0.2-s exposure time and 400-mm focus-film distance. An aluminum step-wedge was exposed simultaneously. The gray levels (pixel density) of the digital images were analyzed, and aluminum equivalence values (mm) of each specimen were recorded [12]. Five additional specimens were obtained for two well-known commercial references of dental adhesives: the bonding resin of Scotchbond Multi-Purpose (SBMP—3M ESPE, St. Paul, MN, USA) and Clearfil SE Bond (CSEB—Kuraray, Osaka, Japan).

2.4. Translucency parameter (TP)

The TP values of five cylindrical specimens (diameter 7 mm, thickness 1 mm) were measured. Polyester strips were used to produce smoothness, both at top and bottom surfaces. The CIEL*a^*b^* color parameters were measured 24 h after polymerization, over white ($L^*=93.07$, $a^*=-1.28$, $b^*=5.25$) and black ($L^*=27.94$, $a^*=-0.01$, $b^*=0.03$) Munsell-like neutral value scale sheet backgrounds (AG-5330; BYK-Chemie, Wesel, Germany) using a spectrophotometer (SP60; X-Rite Inc., Grand Rapids, MI, USA). The translucency parameter (TP) for each specimen was calculated using the formula: $TP=[(L^*_W-L^*_B)^2+(a^*_W-a^*_B)^2+(b^*_W-b^*_B)^2]^{1/2}$, where L^*_W, a^*_W and b^*_W and L^*_B, a^*_B and b^*_B were measured over the white and black backgrounds, respectively.

2.5. Degree of C=C conversion (DC) by FTIR

The DC of the adhesives ($n=5$) was evaluated using real-time FTIR spectroscopy (Prestige21; Shimadzu, Tokyo, Japan) with an attenuated total reflectance (ATR) device. A drop of each material was placed in the ATR cell and a preliminary reading for the uncured material (monomer) was taken, using 24 scans co-addition and 4-cm^{-1} resolution. The adhesive was photoactivated for 40 s and

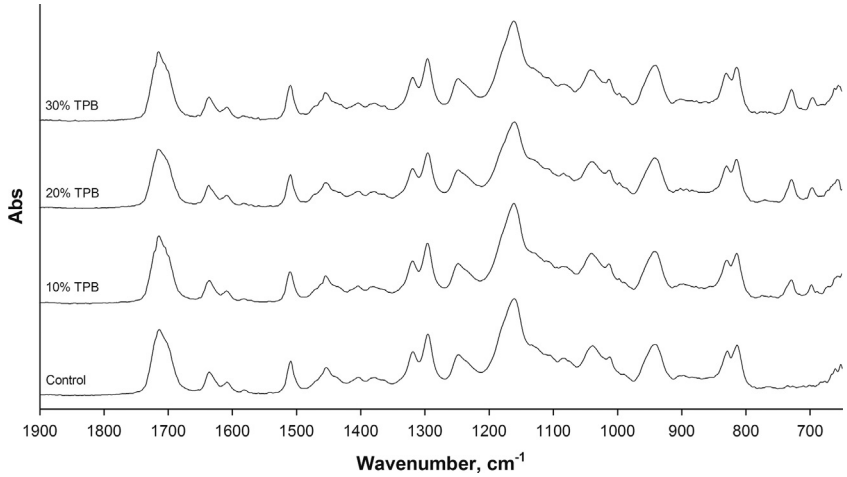

Fig. 2. FTIR spectra of the control and materials loaded with 10%, 20%, and 30% of TPB (24 scans co-addition, 4-cm^{-1} resolution). The spectra were shifted for clarity. The phenyl rings of TPB are identified by the sharp peaks in the region of 700 cm^{-1} to 800 cm^{-1}, with no other appreciable spectral differences.