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Evaporation of low-volatility components in polymeric dental resins

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ABSTRACT

Objectives. This study provides measurement of the volatility of selected photoinitiators and monomers used in dental adhesive resins. A detailed determination of the spatial and temporal character of camphorquinone (CQ) volatilization with respect to air flow conditions as well as media viscosity is assessed to gauge the effect of evaporative loss on the photopolymerization process and the photopolymers formed.

Methods. Vapor pressures of materials are measured by thermogravimetric analysis. A quantitative model assuming one-dimensional Fickian diffusion with surface evaporation is presented and compared with measured photoinitiator volatilization from viscous and non-viscous resin samples, obtained by spectrophotometry and confocal microscopy. Model resins are prepared and subject to airthinning followed by photocuring, monitored in real-time by Fourier transform infrared spectrometry.

Results. Vapor pressure measurements of the individual components of the adhesive resin span nearly four orders of magnitude, with the photoinitiator CQ near the middle (0.6 Pa) and the monomer HEMA at the upper end (10 Pa). We see depth-averaged CQ loss from non-viscous open films, while depthresolved measurements of viscous droplets show strong surface-localized CQ depletion. Good agreement is observed between measurements and the model. Finally, air-thinning of samples prepared with more-volatile photoinitiator and monomer is shown to cause longer induction times, slower early-stage polymerization rates and lower late-stage degree of conversion.

Significance. Widely used compounds with vapor pressures as low as 0.6 Pa (0.001 Torr) undergo significant volatilization from samples ventilated under conditions generally representative to clinically used air-thinning procedures, with the potential to adversely affect the photopolymerization of both viscous and non-viscous resins. The inverse relationship between air-thinning and adhesive bond strength, observed elsewhere, may be partially caused by this same effect.

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1. Introduction

Apart from polymerizable solvated adhesives and coatings for which solvents are meant to evaporate from solution after application to the target surface, the remaining, less-volatile components to coatings and adhesives are often assumed to evaporate so slowly that their volatility is essentially zero or at least negligible. This assumption is justifiable in many instances and applications. However, for situations involving thin films or highly ventilated environments or both, additional study is required to measure the potential for and effects of volatilization of the primary formulation components. Azeotropes aside, the formulation will change as some components volatilize more quickly than others and thus alter the formulation composition and properties.

While pursuing other research [1,2], the authors determined that camphorquinone (CQ), a visible-light photoinitiator widely used in dental materials [3], was preferentially being depleted from thin-films during the course of experiments. Although measurable photoinitiator volatility is not unknown [4], no mention of CQ volatility could be found in the literature (apart from mention of purification by vacuum sublimation [5]), and the questions arose of whether CQ evaporation could significantly affect the performance of dental materials and how the CQ volatilization rate compares to that of other compounds.

Active air thinning is used extensively in the application of dental adhesive systems. Solvents are included in dental adhesives to control initial viscosity, displace water and promote infiltration into demineralized dentin and to moderate the moisture-induced phase separation potential between the relatively hydrophilic and hydrophobic comonomers typically combined in these formulations [6]. In addition to solvent reduction, air thinning also aids placement of uniform adhesive layers. Although complete solvent elimination is not practically achievable under the constraints imposed in clinical dentistry, it is essential to minimize residual solvent in the adhesive at the time of polymerization to avoid reduced performance due to dilution of the monomers, which slows the rate of polymerization and decreases the resulting polymer network density [7,8]. Residual solvent during polymerization of the adhesive layer has the potential to affect both initial and long-term dentin bond strength and integrity. There are many conflicting reports regarding the effect of air thinning on the performance of the dental adhesives. Small amounts of air-drying are reported to increase bond strength while extended air-drying has been reported to actually decrease the bond strength, possibly due to thinning of the adhesive layer that also leads to increased oxygen inhibition and subsequent lowering of monomer conversion [9,10]. The intensity of application of the adhesive, the number of coats applied and also temperature and speed of the air can also result in significant differences in bonding properties. While these already constitute a large number of factors that affect the bond strength in dental adhesive applications, our results suggest that evaporation of the initiator from the formulation is another important factor that has been overlooked.

This paper seeks to answer the questions related to volatility by quantifying the vapor pressures of selected compounds other than solvents that are commonly found in dental resins, and by exploring via experiment and theory the characteristics and effects of volatilization from polymeric resins.

2. Materials and methods

2.1. Materials

Triethylene glycol dimethacrylate (TEGDMA), bisphenol A glycerolate dimethacrylate (BisGMA), 2-hydroxyethyl methacrylate (HEMA), camphorquinine (CQ), ethyl N,N-dimethylaminobenzoate (EDAB), camphor and dibutyl phthalate DBP were all obtained from Sigma-Aldrich. Urethane dimethacrylate (UDMA) was obtained from Esstech and 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TPO) was obtained from BASF. All materials were used without further purification unless otherwise noted.

2.2. Thermogravimetic analysis

A thermogravimetric analyzer (TGA; Perkin-Elmer Pyris 1) was used with 50 mg platinum sample pans, under a constant nitrogen purge flowrate of 20 mL min^{-1}. Evaporation rates were determined by holding each individual component sample at a series of constant temperatures for an interval of 5 to 10 min after temperature stabilization had occurred. Before data collection, moisture was removed by holding the samples under nitrogen at an elevated temperature for approximately 20 min, or until the evaporation rate became completely linear. Sample pans were washed thoroughly and sonicated before use, and were filled with only enough sample material to completely cover the floor of the pan (typically ~10 mg).

Vapor pressure is determined by a method that follows the work of Price [11] and others (see, for example [4,12–17]). Mass loss rate is given as

$$\frac{-\mathrm{d}m}{\mathrm{d}t} = p\alpha\sqrt{\frac{M}{2\pi RT}}, \tag{1}$$

where p is pressure (Pa), α is the vaporization coefficient, M is molar mass (Da), R is the ideal gas constant (m^3 Pa K^{-1} mol^{-1}) and T is temperature (K). For convenience, we write this as

$$p = kv, \tag{2}$$

where $k = \sqrt{2\pi R}/\alpha$ and $v = \mathrm{d}m/\mathrm{d}t\sqrt{T/M}$. For a given setup, k may be experimentally determined so that mass loss rate, temperature and molecular weight can be converted to a vapor pressure p. As in [12], we use glycerol as a reference material using vapor pressure data from [18] to obtain the linear best-fit of log(p) vs. log(v) (R^2 = 0.998).

2.3. Low-speed forced convection

For low viscosity standing droplet tests, resin was prepared by adding 0.4 wt% camphorquinone (CQ) into triethylene glycol dimethacrylate (TEGDMA). When the CQ was fully dissolved, 0.6 g of the resin was spread evenly over a 76 × 50 mm microscope slide. The slides had been previously cleaned in Nano