New insight into the "depth of cure" of dimethacrylate-based dental composites

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ABSTRACT

Objectives. To demonstrate that determination of the depth of cure of resin-based composites needs to take into account the depth at which the transition between glassy and rubbery states of the resin matrix occurs.

Methods. A commercially available nano-hybrid composite (Grandio) in a thick layer was light cured from one side for 10 or 40 s. Samples were analyzed by Vickers indentation, Raman spectroscopy, atomic force microscopy, electron paramagnetic imaging and differential scanning calorimetry to measure the evolution of the following properties with depth: microhardness, degree of conversion, elastic modulus of the resin matrix, trapped free radical concentration and glass transition temperature. These measurements were compared to the composite thickness remaining after scraping off the uncured, soft composite.

Results. There was a progressive decrease in the degree of conversion and microhardness with depth as both properties still exhibited 80% of their upper surface values at 4 and 3.8 mm, respectively, for 10 s samples, and 5.6 and 4.8 mm, respectively, for 40 s samples. In contrast, there was a rapid decrease in elastic modulus at around 2.4 mm for the 10 s samples and 3.0 mm for the 40 s samples. A similar decrease was observed for concentrations of propagating radicals at 2 mm, but not for concentrations of allylic radicals, which decreased progressively. Whereas the upper composite layers presented a glass transition temperature – for 10 s, 55 °C (±4) at 1 mm, 56.3 °C (±2.3) at 2 mm; for 40 s, 62.3 °C (±0.6) at 1 mm, 62 °C (±1) at 2 mm, 62 °C (±1.7) at 3 mm – the deeper layers did not display any glass transition. The thickness remaining after scraping off the soft composite was 7.01 (±0.07 mm) for 10 s samples and 9.48 (±0.22 mm) for 40 s samples.

Significance. Appropriate methods show that the organic matrix of resin-based composite shifts from a glassy to a gel state at a certain depth. Hence, we propose a new definition for the "depth of cure" as the depth at which the resin matrix switches from a glassy to a rubbery state. Properties currently used to evaluate depth of cure (microhardness, degree of conversion or scraping methods) fail to detect this transition, which results in overestimation of the depth of cure.

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1. Introduction

Photopolymerizable resin-based composites (RBC) have improved considerably since they were introduced, and are currently accepted as reliable materials for direct anterior and posterior dental restoration. Their use has now been extended to large and deep cavities [1], which require the build-up of RBC restorations in successive layers, first because of the limited cure depth [2] and second to reduce the consequences of shrinkage stress [3]. Knowledge of the maximum thickness for each layer is crucial for the clinician. Use of excessively thick layers can result in insufficient cure of the RBC at depth, leading to reduced mechanical properties and biocompatibility. The "depth of cure" (DOC) – usually referring to the thickness of a RBC that is "adequately" cured – is limited by light absorption and scatter within the material, which are influenced by numerous factors, including the amount, size and type of fillers [2,4], RBC shade [5–7], photoinitiator type and concentration [8,9], refractive index mismatch [2], light irradiation source and irradiation duration [10].

Several methods have been used to assess the DOC. A simplistic method has been described in the ISO 4049 standard and is based on measurement with a micrometer of the thickness of the RBC that remains after removal of uncured soft material with a plastic spatula [11]. Other groups have used a penetrometer to measure the DOC based on application of a needle with a constant force to the lower side of the RBC sample [7,9,12]. Alternative methods include measurement of the degree of conversion (DC) – by Raman or FTIR spectroscopy [13] – or of the microhardness (MH) [5,14] at regular intervals through the depth of the material. Based on these measurements, the DOC is usually described as the depth at which the MH or DC value equals the surface value multiplied by an arbitrary ratio, usually 0.8 [5,15].

Several factors suggest, however, that these methods might not be appropriate to measure the quality of cure of a RBC at depth. When considering the DC at depth, it is difficult to determine which DC corresponds to "adequate" polymerization. In fact, the DC value on its own is insufficient, as it does not provide any information on the state of network development, i.e., the degree of cross-linking. The highly crosslinked nature of dimethacrylate-based polymers is responsible for a non-linear polymerization process, marked by two macroscopic changes of state: first, gelation, which refers to the change from a viscous liquid to an elastic gel (infinite network) occurring at a relatively low DC (<10%) – the "gel point"; second, vitrification, which refers to the transformation from the rubbery material to a glassy one, accompanied by a considerable increase in elastic modulus (3–4 orders of magnitude) [16]. The DC and the degree of cross-linking determine when the polymer network changes from a liquid to a gel, and then from a rubbery to a glassy state. These two transitions have been very well described by real-time measurement of DC in thin samples (<2 mm): as DC and crosslinking increase with irradiation time, the liquid resin transforms into a gel and then into a glassy material [17].

Given the logarithmic decrease in light transmittance at depth (only 25% overall transmittance at 1 mm depth, 12% at 2 mm and 7% at 3 mm) [18], RBC conversion and/or crosslinking decreases with depth. Hence, similar to what is observed in real-time polymerization experiments, it is conceivable that at a certain depth, the resin would first change from a glassy to a rubbery state, then from a rubbery to a liquid state. The transition between gel and liquid is relatively obvious, as a RBC with a liquid resin matrix is soft and can easily be scraped away. However, the theoretically sharp transition between rubbery and glassy polymer has to our knowledge never been described, possibly because the methods used so far have not been able to measure this event. The size of the micro-indenter, of the penetrometer tip and *a fortiori* of the plastic spatula are indeed disproportionate compared to what needs to be measured. In this regard, it must be remembered that the quality of polymerization concerns only the resin phase of the material, which represents 30–40 vol% of the material for the most highly filled RBCs. Hence, most of the material is composed of fillers, which are tightly packed, leaving very little space for the resin between them. As an example, the width of the indentation left by a Vickers indenter in a dental RBC is around 60 μm, which is considerably larger than the distance between two neighboring fillers that the resin occupies, i.e., less than 1 μm based on scanning electron microscopy (SEM) images [19]. This simple comparison highlights the difficulty in assessing the properties of the resin using hardness, penetrometer and scraping measurements, and suggests that other methods, which can limit any interference of the fillers in the results, should be used.

The working hypothesis of the present study was, therefore, that determination of the DOC of a RBC needs to take into account the depth at which transition between the glassy and rubbery states of the resin matrix occurs. Specific techniques were used to highlight this transition, i.e., atomic force microscopy (AFM) to measure the elastic modulus of the resin between the fillers (E-Mod, MPa), electron paramagnetic resonance (EPR) imaging to determine the trapped radical concentration ($R^\bullet$, a.u.) at each depth, and differential scanning calorimetry (DSC) to determine the glass transition temperature (T_g, °C) at different depths. These results were compared to classical methods, i.e., Vickers MH, DC by Raman spectroscopy, and a "scraping" test similar to the ISO 4049 standard.

2. Materials and methods

A highly filled nano-hybrid RBC, Grandio (Voco, Cuxhaven, Germany) of shade A3 (batch #0952138, ref 1812) was chosen for all experiments. For AFM, EPR imaging, Raman spectroscopy and Vickers MH measurements, the RBC was packed into a rectangular Teflon mold of 3 mm × 3 mm aperture and 6 mm depth, covered by a polyester film and irradiated from one side. For the "scraping" tests, a similar Teflon mold was used but 10 mm deep, similar to the ISO 4049 specifications [11]. For DSC measurements, 6 cylindrical Teflon molds (1 mm depth and 3 mm diameter) were successively filled and superposed on each other, a polyester film separating each mold from its neighbor. Regardless of the mold, the light tip of the LED light BluePhase G2 (Ivoclar-Vivadent, Schaan, Liechtenstein) was then placed against the upper surface film and polymerization was initiated using the low radiation mode (650 mW/cm²) for either 10 or 40 s. In the instructions for