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Polymerization kinetics and impact of post polymerization on the Degree of Conversion of bulk-fill resin-composite at clinically relevant depth

Khold Al-Ahdal[a,b], *Nicoleta Ilie*[c,*], *Nick Silikas*[a], *David C. Watts*[a,d]

[a] *Biomaterials Science Research Group, School of Dentistry, University of Manchester, UK*
[b] *College of Dentistry, King Saud University, Riyadh, Saudi Arabia*
[c] *Ludwig-Maximilians-University of Munich, Germany*
[d] *Photon Science Institute, University of Manchester, UK*

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ABSTRACT

Objective. Since bulk-fill (BF) resin composites should cure efficiently to a depth up to 4 mm, the aim of the study was to determine the time-dependence of degree of conversion (DC) at that depth during 24 h post-irradiation.

Methods. Eight representative BF resin composites were studied [x-tra base (XTB), Venus Bulk Fill (VBF), Tetric EvoCeram Bulk Fill (TECBF), Sonic Fill (SF), Filtek Bulk Fill (FBF), everX Posterior (eXP), Beautifil-Bulk Flowable (BBF), Beautifil-Bulk Restorative (BBR)]. Specimens were fabricated in white Delrin moulds of 4 mm height and 5 mm internal diameter directly on an attenuated total reflectance (ATR) accessory attachment of an (FTIR) spectrometer (Nicolet iS50, Thermo Fisher, Madison, USA). Upper specimen surfaces were irradiated *in situ* for 20 s with an LED curing unit (Elipar S10 with average tip irradiance of 1200 mW/cm^2). Spectra from the lower surface were recorded continuously in real-time for 5 min and then at 30 and 60 min and 24 h post irradiation.

Results. Mean ranges of DC_{4mm} (%) of the materials at 4 mm depth were 39–67; 48–75; 45–74; and 50–72 at 5, 30 and 60 min and 24 h respectively. DCs for XTB, VBF, TECBF, FBF, BBR increased significantly 30 min after irradiation ($p < 0.05$) and were not affected by subsequent time up to 24 h ($p > 0.05$). DC for SF was not affected by subsequent time after 5 min ($p > 0.05$). For eXP and BBF, DC increased 24 h after irradiation ($p < 0.05$). The data were described by the superposition of two exponential functions characterising the gel phase (described by parameters a, b) and the glass phase (described by parameters c and d).

Significance. Post polymerization impact of bulk-fill composites is material dependent. Five materials exhibited their maximum DC_{4mm} already 30 min after starting the irradiation while DC_{4mm} for two materials optimized after 24 h. BF materials were found to exhibit after 24 h a DC between 50 and 72% at 4 mm depth under the stated irradiation conditions.

* *Corresponding author at*: Department of Operative Dentistry and Periodontology Ludwig-Maximilians-University Munich, Germany.
E-mail address: nilie@dent-med.uni-muenchen.de (N. Ilie).

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1. Introduction

The adequate conversion of resin composite materials is essential in determining their mechanical performance. Ideally, during the polymerization reaction all the monomer in the resin composite material would have been converted to polymer. However, dimethacrylate monomers exhibit residual double carbon bonds in the final material, with the Degree of Conversion (DC) ranging from 55 to 75% [1–3]. An ideal resin composite should exhibit a high degree of conversion (DC) and only a minimal polymerization shrinkage [4].

There are many factors that can affect the final degree of conversion: these include intrinsic factors such as the chemical structure and composition of the dimethacrylate monomer and the concentration of the photo-initiator. The DC is also affected by extrinsic factors such as the polymerization temperature [5,6].

Resin composites are conventionally applied in increments of 2 mm thickness [6,7]. However, this is time consuming, especially when applied in deep posterior cavities. Therefore, a new category of resin composite termed "bulk-fill" has been introduced which can be cured in 4 mm thick increments. Compositional modifications have been made to allow such bulk placement that may also change the polymerization kinetics.

Dental resin composites are mostly based on dimethacrylate resins; where the polymerization process is usually activated by applying visible light [8,9]. This free-radical polymerization process is fast in the early stages where the monomer molecules are mobile and able to reach the reactive sites easily. However, the polymerization rate decreases afterwards as the degree of conversion increases and hinders the mobility of monomer molecules to reach the reactive sites [10]. The majority of the polymerization process occurs during the first few minutes after irradiation [6].

Bulk fill composites are receiving attention mainly because they can be placed in 4 mm increments without adverse effects on polymerization shrinkage, cavity adaptation or the degree of conversion (DC) [11]. Additionally their polymerization shrinkage may be lower than conventional composites, so that post-operative problems of gap formation and subsequent caries recurrence may be reduced [12]. A comparison between Surefil® SDR™ flow and Venus® bulk fill showed that Surefil® SDR™ flow exhibited higher mechanical properties despite lower DC values than Venus® bulk fill [11].

Some studies have established and compared the degree of conversion of conventional resin composites and bulk-fill resin composites. Previous research [13] has shown that the surface DC values of bulk-fill resin composites are comparable to those of conventional resin composites and that there is difference in DC between 5 min and 24 h. However, this was done on thin films rather than with 4 mm thick specimens. Li et al. [14] compared the DC of bulk-fill and conventional composites and showed that Filtek Bulk Fill Flowable and everX Posterior showed the highest DC followed by SDR then Tetric EvoCeram Bulk Fill and Herculite XRV Ultra.

The precise nature of the initial photo-cure of resin-composites has an essential role in the post-cure polymerization process. The polymerization reaction starts rapidly after applying the irradiation source, which causes internal mobility restrictions within the growing polymer matrix network, which in turn causes reduction in the polymerization rate [15]. Consequently, the free radicals have reduced movement within the matrix and so the polymerization continues at a slower rate [16].

Some studies reported that the post-cure polymerization continues up to or beyond 24 h after irradiation [17,18]. As long as there are free radicals and reactants, the polymerization process will continue but as the quantity of the free radicals decreases, the polymerization rate decreases. Moreover, post-cure polymerization has been detected up to 1 month after irradiation [19].

Optimum clinical properties of dental composites are significantly affected by their composition. However, properties also depend upon the effective polymerization of the material during, and following, clinical placement. The degree of conversion (DC) of resin composite materials is a key measure of effective polymerization and crosslinking of the multifunctional monomers that are used to create the matrix. Good conversion is thus essential to their long-term functionality [2,20,21] and inadequate DC can be detrimental to the success of dental restorations. Thus several factors affect the DC of resin composites when applied clinically. These include operator-related factors, such as thickness of each layer, irradiance of the light curing unit, and proximity of light curing tip to the restoration [22–24].

The DC is nevertheless influenced by composite formulation, as determined by the manufacturer, through the type of resin-matrix, filler type, size and loading [25–27].

Since 'bulk fill' (BF) resin composites are generally claimed to be suitable for placement in increments of up to 4 mm, it is useful to denote 'the degree of conversion measured at 4 mm' as DC_{4mm}. Measuring this particular parameter was the focus of this investigation.

The aim of this study was to assess and compare the degree of conversion (DC_{4mm}) of some bulk-fill resin composite materials using real time Fourier transform infrared spectroscopy (FTIR) up to 30 min, 60 min and 24 h post cure. Our null hypothesis was that for each composite there is no difference between degree of conversion (DC_{4mm}) at 5 min, 30 min, 60 min and 24 h post cure.

2. Materials and methods

Eight bulk fill resin composites were investigated (Table 1). The DC measurements were conducted using a Fourier transform infrared spectroscopy (FTIR) with an attenuated total reflectance (ATR) accessory (Nicolet iS50, Thermo Fisher, Madison, USA).

2.1. *Real time measurement.*

The un-polymerized composite pastes ($n = 6$) were placed directly on the diamond ATR crystal in molds of 4 mm height and 3 mm internal diameter, filled in one increment. The specimens were covered with plastic matrix strips (Frasaco, Tettnang, Germany) and the light curing unit (LCU), with measured average tip irradiance of 1200 mW/cm^2, was applied