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## Bulk-fill resin composites: Polymerization properties and extended light curing

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### ABSTRACT

**Objectives.** The aim was to evaluate the polymerization properties of bulk-fill resin composites using two different light-curing protocols, in terms of degree of conversion (%DC), Vickers hardness (HV), polymerization volume shrinkage (PVS) and polymerization shrinkage stress (PSS) and compare them to conventional condensable and flowable resin composites.

**Materials and methods.** Filtek BulkFill (FBF, 3MESPE, Germany), SDR (Dentsply, Germany), TetricEvoCeram BulkFill (TBF, Ivoclar-Vivadent, Liechtenstein), Venus BulkFill (VBF, Heraeus, Germany), X-traBase (XTB, Voco, Germany), FiltekZ250 (3MESPE) and Filtek Supreme XTE Flowable (FSF, 3MESPE) were investigated. Light-curing was performed for 30 s or according to manufacturers' instructions (1200 mW/cm<sup>2</sup>, Bluephase20i, Ivoclar-Vivadent). For %DC and HV, discs ( $n = 5$ ) of 2 or 4 mm in thickness were prepared and stored for 24 h in distilled water at 37 °C. %DC was determined by FTIR-ATR-spectroscopy. %DC and HV were measured at the top and bottom of the specimens. PVS was measured using Archimedes method ( $n = 6$ ). PSS measurements ( $n = 10$ ) were carried out using 5 mm diameter PMMA rods as bonding substrates with a specimen height of 1 mm in a universal testing machine. Data were analyzed using one- and two-way ANOVA ( $\alpha = 0.05$ ).

**Results.** Except Z250 in the manufacturers' light-curing mode, all materials showed no significant inferior %DC at 4 mm thickness. When light cured for 30 s Z250 had no significant differences in %DC at 2 or 4 mm when compared to top. FBF, TBF, FSF and Z250 displayed significant reduced HV at 4 mm in both curing modes. Z250 and TBF showed the lowest PVS and FSF the highest PSS in both curing modes.

**Significance.** All investigated bulk-fill composites obtained sufficient polymerization properties at 4 mm depth. Enhanced curing time improved the investigated polymerization properties of bulk-fills and Z250.

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## 1. Introduction

One major goal in research and development of resin-based composites (RBCs) is to enhance their clinical longevity and ease of use. Since their introduction in dentistry RBCs have undergone many improvements in filler [1], matrix [2] and initiator technology [3]. This evolution led to contemporary RBCs showing clinical success rates comparable [4] or higher than those of amalgam [5]. Still one of the main reasons for restoration loss, along with fracture due to mechanical fatigue degradation [6], is secondary caries [7].

One of the shortcomings of RBCs is polymerization volume shrinkage due to radical polymerization. The resulting polymerization shrinkage stress [8] is transmitted to the bonding interface and to the remaining dental tissue causing cuspal deflection [9], enamel cracks, marginal breakdown, gap formation and microleakage [10]. This may ultimately lead to secondary caries and restoration loss. Although clinical evidence of the association between shrinkage stress and in situ failure might be difficult to collect [11], in vitro results show the need of developing strategies reducing shrinkage stress of RBCs [12].

Some practical strategies include alternative light curing protocols [13], the use of flowable cavity liners [14] and incremental filling techniques [15]. As RBCs shrink toward the bonded surfaces during light curing [12], stress relief can be achieved by flow of material in the pre-gel state from free surfaces into the bulk. The ratio of bonded to free surfaces (c-factor) is minimized by reducing the contact area between resin and cavity walls, as advocated in the incremental filling technique [16]. For the clinical procedure, multiple small increments generally mean increased operational time and are difficult to place in small cavities.

Beside the shortcomings related to polymerization volume shrinkage and stress build up in RBCs, the degree of conversion is another limiting factor when placing restorations. It has been shown that an increment thickness of 2 mm should not be exceeded for RBCs with conventional chemistry [17]. When placing restorations with RBCs in cavities deeper than 2 mm, proper cure may only be assured for incremental build-up techniques [17]. Sufficient curing of RBCs is crucial to achieve appropriate physical and mechanical properties [18], wear resistance [19] and biocompatibility [20].

In order to overcome the time consuming incremental cavity filling technique with conventional RBCs, bulk-fill RBCs have been developed. This newly developed kind of RBCs claim to allow the use of material increments up to 4 mm in thickness with low volumetric polymerization shrinkage and resulting low polymerization shrinkage stress [21–24]. Therefore matrix and initiator chemistry as well as filler technology were optimized. The aims of this study were to evaluate degree of conversion (%DC), Vickers hardness (HV), polymerization volume shrinkage (PVS) and polymerization shrinkage stress (PSS) of bulk-fill RBCs and compare these parameters to those of conventional RBCs.

The null hypotheses were: (i) increment thickness has no significant influence on degree of conversion (%DC) or Vickers hardness (HV) of bulk-fill resin composites and conventional resin composites; (ii) bulk-fill resin composites show

no significant lower polymerization shrinkage stress (PSS) and volumetric polymerization shrinkage (PVS) compared to conventional composite resins; and (iii) increased light curing time, compared to manufacturers' instructions, has no significant influence on the evaluated polymerization parameters.

## 2. Materials and methods

### 2.1. Materials used

Five commercially available bulk-fill composites Filtek Bulk Fill Restorative (A2, 3M ESPE, Seefeld, Germany), SDR Surefil (Uni, Dentsply, Konstanz, Germany), Tetric EvoCeram Bulk Fill (IVA, Ivoclar Vivadent, Schaan, Liechtenstein), Venus Bulk Fill (Uni, Heraeus, Hanau, Germany) and X-tra Base (A2, VOCO, Cuxhaven, Germany), a conventional flowable composite Filtek Supreme XTE Flow (A2, 3M ESPE, Seefeld, Germany) and a condensable composite Z250 (A2, 3M ESPE, Seefeld, Germany) were the materials under investigation (Table 1).

### 2.2. Specimen preparation

From each composite, uncured material was inserted into cylindrical stainless steel molds of 8 mm in diameter and 2 mm ( $n=10$ ) or 4 mm ( $n=10$ ) in thickness. To prevent oxygen inhibition, a transparent mylar strip was placed on top and bottom of the mold. Per specimen thickness, half of the specimens ( $n=5$ ) were light-cured from the top as specified by the manufacturer (Table 1), whereas the other half ( $n=5$ ) for an extended light-curing time of 30 s, both with a LED curing unit (1200 mW/cm<sup>2</sup>, Bluephase 20i, Ivoclar Vivadent, Schaan, Liechtenstein). All specimens were polished under profuse water cooling with silicon carbide abrasive paper (4000 Grit) for mirror gloss on top and bottom surfaces. This was performed to create a smooth surface for accurate Fourier transform infrared spectroscopy (FTIR) measurement. All specimens were stored for 24 h in distilled water at 37 °C prior to %DC and HV measurements.

### 2.3. Degree of conversion (%DC)

For each material FTIR spectroscopy (Nicolet 420 FT-IR Spectrometer, Thermo Fischer, Waltham) with attenuated total reflectance method (ATR, DuraSamplIR II, SensiIR Technologies, Danbury, USA) was performed to assess %DC. Absorption spectra on the top (0 mm) and bottom (2 mm or 4 mm) of each specimen ( $n=5$ ), as well as for the uncured material, were measured with 64 scans at a resolution of 4 cm<sup>-1</sup> within a wavelength spectrum of 4000–650 cm<sup>-1</sup>. Peak heights at 1637 cm<sup>-1</sup> (aliphatic carbon double bonds) and 1608 cm<sup>-1</sup> (aromatic carbon double bonds) were measured using the baseline method with the software Origin 8.6 (Origin Lab Corporation, Northampton, USA). The %DC was calculated by the reduction of absorbance at 1637 cm<sup>-1</sup> between uncured and cured material using the equation:

$$\%DC = \left[ 1 - \frac{\left( \frac{1637 \text{ cm}^{-1}}{1608 \text{ cm}^{-1}} \right) \text{ Peak height cured}}{\left( \frac{1637 \text{ cm}^{-1}}{1608 \text{ cm}^{-1}} \right) \text{ Peak height uncured}} \right] \times 100$$

**Table 1 – Materials under investigation (information as disclosed by the manufacturers).**

Code	Material	Manufacturer batch no.	Shade	Photoinitiators/ coinitiators	Monomers	Fillers	Manufacturers' curing time
FBF	Filtek Bulk Fill Flowable Restorative	3M ESPE N428456	A2	n.a.	<ul style="list-style-type: none"> <li>• UDMA 10–20 wt%</li> <li>• Substituted dimethacrylate 10–20 wt%</li> <li>• BisEMA-6 1–10 wt%</li> <li>• BisGMA 1–10 wt%</li> <li>• TEGDMA &lt;1 wt%</li> </ul>	<ul style="list-style-type: none"> <li>• Silane treated ceramic 50–60 wt%</li> <li>• YbF<sub>3</sub> 1–10 wt%</li> <li>• 42.5 vol%</li> </ul>	20 s
SDR	SDR Surefil	Dentsply 6251	Uni	n.a.	<ul style="list-style-type: none"> <li>• Modified UDMA</li> <li>• Dimethacrylate</li> <li>• Difunctional diluents</li> </ul>	<ul style="list-style-type: none"> <li>• Barium and strontium alumino-fluoro-silicate glasses 68 wt%</li> <li>• 44 vol%</li> </ul>	20 s
TBF	Tetric Evo Ceram Bulk Fill	Ivoclar Vivadent R72542	IVA	<ul style="list-style-type: none"> <li>• Acyl phosphine oxide</li> <li>• Camphorquinone</li> <li>• Dibenzoyl germanium derivative</li> </ul>	<ul style="list-style-type: none"> <li>• Bis-GMA</li> <li>• Bis-EMA</li> <li>• UDMA</li> <li>• 19.7 wt% organic matrix in total</li> </ul>	<ul style="list-style-type: none"> <li>• Prepolymer fillers 17 wt%</li> <li>• Barium glass filler, ytterbium fluoride and spherical mixed oxide fillers 62.5 wt%</li> <li>• 60 vol%</li> </ul>	10 s
VBF	Venus Bulk Fill	Heraeus 10031	Uni	n.a.	<ul style="list-style-type: none"> <li>• UDMA</li> <li>• EBADMA</li> </ul>	<ul style="list-style-type: none"> <li>• Barium glass filler, ytterbium fluoride and silica 65 wt%</li> <li>• 38 vol%</li> </ul>	20 s
XTB	X-tra Base	Voco 1250061	A2	n.a.	n.a.	<ul style="list-style-type: none"> <li>• Anorganic fillers 75 wt%</li> <li>• 58 vol%</li> </ul>	20 s
FSF	Filtek Supreme XTE Flowable	3M ESPE N359823	A2	EDMAB <0.5 wt%	<ul style="list-style-type: none"> <li>• Substituted dimethacrylate 15–25 wt%</li> <li>• BisGMA 5–10 wt%</li> <li>• TEGDMA 5–10 wt%</li> </ul>	<ul style="list-style-type: none"> <li>• Silane treated ceramic 50–60 wt%</li> <li>• Silane treated silica 5–10 wt%</li> <li>• YbF<sub>3</sub> &lt;5 wt%</li> <li>• Functionalized dimethacrylate polymer &lt;5 wt%</li> <li>• Titanium dioxide &lt;0.5 wt%</li> <li>• 65 wt%/46 vol%</li> </ul>	20 s
Z250	Filtek Z250 Universal Restorative	3M ESPE N217339	A2	n.a.	<ul style="list-style-type: none"> <li>• UDMA 1–10 wt%</li> <li>• BisEMA-6 1–10 wt%</li> <li>• BisGMA 1–10 wt%</li> <li>• TEGDMA &lt;5 wt%</li> </ul>	<ul style="list-style-type: none"> <li>• Silane treated ceramic 75–85 wt%</li> <li>• 60 vol%</li> </ul>	20 s

UDMA: urethane dimethacrylate, Bis-GMA: bisphenol A glycidyl methacrylate, Bis-EMA: ethoxylated bisphenol A glycol dimethacrylate, EBADMA: ethoxylated bisphenol A dimethacrylate, EDMAB: ethyl-4-dimethylaminobenzoate.

The absorption band at  $1608\text{ cm}^{-1}$  served as internal reference for normalization.

#### 2.4. Vickers hardness (HV)

For each material HV was measured on top (0 mm) and bottom (2 mm or 4 mm) of each specimen ( $n=5$ ) using a Vickers impression tester (15 s indentation time, 1 kg load, ZHV 10, Zwick Roell, Ulm, Germany). The length of the diagonals ( $d_1$  and  $d_2$ ) left by the indenter was digitally measured under a light microscope (Stemi SV6 with Axiovision LE, Carl Zeiss Microscopy, Jena, Germany). Subsequently HV values, bottom-top-ratios ( $HV_{\text{Bottom-Top-Ratio}}$ ) and % of maximal hardness ( $HV_{\text{Max}}$ ) were calculated.

#### 2.5. Volumetric polymerization shrinkage (PVS)

PVS was assessed by Archimedes' principle of buoyancy using a density determination kit, installed on a high accuracy balance (YDK01 and CP124S, Sartorius, Goettingen, Germany). Densities of the uncured materials ( $\rho_u$ , 1 g,  $n=6$ ) were determined measuring weight in air and in buoyancy medium ( $23^\circ\text{C}$ , 0.1% sodium laurylsulfate aqueous solution). Materials were light cured as indicated by the manufacturer (Table 1,  $\rho_c$ , 0.5 g,  $n=12$ ) or for 30 s ( $\rho_c$ , 0.5 g,  $n=12$ ) with a LED curing unit ( $1200\text{ mW/cm}^2$ , Bluephase 20i, Ivoclar Vivadent, Schaan, Liechtenstein). The densities of the light cured materials were weighted after 24 h of storage in distilled water at  $37^\circ\text{C}$ . The volumetric polymerization shrinkage was calculated using the equation:

$$\text{PS [\%]} = \left( \frac{\rho_c - \rho_u}{\rho_c} \right) \times 100$$

#### 2.6. Polymerization shrinkage stress (PSS)

The PSS test was performed in a high compliance system with 5 mm diameter PMMA rods as bonding substrate, following the experimental setup described by Boaro et al. [25]. The rod surfaces were sandblasted (Rocatec Plus, 3M ESPE, Seefeld, Germany), silanized (Monobond Plus, Ivoclar Vivadent), covered with a bonding agent (Heliobond, Ivoclar Vivadent) and light-cured. The rods were placed vertically into their respective holders in a universal testing machine (Z 2.5, Zwick Roell, Ulm, Germany) so that the two bars formed a 1 mm high gap, which was filled with the material under investigation. The lower holding device had an inlet for the light of the curing unit. The upper holding device was attached to the traverse axis and the load cell of the test machine. An extensometer (Mini MFA 2, MF Mess- & Feinwerktechnik GmbH, Velbert, Germany) was clamped to the rods, which served to maintain the gap height at 1 mm during the curing process. The force resulting therefrom served to calculate the resulting PSS. Each material was light cured according to manufacturers' instructions ( $n=10$ , Table 1) or for 30 s ( $n=10$ ) with a LED curing unit ( $1200\text{ mW/cm}^2$ , Bluephase 20i, Ivoclar Vivadent, Schaan, Liechtenstein) and the resulting PSS was measured for 300 s.

#### 2.7. Statistical analysis

All data were analyzed using one- or two- ANOVA and post hoc Student–Newman–Keuls test for multiple comparisons ( $\alpha=0.05$ , IBM SPSS Statistics for Windows, Version 20.0. IBM Corp., Armonk, NY, USA). Independent two sample T-test was performed to evaluate the effect of curing time on PVS, PSS, DC and HV of each material within the same specimen thickness.

### 3. Results

#### 3.1. Degree of conversion (%DC)

The measured %DC values are shown in Table 2. When light-curing following manufacturers' instructions was performed, bulk-fill resin composites had no significant inferior %DC at 2 or 4 mm specimen thickness when being compared to the top. In contrast the conventional condensable composite resin Z250 exhibited 38.90% at 2 mm increment thickness and only 22.20% at 4 mm thickness, compared to 42.19% at top. When extended light-curing for 30 s was performed, the conventional FSF had a significant decreased %DC at 4 mm when compared to top, whereas Z250 had no significant inferior %DC at 4 mm when compared to surface. Independent two-sample T-test revealed that extending the light-curing time resulted in significant increase ( $p < 0.05$ ) of %DC for the bulk-fill SDR at all increment thicknesses and for the conventional condensable Z250 at 2 and 4 mm.

#### 3.2. Vickers hardness (HV)

Measured HV values are presented in Table 2, the calculated bottom-top-ratios ( $HV_{\text{Bottom-Top-Ratio}}$ ) are shown in Table 3. With exception of SDR and XTB all materials had a significant decrease ( $p < 0.05$ ) of HV at 4 mm increment thickness when compared to surface, independent of the light-curing time or type of material. Independent two-sample T-test revealed that extended curing time resulted in a significant ( $p < 0.05$ ) increase of the mean HV for the bulk-fills TBF and XTB at all specimen thicknesses and for FBF and VBF at 2 and 4 mm.

#### 3.3. Volumetric polymerization shrinkage (PVS)

Measured PVS values are shown in Table 4. In both curing modes the condensable materials Z250 and TBF had significantly inferior PVS values, followed by XTB. In the manufacturers' light curing time FSF and VBF had the significantly highest PVS. With exception of FBF, extended light-curing did not significantly affect PVS.

#### 3.4. Polymerization shrinkage stress (PSS)

Measured PSS values are presented in Table 4. In the manufacturers' light curing time TBF and Z250 had the significantly lowest PSS values. Irrespective of the used light-curing time, VBF followed by the conventional flowable resin composite FSF exhibited the significant highest PSS values. Extending the curing time resulted in significantly higher PSS for TBF, XTB and Z250.

**Table 2 – Mean degree of conversion (%DC) and Vickers hardness (HV) with standard deviations ( ) of investigated materials at different specimen thicknesses and curing times after 24 h of storage.**

Material		FBF			SDR			TBF			VBF		
Specimen thickness		0 mm	2 mm	4 mm	0 mm	2 mm	4 mm	0 mm	2 mm	4 mm	0 mm	2 mm	4 mm
%DC [%]	Manufacturers' instructions	65.9 (1.97) A	67.53 (2.03) A	66.4 (4.60) A	56.53 (10.9) A	43.69 (5.92) A	52.04 (12.45) A	67.45 (6.58) A	63.00 (3.88) A	63.40 (4.37) A	73.46 (9.61) A	76.32 (1.27) A	80.07 (2.76) A
	30 s	59.62 (3.22) A	68.13 (6.15) B	69.26 (6.49) B	70.86 (2.09) A	73.02 (1.89) A	72.18 (3.29) A	52.95 (11.07) A	60.05 (6.33) A	54.63 (3.67) A	65.37 (4.61) A	75.74 (1.27) B	73.93 (3.26) B
	Manufacturers' instructions	41.07 (1.62) A	37.60 (1.52) B	33.45 (1.44) C	39.82 (3.64) A	39.70 (2.5) A	38.12 (2.22) A	64.52 (2.45) A	60.55 (3.53) B	41.92 (4.46) C	34.34 (4.34) A	29.21 (1.52) B	29.15 (1.93) B
HV [GPa]	30 s	40.47 (2.40) A	38.60 (0.94) B	36.50 (1.90) C	36.18 (2.87) A	39.68 (2.30) B	35.37 (1.94) A	70.88 (2.50) A	68.39 (3.48) B	62.27 (3.79) C	30.64 (2.12) A	33.40 (1.61) B	34.41 (2.07) B
	Material	XTB			FSF			Z250					
	Specimen thickness	0 mm	2 mm	4 mm	0 mm	2 mm	4 mm	0 mm	2 mm	4 mm			
%DC [%]	Manufacturers' instructions	65.24 (2.51) A	64.52 (1.19) A	62.53 (3.01) A	70.25 (7.92) A	51.12 (10.76) B	65.80 (4.46) A	42.19 (7.56) A	38.90 (9.65) A	22.20 (1.07) B			
	30 s	61.48 (3.96) A	77.65 (3.08) B	61.53 (4.00) A	72.6 (3.55) A	70.15 (0.99) A	58.69 (4.90) B	52.63 (8.17) A	56.20 (3.92) A	48.53 (7.04) A			
	Manufacturers' instructions	57.06 (2.76) A	58.08 (2.75) A	56.96 (3.07) A	52.41 (2.21) A	50.99 (1.98) A	34.80 (1.62) B	93.59 (2.92) A	94.08 (1.77) A	81.39 (2.89) B			
HV [GPa]	30 s	69.86 (9.29) A	74.02 (3.61) B	67.84 (4.7) A	53.14 (4.11) A	51.85 (2.11) A	43.26 (2.08) B	91.66 (7.57) A	93.15 (7.29) A	83.67 (6.48) B			

Letters indicate homogeneous subsets within the same material and curing mode (S-N-K,  $\alpha = 0.05$ ).

**Table 3 – Degree of conversion Bottom-Top-Ratio ( $DC_{\text{Bottom-Top-Ratio}}$  [%]) and Vickers hardness Bottom-Top-Ratio ( $HV_{\text{Bottom-Top-Ratio}}$  [%]) of investigated materials at different specimen thicknesses and curing times after 24 h of storage.**

Material	FBF		SDR		TBF		VBF		XTB		FSF		Z250							
Specimen thickness	0 mm	4 mm	0 mm	4 mm	0 mm	4 mm	0 mm	4 mm	0 mm	4 mm	0 mm	4 mm	0 mm	4 mm						
$DC_{\text{Bottom-Top-Ratio}}$ [%]	100.00	102.47	100.76	100.00	77.29	92.06	100.00	93.40	100.00	103.90	109.01	100.00	99.74	97.22	100.00	72.77	93.67	100.00	92.20	52.63
Instructions																				
30 s	100.00	114.28	116.17	100.00	103.05	101.86	100.00	113.41	103.17	115.86	113.09	100.00	126.30	100.08	100.00	96.63	80.84	100.00	106.78	92.21
$HV_{\text{Bottom-Top-Ratio}}$ [%]	100.00	91.55	81.45	100.00	99.70	95.73	100.00	93.85	64.97	85.06	84.89	100.00	101.79	99.82	100.00	97.29	66.40	100.00	100.52	86.96
Instructions																				
30 s	100.00	95.38	90.19	100.00	109.67	99.42	100.00	96.49	87.85	109.01	112.30	100.00	105.95	97.11	100.00	97.57	81.41	100.00	101.63	91.28

#### 4. Discussion

The first null hypothesis, that increment thickness has no significant influence on degree of conversion (%DC) or Vickers hardness (HV) of bulk-fill resin composites and conventional resin composites has to be partially rejected. The conventional composite Z250, cured as indicated by the manufacturer, showed significant inferior %DC at 4 mm specimen thickness in comparison to top. When being light cured for 30 s Z250 had no significant differences in %DC at 2 or 4 mm compared to top. On the other hand, the investigated bulk-fills showed no significant decrease in %DC at 2 or 4 mm when compared to top, for both light curing times.

In general, bulk-fills display a higher translucency than conventional resin composites [26]. As light transmission is strongly linked to material opacity [27] the observed %DC at 4 mm specimen thickness for the investigated bulk-fills might be a result of their reduced opacity. Higher translucency can also be achieved by reduction in filler content [28]. As disclosed by the manufacturers, all investigated bulk-fills, except TBF show a slightly lower filler volume fraction compared to the conventional low viscosity flowable FSF, with VBF having the lowest (Table 1). For experimental resin composites it has been demonstrated that increasing the filler-to-matrix ratio progressively decreases conversion [29].

The selection of the components of the monomer matrix has an influence on the %DC of resin composites [30]. As far as described by manufacturers' information sheet, several of the investigated materials contain urethane dimethacrylate (UDMA), beside the conventional bisphenol A glycolmethacrylate (Bis-GMA) [21–24]. UDMA was shown to reach higher final %DC values than Bis-GMA, combining relatively high molecular weight (UDMA 470.0, Bis-GMA 510.6) with high concentration of double bonds (UDMA 4.25 mol/kg, Bis-GMA 3.90 mol/kg) and low viscosity (UDMA 23.1 Pa s, Bis-GMA 1200 Pa s) [30]. Co-polymerization of Bis-GMA with UDMA or triethyleneglycol dimethacrylate (TEGDMA) is usually utilized to increase conversion and create highly cross-linked, dense and stiff polymer networks [31]. The elastic modulus, in turn, has an active role in determining %DC and PSS development during polymerization [8]. Elastic modulus is enlarged by increase of the filler fraction [32] and BisGMA concentration [33]. An increased amount of filler particles is an obstacle for polymeric chain propagation [29] and BisGMA due to its high viscosity has decreased mobility [30]. Both factors result in reduced %DC and thus inferior PSS.

With 60% filler volume fraction, TBF is one of the highest filled and the less translucent bulk-fills among the materials under investigation in the present study. The manufacturer recommends 10 s of light curing at 1200 mW/cm<sup>2</sup>. For this material %DC at higher increment thickness is partially reached by the use of a photoinitiator system which combines the conventional camphorquinone (CQ) and acyl phosphine oxide with Ivocerin® (Bis-4-(methoxybenzoyl)diethylgermanium Ge-3) [34] a dibenzoyl germanium derivate similar to dibenzoyldiethylgermane (DBDEGe) [21,35]. When irradiated by visible light dibenzoyl germanium derivates show a cleavage under formation of germyl and benzoyl radicals which initiate the polymerization

**Table 4 – Mean polymerization volume shrinkage (PVS) and shrinkage stress (PSS) with standard deviations (σ) of investigated materials.**

Material	FBF	SDR	TBF	VBF	XTB	FSF	Z250
<b>PVS [%]</b>							
Manufacturers' instructions	3.34 (0.11) B	3.37 (0.55) B	2.36 (0.23)A	4.03 (0.24) C	3.05 (0.3) B	3.92 (0.48) C	2.31 (0.57)A
30 s	3.87 (0.45) C	3.79 (0.23)B, C	2.32 (0.32)A	3.77 (0.28)B, C	3.38 (0.2) B	3.8 (0.24)B, C	2.08 (0.22)A
<b>PSS [MPa]</b>							
Manufacturers' instructions	1.55 (0.11)C, D	1.33 (0.07) B	1.07 (0.1) A	1.65 (0.1) D	1.45 (0.11)C	1.94 (0.2) E	1.23 (0.12)B
30 s	1.47 (0.06) B	1.29 (0.06) A	1.58 (0.13)B	1.74 (0.11) C	1.68 (0.09)C	1.93 (0.15) D	1.48 (0.12)B

Letters indicate homogeneous subsets within the same curing mode (S-N-K,  $\alpha = 0.05$ ).

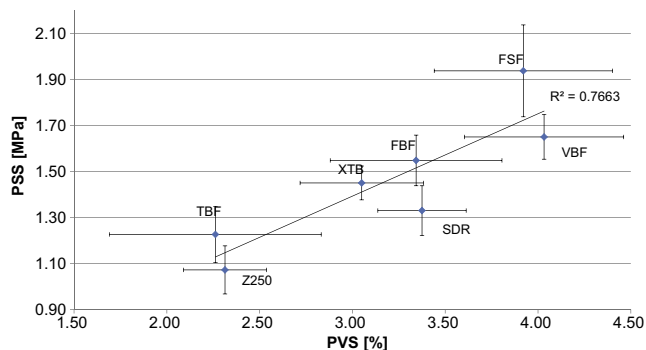
[36], so that no co-initiator, such as a tertiary amine is necessary. Dibenzoyl germanium derivatives are characterized by absorption at lower wavelengths (<350–490 nm, e.g. Ivocerin<sup>®</sup>,  $\lambda_{\max}$  408.2 nm or DBDEGe,  $\lambda_{\max}$  418) than CQ (400–550 nm,  $\lambda_{\max}$  468 nm) and higher quantum yield conversion (DBDEGe 0.85, CQ 0.07) and accordingly more initiating radicals per molecule initiator (DBDEGe 2–3, CQ 1) [3]. The more sensitive the initiator system, the more prone is the polymerization reaction to start, despite less light energy delivered at greater material thickness. Interestingly, all bulk-fills showed inferior %DC at top when compared to 2 and 4 mm when being light cured for 30 s. This is in accordance with literature where similar findings are reported [37,38] and linked to factors, such as the heterogeneity of temperature increase with material thickness during polymerization, variation of the degree of crosslinking with depth, or to oxygen inhibition. However in the present study this is unlikely due to the fact that a transparent mylar strip was placed on top and bottom of the mold to prevent oxygen inhibition and polishing of the sample surface was performed. Studies with unfilled systems showed an inferior %DC on surface when irradiance was increased [39]. In this case the lower %DC on the sample surface was alleged to diffusion-limitation at early stage due to the increased irradiance. However this explanation cannot be transferred directly to filled resin composite systems making further studies necessary to explain this phenomenon.

With exception of SDR and XTB, all investigated bulk-fills and conventional resins presented a significant decrease in HV at 4 mm, irrespective of the curing time. When the 80% bottom-top-ratio (HV<sub>Bottom-Top-Ratio</sub>) [40,41] criterion was applied as a minimum acceptable threshold, all investigated materials, with exception of TBF and FSF in the manufacturers' light-curing time (TBF 10 s, FSF 20 s at 1200 mW/cm<sup>2</sup>), showed adequate hardness at 4 mm. The fact, that TBF did not reach the 80% threshold at 4 mm has been reported in literature [42]. At higher radiant exposure (30 s at 1200 mW/cm<sup>2</sup>) all materials reached at least 80% HV<sub>Bottom-Top-Ratio</sub> (Table 3). For the investigated bulk-fills, these findings are in accordance with the literature [26,41,43]. However, applying the 80% criterion has been questioned in literature [37,44]. Some authors propose that sufficient curing is only reached if there is no significant decrease of HV with increasing material depth. This approach could only be fulfilled by SDR and XTB in both light-curing times and by VBF in the 30 s light-curing mode. As the HV indenter is greater compared to the size of the fillers and the space in between filled with matrix [45], the resulting HV value is a measurement of the whole filler matrix

system, being the filler component the dominating factor over the softer matrix [46]. This can be seen in the present study, where a positive correlation value ( $R^2 > 0.695$ ), between the HV and the filler volume content (as far as provided by the manufacturers) of the materials in question at all specimen thicknesses and curing modes, were calculated. In this respect, HV measurements could be more sensitive than %DC, as HV indirectly considers the matrix network crosslinking, whilst %DC only reveals the amount of remaining carbon double bonds [47].

The second null hypothesis, that bulk-fill resin composites show significant lower polymerization shrinkage stress (PSS) and volumetric polymerization shrinkage (PVS) than conventional composite resins can be partially rejected. For both curing times the conventional flowable composite FSF revealed the significantly highest PSS. On the other hand, the conventional condensable resin composite Z250 ranked among the significant lowest PSS of the investigated composites. This could also be observed for PVS. Two-way ANOVA revealed that the material had a highly significant influence on PSS ( $p < 0.001$ ). According to the literature [31] it was expected that the materials with the higher volume filler loading would exhibit the lowest PSS. This could be corroborated for the investigated materials with the highest filler content. When being cured as instructed by the manufacturer, the condensable bulk-fill TBF had the significantly lowest PSS ( $p < 0.05$ ) followed by the conventional condensable resin composite Z250. Some studies in which stress and conversion are simultaneously measured also provide evidence that the increase in filler content results in slight reduction of %DC [48]. Probably this could be a synergistic effect in reducing the PSS. In contrast, recent studies on PSS of bulk-fills and conventional resins [40] showed significantly higher shrinkage stress values for Z250 when compared to the investigated bulk-fills ( $p < 0.05$ ). This could be partially due to different experimental settings such as system compliance and different material thicknesses. In the present study a high compliance system was chosen in order to simulate the clinical situation [49]. Overall, the investigated flowable bulk-fills could achieve in both light-curing times significant lower PSS than the conventional flowable composite FSF. As far as disclosed by the manufacturers, FSF contains a higher amount of TEGDMA than FBF and Z250 (Table 1). The higher fraction of TEGDMA is probably implemented in order to keep FSF flowable despite the relatively high filler volume fraction in comparison to the other low viscous materials. Low molecular weight monomers reduce the viscosity of resin composites and enhance %DC [50]





**Fig. 1 – Plot of polymerization shrinkage stress (PSS) [MPa] versus volume shrinkage (PVS) [%] of the materials under investigation, when light cured as recommended by the manufacturers, with linear correlation coefficient [ $R^2$ ]. Solid line represents the least squares fit.**

but they increase thereby PSS and PVS [32]. The solution reducing PSS in flowable bulk-fills might be found in the reduction of the amount of low molecular weight monomers like TEGDMA. In order to keep the viscosity low without increasing the amount of TEGDMA, higher molecular weight monomers like UDMA and ethoxylated dimethacrylates are used. In addition most bulk-fill materials, like TBF and SDR, contain undisclosed proprietary monomers with “stress-relievers” [21,22]. In the case of TBF, XTb and Z250, the increase in curing time to 30s resulted in a highly significant rise of PSS ( $p < 0.01$ ), probably due to higher %DC and thus to higher crosslinking resulting in greater PSS values, confirming results from similar studies [51].

By increasing the filler volume content, PVS decreases [52]. This is shown in the present study as the highly-filled materials Z250 and TBF had significant inferior PVS. Although having a higher filler volume load than XTb, FBF and SDR, FSF showed significant higher PVS than those, in the manufacturer’s instruction light curing mode. For FSF monomer matrix seems to be the determining factor for PVS, as FSF contains the most TEGDMA of the materials under investigation. With exception of FBF none of the materials presented significant changes in PVS when being cured for 30s. From this point of view it can be presumed that, for this material, the filler volume fraction is the deciding factor on PVS, which is in accordance with similar studies on commercial resin composites [53]. A linear correlation could be found between PVS and PSS ( $R^2 = 0.7663$ , Fig. 1).

The third null hypothesis, that increased light curing time has no significant influence on the evaluated polymerization parameters, has to be partially rejected depending on the material and the investigated properties. Increased curing time of 30s had positive effects on parameters like %DC and HV, which are predictors for the depth of cure of resin composites. Interestingly the conventional resin composite Z250 profited from extended light curing (with an irradiance of  $1200 \text{ mW/cm}^2$ ) showing no significant differences in %DC at 2 or 4 mm when compared to top, leading to a bulk-fill like performance in terms of %DC. Extended curing time resulted overall in no significant increase of PVS, which is often linked

to leakage and gap formation [9]. Even under extended irradiation time of 30s all investigated bulk-fills performed lower PSS than a conventional flowable resin composite irrespective of their filler volume contents. Under this aspect it could be presumed that increased light curing time is profitable in terms of depth of cure without the adverse effects of higher PSS.

## 5. Conclusion

Within the limits of this study all investigated bulk-fills had sufficient polymerization properties at 4 mm increment thickness in terms of not significant lower %DC compared to 0 mm. Most bulk-fills combined this with inferior PVS and PSS compared to the conventional flowable resin composite. Bulk-fills are promising RBCs because they are useful in clinics for adhesive filling of deep cavities when time consuming incremental techniques are not possible due to low patients compliance. Based on this study, 30s curing time had positive effects on polymerization properties, so that enhanced light curing of bulk-fills in deep cavities is recommended.

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