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Polymerization and shrinkage kinetics and fracture toughness of bulk-fill resin-composites

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ABSTRACT

Objectives: To determine degree of conversion (DC), maximum polymerization rate (RP_{max}), polymerization shrinkage (PS), maximum shrinkage rate ($PS R_{max}$) and fracture toughness (K_{IC}) of different types of bulk-fill (BF) composites plus the effect of viscosity reduction techniques.

Methods: BF specimens were created in 2 mm deep molds: SonicFill 3 (SF3), Viscolor (VC), One Bulk Fill (OBF) and Beautiful Bulk (BBR). SF3 was applied via sonic insertion using a SonicFill handpiece (Kerr Corp. USA). Viscolor was pre-heated in a Caps Warmer in T3 mode (at 68 °C) for 30 s (T3–30 s) and 3 min (T3–3 min), respectively. Specimens were irradiated at zero distance from the upper surface with an Elipar S10 LED unit (3 M ESPE, USA) of mean irradiance 1200 mW/cm² for 40 s. Real-time polymerization kinetics and DC at 5 min and 24 h post-irradiation ($DC_{5 min}$ and $DC_{24 h}$) were measured using ATR-FTIR ($n = 3$). PS was measured up to 1 h on 1 mm thick discs via the bonded-disk technique ($n = 3$) and $PS R_{max}$ obtained by numerical differentiation ($n = 3$). For fracture toughness, single-edge-notched specimens (32 × 6 × 3 mm) of each BF composite were prepared and measured by three-point bending after 7 d water storage ($n = 5$). Data were analysed using One-way ANOVA, independent T-tests and Tukey *post-hoc* tests ($p < 0.05$).

Results: SF3 showed the significantly highest $DC_{5 min}$, $DC_{24 h}$ and RP_{max} ($p < 0.05$), followed by OBF ($p < 0.05$). Regardless of pre-heating, VC showed comparable conversion kinetics to BBR ($p > 0.05$). There was no significant difference in PS of these BF composites, except OBF had the highest PS ($p > 0.05$). However, $PS R_{max}$ significantly varied among materials ($p = 0.047$) and SF3 had the highest $PS R_{max}$. Regarding fracture toughness, BBR had the lowest K_{IC} ($p < 0.05$), whereas other composites showed similar K_{IC} ($p > 0.05$). Strong correlations of filler content (wt%)-PS/ K_{IC} were found. Different pre-heating times had no significant influences on DC %, RP_{max} , PS, $PS R_{max}$ and K_{IC} of VC ($p > 0.05$).

Significance. Different types of bulk-fill composites showed comparable shrinkage. A highly filled BF filler composite (BBR) had the lowest fracture toughness, whereas others had similar K_{IC} . Pre-heating had no adverse effects on Viscolor properties. Sonication and pre-heating are beneficial techniques to enhance composite flowability without either increasing shrinkage or reducing fracture toughness.

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1. Introduction

Secondary caries and bulk fractures are considered major drawbacks of dental resin-based composites (RBCs) [1,2]. The former results from gap formation at the restoration/tooth interface and following bacterial accumulation. The latter relates to insufficient material fracture resistance. During polymerization, inherent volumetric shrinkage occurs [3]. The resultant stress on adhesive bonds can cause micro-leakage and clinical failure. Different measures have been introduced to reduce shrinkage and avoid adverse clinical consequences [4–6].

Dental RBCs can be somewhat brittle and may undergo elastic deformation with catastrophic crack growth under high applied stress [2,7,8]. Fracture resistance of composites are usually characterized by fracture toughness measurements, which express the ability to resist pre-crack/flaw propagation [9]. It is not possible to predict flaw distributions within RBCs since they can be created during light-curing or after specimen preparation [7,9]. Fracture happens when the stress intensity factor, K , exceeds its critical value, K_{IC} [2,7,9]. Subscript numbers refer to different modes of loading and K_{IC} refers to cracks propagating under tensile stress [7,9,10].

Various fracture toughness measurements have been developed and single-edge notch three-point bending (SENB) is commonly used due to its simplicity and acceptance [9]. Theoretically, fracture toughness does not change with the specimen geometry or measurement technique [9]. Filler composition, shape, content and distribution have major influences on the fracture toughness of composites [2,7,11]. Internal flaw distributions, air bubbles and inter-particle bonding also affect crack propagation under stress and the resultant K_{IC} [2]. Different storage and test conditions may lead to diverse results [11,12].

A sufficient degree of conversion (DC) is necessary to enhance the longevity and clinical performance of RBCs. Homogenous crosslinking networks may aid in resisting the applied stress and avoid restoration fracture. Since ca. 2010, bulk-fill (BF) composites have been introduced with translucency to enable 4–5 mm cure depths with a sufficient DC [3,13,14]. Compared to the incremental filling technique, BF composites may show reduced shrinkage stress [3]. Bulk placement also reduces voids between layers relative to increment placement and avoids negatively affecting mechanical properties. However, high-viscosity bulk-fill

composites may entrap air bubbles during manipulation and lead to internal voids [12]. Sonic vibration is employed to reduce the viscosity of SonicFill via a sophisticated handpiece without compromising its depth of cure and mechanical properties [15,16]. Heating composites before placement, also called *pre-heating*, may improve adaptation and possibly monomer conversion and thus enhance synergistic mechanical properties of the tooth/restoration complex [15].

Bulk-fill composites have been investigated extensively, but very few studies compared the effects of pre-heating and sonication on their polymerization and shrinkage kinetics and fracture toughness. This study aimed to measure these properties of sonicated and pre-heated bulk-fill composites and compare them with other BF composites. The Null Hypotheses were: [1] there are no significant differences in conversion, shrinkage and fracture toughness properties of investigated BF composites. [2] pre-heating time does not significantly influence the conversion, shrinkage and fracture toughness properties of Viscalor.

2. Materials and methods

Manufacturer information concerning the investigated bulk-fill composites is shown in Table 1. SonicFill 3 was applied via the sonic insertion method using a SonicFill handpiece (Kerr Corp. USA). Viscalor was pre-heated using a Caps Warmer (VOCO, Germany) in T3 mode (at 68 °C) for 30 s (T3–30 s) and 3 min (T3–3 min), respectively.

Uncured RBC paste was packed into cylindrical Acetal molds (4 mm diameter × 2 mm thickness) above the attenuated total reflectance (ATR) crystal of a FTIR spectrometer. Each specimen was pressed from the top with a Mylar strip followed by a glass slide to remove air bubbles. The degree of conversion at 5 min and 24 h post-irradiation ($DC_{5\text{min}}$ and $DC_{24\text{h}}$) and real-time polymerization kinetics were measured using Fourier Transform Infrared (FTIR) spectroscopy (ALPHA II FTIR Spectrometer, Bruker Optik GmbH). Background readings were collected between 400 and 4000 cm^{-1} using 32 scans at a resolution of 4 cm^{-1} .

For DC % measurements ($n = 3$), the spectrum of uncured RBC was firstly collected. Then light irradiation was applied at zero distance from the upper surface using a calibrated Elipar S10 LED unit (3M ESPE, USA) of mean irradiance 1200 mW/cm^2 for 40 s. Good contact was maintained between the specimen and the ATR crystal. DC spectra were collected after 5 min ($DC_{5\text{min}}$) and 24 h ($DC_{24\text{h}}$) via real-time

Table 1 – Manufacturer information of investigated bulk-fill composites.

Code	Material	Manufacturer	Resin system	Filler vol %	Filler wt%
BBR	Beautifil-Bulk Restorative	SHOFU Inc. Kyoto, Japan	bis-GMA, UDMA, bis-MPEPP, TEGDMA	74.5	87
OBF	Filtek One Bulk fill	3M ESPE, St. Paul, USA	DDDMA, UDMA, AUDMA, diurethane-DMA	58.4	76.5
SF3	SonicFill 3	Kerr Corporation, USA	bis-EMA, triethylene glycol dimethacrylate	–	81
VC	Viscalor	VOCO, Germany	bis-GMA, aliphatic dimethacrylate	–	83

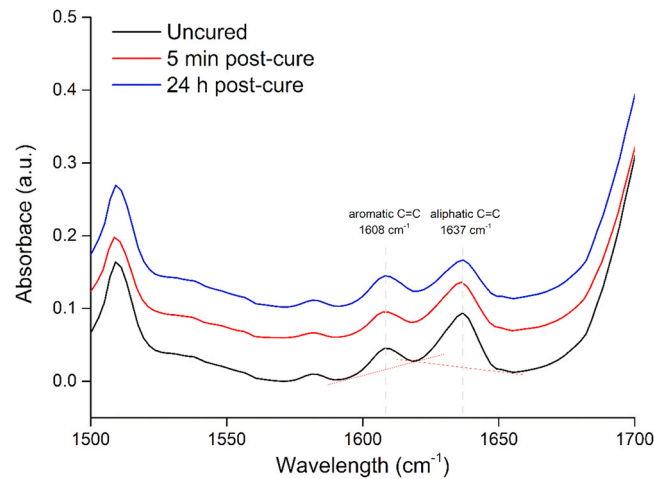


Fig. 1 – FTIR spectra of uncured and post-cured specimens at 23 °C.

acquisition. The peak heights of the aliphatic C=C absorbance peak at 1637 cm^{-1} and the aromatic C=C absorbance peak at 1608 cm^{-1} were selected to calculate the DC %:

$$DC\% = 1 - \frac{(H_{1637\text{ cm}^{-1}}/H_{1608\text{ cm}^{-1}})_{\text{cured}}}{(H_{1637\text{ cm}^{-1}}/H_{1608\text{ cm}^{-1}})_{\text{uncured}}} \times 100\%$$

where $H_{1637\text{ cm}^{-1}}$ was the height of the aliphatic C=C peak and $H_{1608\text{ cm}^{-1}}$ was the height of the aromatic C=C peak.

For real-time kinetic measurements over 15 min ($n = 3$), the spectral acquisition started immediately before irradiation. 40 s irradiation was applied at 5 s after the start of the spectral acquisition. Spectra were collected using 10 scans at a resolution of 4 cm^{-1} . The rates of polymerization were obtained by numerical differentiation of real-time DC % data with respect to time.

Polymerization shrinkage (PS) was measured using the bonded-disk technique [17,18]. The uncured RBC paste was placed centrally within a brass ring (1 mm thickness), which bonded to a 3 mm thick glass baseplate. The upper surface of the RBC paste was covered by a compliant glass coverslip. The specimen was irradiated from the lower surface using an Elipar S10 LED unit (3M ESPE, USA) of mean irradiance 1200 mW/cm^2 for 40 s at $23\text{ }^\circ\text{C}$. The axial strain was continuously measured up to 1 h after irradiation ($n = 3$). The rates of polymerization shrinkage were obtained by numerical differentiation of PS data with respect to time.

For fracture toughness measurement, the critical stress intensification factor, K_{IC} , was measured by fracturing single-edge notched specimens with three-point bending ($n = 6$) [9]. The geometry of the split PTFE-lined brass mold (34 mm length \times 6 mm height \times 3 mm thickness) conformed to British Standard 54, 749: 1978 [19]. A blade was located at mid-length and extended half the height of the specimen to produce the crack during specimen preparation. A pre-crack was made by sharpening the tip of the notch with a razor blade. The specimen was photo-cured for a total of 280 s at zero distance from the top surface. By moving half the diameter of the exit window of the LED-LCU, seven centre-overlapping areas were cured along the length of the specimen. After removing from

the mold, the specimen was additionally cured along the thickness direction with close contact between the curing tip and the specimen, to ensure sufficient curing. The specimen was polished using 1000-grit silicon carbide sandpaper to remove excess material at the edge. The specimen dimensions were measured at three different positions using a caliper with 0.01 mm accuracy. The total crack length for each specimen was determined at $0.7\times$ magnification using a stereomicroscope (EMA-5; Meiji Techno Co. Ltd. Japan) with a calibrated scale bar (0.1 mm accuracy). All specimens were stored in water at $37\text{ }^\circ\text{C}$ for 7 days before testing. A Universal Testing Machine (Zwick/Roell-2020, 2.5 kN load cell) was used to measure K_{IC} at $23\text{ }^\circ\text{C}$. The load was applied at a crosshead speed of 0.5 mm/min to the centre of the notched beam until reaching the fracture point. The load-deflection curves were recorded. The K_{IC} was calculated as:

$$K_{IC} = \left[\frac{PL}{BW^{1.5}} \right] Y$$

$$Y = \left\{ 2.9 \left(\frac{a}{w} \right)^{0.5} - 4.6 \left(\frac{a}{w} \right)^{1.5} + 21.8 \left(\frac{a}{w} \right)^{2.5} - 37.6 \left(\frac{a}{w} \right)^{3.5} + 38.7 \left(\frac{a}{w} \right)^{4.5} \right\}$$

where P = fracture load, L = loading span (20 mm), B = thickness of the specimen, W = width of the specimen, a = total notch length, Y = function of (a/W) .

Data were entered into statistical software (SPSS, SPSS Inc., Illinois, USA) and analysed using One-way ANOVA, independent T-tests and Tukey *post-hoc* tests ($p < 0.05$). Homogeneity of variance was calculated using the Kruskal-Wallis Test ($p < 0.05$).

3. Results

FTIR spectra of uncured and post-cured specimens are shown in Fig. 1. As presented in Fig. 2, polymerization kinetic plots of the composites from 0 to 15 min showed similar development, except for the significantly higher DC % of SF3 and OBF. After 24 h, DC significantly increased. $DC_{5\text{ min}}$, $DC_{24\text{ h}}$ and RP_{max} results are summarized in Table 2, in which SF3 had the highest results ($p < 0.05$), followed by OBF ($p < 0.05$).

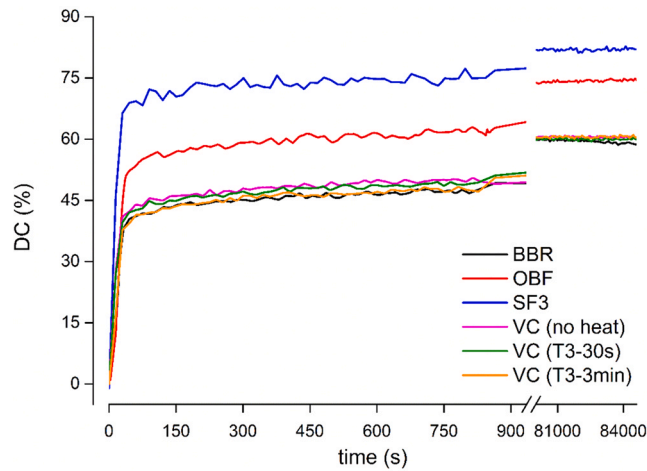


Fig. 2 – DC % vs. time 0–15 min and at 24 h post-irradiation for bulk-fill composites at 23 °C.

Table 2 – Degree of conversion at 5 min and 24 h post-irradiation ($DC_{5\text{ min}}$ and $DC_{24\text{ h}}$) and maximum polymerization rate (RP_{max}) of different bulk-fill composites at 23 °C.

Materials	$DC_{5\text{ min}}$	$DC_{24\text{ h}}$	RP_{max} (%/s)
BBR	43.9 % ^{a A} (2.21)	56.7 % ^{a B} (2.61)	1.95 ^{a C} (0.15)
OBF	62.1 % ^{b A} (2.95)	70.2 % ^{b B} (3.99)	2.37 ^{a C} (0.11)
SF3	71.3 % ^{c A}	80.4 % ^{c B}	3.30 ^{b C} (0.06)
VC (no heat)	40.8 % ^{a A} (0.85)	58.0 % ^{a B} (3.35)	1.79 ^{a C} (0.32)
VC (T3–30 s)	42.8 % ^{a A} (1.22)	58.5 % ^{a B} (0.76)	1.76 ^{a C} (0.49)
VC (T3–3 min)	41.5 % ^{a A} (1.20)	58.4 % ^{a B} (0.80)	1.78 ^{a C} (0.35)

For each property, the same lower case superscript letters indicate homogeneous subsets among the materials.

For each material, the same CAPITAL superscript letters indicate homogeneous subsets among different properties.

Non-preheated and pre-heated VC showed comparable $DC_{5\text{ min}}$, $DC_{24\text{ h}}$ and RP_{max} to BBR ($p > 0.05$). RP_{max} ranged from 1.76 %/s to 3.30 %/s. As shown in Fig. 3, RP_{max} results were all obtained within 20 s of irradiation. Pre-heating had no significant influences on $DC_{5\text{ min}}$, $DC_{24\text{ h}}$ and RP_{max} of VC ($p > 0.05$).

In Table 3 and Figs. 4–5, PS and PS R_{max} data are presented which ranged from 1.39 % to 1.65 % and from 0.14 %/s to 0.23 %/s, respectively. There were no significant differences in PS among these composites ($p > 0.05$), in which OBF had relatively higher PS result. However, PS R_{max} significantly varied in materials ($p = 0.047$) and SF3 had the highest PS R_{max} .

Table 4 summarizes the K_{IC} data for the composites. There were no significant differences among these composites, except BBR had a significantly lower K_{IC} ($p < 0.05$). Different pre-heating times had no significant influence on the K_{IC} of VC ($p > 0.05$).

Scatter plots and correlations between PS/ K_{IC} and filler content (wt%) of these composites are shown in Fig. 6.

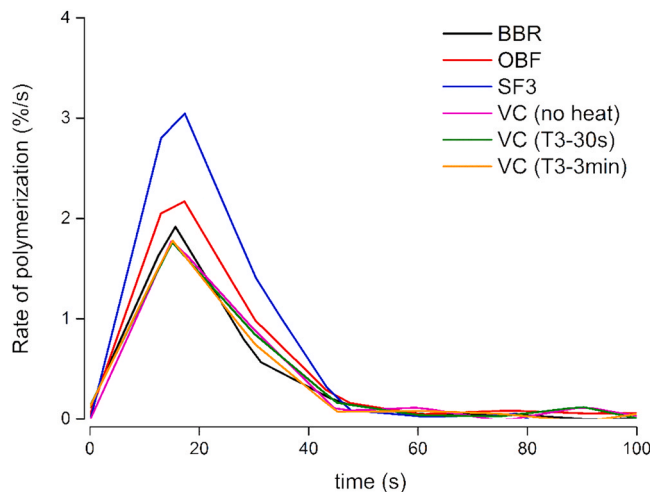


Fig. 3 – Maximum polymerization rates (RP_{max} , %/s) of bulk-fill composites at 23 °C.

Table 3 – Polymerization shrinkage (PS) at 1 h and maximum shrinkage rate (PS R_{max}) of different bulk-fill composites at 23 °C.

Materials	PS _{1h} (%)	PS R_{max} (%/s)
BBR	1.39 % ^a (0.07)	0.14 ^a (0.02)
OBF	1.65 % ^a (0.05)	0.15 ^{ab} (0.02)
SF3	1.45 % ^a (0.06)	0.23 ^b (0.01)
VC (no heat)	1.41 % ^a (0.13)	0.15 ^{ab} (0.04)
VC (T3–30 s)	1.57 % ^a (0.16)	0.17 ^{ab} (0.05)
VC (T3–3 min)	1.45 % ^a (0.15)	0.16 ^{ab} (0.04)

For each condition, the same lower case superscript letters indicate homogeneous subsets among the materials.

Correlation coefficients (r^2) were 0.95 and 0.89, respectively. Both PS and K_{IC} declined with increased filler content (wt%).

4. Discussion

This study compared conversion, shrinkage and fracture toughness of several bulk-fill composites, building upon previous study of polymerization behavior of Viscolor [20]. For these bulk-fill composites, 10 s and/or 20 s curing time is commonly recommended by manufacturers and applied by different studies [21–23]. Moreover, according to the previous study, 20 s irradiation was sufficient to produce an adequate degree of polymerization for Viscolor (no heat, T3–30 s and T3–3 min) [20]. Thus, in the present study, 40 s irradiation was applied in both DC and PS measurements to ensure thorough polymerization. SF3 had the highest DC. All these composites showed similar polymerization shrinkage. K_{IC} for the composites were comparable except BBR was low. Pre-

heated VC showed comparable conversion, shrinkage and K_{IC} results to VC cured at room-temperature. Thus, the first null hypothesis was partly rejected and the second null hypothesis was accepted.

Once irradiated, the photo-initiator system absorbs light energy and triggers free radical formation, which initiates polymerization [4]. As the localized viscosity increases (gel effect), this hinders diffusion-controlled termination reactions of free radicals leading to auto-acceleration [24,25]. Upon further polymerization, the high-viscous crosslinked network limits the mobility of available free radicals/monomers and reduces the reaction rate [26]. RP_{max} is often reached at the early stage of polymerization [27] and this occurred around 20 s post-irradiation. Sonication of SF3 reduced viscosity via monomer mobility and increased RP_{max} . Within the OBF monomer system, the addition-fragmentation monomers (AFM) could cleave and form additional reactive sites. With multiple reactive sites, more free radicals/monomers are consumed and thus higher RP_{max} and DC are achieved.

Real-time DC developed similarly for all composites, although SF3 and OBF reached higher conversion which is beneficial for mechanical properties and long-term clinical performance [28]. DC is influenced by the synergetic effect of both intrinsic and extrinsic factors [29]. The former include: monomer composition, filler content and photo-initiator system and the latter: irradiance, exposure duration and light beam uniformity. The lower initial DCs of BBR and VC may be due to incorporation of rigid bis-GMA. However, their DCs improved after 24 h post-irradiation [30].

During polymerization, polymer units pack more densely with overall reduction in free volume [31]. Depending on the shrinkage magnitude, shrinkage stress develops within composites and at the restoration/tooth interface [32–34]. High PS, often results from high DC [35,36]. For the composites investigated, shrinkage did not vary greatly and was within an acceptable range of 2–6 % [37]. Fig. 6 shows decrease of PS with increasing filler content. The high PS of OBF is consistent with its high DC. However, high-molecular-mass

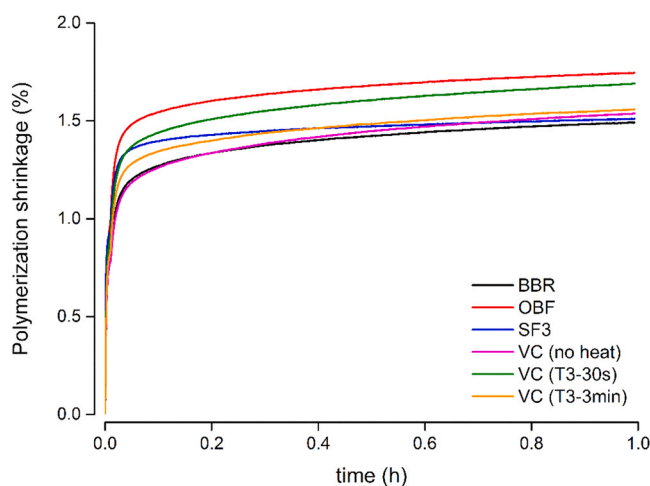


Fig. 4 – Shrinkage vs. time: 0–1 h post-irradiation for bulk-fill composites at 23 °C.

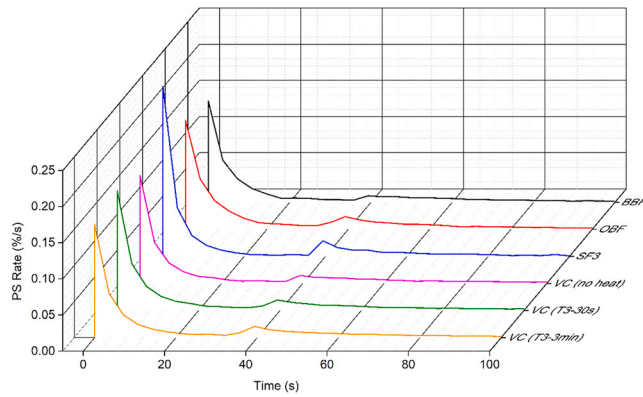


Fig. 5 – Maximum shrinkage rate (PS R_{max} , %/s) of bulk-fill composites at 23 °C.

Table 4 – Fracture toughness (K_{IC}) of different bulk-fill composites after 7 d water storage.

Materials	K_{IC} (MPa $m^{0.5}$)
BBR	1.13 ^a (0.04)
OBF	1.58 ^b (0.20)
SF3	1.44 ^b (0.04)
VC (no heat)	1.38 ^b (0.10)
VC (T3–30 s)	1.44 ^b (0.11)
VC (T3–3 min)	1.45 ^b (0.13)

The same lower case superscript letters indicate homogeneous subsets among the materials.

monomers, such as AUDMA and DDDMA, might increase OBF matrix viscosity and reduce an expected high DC and PS [14, 27, 38].

BBR has a high filler content of 87 wt% reducing the resin matrix portion; this showed relatively low PS as seen in previous studies [6, 13, 32, 39–41]. The rigid bis-GMA monomer within the BBR monomer system may also reduce shrinkage [26, 42–44]. However, it was previously reported that BBR had higher shrinkage than other composites [45]. The addition of low-viscous monomers, such as TEGDMA, may alter the viscosity and increase the PS [26, 27, 32, 40, 41]. Different testing methods could also lead to diverse results, which merits further investigation.

SF3 had the highest PS R_{max} , evidently due to beneficial viscosity reduction after sonication, without increasing shrinkage [16].

The fracture toughness of materials denotes their ability to resist fracture and the amount of stress needed for propagation of flaws or pre-cracks. Previous study has shown that K_{IC} of RBCs may not change significantly over storage periods [46], so this study measured K_{IC} after 7 d water storage. K_{IC} declined with higher filler content (Fig. 6), amongst the materials studied, with BBR and OBF showed the lowest and highest K_{IC} , respectively. BBR is designed as a high-viscosity bulk-fill giomer, intended to incorporate some features of glass ionomers. Its

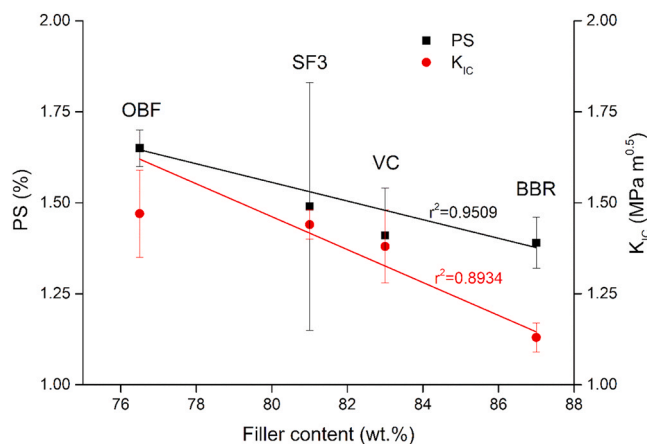


Fig. 6 – Linear regressions between PS (black line)/ K_{IC} (red line) and filler content.

low K_{IC} may be attributed to high filler loading, which impedes light penetration during irradiation and reduces the DC of BBR. However, Ilie et al. suggested *reduced* light scattering at the filler/matrix interface of BBR and reported some enhanced micro-mechanical properties relative to conventional RBCs [21]. BBR restorations have also been reported to have greater fracture resistance, possibly due to high filler load and elastic modulus [47]. Within OBF, addition-fragmentation monomers may produce more homogeneous network structures to resist fracture stress [14,48]. Hence, it showed relatively high K_{IC} , albeit with a lower filler content.

However, some studies report that K_{IC} increases with filler content [7,12]. Crack propagation needs more energy to pass through the randomly distributed particles with higher concentration [11]. Thus, the addition of small particles may improve filler volume and elevate fracture toughness [2,11,46]. In addition to crack branching and deflection caused by filler particles, the toughening mechanism of the filler/matrix interaction also plays a vital role in enhancing K_{IC} [2]. When filler content exceeds the *critical volume fraction* (usually 55–65 vol %), viscosity increases and more voids/porosities are trapped in the structure [2,11,49]. Increased filler loading may also limit plastic deformation of the resin matrix and reduce K_{IC} [50]. Filler size, shape and distribution, air bubbles and inter-particle bonding all have impacts on fracture origins and the resultant K_{IC} [2,11]. Small filler particles may also increase the filler/matrix interface area and make composites more susceptible to water penetration and degradation [2,51]. Thus, a weak resin matrix facilitates crack growth and finally reduces the K_{IC} .

In this study, VC (no heat, T3–30s and T3–3 min) showed comparable shrinkage kinetics, which correlated with the conversion kinetics [20]. The rapid fall in temperature after removal from the heating device resulted in only ca. 4.5 °C temperature rise of VC (T3–3 min) before irradiation [35,52,53]. Therefore, a 3 min pre-heating period effectively reduced VC viscosity during manipulation without causing dramatic shrinkage during irradiation. K_{IC} for non-heated and pre-heated VC were as high as that of OBF. Although VC had lower DC than SF3 and OBF, its comparable K_{IC} demonstrated acceptable mechanical strength. Fracture toughness of composites was reported to decrease with temperature, although this was not significant over the range 32–40 °C [54]. Temperature affects the resin matrix rather than filler particles. Within VC, even after pre-heating for 3 min before irradiation, the resultant resin matrix was sufficiently stable to resist fracture under applied load.

Although different methods (sonication and pre-heating) were used to reduce composite viscosity, SF3 and VC showed comparable shrinkage and K_{IC} results. This outcome may be due to their almost identical filler content of 81 and 83 wt%. However, the more rapid conversion of SF3 was an important difference.

5. Conclusions

- 1) SF3 and OBF had the highest conversion kinetics, while other bulk-fill composites showed comparable results.
- 2) Polymerization shrinkage (PS) was comparable for the bulk-fill composites, except OBF showed a relatively high PS.

- 3) These bulk-fill composites showed similar K_{IC} , except for a lower K_{IC} for bulk-fill giomer (BBR).
- 4) Sonication and pre-heating are beneficial techniques to enhance composite flowability without either increasing shrinkage or reducing fracture toughness.

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