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Effect of exposure time and pre-heating on the conversion degree of conventional, bulk-fill, fiber reinforced and polyacid-modified resin composites

Edina Lempel[a,*], *Zsuzsanna Őri*[b,c], *József Szalma*[d], *Bálint Viktor Lovász*[a], *Adél Kiss*[a], *Ákos Tóth*[e], *Sándor Kunsági-Máté*[b,c]

[a] *Department of Restorative Dentistry and Periodontology, University of Pécs, Pécs, Hungary*
[b] *Department of General and Physical Chemistry, University of Pécs, 6 Ifjúság Street, Pécs, H-7624, Hungary*
[c] *János Szentágothai Research Center, 20 Ifjúság Street, Pécs, H-7624, Hungary*
[d] *Department of Oral and Maxillofacial Surgery, University of Pécs, Pécs, Hungary*
[e] *Faculty of Sciences, University of Pécs Pécs, Hungary*

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ABSTRACT

Objective. To determine the degree of conversion (DC) of different type of resin-based composites (RBC) in eight-millimeter-deep clinically relevant molds, and investigate the influence of exposure time and pre-heating on DC.

Methods. Two-millimeter-thick samples of conventional sculptable [FiltekZ250 (FZ)], flowable [Filtek Ultimate Flow (FUF)] and polyacid-modified [Twinky Star Flow (TS)] RBCs, and four-millimeter-thick samples of flowable bulk-fill [Filtek Bulk Fill Flow (FBF), Surefil SDR (SDR)] and sculptable fibre-reinforced [EverX Posterior (EX)] RBCs were prepared in an eight-millimeter-deep mold. The RBCs temperature was pre-set to 25, 35 and 55 °C. The RBCs were photopolymerized with the recommended and its double exposure time. The DC at the top and bottom was measured with micro-Raman spectroscopy. Data were analyzed with ANOVA and Scheffe post-hoc test ($p < 0.05$).

Results. The differences in DC% between the top/bottom and the recommended/extended exposure time were significant for the materials, except SDR (64.5/63.0% and 67.4/63.0%). FUF (69.0% and 53.4%) and TS (64.9% and 60.9%) in 2 mm provided higher DC% at the top and bottom with the recommended curing time, compared to the other materials, except SDR. Pre-heating had negative effect on DC at the bottom in flowable RBCs (FUF: 48.9%, FBF: 36.7%, SDR: 43%, TS: 54.7%). Pre-heating to 55 °C significantly increased the DC% in fibre-reinforced RBC (75.0% at the top, 64.7% at the bottom).

Significance. Increased exposure time improves the DC for each material. Among bulk-fills, only SDR performed similarly, compared to the two-millimeter-thick flowable RBCs. Pre-heating of low-viscosity RBCs decreased the DC% at the bottom. Pre-heating of fibre-reinforced RBC to 55 °C increased the DC% at a higher rate than the extended curing time.

* *Corresponding author at*: Department of Restorative Dentistry and Periodontology, University of Pécs, 5. Dischka Gy Street, Pécs, H-7621 Hungary.
E-mail address: lempel.edina@pte.hu (E. Lempel).

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1. Introduction

The marginal seal is an essential factor in the longevity of a dental restoration. Leakage at the deep gingival margin can lead to secondary caries development resulting in the failure of the restoration and compromising the health of the vital pulp tissue [1]. In root canal treated teeth the penetration of microorganisms through the coronal orifice of the root canal may also cause recontamination and subsequent failure of the endodontic treatment [2].

Resin-based composite restorative materials (RBC) are widely used among dentists as the most common restorative material. Evolution in both filler and polymer technology led to a wide selection of materials that provide the adequate characteristics required for each clinical situation [3]. Besides the conventional RBCs, bulk-fill and fiber reinforced RBCs are also available in the market as improved materials. Low and high viscosity bulk filling composites usually have higher translucency, and sometimes a modified initiator system to ensure better curing in depth, as compared to conventional composites. These materials are recommended to use in 4 mm or even 5 mm in thickness without stratification [4], and promise adequate curing depth, physical and mechanical properties. Many bulk-fill composite resins have been investigated regarding different parameters like mechanical features, degree of conversion, polymerization stress or microleakage. On the one hand, such studies have shown that bulk-fill composite resins have similar physical and chemical properties as conventional RBCs [5–8], on the other hand, bulk filling RBCs were found to have lower mechanical properties, higher shrinkage rate and lower degree of conversion in the recommended 4 mm thickness compared to 2 mm of the conventional RBC's [9–11].

Fiber reinforcement of conventional dental composites were also introduced with the aim of enhancing their physical properties [12]. The enhancement was due to the stress transfer from the matrix to the fibers depending on the fibers length and diameter, leading to high resistance to fracture [13,14]. Besides the above mentioned developments, manufacturers are looking for continuous improvements to eliminate disadvantageous properties, like the polymerization shrinkage and the inadequate rate of polymerization. The presence of the aforementioned drawbacks adversely affects the marginal or coronal leakage. To avoid it, flowable RBCs could be used at the gingival margins of a proximal cavity or as a barrier to seal the orifices of the root canals [15]. Flowable RBCs have better adaptation to the cavity walls owing to their high tooth surface wetting ability, ensuring penetration into all irregularities [16].

Pre-heating of RBC can also decrease microleakage. Increasing the polymerization temperature leads to lower viscosity thus increasing the fluidity and improving the adaptation of the RBC material to the cavity [17,18]. Pre-heating in turn results in greater mobility of monomer molecules within the resin matrix, enhances free radical formation, which results in a higher value of the DC and shorten curing time [19,20]. The increased mobility of monomers at elevated temperature can lead to delayed autodeceleration stage of the polymerization reaction thus contribute to increased monomer conversion [21]. In addition, pre-heating significantly reduces the generation of shrinkage forces in both high-viscosity bulk-fill and conventional resin composites [22].

Clinical restoring procedures meet complex cavity shapes which could be challenging. Occasionally, cavity preparations that are 7–10 mm deep with a narrow orifice, as well as the angulation of the light curing tip may influence the polymerization rate of RBCs. Incomplete curing can lead to the early degradation, wear of the RBC restoration and also affect the functional durability, eventually leading to failure [23]. Light-curing an RBC is a complex process, as the depth of cure is affected by material composition, layer thickness, irradiance, curing time and variety of other factors [24]. For adequate polymerization the conventional RBC should receive a radiant exposure within the 16–24 J/cm^2 range [25]. This radiant exposure or energy density is calculated by multiplying the irradiance level coming from the light curing unit (LCU) by its duration [25]. Curing time is set depending of the irradiance level of the LCU. The "exposure reciprocity low" proposes reciprocity between the irradiance level and exposure duration to achieve equivalent DC of RBCs. This low has been evaluated in the literature and found not to apply, as it depends on the photoinitiator- and monomer-system of the RBC, the spectral radiant power of the LCU and is even time-dependent [26–28]. Selig et al. showed that an exposure time of only 10 s and above gave a sufficient DC [29], thus increasing the light exposure time results in higher radiant exposure reaching the RBC increment, especially with conservative cavity preparation (small orifice) and increased distance between the LCU tip and the RBC surface [30].

Selecting the proper material from the wide range available in the market is also a hard decision. In deep, occasionally irregular cavities the RBC should be easy to handle – if it is possible without the conventional layering – well adaptable and must be converted at an acceptable degree to provide good sealing and mechanical properties with low solubility. When sealing the orifices in root canal treated teeth, the use of a well distinguished material could be also advisable supposing a possible future re-treatment.

The purpose of this study was to measure the conversion degree with micro-Raman spectroscopy at the top and bottom of the first layer of a conventional sculptable and flowable, two flowable bulk-fill, a fibre-reinforced high-viscosity bulk-fill and a low-viscosity, coloured polyacid-modified RBC applied in a clinically relevant *in vitro* model, where an 8 mm distance from the light guide tip to the bottom side of the cavity was compiled. Further aim was to determine the effect of the recommended and the doubled curing time, as well as the RBC's pre-heating to 35 °C or 55 °C on the polymerization rate of the investigated materials.

2. Materials and methods

2.1. *Preparation of the composite resin specimens*

During this *in vitro* study six brands of resin composite material – a conventional sculptable microhybrid, a flowable nanofill, two flowable bulk-fill RBC, a fibre-reinforced bulk-fill material and a polyacid-modified RBC – were analyzed.

Table 1 – Materials, manufactures and composition.

Group	Material layer thickness	Code	Manufacturer	Shade	Organic matrix	Filler	Filler loading
Conventional RBC	Filtek Z250 2 mm	FZ	3M ESPE, St. Paul, MN, USA	A2	Bis-GMA, UDMA, Bis-EMA, TEGDMA	0.6 μm zirconia-silica	78 wt%
Conventional flowable RBC	Filtek Ultimate Flow 2 mm	FUF	3M ESPE, St. Paul, MN, USA	A2	BisGMA, TEGDMA, Procrylat resin	Zirconia/silica, ytterbium trifluoride	65 wt%
Bulk-fill RBC	Filtek Bulk Fill 4 mm	FBF	3M ESPE, St. Paul, MN, USA	U	BisGMA, UDMA, BisEMA, Procrylat resin	Zirconia/silica, ytterbium trifluoride	64.5 wt%
	SureFil SDR Flow 4 mm	SDR	Dentsply, Milford, DE, USA	U	Modified UDMA, EBPADMA, TEGDMA	Ba-Al-F-B silicate glass, Sr-Al-F silicate glass	68 wt%
Short glass fiber-reinforced RBC	EverX Posterior 4 mm	EX	GC Europe, Leuven, Belgium	U	BisGMA, TEGDMA, PMMA	Barium glass, short E-glass fibers	74.2 wt%
Polyacid-modified RBC	Twinky Star Flow Blue 2 mm	TS	VOCO GMBH, Cuxhaven, Germany	Blue	BisGMA, TEGDMA, UDMA, carboxylic acid modified methacrylate	Ba-Al-F-B silicate glass, silicon dioxide, glimmer	65 wt%

Abbreviation: RBC: resin-based composite; U: universal; UDMA: urethane dimethacrylate; EBPADMA: ethoxylated Bisphenol A dimethacrylate; TEGDMA: triethylene glycol dimethacrylate; BisEMA: Bisphenol A polyethylene glycol diether dimethacrylate; BisGMA: Bisphenol A diglycidil ether dimethacrylate; PMMA: polymethyl methacrylate.

The brand, the chemical composition and the manufacturer are presented in Table 1. According to the sample preparation and polymerization method, four experimental groups of specimens were divided. In each group, from each material, 5 specimens were prepared. Table 2 shows the experimental groups according to the method of polymerization and the abbreviations of the investigated materials.

Cylindrical Teflon molds with 5 mm internal diameter and 8 mm in height (representing a pulp chamber or deep proximal cavity) were constructed from two parts stacked on top of one another, according to the recommended thickness of the investigated materials. The schematic figure of sample preparation is presented in Fig. 1. For conventional sculptable and flowable RBCs and for the polyacid-modified resin composite the mold was built up from a 2 and a 6 mm high parts. For the bulk-fill RBCs the mold was constructed from two 4 mm high parts. Specimen preparation was performed inside a temperature-controlled chamber set at 25 °C. Materials with recommended 2 mm layer thickness were condensed or filled with a canula into the 2 mm high mold part, which was positioned on a glass slide. Thereafter, the uncured RBC was covered with a polyester (Mylar) strip in order to avoid contact with oxygen, which is an inhibitor of the polymerization. Immediately after that the 6 mm mold was positioned on top of the 2 mm mold filled with the investigated material providing the distance between the light curing guide and the material. The specimen was irradiated with a Light Emitting Diode (LED) curing unit ($\lambda = 420$–480 nm; LED.D, Woodpecker, Guilin, China) in standard mode, at an average tip irradiance of 1450 mW/cm^2 with an 8 mm diameter fiberglass light guide. The irradiance of the LED source was monitored before and after curing with a radiometer (Cure Rite, Dentsply, Milford, DE, USA). The curing light guide was centrally positioned directly on the mold entrance and the tip of the light guide was ensured to be parallel to the sample. Recommended curing time was applied for Group 1 (control), whereas double exposure time for group 4 (Table 2). For the bulk-fill RBCs the 4 mm high mold was positioned on the glass slide and was filled with the material in the recommended 4 mm thickness. The top of the sample was covered with a Mylar strip and the second 4 mm high mold was positioned on top of the first one, then the specimen was irradiated as mentioned above. In case of pre-heated groups, the RBC preheating was performed using a resin composite heating device (Ena Heat, Micerium, Avegno, Italy) preset to 35 °C (Group 2) and 55 °C (Group 3). The attained RBC's temperature was measured with a thermocouple probe (Type K thermocouple device; Ø = 0.5 mm; Cu/CuNi; TC Direct, Budapest, Hungary) which was coupled to a digital thermometer (EL-EnviroPad-TC, Lascar Electronics Ltd., Salisbury, UK), with a resolution of 0.1 per 1 °C and a data sampling frequency of 1 measurement per second. The preparation for the pre-heated specimens followed the above described protocol and was photoactivated with the recommended irradiation time for each material, respectively.

Additionally, the irradiance which reached the top of the 2 mm conventional and the 4 mm bulk-fill RBC, was measured with the radiometer. The 6 mm high mold part with 5 mm internal diameter was positioned at the center of the radiometer sensor and the incident irradiance was recorded, representing the radiant power which reaches the top of the conventional sculptable and flowable, or polyacid-modified RBC sample, filled into the 2 mm high mold. Then the procedure was repeated with the 4 mm high mold to indicate the irradiance, that reached the top of the bulk-fill RBC, filled into the 4 mm high mold part. According to this information the radiant exposure (J/cm^2) could be calculated with the product of the irradiance (mW/cm^2) and the exposure time (s).

Table 2 – Methods of polymerization and abbreviations of the investigated materials.

Methods of polymerization		Material temperature	Materials, exposure time, abbreviations, calculated radiant exposure					
			Filtek Z250	Filtek Ultimate Flow	Filtek Bulk Fill Flow	Surefil SDR	EverX Posterior	Twinky Star Blue
Group1	Exposure time recommended by the manufacturer	25 °C	20 s FZ_20 9 J/cm^2	20 s FUF_20 9 J/cm^2	10 s FBF_10 5.1 J/cm^2	20 s SDR_20 10.2 J/cm^2	10 s EX_10 5.1 J/cm^2	40 s TS_40 18 J/cm^2
Group2	Pre-heating to 35 °C and recommended exposure time	35 °C	20 s FZ_35_20 9 J/cm^2	20 s FUF_35_20 9 J/cm^2	10 s FBF_35_10 5.1 J/cm^2	20 s SDR_35_20 10.2 J/cm^2	10 s EX_35_10 5.1 J/cm^2	40 s TS_35_40 18 J/cm^2
Group3	Pre-heating to 55 °C and recommended exposure time	55 °C	20 s FZ_55_20 9 J/cm^2	20 s FUF_55_20 9 J/cm^2	10 s FBF_55_10 5.1 J/cm^2	20 s SDR_55_20 10.2 J/cm^2	10 s EX_55_10 5.1 J/cm^2	40 s TS_55_40 18 J/cm^2
Group4	Double exposure time	25 °C	40 s FZ_40 18 J/cm^2	40 s FUF_40 18 J/cm^2	20 s FBF_20 10.2 J/cm^2	40 s SDR_40 20.4 J/cm^2	20 s EX_20 10.2 J/cm^2	80 s TS_80 36 J/cm^2

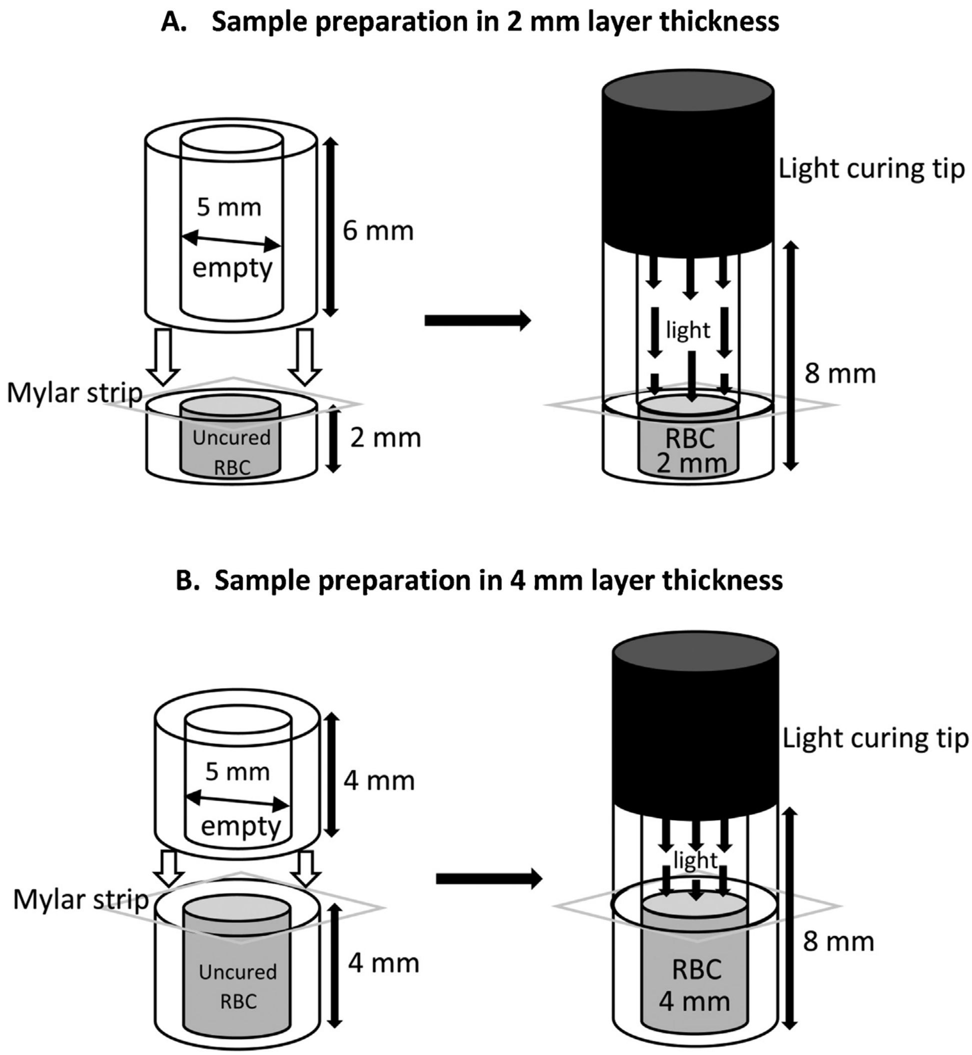

Fig. 1 – Schematic figure of the 2 mm thick (A) and the 4 mm thick (B) sample preparation.

2.2. *Micro-Raman spectroscopy measurement*

The 24 h post-cure DC values of the polymerized composite resin samples were examined using Labram HR 800 Confocal Raman spectrometer (HORIBA Jobin Yvon S.A.S., Longjumeau Cedex, France). The following sets of parameters were applied during the micro-Raman measurements: 20 mW He–Ne laser with 632.817 nm wavelength, spatial resolution ~1.5 μm, spectral resolution ~2.5 cm^{-1}, magnification x 100 (Olympus UK Ltd., London, UK). The spectra were taken on the top surface of the composite specimens at three random locations with 10 s integration time and ten acquisitions were averaged for each geometrical point. Spectra of uncured composite were taken as reference. Post-processing of spectra was performed using the dedicated software LabSpec 5.0 (HORIBA Jobin Yvon S.A.S., Longjumeau Cedex, France). The ratio of double-bond content of monomer to polymer in the composite resin was calculated according to the following equation:

$$DC\% = (1 - (R_{cured}/R_{uncured})) \times 100$$

where R is the ratio of peak intensities at 1639 cm^{-1} and 1609 cm^{-1} associated to the aliphatic and aromatic (unconjugated and conjugated) C–C stretching in cured and uncured composite resins, respectively.

2.3. *Statistical analysis*

The statistical analysis was performed using the SPSS (Statistical Package for Social Science, SPSS Inc., Chicago, USA) software for Windows. The values for degree of conversion between the studied test groups and between each material were compared by one-way analysis of variance (ANOVA) test. For multiple comparisons the significance between the groups, materials and between the top and bottom surfaces was determined by Scheffe's post-hoc test at $\alpha = 0.05$ level.

3. Results

Fig. 2 shows the degree of conversion at the top of the investigated materials according to the method of polymerization.

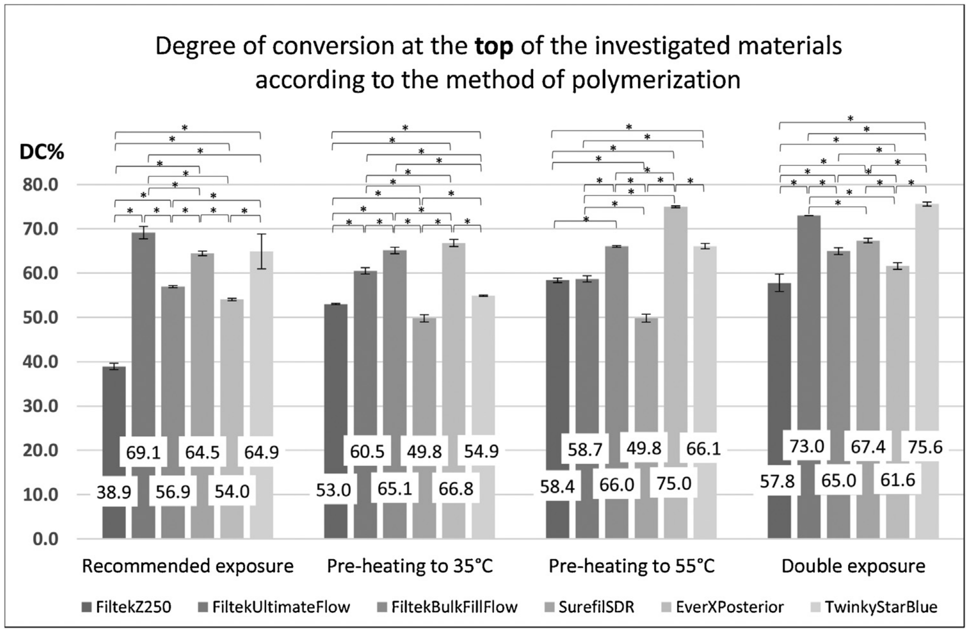

Fig. 2 – Degree of conversion at the top of the investigated materials according to the method of polymerization. The * mark indicates statistically significant difference between the investigated materials.

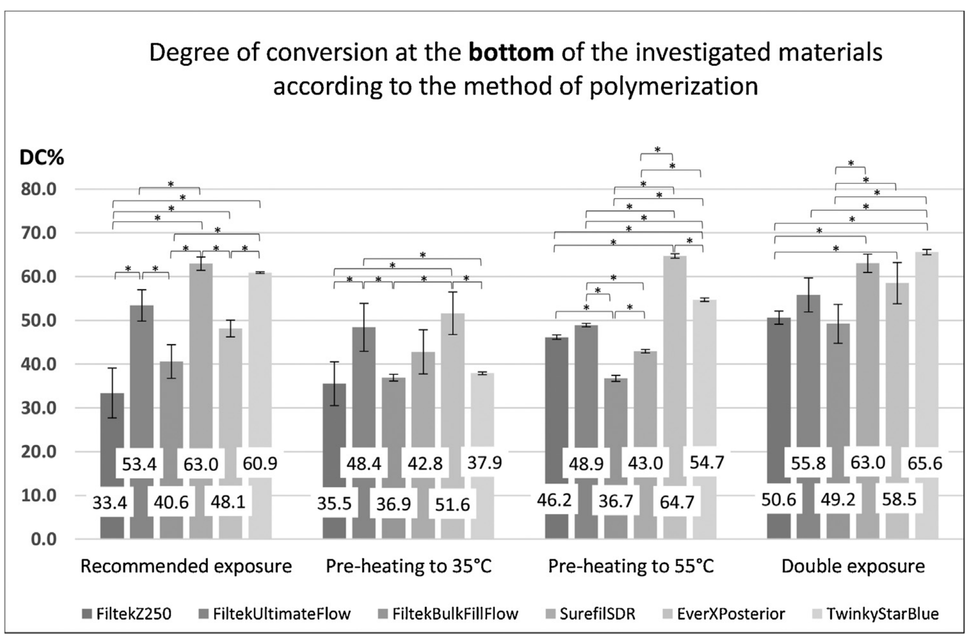

Fig. 3 – Degree of conversion at the bottom of the investigated materials according to the method of polymerization. The * mark indicates statistically significant difference between the investigated materials.

Regarding the top of the samples, conversion degree of the different materials ranged between 38.9% and 75.6%. The lowest value was measured in case of conventional sculptable microhybrid RBC (FZ_20) irradiated with the recommended exposure time at room temperature, meanwhile the highest DC% was detected in the case of the polyacid-modified resin composite (TS_80) with double exposure time at room temperature. In Group 1 the highest DC was measured in case of conventional flowable RBC (FUF_20) in 2 mm layer thickness. Similar values were detected on SDR_20 in 4 mm layer thickness and on TS_40 in 2 mm layer thickness. In Group 2 the effect of pre-heating to 35 °C was divisive. For FZ_35_20, FBF_35_10 and EX_35_10 there was a statistically significant increase in DC% on the top surface compared to the FZ_20, FBF_10 and EX_10 belong to Group 1. On the other hand, in most of the low viscosity materials (FUF_35_20, SDR_35_20 and TS_35_40) a statistically significant decrease was detected. In group 3. similar distribution in DC% was observed. In group 4. significantly higher DC

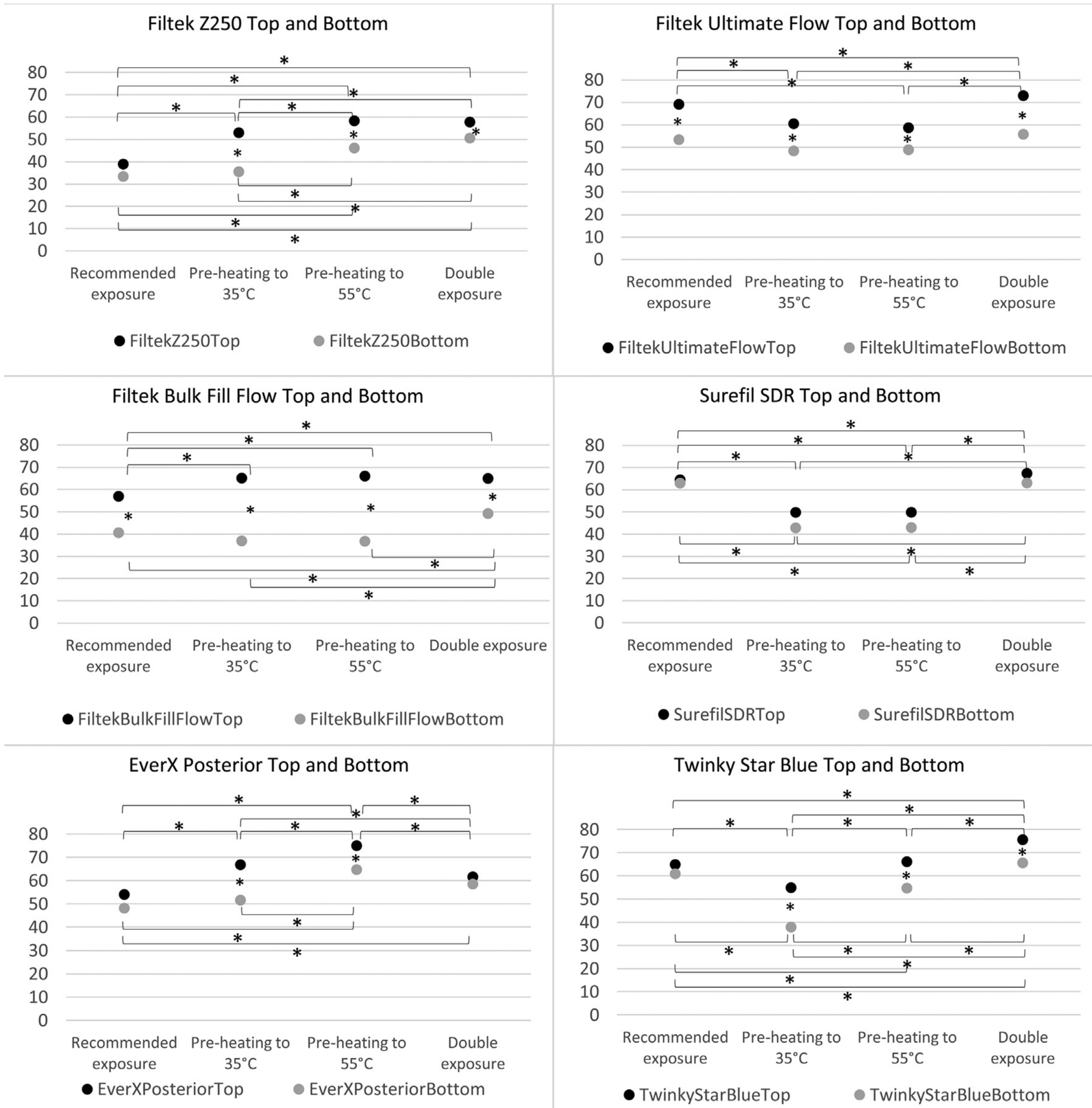

Fig. 4 – Degree of conversion at the top and the bottom of the investigated materials according to the polymerization methods. The * mark indicates a statistically significant difference between the investigated groups and as well as between top and bottom surfaces.

values (5–15% more) were measured compared to the single exposure at room temperature, except for SDR, which showed similar DC values both in Group 1 and 4. Double exposure time provided significantly higher DC for each material compared to the pre heated groups, except for EX, on which the effect of pre-heating to 55 °C dramatically improved the rate of polymerization. Fig. 3 demonstrates the degree of conversion at the bottom of the investigated materials according to the method of polymerization. Focusing on the bottom of the samples, the conversion degree of the different materials ranged between 33.4 and 65.6%. Similarly to the results of the top DC%, the lowest value was measured in case of FZ_20 and the highest was detected on TS_80. In general, at the bottom of the samples, in all cases, a lower value (5–15% less) could be measured than at the top. However, the decrease in DC was not statistically significant in any of the materials. Fig. 4 shows the degree of conversion and the statistical significance at the top and the bottom of the investigated RBCs according to the polymerization methods. In the case of FZ_20, EX_10, TS_40 (Group 1) and in EX_20 (Group 4) the difference was not statistically significant between the top and bottom DCs. In the case of SDR the DC of the top and bottom surfaces was similar in all groups. In the low viscosity materials pre-heating to 35 °C inhibited the DC level at the bottom to reach the DC values of Group 1(FUF_35_20, FBF_35_10, SDR_35_20, TS_35_40) and had no statistically significant effect on the high viscosity materials (FZ_35_20, EX_35_10). In Group 3, the same result was observed in almost all low viscosity materials and a significant increase was detected in the high viscosity RBCs (FZ_55_20, EX_55_10). Double exposure unequivocally increased the DC values at the bottom of the samples compared to Group 1, 2 and 3, except EX_20, where the highest DC was observed in Group 3, when the material was pre-heated to 55 °C.

The irradiance decreased from 1450 mW/cm^2 to 510 mW/cm^2 in the 4 mm deep mold, while in the case of the 6 mm deep mold with 5 mm internal diameter, it decreased to 450 mW/cm^2. The calculated radiant energy delivered to the samples is presented in Table 2.

4. Discussion

In this study a clinically relevant 8 mm deep, 5 mm wide mold was filled with six different RBCs in the recommended layer thicknesses, irradiated with the recommended and its doubled exposure time as well as pre-heated to 35 and 55 °C. The degree of conversion at the top and bottom surfaces was assessed using micro-Raman spectroscopy. Different type of RBC materials were included in this investigation: a commercial sculptable microhybrid RBC (FZ), a conventional flowable nanofill RBC (FUF), a nanofill flowable bulk-fill RBC (FBF), another flowable bulk-fill RBC (SDR), a short glass-fiber reinforced bulk-fill RBC (EX) and a colored polyacid- modified RBC (TS).

The polymerization process has a major influence on the mechanical and biological properties of light cured RBCs [3]. Resin composite polymerization depends on the chemical structure of the monomer, filler particle characteristics, the photoinitiator concentration and the polymerization conditions, such as the spectral irradiance, exposure duration, distance between the curing guide and the material, layer thickness, just to mention a few of them [31,32]. An increment thickness of 2 mm is the gold standard for composite resin placement and curing [23]. It is technique sensitive and time consuming in cases of deeper posterior restorations or during coronal sealing of an endodontically treated tooth. To address these problems, various manufactures have recently introduced the newest type of resins, so called bulk-fill materials which claim to cure at a maximum increment thickness of 4 mm.

According to our results, with the recommended exposure time (Group 1) the commercial sculptable RBC in 2 mm layer thickness with 20 s irradiation showed the lowest DC% at the top and bottom surface of the samples. This RBC has the highest amount of filler content (78 wt%) among the investigated materials, which exhibited the highest light distribution. Halvorson et al. demonstrated, that increasing the filler-matrix ratio progressively decreases conversion, because an increased amount of filler particles is an obstacle for polymeric chain propagation [33]. To provide acceptable depth of cure in 4 mm or more layer thickness, the manufacturers of bulk-fill RBCs were able to improve polymerization depth by the use of potent photoinitiator systems along with an increased translucency [34]. However, with the recommended exposure time, bulk-fill RBCs (except SDR) did not reach the DC level of the 2 mm thick commercial as well as the polyacid-modified flowable RBC's DC value at the top of the samples in our investigation. Each RBC product revealed an inverse correlation between DC and depth. The monomer to polymer conversions showed 5–15% lower values at the bottom, except for SDR, where the DC % reached the value measured at the top. It also exceeded the polymerization rate of the materials used in 2 mm layer thickness. The unique combination of glass filler loading with SDR resin provides high depth of cure in the recommended 4 mm thickness [35]. Besides the filler-matrix ratio, the DC is affected by the viscosity and reactivity of the monomers, as well [36,37]. In our study, only the SDR monomer system does not contain BisGMA, which is considered the most viscous, thus the less mobile monomer. SDR is a UDMA/EBPADMA-based bulk-fill flowable composite with additional TEGDMA, which has a synergistic effect on the rate of polymerization. Thus, the DC value of this monomer is significantly higher than that of the other investigated bulk-fill materials [38]. In addition, a photo-active modulator – embedded in the polymerizable resin backbone of the SDR resin monomer – may cooperate with camphorquinone (CQ), thereby facilitating polymerization.

In Group 4 with double exposure, the materials showed almost the same order, but with a 5–15% higher DC level on the top of the samples. It has been concluded by Zorzin et al., that extended curing time (30 s) had a positive effect on polymerization properties, so enhanced light curing of bulk-fills in deep cavities is recommended [39]. It is well-documented that radiant exposure (irradiance x exposure duration) of the light cure influences the DC and DOC of RBCs, thus a given radiant exposure can be delivered with different combinations of irradiance and exposure duration [25–27,40] Daugherty et al. concluded that the polymerization kinetics have been found to be highly complex, and a simple reciprocal relationship between radiant exposure and exposure time does not exist since irradiance and exposure can independently affect DC and DOC [41]. Increased depth of the cavity implies a radiant exposure reduction, whereas the irradiance of the light exponentially decreases with distance. Rueggeberg et al. and Emami and Söderholm concluded, that in order for a 2 mm thick conventional RBC increment to have adequate polymerization, it should receive a radiant exposure within the 16–24 J/cm^2 range [25,26]. In our study, an 8 mm deep cavity was simulated, where the distance between the light curing tip and the material top surface is increased, thus a decreased irradiance could initiate the polymerization. At 2 mm layer thickness (FZ, FUF, TS) the photons travel through 6 mm to reach the material's surface. This distance decreased the 1450 mW/cm^2 irradiance provided by the LED curing unit to ~740 mW/cm^2, however the small – 5 mm in diameter – orifice of the cavity further decreased the irradiance to 450 mW/cm^2. At 4 mm layer thickness (FBF, SDR, EX) in the 8 mm deep simulated cavity the photons travel through 4 mm distance, which decreases their radiant power to 930 mW/cm^2, and the shuttering effect of the narrow orifice resulted in 510 mW/cm^2 irradiance. The beneficial effect of the longer exposure duration is evident in group 4 in these conditions, however the DC of the different materials was not in correlation with the radiant exposure. The exception was TS, where the doubled exposure time increased the radiant exposure to 36 J/cm^2, resulted in 75.6% DC at the top surface and 65.6% at the bottom of the sample, which was the highest rate of polymerization among the investigated materials. The conventional flowable RBC (FUF) in also 2 mm layer thickness received 18 J/cm^2 radiant exposure and performed well with its 73% DC level at the top surface. The bulk-fill materials failed to reach the DC value of the 2 mm thick flowable RBC's, but exceeded the polymerization rate of the sculptable FZ. At the bottom of the specimens, however, the bulk-fill RBCs performed better than the conventional RBCs used in 2 mm thickness, except FBF. The composition and initiator system of SDR and EX provided a convincing DC% through its 4 mm layer thickness without significant difference between the top and the bottom surfaces, cured in an 8 mm deep simulated cavity. Although, the highest DC was provided by TS (received 36 J/cm^2), there was no significant difference found between TS and SDR (received 20.4 J/cm^2), or TS and EX (received 10.2 J/cm^2) at the bottom surface in Group 4. According to our results, SDR was unique among the investigated materials with its 63% degree of conversion at the bottom of the samples, both in Group 1 and 4. It means, the rate of polymerization was the same (63%) with the recommended (20 s) and its double (40 s) exposure time in an 8 mm deep simulated cavity with 4 mm layer thickness.

Considering EX, in spite of the fact, that the 4 mm thick EX sample received less energy density (10.2 J/cm^2) compared to the 2 mm thick conventional one (18 J/cm^2), provided higher DC% at the bottom of the 4 mm thick sample. In fact, did not differ significantly from the highest values of TS and SDR, which received greater radiant exposure, 36 J/cm^2 and 20.4 J/cm^2, respectively. Certainly the short glass fibers have great significance in providing high depth of cure with the extended curing time (20 s) at the bottom of the samples. Similarity between the fiber/matrix refractive indices may allow light penetration into the deeper parts of the material. Goracci et al. concluded in their experiment, that EX exhibited DOC over 4 mm, the maximum thickness recommended for bulk placement [42]. From the available bulk-fill RBCs, besides SDR and EX, FBF was also investigated in this study. A universal shade was selected for all three brands. The absence or low amount of pigments in universal shaded, more translucent composite resin materials also have a beneficial effect on DC or depth of cure because pigments are opaque particles that will limit light penetration and reduce the degree of polymerization at greater depths [43] Although, Ilie found no correlation among DC and light transmittance. It was concluded, that light transmission changes during polymerization do not alter polymerization kinetics in modern bulk-fill RBCs [44]. Among bulk-fill materials in the present study, FBF has the lowest filler loading and the highest translucency parameter [45]. Despite of these advantageous parameters, FBF failed to reach the DC of the other investigated materials, especially at the bottom of the 8 mm deep simulated cavity in Group 1 and 4, except for FZ. In accordance with previous studies, the DC values for FBF were lower compared to the conventional flowable RBCs or to the other investigated bulk-fill materials [6,44]. Considering the chemical composition of FBF, it has the same filler content than the conventional flowable RBC (FUF) from the same manufacturer, however the matrix composition is different. FUF contains highly viscous BisGMA, low molecular weight, highly mobile and reactive TEGDMA as a diluting monomer and a Procrylate monomer. In case of FBF, besides Procrylate resin, BisGMA was combined with UDMA and BisEMA, instead of TEGDMA. Although the viscosity of UDMA is much lower than that of BisGMA, when it is mixed with the high molecular weight BisEMA, it can significantly restrict the mobility of UDMA monomers and decrease their reactivity and conversion value [6,46]. The other influencing factor of DC is the radiant exposure delivered to the material. With the recommended 10 s curing time and 1450 mW/cm^2 irradiance, the delivered energy density was only 5.1 J/cm^2, which increased to 10.2 J/cm^2 with the extended irradiation time.

In Group 2 and 3 the effect of pre-heating on degree of conversion was investigated. Increasing the temperature of the RBC before application, decreases their viscosity, therefore enhances the marginal adaptation, reduces microleakage [17], and significantly reduces shrinkage force formation [22], while maintaining or increasing the degree of conversion and crosslinking by enhancing free radical and monomer mobility and increasing collisions among molecules [20,21]. The restoration of deep cavities with a narrow orifice – *i.e.* pulp chamber – could be difficult, considering the decreased irradiance of the curing light, that can reach the surface of the first RBC layer. Based on these considerations, the aim of increasing the temperature of the investigated materials was to determine the influence on degree of conversion in 8 mm deep – clinically relevant – simulated cavities. Two temperature values were used, 35 °C and 55 °C. As Fig. 3 shows, both in Group 2 and 3 two main effect was detected. In case of sculptable conventional RBC (FZ) and sculptable glass-fibre reinforced bulk-fill RBC (EX) a significant increase in DC% was found as a positive influence of pre-heating. In Group 2, the increase was remarkable at the top and less, but significant, at the bottom of the samples. In Group 3 the pre-heating to 55 °C increased the DC level by 20% at the top and around 15% at the bottom. This increase at the top of FZ and EX exceeded the DC values found in group 4, however, the DC% was higher at the bottom only for EX, compared to the double exposure. On the other hand, in case of the flowable RBCs, a negative effect on DC% was detected both in Group 2 and 3, especially at the bottom of the samples, compared to Group 1. Interestingly, there was not significant difference in DC values of flowable RBCs at the bottom between Group 2 and 3. At the top, the results were not as homogenous than at the bottom: in case of FUF, SDR and TS_35_40 a significant decrease was detected, meanwhile FBF showed a significant increase. The unexpected decrease of DC level of pre-heated (both 35 °C and 55 °C) flowable RBCs from the top to the bottom may be caused by the rapid cooling process of materials with lower filler content [47]. In our study the material was placed in an 8 mm deep mold under a non-isothermal condition, where the composite temperature reached after pre-heating is not stabilized, in order to simulate a clinically realistic scenario. Plasmans et al. reported an intraoral temperature of 25.1 °C around the treatment area after rubber dam isolation [48]. Studies, that have shown improvement in monomer conversion upon pre-heating generally maintained the resin composite temperature constant during the experimentation [20,21]. Once RBC temperature is elevated, there is a time delay between removing it from the heating device, dispensing it from a canula or syringe, placing it into an occasionally deep cavity, contouring it, and subsequently light-curing it. Our preliminary investigations revealed that during the 40 s manipulation time interval between RBC removal from the heater and start of photoactivation with 20 s, the temperature of the 55 °C pre-heated flowable test materials decreased to 26.2 °C. Results provided by Lohbauer et al. also confirm that RBC's temperature rapidly drops to the physiological level upon removal from the pre-heating device [18]. Polymerization is an exothermic process and the heat liberated tends to accelerate the curing reaction. Generated heat increases the system temperature leading to decrease of viscosity and improves molecular mobility, increasing collision frequency of reactive radicals and postponing diffusion-controlled propagation, also known as autodeceleration, thus increasing final conversion [21]. However, during cooling the polymer formation has an excess heat loss. It deprives energy from the system, which is necessary for polymer chain propagation. The gel-phase interval may be decreased, autodeceleration takes place and leads to early vitrification, decreasing the degree of conversion. The polymerization as an exothermic process is influenced by the environmental temperature, curing time, monomer and filler content and nature of the filler surface [49]. Our results show different effect of pre-heating thermal changes on RBCs, probably depending on their filler content. On highly filled RBCs (FZ, EX) the pre-heating had a positive effect, it could increase significantly the DC% at the top and bottom, however on RBCs with lower filler content, the pre-heating even resulted in a negative effect on the bottom of the samples. These results are contradictious to most of the previous experiments [20,21], however Tauböck et al. reported similar, non-isothermal, real scenario pre-heating experiments and among the five investigated materials, only one showed significant DC% increase resulted from the pre-heating and in case of three materials, a non-significant DC% decrease was presented [22]. The observed DC% values and changes reflect overall result of the temperature dependent complex processes. It is speculated, that, on one hand, the higher volume content of inorganic fillers kept more energy and allowed for a delayed autodeceleration. According to another aspect, Plueddemann stated, that organofunctional silane coupling agents are hybrid organic-inorganic compounds which act as an interface between inorganic filler and organic polymer matrix and can help overcome the obstacle resulting from the mismatch of thermal coefficient [50]. In sculptable RBCs the filler content, thus the filler/matrix interface is higher. The dynamic equilibrium created at the silane interface between the filler and the polymer may provide higher exotherm reaction and dense bond formation at the deeper regions as well. This effect is stronger when the temperature increased to a higher level. On the other hand, in case of the less-filled RBCs, the highest DC% values were resulted on room temperature and most of them showed a negative effect of the pre-heating, indicating that, some part of the exothermic polymerization reaction is shifted towards the reactants, or the chain propagation is inhibited. Itś worth to mention here also, that in most cases of polymerization the entropy change associated with the building of one new segment into the chain continuously decreases since the rotational freedom of the chain decreases with an increasing length of the chain. The large negative entropy change inhibits the spontaneous growth of the chain due to the very small or positive free enthalpy (Gibbs free energy). Due to its complexity, further investigations are necessary to clarify this phenomenon. Preliminary testing of FZ and FUF in 8 mm deep cavity at isothermic (55 °C) condition resulted in 65 DC% and 63 DC% at the top and 59 DC% and 60.5 DC% at the bottom, respectively. These are higher DC values, compared to the results observed in this present study under clinically relevant conditions, therefore supporting the results that were concluded in previous experiments [20,21]. However, the above mentioned measurements are under work, supplemented with continuous testing of thermal changes during the restorative procedures. In some cases of flowable RBCs (FUF and TS_55_40) the preheating provided enough energy to reach higher DC level at the top, however the sudden drop of temperature decreased the diffusion-controlled propagation towards the bottom of the samples leading to lower DC, compared to the control group (Group 1).

The minimum DC% for clinically acceptable restoration has not yet been exactly recognized [51]. Soares et al. reported that, for occlusal restorative layers, DC values should be at least 55% [52]. In our investigation the samples represented the first layer of light-cured RBC, which are covered with more subsequent layers in clinical situation. However, the adequate degree of monomer conversion is also essential at the bottom of the cavity close to the pulp space or at the proximal gingival margin. According to our results in Group 1 only SDR and TS, only EX in Group 3 and FUF, SDR, EX and TS in group 4 provided this DC level at the bottom of the samples in an 8 mm deep and 5 mm wide simulated cavity.

Present study, however, has some limitations. Firstly, this is an *in vitro* study and the specimens were prepared in a teflon mold and irradiated from an "occlusal" direction. In case of *in vivo* circumstances there is a possibility to irradiate the composite resin specimen from a buccal or lingual aspect as well, to improve the DC. Although, indirect polymerization of the RBCs through a substance significantly reduces the radiant exposure delivered to the material, since the tooth absorbs the energy originated from the photocuring device [53]. Secondly, the DC measurements do not yield information about the mechanical properties or the development of contraction stress in the investigated materials in response to recommended or doubled duration exposures and pre-heating. Although, direct correlation existed between hardness and DC, further mechanical testing, like three-point bending is planned to get more information about the relation of DC and mechanical characteristics. Thirdly, a commercial handheld dental radiometer was used in this survey to measure the radiant exitance from the curing unit and to calculate the radiant exposure received by the RBC through the mold with 4 and 6 mm depth and 5 mm internal orifice diameter. Price et al. discourages the use of irradiance values derived from a dental radiometer to describe the real spectral radiant power from an LCU [32]. However, in our study only one type of LCU was used and all the specimens were prepared in molds with the same dimension in diameter and with standardized LCU tip positioning to the mold's orifice, thus the spectral radiant power was similar for all the investigated materials and the received energy density was influenced only by the distance between the light curing tip and the material. Although, the values of the calculated radiant exposure are not accurate due to the usage of a radiometer, it is presumed, that the comparison of resulted DC data for the investigated materials is relevant. Finally, further investigations are necessary to clarify the negative effect of pre-heating on the DC of flowable RBCs.

5. Conclusion

Within the limitations of this *in vitro* study – simulating an eight mm deep clinically relevant simulated cavity – the following conclusions can be stated:

1) Significantly higher DC levels were measured at the top of the samples compared to the bottom in each investigated material, in each experimental group, except SDR in Group 1 and 4.
2) Doubling the exposure time had a significant effect on DC% except for SDR. It provided the highest DC% at the bottom of the samples in Group 1 and 4, regardless the exposure time, thus the radiant exposure.
3) Radiant exposure had no direct correlation with DC especially in bulk-fill RBCs.
4) Pre-heating had a positive effect on the DC% of the high-viscosity RBCs (especially 55 °C on the DC% of EX) and had negative effect on DC% of the low-viscosity RBCs at the bottom of the samples.

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