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**In-vitro-Untersuchung neuartiger fließfähiger Komposite
(selbstadhäsiv, „bulk-fill“ und niedrigrumpfend)**

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1 Einleitung

Die Ansprüche, die an moderne fließfähige Komposite gestellt werden, steigen immer weiter. Neben ausgezeichneten mechanischen Eigenschaften wird besonderer Wert auf zusätzliche Eigenschaften wie Selbstadhäsion, geringe Polymerisationsschrumpfung und immer einfachere Verarbeitbarkeit gelegt. Im Zuge dessen gab es zahlreiche Innovationen: Die Veränderungen im chemischen Aufbau und der Füllkörper führte zu vielen verschiedenen Komposittypen [1].

Vor kurzem wurde eine neue Entwicklung, die sogenannten „bulk-fill“ Komposite, vorgestellt. Es soll die besondere Möglichkeit bestehen, das Material in 4 mm dicken Inkrementen - statt der momentanen Inkrementtechnik mit maximal 2 mm dicken Inkrementen - in den Zahn einzubringen ohne dabei die Polymerisationsschrumpfung, die Konversionsrate oder die Passung zum Kavitätenrand negativ zu beeinflussen. Darüber hinaus behaupten die Hersteller, dass diese Materialien sogar eine deutlich niedrigere Schrumpfung als moderne fließfähige Komposite haben [2]. Die mit hoher Kompositsschrumpfung verbundenen Probleme [3] wie Randspaltbildung [4, 5] oder post-operative Sensibilitätsbeschwerden [6] könnten somit vermieden werden. Laut Hersteller sollen die Materialien sogar eine ausreichende Aushärtung bis zu einer Inkrementdicke von 6 mm erfahren [2]. Leider fehlen hierzu bislang die grundlegenden Studien. Dennoch würde ein an die Kavitätenwände anfließendes Komposit eine enorme Zeit- und Kostenersparnis für die Praxis darstellen. Das „bulk-fill“ Komposit Surefil® SDR™ (Smart Dentin Replacement, shrinkage decreased resin) beinhaltet einen im Polymerisationsgerüst chemisch eingebundenen Polymerisationsmodulator, der zu einer reduzierten Polymerisationsschrumpfung beitragen soll. Der Modulator hat ein hohes molekulares Gewicht. Dank der konformativen Flexibilität um den eingebundenen Modulator herum sollen Flexibilität und Gerüststruktur optimiert werden. Untersuchungen von Kompositen die auf SDR™ Technologie basieren zeigten signifikant niedrigere Schrumpfungswerte, nicht nur im Vergleich mit anderen fließfähigen Kompositen [7] sondern auch mit Nano- und Hybridkompositen [8]. De Biasi et al. untersuchten die mikromechanische Härte eines SDR™ Komposits und äußerten Bedenken bezüglich der praktischen Anwendbarkeit aufgrund der geringen

Vickershärte [9]. Ilie et al. teilten diese Bedenken: sie maßen für das SDR™ Komposit die geringsten Oberflächenwerte verglichen mit anderen oftmals verwendeten Kompositen (EsthetXFlow, Filtek Supreme Plus Flow, EsthetX Plus, Filtek Silorane, Filtek Supreme Plus) [10]. Bezüglich Verschleiß, Oberflächenrauigkeit, Politurfähigkeit und Verfärbungsresistenz wurden vergleichbare Werte mit anderen klinisch erfolgreich verwendeten Kompositen erreicht [7].

Eine der neuesten Entwicklungen zur Vereinfachung des klinischen Behandlungsablaufs sind die selbstadhäsiven fließfähigen Komposite, die weder eine Vorbehandlung der Restzahnhartsubstanz mittels Phosphorsäure noch eines Dentin-Bonding-Agents benötigen [11]. Seit der Einführung der Komposite stellte deren Befestigung an den Kavitätenwänden der Zahnhartsubstanz Forscher und Entwickler vor eine schwere Aufgabe. Nachdem Buonocore eine Methode zur Verbesserung der Restaurationsbefestigung vorstellte [12], entwickelten zahlreiche Forscher neue, einfachere und qualitativ hochwertigere Ätz- und Bondingsysteme [13]. Eines davon ist die Herstellung selbstadhäsiver Komposite [14], Zemente [15] oder Adhäsive [16, 17] mittels eines speziellen Dimethacrylatmonomers: Glycerol Phosphat Dimethacrylat (GPDM). Dieses Monomer erlaubt die chemische Verbindung seiner Phosphatgruppe mit Calciumionen der Zahnhartsubstanz. Zusätzlich dazu trägt die mikromechanische Verankerung zwischen dem sich aufbauenden Polymer und den durch die Phosphatgruppe des GPDM freigelegten Kollagenfasern wie auch die mechanische Verbindung zwischen dem Polymer und dem „Smear layer“ zur Befestigung der Restauration an der Zahnhartsubstanz bei [1]. Wenn man allerdings die Haftkraft selbstadhäsiver Komposite zum Zahnschmelz mit der Haftkraft der state-of-the-art „etch and rinse“ Adhäsive vergleicht, schneiden die Erstgenannten deutlich schlechter ab [18-21]. Ein weiterer Nachteil von Ein-Flaschen-Adhäsiven ist in ihrer relativ hohen Wasseraufnahme zu sehen [22, 23]. Die Haftscherfestigkeit zu oberflächlichem wie auch zu tiefer gelegenem Dentin von GPDM-basierten Adhäsiven wurde in diversen Studien als vergleichbar mit anderen selbstätzenden und „etch-and-rinse“ Adhäsivsystemen befunden [21]. Auch die Hydrolyse des Zahn-Restaurationsüberganges mit den bekannten möglichen Folgen wie Microleakage, Verfärbungen, Sekundärkaries bis hin zur Devitalisierung der Pulpa ist als mögliche Komplikation zu nennen.

Ein weiterer Wunsch der modernen restaurativen Zahnheilkunde ist die Verringerung der Polymerisationsschrumpfung. In einer Untersuchung in der die Polymerisationsschrumpfung eines experimentellen Komposits mit verschiedenen

Monomierzusammensetzungen gemessen wurde, fanden Ellakwa et al. beispielsweise heraus, dass eine negative Korrelation zwischen der Schrumpfung und dem Molekulargewicht des jeweiligen Monomers besteht [24].

Einige der modernen fließfähigen Komposite verzichten zugunsten hochmolekularer Monomere soweit möglich auf niedermolekulare Monomere wie Triethylenglycoldimethacrylat (TEGDMA) (286 g/mol) und 2-Hydroxyethylmethacrylat (HEMA) (130 g/mol). Neben klassischen Monomeren wie Bisphenylglycidylmethacrylat (BisGMA) (512 g/mol) und ethoxyliertem Bisphenol-A-Dimethacrylat (BisEMA) (540 g/mol) [25] werden heutzutage auch die neu entwickelten Dimersäure-Dimethacrylate (574 g/mol) [26-28] verwendet. Diese versprechen eine höhere Konversionsrate, höhere Biegemodulwerte und die Möglichkeit einer dickeren Inkrementplatzierung [29].

Ziel der nachfolgenden zwei Artikel war es, die Auswirkungen der Veränderung von chemischer Struktur und Zusammensetzung von anorganischer und organischer Phase auf mikromechanische (Vickershärte, Eindringmodul) und makromechanische Eigenschaften (Biegefestigkeit, Biegemodul) sowie die Konversionsrate bei verschiedenen Belichtungszeiten und klinisch relevanten Inkrementdicken zu untersuchen. Als Materialien dienten dabei zwei „bulk-fill“ (Inkrementdicke bis zu 4 mm), ein selbstadhäsives (keine Vorbehandlung der Kavität), zwei „low-shrinkage“ (niedrigschrumpfend) und als Kontrollgruppe zwei zur Gruppe der Mikrohybride gehörige fließfähige Komposite.

2 Veröffentlichte Artikel

2.1 „In-vitro comparison of mechanical properties and degree of cure of bulk-fill composites“

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Abstract:

OBJECTIVES: The aim of our study was to measure and compare degree of conversion (DC) as well as micro- (Indentation modulus, E, Vickers hardness, HV) and macromechanical properties (Flexural strength, σ , Flexural modulus, E_{flexural}) of two recently launched bulk-fill RBCs (resin-based composites): Surefil® SDR™ flow (SF) and Venus® bulk fill (VB).

MATERIALS AND METHODS: DC (n=6) was investigated by FTIR-Spectrometry in clinical relevant filling depths (0.1 mm, 2 mm, 4 mm, 6 mm-bulk, 6 mm-incremental) and irradiation times (10s, 20s, 40s). Micro- (n=6) and macromechanical (n=20) properties were measured by an automatic microhardness indenter and a three-point bending test device after storing the specimens in distilled water for 24 h at 37°C. Furthermore, on the 6 mm-bulk samples the depth of cure was determined. A field emission scanning electron microscope was used to assess filler size. Results were evaluated using one-way ANOVA, Tukey HSD post-hoc test, a multi-variate analysis ($\alpha=0.05$) and an independent t-test. Weibull analysis was used to assess σ .

RESULTS: VB showed in all depth significant higher DC (VB: 62.4-67.4%; SF: 57.1-61.9%), but significant lower macro- (VB: $E_{\text{flexural}}=3.6\text{GPa}$; $\sigma=122.7\text{MPa}$; SF: $E_{\text{flexural}}=5.0\text{GPa}$; $\sigma=131.8\text{MPa}$) and micromechanical properties (VB: $E=7.3\text{-}8.8\text{GPa}$, $\text{HV}=40.7\text{-}46.5\text{N/mm}^2$; SF: $E=10.6\text{-}12.2\text{GPa}$, $\text{HV}=55.1\text{-}61.1\text{N/mm}^2$). Both RBCs showed high reliability (VB: $m=21.6$; SF: $m=26.7$) and a depth of cure of at least 6mm at all polymerization times. The factor “RBC” showed the strongest influence on the measured properties ($\eta^2=0.35\text{-}0.80$) followed by “Measuring Depth” ($\eta^2=0.10\text{-}0.46$) and “Polymerization time” ($\eta^2=0.03\text{-}0.12$).

CONCLUSIONS: Significant differences between both RBCs were found for DC, E, σ and E_{flexural} at all irradiation times and measuring depths.

CLINICAL RELEVANCE: Curing the RBCs in 4 mm bulks for 20s can be recommended.

Keywords:

Bulk-fill, composite, macro-mechanical properties, micro-mechanical properties, degree of conversion;

Introduction:

Since the development of resin-based composites (RBCs) several improvements in their chemical composition as well as various filler reinforcements occurred, leading to a large category of materials [1]. Recently a new category of flowable RBCs – so called bulk-fill RBCs- was introduced (Surefil® SDR™ flow, Dentsply, Caulk, USA and Venus® bulk fill, Heraeus Kulzer GmbH, Hanau, Germany) as bulk-fill material and as liner in Class I and II restorations. The particularity of the new material category is stated to be the option to place it in 4 mm thick bulks instead of the current incremental placement technique, without negatively affecting polymerization shrinkage, cavity adaptation or the degree of conversion (=DC). Moreover manufacturers stated that the polymerization shrinkage of those materials is even lower when compared to commonly used flowable and conventional RBCs [2]. Thus, problems related to polymerization shrinkage [3] like gap formation causing secondary caries due to bacteria colonization [4,5], pulp irritation, post-operative sensibility when chewing [6] or cusp deflection when the “C” factor is high [7,8], could be minimized. Manufacturers claimed that bulk-fill materials can achieve a depth of cure of 6 mm [2], though no published investigations are available till now to confirm these statements. Nevertheless the idea of placing a self-adapting material as bulk, saving time as well as improving material handling is of great interest.

The bulk-fill material Surefil® SDR™ (Smart Dentin Replacement, Shrinkage Decreased Resin) flow contains a polymerization modulator, chemically embedded in the center of the polymerizable resin backbone of the SDR™ monomer, to lower polymerization shrinkage. The modulator has a high molecular weight. Due to the conformational flexibility around the centered modulator impart, the modulator is supposed to optimize flexibility and network structure of the SDR™ resin [9]. Investigations on RBCs with SDR™ technology showed significant lower shrinkage stress values [10] not only when compared to regular flowable RBCs, but also to nano- and hybrid RBCs or even to silorane-based composites [11]. De Biasi et al. investigated microhardness and raised concerns about its practical use due to its low Vickers hardness (=HV) [12]. This was also confirmed by Ilie et al. [11] where Surefil® SDR™ flow showed the lowest surface hardness when compared to other commonly used RBCs (EsthetX Flow, Filtek Supreme-Plus-Flow, EsthetX-Plus, Filtek Silorane and Filtek Supreme-Plus). However, when compared to the investigated flowable RBC of the same study, Surefil® SDR™ flow showed significant higher indentation modulus

(=E). In view of wear, surface roughness, gloss, color stability and stain resistance, similar results to clinically successful RBCs were found [10]. Other experimental flowable RBCs with SDR™ technology – P&P-Adaptable and P&P-Universal (both Dentsply) – also showed low shrinkage stress values [13]. Moreover Surefil® SDR™ flow was used for luting fiber posts and resulted comparable regarding retentive strength like a dual resin cement commonly used [14].

This study evaluated and compared two bulk-fill RBCs - Surefil® SDR™ flow and Venus® bulk fill – regarding their micro- and macromechanical properties and DC at different irradiation times and by simulating clinical relevant filling depth.

The tested null hypothesis were that: a) there would be no significant difference between the two materials in view of macro- (flexural strength ($=\sigma$), modulus of elasticity ($=E_{\text{flexural}}$)) and micromechanical properties (Vickers hardness HV, indentation modulus E) and degree of cure (DC) at any measured depth and irradiation time; b) within one material, irradiation time and depth would not influence the measured properties.

Materials and methods:

Two flowable bulk-fill RBCs - Surefil® SDR™ flow (Dentsply, Caulk, USA, Lot No.: 100407, 100507) and Venus® bulk fill (Heraeus Kulzer GmbH, Hanau, Germany, Lot No.: 010026) were analyzed by assessing DC and micromechanical properties (HV, E) as function of depth and polymerization time (10s, 20s or 40s) as well as the macromechanical properties (σ , E_{flexural}). Due to manufacturers' information Surefil® SDR™ flow consists of Ba–Al–F–B–Si–glass and St–Al–F–Si–glass as fillers (68% per weight, 44% per volume) and modified Urethane dimethacrylate (UDMA), Triethyleneglycol dimethacrylate (TEGDMA) and ethoxylated Bisphenol-A-dimethacrylate (EBPDMA) as resin matrix. For Venus® bulk fill, Ba–Al–F–Si–glass and SiO₂ were given as fillers (65% per weight, 38% per volume) and UDMA and EBPDMAs as resin matrix.

Degree of cure measurements:

To evaluate the DC, five different sample geometries were considered. Thin films (100 μm) as well as 2 mm, 4 mm and 6 mm high molds (3 mm diameter) were filled in bulk. Additionally three consecutive increments - each 2 mm high - were prepared in the mold of 6 mm height (6 mm-incremental). Samples were cured by applying the curing unit (Elipar Freelight2, 3M ESPE, 1226 mW/cm²) directly on the top of the particular mould, respectively on the film surface covered by a transparent matrix strip. For each product, irradiation time (10s, 20s, 40s) and geometry (0.1 mm, 2 mm, 4 mm, 6 mm-bulk, 6 mm-increment) six samples were measured (n=6). Real-time measurements were made with a FTIR-Spectrometer with an attenuated total reflectance (ATR) accessory (Nexus, Thermo Nicolet, Madison, USA). Therefore, the non-polymerized RBC paste was put directly on the diamond ATR crystal in the mold as described above. FTIR spectra were recorded in real time for 5 minutes at the bottom of the samples irradiated according to the curing protocol presented above. Diameter of measured surface was 800 μm , wave number of the spectrum ranged between 4000–650 cm^{-1} and the FTIR spectra were recorded with four scans at a resolution of 8 cm^{-1} .

To determine the percentage of the remained unreacted double bonds, the DC was measured by assessing the variation in peak height ratio of the absorbance intensities of methacrylate carbon double bond peak at 1634 cm^{-1} and that of an internal standard peak (=IS) at 1608 cm^{-1} (aromatic carbon double bond) during polymerization, in

relation to the uncured material. For the RBC Surefil® SDR™ flow, the reference peak was set at 1600 cm^{-1} due to the absence of the aromatic carbon bond.

$$DC_{\text{height}} \% = \left[1 - \frac{\left(\frac{1634\text{cm}^{-1}}{\text{IS}} \right)_{\text{Peak after curing}}}{\left(\frac{1634\text{cm}^{-1}}{\text{IS}} \right)_{\text{Peak before curing}}} \right] \times 100$$

Micro-mechanical properties:

The variation in micromechanical properties (HV, E) was assessed on the 6 mm bulk samples prepared for the DC measurements. For this purpose, samples were stored in distilled water after curing for 24 hours at 37°C , ground and polished under water in longitudinal direction from 3 mm diameter to 1.5 mm diameter with diamond abrasive paper (mean grain sizes: $20\ \mu\text{m}$, $13\ \mu\text{m}$, $6\ \mu\text{m}$) in a grinding system (EXAKT 400CS, Exakt, Norderstedt, Germany). Measurements were made with an automatic microhardness indenter (Fischerscope H100C, Fischer, Sindelfingen, Germany) starting from 0.1 mm under the surface, with $100\ \mu\text{m}$ intervals between the measuring points. The test procedure was carried out force-controlled, where the test load increased and decreased with constant speed between 0.4 mN and 500 mN. Load and penetration depth of indenter (Vickers pyramid: diamond right pyramid with a square base and an angle of $\alpha = 136^{\circ}$ between the opposite faces at the vertex) were continuously measured during the load-unload hysteresis. Universal hardness is defined as the test force divided by the apparent area of indentation under the applied test force. From a multiplicity of measurements stored in a database supplied by the manufacturer, a conversion factor (0.0945) between Universal hardness and HV was calculated by the manufacturer and entered into the software, so that the measurement results were indicated in the more familiar HV units. E was calculated from the slope of the tangent adapted at the beginning (at maximum force) of the non-linear indentation depth curve upon unloading.

HV and E variations with depth and irradiation time were calculated for each product (Tables 3 and 4) based on data from six samples (360 measuring points).

The depth of cure, usually acknowledged as the thickness of a RBC that is adequately cured [15] or rather as the depth where HV equals the surface value multiplied by an arbitrary ratio, usually 0.8 (=HV-80%) [16], was calculated. Therefore for each sample

HV in the depth was compared to the related surface value and noted when it became less than 80% (HV-80%).

Flexural strength and flexural modulus:

σ was determined in a three-point-bending test according to ISO/DIN 4049:1998. The samples (n=20) were made by compressing the RBC material between two glass plates with intermediate polyacetate sheets, separated by a steel mould having an internal dimension of (2 x 2 x 16) mm. After curing (with three light exposures of 20 seconds per side, Elipar Freelight2, 3M ESPE) the specimens were removed from the mould and any flash material was trimmed away with sandpaper (grit size P4000 (FEPA)). All specimens were then stored in distilled water at 37°C prior to testing for 24 h. Samples were loaded until failure in the universal testing machine (MCE 2000ST, quick test Prüfpartner GmbH, Langenfeld, Germany). The crosshead speed was 0.5 mm/min. The specimens were placed on a three-point bending test device, which is constructed according to the guidelines of NIST No. 4877 with 12 mm distance between the supports. During testing the specimens were immersed in distilled water at room temperature.

Flexural strength was calculated from formula (1).

$$(1) \quad \sigma = \frac{3Fl}{2bh^2}$$

F is the maximum load [N], l is the distance between the supports [mm], b is the width of the specimen [mm], h is the height of the specimen [mm].

The universal testing machine stored the force during bending and the deflection of the beam in a file. The bending modulus was calculated from formula (2).

$$(2) \quad E_{flexural} = \frac{Fl^3}{4bh^3y}$$

y is the deflection at load point [mm].

Field emission scanning electron microscope (FE-SEM):

For each product one specimen (1cm x 1cm x 0.5cm) was manufactured with an irradiation time of 60s and treated for one hour in a chemical dry cleaning process with oxygen plasma in vacuum (45 - 50 W). Afterwards surfaces were investigated (Magnification: 10000x, Signal: Secondary electrons SE2, Working distance: 4 mm, Electron high tension: 10 kV) with a field emission scanning microscope (FE-SEM)

(Zeiss Supra® 55 VP, Zeiss NTS GmbH, Oberkochen, Germany) and the most representative picture was chosen for assessing fillers' size.

Statistical analysis:

The results for DC, HV and E within each material, each measuring depth and each curing time, respectively, were compared using one-way ANOVA and Tukey's HSD post hoc-test ($\alpha = 0.05$) (SPSS 18.0, Chicago, IL, USA). An ANOVA multivariate analysis and partial eta-square statistic was used to investigate the influence of the parameters "RBC", "measuring depth" and "polymerization time" on E, HV, DC. For the properties E_{flexural} and σ the influence of "RBC" was assessed. Additionally a Weibull analysis was used to assess σ .

A common empirical expression for the cumulative probability of failure P at applied stress is the Weibull model:

$$P_f(\sigma_c) = 1 - \exp\left[-\left(\frac{\sigma_c}{\sigma_0}\right)^m\right]$$

where σ_c is the measured strength, m the Weibull modulus and σ_0 the characteristic strength, defined as the uniform stress at which the probability of failure is 0.63. The double logarithm of this expression gives:

$$\ln \ln \frac{1}{1-P} = m \ln \sigma_c - m \ln \sigma_0$$

By plotting $\ln \ln(1/(1-P))$ versus $\ln(\sigma)$, a straight line results, with the upward gradient m, whereas the intersection with the x-axis gives the logarithm of the characteristic strength.

Results:

The influence of the parameters “RBCs”, “Measuring Depth” and “Polymerization time” as well as their interaction products was analyzed in an ANOVA multivariate test (Table 1). DC and the mechanical properties – HV, E, σ and E_{flexural} - were selected as depended variables. The significance values of these three main effects were less than 0.05, indicating that they contribute all to the model. The “RBCs” was the parameter exerting the strongest influence on all measured properties (higher eta square values). The influence of the “Measuring Depth” was stronger on the micro-mechanical properties (HV, E) than on DC, whereas the influence of polymerization time, though significant, was very low.

A one-way ANOVA was used to identify detailed differences in the measured properties within each material as function of polymerization times (horizontal lines in tables 2 to 4) and geometries (vertical lines in tables 2 to 4).

A significant increase ($p < 0.05$) in DC (Table 2) with increasing polymerization time was found for Surefil® SDR™ flow only at 4 mm (between 10s and 40s) and 6 mm depth bulk placement (between 20s and 40s) whereas for Venus® bulk fill this statement is only valid at 4 mm (between 10s and 20s, respectively 40s) and 6 mm depth (bulk: between 10s and 20s; incremental: between 10s and 40s).

The DC at 6 mm depth bulk versus incremental placement was significantly lower only at low polymerization times (10s and 20s for Surefil® SDR™ and 10s for Venus® bulk fill).

Comparing both RBCs it can be seen that Venus® bulk fill had a statistically significant higher DC (about 5%) for all irradiation times and measuring depths.

Concerning the variation of E (Table 3) results showed for both RBCs significant ($p < 0.05$) lower values for 0.1 mm when compared to 2 mm depth as well as statistically equal values for 2 mm and 4 mm depth at all polymerization times. Similar trend is also valid for HV (Table 4). As for the incremental thickness, the HV-80% was not reached in the 6 mm samples at any polymerization time in both measured RBCs.

Comparing both RBCs, Surefil® SDR™ flow showed statistically significant higher values for E (about 3 GPa) and HV (about 15 N/mm²) at all irradiation times and measured depths.

The investigated macromechanical properties σ and E_{flexural} revealed for Surefil® SDR™ flow a significantly higher σ (131.8 ± 5.8 MPa) and E_{flexural} (5.0 ± 0.4 GPa) when compared to Venus® bulk fill ($\sigma = 122.7 \pm 6.9$ MPa; $E_{\text{flexural}} = 3.6 \pm 0.4$ GPa). For both

materials a very high Weibull modulus was reached (21.6 and 26.7) attesting a high reliability of both RBCs (Figure 1).

Comparing FE-SEM pictures (Figure 3), fillers in Surefil® SDR™ flow are consistently smaller than fillers of Venus® bulk fill.

Discussion:

Two recently launched bulk-fill flowable RBCs - Surefil® SDR™ flow and Venus® bulk fill - considered to be used as cavity liners and bulk fill materials in class I and II restorations were investigated. For this purpose specimens were measured by a FTIR-Spectrometer, a microhardness indenter, a three-point-bending test device and a FE-SEM. It must however be considered that the measurements were done with a modern high intensity LED curing unit which was applied at mould upper surface. Placing clinical restorations often means higher distances [17-19] between less effective curing units [20] and RBC surface. Therefore the clinical values of the measured properties could be lower.

The substantial reduction in polymerization shrinkage and particularly the ability to place the RBCs as 4 mm bulks claimed by both manufacturers has led to further interest about the composition of the measured products. For both RBCs the manufacturers renounced to Bisphenol-A-dimethacrylate (Bis-GMA) and only formed the organic matrix out of other dimethacrylates [21,22]. As a result, the RBCs are supposed to be less viscous because Urethane dimethacrylate (UDMA), Triethyleneglycol dimethacrylate (TEGDMA) and ethoxylated Bisphenol-A-dimethacrylate (EBPDMA) form more flexible polymers than Bis-GMA [23-26]. Moreover, Bis-GMA is said to be more hydrophilic [27] and consequently runs a higher risk of water uptake and degradation than the more hydrophobic EBPDMA [28] - used in both RBCs – thus reducing the risk of discoloration [29].

In our study DC was mainly influenced by the type of RBC ($\eta_2=0.63$). Combined with our results the claimed significant lower DC of Surefil® SDR™ flow in comparison to Venus® bulk fill [2] as well as its stated high DC when compared to other common RBCs (EsthetX Flow, Filtek Supreme Flow, Tetric Evo Flow, Filtek Silorane) [30] can be confirmed within the limitations of our experimental set-up. Unless it has to be pointed out that through different matrix compositions of the two RBCs, DC cannot be rated because each monomer and additional group implicates different properties and different molecular architecture, thus a higher DC does not necessarily mean higher mechanical properties as also confirmed by the measured mechanical properties. Furthermore by increasing the concentration of monomers [31] or diluents [32] the DC can be artificially kept high without improving mechanical properties. This was obviously not done in the analysed materials, since the measured mechanical properties performed well as already investigated and confirmed for Surefil® SDR™ flow when

comparing it to different types of modern RBCs [11]. Scougall-Vilchis et al. claimed that microhardness largely depends on the filler particles (size, weight, volume) as well as on the chemical composition of the RBC when – like in our study - the test device produces larger indents than the size of the fillers [33]. Therefore it can be stated that the measured HV-values present the average microhardness of both, fillers and matrix. Comparing micromechanical properties of Venus® bulk fill - concerning values on surface and in 2 mm depth after curing for 20s - with literature data [11], HV and E result like a commonly used microhybrid flowable RBC (EsthetX Flow) and a nanohybrid flowable RBC (Filtek Supreme Flow) (for E). When comparing the neat dimethacrylates Sideridou et al. showed that DC increases in the order Bis-GMA < Bis-EMA (EBPDMA) < UDMA < TEGDMA [23]. However, there must be an upper limit in increasing concentration of dimethacrylates with lower molecular weight because polymerization shrinkage would either increase [34]. The low polymerization shrinkage for Surefil® SDR™ flow shall result from the addition of the “polymerization modulator”, a chemical moiety in the resin backbone increasing flexibility and thus relaxing the polymerized network without harming DC (when compared to another common flowable RBC (EsthetX Flow, Dentsply)) [30]. Moreover, the extreme lowered polymerization shrinkage stress claimed by the manufacturer has been confirmed in other studies, showing for Surefil® SDR™ flow significant lower polymerization stress (1.1 ± 0.1 MPa) even when compared to the low- shrinkage silorane-based composite Filtek Silorane [11]. Unfortunately there are no published studies concerning the polymerization shrinkage of Venus® bulk fill. But with low contraction stress the cavity adaptation increases and it allows the dentist to place the composite in a favourable way. Nevertheless investigations on polymerization shrinkage in various bulks could be useful as an increased “C”- Factor caused by lower unattached RBC surface raises cusp deflection [8].

Statistics revealed for HV a strong influence ($\eta^2=0.80$) and for σ a moderate influence ($\eta^2=0.35$) of the factor “RBC”; moreover E ($\eta^2=0.84$) and E_{flexural} ($\eta^2=0.80$) were nearly equally strongly depended on the material. Therefore, the first tested hypothesis must be rejected. In the macro- and micromechanical tests Surefil® SDR™ flow proved to be significantly superior to Venus® bulk fill. Reasons for this behaviour might be found in both, inorganic and organic compounds. Surefil® SDR™ flow differs from Venus® bulk fill in the matrix composition as it contains additional TEGDMA and a polymerization modulator [30]. With the addition of the more flexible side groups containing TEGDMA, viscosity can be decreased [35] and with the formation of more

homogenous copolymer networks, polymerization shrinkage decreases either [36]. When comparing experimental composites with different types and contents of fillers Lee et al. found out that viscosity of RBC increases when filler volume increases [37]. Decreased viscosity is desirable for Surefil® SDR™ flow to reach similar levels of flowability, as its filler content (68% per weight, 44% per volume) strongly differs from the filler content of Venus® bulk fill (65% per weight, 38% per volume). With increasing filler volume the flexural strength and modulus as well as hardness improve [38,39]. Comparing the results for the micromechanical properties to a study investigating five nanohybrid RBCs (Miris2, N'Durance, Premise, Simile, Venus Diamond) with the same experimental set-up, Venus® bulk fill and Surefil® SDR™ flow show lower values than all of the measured materials [40]. The recommendation for an irradiation time of 20s and a 4 mm bulk placement for Surefil® SDR™ flow as well as an irradiation time of either 40s and 6 mm bulk placement or 20s and 4 mm bulk placement for Venus® bulk fill, is supported by the measured micromechanical values. Therefore the second hypothesis was rejected.

Assessing FE-SEM pictures (Figure 3), fillers in Surefil® SDR™ flow are consistently smaller than fillers of Venus® bulk fill. Li et al. claimed that decreasing filler size also means harming depth of cure and compressive strength [41] which however is not evident for the measured bulk-fill materials. Further investigations are needed to define the role of the polymerization modulator concerning both, mechanical properties and DC.

The producers' guarantee of placing the RBCs in 4 mm bulks and light curing for 20s without a loss in DC and mechanical properties seems to be of great interest for customers: it saves time and handling would be very easy. Our results confirm this claim and show no improvement when placing thinner bulks than 4 mm or increasing the irradiation time from 20s to 40s up to a measurement depth of 4 mm for both RBCs. Moreover the 80%-HV value - presenting the percentage of the relation of bottom to top surface hardness to be 80% for a properly cured composite [42] and due to Hansen et al. rather important than top surface hardness [43] - was not reached in the 6 mm samples at any of the measured irradiation times. This concludes that both RBCs may be placed in 4 mm bulks without a loss in relevant properties, like mechanical properties or degree of cure.

Besides the factor "RBC", E ($\eta^2=0.46$) as well as HV ($\eta^2=0.24$) were moderately influenced by "measuring depth". Considering the variation of micromechanical properties with depth (Fig. 2), it has to be noted that HV and E values rise with the

depth to a measuring depth of approximately 1.5 mm until then starting to decrease. This behavior is not characteristic for high filled RBCs [44]. Since the oxygen inhibition layer does not exceed 20 – 50 μm [45], the initial decrease in mechanical properties can rather be explained by the fact that non-bonded light-cured RBCs may shrink towards the center of the restoration [46]. Kakaboura et al. shared the same thought when evaluating shrinkage strain of light-cured RBCs using a X-ray microtomography and a bonded-disc method [47]. Therefore the polymerized bulks could reach lower mechanical values at peripheral surfaces because the volumetric shrinkage in the center of the bulk would be compensated by the flow from the periphery. Moreover Baroudi et al. explained the increased edge fracture resistance with the lower viscosity of monomers and the reduced particle size of fillers of flowable RBCs [48].

Regarding the results of the Weibull analysis, both materials exerted a high reliability (m-value). The high values of m (21.6 and 26.7) - indicating a narrow distribution of values and therefore a small error range – were unexpected as consistently lower values were measured for regular flowable RBCs on the market (6.37 to 15.23) [49].

Conclusions:

A strong influence of the material was statistically proven for all measured properties. A polymerization time of 20s instead of 40s as well as placing the RBCs in 4 mm bulks instead of 2 mm bulks neither lowered the micromechanical properties nor DC. Surefil® SDR™ flow showed significantly higher mechanical properties but lower DC values when compared to Venus® bulk fill.

Within the limitations of our study and the experienced high reliability (high Weibull modulus values) and good mechanical properties, a polymerization time of 20s and bulk placement up to 4 mm can be recommended.

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Tables:

Table 1: Influence of material, measuring depth and polymerization time on the micromechanical properties – indentation modulus (E), Vickers hardness (HV) – as well as degree of conversion (DC) and macromechanical properties - flexural strength (σ) and flexural modulus (E_{flexural}) –. The influence of all parameters was statistical significant ($\alpha=0.05$). Table contains the partial eta-square values. The higher the partial eta-squares, the higher the influence of the selected factor on the measured properties.

Factor	E	HV	DC	σ	E_{flexural}
RBCs	0.84	0.80	0.63	0.35	0.80
Measuring depth	0.46	0.24	0.10		
Polymerization time	0.03	0.04	0.12		

Table 2: Degree of Cure [%] 5 minutes after curing of **a)** Surefil® SDR™ flow and **b)** Venus® bulk fill at 0.1 mm, 2 mm, 4 mm, 6 mm (bulk and incremental) depth are detailed in mean values and standard deviations (in parentheses). Same superscripts (within one geometry, vertical line) and subscripts (within one polymerization time, in horizontal line) indicate statistical similar groups (Tukey's HSD Test, $\alpha=0.05$).

a) Surefil® SDR™ flow

Measuring depth	0.1 mm	2 mm	4 mm	6 mm-bulk	6 mm-incremental
Polymerization time					
10s	58.9 ^A _{1,2,3} (2.9)	60.1 ^a _{2,3} (1.8)	58.3 ^A _{1,2} (1.7)	57.1 ^a ₁ (3.0)	61.0 ^A ₃ (3.1)
20s	61.1 ^A ₂ (1.5)	59.5 ^a _{1,2} (2.2)	59.7 ^{AB} _{1,2} (1.7)	58.2 ^a ₁ (1.7)	60.7 ^A ₂ (2.1)
40s	60.4 ^A _{1,2} (3.1)	59.6 ^a ₁ (1.9)	61.2 ^B _{1,2} (2.1)	60.1 ^b _{1,2} (2.0)	61.9 ^A ₂ (2.4)

b) Venus® bulk fill

Measuring depth	0.1 mm	2 mm	4 mm	6 mm-bulk	6 mm-incremental
Polymerization time					
10s	65.0 ^A ₂ (1.9)	65.0 ^a ₂ (1.5)	62.9 ^A ₁ (2.3)	62.4 ^a ₁ (2.5)	65.6 ^a ₂ (1.5)
20s	64.9 ^A ₁ (1.7)	65.0 ^a ₁ (1.5)	66.1 ^B _{1,2} (2.8)	65.6 ^b _{1,2} (2.0)	66.7 ^{ab} ₂ (1.6)
40s	64.6 ^A ₁ (1.6)	65.7 ^a _{1,2} (1.8)	66.2 ^B _{1,2} (1.6)	66.1 ^b _{1,2} (2.8)	67.4 ^b ₂ (1.5)

Table 3: Indentation modulus E [GPa] of **a)** Surefil® SDR™ flow and **b)** Venus® bulk fill at 0.1 mm, 2 mm, 4 mm and 6 mm depth of samples cured for 10s, 20s or 40s as 6 mm high bulk and stored for 24h in distilled water at 37°C, is detailed in mean values and standard deviations (in parentheses). Same superscripts (within one geometry, in vertical line) and subscripts (within one polymerization time, in horizontal line) indicate statistical similar groups (Tukey's HSD Test, $\alpha=0.05$).

a) Surefil® SDR™ flow

Measuring depth	0.1 mm	2 mm	4 mm	6 mm-bulk
Polymerization time				
10s	10.7 ^A ₁ (0.6)	12.0 ^a ₂ (0.5)	12.2 ^A ₂ (0.7)	11.5 ^a ₂ (0.6)
20s	10.6 ^A ₁ (0.4)	11.9 ^a ₂ (0.4)	12.2 ^A ₂ (0.5)	11.1 ^a ₁ (0.7)
40s	10.8 ^A ₁ (0.4)	11.9 ^a _{2,3} (0.4)	12.2 ^A ₃ (0.6)	11.6 ^a ₂ (0.8)

b) Venus® bulk fill

Measuring depth	0.1 mm	2 mm	4 mm	6 mm-bulk
Polymerization time				
10s	7.3 ^A ₁ (1.1)	8.4 ^a ₂ (0.6)	8.6 ^A ₂ (0.9)	7.3 ^a ₁ (0.4)
20s	7.6 ^A ₁ (0.3)	8.6 ^{ab} ₂ (0.4)	8.8 ^A ₂ (0.4)	7.7 ^b ₁ (0.5)
40s	7.7 ^A ₁ (0.9)	8.8 ^b ₂ (0.3)	8.8 ^A ₂ (0.4)	8.5 ^c ₂ (0.3)

Table 4: Vickers hardness HV [N/mm^2] and depth of cure (HV-80%) [N/mm^2] of **a)** Surefil® SDR™ flow and **b)** Venus® bulk fill at 0.1 mm, 2 mm, 4 mm and 6 mm depth of samples cured for 10s, 20s or 40s as 6 mm high bulk and stored for 24h at 37°C in distilled water, is detailed in mean values and standard deviations (in parentheses). Same superscripts (within one geometry, in vertical line) and subscripts (within one polymerization time, in horizontal line) indicate statistical similar groups (Tukey's HSD Test, $\alpha=0.05$).

a) Surefil® SDR™ flow

Measuring depth	0.1 mm	2 mm	4 mm	6 mm-bulk	HV-80%
Polymerization time					
10s	55.1 ^A ₁ (2.3)	57.8 ^a ₂ (3.4)	58.2 ^A ₂ (4.1)	55.4 ^a ₁ (3.8)	44.1
20s	59.1 ^A ₁ (3.3)	61.1 ^b ₂ (2.1)	59.8 ^A _{1,2} (2.9)	59.0 ^b _{1,2} (3.4)	47.3
40s	59.1 ^A ₁ (1.3)	60.2 ^{ab} ₁ (1.8)	59.5 ^A ₁ (2.9)	58.9 ^b ₁ (2.6)	47.3

b) Venus® bulk fill

Measuring depth	0.1 mm	2 mm	4 mm	6 mm-bulk	HV-80%
Polymerization time					
10s	40.7 ^A ₁ (4.0)	46.1 ^a ₂ (3.1)	46.5 ^A ₂ (4.7)	39.1 ^a ₁ (2.9)	32.6
20s	41.4 ^A ₁ (1.5)	45.8 ^a ₃ (1.4)	46.4 ^A ₃ (0.9)	43.0 ^b ₂ (1.4)	33.1
40s	42.7 ^A ₁ (4.9)	46.4 ^a ₂ (2.1)	46.4 ^A ₂ (1.0)	46.0 ^c ₂ (1.9)	34.2

Figures:**Figure 1:**

Evaluation of the Weibull parameter (m) for Surefil® SDR™ flow and Venus® bulk fill using the variables P (probability of failure) and σ (Flexural strength). R^2 is the coefficient of determination.

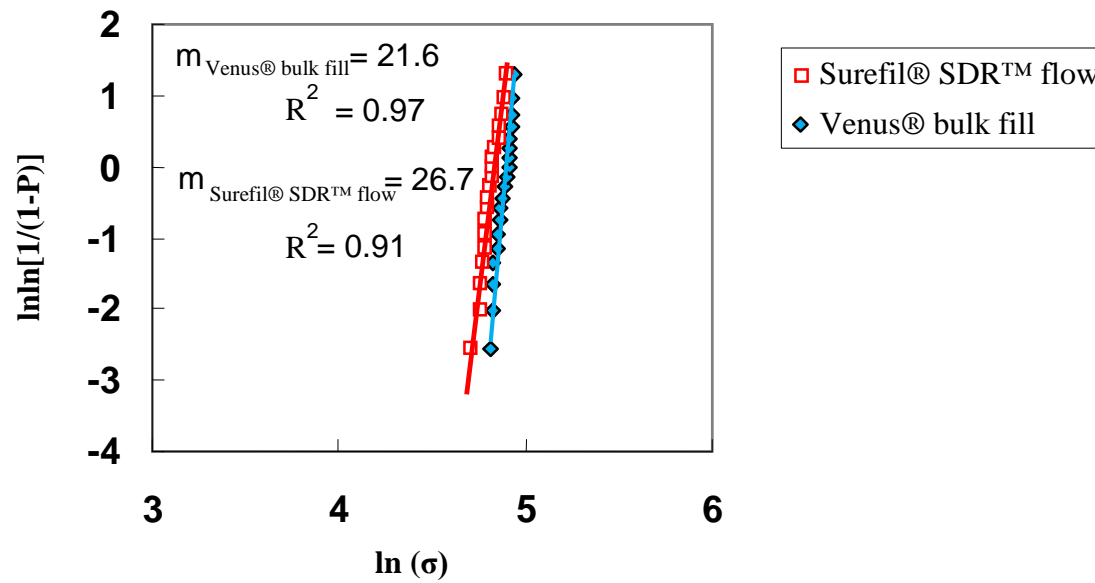


Figure 2:

Evaluation of the Vickers hardness (HV) with increasing specimen-depth for Surefil® SDR™ flow when cured as bulk for 40s (360 measuring points).

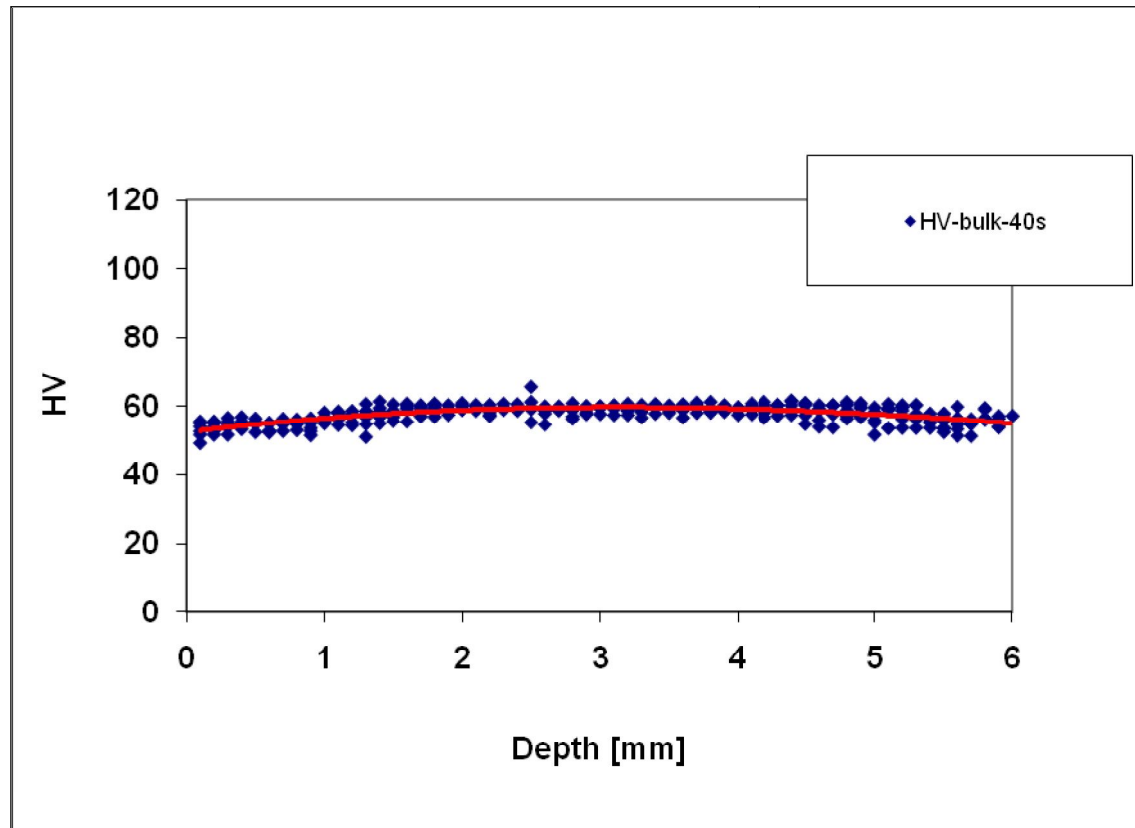
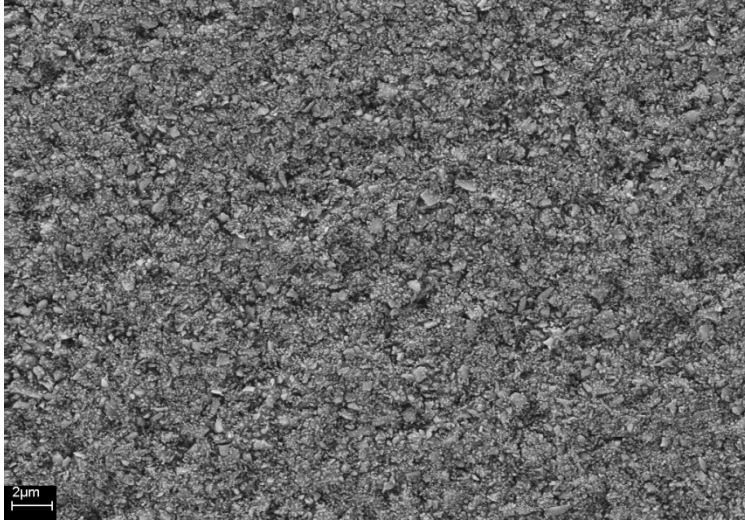
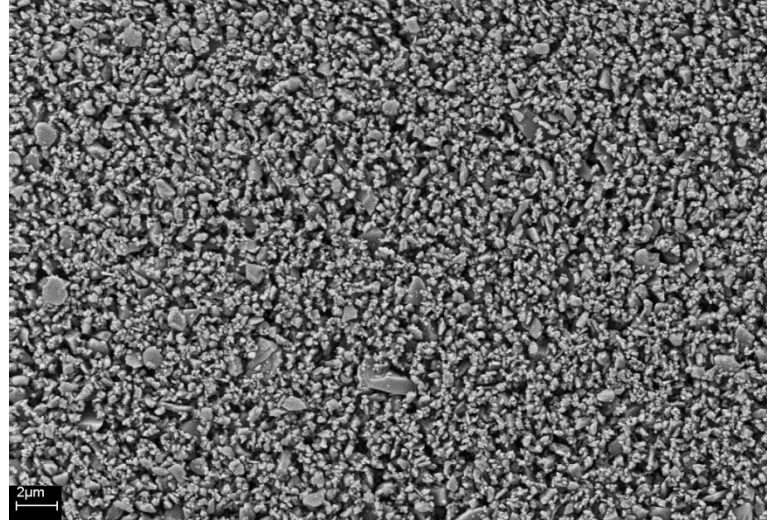


Figure 3:

Fe-SEM pictures of the measured materials.

Surefil® SDR™ flow**Venus® bulk fill**

2.1.1 Deutsche Zusammenfassung

Ziel der Studie war es Konversionsrate (KR), mikromechanische (Eindringmodul (E), Vickershärte (HV)) und makromechanische (Biegefestigkeit (σ), Biegemodul (E_{Biege}) Eigenschaften von zwei neu auf dem Markt erschienenen „bulk fill“ Kompositen zu untersuchen und zu vergleichen: Surefil® SDR™flow (SF) und Venus® bulk fill (VB).

Die Arbeitshypothesen waren:

- (a) Es gibt keinen Unterschied zwischen beiden Materialien bezüglich ihrer makromechanischen (Biegefestigkeit, Biegemodul) und mikromechanischen (Vickershärte, Eindringmodul) Eigenschaften sowie ihrer Konversionsrate in jeder der gemessenen Inkrementdicken und zu jeder Belichtungszeit.
- (b) Die Belichtungszeit und Inkrementdicke haben bei keinem von beiden Materialien einen signifikanten Einfluss auf die gemessenen Materialeigenschaften.

Die KR (n=6) wurde durch eine Fourier-Transformations-Infrarotspektrometrie (FTIR) in klinisch relevanten Inkrementdicken (0,1 mm, 2 mm, 4 mm, 6 mm-Bulk (ein Inkrement), 6 mm-Inkrement (geschichtet aus dreimal 2 mm dicken Inkrementen)) und Belichtungszeiten (10s, 20s, 40s) bestimmt. Mikro- (n=6) und makromechanische (n=20) Eigenschaften wurden nach 24 Stunden Lagerung der Prüfkörper bei 37°C in destilliertem Wasser von einem Universalhärtemessgerät und einer Drei-Punkt-Biegeversuch Anordnung bestimmt. Darüber hinaus wurde mittels der 6 mm-Bulk Prüfkörper die Tiefen Härte gemessen. Ein Rasterelektronenmikroskop wurde zur Evaluation der Füllkörpergröße hinzugezogen. Die Ergebnisse wurden mittels univariater Varianzanalyse, Tukey's honest significance post-hoc-Test, einer multivariaten Varianzanalyse ($\alpha=0.05$) und einem unabhängigen t-Test ausgewertet. Eine Verlässlichkeitsbestimmung wurde für σ mittels Weibullanalyse (m-Parameter) durchgeführt.

Für alle Inkrementdicken zeigte VB signifikant höhere KR (VB: 62,4 – 67,4 %; SF: 57,1 – 61,9 %) und signifikant niedrigere makro- (VB: $E_{\text{Biege}}= 3,6$ GPa; $\sigma= 122,7$ MPa; SF: $E_{\text{Biege}}= 5,0$ GPa; $\sigma= 131,8$ MPa) und mikromechanische (VB: $E= 7,3\text{--} 8,8$ GPa, $HV= 40,7\text{--}46,5$ N/mm²; SF: $E= 10,6\text{--}12,2$ GPa, $HV= 55,1\text{--}61,1$ N/mm²) Eigenschaften. Beide Materialien zeigten eine hohe Verlässlichkeit (VB: m= 21,6; SF: m= 26,7) und eine Tiefen Härte von mindestens 6 mm zu allen Belichtungszeiten. Der Parameter

„Kompositmaterial“ („RBC“) hatte den größten Einfluss auf die untersuchten Eigenschaften ($\eta^2 = 0,35-0,80$) gefolgt von der Inkrementdicke („measuring depth“) ($\eta^2 = 0,10-0,46$) und der Belichtungszeit („polymerization time“) ($\eta^2 = 0,03-0,12$). Signifikante Unterschiede zwischen den beiden Kompositen konnten für KR, E, σ und E_{Biege} bei allen Inkrementdicken und zu allen Belichtungszeiten gemessen werden.

Surefil® SDR™ flow zeigte signifikant höhere Werte für die mechanischen Eigenschaften und signifikant niedrigere KR-Werte als Venus® bulk fill. Somit wurde die erste Arbeitshypothese widerlegt.

Eine Belichtungszeit von 20s und eine 4 mm Inkrementplatzierung von Surefil® SDR™ flow wie auch eine Belichtungszeit von entweder 40s mit einer 6 mm Inkrementplatzierung oder 20s mit 4 mm Inkrementplatzierung von Venus® bulk fill führten zu den besten mikromechanischen Werten. Somit wurde auch die zweite Arbeitshypothese widerlegt.

Durch die gute Verlässlichkeit der Werte (hohe Weibullparameter) und der guten mechanischen Eigenschaften beider Materialien kann mit Rücksicht auf die Limitationen der Studie eine Belichtungszeit von 20s und eine Inkrementplatzierung bis hin zu einer Dicke von 4 mm empfohlen werden.

2.1.2 English summary

The aim of the study was to measure and compare degree of conversion (DC) as well as micro- (indentation modulus (E); Vickers hardness, (HV)) and macromechanical properties (flexural strength (σ); flexural modulus, E_{flexural}) of two recently launched bulk fill resin-based composites (RBCs): Surefil® SDR™flow (SF) and Venus® bulk fill (VB).

The tested null hypotheses were that:

- (a) There would be no significant difference between the two materials in view of macro- (flexural strength (σ), modulus of elasticity (E_{flexural})) and micromechanical properties (Vickers hardness (HV) and indentation modulus (E)) and degree of cure (DC) at any measured depth and irradiation time.
- (b) Within one material, irradiation time and depth would not influence the measured properties.

DC (n=6) was investigated by Fourier transform infrared spectroscopy (FTIR) in clinical relevant filling depths (0.1, 2, and 4 mm; 6 mm-bulk, 6 mm-incremental) and irradiation times (10s, 20s, 40s). Micro- (n=6) and macromechanical (n=20) properties were measured by an automatic microhardness indenter and a three-point bending test device after storing the specimens in distilled water for 24 h at 37°C. Furthermore, on the 6-mm bulk samples, the depth of cure was determined. A field emission scanning electron microscope was used to assess filler size. Results were evaluated using one-way analysis of variance, Tukey's honest significance post-hoc-test, a multivariate analysis ($\alpha=0.05$) and an independent t-test. Weibull analysis was used to assess σ .

VB showed, in all depth, significant higher DC (VB: 62.4–67.4 %; SF: 57.1–61.9 %), but significant lower macro- (VB: $E_{\text{flexural}}= 3.6$ GPa; $\sigma= 122.7$ MPa; SF: $E_{\text{flexural}}= 5.0$ GPa; $\sigma= 131.8$ MPa) and micromechanical properties (VB: $E= 7.3– 8.8$ GPa, $HV= 40.7– 46.5$ N/mm²; SF: $E= 10.6–12.2$ GPa, $HV= 55.1–61.1$ N/mm²). Both RBCs showed high reliability (VB: $m= 21.6$; SF: $m= 26.7$) and a depth of cure of at least 6 mm at all polymerization times. The factor “RBC” showed the strongest influence on the measured properties ($\eta^2= 0.35–0.80$) followed by “measuring depth” ($\eta^2= 0.10–0.46$) and “polymerization time” ($\eta^2= 0.03–0.12$). Significant differences between both RBCs were found for DC, E, σ and E_{flexural} at all irradiation times and measuring depths.

Surefil® SDR™ flow showed significantly higher mechanical properties but lower DC values when compared to Venus® bulk fill. Therefore the first hypothesis had to be rejected.

An irradiation time of 20s and a 4 mm bulk placement for Surefil® SDR™ flow as well as an irradiation time of either 40s and 6 mm bulk placement or 20s and 4 mm bulk placement for Venus® bulk fill led to the best micromechanical values. Therefore also the second hypothesis was rejected.

Within the limitations of our study and the experienced high reliability (high Weibull modulus values) and good mechanical properties, a polymerization time of 20s and bulk placement up to 4 mm can be recommended.

2.2 „In-vitro comparison of mechanical properties and degree of cure of a self-adhesive and four novel flowable composites“

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Abstract:

Purpose: The aim of our study was to compare a self-adhesive with two low shrinkage and two regular flowable resin-based composites (RBCs) in terms of degree of conversion (DC) and mechanical properties measured at microscopic (Indentation modulus, E, Vickers hardness, HV) and macroscopic scale (Flexural strength, σ , Flexural modulus, E_{flexural}).

Materials and Methods: DC was investigated by an ATR-FTIR-Spectrometer in clinical relevant filling depth (0.1 mm, 2 mm, 4 mm, 6 mm-bulk, 6mm-incremental) and irradiation times (10s, 20s, 40s). Micro- and macro-scale mechanical properties were measured by an automatic microhardness indenter and a three-point bending test device after curing the specimens for 20s and storing them in distilled water for 24h at 37°C. Fillers were visualized by a field emission scanning electron microscope. Results were evaluated using one-way ANOVA, Tukey's HSD post-hoc test, Pearson correlation and a multi-variate analysis ($\alpha = 0.05$). A Weibull analysis was used to assess σ .

Results: N'Durance[®] Dimer flow (65.66%) reached the highest DC (at 2 mm depth, 20s irradiation). At macro-scale EcuSphere[®]-Flow (129.82 MPa) for σ and Synergy[®] D6 Flow (3.74 GPa) for E_{flexural} reached highest values. The highest micro-mechanical properties were measured for the self-adhesive RBC (Vertise[™] Flow; E= 10.81 GPa, HV= 60.20 N/mm²). Reliability was highly influenced by filler weight ($\eta^2 = 0.77$) and volume ($\eta^2 = 0.99$) proportion.

Conclusion: In the present study the self-adhesive RBC showed the highest reliability, highest DC (together with one of the low shrinkage RBCs) and highest mechanical properties measured at micro-scale as well as good mechanical properties measured at macro-scale. Moreover a curing time of 40s and an incremental thickness not exceeding 2 mm appeared to be necessary for it.

Introduction:

The demands on modern flowable resin based composites (=RBCs) in their function as restorative materials or liners are permanently extended, asking nowadays for supplementary properties like self-adhesion, low polymerization shrinkage or improved mechanical properties. The latest developments in this subject area are the self-adhering flowable RBCs, as a result of ongoing efforts to simplify clinical treatment. New self-adhesive RBCs are promoted as materials needing neither etching nor a bonding agent (1). Since the development of resin based composites, their adhesion to tooth structure has been challenging clinicians and scientists. After Buonocore published a method of increasing the restorations adhesion (2), various researchers developed new ways to ease and enhance handling and quality of modern etching and bonding systems (3, 4). One modern way to create self-adhesive RBCs (5), self-adhesive resin cements (6) or self-etching adhesives (7, 8), is to use special phosphate dimethacrylate monomers like glycerol phosphate dimethacrylate (=GPDM), allowing thus a chemical interaction of the phosphonate group with the calcium ions of the tooth structure. But also a micromechanical bonding between polymer and the collagen fibers that are exposed through the etching effect of the phosphonate acidic group of GPDM, as well as between the polymer and the integrated smear layer (interdiffusion zone) was ascertained (3). However including GPDM in self-adhesive RBCs did not improve the bond strength to enamel, when compared to etch- and rinse adhesives (9-12). Disadvantages of one-component self-etching adhesives in general are seen in their relatively high water uptake (13, 14) as well as a possible hydrolytic degradation of the tooth-restoration interface (15). Nevertheless concerning shear bond strength to superficial as well as to deep dentin, GPDM-containing adhesives resulted equally to other self-etching and total-etching adhesive systems (12).

Another attempt intensively followed in modern flowable RBCs is to reduce polymerization shrinkage. When measuring polymerization shrinkage of experimental composites with the same filler and initiator concentrations but different fractions of monomers, Ellakwa et al. found out that one way to decrease polymerization shrinkage is to use monomers with higher molecular weights (16). Some modern flowable RBCs therefore renounce to low molecular weight monomers like Triethyleneglycol dimethacrylate (=TEGDMA) (286 g/mol) and are based on monomers with a high molecular weight. Besides traditional monomers like bisphenylglycidyl dimethacrylate

(=BisGMA) (512 g/mol) and ethoxylated bisphenol-A dimethacrylate (=BisEMA) (540 g/mol) (17), also the newly developed dimer-acid dimethacrylates (847 g/mol) (18-20) are used, resulting in higher DC, higher flexural modulus and the possibility of placing thicker increments than traditional RBCs (21). The mechanism of reducing shrinkage by using dimer-acid dimethacrylates in combination with BisEMA and Urethane dimethacrylate (=UDMA) (471 g/mol) is based, besides the higher molecular weight, on a phase separation due to a partial compatibility of the monomers in their polymerized state (20). A higher degree of conversion (=DC) and a lower shrinkage are stated to be the result when the faster polymerizing phase remains in a less reticulated polymer (22).

The aim of our study was to compare a new self-adhesive RBC (Vertise™ flow) as well as two low shrinkage flowable RBCs (N'Durance® Dimer flow and Extra low shrinkage flow) with two traditional flowable microhybrid RBCs (EcuSphere®-Flow, Synergy® D6 Flow) regarding DC and their mechanical properties at macroscopic and microscopic scale at different irradiation times and by simulating clinical relevant filling depth.

The tested null-hypotheses were that: a) there would be no significant difference between the five materials in view of DC at any measured depth and irradiation time; b) there would be no significant difference between the five materials when measuring mechanical properties at macro- (flexural strength ($=\sigma$) and modulus of elasticity ($=E_{\text{flexural}}$)) and micro-scale (Vickers hardness ($=\text{HV}$) and indentation modulus ($=E$)) at a clinical relevant irradiation time of 20s.

Materials and methods:

Five flowable RBCs – composition information as far as they could be collected (17, 18, 23-26) (Table 1) – all in shade A3, were analyzed by assessing DC as function of depth, incremental technique and polymerization time (10s, 20s or 40s). Furthermore, the mechanical properties measured at macroscopic (flexural strength ($=\sigma$) and modulus of elasticity ($=E_{\text{flexural}}$)) and microscopic scale (Vickers hardness ($=HV$) and indentation modulus ($=E$)) were assessed.

Degree of cure measurements:

To evaluate the DC, five different sample geometries were considered. Thin films (100 μm) as well as 2 mm, 4 mm and 6 mm high molds (3 mm diameter) were filled in bulk. Additionally three consecutive increments - each 2 mm high – were prepared in the mold of 6 mm height (6 mm-incremental). Samples were cured by applying the curing unit (Elipar Freelight2, 3M ESPE, 1226 mW/cm^2) directly on the top of the particular mould, respectively on the film surface covered by a transparent matrix strip. For each product, irradiation time (10s, 20s, 40s) and geometry (0.1 mm, 2 mm, 4 mm, 6 mm-bulk, 6 mm-incremental) six samples were measured ($n=6$). Real-time measurements were made with a FTIR-Spectrometer with an attenuated total reflectance (ATR) accessory (Nexus, Thermo Nicolet, Madison, USA). Therefore, the non-polymerized RBC paste was put directly on the diamond ATR crystal in the mold as described above. FTIR spectra were recorded in real time for 5 minutes with two spectra per second at the bottom of the samples irradiated according to the curing protocol presented above. Diameter of measured surface was 800 μm , wave number of the spectrum ranged between 4000–650 cm^{-1} and the FTIR spectra were recorded with four scans at a resolution of 8 cm^{-1} . During testing the specimens were constantly pressed to the ATR refractive element by a fixed stamp to prevent the potential pull-out effect caused by setting shrinkage.

To determine the percentage of the remained unreacted double bonds, DC was measured by assessing the variation in peak height ratio of the absorbance intensities of methacrylate carbon double bond peak at 1634 cm^{-1} and that of an internal standard peak ($=IS$) at 1608 cm^{-1} (aromatic carbon double bond) during polymerization, in relation to the uncured material.

$$DC_{\text{height}} \% = \left[1 - \frac{\left(\frac{1634 \text{cm}^{-1}}{\text{IS}} \right)_{\text{Peak after curing}}}{\left(\frac{1634 \text{cm}^{-1}}{\text{IS}} \right)_{\text{Peak before curing}}} \right] \times 100$$

Flexural strength and flexural modulus:

Flexural strength (σ) was determined in a three-point-bending test in analogy to DIN EN ISO 4049:2010-03 (27). The samples (n=20) were made by compressing the RBC material between two glass plates with intermediate polyacetate sheets, separated by a steel mould having an internal dimension of (2 x 2 x 16) mm. After curing (with three overlapping light exposures of 20 seconds per each side, Elipar Freelight2, 3M ESPE) the specimens were removed from the mould and any flash material was trimmed away with sandpaper (grit size P4000 (FEPA)). Afterwards all specimens were stored in distilled water at 37°C prior to testing for 24 h. Samples were then loaded until failure in the universal testing machine (MCE 2000ST, quick test Prüfpartner GmbH, Langenfeld, Germany). The crosshead speed was 0.5 mm/min. The specimens were placed on a three-point bending test device, which is constructed according to the guidelines of NIST No. 4877 with 12 mm distance between the supports. During testing the specimens were immersed in distilled water at room temperature.

Flexural strength was calculated from formula (1).

$$(1) \quad \sigma = \frac{3Fl}{2bh^2}$$

F is the maximum load [N], l is the distance between the supports [mm], b is the width of the specimens [mm], h is the height of the specimens [mm].

The universal testing machine stored the force during bending and the deflection of the beam in a file. The bending modulus was calculated from formula (2).

$$(2) \quad E_{\text{flexural}} = \frac{Fl^3}{4bh^3y}$$

y is the deflection at load point [mm].

Mechanical properties measured at microscopic scale:

The mechanical properties at micro-scale (HV, E) were assessed on six randomly assigned fragments resulted after the bending test. For this purpose, the fragments were

ground and polished under water with diamond abrasive paper (mean grain sizes: 20 μm , 13 μm , 6 μm) in a grinding system (EXAKT 400CS, Exakt, Norderstedt, Germany). Measurements were made with an automatic microhardness indenter (Fischerscope H100C, Fischer, Sindelfingen, Germany) testing 10 randomly assigned measurement points at one sample (total 60 measurement points per group). The test procedure was carried out force-controlled, where the test load increased and decreased with constant speed between 0.4 mN and 500 mN. Load and penetration depth of indenter (Vickers pyramid: diamond right pyramid with a square base (2.5 μm x 2.5 μm) and an angle of $\alpha=136^\circ$ between the opposite faces at the vertex (calculated mean radius of the tip: 0.5 μm)) were continuously measured during the load-unload hysteresis. Universal hardness is defined as the test force divided by the apparent area of indentation under the applied test force. From a multiplicity of measurements stored in a database supplied by the manufacturer, a conversion factor (0.0945) between Universal hardness and HV was calculated by the manufacturer and entered into the software, so that the measurement results were indicated in the more familiar HV units. E was calculated from the slope of the tangent adapted at the beginning (at maximum force) of the non linear indentation depth curve upon maximum loading.

Field emission scanning electron microscope (FE-SEM):

For each product one specimen (1 cm x 1 cm x 0.5cm) was polymerized for 40s and treated for one hour in a chemical dry cleaning process with oxygen plasma in vacuum (45 - 50 W). Afterwards surfaces were investigated (Magnification: 20000x, Signal: Secondary electrons SE2, Working distance: 4 mm, Electron high tension: 10 kV) with a field emission scanning microscope (FE-SEM) (Zeiss Supra[®] 55 VP, Zeiss NTS GmbH, Oberkochen, Germany) and the most representative picture was chosen to visualise filler shape and dimension.

Statistical analysis:

The results for DC within each material, each measuring depth and each curing time, respectively, were compared using one-way ANOVA and Tukey's HSD post hoc-test ($\alpha=0.05$) (SPSS 18.0, Chicago, IL, USA). Additionally a Weibull analysis was used to assess σ . An ANOVA multivariate analysis and partial eta-square statistic were used to investigate the influence of the parameters "RBCs", "measuring depth", "polymerization time", "Wt%-Filler" (=weight proportion of fillers) and "Vol%-Filler"

(=volume proportion of fillers) on DC, E, HV, E_{flexural} , σ and m. Furthermore a Pearson correlation investigated the linear dependence between wt%-filler, vol%-filler, E, HV, E_{flexural} , σ and m.

A common empirical expression for the cumulative probability of failure P at applied stress is the Weibull model:

$$P_f(\sigma_c) = 1 - \exp\left[-\left(\frac{\sigma_c}{\sigma_0}\right)^m\right]$$

where σ_c is the measured strength, m the Weibull modulus and σ_0 the characteristic strength, defined as the uniform stress at which the probability of failure is 0.63.

The double logarithm of this expression gives:

$$\ln \ln \frac{1}{1-P} = m \ln \sigma_c - m \ln \sigma_0$$

By plotting $\ln \ln(1/(1-P))$ versus $\ln \sigma$, a straight line results, with the upward gradient m, whereas the intersection with the x-axis gives the logarithm of the characteristic strength.

Results:

The influence of the parameters “RBCs”, “Depth”, “Polymerization time”, “wt%-filler” and “vol%-filler” were analyzed in an ANOVA multivariate test (Table 2). DC and the mechanical properties – HV, E, σ , E_{flexural} , m - were selected as depended variables. The significance values of these effects were less than 0.05, indicating that they contribute all to the model. DC was strongly influenced by depth ($\eta^2 = 0.95$, Table 2), RBC (0.94) and polymerization time (0.81). The RBCs exerted the strongest influence (higher η^2 values) on DC followed by the micro-mechanical properties (E (0.88), HV (0.68)) and the mechanical properties measured at macroscopic scale (E_{flexural} (0.48) and σ (0.32)). Vol%-filler strongly influenced m (0.99), E (0.80), HV (0.61) and moderately E_{flexural} (0.47). This statement is equally valid for wt%-filler.

The DC five minutes after photo-initiation as function of samples thickness and polymerization time is expressed in Table 3. Increasing measuring depth from 0.1 mm to 2 mm significantly decreased DC values in all groups except for Vertise™ Flow, N'Durance® Dimer flow and Synergy® D6 Flow at high polymerization times (20s, 40s). As for the differences in DC at 2 mm and 4 mm depth, a significant decrease was measured at 4 mm depth for all materials and polymerization times. At 2 mm depth DC increased with progressive irradiation time in all RBCs, except for N'Durance® Dimer flow which showed similar DC values at 20s and 40s irradiation times. By using an incremental technique, the DC values measured at 6-mm depth were similar to those measured at 2 mm depth, except for Extra low shrinkage flow at low polymerization times (10s, 20s) and N'Durance® Dimer flow at high polymerization time (40s).

Regarding the mechanical properties measured at microscopic scale (HV, E, Table 4), the highest values were measured for Vertise™ Flow, whereas at macroscopic scale (σ , E_{flexural} , Table 4), EcuSphere®-Flow reached the highest values for σ and Extra low shrinkage flow the lowest values for E_{flexural} besides the other statistically similar RBCs. As for the Weibull modulus (Figure 1, Table 4) Vertise™ Flow and Extra low shrinkage flow showed the highest reliability of the investigated RBCs.

The modulus of elasticity measured in both methods – the flexural test and Universal hardness test - correlated moderately (Pearson correlation coefficient = 0.43). An excellent correlation was found between the microscopic mechanical properties (E-HV = 0.91).

Discussion:

A recently launched self-adhesive flowable RBC – Vertise™ Flow – and two low shrinkage flowable RBCs – N'Durance® Dimer flow (a new flowable RBC with a tri-monomer system including dimer-acid dimethacrylates) and Extra low shrinkage flow (a new flowable RBC with a matrix free of low molecular weight monomers) – were investigated and compared with two established flowable microhybrid composites on the market (EcuSphere®-Flow, Synergy® D6 Flow).

When compared with other RBCs (GC Kalore, GC GradiaDirect Anterior, GC Gradia Direct Posterior, Filtek® Silorane), Wei et al. found out that the self-adhesive flowable RBC Vertise™ Flow suffered the greatest hygroscopic expansion (4.82%), the greatest water sorption (71.96 g/mm³) and the greatest solubility (16.95 g/mm³) as well as a significant higher dehydration shrinkage and a significant mass reduction after 42 days in water immersion (28, 29). As shown in our study, good DC values were reached for Vertise™ Flow when compared to the other investigated products (Table 3), thus the above described material behaviour cannot be related to a disproportional high amount of not-polymerized monomers that potentially could be washed out (30). A reason for the high solubility associated with Vertise™ Flow could rather be the usage of GPDM and other methacrylate co-monomers (5), since its hydrophilic acidic phosphate group and the short spacer group are said to exhibit a great hydrophilicity (29). The role of the methacrylate co-monomers cannot be assessed since any clear information is unfortunately available about their chemical composition. Therefore it is questionable if Vertise™ Flow may really be used in restoration parts that are exposed to saliva and other fluids. Moreover it is stated that the self-adhesive flowable RBC Vertise™ Flow requires a longer polymerization time in comparison with conventional adhesives or other marketed flowable RBCs since the included monomers tend to have a slower response to light curing than non-adhesive monomers (31).

For Vertise™ Flow the manufacturer advises the usage in small class I restorations, as liner in class I and II restorations, as fissure sealant and as minor occlusal build-up in non-stress bearing areas. Comparing our results to a recent study, Vertise™ Flow shows lower mechanical properties at macro- and micro-scale than modern non-flowable RBCs (32). Therefore a placement of non-flowable RBCs on top is strongly recommended in occlusal loaded areas. Within the analysed flowable materials however, Vertise™ Flow shows the best values in microscopic mechanical properties. A reason for this can be found in the composition of the inorganic content. Vertise™

Flow contains 1-micron barium glass fillers, nano-sized colloidal silica and nano-sized Ytterbium fluoride (5). Together they represent about 70 percent of total weight (28), which is about 7 percent higher than the given weight percent values of EcuSphere®-Flow and Synergy® D6 Flow and even 17 percent higher than the filler weight proportion of Extra low shrinkage flow (Table 1). This is due to the increase of filler volume being about 6 percent (Synergy® D6 Flow), 7 percent (EcuSphere®-Flow, N'Durance® Dimer flow) or even 20 percent (Extra low shrinkage flow) higher for Vertise™ Flow. When assessing those values it becomes clear that the low mechanical properties of Extra low shrinkage flow are due to its low filler content since statistical results show a high influence (high partial eta-square values) of the filler proportions (weight and volume percent) on the investigated mechanical properties. A positive correlation between filler loading and mechanical properties was also reported by former studies (33, 34).

N'Durance® Dimer flow is said to use a tri-monomer system including dimer-acid dimethacrylates which exhibit a higher molecular weight (847 g/mol) (19, 20) compared to the two dimethacrylates – BisGMA (512 g/mol) and BisEMA (540 g/mol) (35) – the matrix of Extra low shrinkage flow exclusively consists of. Trujillo-Lemon et al. measured in several experimental hydrophobic monomers, that were based on a dimer-acid structure, a higher DC, lower polymerization shrinkage and an increase of flexibility (19). However two other studies stated that high molecular weight monomers in general present lower mobility, thus reducing the final DC reached by the (36, 37). Referring to our results N'Durance® Dimer flow reaches in fact- together with Vertise™ Flow - the highest DC in contrast to Extra low shrinkage flow which presents the lowest DC values. Unfortunately the co-monomers represented in the tri-monomer system of N'Durance® Dimer flow have not been published, but it seems that they contribute to a higher DC.

Referring to the mechanical properties at macro- and micro-scale, it becomes obvious that through different organic and filler compositions of the RBCs, mechanical superiority cannot be predicted by DC. Together with a different filler loading and filler type each monomer and additional group implicates different properties and different molecular architecture, thus a nearly equal DC in the case of Vertise™ Flow and N'Durance® Dimer flow does not necessarily mean equal mechanical values as reflected in the measured mechanical properties (Table 4).

For Weibull modulus (Figure 1, Table 4) - highly influenced by wt%-filler ($\eta^2=0.77$) and vol%-filler ($\eta^2=0.99$) - Vertise™ Flow (11.35) and Extra low shrinkage flow

(11.22) present the highest values thus exhibiting the highest reliability while the lowest reliability was found for Synergy® D6 Flow (6.52).

Lee et al. found out - when comparing experimental composites with different types and contents of fillers - that viscosity of RBCs increases when filler volume increases (38). Following studies could therefore compare the rheological properties of Vertise™ Flow with other flowable RBCs on the market.

Comparing our results to those of Tjandrawinata et al. (6.37 to 15.23) (39), who measured eight flowable RBCs concerning their flexural strength, our investigated RBCs show comparable values.

Assessing FE-SEM pictures (Figure 2), fillers of Vertise™ Flow are obviously bigger than fillers of N'Durance® Dimer flow and Extra low shrinkage flow. The fillers of Synergy® D6 Flow seem to be the smallest of all investigated products, while the majority of fillers of EcuSphere®-Flow are small, with some sporadic fillers that are bigger than 2 µm though. However Li et al. claimed that decreasing filler size in the same monomer system with the same filler amount also means harming depth of cure, compressive strength and resistance to tooth brushing (40). This could be of interest in further studies about Vertise™ Flow.

The indications for use of the investigated products advise a placement up to 2 mm and a curing time of 20s (1, 18, 24, 25), except for Extra low shrinkage flow where a curing time of 30s was suggested (17). For N'Durance® Dimer flow this claim can be confirmed by our data, since no improvement in DC is shown when increasing the irradiation time from 20s to 40s in 2 mm depth. This does not apply for Vertise™ Flow since an improvement of irradiation time from 20s to 40s also increased DC. Moreover significant lower values appeared for both RBCs when raising placement thickness of the specimens from 2 mm to 4 mm, limiting thus the incremental thickness to 2 mm.

It must however be considered that the measurements were done with a modern high intensity LED curing unit which was applied at mould upper surface. Placing clinical restorations often means higher distances between less effective curing units and RBC surface. The DC measured 5 minutes after starting the polymerization was reported to represent 85-90% of the final DC measured after 24 hours (41), legitimating thus the short post-polymerisation period considered in our study. The initial DC after 5 minutes is however of great importance since elution of unreacted monomers by saliva and other fluids starts right after polymerization with all of the already investigated possible toxicological long term consequences (42-44). Because Vertise™ Flow shows the best mechanical properties at micro-scale and good macro-scale results as well as medium

mechanical values for N'Durance® Dimer flow and a further variation in mechanical properties between the investigated flowable RBCs the second hypothesis must be rejected.

Conclusions:

A strong influence of the material on all measured properties, as well as a strong influence of filler proportion (wt%-filler, vol%-filler) on the reliability was statistically proven. All tested null-hypotheses had to be rejected.

Within the limitations of our study the self-adhesive RBC (Vertise™ Flow) showed best performance concerning DC after five minutes of polymerization (together with the dimer-acid based RBC) and mechanical properties measured at micro-scale. The traditional microhybrid flowable RBCs performed best in the macroscopic mechanical properties σ (EcuSphere®-Flow) and E_{flexural} (Synergy® D6 Flow). For the self-adhesive RBC a curing time of 40s as well as an incremental placement not exceeding 2 mm thickness appeared to be necessary.

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Tables:

Table 1:

Materials, manufactures, batch numbers and composition of all investigated materials.

Composite	Manufacturer	Type	Resin matrix	Filler
Vertise™ Flow LOT: 3355213	Kerr	Self-adhesive flowable	GPDM, methacrylate co-monomers	Barium glass, nano-sized colloidal silica, nano-sized ytterbium fluoride 70 wt%, 48 vol%
Extra low shrinkage flow LOT: 21	Saremco	Microhybrid flowable	BisGMA, BisEMA	Barium glass 53 wt%, 28 vol%
EcuSphere®-Flow LOT: 646549	DMG	Microhybrid flowable	Optimized BisGMA	Dental glass 63 wt%, 41 vol%
N'Durance® Dimer flow LOT: 082109A	Septodont	Microhybrid flowable	Tri-monomer system including dimer-acid dimethacrylates	Nano-sized ytterbium fluoride, barium glass, silicium dioxide 57 wt%, 41 vol%
Synergy® D6 Flow LOT: 224304	Coltène/Whaledent	Microhybrid flowable	Methacrylates	Silanized barium glass, hydrophobic amorphous silica 63 wt%, 42 vol%

GPDM: glycerol phosphate dimethacrylate; BisGMA: bisphenylglycidyl dimethacrylate; BisEMA: ethoxylated bisphenol-A dimethacrylate;

Table 2:

Influence of material (RBCs), measuring depth and polymerization time as well as weight (Wt%-filler) and volume proportion (Vol%-filler) of fillers on degree of conversion (DC), macro- (flexural strength (σ) and flexural modulus (E_{flexural})) and micro-scale (Indentation modulus (E), Vickers hardness (HV)) mechanical properties and Weibull modulus (m). The influence of all parameters was statistically significant ($\alpha < 0.05$). Table contains the partial eta-square values. The higher the partial eta-squares, the higher is the influence of the selected factor on the measured properties.

Factor	DC	E	HV	E_{flexural}	σ	m
RBCs	0.94	0.88	0.68	0.48	0.32	
Measuring depth	0.95					
Polymerization time	0.81					
Wt%-filler	0.31	0.88	0.67	0.48	0.09	0.77
Vol%-filler	0.31	0.80	0.61	0.47	0.10	0.99

Table 3:

Degree of Cure [%] of the investigated materials - 5 minutes after curing - measured in various depths is detailed in mean values and standard deviations (in parentheses). Same superscripts (within one polymerization time, in horizontal line) and subscripts (within one geometry, in vertical line) indicate statistically similar groups (Tukey's HSD Test, $\alpha=0.05$).

a) Vertise™ Flow

Measuring depth	0.1 mm	2 mm	4 mm	6 mm-bulk	6 mm-incremental
Polymerization time					
10s	66.92 ^D ₁ (2.6)	60.39 ^C ₁ (3.7)	18.83 ^B ₁ (3.6)	3.67 ^A ₁ (3.3)	58.62 ^C ₁ (3.9)
20s	67.68 ^c ₁ (3.2)	65.12 ^c ₂ (3.2)	49.20 ^b ₂ (3.1)	27.05 ^a ₂ (2.6)	63.68 ^c ₂ (2.7)
40s	70.24 ^D ₂ (2.5)	67.79 ^{CD} ₃ (2.5)	59.32 ^B ₃ (2.2)	48.78 ^A ₃ (3.6)	66.48 ^C ₃ (3.1)

b) N'Durance[®] Dimer flow

Measuring depth	0.1 mm	2 mm	4 mm	6 mm-bulk	6 mm-incremental
Polymerization time					
10s	65.32 ^D ₁ (1.3)	63.02 ^C ₁ (2.2)	53.25 ^B ₁ (1.5)	43.78 ^A ₁ (2.6)	62.23 ^C ₁ (1.6)
20s	64.22 ^c ₁ (2.2)	65.66 ^{cd} ₂ (2.3)	60.77 ^b ₂ (1.9)	54.96 ^a ₂ (2.1)	67.29 ^d ₂ (2.1)
40s	65.00 ^{BC} ₁ (1.5)	66.40 ^C ₂ (1.9)	64.54 ^B ₃ (2.0)	59.27 ^A ₃ (1.5)	69.26 ^D ₃ (1.7)

c) EcuSphere®-Flow

Measuring depth	0.1 mm	2 mm	4 mm	6 mm-bulk	6 mm-incremental
Polymerization time					
10s	62.09 ^D ₁ (1.1)	58.00 ^C ₁ (1.7)	36.86 ^B ₁ (3.0)	21.77 ^A ₁ (2.5)	58.70 ^C ₁ (2.5)
20s	64.72 ^d ₂ (2.9)	62.43 ^c ₂ (1.3)	54.65 ^b ₂ (2.5)	42.70 ^a ₂ (2.9)	62.76 ^{cd} ₂ (2.2)
40s	65.69 ^D ₂ (1.4)	65.21 ^C ₃ (2.1)	59.06 ^B ₃ (1.2)	52.73 ^A ₃ (2.4)	63.68 ^{CD} ₂ (1.3)

d) Extra low shrinkage flow

Measuring depth	0.1 mm	2 mm	4 mm	6 mm-bulk	6 mm-incremental
Polymerization time					
10s	49.01 ^D ₁ (1.9)	39.57 ^C ₁ (2.2)	1.00 ^A ₁ (1.2)	1.65 ^A ₁ (1.6)	33.17 ^B ₁ (3.3)
20s	49.88 ^e _{1,2} (1.5)	43.58 ^d ₂ (1.7)	6.77 ^b ₂ (3.2)	0.77 ^a ₁ (1.1)	39.46 ^c ₂ (3.3)
40s	50.63 ^D ₂ (1.7)	47.43 ^C ₃ (1.9)	28.19 ^B ₃ (3.5)	13.66 ^A ₂ (3.9)	44.71 ^C ₃ (2.8)

e) Synergy[®] D6 Flow

Measuring depth	0.1 mm	2 mm	4 mm	6 mm-bulk	6 mm-incremental
Polymerization time					
10s	57.02 ^D ₁ (1.4)	53.05 ^C ₁ (1.8)	29.05 ^B ₁ (2.9)	3.61 ^A ₁ (2.1)	52.13 ^C ₁ (3.0)
20s	58.62 ^c ₂ (1.5)	55.86 ^c ₂ (2.2)	47.21 ^b ₂ (1.8)	31.03 ^a ₂ (3.1)	57.87 ^c ₂ (2.2)
40s	59.33 ^C ₂ (1.62)	60.64 ^C ₃ (1.4)	52.64 ^B ₃ (1.9)	44.35 ^A ₃ (2.0)	59.43 ^C ₂ (1.6)

Table 4:

Macro-scale (Flexural strength ($=\sigma$) [MPa], flexural modulus ($=E_{\text{flexural}}$) [GPa]), Weibull parameter (m) and micro-scale mechanical properties (Vickers hardness ($=HV$) [N/mm^2], indentation modulus ($=E$) [GPa]) are detailed in mean values and standard deviations (in parentheses). Same superscripts (vertical line) indicate statistically similar groups (Tukey's HSD Test, $\alpha=0.05$).

RBC	σ	m	E_{flexural}	HV	E
Vertise™ Flow	116.07 ^A (12.2)	11.35	3.52 ^B (0.43)	60.20 ^E (4.40)	10.81 ^E (0.38)
N'Durance® Dimer flow	105.06 ^A (12.33)	9.81	3.38 ^B (0.33)	46.51 ^B (9.69)	7.44 ^B (0.89)
EcuSphere®-Flow	129.82 ^B (14.67)	9.21	3.60 ^B (0.71)	55.62 ^D (2.97)	8.99 ^C (0.50)
Extra low shrinkage flow	108.33 ^A (11.57)	11.22	2.49 ^A (0.31)	37.29 ^A (1.42)	6.90 ^A (0.26)
Synergy® D6 Flow	104.54 ^A (18.51)	6.52	3.74 ^B (0.49)	53.04 ^C (1.12)	9.27 ^D (0.20)

Figures:

Figure 1: Evaluation of the Weibull parameter (m) for the five investigated materials, using the variables P (probability of failure) and σ (Flexural strength).

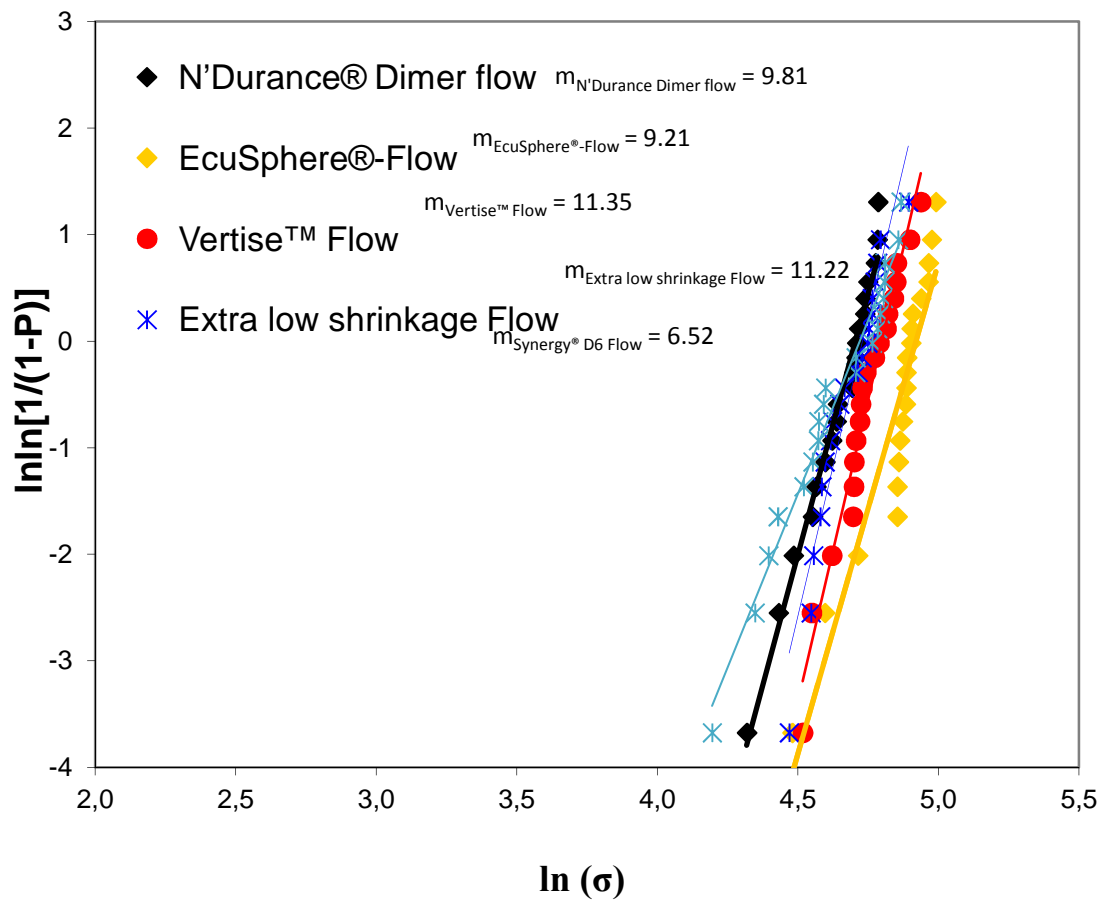
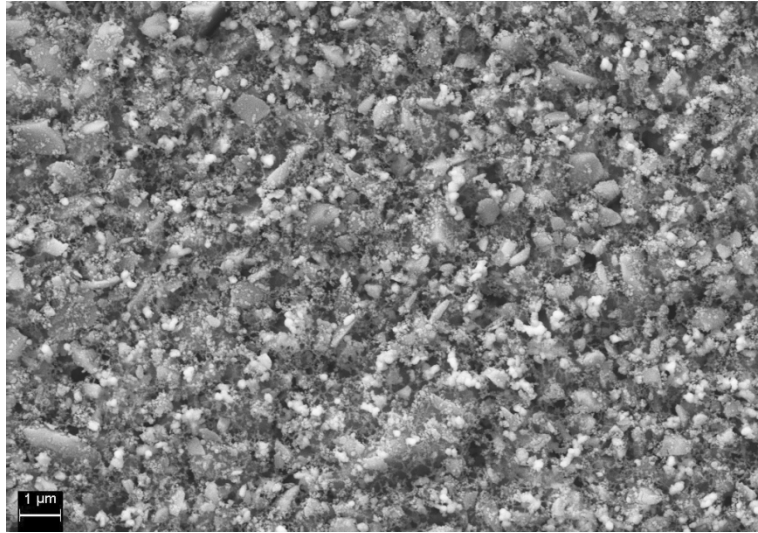
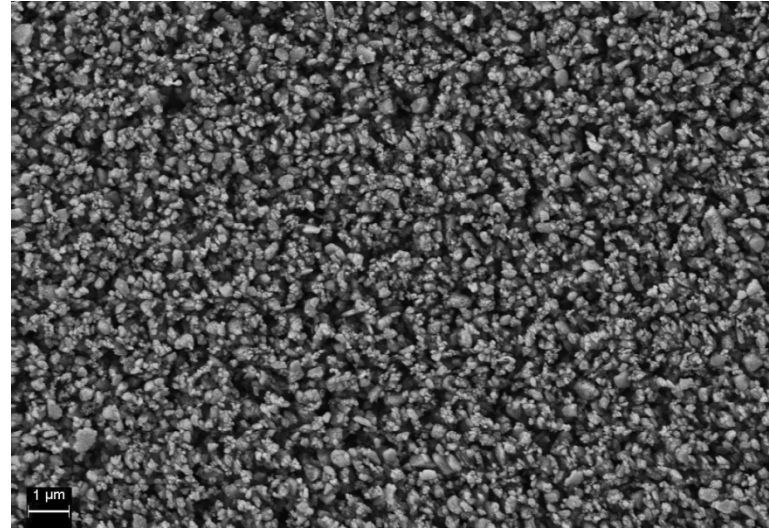


Figure 2: Fe-SEM pictures of the measured materials.

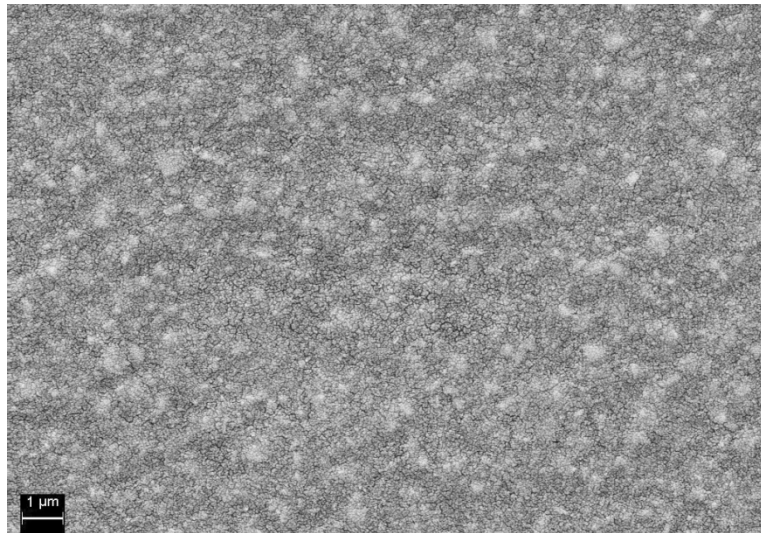
Vertise™ Flow



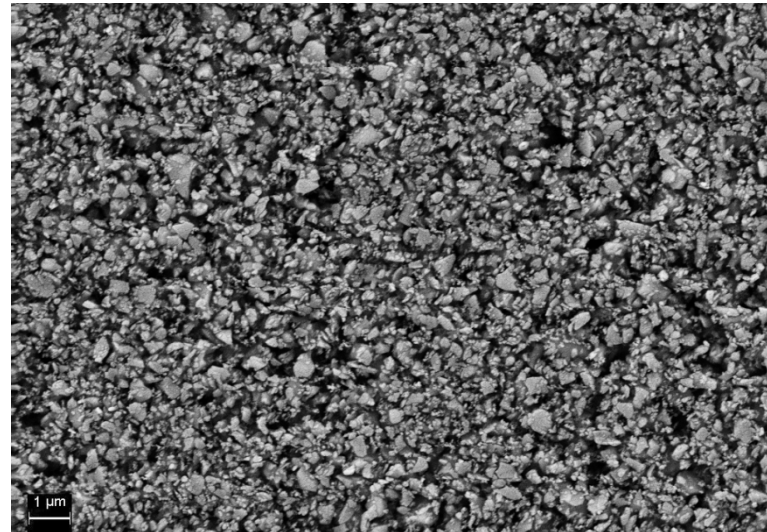
N'Durance® Dimer flow

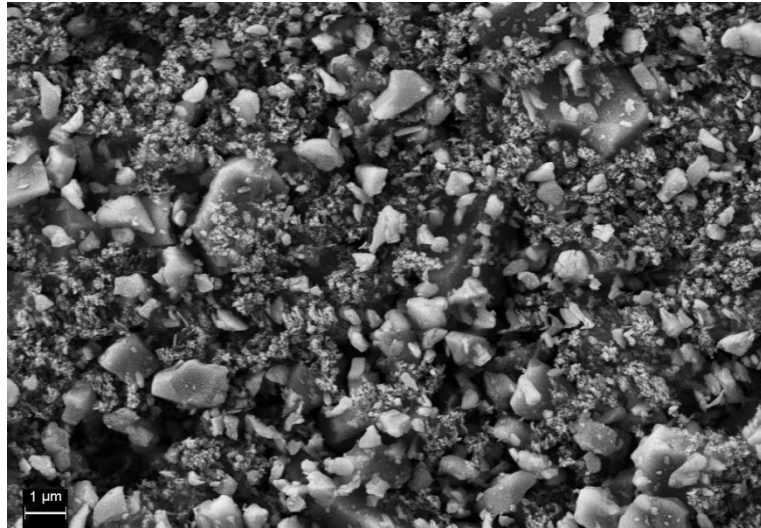


Synergy® D6 Flow



Extra low shrinkage flow



EcuSphere[®]-Flow

2.2.1 Deutsche Zusammenfassung

Ziel der Untersuchung war es ein selbstadhäsives fließfähiges Komposit mit zwei niedrigschrumpfenden Kompositen und zwei Mikrohybridkompositen bezüglich ihrer Konversionsrate (KR), ihrer mikromechanischen Eigenschaften (Eindringmodul (E), Vickershärte (HV)) sowie ihrer makromechanischen Eigenschaften (Biegefestigkeit (σ), Biegemodul (E_{Biege}) zu vergleichen.

Die Arbeitshypothesen waren:

- (a) Es gibt keinen signifikanten Unterschied bezüglich der Konversionsrate zwischen den fünf untersuchten Materialien zu jeder Belichtungszeit und Inkrementdicke.
- (b) Es gibt keinen signifikanten Unterschied zwischen den fünf untersuchten Materialien bezüglich makromechanischer (Biegefestigkeit (σ), Biegemodul (E_{Biege})) und mikromechanischer (Vickershärte (HV), Eindringmodul (E)) Eigenschaften bei einer klinisch praktikablen Belichtungszeit von 20s.

Die KR (n=6) wurde durch eine Fourier-Transformations-Infrarotspektrometrie (FTIR) in klinisch relevanten Inkrementdicken (0,1 mm, 2 mm, 4 mm, 6 mm-Bulk (1 Inkrement), 6 mm-Inkrement (geschichtet in dreimal 2mm dicken Inkrementen) und Belichtungszeiten (10s, 20s, 40s) bestimmt. Mikromechanische und makromechanische Eigenschaften wurden von einem Universalhärtemessgerät und einer Drei-Punkt-Biegeversuch Anordnung gemessen, nachdem die Prüfkörper 24 Stunden lang bei 37°C in destilliertem Wasser gelagert wurden. Ein Rasterelektronenmikroskop diente zur Visualisierung der Füllkörper. Die Ergebnisse wurden mittels univariater Varianzanalyse, Tukey's honest significance post-hoc-Test, einer multivariaten Varianzanalyse ($\alpha=0,05$) und einer Korrelation nach Pearson ausgewertet. Eine Verlässlichkeitsbestimmung wurde für σ mittels Weibullanalyse (m-Parameter) durchgeführt.

N'Durance[®] Dimer flow (65,66%) zeigte die höchsten KR-Werte (bei 2 mm Inkrementdicke, 20s Belichtungszeit). Bezüglich der makromechanischen Eigenschaften zeigten EcuSphere[®]-Flow (129,82 MPa) für die Biegefestigkeit und Synergy[®] D6 Flow (3,74 GPa) für den Biegemodul die höchsten Werte. Die besten mikromechanischen Eigenschaften wurden für das selbstadhäsive Komposit (Vertise[™] Flow; $E= 10,81$ GPa; $HV= 60,20$ N/mm²) gemessen. Die Verlässlichkeit wurde stark von Füllkörpergewicht ($\eta^2= 0,77$) und Füllkörpergröße ($\eta^2= 0,99$) beeinflusst. Außerdem zeigte sich ein starker

Zusammenhang zwischen dem Kompositmaterial und den untersuchten Materialeigenschaften.

Mit Rücksicht auf die Limitationen dieser Studie zeigte das selbstadhäsive Komposit (Vertise™ Flow) die besten KR-Werte nach 5 Minuten Polymerisation (zusammen mit dem Dimersäure- basierten Komposit) sowie die besten mikromechanischen Eigenschaften. Die Mikrohybridkomposite zeigten die besten makromechanischen Eigenschaften: EcuSphere®-Flow für die Biegefestigkeit und Synergy® D6 Flow für den Biegemodul. Aus den genannten Gründen wurden demnach beide Arbeitshypothesen widerlegt. Für das selbstadhäsive Komposit scheinen 40s Belichtungszeit und eine Schichtung in maximal 2 mm dicken Inkrementen zur Erzielung guter mechanischer Eigenschaften nötig zu sein.

2.2.2 English summary

The aim of the study was to compare a self-adhesive with two low shrinkage and two regular flowable resin-based composites (RBCs) in terms of degree of conversion (DC) and mechanical properties measured at microscopic (Indentation modulus (E), Vickers hardness (HV)) and macroscopic scale (Flexural strength (σ) Flexural modulus (E_{flexural})).

The tested null-hypotheses were that:

- (a) There would be no significant difference between the five materials in view of DC at any measured depth and irradiation time.
- (b) There would be no significant difference between the five materials when measuring mechanical properties at macro- (flexural strength ($=\sigma$) and modulus of elasticity ($=E_{\text{flexural}}$)) and micro-scale (Vickers hardness ($=HV$) and indentation modulus ($=E$)) at a clinical relevant irradiation time of 20s.

DC (n=6) was investigated by Fourier transform infrared spectroscopy (FTIR) in clinical relevant filling depths (0.1, 2, and 4 mm; 6 mm-bulk, 6 mm-incremental) and irradiation times (10s, 20s, 40s). Micro- and macro-scale mechanical properties were measured by an automatic microhardness indenter and a three-point bending test device after curing the specimens for 20s and storing them in distilled water for 24h at 37°C. Fillers were visualized by a field emission scanning electron microscope. Results were evaluated using one-way ANOVA, Tukey's HSD post-hoc test, Pearson correlation and a multi-variate analysis ($\alpha = 0.05$). A Weibull analysis was used to assess σ .

N'Durance[®] Dimer flow (65.66%) reached the highest DC (at 2 mm depth, 20s irradiation). At macro-scale EcuSphere[®]-Flow (129.82 MPa) for σ and Synergy[®] D6 Flow (3.74 GPa) for E_{flexural} reached highest values. The highest micro-mechanical properties were measured for the self-adhesive RBC (Vertise[™] Flow; $E = 10.81$ GPa, $HV = 60.20$ N/mm²). Reliability was highly influenced by filler weight ($\eta^2 = 0.77$) and volume ($\eta^2 = 0.99$) proportion.

A strong influence of the material on all measured properties, as well as a strong influence of filler proportion (wt%-filler, vol%-filler) on the reliability was statistically proven.

Within the limitations of our study the self-adhesive RBC (Vertise[™] Flow) showed best performance concerning DC after five minutes of polymerization (together with the dimer-acid based RBC) and mechanical properties measured at micro-scale. The

traditional microhybrid flowable RBCs performed best in the macroscopic mechanical properties σ (EcuSphere[®]-Flow) and E_{flexural} (Synergy[®] D6 Flow). Therefore both null hypotheses had to be rejected. For the self-adhesive RBC a curing time of 40s as well as an incremental placement not exceeding 2 mm thickness appeared to be necessary.

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