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Investigations towards nano-hybrid resin-based composites

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Abstract

Objective Clinical data indicate an increased trend in material fracture as reason for failure in composite restorations, questioning whether modern resin-based composites (RBCs) are able to fulfil the rising aesthetical demands and to provide at the same time a sufficient mechanical stability also in larger cavities. Nano-hybrid RBCs are promoted as materials with improved mechanical properties. The aim of this study was to analyse differences in mechanical properties within and between modern flowable and non-flowable nano-hybrid and micro-hybrid RBCs by measuring mechanical properties at macro- and micro-scale.

Methods Thirty-four RBCs with traditional and new monomer formulation or photo-polymerization initiator technology—15 nano-hybrid, nine micro-hybrid and ten flowable—were therefore considered. Flexural strength, flexural modulus (E_{flexural}), indentation modulus, Vickers hardness (HV) and creep were measured after the samples had been stored in water for 24 h at 37°C. Differences within the materials as well as within material categories were statistically analysed using one-way ANOVA with Tukey HSD post hoc test (α =0.05) as well as partial eta-square statistics.

Results The category of micro- and nano-hybrid RBCs performed in all properties superior compared to the flowable RBCs. The former two categories differ significantly only with regard to three parameters, with nano-hybrid RBCs showing higher HV respectively lower $E_{flexural}$ and filler weight. The micro-mechanical parameters proved to be

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Dental School of the Ludwig-Maximilians-University, Goethestr. 70, 80336 Munich, Germany e-mail: nicoleta.ilie@dent.med.uni-muenchen.de more sensitive to differences in filler amount and RBCs type than the macro-mechanical properties.

Clinical relevance Only few differences were found between nano-hybrid and micro-hybrid RBCs as a material category and thus, from laboratory tests, no clear advantages in the mechanical stability in stress-bearing areas of nanohybrid RBCs are expected clinically. Similar is valid for materials with new monomer formulation or photopolymerization initiator technology. However, several of the measured nano-hybrid RBCs showed consistently higher mechanical properties than the mean values of the micro-hybrid RBCs.

Keywords Flexural strength · Modulus of elasticity · Hardness · Resin-based composites

Introduction

Comprehensive reviews of the last years, searching for reasons of clinical failures in resin-based composite (RBC) restorations, indicate an increased trend in material fracture, questioning thus the sufficient mechanical stability of RBCs in stress-bearing areas [1–4].

In posterior composite restorations, secondary caries and restoration fracture were found to be the most common clinical problems, as reviewed by Sarrett in 2005 [1]. Clinical studies published between 1996 and 2002 regarding direct posterior restorations in service periods up to 5 years showed that RBC fracture was the most frequent type of failure, whereas secondary caries was the most common failure beyond 5 years of clinical service [2]. For RBC restorations placed in larger cavities, the predominant reason for failure was found to be fracture as well, also for periods longer than 11 years [3, 4]. It seems that these actual trends

are a consequence of extending the indication for RBCs to larger multi-surface posterior approximal cavities as well as decreasing the filler size to improve aesthetics. The development of nano- and nano-hybrid RBCs tried to repeal these deficits, promising both, excellent aesthetics and improved mechanical properties. Long-term clinical studies with nano- and nano-hybrid RBCs to certify these advantages are not available until now, forcing practitioners to rely on laboratory data for assessing the material's performance.

Apart from improvements in filler systems, modern nanohybrid RBCs showed a trend in changing the monomer-matrix formulations. Besides traditional monomers like bis-GMA (bisphenol-A diglycidyl ether dimethacrylate), BIS-EMA (bisphenol A polyethylene glycol diether dimethacrylate), UDMA (urethane dimethacrylate) or TEGDMA (Triethyleneglycol dimethacrylate), a series of new monomers are either complete replacing the traditional monomers or only merged in a traditional monomer formulation.

As such an example, dimer acid-based monomers were synthesized in an attempt to reduce volume shrinkage during polymerization by using high molecular weight monomers with decreased initial double-bond concentrations. The monomers are derived from a core structure based on hydrogenated dimer acid, a derivative of linoleic acid, which is an essential fatty acid [5]. Compared to conventional dimethacrylate monomers like bis-GMA or UDMA, the dimer acid dimethacrylate monomers showed higher molecular weights and lower initial double bond concentrations with relatively low viscosities [5]. A higher degree of conversion, a lower polymerization shrinkage and water sorption values in comparison with conventional monomers were also measured. Besides that, the relatively low cross-link density of dimethacrylates constructed from dimer acid was shown to produce polymers with high flexibility but low modulus of elasticity [5]. The commercial nano-hybrid RBC based on this dimer acid derivate (N'Durance, Septodont, France) has included in the organic matrix also traditional monomers like BisGMA, UDMA and dicarbamate.

TCD-urethane monomers TCD-urethane monomers are new methacrylic acid derivatives, containing urethane groups of tricyclodecanes (TCD), being prepared by reaction of hydroxyalkyl (meth)acrylic acid esters with diisocyanates and subsequent reaction with polyols [6] (nano-hybrid RBCs Venus Diamond and Venus Diamond Flow, Kulzer, Germany). Due to the low viscosity of TCD-urethane monomers, no further diluents are needed thus reducing the polymerization shrinkage in comparison to BisGMA-based RBCs [7] but also when compared to the low shrinkage silorane-based RBC [8]. As a result of the steric restriction of the mobility, the urethane derivatives of 1,3-bis(1-isocyanato-1-methylethyl) benzene are very similar in terms of their properties to bis-GMA and can be used in dental RBCs in its place, as described in the

patent EP 0 934 926 [9]. Being an acrylic acid ester, the monomer is described to have a high reactivity, achieving consequently higher degrees of conversion as traditional monomers and also a high biocompatibility [10].

DX-511 Reducing shrinkage through implementation of monomers with a higher molecular weight was also the idea behind the synthesis of the monomer DX-511 from DuPont. The molecular weight of DX-511 is 895 g/mol, being thus consistently higher compared to Bis-GMA (512.6 g/mol) and UDMA (470.6 g/mol). The new methacrylate monomer consists of a long rigid core with flexible side arms and a lower number of C = C double bonds. Besides DX-511, the composite matrix of the nano-hybrid composite (Kalore, GC, Japan) also contains diurethane methacrylate and dimethacrylate co-monomers (manufacturers' information).

The aim of this study was to assess the mechanical properties of modern flowable and non-flowable nanohybrid and micro-hybrid RBCs at a macro- and microscale, with traditional and new monomer formulation or photo-polymerization initiator technology.

The null hypotheses were: (a) there would be no significant difference in micro (Vickers hardness (HV), indentation modulus (E) and creep (Cr)) and macro (flexural strength (FS) and flexural modulus (FM)) mechanical properties among various types of resinbased composites; (b) there would be no significant difference in the above-mentioned properties within RBCs belonging to the same material type.

Materials and methods

The mechanical properties of 34 restorative materials comprising three material categories: nano-hybrid (15), microhybrid (nine) and flowable RBCs (ten) were analysed (Table 1).

Flexural strength and flexural modulus The FS and FM were determined in a three-point bending test (n=20) in analogy to ISO/DIN 4049:1998. The samples were made by compressing the composite material between two glass plates with intermediate polyacetate sheets, separated by a steel mould having an internal dimension of $2 \times 2 \times 16$ mm. Irradiation occurred on top and at the bottom of the specimens, with three light exposures of 20 s per side, overlapping one irradiated section no more than 1 mm of the diameter of the light guide (Elipartm Freelight 2, 3 M ESPE, Seefeld, Germany), in order to prevent multiple polymerization. After removal from the mould, the specimens were ground with silicon carbide sand paper (grit size, P 1200/4000 (Leco)) in order to get rid of disturbing edges or

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Table 1 Materials, manufacturer,	chemical composition of matrix and filler as	s well as filler content by weight and volume p	ercent	
Nano-hybrid RBCs	Manufacturer/batch	Resin matrix	Filler	Filler, wt./vol
CeramX Duo D3	Dentsply Caulk, 0810000250	ORMOCER, DM Ethyl-4 (dimethvlamino)henzoate	Ba-Al-B-Si-glass, SiO ₂ -nanofiller	76/57
CeramX Duo E3	Dentsply Caulk, 0810002674	ORMOCER, DM Ethyl-4 (dimethylamino)benzoate	Ba-Al-B-Si-glass, SiO ₂ -nanofiller	76/57
Empress Direct Dentin	Ivoclar Vivadent, M68447	DM	Ba-Al-Si-glass, YbF ₃ , SiO ₂ /ZrO ₂ - MO. Nanomodifier	75/53
Empress Direct Enamel	Ivoclar Vivadent, M66966	DM	Ba-Al-Si-glass, SiO ₂ /ZrO ₂ MO, Nanomodifier	78/58
Empress Direct Opal	Ivoclar Vivadent, M62836	DM	Ba-Al-Si-glass, YbF ₃ , SiO ₂ /ZrO ₂ -MO, Nanomodifier	60.5/45
Filtek Supreme XT Dentin	3 M-ESPE, 6BE	BisGMA, BisEMA, UDMA, TEGDMA	ZrO ₂ /SiO ₂ cluster SiO ₂ nanofiller	78.5/59.5
Filtek Supreme XTE	3 M-ESPE, N141479	BisGMA, BisEMA, UDMA, TEGDMA, PEGDMA	ZrO ₂ -SiO ₂ cluster SiO ₂ and ZrO ₂ nanofiller	78.5/63.3
Kalore	GC, 0903131	DX-511 monomer, di-UDMA, DM	F-Al-Si-glass, Ba-Sr-glass, SiO ₂ - nanofillers, PPF	82/69
Grandio	Voco, 0921103	BisGMA, UDMA, DM, TEGDMA	F-Si-glass, SiO ₂	87/71.4
Miris 2	Coltène/Whaledent, 0191818	Methacrylates	Ba-glass, SiO_2	80/65
N'Durance	Septodont, G-9020-11	BisGMA, UDMA, dicarbamate dimethacrvlate dimer acid	YbF ₃ , Ba-glass, SiO ₂	80/65
Premise	Kerr, 3120178	TEGDMA, BisGMA	Ba-glass, SiO ₂ , PPF	84/71.2
Simile	Pentron Clinical, 190633	PCBisGMA, BisGMA, UDMA, HDDMA	Ba-Si-glass, Zr-silicate, SiO ₂	75/66
Tetric Evo Ceram	Ivoclar-Vivadent, M69649/ J17761	BisGMA, UDMA, DMDMA	Ba-glass, YbF ₃ , MO, PPF	76/54
Venus Diamond	Heraeus, 010029	TCD-DI-HEA, UDMA	Ba-Al-F-glass	81/64
Micro-hybrid RBCs	Manufacturer/batch	Resin matrix	Filler	Filler, wt./vol
Estelite Posterior	Tokuyama Dental, W216	Bis-GMA, TEGDMA, Bis-MPEPP	ZrO_2 -SiO ₂	84/70
Estelite Sigma Quick	Tokuyama Dental, E654M	Bis-GMA/TEGDMA	ZrO_2 -SiO ₂	82/71
EsthetX	Dentsply Caulk, 505002629	BisGMA, BisEMA, TEGDMA	Ba-F-Al-B-Si-glass, SiO ₂	77/60
Filtek Silorane	3 M, ESPE/203908	3,4-Epoxycyclohexylethylcyclo- polymethylsiloxane Bis-3, 4-epoxycyclohexylethyl- nhenvlmethylsilane	SiO ₂ , YF ₃	76/55
Gradia Direct Anterior	GC, 0901211	UDMA, DM	SiO_{2} , PPF	73/64
Gradia Direct X	GC, 0901096	UDMA, DM	SiO_2 , PPF	-/2/
Tertric Ceram HB	Ivoclar-Vivadent, N03283	BisGMA, UDMA, DDM	Ba-glass, Ba-Al-F-Si-glass, YbF ₃ , SiO ₂ , MO	81/63
Tetric	Ivoclar-Vivadent, D54725	Bis-GMA, UDMA, TEGDMA	Ba-glass, YbF ₃ , SiO ₂ , MO	81/62
Tetric Ceram	Ivoclar-Vivadent, D51302	Bis-GMA, TEGDMA, UDMA	Ba-glass, Ba-Al-F-Si-glass,YbF ₃ , SiO _{2,} MO	78.6/60

Table 1 (continued)				
Flowable RBCs	Manufacturer/batch	Resin matrix	Filler	Filler, wt/vol
Nano-hybrid flowable				
Filtek Supreme XT Flow	3 M ESPE, 20080815	BisGMA, TEGDMA, Bis-EMA	ZrO ₂ , SiO ₂ nanofiller ZrO ₂ /SiO ₂ nanocluster	65/55
Grandio Flow	Voco, 0838114	BisGMA, TEGDMA, HEDMA	SiO ₂ ; Ba-Al-B-Silicate	80/65.6
Tetric EvoFlow	Ivoclar Vivadent, M07441	DM	Ba-glass, Yb ₃ F, SiO ₂ , MO	57.5/30.7
Venus Diamond flow	Heraeus, VP200409HA-K1	multifunctional methacrylate monomers UDMA, EBADMA	Ba-AI-F-Si-glass, YbF ₃ , SiO ₂	65/41
Micro-hybrid flowable				
Gradia Direct Flow	GC, 0906111	UDMA, DM	SiO ₂ , F-Al-Si-glass, PPF	67/45
Gradia Direct LoFlo	GC, 0902041	UDMA, DM	SiO ₂ , F-Al-Si-glass, PPF,	63/
Revolution Formula 2	Kerr, 3192110	Bis-GMA	Filler	60/48
SureFil® SDR TM flow	Dentsply Caulk, QD2-161	Modified UDMA, EBPADMA, TEGDMA	Ba-Al-F-B-Si-glass St-Al-F-Si- glass	68/44
Tetric Flow	Ivoclar Vivadent, J12549	Bis-GMA, UDMA, TEGDMA	Ba-glass, Yb ₃ F, Ba-Al-F-Si-glass, SiO ₂ , MO	64.6/39.7
X-Flow	Dentsply Caulk, 09093001898	Di- and multifunctional acrylate and methacrylate resins, DEMA	Sr-Al-Na-F-P-Si-glass, SiO ₂	60/38
Data are provided by the manufa. BIS-EMA bisphenol A polyethyle	sturers sne elvcol diether dimethacrylate, <i>Bis-GMA</i>	bisphenol-A diglycidyl ether dimethacrylate. Bis	- <i>MPEPP</i> bisphenol A polvethoxy methacrylate	e, <i>DDM</i> decandiol

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bulges. All specimens were then stored in distilled water at 37°C prior to testing for 24 h. The samples were loaded until failure in the universal testing machine (Z 2.5, Zwick/Roell, Ulm, Germany) in 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 the testing, the specimens were immersed in distilled water at room temperature. The crosshead speed was 0.5 mm/min. The universal testing machine measured the force during bending as function of deflection of the beam. The bending modulus was calculated from the slope of the linear part of the force deflection diagram.

Micro mechanical properties

Fragments (n=10) of the three-point bending test specimens were used to determine the micro-mechanical properties-Vickers hardness (HV), indentation modulus (E) and creep (Cr)-according to DIN 50359-1:1997-10 by means of a universal hardness device (Fischerscope H100C, Fischer, Sindelfingen, Germany). Prior to testing, the samples were polished with a diamond suspension (mean grain size, 1 µm). Measurements were done on the first polymerised side of the slabs (six measurements per sample, 60 measurements for each material). The test procedure was carried out force controlled; the test load increased and decreased with constant speed between 0.4 and 500 mN. The load and the penetration depth of the indenter were continuously measured during the load-unload hysteresis. The universal hardness is defined as the test force divided by the apparent area of the indentation under the applied test force. From a multiplicity of measurements, a conversion factor between universal hardness and Vickers hardness was calculated and implemented in the software, so that the measurement results were indicated in the more familiar HV units. The indentation modulus (E) was calculated from the slope of the tangent of indentation depth curve at maximum force. By measuring the change in indentation depth with constant test force, a relative change in the indentation depth can be calculated. This is a value for the creep of the materials.

Statistical analysis

Results were statistically compared using one-way ANOVA and Tukey HSD post hoc test (α =0.05) as well as a Pearson correlation analysis. A multivariate analysis (general linear model with partial eta-squared statistics) tested the influence of the parameters RBCs type, filler volume and filler weight on the considered properties (SPSS Inc.; Chicago, IL, USA, version 18.0).

Results

The results of the investigated properties for the examined materials are summarized in Tables 2, 3, 4, 5 and 6. Post hoc multiple pairwise comparisons with Tukey's HSD test (p < 0.05) (Table 5) showed that, within the tested material categories, the micro- and nano-hybrid RBCs performed superior in all properties compared to the flowable RBCs. Comparing the former two categories, significant differences were calculated only for HV, $E_{flexural}$ and filler weight, showing higher HV respectively lower $E_{flexural}$ and filler weight for the nano-hybrid RBCs.

The influence of the parameters RBCs type, filler volume and filler weight were analyzed in an ANOVA multivariate test. The filler volume and filler weight data were taken as indicated by manufacturer. The macro-mechanical properties-flexural strength and modulus of elasticity in flexural test-and micromechanical properties-modulus of elasticity in universal hardness test, Vickers hardness and creep-were selected as dependant variables. The significant values of these three main effects were less than 0.05, indicating that they contribute all to the model. The results of the ANOVA multivariate test are summarised in Table 6, showing that the strongest influence on the mechanical properties (higher eta square values) was performed by the filler volume, followed by RBC type, whereas the influence of filler weight was, except for the parameter creep, lower. Furthermore, the micro-mechanical parameters proved to be more sensitive (higher eta square values) to differences in filler amount and RBCs type than the macromechanical properties.

The modulus of elasticity measured in both methods flexural test and universal-hardness test —correlated well (Pearson correlation coefficient=0.8). There was a good correlation within the micro-mechanical properties (E– HV=0.9; E-Cr=-0.7; HV-Cr=-0.8) and macromechanical properties (FS– $E_{flexural}=0.7$) as well.

Discussion

Like in almost all fields of science, nanotechnology found application also in restorative dentistry. Defined as the creation of functional materials with structures sized between 1 to 100 nm in at least one dimension, nanotechnology developed materials with fundamental new physical, chemical or biological behaviour, difficult to be fully explained by current theories [11].

The implementation of nano-filler in dental RBCs was motivated by the wish to increase the filler amount, without necessarily changing the composite's viscosity, and to enhance the mechanical properties. Having dimensions below the wavelength of visible light (390 to 750 nm) nanoparticles are unable to scatter or absorb visible light, an

Table 2 Nano-hybrid RBCs

Micro-mechanical properties (Vickers hardness HV [N/mm²], modulus of elasticity E [GPa] and creep Cr [%]) as well as macro-mechanical properties (flexural strength FS [MPa] and modulus of elasticity in flexural test E_{flexural} [GPa]) are detailed in mean values and standard deviations (in parentheses). Letters indicate statistically homogeneous subgroups (Tukey's HSD test, α =0.05)

Nano-hybrid composite	Е	HV	Cr	FS	E _{flexural}
Empress Direct Opal	6.0a (0.4)	35.6A (2.9)	4.6h (0.2)	73.8 A (5.3)	2.9a (0.2)
N'Durance	10.7b (0.5)	73.5B (6.4)	3.4de (0.2)	123.5EF (15.0)	5.3bc (0.7)
Tetric Evo Ceram	12.4c (0.3)	70.9B (3.2)	3.8g (0.1)	115.3DE (11.3)	6.7de (1.1)
Premise	12.5c (0.5)	73.8B (4.2)	3.7f (0.1)	91.0BC (10.2)	4.8b (0.8)
CeramX E3	12.9cd (1.5)	90.9DE (5.6)	3.4d (0.2)	103.3CD (21.6)	5.3bc (0.9)
Empress Direct Dentin	13.1de (0.3)	73.5B (1.7)	3.9g (0.1)	132.1FG (13.7)	5.3bc (0.9)
Kalore	13.4ef (0.5)	73.0B (5.2)	3.8e (0.2)	103.3A (13.2)	5.0bc (0.9)
Empress Direct Enamel	13.6ef (0.3)	85.6C (3.1)	3.8g (0.1)	104.8CD (8.5)	4.5b (0.8)
Ceram X D3	13.9fg (0.9)	88.0CD (3.8)	3.4d (0.1)	82.8AB (15.6)	5.6bc (0.6)
Simile	14.1g (0.2)	91.9E (2.4)	3.4d (0.1)	136.4FG (10.9)	5.4bc (0.7)
Miris 2	15.0h (0.8)	90.3DE (3.9)	3.5e (0.1)	131.3FG (15.2)	5.9cd (1.3)
Filtek Supreme XTE	15.9i (0.5)	115.9F (2.7)	3.1c (0.1)	168.9H (13.0)	8.4f (0.5)
Filtek Supreme XT Dentin	16.8j (0.2)	123.0G (2.6)	2.9b (0.1)	163.7H (18.1)	10.0g (1.4)
Venus Diamond	17.3 ^k (0.8)	91.5 ^{DE} (7.1)	3.8 ^g (0.2)	157.6 ^H (12.7)	7.1 ^e (1.2)
Grandio	23.5 ¹ (1.5)	161.3 ^H (12.2)	$2.6^{a}(0.2)$	141.8 ^G (16.0)	8.8 ^f (1.2)

important aspect in light curing and aesthetics. Almost all dental companies have consequently introduced on the market so-called nano-hybrid RBCs, promising a consistently improvement in the materials' behaviour. But nano-particles have been used for years in dental RBCs, for instance as colloidal silica particles in microfilled and micro-hybrid RBCs, questioning if the promised jump toward increasing mechanical properties in nano-hybrid RBCs is possible at all.

The present study showed that nano-hybrid RBCs, as material type, perform quite similar compared to microhybrid RBCs. The filler volume of the two material categories do not differ significantly, whereas the filler weight was less but significantly higher in the micro-hybrid RBCs group (Table 5). Thus both results stay in contrast to the initial proposals in the development of nano-hybrid RBCs, as mentioned above. It must, however, be pointed out that

Table 3	Micro-h	ybrid	RBCs
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the interpretation of the effect of filler on the mechanical properties is hindered by the incertitude of whether the manufacturer has indicated only the inorganic filler content or the total filler content, which comprise additionally the pre-polymerized fillers. Despite lower filler weight and comparable filler volume, the Vickers hardness of nanohybrid RBCs, as a material category, was higher. One reason therefore could be found in the chemical nature of nanofillers, being predominantly made of crystalline silica and zirconia (Table 1) and thus harder then amorphous glasses, predominantly used in micro-hybrid RBCs. But more probable, this behaviour is due to changes which occurred in the organic matrix between the particles as a consequence of decreasing filler size and thus decreasing inter-particle distances. This so-called interfacial region is responsible for the communication between the matrix and the filler, and its conventionally ascribed properties are different from the

Micro-hybrid Composite	E	HV	Cr	FS	E _{flexural}
Gradia Direct Anterior	7.5a (0.5)	46.5A (3.0)	4.3f (0.1)	98.0A (8.4)	3.4a (0.4)
Gradia Direct X	9.2b (0.6)	46.9A (5.4)	4.5g (0.2)	96.0A (8.0)	3.9a (0.5)
Estelite Sigma Quick	11.5c (0.4)	75.5C (4.5)	3.5d (0.1)	106.4AB (9.1)	5.2b (0.8)
Filtek Silorane	12.5d (0.3)	70.5B (2.6)	3.3b (0.1)	131.0C (14.8)	7.9d (1.1)
Esthet.X	13.7e (0.3)	81.8D (4.7)	3.4c (0.1)	119.3BC (14.7)	8.2d (1.5)
Tertric Ceram HB	15.2f (0.5)	86.0E (3.3)	3.6d (0.1)	122.4C (21.1)	6.6c (0.4)
Tetric Ceram	15.2f (0.3)	82.4D (2.3)	3.7e (0.1)	134.7C (11.0)	7.9d (0.9)
Tetric	17.7g (0.5)	98.0F (4.8)	3.5d (0.1)	153.6D (21.2)	9.3e (1.7)
Estelite Posterior	21.5h (0.6)	119.6G (4.9)	3.2a (0.1)	167.1D (16.9)	10.7f (0.7)

Micro-mechanical properties (Vickers hardness HV [N/mm²], modulus of elasticity E [GPa] and creep Cr [%]) as well as macro-mechanical properties (flexural strength FS [MPa] and modulus of elasticity in flexural test $E_{flexural}$ [GPa]) are detailed in mean values and standard deviations (in parentheses). Letters indicate statistically homogeneous subgroups (Tukey's HSD test, α =0.05)

Table 4 Flowable RBCs

Flowables Composite	Е	HV	Cr	FS	E _{flexural}
Revolution Formula 2	5.8a (0.7)	33.3AB (2.8)	4.4e (0.3)	76.5A (7.9)	2.8a (0.3)
Tetric EvoFlow	6.1 ab (0.5)	37.4C (1.5)	4.5e (0.1)	104.2BC (10.2)	2.8a (0.4)
Gradia Direct LoFlo	6.6b (0.2)	32.3A (2.9)	4.5e (0.3)	95.6B (7.7)	2.7a (0.3)
VENUS Diamond flow	7.1c (0.7)	37.9C (3.3)	4.7f (0.2)	106.8BCD (8.5)	4.4bc (0.5)
Tetric Flow	8.2d (0.8)	50.1D (2.4)	4.2d (0.1)	118.1DE (9.9)	5.0d (0.4)
X-Flow	9.0e (0.7)	56.3E (4.9)	3.9c (0.2)	108.9CD (6.8)	4.3bc (0.3)
SureFil® SDR [™] flow	9.2ef (1.0)	36.3BC (3.6)	5.4g (0.3)	125.9EF (19.9)	4.9cd (1.2)
Filtek Supreme XT Flow	9.3ef (0.3)	59.1 E (3.8)	3.6b (0.2)	110.3CD (11.0)	4.7cd (0.6)
Gradia Direct Flow	9.7f (0.5)	49.3D (3.6)	4.9f (0.2)	135.6F (8.1)	3.9b (0.6)
Grandio Flow	15.8g (0.7)	108.3F (7.9)	3.0a (0.2)	115.7CDE (21.0)	5.1d (0.6)

Micro-mechanical properties (Vickers hardness HV [N/mm²], modulus of elasticity E [GPa] and creep Cr [%]) as well as macro-mechanical properties (flexural strength FS [MPa] and modulus of elasticity in flexural test $E_{flexural}$ [GPa]) are detailed in mean values and standard deviations (in parentheses). Letters indicate statistically homogeneous subgroups (Tukey's HSD test, α =0.05)

bulk matrix because of its proximity to the surface of the filler [12]. It was also shown that nano-particles create local specific properties in RBCs, with a spatial distribution of the nano-dynamic–mechanical properties, suggesting a graduated structure, with a smooth transition from the stiff filler to the softer matrix [13].

The other measured micro-mechanical properties—modulus of elasticity and creep—were comparable for both material categories. At macroscopically scale, the modulus of elasticity measured in flexural test was significant lower in nano-hybrid RBCs compared to micro-hybrid RBCs, being in accordance with previous measurements [14].

At an equivalent filler volume, decreasing the particle dimension in nano-hybrid RBCs will lead in larger filler surfaces relative to the volume size, resulting in a larger interface between filler and organic matrix, when compared to micro-hybrid RBCs. The interface between filler and organic matrix is thus the critical point for the hydrolytically stability of an RBC. Trends are evident suggesting a faster degradation of mechanical properties by aging in nanohybrid RBCs when compared to micro-hybrid RBCs [14].

Within the nano-hybrid RBCs, the material with the highest filler weight and volume content —Grandio—also reached the best micro-mechanical properties as well as very good macro-mechanical properties, achieving thus the initial proposal in the development of nano-hybrid RBCs. Though having a higher filler volume and the same filler weight, Filtek Supreme XTE, the last development in the Filtek Supreme RBC series, showed slightly but significantly lower mechanical properties (E, HV, E_{flexural} and lower creep resistance) compared to Filtek Supreme XT Dentin (Table 2). Both materials have almost the same chemical formulation, with small amounts of PEGDMA in Filtek Supreme XTE as a substitute for a portion of the TEGDMA resin in Filtek Supreme XT to moderate shrinkage (manufacturer information). The assumed lower shrinkage in Filtek Supreme XTE, albeit no publications are available, therefore could have led to lower stresses in the RBCs and also to lower mechanical properties, despite higher filer content. Compared to other nano-hybrid materials. the filler in the former two materials consists, besides nanoparticles, also of nano-clusters, which have demonstrated to provide a distinct fracture mechanism in RBCs [15] significantly improving the strength and reliability, when subjected to cyclic pre-loading [16]. The potential consequence could be an improvement in fatigue behaviour and thus an enhanced clinical longevity of the material [17].

Though having high filler content, the modulus of elasticity in the dimer acid-based composite N'Durance was

Table 5 Material category, including filler volume and weight percent

	•	• ·				
Е	HV	Cr	FS	E _{flexural}	Vol%	Wt%
9.3a (3.1)	53.4A (25.4)	4.3a (0.8)	110.0A (19.5)	4.1a (1.1)	47.5A (9.5)	66.6a (6.4)
13.8b (4.1)	78.7B (22.1)	3.7b (0.4)	124.5B (27.4)	6.9c (2.6)	63.1B (5.0)	78.9c (3.3)
14.1b (3.7)	86.6C (26.9)	3.6b (0.5)	124.9B (30.8)	6.2b (1.9)	62.5 B (7.8)	77.4b (7.6)
	E 9.3a (3.1) 13.8b (4.1) 14.1b (3.7)	E HV 9.3a (3.1) 53.4A (25.4) 13.8b (4.1) 78.7B (22.1) 14.1b (3.7) 86.6C (26.9)	E HV Cr 9.3a (3.1) 53.4A (25.4) 4.3a (0.8) 13.8b (4.1) 78.7B (22.1) 3.7b (0.4) 14.1b (3.7) 86.6C (26.9) 3.6b (0.5)	E HV Cr FS 9.3a (3.1) 53.4A (25.4) 4.3a (0.8) 110.0A (19.5) 13.8b (4.1) 78.7B (22.1) 3.7b (0.4) 124.5B (27.4) 14.1b (3.7) 86.6C (26.9) 3.6b (0.5) 124.9B (30.8)	E HV Cr FS E _{flexural} 9.3a (3.1) 53.4A (25.4) 4.3a (0.8) 110.0A (19.5) 4.1a (1.1) 13.8b (4.1) 78.7B (22.1) 3.7b (0.4) 124.5B (27.4) 6.9c (2.6) 14.1b (3.7) 86.6C (26.9) 3.6b (0.5) 124.9B (30.8) 6.2b (1.9)	E HV Cr FS E _{flexural} Vol% 9.3a (3.1) 53.4A (25.4) 4.3a (0.8) 110.0A (19.5) 4.1a (1.1) 47.5A (9.5) 13.8b (4.1) 78.7B (22.1) 3.7b (0.4) 124.5B (27.4) 6.9c (2.6) 63.1B (5.0) 14.1b (3.7) 86.6C (26.9) 3.6b (0.5) 124.9B (30.8) 6.2b (1.9) 62.5 B (7.8)

Micro-mechanical properties (Vickers hardness HV [N/mm²], modulus of elasticity E [GPa] and creep Cr [%]) as well as macro-mechanical properties (flexural strength FS [MPa] and modulus of elasticity in flexural test $E_{flexural}$ [GPa]) are detailed in mean values and standard deviations (in parentheses). Letters indicate statistically homogeneous subgroups (Tukey's HSD test, α =0.05)

Table 6 Influence of fillers—weight and volume—and RBC type on the micro-mechanical properties (modulus of elasticity E, Vickershardness HV, Creep Cr) as well as on macro-mechanical properties (flexural strength FS and modulus of elasticity in flexural test $E_{flexural}$)

Parameters	Е	HV	Cr	FS	E _{flexura}
% Filler volume	0.374	0.445	0.488	0.173	0.203
% Filler weight	0.168	0.006	0.444	0.095	0.104
RBC type	0.328	0.310	0.262	0.107	0.255

The higher the partial eta-squared values, the higher the influence of the selected variables on the measured properties

lower than in other products, confirming measurements showing a lower cross-link density compared to regular methacrylates [5]. Kalore also performed in a comparable way, showing moderate mechanical properties, albeit high filler content, partly due to a lower cross-link density as a result of the high molecular weight but also to the presence of pre-polymerised fillers. There is less information until now regarding the performance of this material. Recent conference presentations confirmed a lower shrinkage stress compared to regular RBCs [18, 19] but also a higher water sorption and radial expansion when compared to the low shrinkage silorane-based composite (Filtek Silorane; 3M ESPE, Germany/USA) [20].

The new TCD-urethane monomer incorporated in Venus Diamond helped to create a composite with excellent mechanical properties, especially a high modulus of elasticity. Vickers hardness was significantly lower compared to other nano-hybrid RBCs (Grandio, Filtek Supreme XT, Filtek Supreme XTE). The reason therefore must be searched in the filler system composed of glasses with no crystalline silica or zirconia compounds.

As for Empress Direct Opal, the nano-hybrid RBC with the lowest mechanical properties as a consequence of the lowest filler content, the material was developed to mimic the opalescent effect, especially for adolescent patients and is not supposed to be applied in stress-bearing areas. The measured enamel and dentin shades of the same brand ranged within the average values of the measured nanohybrid RBCs, showing similar elastic modulus and a higher Vickers hardness in the enamel shade.

The category of micro-hybrid RBCs exhibits a lower variation in mechanical properties when compared to the nano-hybrid materials, although showing consistent differences in the chemical composition of both—filler and matrix. With a completely different monomer matrix when compared to traditional RBCs, the silorane-based composite Filtek Silorane [21] showed average mechanical properties within the range of micro-hybrid RBCs. Particularly the creep resistance (=time dependent plastic deformation occurring under stresses lower than the yielding stress) was shown to be considerably superior (=low creep values, Table 3) to regular methacrylate-based RBCs with similar filler content (Table 3), being solely outclassed by Estelite Posterior, a high filled material. Other than di-methacrylates, siloranes were developed as monomers with four polymerisable cycloaliphatic oxirane moieties [21], giving a higher cross-link density and thus a better creep resistance. Besides that, a key factor affecting the long-term stability of a resinbased composite is water sorption [22]. Due to the hydrophobic siloxane structure, the silorane-based composite exhibited significantly lower water sorption, solubility and associated diffusion coefficient than established methacrylate-based dental RBCs [23] and were proven to be also very stable during aging in aggressive storing conditions [14].

The demand for even faster polymerization of RBCs constrains manufacturers to change the photo-initiation process. Advertised as materials having implemented a radical amplified photo-polymerization initiator technology (RAP technology), which is supposed to reduce curing time and the amount of photo-initiator CQ (manufacturer information), Estelite Sigma Quick and Estelite Posterior differ consistently in their properties. As an RBC for posterior restorations, Estelite Posterior indeed showed the best mechanical properties within the measured micro-hybrid RBCs, but performed comparably or even inferior to several nano-hybrid RBCs. A particularity of the material is the highest filler load within all the tested RBCs containing exclusive spherical-shaped fillers. Besides an increased filler load [24], this also allows to enhance the material's fracture strength compared to materials with irregularly shaped fillers, since mechanical stresses tend to concentrate on the angles and protuberances of the filler particles [25].

In the material SureFil SDR Flow, the polymerization kinetics is controlled by a photo-initiator being incorporated into a urethane-based methacrylate resin. A 60-70% reduction in shrinkage stress in the unfilled resin when compared to conventional methacrylate-based resins was measured as well as a relatively slow radical polymerization rate, suggesting that the photo-initiator incorporated into the resin is affecting indeed the radical polymerization process [26]. This lower curing stress was shown to be retained also in filled compositions [26, 27]. Indicated as a bulk fill flowable base, the material was supposed to be adequately cured also in increments of up to 4 mm. The material performance is particular, showing within the group of flowable RBCs a high rigidity (=high modulus of elasticity), a moderate Vickers hardness but also the highest creep value, meaning a high plastic deformability thus making difficult to predict its clinical behaviour.

The category of flowable RBC performed significantly inferior in all measured properties compared to nano- and micro-hybrid RBCs. A clear improvement in mechanical properties in the nano-flowables (Filtek Supreme XT Flow, Grandio Flow, TetricEvoFlow, Venus Diamond flow) when compared to the micro-hybrid flowables is, however, not evident. With a particular behaviour, Grandio Flow showed distinguished properties exceeding several materials of the non-flowable RBCs.

Conclusions

Albeit showing a significant and high influence on the mechanical properties—with a stronger influence on the micro-mechanical than on the macro-mechanical properties (Table 6)—the type of RBC is not a guarantor for good mechanical properties of a material since the variation in mechanical properties was found to be very high within a material category. Few differences were found between nano-hybrids and micro-hybrid RBCs suggesting no clear advantages of the former, clinically. Similar is valid for materials with new monomer formulation or photo-polymerization initiator technology. However, several nano-hybrid RBCs exceed the average mechanical properties of micro-hybrid RBCs. Both tested hypothesis were thus rejected.

Conflict of interest The authors declare that they have no conflict of interest.

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