

The effect of aging on the mechanical properties of nanohybrid composites based on new monomer formulations

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Abstract

Objectives Nanohybrid resin-based composites (RBCs) containing new types of matrix monomers such as dimer acid-based dimethacrylate or tricyclodecane-urethane are assumed to show decreased water uptake and therefore better resistance to hydrolytic degradation than RBCs using bisphenol A diglycidyl methacrylate (BisGMA) due to their hydrophobic nature. Our study aimed to analyze the effect of aging on six nanohybrid RBCs, of which two are using these new types of monomers, with regard to differences in the mechanical properties of the materials.

Materials and methods Diametral tensile strength (DTS), Vickers hardness (HV), and creep were measured. Mechanical tests were performed after storing samples for 24 h in distilled water, as well as after aging (thermocycling for 5,000 cycles at 5–55°C and storage for 4 weeks either in distilled water, artificial saliva, or ethanol).

Results The effect of aging on all test parameters was lower than the effect of the material. This information was provided by a general linear model, showing higher partial η^2 values for the influence factor material than for the factor aging. The influence of aging on the micromechanical properties HV and creep was proven to be more sensitive than on the macromechanical property (DTS). This was also illustrated by lower η^2 values for the variable aging for DTS. An increase of the creep of all materials was observed after storage in alcohol.

Conclusions The use of new types of monomers could not be shown to be a significant advantage to the other examined materials containing BisGMA.

Clinical relevance Nanohybrid composites can be recommended as universal filling materials, whether based on new or conventional monomers.

Keywords Nanohybrid composites · Monomers · Aging · Storage · Mechanical properties

Introduction

The effects of water on resin-based composites (RBCs) are known to be responsible for a decrease of the mechanical properties caused by degradation of the silane interface [1]. The extent to which RBCs are influenced by this water-dependent degradation seems to be different for each material, but the physical and mechanical properties of dental polymer networks may be significantly altered by the effects of solvent uptake and component elution [2] such as the leaching of fillers or unreacted monomers. Although clinical data indicate that hydrolytic and hygroscopic effects are not the most common reasons for the failure of composite restorations, the long-term stability of RBCs within the wet oral environment is a matter of concern, since the principal reason for the replacement of restorations of amalgam and composite has remained secondary caries as diagnosed clinically [3]. Schwartz and Söderholm [4] assumed that finer filler particles and consequently shorter filler spacing slow down the diffusion of plasticizing agents, such as water and ethanol, and contribute to a lower plasticizing effect. Nanoscale-sized fillers, which are smaller than the wavelength of light, prove the most decreased filler particle size and have been utilized in composites to provide a

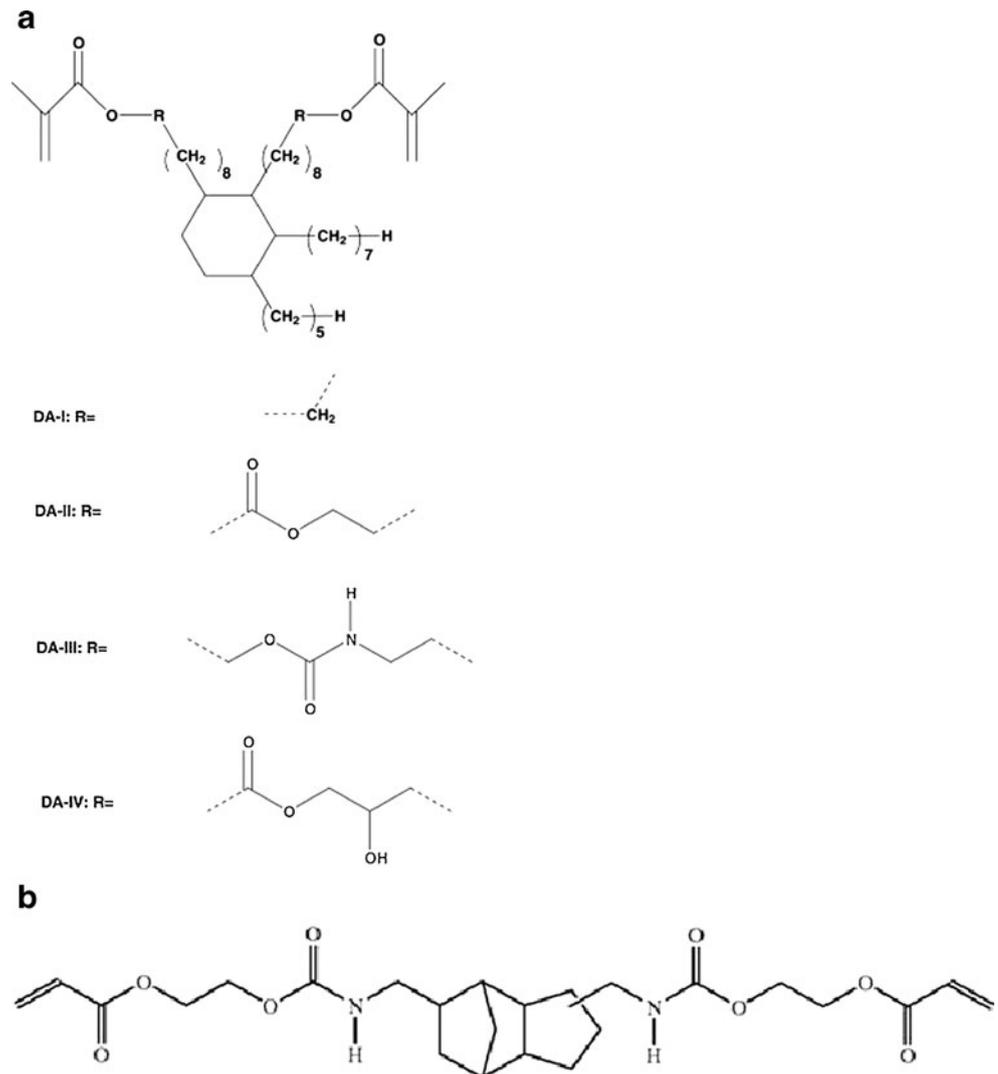
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combination of the good mechanical properties of macrofilled composites with the excellent optical qualities of microfilled RBCs [5]. More recently, nanohybrid composites have been introduced containing a range of different sizes of macrofillers and microfillers to which some nanoscale-sized fillers have been added, which occupy the spaces between the larger particles and therefore may lead to shorter particle spacing.

Changes within matrix compositions of RBCs promise improvements of mechanical properties, reduction of water uptake, polymerization shrinkage, and increased degree of conversion. Such new types of matrix monomers, e.g., dimer acid-based dimethacrylates (N'Durance, Septodont, which is based on a patented resin matrix system owned by the University of Colorado [6]) or special urethane monomers such as TCD-urethane (Venus Diamond, Hereaus Kulzer, European Patent 1935393 [9]) incorporated in nanohybrid composites, are promoted as alternatives to the

conventional BisGMA monomers. Dimer acid dimethacrylates are derived from cycloaliphatic carboxylic acids with high molecular weight [6]. Additional linear aliphatic structures contribute to the bulky core structure of the monomer (see Fig. 1a). Figure 1b illustrates the chemical structure of the TCD-urethane monomer. It consists of a special aliphatic structure containing high reactive urethane groups of tricyclodecanes which are prepared by reaction of hydroxyalkyl (meth)acrylic acid esters with diisocyanates and subsequent reaction with polyols [7]. Dimer acid monomers were proven to have significantly higher final double-bond conversion than common dimethacrylate monomers [8], and TCD-urethanes are also claimed to have high degrees of conversion [9] which might, besides the hydrophobic nature of these two new monomers, contribute to a reduction of their water uptake due to a reduced amount of free leachable monomer. Furthermore, high degrees of conversion are associated with improved mechanical properties [10].

Fig. 1 **a** Dimer acid-derived monomer as described in [6]. **b** Urethane diacrylate as described in [28]



These considerations led to the following null hypotheses of our study: All examined nanohybrid RBCs, whether containing BisGMA or new types of matrix monomers such as dimer acid-based dimethacrylates or TCD-urethane, show no differences with regard to the mechanical properties, and their behavior is similar after aging (thermocycling and storage in three different solutions, namely distilled water, artificial saliva, and a 1:1 mixture of ethanol and distilled water).

Materials and methods

All six measured materials were nanohybrid RBCs. Information about material composition, lot numbers, colors, and manufacturers are summarized in Table 1.

Tests for diametral tensile strength (DTS) were performed using a universal testing machine (MCE 2000ST, Quicktest Prüfpartner GmbH, Langenfeld, Germany). The disk-shaped specimens were loaded until fracture at a crosshead speed of 0.5 mm/min, being compressed between the two supporting plates of the machine, while the outside surfaces of the specimens were in contact with the plates. The samples, measuring 3 mm in height and 6 mm in diameter, were produced in a round Teflon mold. The materials were therefore applied into the mold, shaped between two parallel glass plates and were then light-cured for 20 s per side (Elipar™ Freelight 2, 3 M ESPE, light intensity 1,241 mW/cm²) through transparent plastic sheets. Eighty such specimens were made for each nanohybrid RBCs and finished with a silicon carbide sand paper (Leco, grit size 1200/4000) in order to secure smooth surfaces. Besides the geometry of the specimens (diameter and height), the force causing fracture was measured. According to the formula $\sigma = \frac{F}{rd\pi}$ (r and d being diameter and height of the samples and F , the force needed for failure), the diametral tensile strength σ was calculated.

Rectangular specimens measuring 2×2×8 mm were used for the micromechanical tests. These samples were produced in a stainless steel mold. Irradiation occurred, overlapping for 20 s per side using the same light guide as for the DTS samples. The parameters Vickers hardness (HV) and creep (Cr) could be determined for each material by carrying out a force-controlled test procedure using an automatic microhardness indenter (Fischerscope H100C, Fischer, Germany). Prior to testing, the bars were polished with a P 4000 grit silicon carbide sandpaper (Leco) and 1 μm diamond spray. During the tests, the load increased and decreased with a constant speed between 0.4 and 500 mN. The load and the penetration depth of the diamond indenter were continuously recorded during the load–unload cycle. The test force divided by the apparent area of the indentation under the applied force is defined as the universal hardness. In order to obtain the more familiar Vickers hardness units from the universal hardness data, a conversion factor between these two parameters could be calculated from a multiplicity of measurements stored in a database supplied by the manufacturer and integrated in the software. The value for the creep of the six nanohybrid RBCs was expressed by the relative change in indentation depth for 5 s while the test force was kept at the constant level of the maximum 500 mN.

All samples for both DTS and micromechanical tests were first stored for 24 h in distilled water at 37°C. Twenty samples of each material were, as a reference, measured after 24 h of storage time. The remaining 60 specimens were thermocycled for 5,000 cycles at 5–55°C, before being randomly divided into groups of 20. These three groups of each material were stored either in distilled water, artificial saliva, or a 50:50 mixture of 96 % ethanol and distilled water for 28 days at 37°C. Solutions were renewed daily.

Table 1 Materials, manufacturers, chemical composition of the matrix and the filler and filler content by weight and volume percentage (content (w/v))

Material	Manufacturer	Color	Lot no.	Matrix	Filler	Content (w/v)
Grandio	Voco	A 3	0921103	BisGMA, UDMA, dimethacrylate, TEGDMA	fluorosilicate glass, SiO ₂	87/71.4
N'Durance	Septodont	A 3	G-9020-11	BisGMA, UDMA, dicarbamate dimethacrylate dimer acid	ytterbium-fluoride, bariumglass, quartz	80/65
Venus Diamond	Heraeus	A 3	010029	TCD-DI-HEA, UDMA	barium-aluminum-fluoride glass	81/64
Miris 2	Coltène/Whaledent	S 2	0191818	methacrylates	bariumglass, SiO ₂	80/65
Premise	Kerr	A 3	3120178	TEGDMA, BisGMA	bariumglass, SiO ₂ , prepolymerized fillers	84/71.2
Simile	Jeneric Pentron	A 3	190633	PCBisGMA, BisGMA, UDMA, HDDMA	barium silicate glass, circonium-silicate, SiO ₂	75/66

Data are provided by the manufacturers

BisGMA bisphenol A diglycidyl methacrylate, *UDMA* urethane dimethacrylate, *TEGDMA* triethylene glycol dimethacrylate, *TCD-DI-HEA* 2-propenoic acid, (octahydro-4,7-methano-1H-indene-5-diyl) bis(methyleneiminocarbonyloxy-2,1-ethanediyl) ester, *PCBisGMA* pentron clinical-bisphenol A diglycidyl methacrylate, *HDDMA* hexanediol dimethacrylate

Statistical analysis

One-way ANOVA and Tukey HSD post hoc test ($\alpha=0.05$) were used for statistical analysis, allowing a comparison of the results within each material, among all materials, and storage conditions. A Pearson correlation analysis was also performed (SPSS Statistics 17, Chicago, IL). Furthermore, a multivariate analysis (general linear model) gave information about the influence of the variables' filler volume, filler weight, aging, and material on all tested parameters (DTS, HV, and Cr). Results of this analysis are to be interpreted by the partial η^2 values for the variables. The higher the partial η^2 ($= \text{eta}^2$) value, the higher is the impact on the tested parameters.

Results

The statistical analysis showed different trends for each test parameter. Results are illustrated in Table 2.

Venus Diamond showed the highest values for the diametral tensile strength after 24 h, followed by a statistically homogeneous group of Grandio, Miris 2, and Simile. N'Durance and Premise performed worst. No significant

differences between the three long-term storage conditions could be detected within one material: Except for Simile, of which results of the saliva and alcohol storage were significantly worse than after storage in water, the specimens showed similar behavior after being stored in distilled water, artificial saliva, or ethanol. For Grandio and Venus Diamond, no significant differences could be noticed between the 28-day storage and the control group at 24-h storage.

As for the Vickers hardness results, N'Durance and Premise were also at the bottom of the table. Grandio proved to have the highest values for HV. For all six materials, there was no significant difference between the samples stored in water or saliva for 4 weeks. However, a more pronounced, significant decrease of the Vickers hardness could be noticed for specimens stored in alcohol compared to the other storage conditions. This tendency did not apply to Grandio, of which results after being stored in alcohol were comparable to water and saliva data. Results of Grandio and Simile after 24 h were significantly better than those after 4 weeks of storage in water. These results did not differ from the 24-h water storage for N'Durance, Venus Diamond, and Miris 2. Premise showed consistent values for all except the alcohol storage.

Table 2 Diametral tensile strength and micromechanical properties Vickers hardness and creep

Material	Storage	DTS (MPa)	HV	Cr (%)
Grandio	24 h water	42.9fgh (7.3)	161.31 (12.2)	2.6a (0.2)
	4 weeks water	41.2efg (7.7)	150.7 e (18.0)	2.6a (0.2)
	4 weeks saliva	36.3bcdef (8.5)	150.6 k (11.4)	2.6a (0.2)
	4 weeks alcohol	41.1efg (8.1)	140.1j (14.3)	2.8b (0.3)
N'Durance	24 h water	38.4cdef (8.7)	73.5cd (6.4)	3.4de (0.2)
	4 weeks water	28.9ab (6.9)	77.9de (3.5)	3.3 cd (0.1)
	4 weeks saliva	30.9abc (6.7)	79.1e (2.5)	3.3c (0.1)
	4 weeks alcohol	32.4abc (4.9)	59.5b (2.5)	3.9ij (0.1)
Venus Diamond	24 h water	57.3 k (9.2)	91.1gh (7.1)	3.9ij (0.2)
	4 weeks water	54.9jk (4.6)	88.7fg (5.1)	3.8hij (0.2)
	4 weeks saliva	53.3ijk (5.5)	85.5f (3.9)	3.9j (0.2)
	4 weeks alcohol	60.5k (5.3)	60.4b(6.7)	4.9 m (0.2)
Miris 2	24 h water	49.2hij (7.6)	90.3gh (3.9)	3.5ef (0.1)
	4 weeks water	38.3cdef (6.2)	88.1 fg (3.9)	3.5ef (0.1)
	4 weeks saliva	34.1abcde (5.8)	85.0f (3.4)	3.6f (0.1)
	4 weeks alcohol	40.5defg (3.3)	61.0b (2.8)	4.2 k (0.2)
Premise	24 h water	38.1cdef (6.0)	73.8 cd (4.2)	3.7 g (0.1)
	4 weeks water	27.2a (4.3)	69.6c (3.9)	3.7gh (0.2)
	4 weeks saliva	29.7ab (4.2)	69.2c (6.1)	3.8ghi (0.2)
	4 weeks alcohol	27.9a (3.7)	49.4a (2.9)	4.4 l (0.3)
Simile	24 h water	46.4ghi (9.0)	91.9gh (2.4)	3.4de (0.1)
	4 weeks water	46.4ghi (9.0)	97.7i (3.7)	3.2c (0.1)
	4 weeks saliva	28.9ab (6.5)	94.7hi (2.7)	3.3c (0.1)
	4 weeks alcohol	33.1abcd (7.3)	73.4 cd (3.4)	3.8hij (0.1)

Lowercase letters indicate statistically significant subgroups; standard deviations in brackets; Tukey HSD post hoc test ($\alpha=0.05$)

The results for the creep of the nanohybrid composites showed different trends than for the parameter HV. Creep values after storage in alcohol were significantly higher than those of all other storage conditions. Grandio, Venus Diamond, Miris 2, and Premise showed no significant differences between the 24-h water and 4-week water and saliva storage.

Regarding the information provided by the general linear model, the material, showing the highest partial η^2 values in the multivariate analysis, was proven to be the most sensitive factor of influence on all test parameters. HV and creep were also influenced greatly by thermocycling and the different storage conditions (0.770). The impact of the volume and weight percentages of the filler on the Vickers hardness was even more pronounced (0.843). See Table 3 for all variables.

Pearson correlation analysis showed moderate correlation between Vickers hardness and filler volume (0.438) and weight (0.469) and inverse correlation between filler volume and weight and Cr (−0.411, −0.291). Inverse correlations were furthermore registered between DTS and filler volume (−0.338) and between HV and Cr (−0.794), while no significant correlation could be noticed between DTS and filler weight (see Table 4).

Discussion

The diametral tensile strength is a mechanical parameter providing information about the behavior of brittle materials, such as RBCs, once exposed to tensile stresses. It is therefore a clinically relevant factor since RBCs would be expected to fail under tensile stresses during mastication [11] because of the forces they are subjected to in functional areas. Although there are critical voices questioning the validity of DTS testing [26], it is still regarded as a valuable method to analyze the mechanical properties of modern restorative resin-based materials [27].

Table 3 Multivariate analysis (general linear model) showing the influence of the material, aging, and volume and weight percentages of the fillers on the test parameters

Variables	Material	Aging	Vol. %	Weight %
DTS	0.616	0.218	0.474	0.474
HV	0.965	0.770	0.843	0.843
Cr	0.920	0.770	0.664	0.664

The higher the partial η^2 values, the higher is the influence of the selected variables on the mechanical properties

The influence of all parameters was statistically significant ($p < 0.05$); thus only the η^2 values are indicated in the table

Table 4 Pearson correlation analysis showing correlations between all parameters

	Vol. %	Weight %	Cr	DTS	HV
HV	0.438	0.469	−.794	0.098	1
Cr	−0.411	−0.291	1	0.208	−0.794
DTS	−0.338	n.s.	0.208	1	0.098

n.s. not significant

The measured DTS values in our study were not affected greatly by storage for 4 weeks, not even after storage in more aggressive solutions such as ethanol. Only three materials showed significantly worse DTS values after storage in water for 4 weeks. All of them except Simile did not differ within all three long-term storage conditions. This was also shown in the general linear model by low values for η^2 , for the variable “aging,” which are to be interpreted as a low influence of the variable on the test parameter (see Table 3). Results of studies on radiopaque dental composites [12] match our data, showing that the effect of aging samples in alcohol was not as dramatic for DTS values compared to a pronounced deterioration in transverse strength and microhardness. Other researchers, however, were able to show a decrease of DTS values for hybrid composite resins after immersion in ethanol [13].

The substitution of bisphenol A diglycidyl methacrylate (BisGMA) or triethylene glycol dimethacrylate (TEGDMA) by urethane dimethacrylate (UDMA) has been reported to result in an increase in tensile strength due to an increased degree of conversion of the UDMA monomer [14]. This might be an explanation for the highest DTS values of Venus Diamond, containing UDMA and a special urethane monomer, namely TCD-urethane, and the lowest DTS values for Premise, having no UDMA content at all. Other studies showed that with increasing urethane content, the solubility values of RBCs tend to decrease, indicating that the degree of conversion and rate of cure is higher for urethane-rich composites compared to BisGMA-based composites [12]. Long-term water sorption has furthermore been reported to be lower for UDMA than for BisGMA and TEGDMA due to the presence of hydrophilic ether linkages in TEGDMA [15]. These observations might contribute to the very consistent behavior of Venus Diamond during storage. The 24-h results did not differ significantly from the ones stored for 4 weeks.

High microhardness values correlate with high degrees of conversion [16] which limits the elution of any residual rest monomer and so improves the biocompatibility of a material. The highest values of Grandio for HV might be explained by the high filler content of the material. However, also the composition of the inorganic phase, the very nature of the varied filler sizes and distributions are

influence factors on the parameter HV, which need to be considered. Also, the use of prepolymerized fillers (Premise) might result in an actual lower percentage of the filler and might lead to lower mechanical properties of a material. Showing very high values for η^2 , the filler weight and volume percentages are proven to have a great influence on the microhardness. The weight and volume filler content was furthermore shown to be directly correlated to microhardness values, and a positive correlation was registered (0.469 for weight and 0.438 for volume content). These findings are confirmed by other studies performing microhardness tests, where composites with the highest filler by volume exhibited the highest hardness values (101–117 HV) [17]. However, this explanation cannot be applied to all measured materials, since Premise, due to the presence of prepolymerized fillers, showed almost the lowest microhardness values but presented the second highest filler volume and weight percentages. N'Durance and Miris 2, having identical filler percentages, differed significantly in their HV values. A reason for the lower HV values of N'Durance might be the relatively low crosslink density of the dimer acid dimethacrylate matrix monomers [8].

The decrease of HV after 4 weeks of storage in alcohol was pronounced for all measured nanohybrid RBCs. This observation correlates well with previously conducted studies by Deepa [12], showing a deterioration of microhardness for radiopaque dental composites with varying resin matrix ratios after storage in alcohol, and with investigations done by Aguiar [13], where samples of hybrid composite resins presented lower microhardness values for almost all groups after immersion in ethanol medium. The microhardness of the top surface was hereby shown to be higher than that at the bottom of specimens. Just like water, alcohol serves as a plasticizer of the composite matrix. The reduction of mechanical properties such as hardness is a consequence of the separation of the polymer chains by molecules that serve as space occupiers instead of forming primary chemical bonds with the chain [2]. Bulk properties such as DTS are affected later than surface properties, such as hardness, since the effect initially would be greatest for surface layers and later involve more of the polymer network [2]. This idea is supported by a study which showed a decrease in surface hardness for nanohybrid RBCs after storage in artificial saliva but an increase in the hardness of the materials bulk, which was explained by resin matrix post-cure [18].

Schwartz et al. [4], who observed a more pronounced decrease of microhardness values for coarse composites than for fine composites after water and alcohol storage, assumed that the differences in filler sizes affect the ease with which water and ethanol molecules reach deeper layers by diffusion. Due to shorter particle spacing and larger surface area of finer filler particles (in our case, nanosized fillers)

diffusion into deeper layers occurs more slowly for fine composites.

The values for the creep of the materials after storage in alcohol were significantly higher compared to all other storage conditions. This was accompanied by a negative correlation between Cr and HV (-0.794). When subjected to a constant force (in our study 500 mN for 5 s), viscoelastic materials experience a time-dependent increase in strain [19]. The abovementioned plasticizing effect of all three storage solutions, being most pronounced for alcohol, leads to an increased deformability of the RBCs and therefore higher creep values expressed by a deeper sinking of the indenter into the sample under the constant test load. A reduced amount of the resin matrix due to a high filler content and homogeneous filler distribution has been found to lead to higher creep resistance [20]. Grandio, showing the lowest creep values after 24 h, therefore seems to be able to withstand viscoelastic deformation best.

Taking all test parameters into consideration, the effect of storage in water on the mechanical behavior of all measured materials was not meaningful. Grandio showed significantly worse values for HV after 4 weeks of water storage compared to the 24-h results, N'Durance, Miris 2, and Premise exhibited deteriorated DTS values after 4 weeks water storage, and Simile performed worse for Cr and HV. As for the difference of the two storage conditions water and artificial saliva, there was no significant difference for all Cr and HV data. Only the DTS values of the Simile samples stored in saliva were significantly worse compared to the specimens stored in water. Söderholm et al. [21] observed the increased leaching of fillers in saliva compared to water, and therefore more degradation of the materials in saliva. This cannot be confirmed by our data. However, human saliva might impair RBCs much more than artificial solutions, since enzymatic reactions, which lead to attacks on the side chains of RBCs producing harmful by-products [22], are not simulated in artificial saliva. Salivary enzymes, such as esterase and hydrolase, have been found to be capable of increasing the rate of diffusion of plasticizer from the materials [23] and of softening the surface of dimethacrylate polymers, resulting in a gradual decrease of the hardness of BisGMA and TEGDMA [24, 25].

A superiority of the materials N'Durance and Venus Diamond, containing new types of monomers, can hardly be claimed. N'Durance proved the lowest values for HV and second lowest results for DTS, which decreased significantly after 24-h water storage. Therefore, neither the hydrophobic character of the dimethacrylates conducted from dimer acid [8] nor the high final double-bond conversion of the monomer mentioned above seemed to contribute to predominant mechanical characteristics of the material or consistence after aging compared to the other examined nanohybrid RBCs. Venus Diamond, which yielded the

highest DTS results after 24 h and showed consistent behavior during all storage conditions, was, however, just as affected by alcohol as the other nanohybrids. The TCD-urethane-based material showed significantly lower Vickers hardness values and higher creep values than that of Grandio after 24 h. Therefore, part of our null hypothesis can be upheld. All examined nanohybrid RBCs, whether containing BisGMA or new types of matrix monomers such as dimer acid-based dimethacrylates or TCD-urethane, showed similar behavior after aging. Disregarding few exceptions, DTS values did not differ significantly within one material for all three storage conditions. HV results of all materials, except Grandio, were affected by storage in alcohol, and for all materials, an increase in Creep values could be detected after the alcohol storage. However, regarding the mechanical properties of all six examined materials, the first part of our null hypothesis needs to be rejected. From the six materials, three significantly different groups can be separated for each test parameter (DTS, HV, and Cr), even four regarding the creep values. Therefore, the examined materials do show significant differences with regard to their mechanical properties.

Conclusion

The effect of aging on all test parameters was lower than the effect of the material. The micromechanical properties HV and creep were proven to be more influenced by thermocycling and storage than the macromechanical property (DTS). An increase of the creep of all materials was observed after storage in alcohol. The use of new types of monomers could not be shown to be a significant advantage to the other examined materials containing BisGMA.

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

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