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ORIGINAL ARTICLE

Effect of polymerisation and ageing on the incremental bond strength of ormocer-based dental materials

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Abstract
Objective The aim of this study was to investigate the effect of polymerisation and ageing on the incremental bond strength (IBS) and fracture mechanics of experimental and commercial, well established ormocer-based materials.
Methods An experimental dimethacrylate-diluent-free ormocer was compared with two commercial products (Admira (VOCO); Ceram X Duo (Dentsply)). For Ceram X Duo, the strength between dentin shades (DD) and between dentin and enamel shades (DE) was measured. In order to simulate clinical conditions, when a direct access to the composite surface is impeded, the curing unit was applied at different distances (1, 3 or 6 mm) from the sample's surface. IBS was measured after the samples were stored in distilled water (24 h/37 °C) and after ageing (5,000 cycles between 5 and 55 °C followed by storage (28 days/37 °C) in distilled water). Additionally, the degree of cure (DC) was measured in a thin film (~50 µm). A multivariate analysis, an additional one-way ANOVA with Tukey HSD post hoc test ($\alpha=0.05$), an independent *t* test ($\alpha=0.05$), and Weibull statistics were used to assess the results.
Results After 24 h, the values for IBS were statistically the same. Differences revealed after ageing, whereby the experimental material achieved the significant highest and Admira the lowest results. By evaluating after 24 h and after ageing, the experimental material obtained the smallest Weibull modulus "m". The predominant breaking mechanism is cohesive, even though the number decreases in favour for the mixture and adhesive fractures after ageing. Clear differences arose with regard to DC. The experimental material reached considerably lower values (31.9–33.2 %) unlike Ceram X Duo (45.6–48.3 %) and Admira (52.9–58.8 %).
Conclusions The IBS and the DC are far more dependent on the parameter filler volume percent and material than on the polymerisation distance.
Clinical significance A dimethacrylate-diluent-free ormocer matrix offers a better stability opposite ageing but achieves a lower DC and reliability.

Keywords Shear-bond strength · Degree of cure · Ormocers

Introduction

The modern resin-based composites (RBC), which are used in the restorative dentistry, have continuously been amended in order to fulfil the rising mechanical and esthetical demands. Still, the polymerisation shrinkage stress is considered as one of the main problems in the filling therapy that has to be solved. Since polymerisation shrinkage still remained a main drawback of methacrylate-based RBC, the Ormocers® (organically modified ceramics) were developed by the Fraunhofer ISC (research institute in Würzburg, Germany) as a new material class with reduced polymerisation shrinkage stress and have been marketed under the name Definite® (Degussa AG, Hanau, Germany) [1]. Having a very similar coefficient of thermal expansion to natural tooth structure [2], the materials were formulated as a novel three-dimensionally cross-linked inorganic–organic polymer, synthesised from multi-functional urethane- and thioether(meth)acrylate alkoxysilanes as sol–gel precursors [1, 3]. These materials proved to generate lower wear rate compared with traditional methacrylate-based composites [4, 5] and a shrinkage stress equal to that of hybrid RBC, at lower filler content [6]. Although, the manufacture of Ormocers® by using various polymers is well documented in the literature, there are

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still ongoing challenges such as processibility, upscaling of prototypes and handling properties, thus additionally necessitating conventional methacrylate monomers to be added to the ormocer matrix in commercial products, thereby diminishing the initial promising advantages [1]. Measurements on mechanical properties regarding flexural strength, flexural modulus, diametric tensile and compressive strength have shown that, as a material type, the ormocer-based composites do not differ significantly compared to the micro-hybrid, nanohybrid or packable RBCs [7].

The inorganic–organic network of conventional Ormocers® exhibits a similar viscosity to bisphenol A glycidyl methacrylate (Bis-GMA), requiring dilution for dental purposes to adapt rheological behaviour and to allow filler inclusion, that may negate initial expected advantages such as an improved biocompatibility [8] or low polymerisation shrinkage stress [9, 10]. For example, Definite® contains about 30 wt% of mixtures of decanediol dimethacrylate and glycerol dimethacrylate as diluents in the monomer matrix [1]. Thus, with regard to the toxicity, the ormocer-based and traditional dimethacrylate-based composites obtained similar results [11]. Therefore, the new, still-experimental Ormocers®, which are synthesised from amine or amide dimethacrylate trialkoxysilanes and which are dimethacrylate-diluent-free, were developed. These materials showed a noticeably improved flexural modulus of elasticity compared to the commercial ormocer-based composite Definite® [1]. In contempt of the increase of the physical properties of the RBC, clinical studies revealed that, within the first years, fracture is the main cause for failure in the filling therapy [12–14]. Therefore, the design of this in vitro study is highly clinically related in order to find out factors that might influence the incremental bond strength and increase the longevity of a direct restoration, respectively.

The aim of the study was therefore to compare an experimental ormocer-based composite without an addition of conventional methacrylates, with other ormocers that are well established on the market. Differences with regard to the incremental bond strength, the degree of cure and the type of fracture should be revealed by varying the distance between the polymerisation curing unit and the sample surface and by an artificial ageing.

The null hypotheses tested were the following:

1. The experimental Ormocer®, with a dimethacrylate-diluent-free matrix, behaves similarly to conventional ormocer-based materials with regard to the incremental bond strength, the type of fracture, and the degree of cure.
2. The incremental bond strength and the type of fracture of the tested materials are not influenced by thermocycling and storage in 28 days, which are models for artificial ageing.
3. The distance between the curing unit and incremental surface which is 1, 3 or 6 mm, respectively, does not influence the mentioned parameters and the degree of cure of the tested ormocer-based dental materials.
4. The incremental bond strength of Ceram X Duo is independent of whether dentin or enamel shades are used for the second and third increment.

Materials and methods

An experimental and two commercial ormocer-based resin composites (Table 1) were investigated. The incremental bond strength was examined in a shear test (Fig. 1). Therefore, the composite was applied in a shaped cavity (2-mm depth, 6-mm diameter) of an acrylic cylinder and cured for 20 s with a LED curing unit (Bluephase, Ivoclar-Vivadent, Schaan, Liechtenstein; 1,200 mW/cm^2) by applying the curing unit at different distances (1, 3 or 6 mm) from the sample's surface to simulate clinical conditions, when a direct access to the composite surface is impeded. A second composite layer (2-mm thickness and 3-mm diameter) was then applied 30 s after the first increment was cured and polymerised under identical conditions (20 s/distance 2 mm) followed by a third composite layer with the same size and polymerisation (20 s/0 mm).

Four hundred eighty samples were, thus, totally prepared, with 40 samples for each polymerisation distance and the material being stored for 24 h at 37 °C in distilled water.

Table 1 Investigated ormocer-based composites

RBC	Manufacturer	Batch	Filler wt/vol (%)	Matrix	Filler
Ceram X Duo Dentin (D3)	Dentsply	0804001568	77/60	Methacrylate-modified polysiloxane, Bis-GMA, TEGDMA	SiO$_2$, Ba-Al-B-Si-glass
Ceram X Duo Enamel (E2)	Dentsply	0804002851	77/60	see above	see above
Admira (A3)	VOCO	0833396	78/56	Acid-modified (di)methacrylate: Bis-GMA, UDMA, TEGDMA, BHT	SiO$_2$, Ba-Al-B-Si-glass (0.7 μm)
Experimental Ormocer (A2)	VOCO	V37877	87/72	100 % ormocer resin	SiO$_2$ nano-particles (20–50 nm), Ba-Si-glass (0.7–3.0 μm)

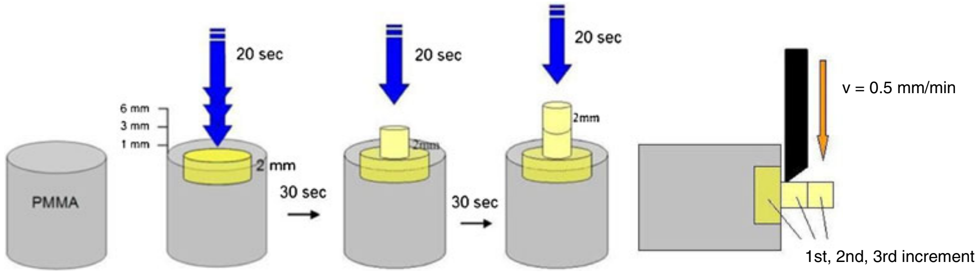

Fig. 1 Preparation and loading of the specimens

Half of the specimens were additionally aged (5,000 cycles between 5 and 55 °C followed by storage for 28 days at 37 °C in distilled water).

The specimens were loaded in a universal testing machine (MCE 2000ST, Quicktest Prüfpartner GmbH, Langenfeld, Germany) at a constant crosshead speed of 0.5 mm/min until fracture.

Type of fracture

The fragments of every sample were examined under the magnifying glass in regard to the breaking mechanism. Exemplarily, characteristic tests were examined by scanning electron microscopy (field emission scanning electron microscope AMK 1200; Leitz, Germany). The fracture mechanism was divided into three different types: if the fracture line runs exactly straight between the two increments, the type of fracture is called adhesive; a fracture line that runs only in parts between the increments to proceed through one layer indicates a mixture fracture. In the case of a fracture line that does not run along the bonding surface at all but solely through one or both increments, the fracture is termed cohesive.

Degree of cure

FTIR spectra were recorded in real time for 2 min with two spectra per second in an FTIR spectrometer with an attenuated total reflectance (ATR) accessory (Nexus, Thermo Nicolet, Madison, WI, USA). Therefore, the non-polymerised composite paste was put directly on the diamond ATR crystal as approximately 50-μm-thin film (n=5) (Fig. 2). In order to determine the percentage of the remained unreacted double bonds, the degree of cure (DC) was measured by assessing the variation in peak height ratio of the absorbance intensities of methacrylate carbon double bond peak at 1,634 cm^{-1} and that of internal standard peak at 1,608 cm^{-1} (aromatic carbon double bond) during polymerisation, in relation to the uncured material:

$$\mathrm{DC_{peak}}\% = \left[1 - \frac{(1,634\mathrm{cm}^{-1}/1,608\mathrm{cm}^{-1})_{\text{Peak height after curing}}}{(1,634\mathrm{cm}^{-1}/1,608\mathrm{cm}^{-1})_{\text{Peak height before curing}}}\right] \times 100$$

Statistical analysis

Multivariate analysis (general linear model with partial eta-squared statistics) tested the influence of the parameters "*RBC*" (*resin-based composite*), "*vol%-filler*" (*filler volume*), (*polymerisation*) "*distance*" and "*ageing*" on the considered properties (bond strength, degree of conversion and type of fracture) (SPSS Inc., Chicago, IL, USA; Version 18.0). Additionally, results were statistically compared using one-way ANOVA and Tukey HSD post hoc test (α= 0.05). A Weibull analysis was performed for the incremental bond strength data (Table 3). A common empirical expression for the cumulative probability of failure P at applied stress is the Weibull model [15]:

$$P_{\mathrm{f}}(\sigma_{\mathrm{c}}) = 1 - \exp\left[-\left(\frac{\sigma_{\mathrm{c}}}{\sigma_0}\right)^m\right]$$

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 $\ln(\ln(1/(1-P)))=m \ln \sigma_c - m \ln \sigma_0$. By plotting $\ln(\ln(1/(1-P)))$ versus $\ln \sigma_c$, a straight line results with the upward gradient m, whereas the intersection with the x-axes gives the logarithm of the characteristic strength [15].

A t test for independent samples compares the mean values of the incremental bond strength with and without artificial ageing (p<0.05).

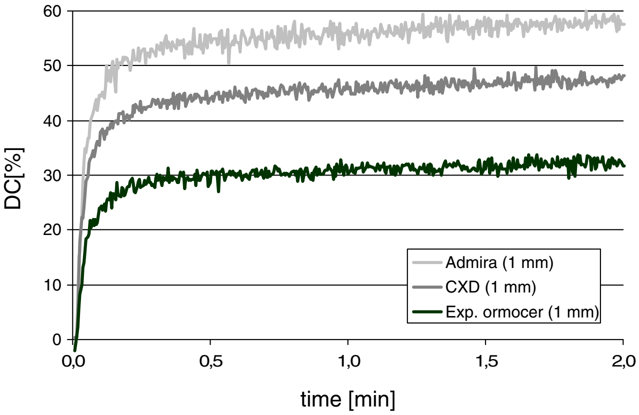

Fig. 2 Mean curves (n=5) of the degree of cure as function of time and material for a distance of 1 mm between the curing unit and sample

Results

Incremental bond strength

Table 2 summarises the results of the shear test. After 24 h, the values for the incremental bond strength vary from 30.8 to 44.4 MPa. Statistically, there is no significant difference between the tested materials. After thermocycling and storage, values from 13.5 to 46.3 MPa were reached. Thereby, the experimental material achieved a statistically higher significance, and Admira (at 1 and 3 mm), a lower bond strength compared to Ceram X Duo.

The polymerisation distance has a significant but slight influence (Table 4; eta-squared value, 0.058) on the bond strength. With the exception of the experimental material, the tested RBC reached the highest bond strength values at a distance of 6 mm, by evaluating after 24 h. This effect, however, is not recognised after ageing.

The Weibull modulus (Table 3) attained values of 0.8–6.3. Thereby, the experimental material reached the lowest values after 24 h as well as after ageing and, therefore, is regarded as less reliable. Figure 3 shows, exemplarily, the reliability of the tested materials after 24 h and at a polymerisation distance of 3 mm.

Table 3 Weibull analysis: reliability of the ormocer-based materials

RBC	Distance (mm)	Reliability without thermocycling		Reliability with thermocycling	
		m	Sigma-0	m	Sigma-0
Ceram X Duo DD	1	2.1	37.5	4.8	25.6
	3	3.6	38.8	2.4	22.4
	6	2.8	50.3	2.9	27.4
Ceram X Duo DE	1	3.3	39.2	4.1	34.4
	3	3.6	38.4	4.2	29.7
	6	5.6	45.2	6.3	31.6
Admira	1	3.2	35.6	2.6	15.5
	3	2.5	34.8	2.7	16.6
	6	4.6	38.1	2.5	34.1
Experimental Ormocer	1	0.8	8.2	1.6	20.2
	3	1.3	15.1	1.4	17.1
	6	0.8	8.0	1.7	21.8

Type of fracture

Considering the type of fracture of the non-aged specimens, the predominant breaking mechanism was cohesive, followed by mixed, whereas no adhesive fracture was observed. The percentage of cohesive failures was highest in Ceram X Duo. The values for Admira, as well as for the experimental Ormocer®, were, however, considerably lower. In the direct comparison, one recognises that the number of cohesive fractures decreases in favour of the mixed and the adhesive type of fracture if the samples were exposed to an artificial ageing, but the adhesive fracture was an exception furthermore and did not come onto

Table 2 Incremental bond strength and degree of cure are detailed in mean values and standard deviations (in parentheses)

RBC	Distance (mm)	Incremental bond strength (MPa)		p value	DC (%)	Type of fracture (%)					
		24 h	Ageing			24 h			Ageing		
						c[a]	m[b]	a[c]	c	m	a
Ceram X Duo Dentin	1	31.9 (11.7)ab	23.4 (6.2)bc	0.006	47.9 (1.6)B	95	5	0	70	30	0
	3	34.9 (11.0)ab	19.6 (7.8)ab	<0.001	48.3 (1.7)B	95	5	0	40	55	5
	6	44.4 (16.0)b	24.0 (7.2)bc	<0.001	45.6 (2.5)B	100	0	0	90	10	0
Ceram X Duo Enamel	1	35.1(12.0)ab	31.2 (9.1)c	0.261	–	100	0	0	75	25	0
	3	32.8 (10.4)ab	27.0 (8.2)bc	0.06	–	85	15	0	80	20	0
	6	41.8 (8.9)ab	29.4 (5.4)c	<0.001	–	95	5	0	95	5	0
Admira	1	31.9 (11.8)ab	13.5 (4.7)a	<0.001	58.8 (2.7)D	55	45	0	20	70	10
	3	30.8 (13.2)a	14.6 (5.1)a	<0.001	58.7 (2.9)D	55	45	0	10	90	0
	6	34.7 (9.5)ab	29.3 (9.1)c	0.072	52.9 (3.5)C	90	10	0	95	5	0
Experimental Ormocer	1	38.6 (13.1)ab	43.9 (8.1)d	0.197	31.9 (1.9)A	67	33	0	100	0	0
	3	39.3 (8.6)ab	43.2 (8.9)d	0.236	32.0 (1.5)A	80	20	0	93	7	0
	6	40.7 (14.1)ab	46.3 (8.1)d	0.199	33.2 (2.1)A	87	13	0	93	7	0

Different lowercase and uppercase letters indicate statistically homogeneous subgroups (Tukey's HSD test, $\alpha=0.05$). An independent t test analysed differences within one material and polymerisation distance as function of storage

[a] Cohesive type of fracture

[b] Mixed type of fracture

[c] Adhesive type of fracture

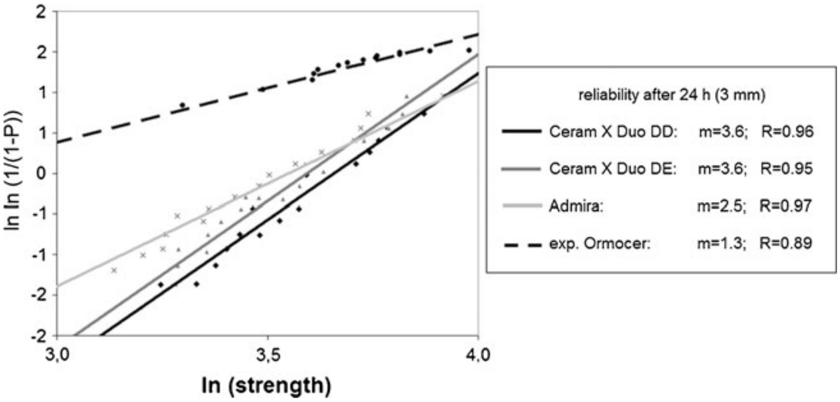

Fig. 3 Example for Weibull analysis. Reliability after 24 h of storage is shown (3 mm)

over 10 %. Statistically, all measured parameters have a comparable influence (Table 4) on the type of fracture. Figure 4 shows electron micrographs of sample fragments as examples for different breaking mechanisms. In Fig. 4 (a), the surface of the second increment of a sample after an adhesive fracture is illustrated. The high number of voids in the area of the bonding surface is noticeable. Firstly, a very big void and, secondly, a crack that runs inside the second increment are marked. In Fig. 4 (b1), an example for a cohesive fracture is shown. The fracture line runs through the second increment and crosses the bonding surface near the point of force application. The marked area is shown enlarged in Fig. 4 (b2). The fracture surface shows homogenous, almost void-free structure of the two increments, apart from a very small exposed area of the bonding surface. The mixture type of fracture is, exemplarily, demonstrated in Fig. 4 (c1, c2). The fracture line runs mostly between the two layers to finally proceed through the first increment. In comparison to the surface of the first increment, a lot of irregularities can be detected on the surface of the second increment, which might indicate a weaker bonding in this area.

Degree of conversion

The values for the DC, which were measured in an approximately 50-μm-thin layer, varied from 31.9 to 58.8 % (Fig. 2). The experimental material reaches significantly lower and Admira, significantly higher DC values compared to Ceram X Duo. Figure 2 shows the course of the DC rates of the three ormocer-based materials with time. Statistically, the parameters RBC (0.940) and vol% filler (0.910) have the strongest influence on DC, whereas the effect of the polymerisation distance (0.208) is significant but modest.

Table 4 Influence of parameters RBC, ageing, distance and vol% filler on the incremental bond strength, the degree of cure and the type of fracture

Parameters	Bond strength	Type of fracture	Degree of cure
RBC	0.272	0.177	0.940
Ageing	0.161	0.117	–
Distance	0.058	0.105	0.208
Vol% filler	0.185	0.121	0.910

All influences were significant ($\alpha=0.05$). The higher the eta-squared value in the table, the stronger the influence

Discussion

In order to simulate the visual qualities of a natural tooth, a filling has to be inserted by using an incremental layering technique; thus, materials of different colour and opacity can be used. The oxygen inhibition layer (OIL) is accepted as reason for the incremental bond. This layer develops on the surface of a composite shade during polymerisation [16]. Oxygen is said to be an effective inhibitor of the polymerisation reaction, stabilising radicals to peroxo radicals. The latter ones cannot initiate the polymerisation reaction, resulting in a higher residual monomer content [17]. Also the reduced space for chemical reactions on the surface supports the effect, that more monomers remain unpolymerised [18]. The thickness of the OIL is indicated from 4 μm [17] to 40 μm [19]. There are different factors, such as the filler amount, concentration of radicals, temperature, oxygen content, polymerisation time and light intensity, that demonstrably have an influence on the OIL [20]. How far the residual monomer content has a beneficial effect on the incremental bond strength is well documented in the literature. Some authors declared in their studies that OIL is a requirement for a sufficient incremental bond [21–23]. Others could not find a beneficial effect for the bond strength [24–26], and older studies even suspect the OIL, being incompletely cured, as unfavourable for the incremental bond [27]. Therefore, in this study, additionally to incremental bond strength, also the DC was measured in a thin layer. This thin layer was exposed to air at different polymerisation distances, in order to possibly create samples with different residual monomer content and to find an effect on the bond strength.

In this thin layer, the DC of the different ormocer-based materials differed significantly. The experimental material reached by far the lowest values. The big molecule size of

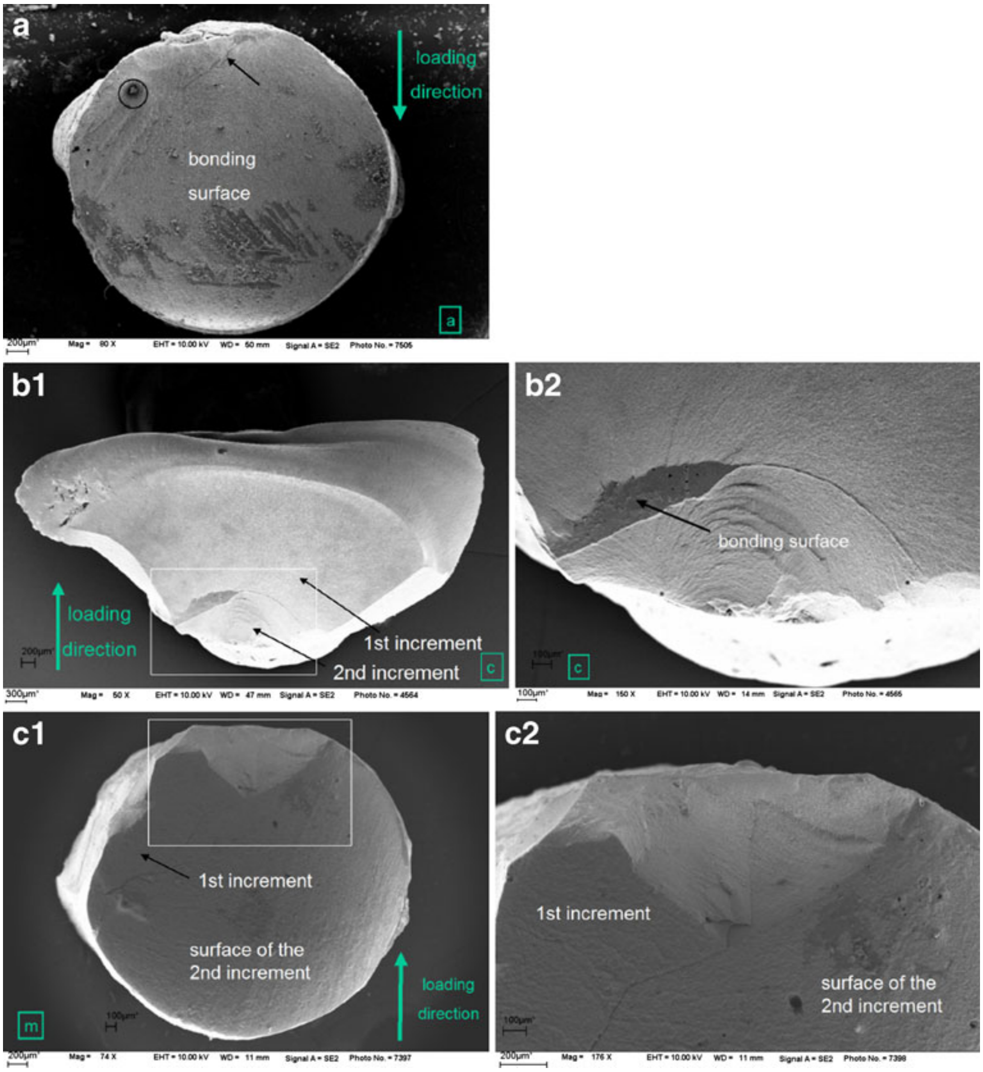

Fig. 4 Electron micrographs of sample fragments as examples for different types of fracture. *a* Admira; type of fracture, adhesive; distance, 1 mm; evaluation after artificial ageing; incremental bond strength, 11.0 MPa. *b* Experimental ormocer; type of fracture, cohesive; distance, 6 mm; 24 h; incremental bond strength, 45.9 MPa. *c* Ceram X Duo DD; type of fracture, mixture; distance, 3 mm; artificial ageing; incremental bond strength, 31.3 MPa

the monomers in the matrix of the experimental material and the absence of smaller dimethacrylate diluent can be reasons for the considerably lower DC values. Due to their size and bulkiness, the organic–inorganic copolymers seem to be confronted with a sterical hindrance at the polymerisation, so that it comes in the restricted time to a less cross-linked network. One must take into account, though, that the measuring of the DC took place during the first 2 min after photoinitiation, and a post-polymerisation therefore remained unnoticed. But it is doubtful whether the low DC has clinically relevant physical consequences. Due to their size, it seems improbable that unconverted ormocer molecules can be eluted. However, it was shown that highly cross-linked polymers are more resistant to degradation and to solvent uptake, whereas linear polymers present a less dense polymer network, allowing solvent molecules to diffuse more readily [28]. Studies that examined the toxicity of conventional ormocer-based dental materials came to contradictory conclusions: on the one hand, a higher toxicity of this material class was detected [11] in comparison to conventional methacrylate-based composites; on the other hand, a significantly lower release of monomers was established [29]. Moreover, some authors described the experimental, dimethacrylate-diluent-free ormocer assessed in this study as a dental material with an enhanced biocompatibility and long-lasting polymer matrix stability, thus, eliminating the risk of allergic reactions [5, 23]. However, the stability of this new experimental material when challenged by fluids encountered in the oral environment is not well known [30], and the necessity to use a dentin adhesive system, containing organic monomers, could negate a higher biocompatibility.

In this study, the polymerisation distance, however, has a slight but statistically significant effect on the DC (0.208), as well as on the incremental bond strength (0.058). The paramaters RBC (0.940) and vol% filler (0.910) predominate the DC. Also, more other studies showed that, unlike the polymerisation distance, other factors, such as the monomer composition [31], the manner of the filler [32, 33] as well as the photo initiator system [34] have influence on the DC very strongly [35]. Furthermore, a reduction of the light intensity will not necessarily result in a lower DC [36]. The exposure time seems to play a larger role in comparison with the intensity [37].

Despite the different DC, the tested ormocer-based composites attain statistically the same bond strength values, by evaluating after 24 h. These data are consistent with previous findings showing that the composition of the superficial OIL hardly influences the strength if fresh increments are analysed [26]. The parameter RBC showed the strongest effect on the incremental bond strength in this study. Also the parameter vol% filler has a significant effect on the bond strength, as well as the artificial ageing. Table 2 shows that, in this study, a higher number of fillers result in also higher bond strength values. It was shown that the filler share in vol% has the strongest influence on mechanical properties of dental composites, whereas the influence of the material category was low but still significant [7]. Leprince analysed in a recent study the mechanical properties of modern low-shrinkage dental resins [8]. Among others, Admira and a comparable experimental material with a pure ormocer matrix were investigated [8]. The experimental material exhibited a significant increased dynamic modulus and upper surface micro-hardness compared with Admira, which can be attributed in part to an increased filler content (84.3–86.7 wt%) in his opinion [8]. Also, Masouras suggested that the filler load was the main factor for determining elastic modulus properties [38]. To analyse the linkage of two layers of composite material, it is important to examine the integrity of the linkage because, among other things, the vulnerability for hydrolysis processes depends on it [39]. Because of this, the tested materials were subjected to an artificial ageing by thermocycling followed by storage for 28 days in distilled water. This has a noticeable influence on the bond strength. A study in which specimens were subjected to an artificial ageing in an identical way showed that through this the mechanical qualities such as modulus of elasticity, flexural strength, Vickers hardness and creep learned a significant reduction [40]. It was shown that water uptake can result in a deterioration of the mechanical properties of composites because of the degradation of filler particles [41], the weakening of polymer matrix [42–44] or the debonding of filler–matrix interfaces [45, 46]. Moreover, repeated temperature changes may induce degradation of matrix–filler bonds due to the different thermal expansion coefficients of fillers and the resin matrix, which has an impact on mechanical properties such as flexural strength [47]. In this study, either a clear decrease of the bond strength due to ageing or at least the tendency toward it can be recorded at the two commercially available materials. The experimental material, whose matrix consists of ormocer molecules to 100 %, however, proves to be extremely stable. It reaches statistically the same strength values after an artificial ageing. Similar results could be seen in a recent study, in which the same experimental material with a pure ormocer matrix, had the lowest percentage of hardness change after ageing and thus proved to be more resistant to solvent degradation (regardless of the light exposure method) [30]. Also, Hahnel attributes in his investigations the highest Vickers hardness and a low flexural strength to the experimental ormocer-based material in comparison with the traditional ormocer-based composite Ceram X [47]. As reason for the high stability, the matrix composition can be named. It is valid, generally, that the water sorption of a resin-based dental material increases provably with the hydrophilicity of its monomers and provides increased hydrolysis processes also in the area of the linkage [48, 49]. Bis-GMA (component of Ceram X Duo and Admira) and UDMA (component of Admira) are said to be strongly proportional hydrophilically [50, 51]. For this reason, it might be speculated that the modifications made in the pure ormocer matrix formulation were significantly important to produce more water stable material compared to the admixed ormocer matrix and dimethacrylate matrix composite materials [30]. The fact that the experimental composite has a considerably higher filler volume (72 in comparison with 56 (Admira) and 60 % (Ceram X Duo)) also favours this effect. Thermocycling is a generally accepted and often used method to simulate a clinical ageing process, so it can be assumed that as far as the resistance against water uptake is concerned, comparable qualities occur in the oral cavity. Therefore the experimental material promises a good chemical stability and high mechanical properties even after a longer period in the patient's mouth. In respect of the fact that practitioners attempt to extend the longevity of direct restorations, these results have a very high clinical relevance, though necessitate a validation in clinical studies. Even so, in this study, where the pure ormocer matrix achieved a considerably lower DC, the relatively bigger ormocer molecules could result in a higher cross-link density, offering a high resistance to degradation and solvent uptake [28].

The high stability of the experimental material opposite an artificial ageing can also be seen in the high number of cohesive fractures after thermocycling. When the frequency of the different breaking mechanisms was examined, it could be seen that the cohesive fracture considerably predominates, and mixture and adhesive fractures occur mainly at samples that achieve proportionally low bond strength. Moreover Table 3 shows that all measured parameters have a comparable and relatively little influence on the type of fracture (eta-squared value, 0.105–0.177). It seems that the bond strength determines the type of fracture accordingly that a high strength increases the probability of a cohesive fracture. Also, other studies arrive at comparable conclusions [52, 53]. Also, on closer consideration of the electron micrographs, it is noticeable that samples with a high homogeneity and a sufficient adaptation to the cavity margin result in a higher bond strength or a high number of cohesive fractures, respectively. Interestingly, the experimental material was the only material that achieved a little higher percentage of cohesive fractures after thermocycling (67–87 % without ageing vs. 93–100 % after ageing). However, at the evaluation both after 24 h and after artificial ageing, the experimental material achieves a lower Weibull modulus m, suggesting a lower reliability.

Applying Ceram X Duo, it is ascertainable that after an artificial ageing, significant but slight differences exist between the DD and the DE combination. The latter ones reach a little higher bond strength values after thermocycling and storage at all polymerisation distances. One could assume that this is due to the higher transparency of the enamel mass. So, a higher light intensity achieves the bonding surface during the polymerisation of the second and third increment, with the consequence that the final polymerisation can turn out a little higher, too. Moreover, an independent *t* test shows that samples made of enamel mass proved to be more resistant to an artificial ageing, at a distance of 1 mm (p=0.261) and 3 mm (p=0.060), and the reliability indicated by the Weibull modulus is also higher.

Within the limitations of this study, the following conclusions were drawn:

1. The experimental dimethacrylate-diluent-free, ormocer-based material showed no decrease in incremental bond strength after thermocycling and storage for 28 days and is therefore regarded as more resistant opposite ageing than the two commercially available materials. Nevertheless, the DC was statistically lower, and small values for the Weibull modulus m were reached, questioning the reliability. The first null hypothesis was therefore rejected.
2. An artificial ageing has a noticeable influence on the incremental bond strength and the type of fracture. Admira and Ceram X Duo reached considerably lower strength values and a higher number of mixture and adhesive fractures after thermocycling and storage, whereby the experimental material turned out to be very stable. So the parameter ageing has a statistically significant influence, and the second null hypothesis has to be rejected, even if the parameters resin-based composite and vol% filler predominate.
3. The distance of a modern LED curing unit, with a performance of 1,200 mW/cm^2 to the increment surface has a slight influence on the degree of cure and the type of fracture as long as it is within 1–6 mm. Its effect on the incremental bond strength, however, was shown to be negligible in comparison to the dominating influence of the parameters RBC and vol% filler, thus the third null hypothesis was partly rejected.
4. At evaluating after 24 h, no difference between the DD and the DE combination for Ceram X Duo could be revealed as far as the bond strength and the type of fracture were concerned. Only after ageing that the DE combination reached statistically higher values for bond strength and reliability at a polymerisation distance of 1 and 3 mm, and the fourth null hypothesis can therefore be partly accepted.

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

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