

Evaluation of a conventional glass ionomer cement with new zinc formulation: effect of coating, aging and storage agents

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Abstract

Objective The study focused on a recently launched conventional glass ionomer cement (GIC) with a particular chemical formulation of both, filler and acrylic liquid, by analysing its mechanical behaviour in comparison to three conventional GICs. Furthermore, the effect of resin coating and storage conditions was evaluated.

Materials and methods Three commercially available GICs were chosen: Riva Self Cure (SDI), Fuji IX Fast (GC) and Fuji IX GP Extra/Equia (GC). Additionally a newly developed zinc-containing GIC—ChemFil Rock (Dentsply)—was tested. Mechanical properties were determined at macro- [flexural strength (FS) and modulus of elasticity (E_{flexural})] and micro-scale [Vickers hardness (VH) and indentation modulus (E)] after storing coated and uncoated specimens in artificial saliva and distilled water for 7 and 30 days.

Results ChemFil Rock revealed the highest FS, but the lowest VH and E . The micro-mechanical properties of the analysed GICs did neither benefit from the new zinc formulation nor from resin coating. A resin coating is nevertheless a valuable support for GIC fillings, since it offers the absence of visible surface defects like crazing and voids, and thus, it led to significant improvements in flexural strength. This statement is also valid for ChemFil Rock, contrary to manufacture recommendation. The impact of storage agent and storage duration on the measured properties was low.

Conclusions The new development (ChemFil Rock) might represent a promising approach regarding longevity of GIC

fillings in molar regions, due to the high flexural strength and the absence of visible surface defects like crazing and voids.

Clinical relevance All GICs should receive surface protection in order to perform their maximum in stability.

Keywords Glass ionomer cements · Coating · Storage · Micro-mechanical properties

Introduction

In the field of dentistry, glass ionomer cements (GICs) are a common and useful choice for restorative therapy concerning fillings which are not situated in high-stress sites. However compared to permanent filling materials like resin-based composites, GICs show several advantages, such as the ability to adhere to moist enamel and dentin without necessitating an intermediate agent and anti-cariogenic properties such as the long-term fluoride release. Other clinical advantages like biocompatibility and low coefficient of thermal expansion support their valuable position in the daily dental practice [1–5].

These positive properties are unfortunately dwarfed by a poor surface polish, a high porosity and rather weak mechanical properties, such as brittleness, surface wear or fracture toughness [5, 6]. Therefore it is doubtful that GIC represents a capable counterpart of amalgam or resin-based composites in high-stress sites.

The first 10 min of the hardening process of GICs is characterised by a slow release of calcium ions within the matrix, followed by aluminium ions [7]. During this time period, the material is very much frail to dehydration [5], meaning in clinical conditions that a gain or loss of liquid in this phase can tremendously affect the final properties of the restoration.

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One advance in strengthening GICs was the application of surface protection in order to preserve the balance of the amount of liquid [8–11]. Reviewing the literature, only a few studies are dealing with the effect of resin coating on conventional GICs. Earl et al. [8] found that immediate covering of the immature GIC surface with light-activated bonding resin is the most effective method of limiting water movement across the surface. This supports the balance between water uptake and loss, leading to better clinical results. In a study by Ribeiro et al. [10], in analysing the effectiveness of surface protection for resin-modified GICs, it was stated that all tested materials required surface protection. Furthermore they found that Heliobond light-activated bonding resin displayed superior results than nail varnishes and surface coatings suggested by the manufacturer.

The manufacturer of a recently launched GIC (ChemFil Rock, Dentsply) followed a different approach to enhance material's stability, claiming that surface protection in the form of resin coating is irrelevant for product's performance. An enhanced setting reaction in the new GIC is supposed, due to the zinc content as part of its glass particles, leading thus to higher strength, by similar working time and application comfort as regular GICs [12].

Our present study aimed therefore primarily to verify if the zinc-containing material performed comparable to traditional alumina–silicate GICs. The influence of resin coating, aging and aging agent, such as artificial saliva and distilled water, are evaluated. The null hypotheses tested were that: (a) the new GIC would perform similar to the traditional GIC in terms of macro- (flexural strength and modulus of elasticity in flexural test) and micro- (Vickers hardness and modulus of elasticity) mechanical properties, (b) applying resin coating on the GICs surface would not influence the above-mentioned properties, (c) aging (7 and 30 days) would not affect the measured mechanical properties and (d) storing the GICs in artificial saliva or distilled water would result in similar mechanical properties.

Materials and methods

Three commercially available conventional restorative GICs—Riva Self Cure (SC), Fuji IX GP Fast and Fuji IX GP Extra (Equia)—and a new conventional GIC, ChemFil Rock, were selected (Table 1). Additionally, the corresponding light-cured resin coating for each material was chosen (Table 1). It should be noticed that for ChemFil Rock, no surface protection is indicated by the manufacturer. We still choose to apply an experimental resin coating supplied by the same manufacturer in order to confront every material with the same conditions. The mechanical properties were determined at macro- [flexural strength (FS) and modulus of elasticity (E_{flexural})] and micro-scale [Vickers hardness (VH) and indentation modulus (E)] for

coated and uncoated specimens after storing the samples in artificial saliva or distilled water for 7 and 30 days, respectively. In order to evaluate the size and shape of the glass particles, a scanning electron microscope (SEM) was used.

Macro-mechanical characteristics

Using a three-point bending test (in analogy to ISO 4049:2009) on bar-shaped specimens (16×2×2 mm), FS and E_{flexural} ($n=20$) were evaluated. Four materials (Table 1), two coating conditions (with and without coating), two aging times (7 and 30 days) and two aging agents (distilled water and artificial saliva) resulted in 32 groups, summarising 640 samples.

The encapsulated GICs were mixed by rotating in a RotoMix (3M-ESPE, Seefeld, Germany) apparatus and fabricated at room temperature, according to the manufacturer instructions. The specimens were prepared in a stainless steel mould, allowing them to set for 20 min at room temperature in the mould. In order to achieve plane and possibly voids free specimens, a transparent foil (US-120 KE; Frasco, Tettang, Germany) was placed on the surface of the unset material, by pressing it with an object slide. The foils were removed about 2.5 min after mixing. Specimens, receiving resin coating, were prepared in the same way, except for the application of the coating. The latter was applied 3 min after activation of the GIC capsules. Thereby the transparent foils were removed and the coating product was applied. Another foil was gently pressed on the coated surface of the specimen followed by light curing the coating for 20 s (Mini L.E.D, SATELEC SED-R, France) by three overlapping irradiations. After 20 min the specimens were taken out of the moulds and conditioned either in artificial saliva or in distilled water at 37°C, and stored for 7 or 30 days.

Previously to loading into a universal testing machine (MCE 2000ST; Quicktest Prüfpartner GmbH, Langenfeld, Germany), each specimen was gently grounded with 1,200-grit silicon carbide (SiC) paper (LECO, St. Joseph, MI, USA) and the exact dimension was recorded. The load was applied at a constant crosshead speed of 0.5 mm/min until fracture. The distance between the supporting points was 12 mm. During loading, the specimens were immersed in distilled water at room temperature. The coated side of the specimen was facing towards the tensile zone. E_{flexural} was calculated from the linear part of the force–deflection diagram.

Micro-mechanical characteristics

Fragments of the three-point bending test were used to determine VH and E by means of an automatic micro-hardness indenter (Fischerscope H100C, Fischer, Germany). Ten randomly selected specimens of each group were wet grounded with 2,500 and 4,000-grit SiC paper (FEPA). The coating was

Table 1 Materials, manufacturer and chemical composition of glass ionomer cements (all encapsulated) and coating materials

	Manufacturer	Composition
Glass ionomer cement		
Riva Self Cure; Lot: B1004281	SDI Limited, Victoria, Australia	Fluoro-aluminosilicate glass Polyacrylic acid + tartaric acid, polyacrylic acid
ChemFil Rock; Lot: 1005004004	Dentsply, Konstanz, Germany	Calcium-aluminium-zinc-fluoro-phosphor-silicate glass, polycarboxylic acid, iron oxide pigments, titanium dioxide pigments, tartaric acid, water
GC Fuji IX GP Fast; Lot: 1005211	GC Europe N.V., Leuven, Belgium	Alumino-fluoro-silicate glass, polyacrylic acid, distilled water, polybasic carboxylic acid
GC Fuji IX GP Extra (Equia); Lot: 1005281	GC Europe N.V., Leuven, Belgium	Polyacrylic acid, aluminosilicate glass, distilled water
Coating		
Riva Coat; Lot: 091103	SDI Limited, Victoria, Australia	Acrylic monomer
Seal&Protect TF; Lot: MTO-3-27-1	Dentsply, Konstanz, Germany	Di- and trimethacrylate, acetone, dipentaerythritol penta acrylate monophosphate
GC Fuji Coat LC; Lot: 1005061	GC Europe N.V., Leuven, Belgium	Methylmethacrylate, multifunctional methacrylate, camphorquinone
GC G-Coat Plus; Lot:1004091	GC Europe N.V., Leuven, Belgium	Methyl methacrylate, colloidal silica, camphorquinone

completely removed by this procedure. Six indentations were accomplished on each sample's coated sight, with a total of 60 measurements in each group. The measurements were 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 stored in a database supplied by the manufacturer, a conversion factor between universal hardness and Vickers hardness was calculated and implemented into the software, so that the measurement results were indicated in the more familiar Vickers hardness. The indentation modulus was calculated from the slope of the tangent of indentation depth curve at maximum force (DIN-50359-1 (1997) Testing of metallic materials—universal hardness test—part 1: test method).

The samples used for the SEM analysis (Zeiss Supra 55 VP, Oberkochen, Germany) were stored for 7 days in distilled water and received no sputtering. The images were taken by using a backscatter signal (RBSD).

Statistical analysis

The Kolmogorov–Smirnov test was applied to verify if the data were normally distributed. Results were compared using one and multiple-way ANOVA and Tukey's HSD post hoc test ($\alpha=0.05$). An independent *t* test additionally analysed the differences in mechanical properties as function of coating, aging duration and aging agent (SPSS Inc.;

Chicago, IL, USA, Version 19.0). An additional Weibull analysis was performed for the flexural strength data. A multivariate analysis (general linear model with partial eta-squared statistics) assessed the effect's strength of the parameters GIC, coating, storage agent and storage duration on the considered properties. The partial eta-squared statistic reports the practical significance of each term, based upon the ratio of the variation accounted for by the effect. Larger values of partial eta squared indicate a greater amount of variation accounted for by the model effect, to a maximum of 1.

Results

Post hoc multiple pairwise comparisons with Tukey's HSD test ($p<0.05$) revealed the highest values in FS for ChemFil Rock under all measured conditions (Tables 2 and 3). The influence of coating on the flexural strength was proved to be significant ($p<0.05$) for almost all tested conditions (exception: Riva Self Cure, saliva, 1 month and Riva Self Cure water, 1 week). Furthermore it could be verified that aging has no significant effect on FS (exception: Riva Self Cure with coating, stored in water) in both of the analysed storage agents. As for the Weibull parameter *m*, the reliability of the material, no clear dependency from material, coating condition, aging agent or duration can be emphasized. The highest value (*m*) was generated in ChemFil Rock, coated and stored for 30 days in artificial saliva.

Regarding the flexural modulus, E_{flexural} , the difference among materials was lower. Similar is valid also for the influence of the storage agent. A significant higher flexural

Table 2 Macro-mechanical properties of flexural strength (in newtons per square millimetres) are detailed in mean values and standard deviations (in parentheses)

Material	Storage	Coating			No coating			Water	Water	Saliva	Water	Water	
		Saliva	<i>m</i>	p1	Saliva	<i>m</i>	p2						<i>m</i>
Riva Self Cure	IW	19.3 α (4.9)	4.32	14.3A (8.3)	1.73	0.033	13.8a (4.4)	4.12	13.3A (3.7)	4.29	0.73	0.001	0.641
	IM	17.6 α (9.9)	1.52	22.8B (7.8)	2.47	0.072	15.5a (5.8)	3.22	12.8A (3.4)	4.64	0.09	0.414	0
ChemFil Rock	IW	38.7 β (12.5)	3.77	39.1C (7.7)	5.66	0.908	28.2b (11.1)	2.74	31.7B (9.6)	3.15	0.308	0.008	0.011
	IM	41.5 β (3.8)	13.1	39.4C (6.6)	7.08	0.22	30.9b (8.2)	4.19	30.4B (10.5)	3.23	0.867	0	0.003
Fuji IX GP Fast	IW	19.4 α (6.2)	3.74	16.7AB (5.9)	4.39	0.17	12.7a (8.2)	1.97	9.1A (1.6)	6.88	0.079	0.007	0
	IM	23.0 α (4.7)	5.76	15.5A (4.3)	4.59	0	9.7a (2.6)	4.17	9.2A (1.9)	5.53	0.539	0	0
Equia	IW	20.4 α (3.4)	6.81	20.1AB (4.9)	4.63	0.815	12.0a (7.4)	2.21	9.7A (4.1)	3.04	0.221	0	0
	IM	22.4 α (4.7)	5.83	18.5AB (5.8)	3.63	0.027	9.2a (5.0)	2.51	12.6A (6.9)	2.13	0.1	0	0.007

Symbols/letters indicate statistically homogeneous subgroups within a column (Tukey's HSD test, $\alpha=0.05$). A *t* test analysed differences as function of storage (difference saliva vs. water storage for samples with coating (p1) and without coating (p2)) and coating (difference coating vs. no coating for samples stored in saliva (p3) and in water (p4)). The Weibull parameter *m* is indicated

modulus ($p<0.05$) when samples were stored in artificial saliva compared to samples stored in water was found only in few groups (both, coated and uncoated samples of Riva Self Cure, 1 week and Fuji IX GP Fast, 1 month of storage). The positive influence of coating on the modulus of elasticity was more frequent evident in samples stored in water (Fuji IX GP Fast and Equia all storage durations) than in saliva (Riva Self Cure and Equia, both materials 1 week of storage).

The micro-mechanical properties, in contrast, varied consistently among the tested materials [Table 4 (a and b)], achieving the highest VH in Fuji IX Fast with coating, stored for 4 weeks in water. Generally this GIC reached the significant highest VH and *E* values under all measured conditions, whereas ChemFil Rock the significant lowest.

A significant increase in both measured micro-mechanical properties, VH and *E*, with storage duration was measured only for Riva Self Cure stored in saliva and uncoated. The influence of coating and storage agent on the micro-mechanical properties was in most cases not significant. Considering the multivariate analysis (Table 5), the flexural strength was proved to be stronger influenced by the material itself ($\eta^2=0.915$) than by the coating condition ($\eta^2=0.740$), whereas the effect on the flexural modulus was consistently lower (lower η^2 values, Table 5), with the coating condition ($\eta^2=0.236$) exerting a stronger influence than the storage duration ($\eta^2=0.190$).

The SEM images display small glass particles size in ChemFil Rock (Fig. 1). The diameter of the particles differs consistently from the larger diameter of the other three measured materials, demonstrating a greater particle surface area in ChemFil Rock. The glass particles in ChemFil Rock appeared rather homogenous in size and shape (SEM images, Fig. 1). More erratically glass particles were found in Riva SC, Fuji IX Fast and Equia.

Discussion

The study evaluated whether a new developed GIC (ChemFil Rock, Dentsply) can provide higher mechanical properties than conventional GIC containing alumina silicate glasses. According to the manufacturer, this new material should present an enhanced durability due to a zinc-containing glass with an accelerated ion release pattern, when compared to conventional GICs. Besides changes in the chemical composition of the glass particle, also a novel acrylic acid copolymer with a high molecular weight was incorporated in the material [12].

Generally, the setting process in a GIC is characterised by an interaction between a polyacid liquid and a glass powder in form of an acid–base reaction [13]. Upon an initial build-up of calcium polyalkenoate, the formation of aluminium

Table 3 Macro-mechanical properties of modulus of elasticity in flexural test ($E_{flexural}$, in gigapascals) are detailed in mean values and standard deviations (in parentheses)

Material	Storage	Coating			No Coating			Saliva	Water
		Saliva	Water	p1	Saliva	Water	p2	p3	p4
Riva Self Cure	1W	6.3αβ (1.3)	4.3A (1.3)	0	5.4a (0.8)	4.4A (0.9)	0.001	0.016	0.72
	1M	5.4α (1.7)	6.4B (1.5)	0.062	5.5a (2.5)	5.8BC (0.8)	0.538	0.933	0.167
ChemFil Rock	1W	5.9αβ (2.1)	5.9B (1.1)	0.919	5.3a (1.0)	5.3AB (1.0)	0.979	0.286	0.141
	1M	6.4αβ (1.1)	6.1B (1.0)	0.367	6.0a (1.2)	6.6C (1.0)	0.072	0.203	0.133
Fuji IX GP Fast	1W	6.6αβ (2.0)	7.0B (2.3)	0.548	5.9a (1.5)	5.8BC (0.8)	0.878	0.238	0.045
	1M	7.2β (2.0)	6.0B (1.1)	0.02	6.4a (1.0)	5.0AB (1.1)	0	0.134	0.011
Equia	1W	6.3αβ (1.0)	6.1B (1.0)	0.403	5.3a (1.4)	5.0AB (1.0)	0.489	0.01	0.003
	1M	6.5αβ (1.1)	6.6B (1.0)	0.74	5.9a (1.1)	5.4B (1.2)	0.176	0.145	0.004

Symbols/letters indicate statistically homogeneous subgroups within a column (Tukey’s HSD test, $\alpha=0.05$). A *t* test analysed differences as function of storage (difference saliva vs. water storage for samples with coating (p1) and without coating (p2)) and coating (difference coating vs. no coating for samples stored in saliva (p3) and in water (p4)). The Weibull parameter *m* is indicated

polyalkenoate occurs. This reaction is characterised by a stepwise, rather long-lasting setting, where changes in mechanical properties occur, mainly characterised by a rise in strength within the first 24 h. A continuing altering of strength can be observed over several weeks and months [14–16].

At first, the precipitation of the cement is continuing until most of the ions are in insoluble form. This period can be observed 3 to 6 min after the mixing process [17, 18].

Considering clinical conditions, both, water contamination and dehydration in this phase can be compromising for the cement applied in a cavity [5]. Crack propagation, frequently observed in GIC fillings, is a typical mechanical failure resulting from desiccation [19]. Gemalmaz et al. [20] observed that due to early moisture contamination, the mechanical properties of GICs decreased and their surfaces became more susceptible for erosion and abrasion. Naasan and Watson [5] emphasizes that water contamination must

Table 4 Micro-mechanical property of (a) Vickers hardness and (b) indentation modulus is detailed in mean values and standard deviations (in parentheses)

	Material	Storage	Coating			No Coating			Saliva	Water	
			Saliva	Water	p1	Saliva	Water	p2	p3	p4	
(a) Vickers hardness (N/mm ²)	Riva Self Cure	1W	105.6βγ (7.4)	116.1BC (7.4)	0.034	85.3bc (6.1)	101.8CD (33.8)	0.289	0	0.354	
		1M	114.5βγδ (11.4)	115.5BC (11.3)	0.886	111.5de (23.6)	92.5BC (9.6)	0.112	0.789	0.004	
	ChemFil Rock	1W	59.1α (5.3)	67.6A (5.9)	0.024	56.4a (3.0)	60.8A (2.1)	0.016	0.313	0.036	
		1M	68.4α (5.1)	66.8A (1.9)	0.498	64.8ab (2.6)	67.1AB (2.2)	0.127	0.161	0.814	
	Fuji IX GP Fast	1W	119.3γδ (3.0)	119.3BC (11.3)	0.998	113.0de (6.7)	118.5CD (13.9)	0.406	0.073	0.921	
		1M	124.6δ (11.9)	125.9C (19.0)	0.896	115.0e (14.6)	122.1D (10.0)	0.349	0.24	0.683	
	Equia	1W	103.0β (9.2)	99.3B (14.3)	0.603	90.7cd (16.5)	97.6CD (7.5)	0.383	0.149	0.802	
		1M	110.9βγδ (5.2)	109.7BC (13.8)	0.846	97.9cde (10.4)	103.3CD (11.8)	0.423	0.027	0.407	
	(b) Indentation modulus (E, GPa)	Riva Self Cure	1W	24.1δϵ (1.1)	24.3CD (1.3)	0.746	19.6b (2.5)	22.0CD (2.2)	0.119	0.003	0.061
			1M	22.5γδ (1.6)	23.1C (0.8)	0.437	23.1c (1.7)	20.5BC (1.5)	0.018	0.571	0.006
ChemFil Rock		1W	17.4α (0.6)	18.9AB (0.9)	0.008	17.0a (0.6)	17.8A (0.7)	0.072	0.31	0.039	
		1M	16.5α (1.3)	17.1A (0.8)	0.34	17.1a (0.4)	17.2A (0.45)	0.907	0.279	0.856	
GC Fuji IX GP Fast		1W	24.3δϵ (0.7)	25.6D (1.7)	0.129	23.9c (0.6)	23.7DE (1.2)	0.642	0.291	0.044	
		1M	25.3ϵ (1.1)	25.7D (1.7)	0.657	24.5c (1.7)	24.4E (1.2)	0.87	0.371	0.159	
Equia		1W	19.9β (1.1)	18.7AB (1.2)	0.115	18.1ab (0.8)	18.7AB (0.8)	0.189	0.01	0.977	
		1M	20.9βγ (1.0)	20.0B (1.2)	0.218	19.3ab (0.8)	19.4AB (0.6)	0.885	0.018	0.276	

Symbols/letters indicate statistically homogeneous subgroups within a column (Tukey’s HSD test, $\alpha=0.05$). A *t* test analysed differences as function of storage (difference saliva vs. water storage for samples with coating (p1) and without coating (p2)) and coating (difference coating vs. no coating for samples stored in saliva (p3) and in water (p4))

Table 5 Influence of material, storage agent, storage duration and coating on flexural strength (FS), modulus of elasticity in flexural test (E_{flexural}), Vickers hardness (VH) and indentation modulus (E)

Parameter	E_{flexural}	FS	VH	E
Material	NS	0.915	0.775	0.911
Storage agent	NS	NS	NS	NS
Storage duration	0.190	NS	NS	NS
Coating	0.236	0.740	NS	NS

The higher the partial eta-squared values, the higher is the influence of the selected variables on the measured properties [general linear model (η^2)]

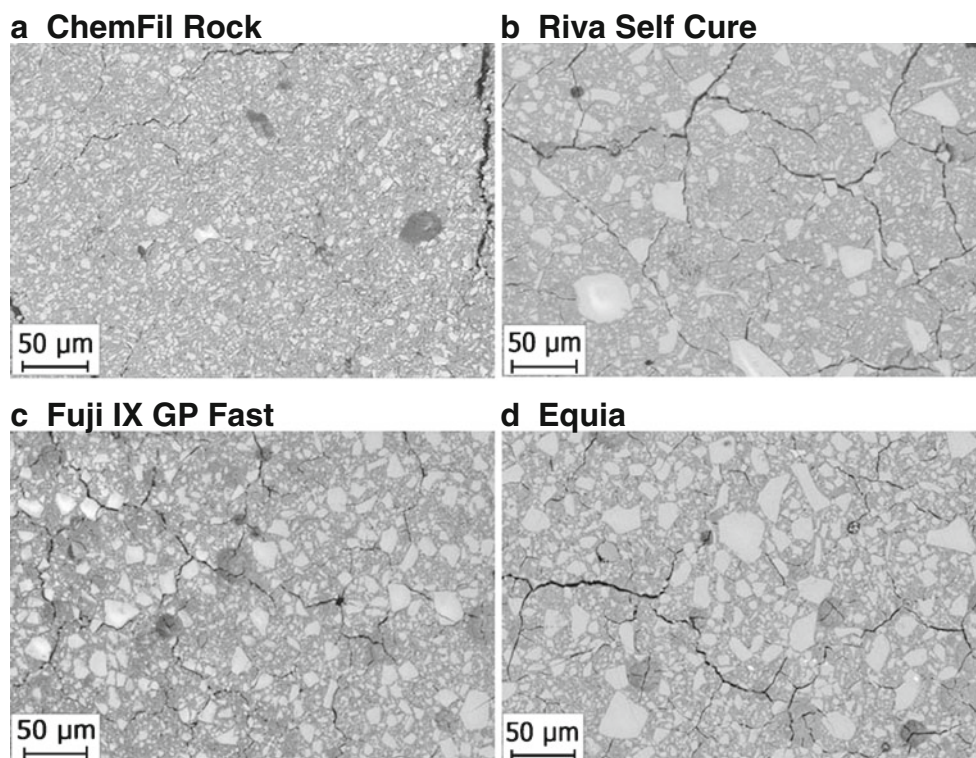
NS nonsignificant

be prevented during the delicate phase of the setting, which is referred by the author to endure 1 day up to 2 weeks. The same author [5] also claims that as time progresses, surface coatings fade away on the strength of mastication wear. Within this process, the resistance of the cement increases towards variations in water balance due to post hardening [5].

Regarding the results of our study, it becomes obvious that once the materials were protected from the influence of aqueous solutions by light-cured resin, FS could be improved. Hereby, it has to be pointed out that all samples prepared in this study were protected by a transparent foil in the initial phase of setting, which in this case was about 150 s. Thus, an initial surface protection was actually

supplied for all specimens, coated and uncoated, which cannot be directly transcribed to real clinical conditions. This step was however necessary to allow correct sample preparation for the three-point flexural strength test, which is seen as the most meaningful test to evaluate the mechanical behaviour of GICs [21, 22]. As described in former investigations [21], FS shows a high sensitivity towards surface irregularities, resulting in erosions caused by water. Crisp and Wilson [7] presumed that the high affinity of water to GICs is caused by the ion-depleted siliceous phase, whose behaviour is analogical to silica gel, taking up water from the surroundings. Xie et al. [23] conclude that a less dense surface, or rather larger and higher amounts of voids result in worse mechanical properties. The assumption can be made that FS usually rises when surface protection is applied. But the strength of GIC is deciding influenced by its glass composition as well [24]. Especially a high content of fluoride was proved to induce a higher compressive and flexural strength [24]. Similar is valid also for GIC containing high amounts of zinc embodied in the glass powder, since an enhanced network connectivity will occur, thus raising the ability of the material to form a cement with acrylic acid. The setting time was also shown to decrease, making the resulting GIC more resistant against hydrolysis and, finally, inducing in the material a higher strength [25]. The high FS measured for ChemFil Rock compared to the other materials in this study supports this thesis. Further examinations upon the cross-link density in GIC by using,

Fig. 1 Scanning electron microscopy images (back-scattered modus on not sputtered samples). **a** ChemFil Rock, **b** Riva Self Cure, **c** Fuji IX GP Fast and **d** Equia



among others, MAS-NMR spectroscopy figured out that zinc oxide is primarily a network modifier than a network former [26]. It was also evidenced that an increasing amount of zinc is directly connected to an enhanced reactivity [27]. As a network modifier, zinc oxide contributes to the Si–O–Si bond disruption in the glass and thus increases the vulnerability of the glasses to acid attack. According to the manufacturer [12] and confirmed by our data, the formation of zinc–polycarboxylate complexes during the setting of the novel GIC enhances the strengths more than other complexes consisting of bivalent ions like calcium or strontium.

Besides the chemical composition of glasses, also the polyacrylate acids in GIC can influence the setting reaction and the resulting properties of GIC [27]. In ChemFil Rock, a new acrylic acid copolymer with a high molecular weight was incorporated as well. The material also has included in its chemical composition itaconic acid as a co-monomer, which when incorporated in a conventional commercial GIC was shown to improve the biaxial flexural strength and diametral tensile strength compared to compositions without this copolymer [28]. The itaconic acid as a co-monomer to the high molecular polycarboxylic acid contained in ChemFil Rock is supposed to reduce the interaction between the high molecular polyacids in form of hydrogen bridges, and thus to delay the building of a gel phase which would worsen the storage stability [12]. The working properties of composition with or without itaconic acid as a co-monomer were proved to be comparable and acceptable for water-based cements [28].

Another approach to explain the high flexural strength of ChemFil Rock is suggested by Prentice et al. [29] who found that improved strength of GIC is related to a decrease in mean particle size and thus an increase in glass surface area. This thesis might correspond to our results within the SEM imaging. Moreover, the visual inspection of the GIC samples previously to loading in the three-point bending showed crazing and surface imperfections for the materials Riva Self Cure, Fuji IX Fast and Equia, but none for ChemFil Rock. There is thus evidence that macro-defects in GICs, such as crazing and voids, are responsible for the weak mechanical properties.

Turning our attention towards the aqueous solutions used in this study, distilled water and artificial saliva, higher flexural strength was measured in both solutions under coating conditions. Within a coating condition, the storage media were proved to have only scattered significant effect on the physical properties measured. Our finding of a low effect of the storage agent on the measured mechanical properties is in agreement with Nicholson and Wilson, who stated that there are no statistically significant differences of strengths measured between the storage media, among others deionized water and artificial saliva, concerning the time period from 24 h to 30 days [30]. Focusing on the condition of storage time, the different materials evolved distinguished behaviour of mechanical strength.

In view of the measured micro-mechanical properties, VH and E [Table 4 (a and b)], these properties are likely to depend stronger on the composition of the selected materials than the measured macro-mechanical properties. Many studies [22, 31–34] discussed this assumption as they described the influence of the chemical composition, concentration and molecular weight of the polycarboxylic acid, the glass structure and the power/liquid ratio.

In contrast to the flexural strength, the effect of resin coating on the micro-mechanical properties was mostly not significant. A particular behaviour was observed for ChemFil Rock. Though reaching significant higher macro-mechanical properties when compared to the other GICs, the micro-mechanical properties were the lowest. The reason for lower micro-mechanical properties must be searched in the filler size and morphology [23] of the glass particles in ChemFil Rock. Analysing the micro-mechanical attributes of GIC and the effect of coating, it has to be ascertained that surface protection in the form of resin coating did not show the expected effect of a significant improvement in hardness and indentation modulus.

Conclusion

The new GIC might represent a promising approach of granting GICs' higher longevity, which turns it into a more favourable filling material in class I and II cavities. In contrast to the other materials tested, it showed no crack propagation and visible surface irregularities and thus improved macro-mechanical characteristics, but lower micro-mechanical properties. The micro-mechanical properties of the analysed GICs did neither benefit from the new zinc formulation nor from resin coating. A resin coating is nevertheless a valuable support for GIC fillings, since it led to significant improvements in flexural strength. This statement is valid also for ChemFil Rock, contrary to the manufacture indication. The impact of storage agent and duration on the measured properties was low.

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

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