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# Time-dependent strength and fatigue resistance of dental direct restorative materials

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Elastic modulus (EM), initial fracture strength (FS) and flexural fatigue limit (FFL) of dental restorative materials were measured in a simulated oral environment to correlate mechanical response under the influence of water with the chemical nature of the test materials under investigation. One resin composite (RC; Tetric® Ceram, Ivoclar-Vivadent Corp., Liechtenstein), an ion-leaching resin composite (ILRC; Ariston® pHc, Ivoclar-Vivadent Corp., Liechtenstein) a compomer (CO; Dyract® AP, Dentsply Corp., USA) and a glass-ionomer cement (GIC; Ketac® Molar, 3MEspe Corp., Germany) were tested. Static EM, FS and dynamic FFL experiments were performed. The FFL was determined under cyclic loading for $10^5$ cycles in terms of a staircase approach. The materials were stored for 1, 8, 30, 90 and 180 days in 37 °C distilled water, respectively. The RC degraded over time due to water adsorption followed by failure within the resin matrix. The ILRC suffered from a pronounced decrease in FS as well as in FFL due to a constant ion-leaching and macroscopic crack growth. CO failed over time due to resin-filler interface cracking. The GIC exhibited improved mechanical performance over time due to a post-hardening mechanism. The results reveal the necessity for substantial preclinical evaluation of direct restorative materials. The material parameters under investigation are capable of predicting clinical performance over time.

## 1. Introduction

Within the last decades, modern restorative materials were developed with a focus on amalgam-like mechanical properties as well as excellent esthetics and acceptable biocompatibility. Different strategies, such as adhesively bonded, high strength resin composite materials or self adhesive and fluoride releasing glass–ionomer cements (GICs) were established as substitutes for amalgam. A combination of the advantages of both materials resulted in the so-called compomers (*compo*site and glass–iono*mer* cement). Ion-releasing materials were developed to prevent sound tissue from secondary caries. All materials were further improved for an application in stress-bearing areas [1]. However, there is often a lack of time for substantial clinical evaluation and therefore preclinical investigation of the materials becomes more and more important. Material parameters such as initial mechanical properties and fatigue resistance measured under simulated oral environment might be capable of predicting clinical performance over time [2].

Fatigue fractures after several years of clinical service were reported to be a common failure reason. Damages of restorations such as bulk, cusp or marginal fractures were observed frequently [3]. Using resin composite materials, Burke *et al.* [4] reported marginal fracture (18%) and bulk fracture (7%) as the most prevalent reasons for re-restoration. Hickel *et al.* [5] reviewed annual failure rates in posterior stress-bearing cavities from literature findings. They determined median annual failure rates of 0–9% for resin-based composites, 0–7% for amalgam and 1.9–14.4% for GICs. They all stated bulk, cusp and marginal fractures as a main reason for failure.

Fatigue of dental restoratives is mainly influenced by hydrolytic degradation. Soderholm *et al.* [6] showed the degrading influence of hydrolytic water adsorption on mechanical strength. They observed microcrack formation at the resin-filler interface due to leakage of filler elements under water exposure. Ferracane *et al.* [7] and Ritter *et al.* [8] also identified the resin-filler interface to be the weak link under water attack. They stated a chemical degradation caused by leakage of the interfacial silane coupling agent.

Clinical fatigue is mainly driven by cyclic masticatory forces. Slow crack propagation in brittle materials such as resin composites and glass–ionomer cements was observed in *in vitro* cyclic fatigue studies [9, 10]. A

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TABLE I Material specifications

| Material | Matrix ingredients | Filler size | Filler content (vol%) |
|---|---|---|---|
| RC (Tetric® Ceram) | Bis-GMA, UDMA, TEGDMA | $d_{50} = 1.0\,\mu m$ | 60 |
| ILRC (Ariston® pHc) | BisGMA, UDMA, spec. DMA | $d_{50} = 1.3\,\mu m$ | 59 |
| CO (Dyract® AP) | UDMA, TCB | $d_{50} = 0.8\,\mu m$ | 50 |
| GIC (Ketac® Molar) | Acrylic/maleic/tartaric acid | $d_{50} = 2.8\,\mu m$ | 56 |

BisGMA: Bisphenol glycidyl methacrylate; UDMA: Urethane dimethacrylate; TEGDMA: Triethyleneglycol dimethacrylate; TCB: Tetracarboxylic acid butane.

dramatically decreased strength performance, due to stress corrosion under load or due to visco-elastic creep was observed after the applied combination of water aging and cyclic loading [11, 12]. Fracture was detected both at the resin–filler interface and within the resin itself [10]. Creep deformation and dynamic mechanical properties in dental restoratives were attributed to variations in filler configuration, such as filler size and fraction [12].

However, the combined hydrolytic and mechanical behavior of the broad variety of direct dental restoratives has not been fully explained. The objective of this *in vitro* study was to describe further mechanical fatigue resistance after long-time exposure in water, increasing the reliability and predictability of this class of dental materials. A selection of direct filling materials, representing different chemical nature, such as resin composite (RC), ion-leaching resin composite (ILRC), compomer (CO) and GIC materials, were included. Elastic modulus (EM), initial fracture strength (FS) and flexural fatigue limit (FFL) were measured and the mechanical response to fatigue and chemical nature of the tested materials.

## 2. Materials and methods

### 2.1. Materials

Four different commercially available dental restorative materials for the direct filling technique were selected. The represented material classes were: resin composite (RC; Tetric® Ceram, Ivoclar-Vivadent Corp., Liechtenstein), ion-leaching resin composite (ILRC; Ariston® pHc, Ivoclar-Vivadent Corp., Liechtenstein), compomer (CO; Dyract® AP, Dentsply Corp., USA) and glass-ionomer cement (GIC; Ketac® Molar, 3M Espe Corp., Germany). Their chemical structure and filler configuration are displayed in Table I.

### 2.2. Specimen preparation

Bending bars with the dimension $2 \times 2 \times 25\,\text{mm}^3$ were produced using a metal/glass mold. The GIC was a two component system that had to be hand spatulated using a powder:liquid ratio of 2.85. The other materials were light-cured on five overlapping spots of 8 mm diameter on each upper and lower side of the bar with a commercial halogen light-curing unit (Elipar® Trilight (800 mW/cm$^2$), 3M Espe Corp., Germany). The illumination time on a single spot was 40 s. The procedure followed the manufacturer's recommendation and ISO 4049 standard. The specimens' surfaces were ground with silicon carbide paper of 1000 grit to avoid and remove surface cracks. All specimens were stored in distilled water of 37 °C.

### 2.3. Experimental procedure

To evaluate the initial flexural strength, the four-point-bending test was used ($n = 12$). Bars of 25 mm in length were fixed between four fins ($\varnothing = 2\,\text{mm}$; distance of inner fins: 10 mm; distance of outer fins: 20 mm) and were subsequently loaded until fracture with a crosshead speed of 0.75 mm/min in a universal testing machine (Z 2.5, Zwick, Germany). The elastic modulus was calculated from the linear-elastic range between bending force and specimen displacement before fracture.

The FFL of the composite materials were determined for $10^5$ cycles under equivalent test conditions at a frequency of 0.5 Hz ($n = 22$). The ''staircase'' approach method [13] was used for fatigue evaluation: for each cycle, the stress alternated between 1 MPa and maximum stress. Tests were conducted sequentially, with the maximum applied stress in each succeeding test being increased or decreased by a fixed increment of stress, according to whether the previous $10^5$ cycle run resulted in failure or not. The first specimen was tested at 50% level of the initial flexural strength value. As the data are concentrated around the mean stress, the number of specimens required is less than with other methods [14]. All tests were carried out in distilled water of 37 °C temperature. The schematic staircase approach is shown in Fig. 1, indicating initial FS, all single cyclic measurement with the number of cycles survived, and the calculated FFL with its standard deviation.

The FFL and SD were determined using Equation 1 and standard deviation, respectively using Equation 2:

$$\text{FFL} = X_0 + d\left(\frac{\sum in_i}{\sum n_i} \pm 0.5\right) \qquad (1)$$

$$\text{SD} = 1.62\,d\left(\frac{\sum n_i \sum i^2 n_i - \left(\sum in_i\right)^2}{\left(\sum n_i\right)^2} + 0.029\right) \qquad (2)$$

where $X_0$ is the lowest stress level considered in the analysis and $d$ is the fixed stress increment. To determine the FFL, the analysis of the data is based on the least frequent event (failures versus non-failures). In Equation 1, the negative sign is used when the analysis is based on failures, otherwise the positive sign is used. The lowest stress level considered is designated as $i = 0$, the next as $i = 1$, and so on and $n_i$ is the number of failures or non-failures at the given stress level. A complete interpretation of the staircase approach is plotted in Fig. 1.

The initial FS and FFL data were statistically computed by an ANOVA test ($p < 0.05$). However, to

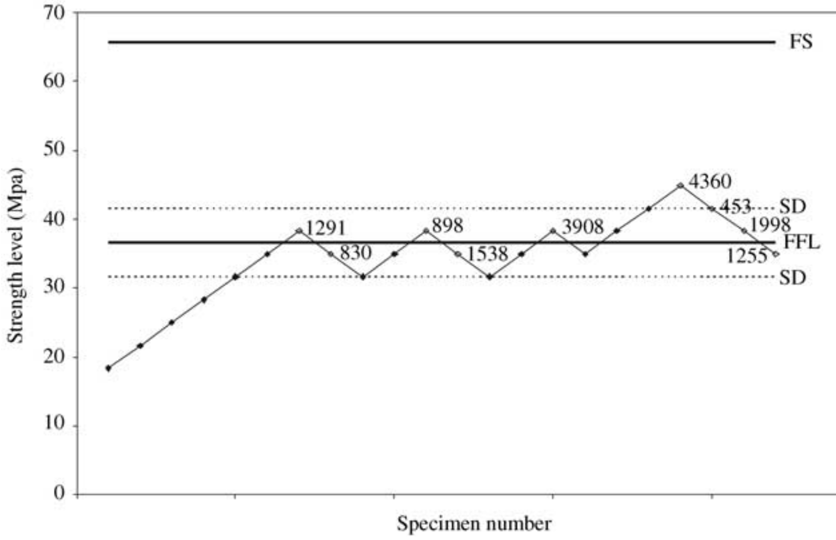

*Figure 1* Staircase approach indicating the characteristic values FS, FFL ( ± SD) and for every broken specimen the number of cycles.

generate significant differences between the tested groups a Bonferroni post-hoc routine was applied.

Fractographic examination was performed under a light microscope (SV 11, Zeiss, Germany) and under a scanning electron microscope (SEM, Leitz ISI SR 50, Akashi, Japan) on representative samples.

## 3. Results

All measured data, including their standard deviations (SD) are summarized in Table II. Fig. 2 exhibits the time-dependent development of the elastic moduli. The time-dependent data for FS are summarized in Fig. 3 (heavy lines). The dotted lines in Fig. 3 represent the FFL data over time. The tests were performed after 1, 8, 30, 90 and 180 days, respectively in water of 37 °C.

### 3.1. Elastic modulus

The RC material exhibited a statistically significant decrease from 9.4 GPa after 1 day to 8.5 GPa after 90 days water storage. ILRC and CO were found to behave significantly constant through a period of 180 days. An intermediately increased EM (11.0 GPa) was observed for CO after 90 days. The significantly lowest values were measured for the GIC material with a pronounced increase of EM from 3.1 GPa up to 5.7 GPa which has been determined within the first 30 days of water storage.

### 3.2. Initial fracture strength

The RC material clearly revealed the highest initial FS (102.3 MPa) after 1 day. However, FS significantly decreased to 73.9 MPa after 90 days water storage. A significant decrease was also observed for the ILRC and for the CO material. ILRC showed a stable behavior from 91.2 MPa (one day) to 50.5 MPa (180 days) and CO from 67.2 MPa (one day) to 36.6 MPa (180 days). CO had a temporary peak of 90.0 MPa at 8 days water storage. In contrast, the FS of the GIC significantly increased from 19.7 MPa after one day up to 36.7 MPa after 90 days. Since a pronounced increase took place, this material still points out the lowest FS after 90 days.

### 3.3. Flexural fatigue limit

After 1 day, the highest FFL was measured for the ILRC material (50.0 MPa), the lowest FFL for the GIC

TABLE II Elastic moduli (EM) data ( ± SD) in GPa (a), fracture strength (FS) data ( ± SD) in MPa (b) and flexural fatigue limit (FFL) data ( ± SD) in MPa (c)

| Material | 1 d | 8 d | 30 d | 90 d | 180 d |
|---|---|---|---|---|---|
| (a) | | | | | |
| RC | 9.4 ± 0.6 | n.m. | n.m. | 8.5 ± 0.5 | n.m. |
| ILRC | 10.6 ± 0.4 | 10.4 ± 0.6 | 10.1 ± 0.6[a] | 10.1 ± 0.7 | 10.7 ± 0.7 |
| CO | 9.9 ± 1.0 | 9.6 ± 1.0 | n.m. | 11.0 ± 0.7 | 9.6 ± 0.6 |
| GIC | 3.1 ± 0.9 | 4.9 ± 1.2 | 5.7 ± 0.7 | 3.7 ± 0.8 | n.m. |
| (b) | | | | | |
| RC | 102.3 ± 6.9 | n.m. | n.m. | 73.9 ± 6.7 | n.m. |
| ILRC | 91.2 ± 15.7 | 86.1 ± 10.1 | 68.9 ± 10.0 | 59.0 ± 11.5 | 50.5 ± 14.1 |
| CO | 67.2 ± 11.9 | 90.0 ± 23.6 | n.m. | 65.7 ± 15.0 | 36.6 ± 8.7 |
| GIC | 19.7 ± 3.1 | 33.0 ± 4.2 | 35.2 ± 9.1 | 36.7 ± 6.3 | n.m. |
| (c) | | | | | |
| RC | 40.6 ± 1.9 | n.m. | n.m. | 40.4 ± 1.9 | n.m. |
| ILRC | 50.0 ± 5.5 | 43.0 ± 5.5 | 35.9 ± 5.2 | 26.8 ± 3.5 | 25.7 ± 3.6 |
| CO | 35.3 ± 4.2 | 40.8 ± 3.6 | n.m. | 31.8 ± 5.7 | 36.6 ± 4.9 |
| GIC | 13.2 ± 2.9 | 17.5 ± 1.9 | 21.4 ± 2.8 | 29.4 ± 14.6 | n.m. |

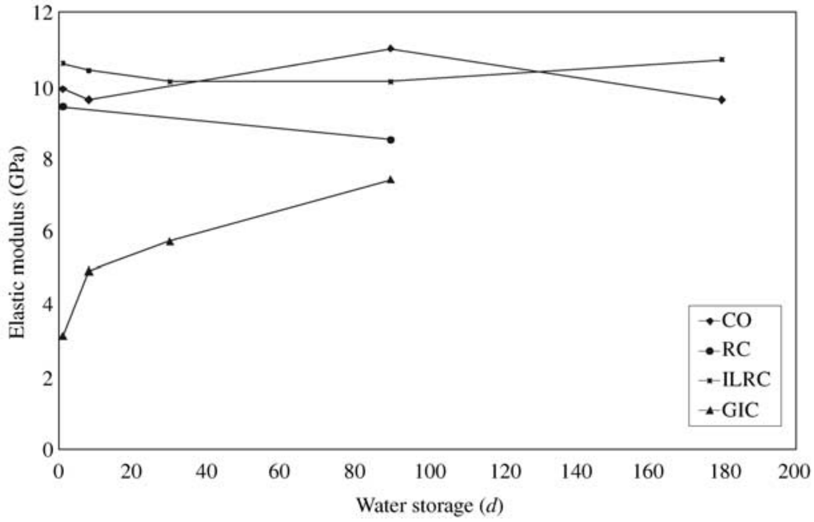

*Figure 2* Time-dependent elastic moduli (EM).

(13.2 MPa). After 90 days of water storage, the GIC fatigue resistance (29.4 MPa) increased to the level of the ILRC (26.8 MPa) and CO (31.8 MPa). The fatigue resistance of the ILRC dropped linearly to that level of FFL, while in contrast the GIC constantly increased. For CO, a prominent peak was observed after 8 days. The RC followed a constant development of FFL from 40.6 MPa after 1 day to 40.4 MPa after 90 days. However, after 90 days this material still revealed the most pronounced fatigue resistance of all tested materials.

## 4. Discussion

All investigated materials suffered from changes in fracture strength and fatigue resistance over time. The mechanical properties of all resin-based materials decreased while those of the GIC increased during water storage. The EM clearly followed mechanical strength and fatigue resistance in RC and GIC. However, in ILRC and CO the long-time elastic moduli remained approximately constant over time.

Mechanical properties of direct filling materials are thoroughly investigated in dental research. FS of approximately 100 MPa was reported for resin composite and ion-leaching resin composite materials after 1 day in water [15]. The authors observed a slightly higher EM for ILRC compared with RC. For CO, a decrease in FS with a constant EM was found after 90 days of water storage [16]. A pronounced increase for GIC materials was reported according to EM and FS within the first month [16]. The authors proposed a post-hardening mechanism of the matrix layer at the filler particle surface to be responsible for that strengthening effect in water. Dynamic properties such as fatigue resistance was investigated by Braem *et al*. [17]. They found a distinct decrease in mechanical strength for RC and CO materials after cyclic loading for $10^5$ cycles. The degradation was addressed to the hydrolytic influence of water.

However, the mechanical behavior of RC, ILRC, CO and GIC materials under investigation correlate with literature findings. The time-dependent development of the measured parameters EM, FS and FFL is supported by related literature. It was shown that water dominantly effected the development of mechanical properties over time. Soderholm *et al*. [6] described the detrimental effect of water on resin-based materials in two ways: water adsorption occurs within the matrix itself and at the resin-filler interface.

A plasticizing effect in the matrix is reported to result

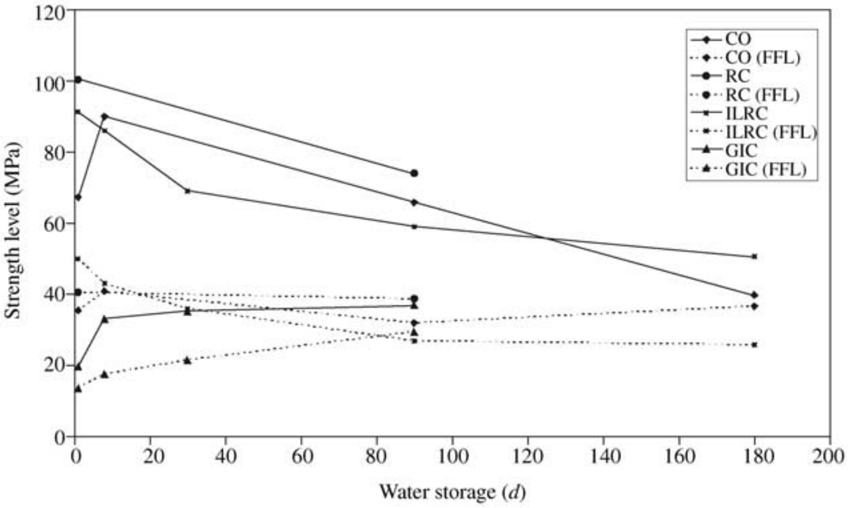

*Figure 3* Development of fracture strengths (FS) and flexural fatigue limits (FFL) over a period of 180 days in water.

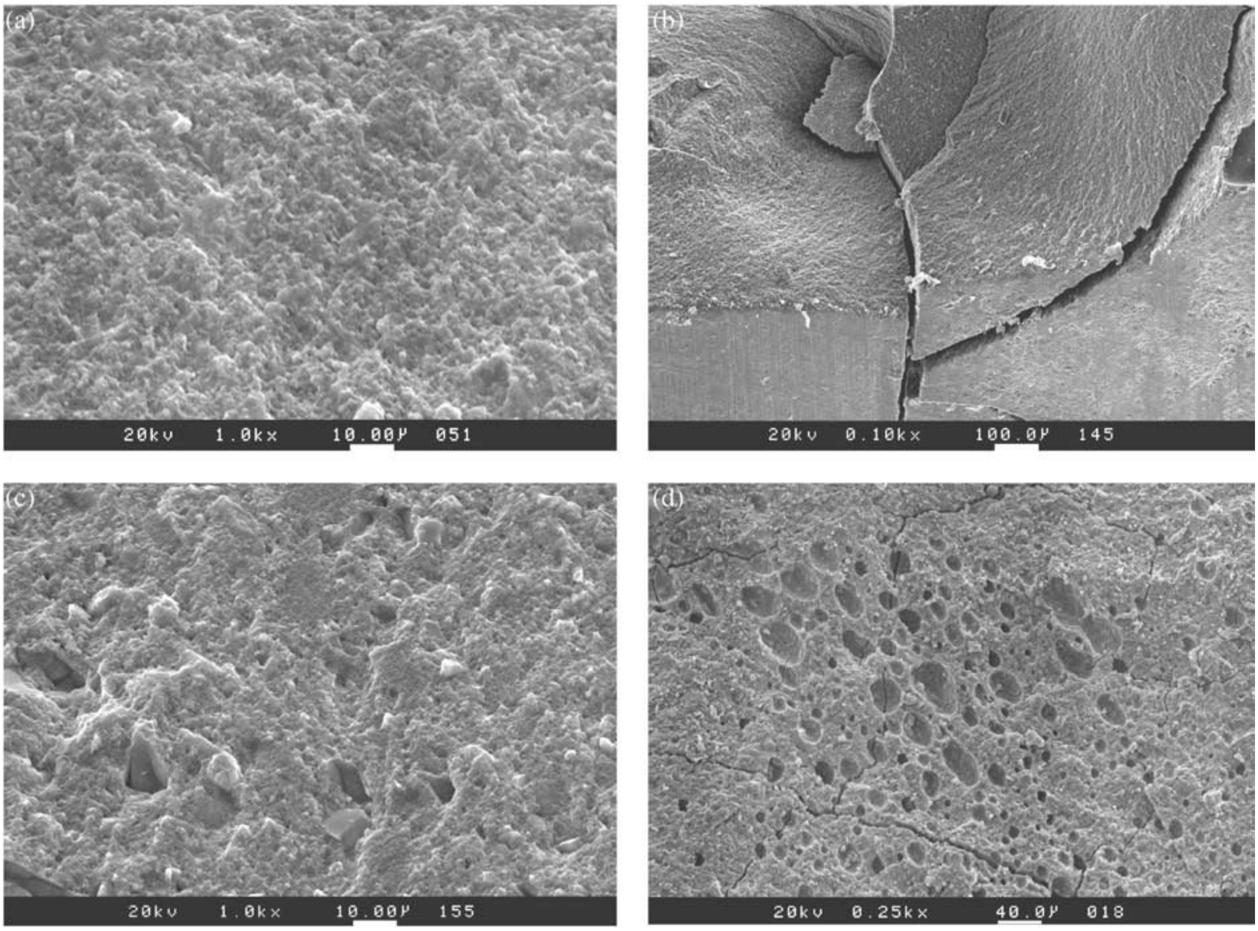

*Figure 4* Fractographic surfaces of the tested materials RC (a), ILRC (b), CO (c) and GIC (d).

in decreased elastic properties as well as swelling of the matrix [7]. On the other hand, a decreased FS has been explained by a slow crack growth mechanism [8].

The elastic modulus and the fracture strength of the RC decreased, due to water absorption from 1 day to 90 days. A supposed cohesive failure of the resin matrix is shown in Fig. 4(a) for the RC. The FFL has not been influenced from water absorption since it remained constant at 1 day and 90 days. A different failure mechanism is shown in Fig. 5. The typical fractographic patterns of a brittle failure, such as the fracture origin (I), the mist and hackle region (II) and the lance hackle mark (III) are only found for initial FS measurements [18]. A smooth fracture surface in Fig. 5(b) indicates a changed failure mechanism, due to slow crack growth under cyclic fatigue conditions [19].

Water attacks and hydrolyzes the silanization of filler particles and allows for crack growth. The CO material, after an initial FS peak at 8 days, suffered from a decrease in strength due to the corrosive attack of water at the resin–filler interface. The composition of CO is based on reactive glass fillers in a mainly anhydrous UDMA matrix. However, the hydrophilic TCB monomer enables water uptake and the glass–ionomer phase to be formed. The amount of absorbed water varies within the tested materials. High water uptake was measured for the partly glass–ionomer reacted CO and highest for the GIC. The lowest value was documented for RC materials [20].

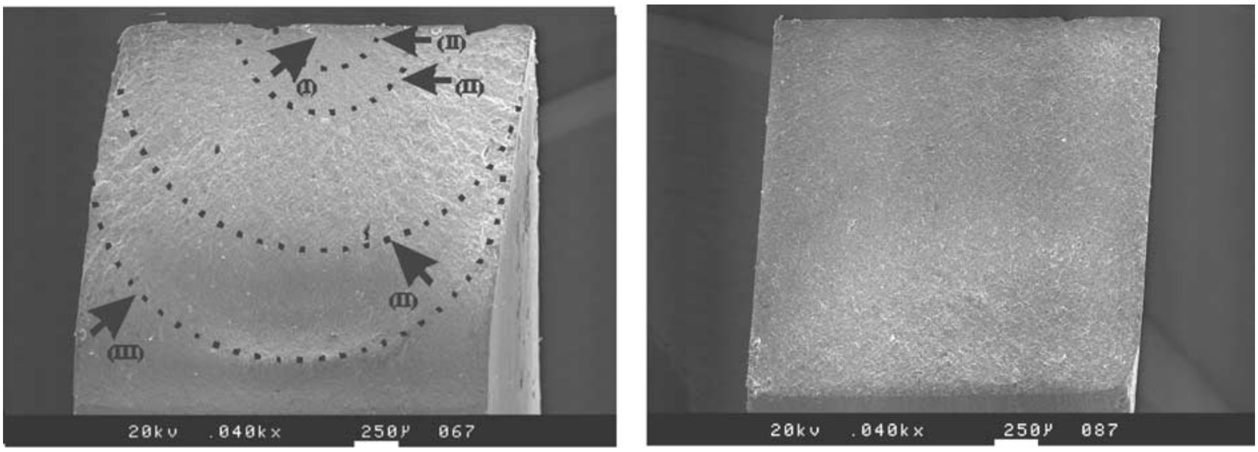

*Figure 5* Typical fractographic patterns of a FS (a) and FFL (b) fracture surface of the resin composite. The arrows indicate the initial fracture origin (I), the typical mist and hackle regions (II) and the lance mark (III) of a brittle failure mode.

A typical fracture surface of CO (Fig. 4(c)) exhibits the exposed filler particles due to an adhesive interfacial fracture mode. CO, as the material with the lowest filler content reveals a reduced long-time FS compared with RC and ILRC. Drummond [10] discussed an increase in fracture resistance for RC with a higher filler fraction. Around filler particles, higher localized polymerization stresses occurred and led to a reduced crack growth potential. Ferracane *et al.* [7] supported these findings for RC materials by measuring an increase in FS and EM in terms of higher filler volumes. A delayed glass–ionomer reaction was suggested for CO since a significant peak in FS and FFL was measured after 8 days in water. The ultrastructural and analytical evidence of the glass–ionomer reaction in CO was shown from Eliades *et al.* [21].

A macroscopic crack growth mechanism was found in ILRC. Fig. 4(b) shows a fracture surface after six months in water. In that material, macroscopic cracks nucleate and grow, driven by the ion-leaching process. Depending on the pH of the storage medium, $Ca^{2+}$, $OH^-$, and $F^-$ ions are leached out of the matrix network in order to prevent from secondary caries [15]. Light polymerization of the ILRC causes a stress gradient from the surface to the core of a specimen. The influence of polymerization stresses and ion-leaching might be responsible for a continuous degradation of FS and FFL over 180 days. The elastic modulus remained constant during that period which supports a linear-elastic crack growth mechanism [10].

The GIC differs from the resin-based materials since mechanical properties have been reported to increase with long-time water storage [17]. A post-hardening mechanism in GIC's and a high water uptake was explained from a change of loosely to firmly bound water caused by the ongoing acid–base reaction [20]. Fig. 4(d) exhibits a high inherent porosity on the fracture surface. This porosity might be incorporated in the GIC matrix during hand mixing and might account for a reduced strength level.

The results of this investigation substantially influence dental practice. The limitations for clinical indications especially in stress bearing areas differ within the materials. RC materials are less restricted since they exhibit a well suited mechanical performance. However, they suffer from expensive and technique-sensitive adhesive procedures. CO materials are partly limited in the posterior region in terms of extended restorations in stress-bearing areas. They also have to be adhesively bonded to tooth structures. Due to their reduced fracture strength, GIC's are mainly used in pediatric dentistry or as a temporary filling material. The promising development of mechanical properties over time is limited in dentistry due to an immediate occurrence of mastication stresses. The concept of pH-dependent ion-leaching resin composites failed in clinical practice and is now retracted from the market [22]. The long-time measurement of FS and FFL significantly degrade the mechanical resistance of the ion-leaching resin composite and might have previously helped to predict its clinical failure. This example clearly reveals the necessity of preclinical evaluation of time-dependent properties.

Cyclic flexural fatigue of the bulk material was investigated in this study. For a clinical successful material performance, the adhesion of the materials to sound tissue should be considered. Especially in adhesively bonded, resin-based materials, the fatigue of the interface to enamel and dentin might play an important role in preventing microleakage and secondary caries. It has to be mentioned that flexural bending experiments are limited for preclinical assessment since sample preparation is not influenced by a C-factor situation [23]. Setting stresses during polymerization shrinkage of resin-based materials have to be considered for reliable clinical predictions.

## 5. Conclusions

This study has shown that the tested physical properties differ considerably among dental materials. EM was found to behave constantly within the ILRC and CO materials. The RC showed decreasing, the GIC increasing elastic moduli over long-term storage in water. FS decreased for all resin-based materials since water adsorption leads to hydrolysis following material degradation. For the GIC, post-hardening due to a change of the adsorbed water from loosely to firmly bound structure was observed and the FS significantly increased over time. This post-hardening effect of the glass-ionomer phase was detected after 8 days in the CO, too. The fatigue behavior of ILRC, CO and GIC followed the initial FS development. However, cyclic fatigue remained constant in RC since different fracture mechanics of initial and dynamic testing were suggested to be responsible. The ILRC suffered from a pronounced decrease in FS as well as in FFL due to a constant ion-leaching followed by macroscopic crack growth. A slow crack growth mechanism was stated in the ILRC since over time the FS and FFL decreased, while the EM remained constant. Fractographic examination exhibited a resin–resin matrix cracking in RC compared with a resin–filler interface cracking in CO. A high porosity of hand mixed GIC's and was found to be responsible for the reduced strength level.

The results shown in this study point out the importance of preclinical assessment of direct filling materials not only in terms of short time strength measurement but in terms of time-dependent fatigue mechanisms.

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