

# Surface hardness change of restorative filling materials stored in saliva

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## Abstract

**Objectives:** This study was to investigate the effect of saliva used as storage liquid and the length of storage effect on surface hardnesses of Fuji IX<sub>GP</sub> (FIX), Dyract (DR), Z-100 and Estio LC (ELC).

**Methods:** The materials were mixed according to the manufacturers' instructions and immersed in distilled water or human parotid saliva. Vickers hardness number (HVN) was measured 1, 7, 20 and 40 days after the materials were mixed. HVN was calculated from the indentation diameter after 100 or 300 g loading on their surface for 15 s. The two methods of characterization used in this work were X-ray photoelectron spectroscopy (XPS) for surface chemical composition and electron probe microanalysis (EPMA) for depth profile analysis.

**Results:** Only in FIX, did HVN increase with time at both storage conditions, distilled water and saliva. The increase rate of the value was higher when stored in saliva than distilled water. After 40 days storage in saliva, the HVN value of FIX increased by 39%. The increase for storage in saliva for DR was 22%, ELC 16%, and Z100 3%, compared to 1 day storage in distilled water. Ca and P peaks caused by saliva were detected by XPS and EPMA analysis, but these peaks did not exist in either composite resin or polyacid-modified composite resin by EPMA analysis.

**Significance:** Saliva has the remarkable effect of increasing surface hardness of Fuji IX<sub>GP</sub>. © 2001 Academy of Dental Materials. Published by Elsevier Science Ltd. All rights reserved.

**Keywords:** Dental materials; Hardness; Saliva; Glass ionomer cement; X-ray photoelectron spectroscopy

## 1. Introduction

Restorative filling materials used in dentistry are required to have long-term durability in the oral cavity. This is a complex environment where the material is in contact with saliva, a fluid that contains a variety of inorganic and organic species, together with a bacterial flora complex. One of the most important physical properties of restorative filling material is surface hardness, which correlates well to compressive strength and abrasion resistance. Strength, setting behavior and wear of glass ionomers have been evaluated using hardness testing. To prevent specimen desiccation, water is most commonly the selected storage medium [1–3]. Tsuruta and Viohl [4] reported the influence of humidity on hardness of light-cured polyalkenoate cements stored in air. In their report, hardness of cements stored in dry conditions (36% RH at 37°C) increased with

time, but in high humidity (100% RH) and in water, no increase occurred. They concluded that the hardness of the cements corresponds to the humidity of the storage environment. Humidity alone, however, does not closely mimic the oral environment. Investigation of long-term surface hardness of tooth-colored restoratives stored in saliva is needed as an indicator of clinical behavior.

Saliva is composed of various chemical components, hormones, proteins enzyme and bacteria such as *Streptococcus mutans* and *Lactobacilli* [5]. Söderholm et al. [6] reported leaching of filler constituents from composites stored either in artificial saliva or distilled water. They concluded that the greatest effect of storage medium on composites was the increased leaching of filler constituents into artificial saliva. As for surface hardness, the effect of human saliva on tooth-colored restorative materials, including glass ionomer cement (GIC), composite resin and polyacid-modified composite resin has not been reported. Yao et al. [7] reported the effect of water isolation and early finishing on hardness of GICs with time. They measured the surface hardness of their sample, immersed in water for

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Table 1  
Materials used

Code	Materials	Classification	Batch. No.	Manufacturer
FIX	Fuji IX <sub>GP</sub>	Glass ionomer	190271	GC Corporation (Tokyo, Japan)
DR	Dyract	Polyacid-modified composite resin	950810	Dentsply (Konstanz, Germany)
Z100	Z100	Composite resin	5904	3M (St. Paul, MN, USA)
ELC	Estio LC	Composite resin	970224	GC Corporation (Tokyo, Japan)

periods ranging from 1 to 40 days. Hardness of all samples they had used reached a maximum value at 40 days. Investigation of the effects of human saliva and storage time in saliva on surface hardness is warranted to enhance understanding of clinical behavior.

In this study, we investigated the effect of the storage medium (saliva or water) and time on the surface hardness (Vickers Hardness Number, HVN) of GIC, composite resins and polyacid-modified composite resins. We also investigated the chemical composition of each material's surface after exposure to human saliva using X-ray photoelectron spectroscopy (XPS) and electron probe microanalysis (EPMA).

## 2. Materials and methods

The materials used in this study, including a conventional GIC, polyacid-modified composite resin and two dental composite resins, are shown in Table 1. Fuji IX<sub>GP</sub> (FIX) is a GIC for restorative filling, Dyract (DR) is a polyacid-modified composite resin, and both Estio LC (ELC) and Z100 are dental composite resins.

Twelve acrylic molds, each having an internal diameter of 6 mm and height of 1 mm were placed on flat glass plates on top of a plastic sheet. These molds were filled with the various materials and mixed in accordance with the manufacturers' directions for use. Excess material was pressed flush with the mold top and bottom using a glass plate with plastic sheet separating the glass plate from the specimen. No surface treatment or barrier was placed on the specimen. The prepared specimens were stored in a chamber at 37°C and 100% relative humidity for 1 h before removal of the plastic sheets from the specimen surfaces. Each specimen was immersed in either distilled water or in human saliva at 37°C.

Ben-Aryeh et al. [8] reported that no significant differences were found in salivary concentrations of sodium, potassium, calcium, magnesium and total protein between whole and parotid, resting and stimulated saliva. In this study, 10–12 ml human whole saliva stimulated by chewing-gum was pipetted at 10 o'clock in the morning from the same person, whose eating pattern was controlled for 1 day before saliva collection. This person normally has breakfast at 7 o'clock, eats rice at least 2 times a day, and

does not smoke tobacco. Saliva was changed once a week. Additionally, to investigate the influence of fresh saliva, using a separate group of specimens, saliva was changed daily for FIX only.

The HVN values were calculated from the indentation measurements observed through the diamond indenter point while loading. The hardness test was conducted under a load of 100 or 300 g, depending on the material. All loading times were 15 s. These conditions created indentation depths of 10–25 µm. In order to investigate change of surface hardness with time, the test was performed 1, 7, 20 and 40 days after the start of storage. Precipitate was observed with all the materials investigated and stored in saliva. Prior to hardness testing, each specimen was sonically cleaned for 10 min to remove any influence of precipitate on surface hardness. The mean hardness values and standard deviations were obtained from 12 indentations on six specimens for each condition. The average HVN values for each day for all materials were analyzed for significant differences using mostly one-way ANOVA to investigate the HVN difference between storage time or media.

The chemical composition of the surface was analyzed with XPS and also with EPMA for all materials. The XPS equipment used in this study was a Surface Science SSX-100 model. All spectra were obtained with the AlK $\alpha$  line. EPMA analyses were performed with a JEOL JED-2001 (JEOL DAJUM LTD Tokyo, Japan) by which we could also observe the microstructure of subsurface material. Additional details of the analysis parameters are given in connection with the presentation of results below.

## 3. Results

### 3.1. Vickers hardness number

Table 2 shows the HVN versus time of the four restorative filling materials. The HVN of a conventional GIC (FIX), which was also stored in saliva that was changed daily, showed values comparable to those where the saliva was changed once a week. There was no statistical difference ( $p > 0.01$ ), i.e. frequency of changing saliva in this experiment did not influence the HVN values. All materials showed higher values after storage in saliva compared to

Table 2  
The HVN mean values and changes by storage condition

Storage medium	Materials		1 day	7 days	20 days	40 days
Distilled water	Fuji IX <sub>GP</sub>	Hv	64.5	74.2	76.3	77.7
		Change (%) <sup>a</sup>	(0)	(+15)	(+18)	(+21)
	Dyract	Hv	39.9	38.6	41.1	42.7
		Change (%) <sup>a</sup>	(0)	(−3)	(+3)	(+7)
	Z100	Hv	105.1	102.0	99.8	102.9
		Change (%) <sup>a</sup>	(0)	(−3)	(−5)	(−2)
	Estio LC	Hv	63.5	60.8	62.7	62.7
		Change (%) <sup>a</sup>	(0)	(−4)	(−1)	(−1)
Saliva	Fuji IX <sub>GP</sub>	Hv	64.3	75.0	85.4	89.7
		Change (%) <sup>a</sup>	(0)	(+16)	(+32)	(+39)
	Fuji IX <sub>GP</sub>	Hv <sup>b</sup>	64.3	76.1	88.3	88.7
		Change (%) <sup>a</sup>	(0)	(+18)	(+37)	(+38)
	Dyract	Hv	44.1	40.3	48.9	48.8
		Change (%) <sup>a</sup>	(0)	(−10)	(+12)	(+11)
	Z100	Hv	109.4	107.0	108.2	108.0
		Change (%) <sup>a</sup>	(0)	(−2)	(−1)	(−1)
	Estio LC	Hv	67.3	67.9	72.3	73.5
		Change (%) <sup>a</sup>	(0)	(1)	(+8)	(+10)

<sup>a</sup> Hardness change percentage which based the data of 1-day storage in distilled water or saliva of each materials.

<sup>b</sup> Frequency of changing saliva is once a day.

storage in distilled water ( $p < 0.05$ ). The values for all materials after 1 day in saliva showed 8–10% hardness increase compared to distilled water except in the case of FIX which showed no increase ( $p < 0.05$ ). Only FIX showed an additional and continual increase between day 1 and day 40 after storage in saliva and distilled water

( $p > 0.05$ ). These results suggest that composite resin and polyacid-modified composite resin setting reactions are completed 1 day after light-curing.

In the case of FIX, hardness values after 1 week storage in saliva and storage in distilled water showed significant increase ( $p < 0.001$ ) and did not differ according to medium ( $p > 0.05$ ). After 20 days storage, hardness of the saliva-stored specimens increased beyond that of the water-stored specimens ( $p < 0.001$ ) and differences remained throughout this investigation ( $p > 0.05$ ). Hardness values of FIX increased with storage period and the increase was influenced by the storage medium (two-way ANOVA;  $p < 0.001$ ).

As for the absolute value of the HVN after saliva storage for 40 days, the composite resin (Z100) showed the highest value of all investigated materials. On the other hand, the greatest increase in surface hardness was observed at 40 days with FIX specimens as shown in Fig. 1(a) and (b). At 40 days storage in distilled water, the value of FIX increased 21%, DR increased 7%, Z100 increased −2% and ELC increased −1%. At 40 days storage in saliva, the value of FIX increased 39%, DR increased 11%, Z100 increased −1%, and ELC increased 10%.

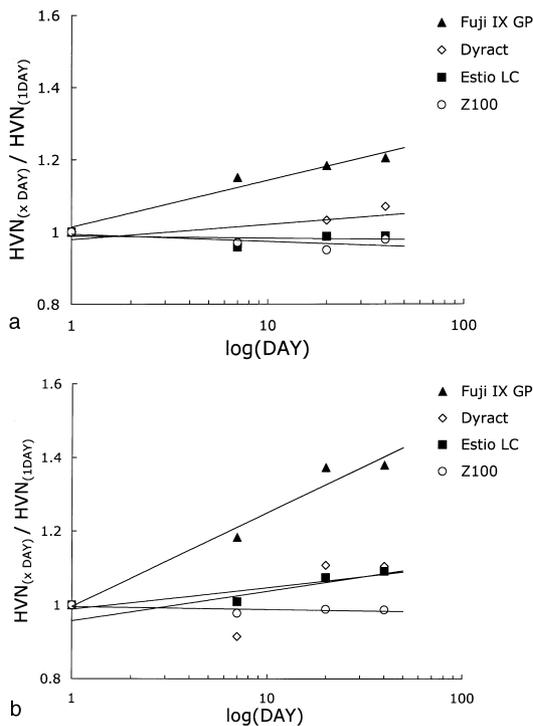


Fig. 1. (a) Hv increase with time for storage in distilled water. Calculated best fit lines for each material were plotted. (b) Hv increase with time for storage in saliva. Calculated best fit lines for each material were plotted.

### 3.2. Surface chemical composition by XPS (ESCA) analysis

An XPS survey spectrum was determined from the surface of restorative filling materials stored for 1, 7 and 40 days both in distilled water and saliva. With samples stored in distilled water, there were no additional chemical elements detected at 40 days' storage. Fig. 2 shows a 1 day storage sample in distilled water referred as a control and

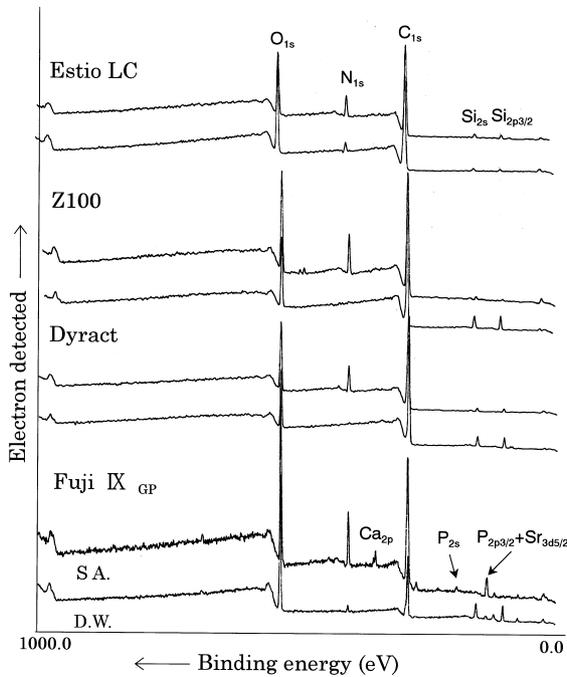


Fig. 2. XPS survey spectrum of restorative filling materials.

40 days storage sample in saliva of all materials. The averages of all binding energy measurements are reported in Table 3.

For FIX, the main spectrum detected in distilled water condition was Si2s, Si2p, Al2s, Al2p, C1s, O1s, P2p and Sr2p. The quantity of Sr3d<sub>5/2</sub> and P2p<sub>3/2</sub> (134.2 eV) elements were not distinguished because binding energy values are similar. The surface chemical composition of FIX samples stored 40 days in saliva was different from that of specimens stored in distilled water. FIX does not contain intrinsic calcium in the formulation. The Ca peak (347.1 eV) was observed only in the sample stored in saliva at 40 days. The P2p<sub>3/2</sub> peak increased with the lapse of time and showed an energy shift from 134.2 to 133.3 eV. These components can be related to the form of phosphate, that is, HPO<sub>4</sub><sup>2-</sup> to PO<sub>4</sub><sup>3-</sup> by considering the energy shift.

This suggests that Ca<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup> ions from saliva

adsorbed onto the surface of the cement, which contains the HPO<sub>4</sub><sup>2-</sup> ion. On the other hand, the peaks of Si and Al were decreased in the samples of 40 days storage and N1s peak appeared. Wilson et al. [9] reported, on the basis of adsorption and infrared spectroscopic studies, that the calcium ions of GIC are displaced from hydroxyapatite along with phosphate as part of a complex series of ionic exchanges. Saliva also contains these ions as complex components. Our findings are quite similar to those of Wilson. However, we could not confirm whether these components formed hydroxyapatite although some reference data showed similar binding energy [10,11].

For the other materials we investigated, (DR, Z100 and ELC), Ca and P peaks were not observed at all in the saliva-stored samples. Only N1s peak was detected on the sample stored in saliva as well as that of FIX.

### 3.3. Subsurface chemical composition by EPMA analysis

In order to investigate the subsurface, additional analysis using EPMA was conducted. Fig. 3 shows the chemical composition of the subsurface of all materials. EPMA analyses were compared for each material and each storage condition.

For the composite resin (ELC) and the polyacid-modified composite resin (DR), Si and Al were observed strongly, and for the composite resin (Z100), Si and Zr were observed. These subsurface spectra were no different between samples stored in distilled water and saliva. This suggests that any chemical elements from saliva did not affect the subsurface of the composite resin and the polyacid-modified composite resin. These materials' setting reactions were completed immediately after visible light activation, unlike GIC. It is likely that saliva components such as Ca and P could not react with the subsurface of these materials. The HVN increase of the material samples immersed in saliva for a day is not enhanced by Ca and P components from saliva.

For FIX, the spectrum dominated by the strong Si, Al, Sr and P peaks in the sample of stored in distilled water. In addition, Ca and K peaks were detected and the P peak

Table 3  
Average binding energy in eV per atom

	O1s	P2p	Si2p <sub>3/2</sub>	Al2p <sub>3/2</sub>	Ca2p <sub>3/2</sub>	N1s	Ref.
FIX 1 day DW <sup>a</sup>	531.7	134.2	102.0	74.6	–	–	This study
FIX 7 days DW	531.7	134.2	102.0	74.6	–	–	This study
FIX 40 days DW	531.7	134.2	102.0	74.6	–	–	This study
FIX 1 day SA <sup>b</sup>	531.7	134.2	102.0	–	–	399.8	This study
FIX 7 days SA	531.7	133.2	102.0	–	347.1	399.8	This study
FIX 40Days SA.	531.7	133.2	102.0	–	347.1	399.8	This study
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	531.5	133.2	–	–	347.4	–	[10]
AlPO <sub>4</sub> ·2H <sub>2</sub> O		134.8					[10]
Ca <sub>8</sub> H <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> ·5H <sub>2</sub> O	531.1	133.2			347.2		[11]

<sup>a</sup> DW = distilled water.

<sup>b</sup> SA = saliva.

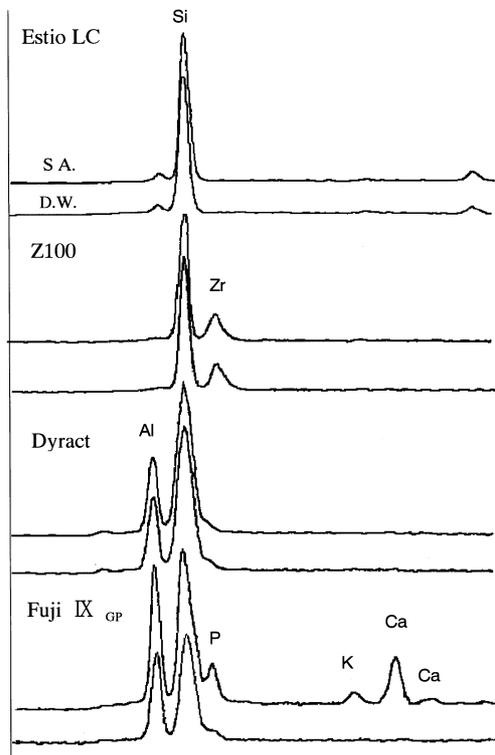


Fig. 3. Subsurface composition analyzed by EPMA.

increased in the sample stored in saliva. For Ca and P, almost the same trend was observed from that of XPS analysis. Potassium was detected only in this analysis. EPMA looked at the deeper point of the surface which was about 1–3  $\mu\text{m}$  depth. Thus, Si and Al in addition to Ca, P and K were observed even in the 40 day storage sample. It can be inferred from this data that Ca, K and P elements penetrated into the GIC matrix to a depth from the surface of a few  $\mu\text{m}$  at least.

#### 4. Discussion

In this study, we found that surface hardness of FIX after 40 days storage in saliva increased significantly. XPS and EPMA analysis revealed hardening was very probably the result of salivary components, including calcium and phosphate, diffusing into the cement structure. The effect of saliva improved the surface structure of FIX after immersion for more than 7 days. This outcome is predictable based on an understanding of FIX setting chemistry. The acid–base reaction and cross-linking of polymers of FIX reportedly continues for an extended time after initial setting under water. Set GICs have a very complex physical chemistry consisting of a glass core, silica gel and hydrogel matrix. This matrix consists of the cement-forming aluminum, strontium, fluoride and polyacrylate ions, which might be changeable and more active in the setting process.

Aqueous ions, e.g.  $\text{H}^+$  and  $\text{OH}^-$  ions can be mobile in the hydrogel matrix.  $\text{Ca}^{2+}$  and ions originated from  $\text{PO}_4^{3-}$  saliva also can diffuse into the matrix. Some metal ions diffused from glass core, that is,  $\text{Al}^{3+}$  and  $\text{Sr}^{2+}$  ions, have a coordination number of either six, seven or eight. This means that six to eight ligands have to be attached to these ions. The ligands could be  $\text{COO}^-$  in polyacrylate,  $\text{F}^-$  ion,  $\text{OH}^-$  ion and water molecules in this case. These ligands could be exchangeable with each other in an aqueous environment.

$\text{H}_2\text{O}$  ligand attached to aluminum and strontium ions in the hydrogel matrix could easily switch to the phosphorus ion originated from saliva. This connection might effectively strengthen the surface of the GIC matrix. Crisp et al. [12] investigated the long-term surface hardness of GIC. They found that the hardness was less than the dental silicate cement, which contains aluminum in the cement powder and phosphoric acid as a main constituent in aqueous liquid. This result might be explained mainly in terms of the degree of cross-linking or connectivity. The connectivity of the ionic aluminum phosphate matrix is high, both the aluminum and phosphorus atoms being four or six coordinates in the hydrogel matrix. Thus, it can be considered that some phosphate ion originated from saliva might connect with aluminum in some surface region of the matrix.  $\text{Ca}^{2+}$  ion, which exists in saliva and not in FIX, also would have a coordination number of six [13]. It might diffuse into the matrix and have the ligands which might be carboxylate groups of polyacrylic acid, phosphorus ion in saliva and water molecules. Our data indicates that these connections occurred at the subsurface region of GIC. A thin layer would result on the surface of the cement, which differs in chemical composition from the bulk of the cement. This thin layer may contain calcium phosphate, aluminum phosphate and polyacrylate salts. These compounds have high ionic bonding and low solubility against water including saliva. Many researchers [11,14] have reported that calcium and phosphorus ions have an important role in forming an intermediate layer that is attached to both the tooth surface and to GIC. Our data shows that saliva contributed to make the surface of GIC harden, very probably because of similar chemical interactions with ions from saliva.

To take osmotic pressure into consideration, acrylic polymers in the hydrogel matrix immersed in distilled water should absorb more water than those in saliva. Surface hardness is related to the amount of water taken up, the greater the uptake the weaker the resulting swollen hydrogel. Some papers have been published where resin-modified GICs were exposed to both water and ionic solution or saliva. Nicholson and co-workers [15,16] showed greater equilibrium water uptakes in pure water than in salt solution, results which were consistent with the above theory. In contrast, Kanchanasavita et al. [17] reported resin-modified GICs exhibited higher weight increase in artificial saliva than in distilled water. This might be caused

by the occurrence of changes in concentration of saliva as it passes through the cement. Kanchanasita et al. [18] also found resin-modified GICs showed less hardness when they were immersed in artificial saliva than in distilled water because the hydrophilic resin content absorbed a great amount of water. In their results, the amount of water uptake and the relation to surface hardness of resin-modified GICs has not yet been clarified. However, there is no doubt that excess water acts as a plasticizer in resin-based materials, including polyacid-modified composite resins. In our study, a conventional GIC, FIX, absorbed some inorganic ions and increased the surface hardness. The increase of surface hardness in saliva might not be explained only by the amount of water uptake.

Söderholm et al. [6] reported that filler leaching of composites was much higher in artificial saliva than in distilled water. We found that resin-modified GIC did not show the increase of surface hardness in saliva with time, but we did not show the data in this paper. Higher filler leaching of resin-modified GICs in saliva might be the cause of a minus effect on the surface hardness. In the case of FIX, the surface hardness increased even in distilled water after the initial setting stage. The removal of some metal cations from the surface stored in saliva could be less than in distilled water because of its absorption in the matrix of some inorganic ions. Thus, saliva has little apparent effect on the surface strength of resin-based materials, yet GIC's surface strength is apparently enhanced by exposure to saliva. In our study, surface hardness of the composite resin and the polyacid-modified composite resin showed slight increases after 1 day storage in saliva. XPS and EPMA analysis did not detect calcium or phosphorus ions on the surface layer. This result suggests that neither the composite resin nor the polyacid-modified composite resin reacted with  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$  ions from saliva as did GIC. Polyacid-modified composite resin seems to have a different matrix from GIC. Such a matrix would not absorb metal ions from saliva.

## 5. Conclusions

We investigated the changes with time of the HVN of FIX, ELC, DR and Z100 when stored in distilled water or saliva. For all materials, the HVN after storage in saliva for more than 1 day showed greater increase than that of distilled water, but this increase only continued beyond the first day, in the case of the GIC (FIX). For FIX, the HVN increased until 20 days storage for both storage mediums and also showed the biggest difference between media. By analyzing the surface using XPS and EPMA, it was clear that the components of saliva, *e.g.* calcium and phosphorus ions, were diffused into the hydrogel matrix and strengthened the surface.

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