The effect of saliva on surface hardness and water sorption of glass–ionomers and "compomers"

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A study is reported in which commercial dental materials (glass–ionomers, resin-modified glass–ionomer and polyacid-modified composite resins) in the form of discs of dimensions 6 mm diameter × 1 mm thickness were prepared and exposed to natural salivas (parotid and unstimulated whole), artificial saliva and water for up to 1 year. Surface hardness was measured at various time intervals, and water sorption characteristics were determined. For all types of material, storage in artificial saliva gave specimens of lowest surface hardness by amounts that were generally significant to $p < 0.05$, whereas no differences were found between specimens stored in water or either of the natural salivas. Water sorption characteristics were found to be unaffected by the nature of the storage medium. These results contrast with some previous findings and were not expected, given the known surface reactions between salivas and glass–ionomers, or the known enzymic degradation of composite resins. They demonstrate, however, that the current widespread practise of employing pure water for storage of specimens in laboratory studies is acceptable.

1. Introduction

In the course of their service life, dental restorative materials come into contact with saliva. This fluid is the most important of the natural defences against dental caries [1] and it is essential for a variety of physiological needs for the maintenance and protection of the dentition and soft tissues of the oral cavity [2, 3]. It is recognized to play a crucial role in the equilibrium between demineralization and remineralization of enamel in a potentially cariogenic oral environment [4]. Due to its large volume and continuous flow, saliva has a mechanical cleansing effect on the hard and soft tissues. Its protective function is augmented by its buffering capacity, the presence of calcium and phosphate, which play a role in the remineralization of teeth, and antimicrobial factors such as salivary lysozyme, lactoferrin, peroxidase system, sIgA, histatins, mucins and phagocytic leukocytes [5]. Other organic substances present include mucins, glycoproteins that lubricate the food and protect the oral mucosa, IgA which is the first immunologic defence against bacteria and viruses, lysozyme that attacks the walls of bacteria, lactoferrin that binds iron and is bacteriostatic, and proline rich proteins that protect enamel and bind toxic tannins [6].

Despite its importance, there have been only a few studies on the effect of saliva on dental restorative materials. There is some evidence that enzymes in saliva caused surface degradation on composite resins [7]. The behavior of glass–ionomer cements has been found to be different in water compared with saliva [8]. This study showed that contamination of glass–ionomer cements at 5 min with pure water had a greater softening effect than either natural saliva and artificial saliva. More recently, it has been reported that 40 days storage in human saliva caused surface hardening on conventional glass–ionomer with no significant effects observed on resin composite and resin-modified glass–ionomer cements [9].

The present *in vitro* study was designed to answer the question of whether the known interactions of saliva with modern tooth colored dental restorative materials (glass–ionomers, resin modified glass–ionomers and compomers) cause differences in their physical properties, in particular, their surface hardness and water sorption. Two different natural salivas (parotid and unstimulated whole saliva) and one artificial saliva were examined, and materials were exposed to them for various time intervals. Results were compared with results for the same materials stored in deionized water.

TABLE I List of materials used in the study

Material	Classification	Contents	Manufacturer
ChemFil Superior Shade: L(2)	Conventional glass–ionomer	Aluminum, sodium, calcium, fluoride, phosphorus, silicate and polyacrylic acid.	DeTrey Dentsply, De-Trey-Str.1 D-78467, Konstanz, Germany
ChemFlex Shade: A3	Conventional glass–ionomer	Strontium, aluminum, fluoride, silicate, tartaric acid, pigments and polyacrylic acid	DeTrey Dentsply, De-Trey-Str.1 D-78467, Konstanz, Germany
Dyract AP Shade: A3	Compomer	Polymerizable resins (methacrylates), TCB resin, strontium, fluoride, silicate, photoinitiators, stabilizers, cetylamine hydrofluoride and acetone.	DeTrey Dentsply De-Trey-Str.1 D-78467, Konstanz, Germany
F2000 Shade: A3	Compomer	Multidose syringe acrylate resin with methacrylates.	3M Dental Products, St. Paul, MN USA
Fuji II LC Shade: A3	Resin-modified glass–ionomer	Light-cured reinforced glass–ionomer restorative in capsules.	GC Corporation, Tokyo, Japan
Vitremer CoreBuildup/ Restorative Shade: A3	Resin-modified glass–ionomer	Powder: radiopaque fluoroaluminosilicate glass. Liquid: light sensitive, aqueous solution of a modified polyalkenoic acid.	3M Dental Products, St. Paul, MN USA

2. Materials and methods

The materials used were:

(i) two conventional glass–ionomers, ChemFlex and ChemFil Superior, both were prepared in accordance with manufacturer's instructions;

(ii) two resin-modified glass–ionomers Vitremer Core Buildup/Restorative and Fuji II LC (capsulated). These were also mixed in accordance with manufacturers' instructions, and cured as appropriate;

(iii) two polyacid-modified composite resins, F2000, supplied in single paste 4 g per syringe, and Dyract AP supplied in single paste capsule.

Full details of all these materials are given in Table I.

Following manufacturers' instructions for the manipulation/mixing of the materials, unset pastes were placed in six ring metal molds of 6 mm in diameter and 1 mm depth and cured. Polymerization for resin-modified glass–ionomers and polyacid-modified composite resins was achieved by using Prismetics® Lite II light-curing machine (DeTrey Dentsply, Konstanz, Germany) at 30 s exposure on each side. All specimens for each material were made from a single batch and preparation was done on the same occasion for each material. Six specimens from each material were randomly selected and stored in individual bottles containing 5 cm^3 of storage medium in the oven at 37 °C for the required time of storage.

The surface hardness test (Vickers Hardness Number) was performed at 1 day, 1 week, 1 month, 3 months, 4 months, 6 months and 1 year after start of immersion. A load of 100 g applied for 25 s (twice for each side) employing a Leitz Miniload 2 Micro Hardness Tester (Ernst Leitz Wetzlar GMB13 D-6330 Wetzlar 1-Germany) was carried out; and with the use of an optical microscope equipped with polarized light, the diamond indentations were measured to evaluate the surface hardness.

TABLE II Composition of artificial saliva (Nicholson and Wilson, 2000)

Reagent	Grade (Supplier)	Concentration, g/l
NaCl	AnalaR (BDH)	0.50
$NaCO_3$	ACS Reagent (Aldrich)	4.20
$NaNO_2$	SLR (Fisons)	0.03
KCl	AnalaR (BDH)	0.20

Details of the composition of the particular artificial saliva formulation used appear in Table II.

The storage media used for immersing the materials were: (i) unstimulated whole saliva (female donor), (ii) stimulated parotid saliva (male donor), (iii) artificial saliva (Table II), and (iv) water as control. The unstimulated whole saliva was collected from a female donor by spitting into a sterile vial between 9:00 in the morning and 12:30 in the afternoon after over an hour of the last food intake and brushing of teeth. The donor's diet was mainly rice, fish and cooked vegetables with no consumption of alcohol or acidic beverages. The regular fluid intake included still mineral water and tea. The donor of the stimulated parotid saliva was a male and collection was straight from the duct using a modified plastic cannula [10] between 10:00 and 11:00 in the morning at least two hours after the last meal. The stimulus was a combination of mastication and gustation using a base gum and citric acid. The donor's diet was not standardized, with alcohol and acidic beverages being consumed. Two different donors were used because this was more convenient than using a single donor, and increased the speed with which the appropriate salivas could be collected. In the case of the unstimulated whole saliva, the medium had to be changed on a weekly basis because of the presence of bacteria and possible food particles in the whole mouth volume.

2.1 Sorption/Solubility

The sorption test was intended to determine the water uptake of the materials considering the viscosity of unstimulated whole saliva compared to the other media. The specimens for sorption were determined using disc-shaped specimens of dimensions 4.0 mm in diameter and 1.0 mm in depth, which were prepared by using silicone rubber molds of the appropriate dimensions between glass microscope slides. Two specimens were made from every material for each combination of medium and time, and these were placed in 5 cm^3 of their respective solutions and weighed at regular intervals until they had equilibriated, after which they were dried to constant weight in the incubator at 37 °C. They were then re-exposed to the relevant storage medium in stoppered glass vials and weighed at hourly intervals for up to 8 h, after which they were weighed on a daily basis for up to 7 weeks until they reached equilibrium again. Weighing was performed with each specimen blotted dry using absorbent tissues; determination was made to the nearest 0.0001 g. After weighing, the specimens were returned to the storage medium and stored at 37 ± 0.5 °C between weighings. The formula used in obtaining water sorption/solubility was:

1. Net mass gain, 1st cycle:

Initial mass : Xg

After water uptake + drying, the new mass was $(X + \delta X)$g

$$\text{Mass gain} : \frac{\delta X}{X} \times 100\%$$

2. Equilibrium:

At equilibrium, new mass $(X + Y)$ g

$$\text{Water uptake} = \frac{Y}{X} \text{ g}$$

2.2 Statistical analysis

SigmaStat 5.25 software by SPSS Science (Software UK Ltd.) was employed in a one-way ANOVA followed by Student–Newman–Keuls method used for the statistical analysis of the results at $p < 0.05$ significance.

3. Results

Results for surface hardness of each of the materials at time periods of up to 1 year are given in Tables III–VIII. For all materials, similar trends were found, though the actual values of surface hardness varied slightly depending on the material type and brand. The pattern showed that there were no significant differences in values for different storage media at 1 day or 1 week, but by 1 year, specimens stored in artificial saliva had the lowest values, and specimens stored in water, parotid saliva and unstimulated whole saliva showed no significant differences. The low mean value in artificial saliva at 1 year was significant $(p < 0.05)$ for all materials except Dyract, where the difference was not statistically significant.

Water sorption data also varied between materials (Tables IX–XIV), but showed only slight variations

TABLE III Vickers hardness number for ChemFil Superior after various storage times (Standard deviation in parentheses)

Length of time	Unstimulated wholesaliva	Stimulated parotid saliva	Artificial saliva	Distilled water
1 day	85.5 (5.2)	77.8 (8.5)	73.9 (8.3)	78.7 (9.3)
1 week	89.9 (4.3)	80.6 (7.7)	62.6 (4.1)	74.1 (6.5)
1 month	89.2 (9.1)	91.3 (11.8)	89.2 (13.9)	92.4 (7.2)
3 months	93.8 (5.1)	82.0 (6.1)	67.2 (9.1)	80.1 (5.7)
4 months	96.8 (4.9)	89.6 (7.1)	53.7 (6.0)	85.1 (7.7)
6 months	109.9 (5.4)	107.7 (14.3)	104.6 (5.1)	109.1 (4.7)
1 year	104.2 (4.0)	104.6 (14.8)	71.0 (18.8)	107.0 (4.9)

TABLE IV Vickers hardness number for ChemFlex after various storage times (standard deviation in parentheses)

Length of time	Unstimulated whole saliva	Stimulated parotid saliva	Artificial saliva	Distilled water
1 day	52.8 (4.2)	51.3 (5.6)	44.4 (1.7)	49.2 (8.2)
1 week	67.3 (10.4)	72.2 (12.6)	53.4 (3.8)	60.5 (11.0)
1 month	84.1 (7.0)	75.8 (5.8)	53.0 (3.9)	77.9 (13.5)
3 months	65.9 (7.3)	63.3 (3.9)	51.8 (4.4)	70.1 (7.9)
4 months	66.7 (4.2)	66.9 (5.2)	51.8 (4.4)	66.0 (3.4)
6 months	85.3 (5.6)	74.7 (3.7)	74.0 (14.9)	89.3 (5.8)
1 year	99.9 (7.0)	101.5 (7.2)	69.8 (9.8)	100.3 (8.6)

TABLE V Vickers hardness number for Fuji II LC after various storage times (standard deviation in parentheses)

Length of time	Unstimulated whole saliva	Stimulated parotid saliva	Artificial saliva	Distilled water
1 day	49.8 (1.7)	45.2 (4.4)	43.8 (4.7)	43.9 (5.2)
1 week	50.3 (2.5)	47.0 (5.9)	31.5 (2.3)	46.3 (4.2)
1 month	49.5 (1.8)	35.5 (5.5)	31.8 (3.0)	44.0 (2.5)
3 months	49.6 (3.4)	50.2 (3.3)	31.6 (4.6)	52.3 (3.8)
4 months	49.7 (0.8)	50.0 (4.4)	27.9 (4.7)	51.7 (2.2)
6 months	71.1 (10.3)	76.0 (11.8)	40.6 (4.5)	71.2 (9.5)
1 year	69.9 (9.4)	72.2 (7.2)	48.1 (5.3)	68.9 (6.9)

TABLE VI Vickers hardness number for Vitremer after various storage times (standard deviation in parentheses)

Length of time	Unstimulated whole saliva	Stimulated parotid saliva	Artificial saliva	Distilled water
1 day	55.2 (2.5)	54.9 (2.6)	51.0 (2.2)	51.7 (1.0)
1 week	62.8 (4.3)	53.2 (1.3)	49.0 (2.4)	55.7 (5.7)
1 month	66.3 (9.1)	62.5 (9.7)	51.4 (4.6)	51.5 (4.1)
3 months	60.8 (7.3)	57.7 (5.7)	53.0 (4.5)	64.3 (7.6)
4 months	59.2 (7.5)	62.3 (8.5)	52.2 (5.8)	56.0 (4.5)
6 months	92.3 (8.9)	89.3 (7.7)	63.5 (15.6)	81.2 (4.2)
1 year	84.3 (5.6)	80.6 (15.8)	59.4 (12.3)	83.7 (18.9)

TABLE VII Vickers hardness number for Dyract AP after various storage times (standard deviation in parentheses)

Length of time	Unstimulated whole saliva	Stimulated parotid saliva	Artificial saliva	Distilled water
1 day	62.1 (3.9)	61.2 (5.6)	55.9 (2.5)	58.6 (3.4)
1 week	55.0 (3.9)	50.6 (1.6)	51.2 (3.0)	53.6 (2.4)
1 month	67.9 (7.1)	66.3 (4.7)	44.7 (1.0)	48.1 (2.2)
3 months	94.3 (12.9)	75.8 (6.1)	41.7 (2.7)	53.7 (2.2)
4 months	93.5 (8.5)	74.9 (6.9)	36.3 (3.3)	47.2 (4.0)
6 months	98.2 (7.9)	67.7 (17.3)	43.0 (3.8)	55.1 (2.8)
1 year	92.9 (5.7)	62.9 (5.7)	34.9 (4.0)	54.1 (4.9)

TABLE VIII Vickers hardness number for F2000 after various storage times (standard deviation in parentheses)

Length of time	Unstimulated whole saliva	Stimulated parotid saliva	Artificial saliva	Distilled water
1 day	109.1 (3.0)	108.7 (2.9)	107.7 (3.2)	110.1 (2.4)
1 week	109.1 (5.6)	107.6 (4.6)	101.1 (8.6)	102.3 (6.2)
1 month	99.2 (6.1)	105.4 (4.6)	66.8 (6.1)	72.5 (7.8)
3 months	115.4 (6.6)	96.3 (15.1)	79.2 (6.3)	82.0 (7.4)
4 months	116.3 (6.9)	84.0 (17.5)	68.2 (8.2)	88.2 (9.9)
6 months	114.1 (1.6)	85.8 (4.1)	84.7 (6.9)	90.8 (5.8)
1 year	111.2 (2.0)	106.2 (16.0)	84.3 (8.8)	109.2 (6.9)

TABLE IX The sorption characteristics of ChemFil Superior

Storage medium	Net mass gain	Equilibrium water uptake
0.9% NaCl (saline)	1.07%	3.47%
Distilled water	0.47%	3.32%
Artificial saliva	0.59%	3.69%
Parotid saliva	0.72%	4.20%
Unstimulated whole saliva	0.44%	3.30%

TABLE X The sorption characteristics of ChemFlex

Storage media	Net mass gain	Equilibrium water uptake
0.9% NaCl (saline)	0.30%	4.87%
Distilled water	0.39%	4.71%
Artificial saliva	0.12%	4.55%
Parotid saliva	0.19%	5.06%
Unstimulated whole saliva	0.50%	5.46%

TABLE XI The sorption characteristics of Fuji II LC

Storage media	Net mass gain	Equilibrium water uptake
0.9% NaCl (saline)	0.00%	3.83%
Distilled water	0.17%	4.21%
Artificial saliva	0.23%	4.31%
Parotid saliva	0.35%	4.36%
Unstimulated whole saliva	0.24%	4.38%

TABLE XII The sorption characteristics of Vitremer

Storage media	Net mass gain	Equilibrium water uptake
0.9% NaCl (saline)	0.52%	5.09%
Distilled water	0.43%	4.55%
Artificial saliva	0.57%	5.38%
Parotid saliva	0.62%	5.36%
Unstimulated whole saliva	0.49%	4.64%

between storage media for any material. This included the artificial saliva, in which both measures of water uptake did not vary significantly from other storage media, despite other differences noted in surface hardness.

TABLE XIII The sorption characteristics of Dyract

Storage media	Net mass gain	Equilibrium water uptake
0.9% NaCl (saline)	0.45%	0.85%
Distilled water	0.54%	0.85%
Artificial saliva	0.45%	0.81%
Parotid saliva	0.50%	0.95%
Unstimulated whole saliva	0.48%	0.91%

TABLE XIV The sorption characteristics of F2000

Storage media	Net mass gain	Equilibrium water uptake
0.9% NaCl (saline)	0.69%	1.29%
Distilled water	0.68%	1.27%
Artificial saliva	0.70%	1.24%
Parotid saliva	0.61%	1.27%
Unstimulated whole saliva	0.72%	1.45%

4. Discussion

Neither parotid saliva as a storage medium nor compomers as materials immersed in human saliva have been studied previously. However, glass–ionomer cements have been studied for their interaction with stimulated whole saliva [9]. It was found that the surface chemical composition of the glass–ionomer was altered by this storage in stimulated whole saliva after 40 days. Most significantly, calcium was detected in the surface, though the cement had not originally contained any of this element. This change in surface composition was associated with significant increases in surface hardness with time compared with specimens stored in water. The authors concluded that the calcium and phosphate contents of the saliva were responsible for the hardening effect on the glass–ionomer surface because they did not find the same thing happening with composite resins or resin-modified glass–ionomer cements.

Our findings show some contrast with these, in that no differences in surface hardness were found between specimens stored in either of the natural salivas and water. This was despite similar amounts of material and storage medium being used, and does not imply that there were no similar interactions to those observed previously [9]; merely that for these materials, any such surface reactions do not lead to differences in hardness. Our results were similar to the previous ones in that glass–ionomer and resin-modified glass–ionomer specimens did show a gradual increase in hardness over time, and this was generally significant to at least $p < 0.05$. However, specimens stored in water also showed this change, which implies that for these materials, the increase is due to the maturation processes taking place throughout the material, rather than to changes in the surface.

The compomers Dyract AP and F2000 showed no significant changes in surface hardness in any storage medium with time, despite the capability of some neutralization occurring as these materials mature in aqueous media [12]. Our results confirm previous findings, since surface hardness of the compomer Dyract AP and also of the resin-modified glass–ionomer Vitremer

have been shown to remain essentially unchanged with time, at least over short storage periods [11].

Enzymes in saliva have been shown to cause surface degradation on composite resins [7]. Since compomers are mainly composite resin materials [12, 13], a similar result might have been expected here. Instead, the current results showed that specimens from the two compomers stored in unstimulated whole saliva showed no evidence of surface degradation. In fact, they exhibited the highest values from one month onwards compared with specimens stored in water and artificial saliva, which suggests that there is no evidence for degradation in this medium.

Water sorption was shown to be consistent for each material regardless of the nature of the aqueous storage medium. This is contrast with the previous findings of Kanchanavasita *et al*. [14], who reported that in their particular artificial saliva, neither Fuji II LC and Vitremer had equilibrated after nine months. They suggested that the breakdown of the cement structures and the clustering of water in the cement matrix or possibly uptake of species from the artificial saliva might have caused this. This highlights a problem discussed previously in the literature [15], that there is a wide variation in compositions of artificial salivas reported in the literature, and their effects on materials may vary widely. This becomes an even more pressing problem with materials possessing even slight hydrogel character, as with resin-modified glass–ionomers [16], because their water uptake is strongly influenced by the chemical composition of the storage medium. In the light of this, it was surprisingly that there were no significant differences between the natural salivas and pure water.

Differences have been found in other studies in both the surface reaction of glass–ionomers with saliva [9] and in water uptake from solutions of differing ionic strength [14, 16, 17]. These differences between pure water and saliva imply that differences were to be expected in ultimate surface composition and other properties of the materials in our experiments. Yet, despite this, no differences could be detected in surface hardness or water sorption properties. Whatever the origin of these similarities, it is clear that water is an acceptable storage medium for these materials for laboratory studies. However, whether this would prove to be the case of all materials of the types we have studied is not clear. Further work is clearly necessary to understand how modern restorative materials interact with natural saliva, and to determine whether these interactions are capable of causing significant alterations in the mechanical and other properties of these materials.

5. Conclusions

The present study has shown that glass–ionomer, resin-modified glass–ionomer and compomer specimens behave in broadly the same way in water, unstimulated whole saliva and parotid saliva in terms of surface hardness and sorption. This suggests that water is probably an acceptable medium for storing specimens of dental restorative materials in laboratory investigations, as recommended in current ISO Standards. By contrast, the particular artificial saliva used was shown to be a poor storage medium since it caused specimens to behave differently from the natural salivas at some time intervals.

The similarity of the results in natural salivas and water were unexpected, given the complexity of the possible interactions of these materials with the salivas. These interactions include water uptake and dissolution, protein deposition and ion deposition in the surface, all of which might have led to alterations in the mechanical and other properties of the materials. However, under the conditions of our experiments, they did not. It should be noted that surface hardness was the only mechanical property considered in the current study, and it is not possible to predict on the basis of these results whether results for other mechanical properties (e.g. flexural strength or fracture toughness) might be similar.

Despite the variations in composition, natural salivas did not show significant differences in sorption and solubility for the materials compared with pure water. For glass–ionomers, there was a net gain mass from the first cycle after storing the materials in salivas and water, which proved that there was additional water taken up from the surroundings which readily became incorporated into the ‘‘bound water’’ fraction.

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