

Changes in surface hardness of conventional restorative glass ionomer cements

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Abstract

The effect of a contact with an aqueous solution on the surface hardness of glass ionomers has been investigated in a few studies and for a limited number of formulations. As there is no information on the long-term changes of the surface hardness in this respect, the aim of this study was to determine these long-term changes in 10 conventionally setting glass ionomer formulations after storage in water as compared to maturation in a humid atmosphere (85% RH).

After setting for 15 min different series of glass ionomer specimens were stored at 37°C in both experimental media for 1, 7, 28 and 140 days. At the end of the specific maturation times, the mean surface hardness was determined on the basis of Knoop Hardness (KHN). Data were analyzed using ANOVA.

In a humid atmosphere the surface hardness generally increases rapidly initially, followed after 1 day by a more gradual increase. In contact with water, the hardness also increases up to one day but not to the same extent. The surface hardness then remains constant or slightly decreases. Evidence of a detrimental softening of the surface ascribed previously to the loss of matrix forming ions was not found. A surface erosion is not likely to occur. © 1998 Published by Elsevier Science Ltd. All rights reserved

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1. Introduction

The popularity of glass ionomer cements in restorative dentistry arises mainly from their behaviour as adhesive bioactive materials with therapeutic action [1]. They set by an acid–base reaction between a degradable glass and a homo- or copolymer of acrylic acid [2–5]. Although the physical properties of glass ionomers vary depending on the specific chemical and physical formulation [6–11], their use is generally restricted to specific indications and restorations such as Class III and V lesions [1]. These limitations are due to the fact that glass ionomer cements are brittle materials with a relatively low physical strength and wear resistance [6–12].

On the other hand, the physical properties of glass ionomers change with time [11–18]. This phenomenon could be correlated to a slow long-term continuation of the acid–base setting reaction [3–5, 19] and could indicate that early time properties are not well suited for a long-term prognosis [14]. In this respect a remarkable increase in wear resistance was observed over a period of one year for conventional glass ionomer cements [12]. Such increasing wear stability could be associated at least partly to the observation that the surface hardness tends to increase with time for glass ionomers setting in a humid atmosphere [13, 20–25]. On the other hand, due to the prolonged setting reaction, hydration of conventional glass ionomers by a contact with an aqueous solution after the initial setting, has been reported to affect their surface hardness [20, 21, 24, 25]. However, the few investigations of this effect on the surface hardness as a function of time are restricted to only a few glass ionomer formulations and the results are not consistent.

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Table 1
Glass ionomer formulations used in the present study

Product	Powder	Liquid	P/L	Batch No.
Fuji II (hand-mixed)	CAFS-glass + PAA	PAA + TA + water	2.7:1	P: 911212 A L: 911017 A
Fuji Cap II (capsule)	CAFS-glass + PAA	PAA + TA + water	2.8:1	Cap: 220411
Miracle Mix (hand-mixed)	CAFS-glass + PAA + AA-powder	PAA + A + water	5.9:1	P: 270121 L: 280121 AA: 071891
Chemfil II (hand-mixed)	CAFS-glass + PAA + TA	Water	6.8:1	P: 880522 L: water
Chemfil Cap II (capsule)	CAFS-glass + PAA + TA	PAA + water	3.3:1	Cap: 900129
Chelon-Fil (hand-mixed)	CAFS-glass (Ca:Na:F:P:Al:Si = 11:2:13:2:16:56)	PAMA + TA + water	3.2:1	P: W008 L: V274
Ketac-Fil (capsule)		PAMA + TA + water	2.95:1	Cap: W029
Chelon-Silver (hand-mixed)	CAFS-glass	PAMA + TA + water	3.2:1	P: V274 L: V274
Ketac-Silver (capsule)	(Ca:Na:F:Al:Si = 11:2:13:2:16:56) + sintered Ag (0.92:1)	PAMA + TA + water	3.72:1	Cap: W085
Shofu II (hand-mixed)	CAFS-glass	PACA + TA + water	2.5:0.8	P: 068807 L: 768808

CAFS-glass: Calcium aluminofluoro silicate glass; PAA: Poly(acrylic acid); TA: Tartaric acid; AA: Amalgam alloy; PAMA: Copolymer of acrylic and maleic acid; PACA: Copolymer of acrylic and tricarboxylic acid.

Moreover, no information is available on the long-term changes in surface hardness when storing glass ionomers in aqueous solutions.

In view of the time-dependent changes in physical properties, the purpose of this study was to investigate the long-term changes of the surface hardness of conventional restorative glass ionomer cements with a different chemical and physical formulation and to evaluate the effect of a prolonged storage in water.

2. Materials and methods

2.1. Materials and specimen preparation

The restorative glass ionomer cements used in the present study are Fuji II, Fuji Cap II and Miracle Mix (GC Dental Corp., Tokyo, Japan); Chemfil II and Chemfil Cap II (De Trey Dentsply, Konstanz, Germany); Chelon-Fil, Ketac-Fil, Chelon-Silver and Ketac-Silver (ESPE, Seefeld/Oberbayern, Germany); and Shofu II (Shofu, Kyoto, Japan). The composition as provided by the manufacturer, batch numbers and mixing procedure are summarized in Table 1. The glass ionomers supplied in a powder/liquid type requiring hand-mixing were mixed and handled according to the prescriptions of the manufacturer (filling consistency). The glass ionomers in capsules, requiring mechanical mixing, were mixed by the use of a Silamat (Vivadent, Schaan, Liechtenstein) for 10 s.

For each glass ionomer formulation 9 series of five cylindrical specimens (6 mm in diameter and 3 mm thick)

were made at different times using a fresh mix for each sample. The cement paste was then transferred or injected (capsules) into a split stainless-steel mold. After being filled, the mold was closed (separation with celluloid strips), excess of material removed and the material was allowed to set under pressure at room temperature for 15 min. Previous studies [22] have shown that the 15 min time interval before contact with the storage medium appears to be clinically relevant.

After setting for 15 min one series was immediately submitted to microhardness measurement. Four other series were stored at 37°C in a humid atmosphere (85% relative humidity) for 1, 7, 28 and 140 days, respectively. The samples of the remaining four series were individually stored for 1, 7, 28 and 140 days, respectively, in polyethylene flasks containing 25 ml double-deionized water (Milli-Q System, Millipore, Bedford, MA, USA), which were shaken in a water bath at $37.0 \pm 0.1^\circ\text{C}$. The water was regularly renewed at specific times according to the scheme used in a previous study of the fluoride release profiles of conventional glass ionomer cements [26].

2.2. Microhardness measurements

At the end of the specified storage times, the surface hardness of the glass ionomer samples was determined on the basis of Knoop hardness. The microhardness measurements were performed with a Shimadzu microhardness tester (HMV-2000, Shimadzu Corporation, Kyoto, Japan) at room temperature (23°C). For each sample the Knoop hardness number (KHN) was

determined on the basis of at least five indentation measurements on the flat surface of the specimen.

The indentations were made with a 50 g load applied for 5 s. Under these conditions sharply defined indentation marks were obtained with a size allowing the determination of the surface hardness of all tested materials with a sufficient accuracy. The application of higher loads or a longer contact time invariably initiated cracks in the surface of the materials.

2.3. Statistical evaluation

Surface hardness data were evaluated for significant differences related to formulation and/or time at a given storage condition using a one-way or two-way ANOVA where appropriate. The Newman–Keuls method ($P = 0.05$) was used for multiple comparisons of the means. For a given formulation significant differences in the surface hardness related to the storage medium were determined at a specific storage time using a *t*-test.

3. Results

The mean Knoop hardness values (KHN) and the corresponding 95% confidence interval are represented in Figs. 1–5 as a function of the glass ionomer formulation, the storage time and the medium. In a humid atmosphere as well as in water, the surface hardness depends on the glass ionomer formulation and the time ($P < 0.001$). Moreover, there is a significant interaction ($P < 0.001$) between the effect of formulation and time indicating that the differences in surface hardness among the glass ionomer formulations change with time.

A comparison of Figs. 1–5 shows that the surface hardness increases drastically after 1 day in a humid atmosphere. This initial surge is followed by a less

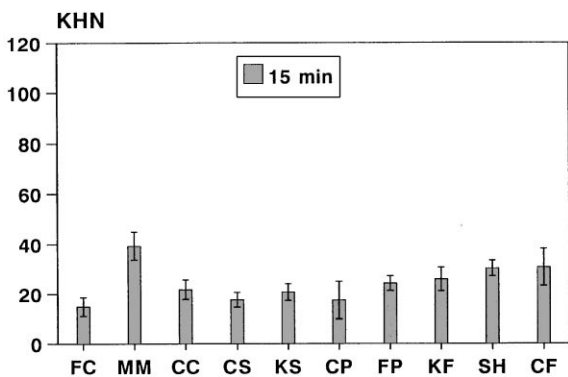


Fig. 1. Mean and corresponding 95% confidence interval of the Knoop hardness number (KHN) of glass ionomer cements after an initial setting of 15 min: Fuji Cap II (FC), Miracle Mix (MM), Chemfil Cap II (CC), Chelon-Silver (CS), Ketac-Silver (KS), Chemfil II (CP), Fuji II (FP), Ketac-Fil (KF), Shofu II (SH) and Chelon-Fil (CF).

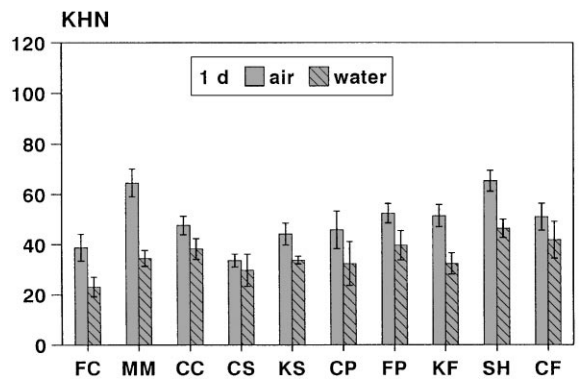


Fig. 2. Mean and corresponding 95% confidence interval of the Knoop hardness number (KHN) for glass ionomer cements stored for 1 day in a humid atmosphere (air) or in water after an initial setting of 15 min: Fuji Cap II (FC), Miracle Mix (MM), Chemfil Cap II (CC), Chelon-Silver (CS), Ketac-Silver (KS), Chemfil II (CP), Fuji II (FP), Ketac-Fil (KF), Shofu II (SH) and Chelon-Fil (CF).

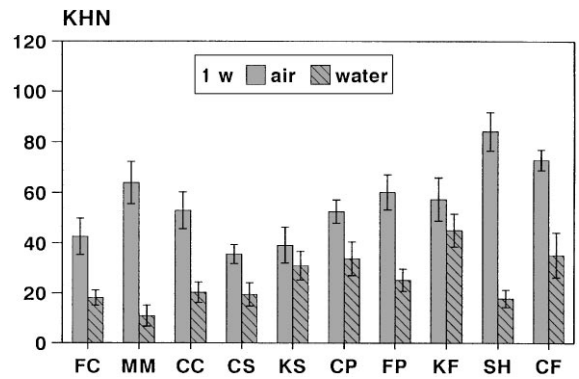


Fig. 3. Mean and corresponding 95% confidence interval of the Knoop hardness number (KHN) for glass ionomer cements stored for 1 week in a humid atmosphere (air) or in water after an initial setting of 15 min: Fuji Cap II (FC), Miracle Mix (MM), Chemfil Cap II (CC), Chelon-Silver (CS), Ketac-Silver (KS), Chemfil II (CP), Fuji II (FP), Ketac-Fil (KF), Shofu II (SH) and Chelon-Fil (CF).

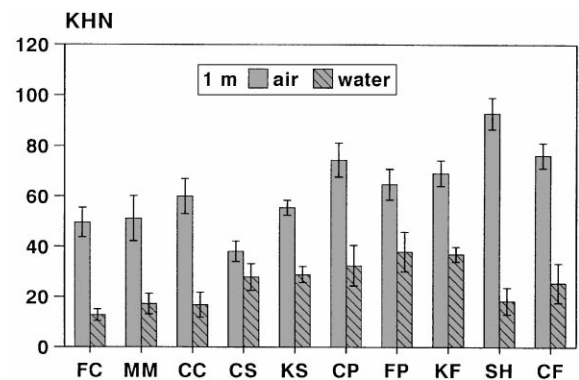


Fig. 4. Mean and corresponding 95% confidence interval of the Knoop hardness number (KHN) for glass ionomer cements stored for 1 month in a humid atmosphere (air) or in water after an initial setting of 15 min: Fuji Cap II (FC), Miracle Mix (MM), Chemfil Cap II (CC), Chelon-Silver (CS), Ketac-Silver (KS), Chemfil II (CP), Fuji II (FP), Ketac-Fil (KF), Shofu II (SH) and Chelon-Fil (CF).

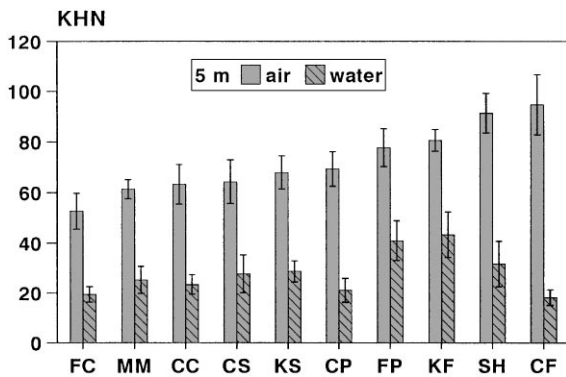


Fig. 5. Mean and corresponding 95% confidence interval of the Knoop hardness number (KHN) for glass ionomer cements stored for 5 months in a humid atmosphere (air) or in water after an initial setting of 15 min: Fuji Cap II (FC), Miracle Mix (MM), Chemfil Cap II (CC), Chelon-Silver (CS), Ketac-Silver (KS), Chemfil II (CP), Fuji II (FP), Ketac-Fil (KF), Shofu II (SH) and Chelon-Fil (CF).

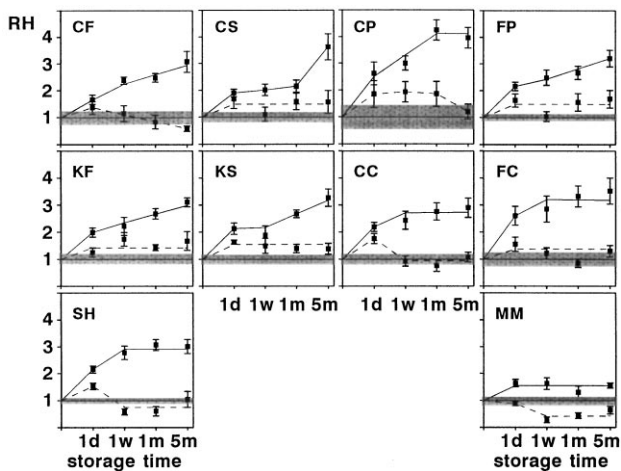


Fig. 6. Mean and corresponding 95% confidence level of the relative Knoop hardness number (RH) with respect to the KHN after an initial setting of 15 min as a function of the time stored in a humid atmosphere (—) and in water (---). The shaded areas give the respective 95% confidence interval for the KHN at 15 min for Fuji II (FP), Miracle Mix (MM), Chemfil II (CP), Chelon-Fil (CF), Chelon-Silver (CS), Shofu II (SH), Fuji Cap II (FC), Chemfil Cap II (CC), Ketac-Fil (KF) and Ketac-Silver (KS).

pronounced, but gradual increase of the KHN for Chelon-Fil, Ketac-Fil, Chelon-Silver, Ketac-Silver and Fuji II. However, for Chemfil II, Chemfil Cap II, Fuji Cap II and Shofu II the surface hardness tends to a constant level which is generally reached after 1 week. These changes of the surface hardness with time are more clearly illustrated in Fig. 6. This figure gives the relative KHN with respect to the surface hardness after an initial setting of 15 min. The lines in Fig. 6 are merely drawn for illustrating the observed trends. The indicated error bars correspond to a confidence level of 95% and were calculated with error propagation theory. The shaded

area represents the 95% confidence interval of the relative KHN at 15 min.

When stored in water for 1 day, the surface hardness of the glass ionomers generally increases with the exception of Chelon-Fil, Chelon-Silver and Miracle-Mix for which the KHN remains constant after an initial setting of 15 min (see Figs. 1, 2 and 6). However, this initial increase of the surface hardness is, in general, significantly smaller ($P \leq 0.01$) compared to that observed in a humid atmosphere after 1 day. A prolonged contact with water (> 1 d) apparently has no further influence on the KHN of Chelon-Silver, Ketac-Fil, Ketac-Silver, Fuji II and Fuji Cap II. These glass ionomer formulations retain the surface hardness reached after 1 day for up to 5 months in contact with water (see Fig. 6). For the other glass ionomer formulations investigated, however, a contact with water for more than 1 day results in a decrease of the KHN. Whereas the surface hardness of Chelon-Fil slightly, but gradually decreases with time, the KHN of Miracle Mix, Shofu II and Chemfil Cap II reaches a constant value after 1 week.

The effect of the contact with water on the surface hardness of Chemfil II is comparable to that for Chemfil Cap II with the exception that the decrease of the KHN is delayed for 1 month (see Fig. 6). When the hand-mixed and capsulated versions of the other glass ionomer formulations are compared, there appeared only a systematic difference with time between the surface hardness of Fuji II and Fuji Cap II (see Figs. 1–5). After an initial setting of 15 min, the surface hardness of the hand-mixed Fuji II is always significantly greater than that of the capsulated Fuji Cap II independent of the storage medium.

4. Discussion

Some investigators have determined the surface hardness of some specific glass ionomer cements with a Vickers indenter [23, 27]. Although a direct comparison with the values found in this study is rather difficult, the hardness numbers generally are in the same range. Brackett and Johnston [22] report a KHN of 42.2, 54.1, 51.0 and 62.7, respectively, for Chemfil II, Ketac-Fil, Fuji II and Shofu II stored for 1 day in a humid atmosphere which agree with the values 45.8, 51.5, 52.4 and 65.3 found in this study.

The setting reaction of a conventional glass ionomer cement is the result of an acid–base reaction between a polyacid liquid and a glass powder [1]. Although an initial setting occurs rapidly, the reaction apparently continues for a long time. This is reflected in the variation of the mechanical properties with time. Glass ionomers gain most of their mechanical strength during the first 24 h of setting, but change in strength as they age over periods of several weeks and months [13–16, 18, 28]. This

study corroborates the results of some short-term investigations [20, 23, 24] and demonstrates in a more general, but distinct way that a long-term ageing effect also occurs for the surface hardness of glass ionomers when matured in a humid atmosphere. Ageing of conventional glass ionomer cements in a humid atmosphere for 5 months after an initial setting of 15 min results in an increase of the KHN by a factor 3–4 (see Fig. 6). However, subtle but distinct time-dependent differences in the KHN are observed (see Figs. 1–5) which can be attributed to differences in the chemical and physical formulation among the different glass ionomers.

Most remarkable in this respect is the effect of metal reinforcement on the surface hardness. The mean KHN of Ketac-Silver and Chelon-Silver (Figs. 1–5) are in general significantly lower than those of the non-reinforced parents Ketac-Fil and Chelon-Fil corroborating the results of other investigators [21, 27]. Despite the metal reinforcement, both Ketac-Silver and Chelon-Silver have a comparable or even a lower surface hardness than conventional glass ionomers on both the short-term and long-term. This indicates that the polysalt matrix formed with these formulations apparently is weaker compared to the non-reinforced formulations Ketac-Fil and Chelon-Fil. Most probably the reduced contact area between the glass and the polyalkenoic acid solution caused by the sintering of particulate silver to the surface of the glass particles results in a less effective degradation of the glass and hence in a less developed polysalt matrix [26, 29].

The amalgam alloy reinforced Miracle Mix is based on the powder and liquid formulation of Fuji II. This metal-reinforced glass ionomer develops a maximum surface hardness after 1 day which then remains unchanged for 5 months (see Fig. 6). The surface hardness of Fuji II, however, is considerably lower initially (Figs. 1 and 2) but gradually increases over a period of 5 months so that it becomes greater than that of Miracle Mix (Fig. 5). As the glass/polyalkenoic acid ratio is lower for Miracle Mix, this behaviour most probably is mainly the result of the indentation of the large amalgam alloy particles and not of differences in the polysalt matrix formation.

The beneficial effect of encapsulation for powder/liquid proportioning and mixing apparently is not reflected in the development of the surface hardness. Increasing the mixing efficiency by encapsulation could be expected to increase the reaction and setting rate and hence to result in a faster increase of the surface hardness with time and possibly in a higher KHN for the encapsulated systems. Only for the Fuji II formulations the surface hardness significantly differs for the hand-mixed and encapsulated versions, the latter having systematically a lower surface hardness. As the qualitative composition of the powder and liquid is the same for both versions according to the manufacturer, such a difference can only be explained by the design of the capsule. In fact,

Fuji Cap II is the only system where the cement mix is ejected through the acid pellicle. Apparently, this has a profound effect on the properties of the cement [16, 26].

Surface hardness is one of the factors that is associated with the wear stability of a material. In this respect, the increase of the surface hardness with time correlates well with the increasing wear stability of conventional glass ionomer cements with time as observed by de Gee et al. [12] and Soltész and Leupolz [30]. On the other hand, some studies [21, 24, 25] report a softening of the surface with time when a glass ionomer cement is stored in an aqueous solution. Figure 6 demonstrates that in water a surface softening generally occurs after an initial setting of 15 min. This has been ascribed to a loss of matrix-forming ions when the cement comes into contact with an aqueous solution before it has fully hardened [1]. These ions result from the degradation of the glass particles by the aqueous polyalkenoic acid solution and react with the carboxylate groups to form a rigid polyalkenoate network. It was assumed that as long as these matrix forming ions are not bound, they are relatively free to move and can be leached out of the material resulting in a weaker cement with a softer surface. The latter would cause a decreased wear resistance.

According to Fig. 6 the surface hardness increases when the glass ionomers are stored in water for 1 day after an initial setting of 15 min. This indicates that the polysalt formation in the surface layer and hence the setting reaction continues even in contact with water. On the other hand, the fact that the KHN is generally lower compared to that obtained in a humid atmosphere suggests that the setting caused by the polyalkenoate formation occurs to a lesser extent due to some loss of matrix forming ions. Further storage in water either has no effect or results in a slight decrease of the surface hardness compared with the value reached after an initial set of 15 min. The reason for these opposite trends is not clear. A gradual softening of the surface with time could be explained by a hydrolytic breakdown of the polyalkenoate matrix at the surface, i.e. a surface erosion, when the cement is stored for a long time in water. In this respect, some authors [14, 15] argue that glass ionomers based on acrylic/maleic acid copolymers have an increased tendency for hydrolysis of the polyalkenoate matrix compared to those based on acrylic acid homopolymers. However, such distinction is not seen from Fig. 6. Moreover, recent studies [16, 18, 26] demonstrate that a hydrolysis of the polyalkenoate matrix during ageing in water for several months is not likely to occur.

A more probable explanation of the surface softening in water with time might be that the post-hardening reaction which is thought to be responsible for the long-term maturation and changes in physical properties is reduced or even hampered by the contact with water. Originally, it was proposed that this post-hardening

reaction was caused by additional cross-linking and hydration of the metal–polyalkenoate bonds [1]. More recently, evidence has been presented that the post-hardening reaction is more likely a secondary setting reaction caused by the formation of a silica gel matrix within the polyalkenoate network [3, 31]. Whereas the latter is formed rather rapidly and is responsible for the early stabilization of glass ionomer cements, the former occurs more slowly and causes the changes in strength with time. On this basis, a leaching of siliceous species originating from the degradation of the glass particles could explain the decrease of the surface hardness in water with time.

According to Dupuis et al. [25] the softening caused by water is restricted to the surface layer and does not affect the bulk material whose hardness increases with time. This is in line with the findings that the strength of recent glass ionomer formulations stored in water generally tends to increase with time [11, 16, 18, 23, 31]. Consequently, as the surface softening is limited to a superficial layer and hardly changes with time (see Fig. 6) a prolonged contact with water is expected to have little or no effect on the change in wear stability with time as observed by de Gee et al. [12] and Soltész and Leupolz [30].

5. Conclusions

This study shows that the surface hardness of glass ionomer cements when stored in a humid atmosphere generally increases with time. However, subtle but distinct time-dependent differences in KHN, which can be attributed to differences in chemical and physical formulation, are observed.

When glass ionomer cements are stored in water after an initial setting of 15 min, a surface softening occurs independent of the formulation. The changes in surface hardness with time suggest that this softening most probably is caused by an inhibition of the secondary setting reaction in a superficial layer of the cement and not by erosion.

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References

[1] Wilson AD, McLean JW. *Glass ionomer cement*. Chicago: Quintessence Publishers, 1988.

- [2] Wasson EA, Nicholson JW. Studies in the setting chemistry of glass-ionomer cements. *Clin Mater* 1991;7:289–93.
- [3] Wasson EA, Nicholson JW. New aspects on the setting of glass-ionomer cements. *J Dent Res* 1993;72:481–3.
- [4] Matsuya S, Maeda T, Ohta M. IR and NMR analyses of hardening and maturation of glass-ionomer cement. *J Dent Res* 1996;75:1920–7.
- [5] Crisp S, Wilson AD. Reactions in glass ionomer cements. III. Precipitation reaction. *J Dent Res* 1974;53:1420–4.
- [6] Prosser HJ, Powis DR, Brant P, Wilson AD. Characterization of glass-ionomer cements. 7. The physical properties of current cements. *J Dent* 1984;12:231–40.
- [7] Prosser HJ, Powis DR, Wilson AD. Glass-ionomer cements of improved flexural strength. *J Dent Res* 1986;65:146–8.
- [8] Beyls HMF, Verbeeck RMH, Martens LC, Lemaitre L. Compressive strength of some polyalkenoates with or without dental amalgam alloy incorporation. *Dent Mater* 1991;7:151–4.
- [9] Kerby RE, Bleiholder RF. Physical properties of stainless-steel and silver-reinforced glass-ionomer cements. *J Dent Res* 1991;70:1358–61.
- [10] Cattani-Lorente MA, Godin C, Meyer JM. Early strength of glass ionomer cements. *Dent Mater* 1993;9:57–62.
- [11] Cattani-Lorente MA, Godin C, Meyer JM. Mechanical behavior of glass ionomer cements affected by long-term storage in water. *Dent Mater* 1994;10:37–44.
- [12] de Gee AJ, van Duinen RNB, Werner A, Davidson CL. Early and long-term wear of conventional and resin-modified glass ionomers. *J Dent Res* 1996;75:1613–9.
- [13] Crisp S, Lewis BG, Wilson AS. Characterization of glass-ionomer cements. 1. Long-term hardness and compressive strength. *J Dent* 1976;4:162–6.
- [14] Williams JA, Billington RW. Changes in compressive strength of glass ionomer restorative materials with respect to time periods of 24 h to 4 months. *J Oral Rehab* 1991;18:163–8.
- [15] Pearson GJ, Atkinson AS. Long-term flexural strength of glass ionomer cements. *Biomaterials* 1991;12:658–60.
- [16] Mitra SB, Kedrowski BL. Long-term mechanical properties of glass ionomers. *Dent Mater* 1994;10:78–82.
- [17] Miyazaki M, Moore BK, Onose H. Effect of surface coatings on flexural properties of glass ionomers. *Eur J Oral Sci* 1996;104:600–4.
- [18] Nicholson JW, Abiden F. Changes in compressive strength on ageing in glass polyalkenoate (glass ionomer) cements prepared from acrylic/maleic acid copolymers. *Biomaterials* 1997;18:59–62.
- [19] Cook WD. Degradative analysis of glass ionomer polyelectrolyte cements. *J Biomed Mater Res* 1983;17:1015–27.
- [20] McKinney JE, Antonucci JM, Rupp NW. Wear and microhardness of glass-ionomer cements. *J Dent Res* 1987;66:1134–9.
- [21] McKinney JE, Antonucci JM, Rupp NW. Wear and microhardness of a silver-sintered glass-ionomer cement. *J Dent Res* 1988;67:831–5.
- [22] Brackett WW, Johnston WM. Relative microhardness of glass ionomer restorative materials as an indicator of finishing time. *J Am Dent Assoc* 1989;118:599–602.
- [23] Soltész U, Leupolz M. Härte- und Festigkeitsverhalten von Glasionomerzementen. *Dtsch Zahnärztl Z* 1993;48:237–41.
- [24] Mojon P, Kaltio R, Feduik D, Hawbolt EB, MacEntee MI. Short-term contamination of luting cements by water and saliva. *Dent Mater* 1996;12:83–7.
- [25] Dupuis V, Moya F, Payan J, Bartala M. Depth microhardness of glass ionomer cements. *Biomaterials* 1996;17:71–4.
- [26] De Moor RJG, Verbeeck RMH, De Maeyer EAP. Fluoride release profiles of restorative glass-ionomer formulations. *Dent Mater* 1996;12:88–95.

- [27] Forss H, Seppa L, Lappalainen R. In vitro abrasion resistance and hardness of glass-ionomer cements. *Dent Mater* 1991;7: 36–9.
- [28] Williams JA, Billington RW. Increase in compressive strength of glass ionomer restorative materials with respect to time: a guide to their suitability for use in posterior primary dentition. *J Oral Rehab* 1989;16:475–9.
- [29] De Maeyer EAP, Verbeeck RMH. Reactivity of fluoride-containing calcium aluminosilicate glasses used in dental glass ionomer cements. *J Dent Res*, in press.
- [30] Soltész U, Leupolz M. Abriebverhalten von glasionomerzementen. *Dtsch Zahnärztl Z* 1993;48:379–82.
- [31] Wilson AD. Secondary reactions in glass-ionomer cements. *J Mater Sci Lett* 1996;15:275–6.