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Post-irradiation hardness of resin-modified glass ionomer cements and a polyacid-modified composite resin

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This study examined the post-irradiation hardness of resin-modified glass ionomer cements and a polyacid-modified composite resin using a digital microhardness tester. Change in hardness of these materials over a period of 6 months was compared to that of conventional glass ionomer cements and a composite resin. With the exception of the composite resin, all materials showed a significant increase in hardness over 24 h after their initial set. Dual-cure resin-modified glass ionomer cements showed decreased hardness with increased storage time in saline at 37 °C. Results suggest that the addition of resins to glass ionomer cements does not improve initial hardness and does not negate the acid-base reaction of conventional cements. Resin addition may, however, lead to increased water sorption and decreased hardness.

1. Introduction

The ongoing search for biologically and aesthetically acceptable adhesive restorative materials has brought new varieties of materials onto the dental market. Two classes of new materials are resin-modified glass ionomer cements and polyacid-modified composite resins. Both materials were developed to overcome the problems of conventional glass ionomer cements which include early low mechanical strengths and poor aesthetics resulting from moisture sensitivity [1]. A true resin-modified glass ionomer cement hardens by two reactions: (1) the comparatively slow acid-base reaction between glass powder and organic acid; and (2) an immediate photochemically induced polymerization of the resin component [2]. Polyacid-modified composite resins, however, differ in their setting characteristics. These materials are a type of composite resin in which the filler and matrix resin undergo an acid-base reaction over a period of time after hydration. The acid-base reaction has been claimed to promote further crosslinking and thus hardening of the entire matrix [3].

This study examined the post-irradiation hardness of resin-modified glass ionomer cements and a polyacid-modified composite resin. The change in hardness of these materials over time was also compared to that of conventional glass ionomer cements and a composite resin.

2. Materials and methods

Materials selected for the study included two conventional glass ionomer cements – Fuji Cap II (FC) (GC Corporation, Tokyo, Japan) and Ketac Fil (KF) (Espe Dental-Medizin, Oberay, Germany); two dual-cure resin-modified glass ionomer cements – Fuji II LC (F2) (GC Corporation, Tokyo, Japan) and Photac Fil (PF) (Espe Dental-Medizin, Oberay, Germany); a tri-cure resin-modified glass ionomer cement – Vitremer (VM) (3M Dental Products, Minnesota, USA); a poly-acid-modified composite resin – Dyract (DY) (Dentsply, Weybridge, UK), and a composite resin – Z100 (3M Dental Products, Minnesota, USA). With the exception of the two conventional glass ionomer cements, all other materials are or can be light-cured and were of the A2 Vita shade. All materials were manipulated according to manufacturers' instructions.

A split ring mould was fabricated for the preparation of specimen discs which were 10 mm in diameter and 1.5 mm thick. The mould was first slightly overfilled with the material under evaluation and then sandwiched between two quartz glass plates to extrude the excess material. Light-cured materials were then polymerized using a calibrated Max Polymerization unit (Dentsply, Milford, USA) for 40 s through both glass plates. After the initial set, all materials were stored in 100% humidity at 37 °C for 10 min prior to finishing of the periphery, which was carried out using 1000 grit abrasive paper on a Metaserv hand grinder (Metallurgical Services, Surrey, London). Ten specimens of each material were made. The Vicker's hardness (H_V) of the materials was subsequently measured using an MXT50 digital microhardness tester (Matzuzawa, Tokyo, Japan) at the following time periods: 1 h; 1 day; 1 week; 1 month; 3 months and 6 months after mixing or light polymerization. A 50 gf load was applied through the indentor with a dwell

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TABLE I Mean Vickers hardness number (H_V) for the different materials at the various time periods

Material	1 h Mean H_V (SD)	1 day Mean H_V (SD)	1 week Mean H_V (SD)	1 month Mean H_V (SD)	3 months Mean H_V (SD)	6 months Mean H_V (SD)
Z100 (ZO)	65.84 (6.71)	79.76 (9.66)	76.52 (5.40)	73.7 (1.67)	74.24 (1.12)	76.56 (2.72)
Fuji Cap II (FC)	23.96 (3.68)	70.38 (6.86)	68.16 (7.87)	64.12 (4.60)	58.8 (8.09)	49.50 (6.17)
Ketac Fil (KF)	25.18 (3.06)	107.16 (13.14)	102.18 (19.19)	101.56 (8.93)	100.94 (15.58)	106.56 (18.77)
Fiji II LC (F2)	15.36 (3.01)	71.64 (12.17)	56.26 (9.92)	51.48 (5.01)	49.58 (6.08)	47.72 (3.16)
Photac-Fil (PF)	22.04 (3.51)	63.64 (7.29)	50.68 (7.41)	38.82 (9.02)	46.42 (2.73)	49.42 (3.66)
Vitremer (VM)	12.46 (2.37)	32.12 (7.53)	36.82 (3.78)	43.70 (7.60)	43.88 (3.05)	48.92 (5.73)
Dyract (DY)	30.14 (2.76)	48.58 (6.81)	40.72 (3.54)	41.16 (5.35)	40.12 (2.27)	50.72 (2.77)

time of 10 s. Hardness measurements were taken in the central area of each specimen and readings were recorded immediately after removal of the indentor to minimize the effects of elastic recovery of polymers on the results. The same specimens were read after the different time periods and the mean H_V and standard deviation was calculated and tabulated (Table I). Storage medium between the various time intervals was saline at 37 °C.

3. Results

The mean H_V of the different materials at the various time periods are reflected in Fig. 1. Data was subjected to one-way ANOVA and Duncan's test at 0.05 significance level. ZO showed no significant change in hardness over the evaluation period. The conventional and resin-modified glass ionomers and polyacid-modified composite resin had significantly lower hardness at 1 h compared to all other test times. FC was significantly harder at 1 day and 1 week than at 1 h and 6 months. There was no significant change in hardness after 1 day for KF. For the resin-modified glass ionomer cements, F2 and PF, hardness at 1 day was significantly higher than that at 1 h, 1 month, 3 months and 6 months. VM, however, was significantly harder at 6 months than at 1 h and 1 day. DY was significantly harder at 6 months compared to evaluation at 1 h, 1 week and 3 months.

At 1 h, ZO was significantly harder than all the other materials evaluated. KF, DY were significantly harder than F2, VM; and FC, PF were significantly harder than VM. There was no significant difference in hardness between the conventional glass ionomer cements KF, FC and their resin-modified counterparts PF, F2 at 1h. At 1 day, KF was significantly harder than all the other materials evaluated including ZO. ZO, F2 were significantly harder than VM, DY; and FC, PF were again significantly harder than VM. At 1 week, KF was still significantly harder than the other materials evaluated. ZO was significantly harder than PF, VM, DY and FC was significantly harder than VM, DY. At 1 month, KF remained significantly harder than all the other materials. ZO was significantly harder than F2, PF, VM, DY. FC was significantly harder than PF, VM, DY. At 3 months, the results were similar to those obtained at 1 month with the exception of FC being only significantly harder than DY. At 6 months, KF and ZO were significantly harder than all the other materials examined and KF was significantly harder than ZO.

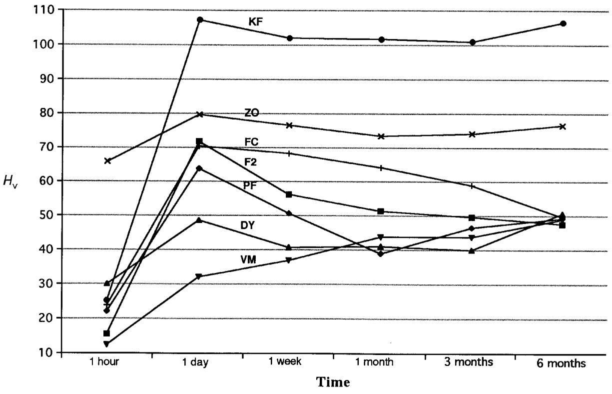

Figure 1 Mean Vickers hardness number (H_V) for the different materials plotted against time of evaluation.

4. Discussion

Hardness may be defined as the resistance to permanent indentation or penetration. It is, however, difficult to formulate a definition that is completely acceptable, since any test method will involve complex stresses in the material being tested from force applications, with the result that a variety of qualities are involved in any single hardness test [4]. Despite this condition, the most common concept of hard and soft substances is the relative resistance they offer to indentation. Change in hardness may reflect the state of cure of a material and the continuation of a setting reaction [5]. It has been shown that at depths of 2 mm or more, the overwhelming influences on cure of composite resins were related solely to light source intensity and exposure duration. Material shade and type was also shown to have minimal influence on cure at this depth [6]. Bourke and co-workers [5], in addition, found that a 30 s exposure with a visible light source produced some immediate hardening up to 1.5–2.0 mm below the surface of resin-modified glass ionomer cements. A 1.5 mm thickness was thus chosen to ensure maximum light polymerization of the specimens.

The dual setting reaction of resin-modified glass ionomer cements is achieved by replacing the water component with a water/HEMA (hydroxyethylmethacrylate) mixture. The acid-base reaction results in the formation of a calcium and aluminium polysalt hydrogel matrix while the polymerization reaction forms a polyHEMA matrix. The initial set of these materials is predominantly the result of the polymerization of HEMA and not the acid-base reaction characteristic of true glass ionomer cements. The slower acid-base reaction serves to additionally harden and strengthen the material. This is the cause of the increase in hardness of the resin-modified glass ionomer cements F2, PF and VM after 1 day. This increase in hardness was also observed with the conventional chemical cure glass ionomer cements KF and FC. This suggests that the acid-base reaction in resin-modified glass ionomer cements is not negated by the addition of resin. This is contrary to the belief that the acid-base reaction of resin-modified glass ionomer cements is severely inhibited because of the lack of water [2]. However, hardness measurement alone does not provide a definite analysis of the setting mechanism. The dual cure resin-modified glass ionomer cements were significantly harder at 1 day than that at 1 month, 3 months and 6 months. The results are consistent with the observations of Bourke and co-workers [5] who reported an increase of hardness of resin-modified glass ionomer cements after light-activation up to 1 day, after which there was no significant increase. Fully hardened resin-modified glass ionomer cements contain a high proportion of hydrophilic functional groups in a highly cross-linked matrix and can be likened to the structure of a synthetic hydrogel [7] which has been shown to take up large amounts of water [8]. When water is absorbed by the matrix, it may act as a plasticizer, resulting in the measured decrease in hardness. The significantly lower hardness of FC after 6 months when compared with 1 day and 1 week may be caused by early water contact [9, 10] as the conventional glass ionomer cements were stored in saline at 37 °C immediately after the initial set without a protective resin layer to standardize testing conditions. The hardness of KF was not affected by early contact with water.

The tri-cure resin-modified glass ionomer VM, differed from its dual cure counterparts, in that it continued to harden over 6 months. This increase in hardness is probably due to the third polymerization reaction, which involves the use of water-activated redox catalysts [11]. This allows the curing of the methacrylate to proceed in the absence of light and hence the gradual increase in hardness. The effects of water sorption may be totally mitigated by the increase in hardness from this polymerization reaction.

The unpolymerized polyacid-modified composite resin DY used in the study contains fluoro-silicate glass in a matrix of TCB (reaction product of butane tetracarboxylic acid and hydroxyethylmethacrylate) and other light-curing monomers. The TCB resin contains two methacrylate as well as two carboxyl groups. This monomer is able to crosslink via free-radical polymerization and subsequently exhibits an acid-base reaction when water is present. The material is initially hardened by a photopolymerization setting mechanism identical to that occurring in composite resins, and the carboxyl groups of the TCB resin are inactive so long as the material is anhydrous. As the polymerized material absorbs water, an acid-base reaction similar to that found in true glass ionomer cements occurs. Since post-curing reactions of the composite resin component is minimal [4], the acid-base reaction in the polyacid-modified composite resin accounts for the significant delayed increase in hardness after 1 day. Diffusion of water into the set restorative continues for several months until the entire filling material has reached its maximum saturation. This sorption of water apparently decreases the hardness up to 3 months. Hardness at 6 months was, however, greatest. A possible hypothesis for this observation is that once the maximum content of water is reached, the decrease in hardness caused by water sorption will cease. Further acid-base reaction that occurs may result in additional crosslinking of the entire matrix leading to the increase in hardness observed at 6 months.

The composite resin control Z100 showed no significant changes in hardness over the evaluation time period. Approximately 75% of the polymerization of photoinitiated composite resins take place during the first 10 min. The curing reaction may continue for a period of 24 h which explains the slight increase in hardness after 1 day [4]. This post-curing reaction is, however, minimal and reliance on this to compensate for inadequate initial photopolymerization is unwise. Even under ideal conditions the conversion rate from monomer to polymer is rarely greater than 60% [12]. The results may also be explained in part by the fact that the composite resin Z100 had significantly less water sorption than resin-modified glass ionomer cements after both 1 week and 1 month water storage [13].

5. Conclusions

The addition of resins to glass ionomer cements does not appear to improve initial hardness. With the exception of the composite resin, all materials showed a significant increase in hardness over 24 h after their initial set. The initial hardness was also significantly lower than that at other time periods. As both conventional glass ionomer cements KF, FC and dual cure resin-modified glass ionomer cements F2, PF were hardest at 1 day, it may be concluded that the acid-base reaction in resin-modified glass ionomer cements was not negated by the replacement of water with a water/HEMA mixture. The dual cure resin-modified glass ionomer cements, however, showed decreased hardness with increased storage time in saline at 37 °C. This decrease in hardness may be attributed to the plasticizing effects of water absorbed by the resin component of these cements. The phenomenon may, however, be compensated for by the addition of a third polymerization involving the use of water-activated redox catalysts, as with the tri-cure resin-modified glass ionomer cement VM.

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