Strength and setting behavior of resin-modified glass ionomer cements

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Diametral tensile strength (DTS), fracture strength, and Vickers microhardness were tested in three resin-modified glass ionomer cements (GICs), one chemically set GIC, and one dental composite. For the DTS studies test discs were immersed in deionized water at 37°C for 10 min, 1 day, and 28 days, respectively. Cured discs were also implanted in back muscles of rats for 28 days before testing. The effects of light irradiation time and delayed curing on the DTS of the cements were also studied. Significantly higher strength was observed in the resin-modified GICs in comparison with the chemically set GIC at all observation periods. K71 showed the highest strength among the GICs. No strength reductions were detected after 28 days for the specimens in vivo. An illumination time of 20 sec was enough to obtain final strength in the PFA and K71 specimens, and 40 sec was needed in the VI specimens. The strength of the resin-modified GICs when light-cured was significantly higher than when the same cements were allowed to set without irradiation. The microhardness of the light-cured GICs was similar to that of the dental composite. Considering the improved fracture strength and surface hardness, it was concluded that the resin-modified GICs present an interesting material for further development. □ *Composite resins; dental cements; dental restoration; light-curing*

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The conventional glass ionomer cement (GIC) is based on an acid-base reaction derived from aqueous polymeric acids, such as poly(acrylic acid) homopolymer or acrylic/itaconic/maleic copolymers. The glass component is usually a fluoroalumino-silicate (1). Relatively high bonding strength to tooth mineral tissue compared with other dental cements and slow release of fluoride are the main advantages of the conventional GIC. However, the initial sensitivity to water and the low strength, particularly the low fracture strength and toughness (2), are problems for the conventional GIC. Efforts have been made to improve the strength of the cement using fiber and powder reinforcements (3, 4). Silver powder-reinforced GIC is an example with some improvements in strength (5, 6). Different glasses or fillers have also been tested (7) to obtain a GIC with a higher fracture strength. These new materials have shown improved strength but are still not strong enough to be used generally as a permanent dental filling material in stress-bearing situations, such as posterior restorations.

The setting behavior of light-curing systems such as those used in dental composites has advantages compared with a chemically set system. The introduction of the light-curing system in the GIC materials presents a way to overcome the low initial strength of the conventional GICs (8). Mitra (9, 10) reported that the resin-modified GIC material had higher bonding ability to tooth substance and fluoride release than the self-curing reference. Other investigators reported similar findings (11, 12), but the fluoride release from the resin-modified materials differed considerably (12).

The resin-modified GICs, also called compomers, consist of a mixture of components in which a photo-curable monomer is introduced into the conventional composition of polyacrylic acid and ion-leachable glass (13). Consequently, several competing reactions will create a more complex structure (14), which will influence the properties of the material. The purpose of this investigation was to evaluate the strength and setting behavior of three light-curing GICs.

Materials and methods

Materials

The materials used in this study, including three resin-modified GICs, a chemically set GIC, and a dental composite, are listed in Table 1.

Diametral tensile strength (DTS)

Cement discs, 4 mm in diameter and 2 mm in height, were prepared in a dismountable stainless steel mold. The cements were mixed in accordance with the manufacturer's instructions. An activating light (VLC 400, Demetron, USA) was used for light-curing. A CL tester

Table 1. Tested materials

Code	Materials	Batch no.	Manufacturer
K71*	K71	Experimental	DeTrey
PFA	Photo-fil Aplicap	Lot 0003	ESPE
VI	Vitremer	3303L	3M Company
P50	P-50 (composite)	Lot 92FO9A	3M Company
FJ	Fuji Ionomer Type II	P : 230271 GC L : 110360	Dental Indus., Japan

* K71 is on the market under the name Dyract.

(Dendema AB, Sweden) was used regularly to check the light intensity of the curing light. In most cases the specimens were immersed in deionized water at 37°C for 24 h before strength testing, but other conditions were used and are given below. The measurements were performed on a universal test machine (Alwetron 50T, AB Loretze, Sweden) at a crosshead speed of 1 mm/min. Eight specimens were used for each condition and material. The specimens were divided into the following groups: I: The specimens were kept in deionized water at 37°C for 10 min, 1 day, and 28 days, after the cements had been irradiated for 60 sec; II: The specimens were irradiated for 60 sec and implanted by the method of Therin et al. (15) in a back muscle of 10 Sprague–Dawley rats for 28 days; III: Specimens of the resin-modified GIC were illuminated for 0, 5, 10, 20, 40, and 60 sec and kept in deionized water at 37°C for 24 h; IV: Specimens of VI and PFA were mixed and kept in 100% relative humidity at 37°C for 3, 6, 10, 60, and 180 min before they were illuminated for 60 sec; and Control: Specimens of P50 were cured and immersed in water like the resin-modified glass ionomer cements, and specimens of FJ were kept in a humidity chamber (100% relative humidity) at 37°C for 1 h after being mixed and then immersed in water at 37°C for 23 h and 28 days.

Three-point bending strength

Test bars, 25 × 2 × 2 mm in size, were prepared in a dismountable stainless steel mold with one 25 × 2-mm side open to the curing light. The VCL 400 curing lamp with a 12-mm diameter wand was used for curing the resin-modified GICs and the composite. The light was applied first at the center of the bar for 60 sec and then for the same time at both ends of the bar. The illuminated areas overlapped. The test bars were removed from the mold after curing and immersed in deionized water at 37°C for 24 h. The bending test was conducted on the universal testing machine with a span of 22 mm at a crosshead speed of 1 mm/min. Six test bars were used for each material.

Vickers microhardness testing

Two discs of each material, 10 × 1 mm in size, were prepared and stored in deionized water for 24 h at 37°C. Twenty indentations were made for each material in a Shimadzu microhardness meter (Shimadzu Corp., Japan) at a load of 100 *g* for 15 sec.

Infrared spectrometry

A drop of each cement liquid was placed on an NaCl crystal. Paste K71 was dissolved in chloroform, and the clean solution on top was collected after centrifugation. The following infrared spectra were taken on an FTIR spectrometer (1600 Series, Perkin Elmer, USA): 1) the three resin-modified GICs; 2) 2-hydroxyethyl methacrylate (HEMA) (Merck, Germany); 3) a mixture of HEMA and polyacrylic acid (PAA) (25% PAA, mol. wt. 50,000; Polyscience, USA).

Statistical analysis

The *t* test and one-way ANOVA were applied to the results, and $P < 0.05$ was used as the statistically significant level.

Results

Diametral tensile strength

The DTS of group I and the control group are listed in Table 2. In general, the resin-modified GICs were stronger than the chemically set GIC. Among the resin-modified GICs, K71 was significantly stronger than PFA and VI for the test periods; its strength was comparable to that of P50. The strengths of the GICs at 1 day and 28 days were significantly higher than their initial strength at 10 min.

Fig. 1 illustrates the DTS of the group-II cements after 28 days' implantation in vivo compared with the corresponding specimens kept in vitro. No statistically significant differences were found between the specimens of the same material implanted in vivo and kept in vitro.

The final strength of PFA and K71 (group III) was

Table 2. Diametrial tensile strength (MPa) of the tested materials

Material	Time		
	10 min	1 day	28 days
K71	29.4 ± 2.2	40.3 ± 2.6	39.5 ± 1.3
PFA	15.6 ± 0.4	25.5 ± 1.0	25.2 ± 1.1
VI	20.1 ± 0.6	26.3 ± 1.1	26.4 ± 1.9
P50	ND*	49.3 ± 1.2	ND*
FJ	10.0 ± 0.8†	13.3 ± 0.3	13.2 ± 0.9

The results are presented as the mean of eight measurements and standard error.
* Not determined.
† The specimens were kept in a humidity chamber (100% relative humidity) at 37°C for 10 min.

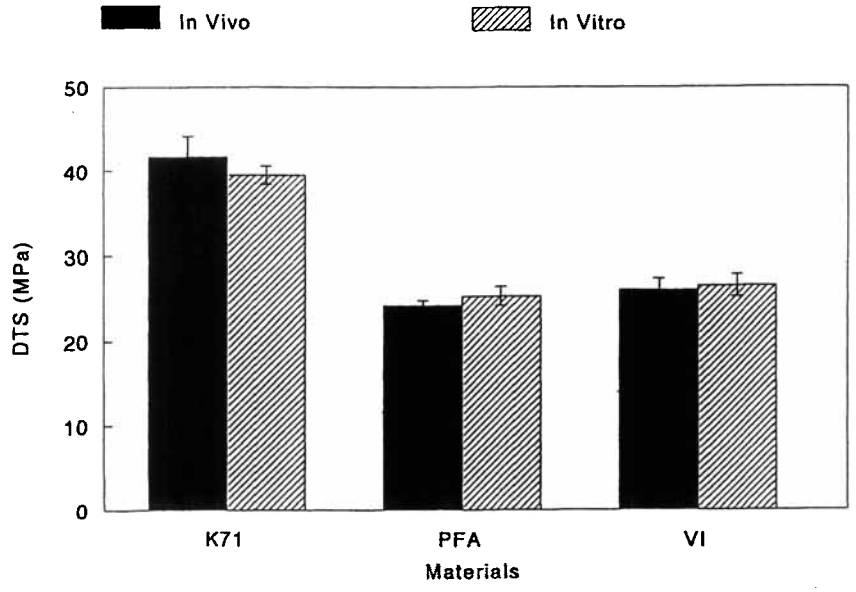

Fig. 1. Diametral tensile strength (DTS) of resin-modified glass ionomer cements in vivo and in vitro 28 days after curing.

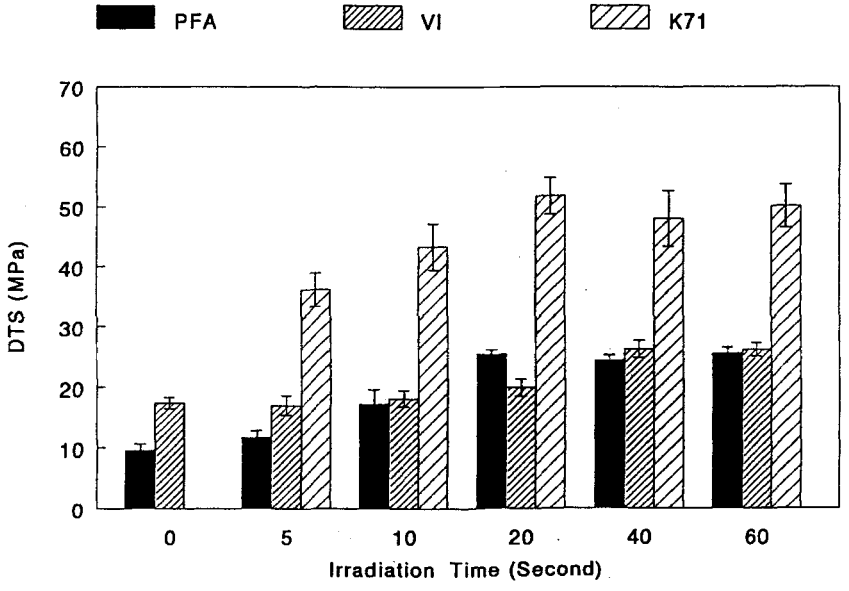

Fig. 2. The influence of irradiation time on the diametral tensile strength (DTS) of resin-modified glass ionomers.

obtained for specimens illuminated for 20 sec or more (Fig. 2). The strength of PFA without light curing was less than 50% of the PFA light-cured for 20 sec. No increase was found with extended light irradiation. A similar comparison cannot be made for K71, since this is a single-paste system and does not set without illumination. However, K71 obtained a significantly increased strength at 20 sec of illumination compared with 5 and 10 sec. In the case of VI, 40 sec was needed to obtain the final strength.

The effect of delayed illumination on the DTS of PFA and VI (group IV) is shown in Fig. 3. The reduction in strength was significant for PFA after a 10-min delay. The decrease in strength with delay time is almost

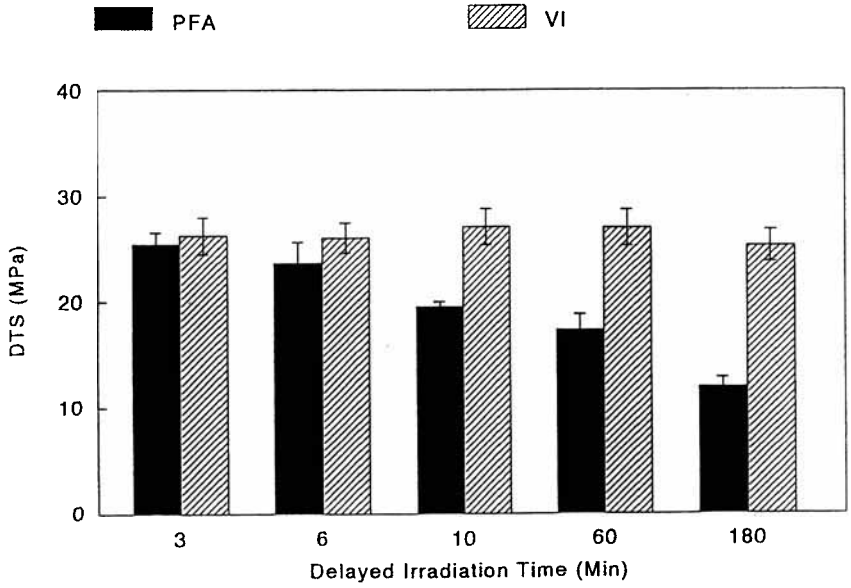

Fig. 3. The influence of delayed irradiation time on the diametral tensile strength (DTS) of resin-modified glass ionomer cements.

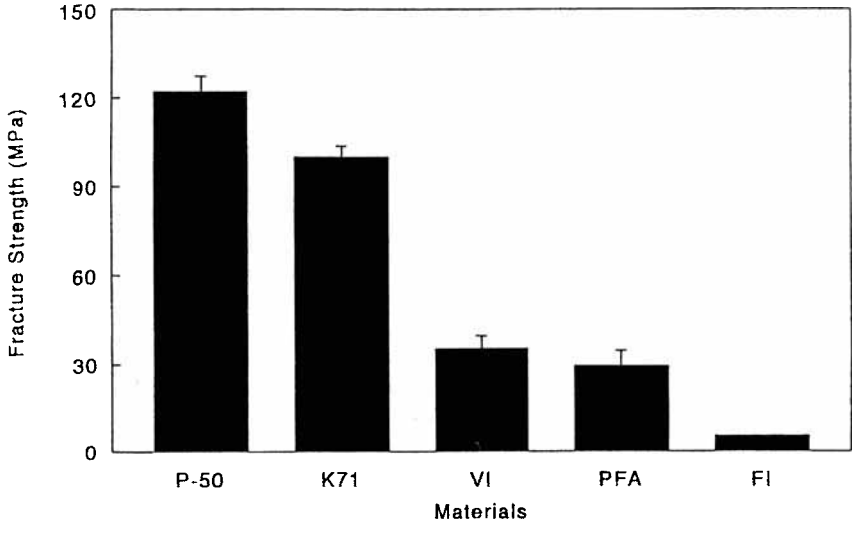

Fig. 4. The fracture strength of dental composite, resin-modified glass ionomer cements and chemically set glass ionomer cement 24 h after curing.

linear. However, VI showed a different pattern, in which no significant reduction of strength was found during this test.

Three-point bending strength

The fracture strength of the materials, presented in Fig. 4, followed a pattern similar to that of the DTS. The K71 showed the highest strength among both the resin-modified and the chemically set GIC, close to the strength of the hybrid composite (P50). The chemically set GIC showed the lowest fracture strength.

Microhardness testing

The hardness of the resin-modified GICs and the dental composite were similar and significantly higher than that of the conventional GIC (Table 3).

Table 3. Vickers microhardness number (VHN) of the tested materials

	Materials				
	P50	FJ	K71	PFA	VI
VHN	47 ± 2	9 ± 1	44 ± 1	52 ± 2	46 ± 1

The results are presented as the mean of 20 measurements and standard error.

Infrared spectrometry

The infrared spectra of the resin part of the PFA and the HEMA/PAA mixture are shown in Fig. 5. They have the characteristic features of the spectrum of an ester, such as the strong C=O (1720 cm^{-1}) C—O (1180 cm^{-1}), and also C—H (2865–2975 cm^{-1}) stretching vibrations. The C=C stretching absorption band at 1636 cm^{-1}cm can be seen in all the materials. A broader absorption band around 3450 cm^{-1} represents stretching vibrations of O—H in water, HEMA, and polyacrylic acid.

Discussion

The DTS strength of the resin-modified GICs investigated was significantly higher than that of the chemically set GIC. The high initial strength of resin-modified GICs reflects the function of photocurable polymers in the cements. The increase of strength with time reflects the continuing setting reactions. It will be of great interest to identify these reactions and their contribution to the mechanical strength. The strengths of the cements tested differed, which may be due to the differences in chemical composition. K71 showed the greatest strength, close to that of the dental composite. K71 is a 'single-paste system', and the speculative components of the paste may be a mixture of HEMA and powder of chemically set GIC, which resembles the resin-filler combination of the dental composite rather than of the GIC.

IR spectra of the resin part of the resin-modified GICs were similar to those of the PAA-HEMA mixture, indicating that HEMA monomer was included in these cements. Whether HEMA is just physically mixed with PAA solution or grafted on the PAA backbone could not be concluded from these investigations. The presence of small amounts of other polymerizable components cannot be excluded. These cements do not contain any aromatic C=C (1606 cm^{-1}), which can be found in the dental composites, reflecting the content of Bis-GMA resin. Only aliphatic C=C (1636 cm^{-1}) vibration was detected for the resin-modified GICs.

Stability of the resin-modified GICs was shown both in vitro and in vivo. To study the sensitivity of the cements to water in an early stage, the test discs were immersed in water immediately after curing. The DTS strength of these specimens at 10 min indicates that the resin-modified GICs have overcome the initial sensitivity to water of the chemically set GIC. The strength of the cements increased significantly in the first 24 h, indicating the continuing setting reaction. Furthermore, no reduction in DTS strength of the new GICs was observed after 28 days' implantation in vivo, which indicated stability of these cements in the biologic environment. This is of particular interest in the field of applications where the GIC will be in direct and continuous contact with living tissue, such as an obturator in apical surgery or alveolar bone substitutes (16) and as a suggested bone cement in orthopedics (17).

The improvement in DTS strength with the resin-modified system is also demonstrated in Fig. 2, where the effects of the light duration are presented. A doubling in strength for PFA was seen when the cement was illuminated for 20 sec compared with no illumination. The strength of the cement without illumination probably reflects the strength of the conventional ionic setting reaction. However, for the VI cement the gain in strength by light curing was not as great as for the PFA. This may be explained by differences in the initiator systems or resin content. The relatively higher strength of VI obtained without light-curing indicated a contribution of a chemical curing initiator and/or acid-base reaction in this cement. The results of these tests indicate roughly the effects of the different setting reactions on the strength of the cement.

Since both chemical and light-curing set mechanisms are involved in the resin-modified GIC, the time when the light is applied on the mixed cement paste should be critical. The viscosity of the cement increases with the acid-base chemical reaction, which may impair the effectivity of the light-curing by limiting the mobility of the radicals. This effect was not significant until the light irradiation was delayed for more than 10 min (Fig. 3). With the specimens of VI no significant reduction in strength due to the delay was recorded. The results indicate that the time to insert and form the fillings can be rather long without impairing the strength of the cement. However, the delayed light-curing may influence other properties of the material, which should be further studied.

The improvements in fracture strength for the resin-modified GICs compared with the chemically set GIC were significant. However, the fracture strength of the resin-modified GICs, except for K71, is still low compared with the dental composites. It is therefore of interest to study further the properties of single-paste systems like K71 with regard to, for example, adhesion to tooth substance and fluoride release.

A significantly higher microhardness was observed for all three resin-modified GICs than for the chemically set GIC. The surface hardness of the resin-modified GICs was at the same level as for P50 and other dental

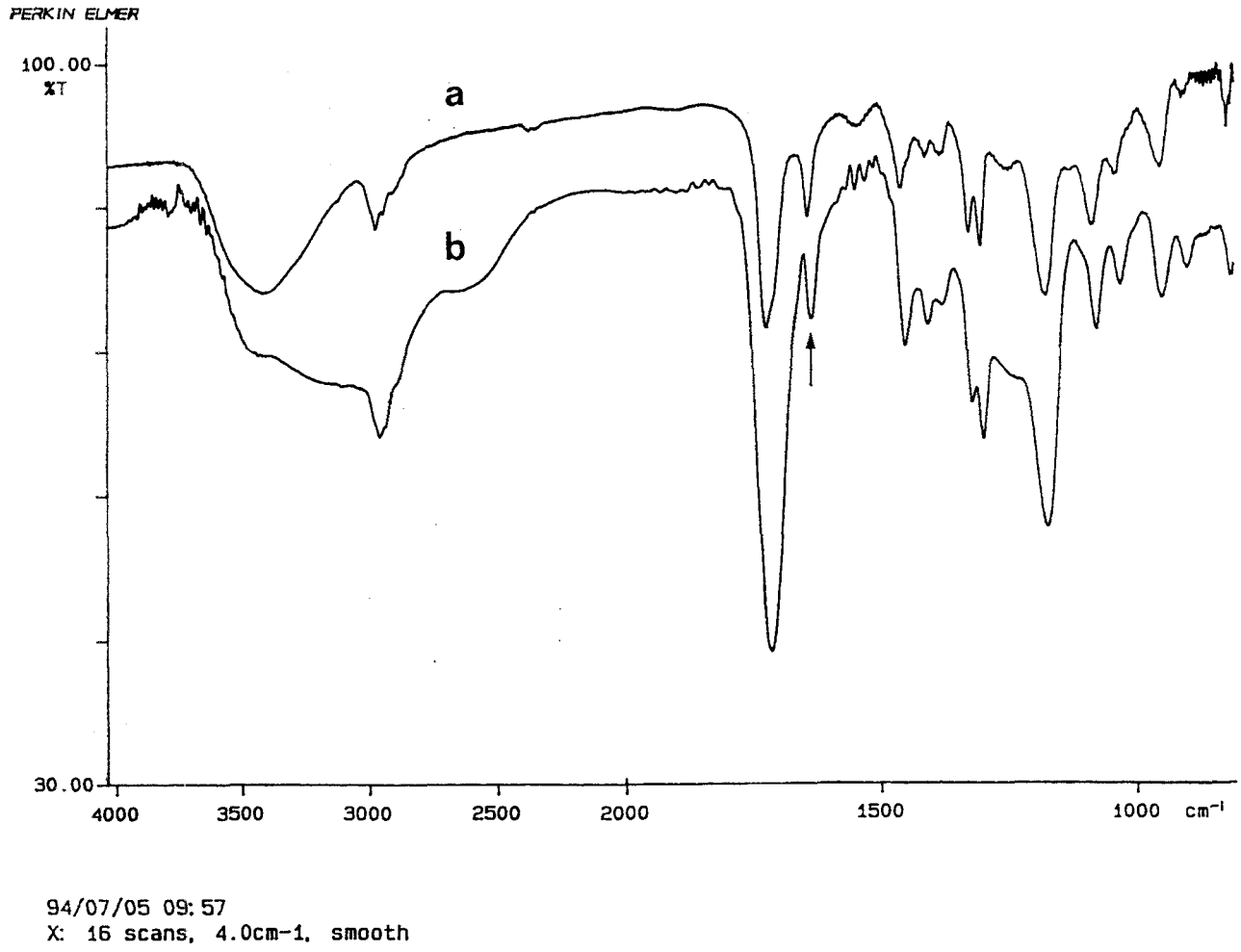

Fig. 5. Infrared spectra of uncured resin components in the resin-modified material PFA (a) and the 2-hydroxyethyl methacrylate (HEMA)/polyacrylic acid (PAA) mixture (b). The arrow indicates the aliphatic C=C (1636 cm^{-1}) absorption.

composites reported in the literature (18). The increased hardness, due to the cross-linking reaction in the resin-modified GIC, may improve the wear resistance of the GICs. Furthermore, unlike the dental composite there is minimal internal stress between the glass particles and resin matrix due to the presence of a silica-gel layer on the partially dissolved glass particles (19); this may improve the wear resistance of the GIC. Consequently, it is of interest to study further the microstructure of the resin-modified GIC and to correlate it with the mechanical and clinical performance of the material.

The light-cured GICs are stronger than the conventional GIC, although the strength varies between different brands. With good initial stability and surface hardness, together with adhesion to tooth substance and fluoride release, they already represent an alternative both to the chemically set glass ionomer and to the dental composite in many applications. Further improvements have to be made before the resin-modified GICs can be generally used instead of the dental composite in applications in which considerable load is involved, such as posterior restorations. The test values obtained in this and other investigations indicate that developments are possible, but since the present dental composites also have limitations in strength, fundamental changes in composition are probably needed if the compomers are to be brought considerably above their level.

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