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Effect of Insertion Method on Knoop Hardness of High Viscous Glass Ionomer Cements

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The aim of this study was to assess the Knoop hardness of three high viscous glass ionomer cements: G1 - Ketac Molar; G2 - Ketac Molar Easymix (3M ESPE) and G3 - Magic Glass ART (Vigodent). As a parallel goal, three different methods for insertion of Ketac Molar Easymix were tested: G4 - conventional spatula; G5 - commercial syringe (Centrix) and G6 - low-cost syringe. Ten specimens of each group were prepared and the Knoop hardness was determined 5 times on each specimen with a HM-124 hardness machine (25 g/30 s dwell time) after 24 h, 1 and 2 weeks. During the entire test period, the specimens were stored in liquid paraffin at 37°C. Significant differences were found between G3 and G1/G2 (two-way ANOVA and Tukey's *post hoc* test; $p<0.01$). There was no significant difference in the results among the multiple ways of insertion. The glass ionomer cement Magic Glass ART showed the lowest hardness, while the insertion technique had no significant influence on hardness.

Key Words: glass-ionomer cement, Knoop hardness, insertion, Atraumatic Restorative Treatment.

INTRODUCTION

Glass ionomer cements (GICs) were first described 40 years ago by Wilson and Kent (1). Since then, many researchers have studied and modified their composition to enhance the mechanical properties.

GIC became the material of choice for Atraumatic Restorative Treatment (ART) due to its well-known properties, i.e. chemical bonding to enamel and dentin, fluoride release and uptake, biocompatibility and chemical set reaction (1,2).

The GIC used in ART restorations is called "condensable" or "highly viscous" (3) and was developed for use in occlusal bearing areas. Even though manufactures have reduced the wear rate and the setting time required for this material (4), hand-mixing is not very easy. A successful mixture, required to achieve the best mechanical properties (2), depends on correct dosage and manipulation. If the mixture is too thin and fluid, one may expect that the mechanical properties and wear resistance will be negatively affected. On the other hand, if the mix is too thick or dry, it will not bond satisfactorily to the tooth structure due to the lack of polyacrylic acid available to wet the tooth substance. This is in line with the conclusion that insufficient polyacrylic acid reduces the bond strength (5).

Based on these assumptions, 3M ESPE has developed a GIC called Ketac Molar Easymix. The main difference between this GIC and its predecessors is the type of powder particles (granules) used. According to the manufacturer, this new component standardizes the amount of powder used to fill the dosage scoop, reflecting on the mixture result. Furthermore, the particles of this type of powder are linked through sphere clusters, which enhance the polyacrylic acid penetration by capillary force in the tooth structure, making mixing easier due to an increased wettability.

Another discussion regarding GIC is the use of

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a syringe to insert the material. The use of a syringe could be useful to reduce voids incorporation and gap formation between the tooth and the filling material, reducing the chance of restoration failure, particularly in proximal restorations. A commercial syringe is expensive to be used in oral health programs or at health centers in developing countries. A low-cost syringe would be of great interest to ART.

The aim of this *in vitro* study was to evaluate the Knoop hardness of: Ketac Molar (3M ESPE), Ketac Molar Easymix (3M ESPE) and Magic Glass ART (Vigodent). Additionally, the Knoop hardness was evaluated regarding three different ways of insertion for Ketac Molar Easymix: a conventional spatula, a commercial syringe (Centrix), a low-cost syringe (Injex 1 mL, with a BD 1.60 x 40 needle). Scanning electronic microscopy (SEM) was used to analyze particle appearance in the specimens.

MATERIAL AND METHODS

The restorative GICs used are listed in Table 1. The materials are hand-mixed versions and were used in accordance with the manufacturers' instructions. One powder scoop was mixed in one drop of liquid, in mixing paddle, and then the mixture were inserted in the molds, accordingly to the insertion method group.

Specimens were prepared using PVC molds (2.5 mm height and 7.5 mm diameter), which were slightly overfilled and covered with mylar strips. A glass plate was used to compress the surface in order to avoid air bubbles. The mylar strip was maintained in position for 10 min, and then stored in lubricant (Liquid Paraffin; Merck KGaA, Darmstadt, Germany) at 37°C. After 24 h, the specimens were polished with a 1,200-grit silicon carbide paper (Buehler, Lake Bluff, IL, USA) until the excesses were removed.

Ten specimens of each material were prepared and the Knoop hardness test was performed after 24 h, one week and two weeks on a hardness test machine (HM 124; Mitutoyo Corp., Kanagawa, Japan), with 25 g load and 30 s dwell time (6). Five indentations were made on each specimen.

Three different insertion techniques were used only with Ketac Molar Easymix, also with 10 specimens in each group: G4: Conventional spatula; G5: Commercial syringe (Centrix, Shelton, CT, USA); G6: Low-cost syringe. This low cost syringe was obtained combining a syringe for insulin application with a needle (BD 1.60 x 0.40).

Knoop hardness measurements and the storage conditions were the same as described for the other groups.

For the SEM analysis, one specimen of each group was broken in its center, glued in metal stubs, dehydrated and gold sputtered for SEM observation of particle's size and voids incorporation. The specimens were evaluated at ×15, 250, 1000 magnifications using a JEOL scanning electronic microscope (JEOL XL Series, 10 Kv; Philips SEM XL 20, Eindhoven, The Netherlands).

The mean Knoop hardness data was assessed by two-way ANOVA and Tukey's *post-hoc* tests (α=0.05).

RESULTS

The averages of the Knoop hardness test are shown in Table 2. The data analysis showed statistically significant differences ($p<0.05$) between the measurements after 24 h and the other two time frames (1 week and 2 weeks), demonstrating an increase of the

Table 1. Materials used in this study with their composition and batch number.

Material (Manufacturer)	Composition	Batch number
Ketac Molar - Group 1 (3M ESPE, Seefeld, GE)	Powder: Al-Ca-La fluorosilicate glass, 5% copolymer acid (acrylic and maleic acid) Liquid: Polyalkenoic acid, tartaric acid, water	GES TA 002
Ketac Molar Easymix - Group 2 (3M ESPE, Seefeld, GE)	Powder: Al-Ca-La fluorosilicate glass, 5% copolymer acid (acrylic and maleic acid) Liquid: Polyalkenoic acid, tartaric acid, water	165737
Magic Glass ART - Group 3 (Vigodent, Rio de Janeiro, BR)	Powder: strontium, aluminum, fluoride, silicate, polyacrylic acid, tartaric acid and pigments Liquid: Polyacrylic acid, water	007-03

Knoop hardness after 24 h.

Ketac Molar and Ketac Molar Easymix showed similar hardness behavior, but distinct performance from Magic Glass ART (Table 2).

No statistically significant difference ($p<0.05$) was found in the Knoop hardness when the insertion techniques were compared (Table 3). The only difference found was between time frames (24 h<1 week = 2 weeks).

DISCUSSION

Frencken and Holmgren's proverb (2) "necessity is the mother of invention" could not be more opportune to explain the constant research for materials and efficient dentistry techniques targeting underprivileged communities. ART was idealized in support of such belief with the challenge to modify the dentistry situation in Tanzania during the 1980's (7).

The low wear and fracture resistance of the first materials used in ART redirected researchers to use materials that presented higher resistance. Later on, manufacturers instigated research to modify the conventional GIC until a material tailored for ART was established. Such material presented increased wear resistance with higher powder-liquid ratio and was called high-viscous GIC (2,8). The manufacturers of high-viscous GIC were also able to reduce the setting time, facilitating its use in areas that lack electricity for saliva suction (2).

Published researches show a great "operator effect" in the restorations survival (9,10), which can have influence in several issues related to ART, such as: unsatisfactory carious tissue removal (mainly in the edges - dentinoenamel junction), dosage and manipulation of the material, insertion, contamination with saliva and an improper surface protection (2). The way found by one manufacturer (3M ESPE) to achieve better mixing and proportion of GIC's components was through changes in the structure of the powder, by keeping it in the granule form with the use of a granulation agent. In such approach, the powder cannot be easily aggregated, being improbable that more powder can be added to the mixture with the movement of pushing the spoon against the bottle, fact easily observed with the classic GIC powder. Besides this change in the powder, the liquid composition was also modified. By reducing a fraction of the acid in the liquid and by drying it in the powder, the liquid became less viscous. These changes enabled a reduction in the contact angle, increasing the wettability.

Taking into account this new characteristics of the powder and liquid, it can be concluded that the dosage was successfully standardized, reducing the operator influence. The hand mixing became easier, faster and efficient because of the increased wettability of the liquid and the absorption of powder granules

Table 2. Means (MPa) (and standard deviations) of GIC's Knoop hardness across different time frames.

Material	24 h	1 week	2 weeks
Ketac Molar	67.9 (14.2) a, B	107.7 (30.8) b, B	105.7 (20.5) b, B
Ketac Molar Easymix	67.9 (9.0) a, B	113.6 (8.3) b, B	93.5 (15.5) b, B
Magic Glass ART	35.1 (4.4) a, A	58.9 (16.9) b, A	71.5 (20.1) b, A

Different lowercase letters in rows and uppercase letters in columns indicate statistically significant differences ($p<0.01$).

Table 3. Knoop hardness means (and standard deviation) of each way of insertion across different timeframes.

Insertion technique	24 h	1 week	2 weeks
Conventional spatula	67.9 (9.1) a	113.6 (8.3) b	93.5 (15.5) b
Centrix syringe	63.4 (11.6) a	89.5 (22.6) b	135.1 (11.8) b
Low cost syringe	50.3 (15.3)a	78.9 (8.5) b	116.6 (32.0) b

Different letters indicate statistically significant difference ($p<0.01$).

for capillarity.

Evaluating the Knoop hardness, it was observed that Ketac Molar Easymix presented similar hardness to Ketac Molar, as described in Table 2.

It is possible that materials with easier manipulation and more standardized dosage, which already present the favorable mechanical properties introduced by its predecessor, will have great value in clinical use, as they minimize the impact of the material in the success/failure of the ART.

It is also interesting to observe in Figure 1 the microstructure of the materials previously cited. Both present the same standards of cohesiveness, density mass and particles with similar size.

These findings are in accordance with Xie et al. (6). The authors raised the hypothesis that the "Ketac family" - Ketac Fil, Ketac Molar and Ketac Bond - presented higher values of Knoop hardness when compared to other materials (11), though without statistically significant difference between them. The positive correlation between cohesive structure and superficial hardness was evidenced by the same authors, which suggests an explanation for the low superficial hardness demonstrated by the Magic Glass ART. Ketac Molar (Fig.2A) and Ketac Molar Easymix (Fig. 2B) can be seen presenting more cohesive patterns than Magic Glass ART (Fig. 2C). In contrast, the Magic Glass ART SEM evaluation proved to be more difficult. Prior to SEM, the GIC samples were caught by 2 Orthodontic pliers, then, a single force was applied to break the samples in the middle. However, in the case of Magic Glass ART, as the material was very brittle, the minimal force of apprehension of the pliers in the edges sometimes already breached the specimen in very small parts, making the sample unusable.

The Magic Glass ART was launched in Brazil to be commercialized as a material indicated for ART by presenting lower cost than its imported competitors. It is known that superficial hardness presents negative correlation with the wear, so, the lower the hardness, the higher the wear (12). Therefore, it is probably that the material Magic Glass ART that presented average of Knoop hardness of 55.19 (KHN) (a relatively low hardness) would worn out more quickly than the other materials tested. Due to such high wear, repair of ART restoration made with this material may be necessary from time to time (2), turning it in a temporary restorations, which is not the purpose of ART. Nevertheless, the material still complies with the American Dental Association's specifications, which regulates the number of Knoop hardness of ionomer material indicated for restoration in 48 KHN (13).

Shintome et al. (14) investigated the microhardness of five GICs. They found higher values to the high viscous GICs, except for Magic Glas ART, which showed low values, similar to the low-viscosity GICs.

Towler et al. (15) and Ellakuria et al. (16) verified an increase in superficial hardness with the increase in time spam. In the present study, a statistically significant increase in the hardness (Tables 2 and 3) was observed from the 24 h to the 7 and 14 days timeframes. However, there was no significant difference between the 7 and the 14 days time spam. This contradicts the findings of Ellakuria et al. (16) that observed increase of the superficial hardness for the Molar Ketac after 7 and 15 days, steadiness in the 30 days reading and increasing again after 60 days.

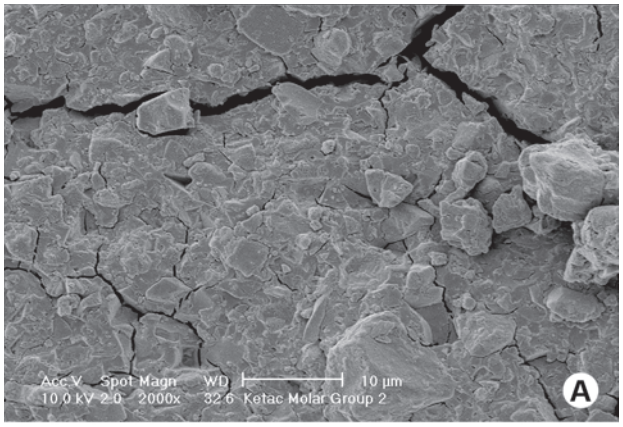
A possible explanation for such differences would be that the samples in the study of Towler et al. (15) and Ellakuria et al. (16) were stored in water, which modifies the surface of the ionomer materials by increasing the chain of polysalts formed (6). In the present study, the material was kept in oily solution (5) to prevent the water to penetrate or leave the interior of the material.

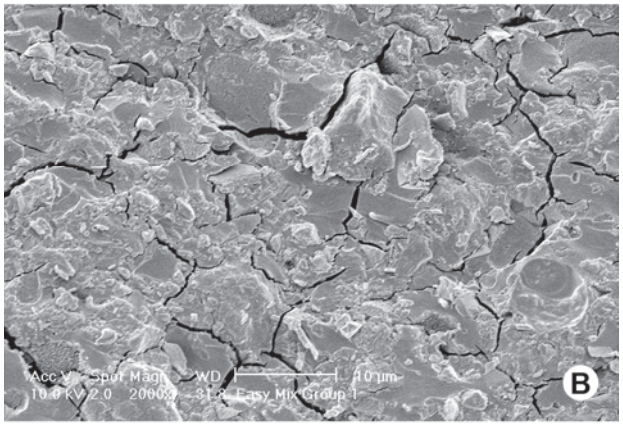
Another study (17) did not find alterations in the hardness of Ketac Molar immersed in water, suggesting that this material would not suffer decrease in its hardness with the precocious exposition to water. The higher powder-liquid ratio relative to other materials used in their study (Hi Fi, Vivaglass Fil, Ketac Fil, Diamonnd Carve) is the most probable responsible for this fact. De Moor and Verbeeck (18) also found small effect of water after 1 week, suggesting that, after this period, the material would be totally mature, presenting no significant alterations in the superficial hardness, fact observed in the present study.

The use of surface protection material was not carried out in our study. Therefore, the samples were immersed in the oily solution (liquid paraffin), which prevented the possibility of water interaction from external sources. The water from the cement could be lost during the initial setting phase (19), in the first minutes, however, as described previously, the material was wrapped and isolated from the environment with polyester strips for 10 min, being placed immediately after in the oily medium, remaining for 14 days at 37ºC.

The type of insertion of the material did not demonstrate to be relevant for the superficial hardness

(Table 3). There are not so many published researches addressing the insertion of GIC. Thus, the question if the insertion method influence on the mechanical properties of the material still remains. Esteves Barata (20) found that the use of a syringe could influence in the strength of proximal restorations in pre molars. The syringe used by those authors was the Centrix syringe, also used in the present study. However, the syringe kit, which comprises the syringe and disposable tip is of high cost. The price of the complete set is around US$





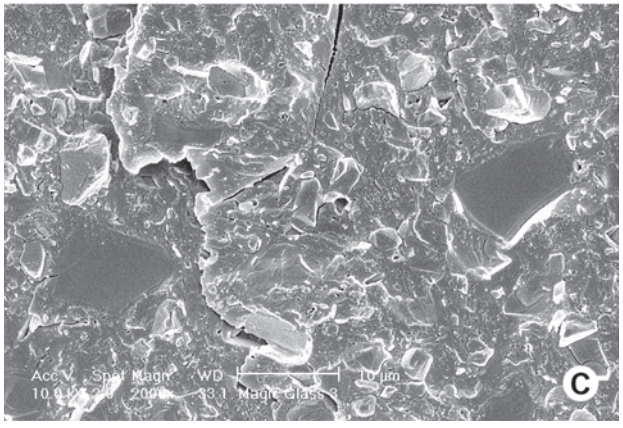
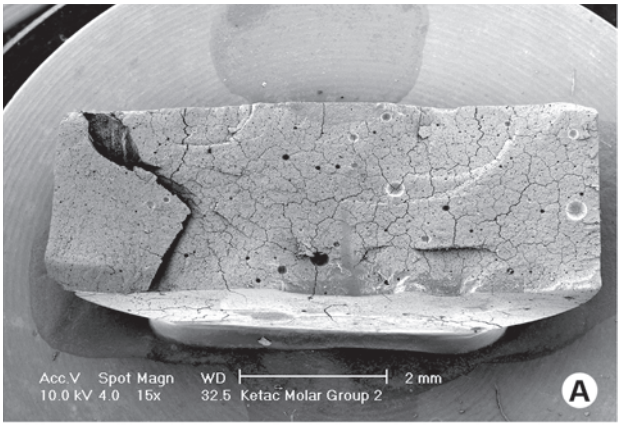
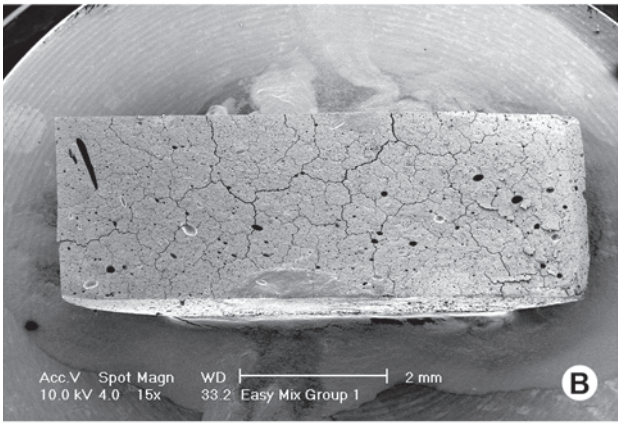


Figure 1. SEM micrographs (×2000 magnification) of the internal surfaces of: (a) Ketac Molar, (b) Ketac Molar Easymix and (c) Magic Glass ART.





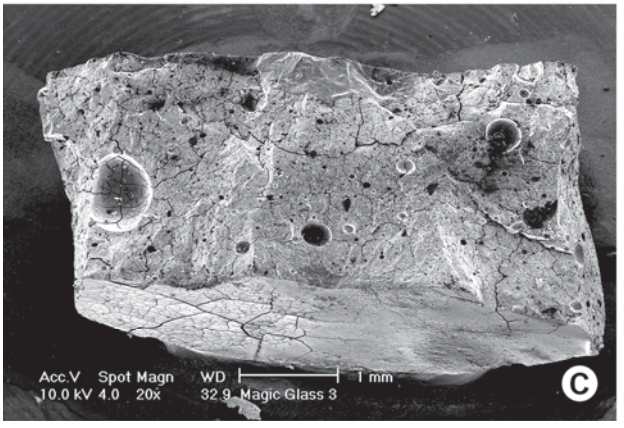


Figure 2. SEM micrographs of the internal surfaces of: (a) Ketac Molar (×15 magnification); (b) Ketac Molar Easymix (×15 magnification); and (c) Magic Glass ART (×20 magnification).

125.00. The set of 30 replacement tips costs US$ 65. The syringe developed for this study has an approximate cost of US$ 0.16. Given the fact that this syringe can be sterilized by chemical liquids and reused, costs can be decreased considerably, facilitating the insertion. The needle 1.60 x 40 (US$ 0.08) cannot be reused.

The use of low-cost syringes did not influence the surface hardness of GIC (Table 3), nor demonstrated significant differences in the SEM micrographs (Fig. 1).

As this research has been carried out *in vitro*, it must be pointed that, in field, where unfavorable conditions of clinical attendance play a role, a good quality injector syringe undoubtedly assists the material insertion. Therefore, further research must be carried out *in vivo* to test the hypothesis that the insertion can influence in the result and the survival rate of ART restorations.

One of the factors related to operator is also regarding inadequate insertion (2). The use of injector syringes is a way to help solving this problem. By using this low cost syringe, the insertion can be carried through repeatedly in the same way, which may help to improve the clinical performance of restorations and reduce costs.

A common finding in the images produced by the scanning electronic microscopy of GICs was the presence of bubbles and cracks, in line with Xie et al. (6). As this material presents water in its composition, after dehydration for SEM evaluation, we could observe the presence of small traces of fractures and cracks. A way to eliminate this inconvenience would be the use of replication technique for a reliable view of the surface. As observation of fractures was not a primary aim of this study, the replica technique was not used.

It is extremely important for dental professionals that further *in vitro* and *in vivo* studies are carried out with the new materials as well as with the new techniques with the purpose of facilitating the handling and use of GICs.

In conclusion, Ketac Molar and Ketac Molar Easymix presented similar Knoop hardness, which wass higher than that of Magic Glass ART. The insertion technique did not influence the Knoop hardness of the tested GICs.

RESUMO

O objetivo deste estudo foi avaliar a microdureza Knoop de três cimentos de ionômero de vidro de alta viscosidade: G1 - Ketac Molar; G2 - Ketac Molar Easymix (3M ESPE) and G3 - Magic Glass ART (Vigodent). Adicionalmente, como um co-objetivo, três diferentes formas de inserção do Ketac Molar Easymix foram avaliadas: G4 - espátula conventional; G5 - seringa comercial (Centrix) e G6 - seringa de baixo custo. Dez corpos de prova de cada grupo foram preparados e a microdureza Knoop foi determinada com 5 indentações por espécime com o aparelho HM-124 (25 g/30 s tempo de identação) após 24 h, 1 e 2 semanas. Durante todo o período de teste, os espécimes foram mantidos em parafina líquida a 37°C. Diferenças estatísticas significantes foram encontradas entre G3 e G1 / G2 (ANOVA a 2 critérios e teste de Tukey *post hoc*; p<0,01). Não houve diferença nos resultados no que se refere às diferentes formas de inserção. O cimento de ionômero de vidro Magic Glass ART apresenta os valores mais baixos de dureza enquanto o método de inserção não influencia nos resultados de dureza.

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