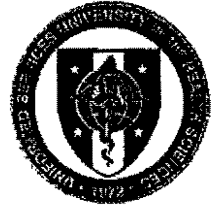




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Physical Property Investigation of Three  
Contemporary Glass Ionomer Restorative  
Materials

Joseph L. Gedge, Maj, USAF, DC

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## Abstract

**Objective:** To investigate the flexural properties and fracture toughness of two recently-marketed, high-viscosity conventional glass ionomer restorative materials compared to a contemporary product.

**Methods:** Specimens (n=12) were fabricated for fracture toughness and flexure strength using standardized, stainless steel molds following manufacturer recommendations, placed in (WHAT %) phosphate buffered saline, and stored at 37 °C until the appointed testing time. Specimens were tested to fracture in three-point bend mode at a rate of 0.5 mm/min on a universal testing machine. Results were recorded in Newtons and values for flexural strength, modulus, and fracture toughness were calculated with mean values recorded. Testing was accomplished at 24 hours, 1, 3 and 6 months after fabrication. Mean data was analyzed with Kruskal Wallis and Dunn's post hoc test ( $\alpha=0.05$ ).

**Results:** Physical properties were material dependent. While slight improvements in selected physical properties were noted between 24 hours and subsequent test points, most tests exhibited little difference between initial and final evaluation.

**Conclusions:** Under the conditions of this study, select physical properties between the glass ionomers evaluated in this study showed a significant difference between the glass ionomers evaluated different time points with the following notable results.

1. Recently developed glass ionomers showed a significantly significant increase in flexural strength compared to Ketac Molar and no difference in fracture toughness at 6 months.
2. Although differences in GIC physical properties were noted, the divergences were of such small magnitude that it is unlikely that it would be of clinical significance.

# Manuscript

## Introduction

Conventional glass-ionomer (GI) restorative materials were formulated in the early 1960's in an attempt to overcome the limitations of silicate restorative materials of that era. <sup>1</sup> GI materials are formed from an acid-base reaction and afford a durable bond to tooth due to the interactions between the polyalkenoic carboxyl groups and hydroxyapatite calcium ions. <sup>2, 3, 4, 5</sup>

During the GI acid-base reaction, an aqueous solution of polyalkenoic acid reacts with the glass component (typically a calcium fluoro-aluminosilicate) that releases first  $\text{Ca}^{2+}$  and later  $\text{Al}^{3+}$  ions which form metallic ion cross-linkage between the polyalkenoic polymer chains. The continued cross-linkage results in the GI material's increase in viscosity that facilitates the improvement in physical properties. <sup>6</sup> Although the initial acid-base reaction is essentially complete by 24 hours, <sup>7-11</sup> Additional maturation continues consisting of continuation of polyalkenoate polymer cross linking and formation of a hydrogel matrix. <sup>10, 11, 12</sup>

Conventional GI restorative materials have undergone changes to improve their physical properties and clinical handling characteristics, to include polyalkenoate acid modifications <sup>8,13, 14</sup> but a significant change in conventional GI formulation was the advent of what has been described as "small particle" or "viscous" materials. <sup>3,15</sup> These GI materials consist of a smaller mean particle glass size, were originally developed for the Atraumatic Restorative Technique, and have displayed impressive clinical results in spite of adverse treatment conditions. <sup>16-18</sup> In addition, these newer conventional GI restorative materials have shown promise as definitive restorations involving functional surfaces for both the primary and permanent dentition. <sup>19-23</sup> Several of these "viscous" or "small particle" conventional GI restorative materials have been recently marketed but lack independent research of these materials'

physical properties over time. The purpose of this study was to evaluate selected physical properties, namely flexural strength, flexural modulus and fracture toughness, of two newer conventional GI restorative materials compared to a similar material that has considerable market tenure. The null hypothesis is that there will be no difference in the physical properties between the tested restorative materials.

## Materials and Methods

The materials used in this study are listed in Table 1.

**Table 1. GIC Restorative Products**

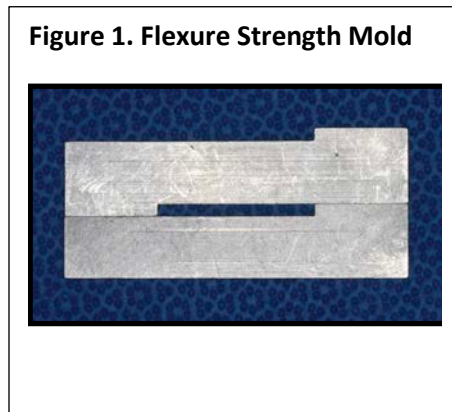
Material	Manufacturer	Powder/Liquid Ratio (g/g)	Powder Content	Liquid Content
Ketac Molar Quick Aplicap	3M ESPE (St. Paul, MN, USA)	*	Oxide Glass Chemicals (non-fibrous) 85-95% Copolymer of Acrylic Acid-Maleic Acid 1-5% Dichlorodimethylsilane Reaction Product with Silica <2%	Water 60-65% Copolymer of Acrylic Acid-Maleic Acid 30-40% Tartaric Acid 10%
Equia Forte	GC Corporation (Tokyo, Japan)	Trade Secret	Trade Secret	Trade Secret
Ketac Universal Aplicap	3M ESPE (St. Paul, MN, USA)	*	Oxide Glass Chemicals (non-fibrous) >95%	Water 40-60% Copolymer of Acrylic Acid-Maleic Acid 30-50% Tartaric Acid 1-10% Benzoic Acid <0.2%

\* Not available from manufacturer information; Content information obtained from manufacturer information

Twelve specimens (n = 12) were fabricated for each test using standardized, stainless-steel molds (Sabri Dental Enterprises, Downer’s Grove, IL) that were placed on a Mylar stripped glass slab. Prepared materials were inserted into the respective mold and immediately covered with a second Mylar strip with digital pressure applied using a microscopic glass slide to form a flat surface. Specimens were allowed

to set for the manufacturer recommended setting time, and were refined as necessary with surgical scalpel blades after removal. Specimens were stored under dark conditions in 0.2M physiologic phosphate buffered saline solution at 37 °C until appointed testing time. Testing occurred at 24 hours and then at 1, 3 and 6 months after fabrication.

**Flexural Strength:** Specimens were formed as previously described in a 2 x 2 x 25 mm mold (Figure 1)



and were tested on a three-point bend fixture mounted on a universal testing machine (Alliance RT/5, MTS Corporation, Eden Prairie, MN, USA). Specimens were stressed until failure at a cross head speed of 0.5mm/min with the maximum force recorded in Newtons. Flexure strength results was determined using the formula

$$\underline{F = 3Fl/2b}$$

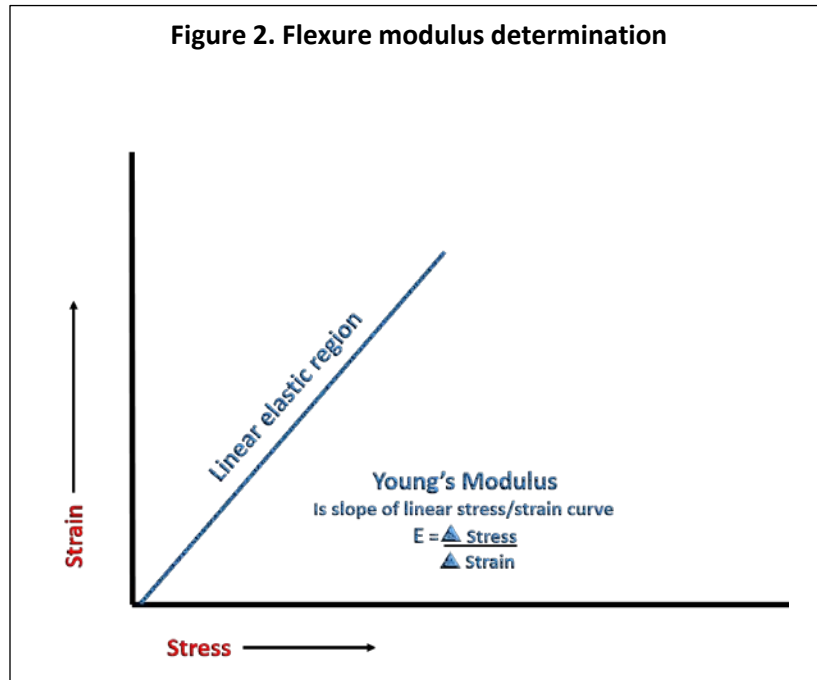
**F = maximum load recorded (N)**

**l = distance between supports (mm)**

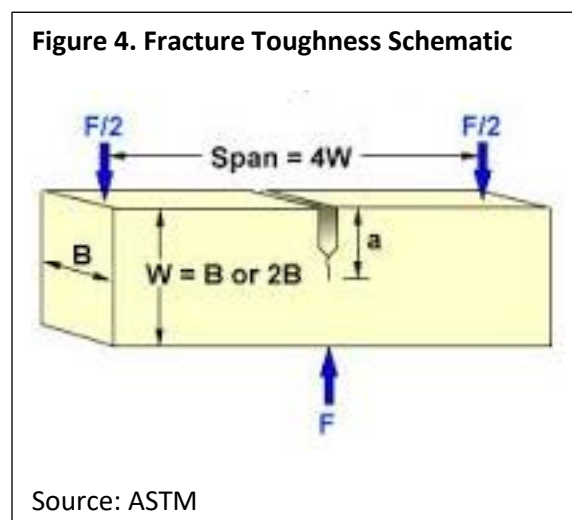
**b = width of specimen (mm)**

**h = height of specimen (mm)**

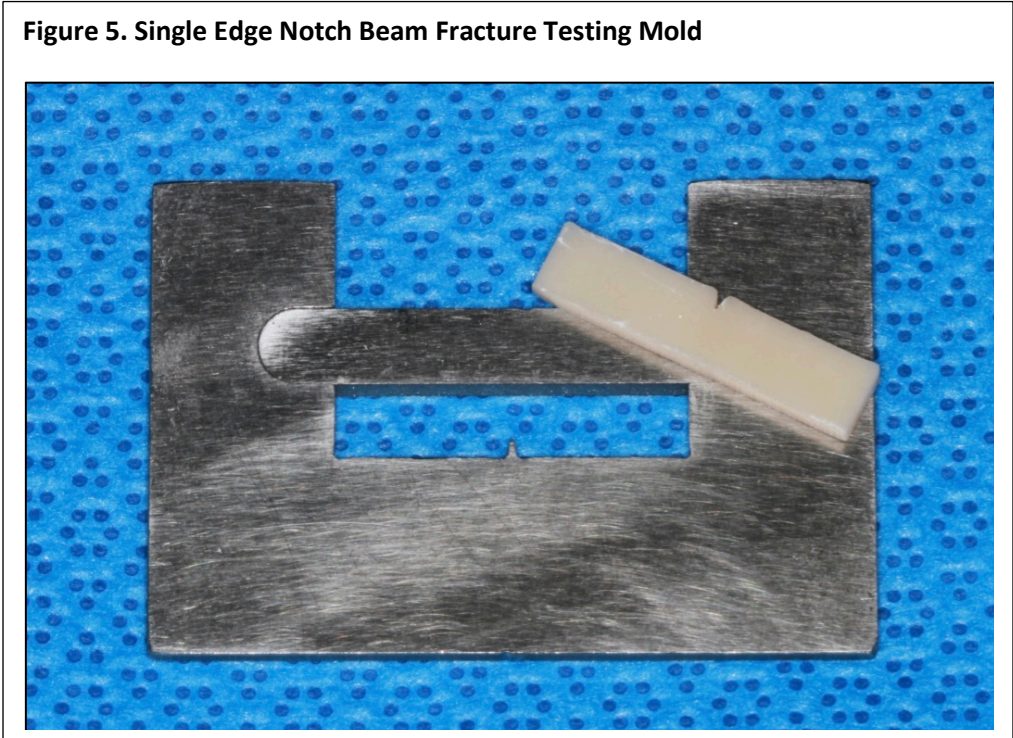
**Flexural Modulus:** Modulus was determined by the slope of the linear portion of the flexure strength stress-strain curve (Figure 2). Mean results were determined and recorded.



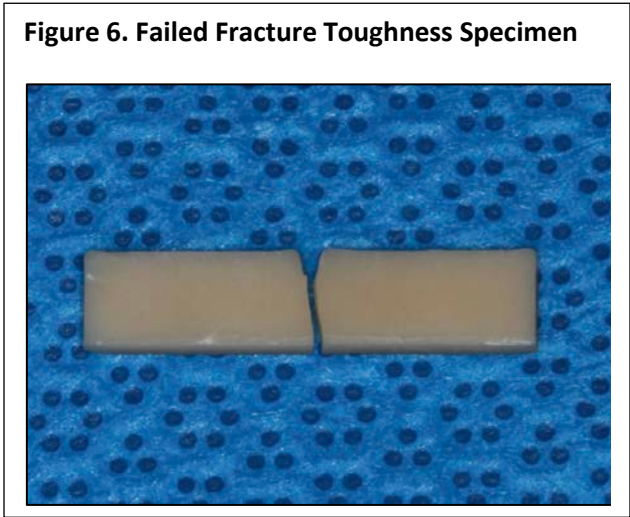
**Fracture Toughness:** Specimens were fabricated in accordance with the single edge notch beam method as described in ASTM Standard E399 (Figure 4).



The specimens were fabricated as described earlier using a custom stainless-steel mold as seen in Figure 5. Each specimen's dimensions were measured along the specimen and recorded.



As with flexure strength testing, specimens were tested in 3-point bending apparatus with a crosshead speed of 0.5mm/min in a universal testing machine (Alliance RT/5) until failure (Figure 6).



Prior to testing, the true notch length was measured with digital measuring microscope (Hirox KH-8700, Hirox USA, Hackensack, NJ, USA). Fracture toughness ( $K_{IC}$ ) was determined using the following equation:

$$K_{IC} = (3PLa^{1/2}/2tw^2) \times f(a/w)$$

**P = failure load (N)**

**L = distance between the support rollers (mm)**

**a = measured notch length (mm)**

**t = specimen thickness (mm)**

**w = specimen width (mm)**

**f(a/w) = 1.93 - 3.07(a/w) + [14.53(a/w)<sup>2</sup> - 25.11(a/w)<sup>3</sup>] + 25.80(a/w)<sup>4</sup>**

**Statistical Analysis:** As the data obtained did not follow a normal distribution, analysis was accomplished using non-parametric Kruskal-Wallis with Dunn’s post hoc testing with a 95 percent level of confidence ( $\alpha = 0.05$ ). Statistical analysis was performed using SPSS 21 (IBM/SPSS, Chicago, IL, USA).

## Results

The mean results for the physical property testing of the GIC restorative materials are listed in Tables 3-5.

Table 3

### Flexural Strength

Material	24 hours	1 Month	3 Months	6 Months
Equia Forte	22.517 A b	18.8 A b	31.433 A a	24.658 A b
Ketac Molar	22.925 A a	11 B c	15.45 C b	15.45 B b
Ketac Universal	16.467 A ab	13.608 B b	18.7 B a	21.308 B a

n=12; Capital letters annotate statistically similar groups per column, lower case letters annotate statistically similar groups per row ( $p = 0.05$ )

**Table 4**

**Fracture Toughness**

Material	24 hours	1 Month	3 Months	6 Months
<b>Equia Forte</b>	0.172 (0.035) B b	0.272 (0.026) A a	0.261 (0.02) A a	0.258 (0.019) A a
<b>Ketac Molar</b>	0.195 (0.028) B b	0.236 (0.017) B b	0.234 (0.029) A a	0.248 (0.017) A a
<b>Ketac Universal</b>	0.246 (0.033) A a	0.244 (0.057) A a	0.245 (0.034) A a	0.252 (0.022) A a

n=12; Capital letters annotate statistically similar groups per column, lower case letters annotate statistically similar groups per row (p = 0.05)

**Table 5**

**Flexural Modulus**

Material	24 hours	1 Month	3 Months	6 Months
<b>Equia Forte</b>	13.89 (2.3) A a	13.44 (2.5) A a	13.82 (1.8) A a	12.18 (1.9) A a
<b>Ketac Molar</b>	16.13 (2.6) A a	11.21 (3.2) B b	10.77 (2.4) B b	10.77 (2.4) B b
<b>Ketac Universal</b>	14.38 (3.8) A a	13.53 (2.7) A a	13.78 (1.5) A a	14.49 (3.2) A a

n=12; Capital letters annotate statistically similar groups per column, lower case letters annotate statistically similar groups per row (p = 0.05)

## Discussion

In this evaluation, three conventional GI restorative products were evaluated over a period up to 6 months. This study investigated selected physical properties of two newly-marketed materials and was compared to a conventional GI material that has been marketed for many years. Notably, one conventional GI material has had scant independent evaluations in the peer-reviewed scientific literature.

Ketac Universal was released in 2016 and advertised as having similar mechanical properties to Ketac Molar, another high-viscous conventional GI, with a reduced number of steps required during placement and improved handling characteristics. While specific components of the materials are not published by the manufacture, Ketac Universal differs in its chemical makeup from Ketac Molar with the addition of benzoic acid. The manufacture claims improvements in the ability to manipulate the material to preparation adaptation, improved fluoride release, and elimination of the conditioning step to remove the smear layer before placement.

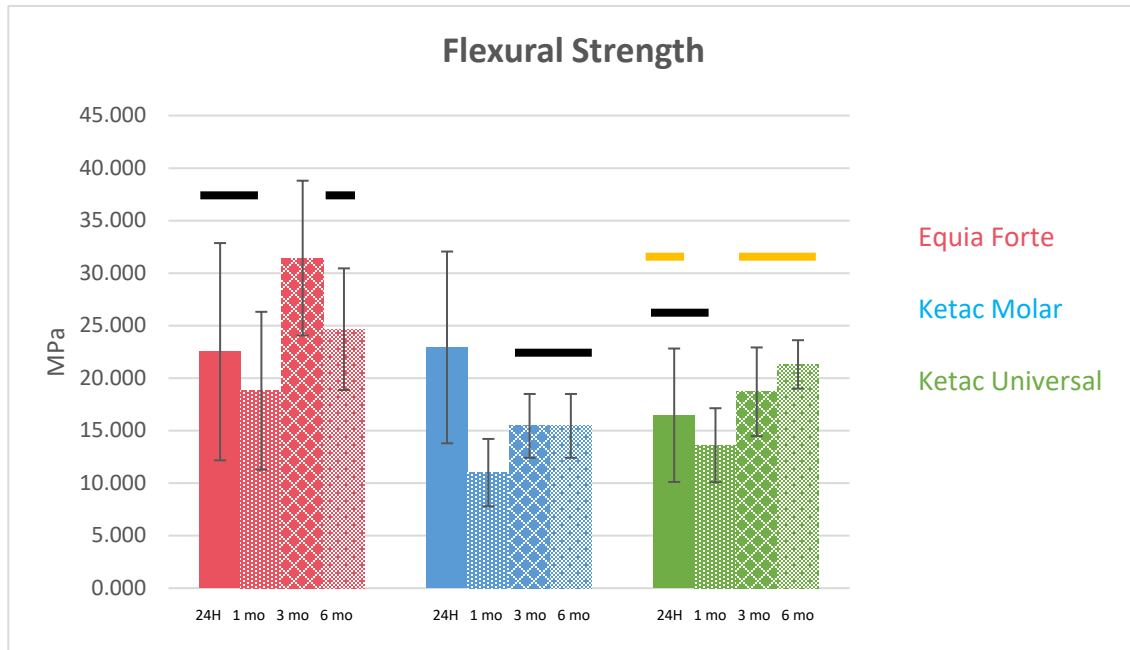
Equia Forte also claims significant improvements over its predecessor, Equia. Improvements include higher fluoride release, higher flexural strength and wear resistance. A higher molecular weight polyacrylic acid and micron-sized fillers are thought to contribute to the increased physical properties.

Only precapsulated materials were chosen for this study due to potential variation that can occur by hand-mixing.<sup>25, 26</sup>

Specimens were stored in 0.2M phosphate-buffered saline solution as this media represents a more physiologic as well as being recommended by international standards.<sup>24</sup> The selected physical properties evaluated were flexure strength, flexural modulus and fracture toughness. Flexural strength

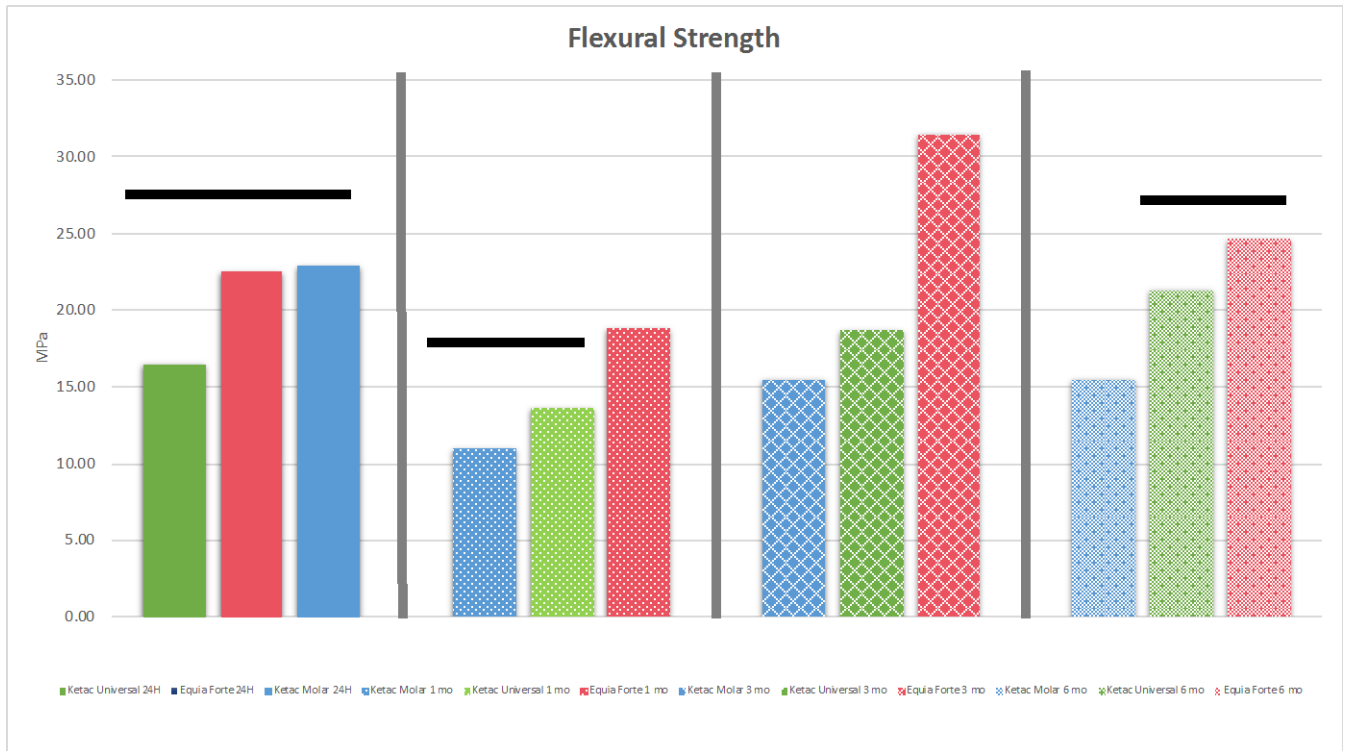
testing has been suggested as possibly a more discriminating *in vitro* evaluation that involves complex failure modes as it involves both tensile and compressive stresses is a beam structure. <sup>27, -28</sup>

Figure 7



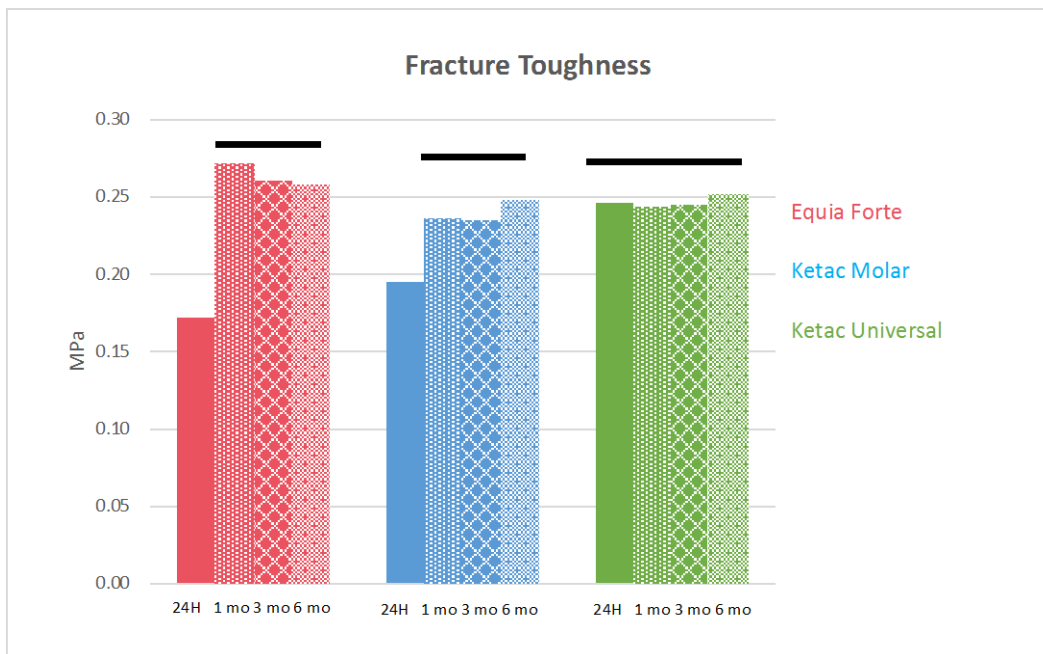
n=12; horizontal lines indicate statistically similar groups per row (p = 0.05)

Figure 8



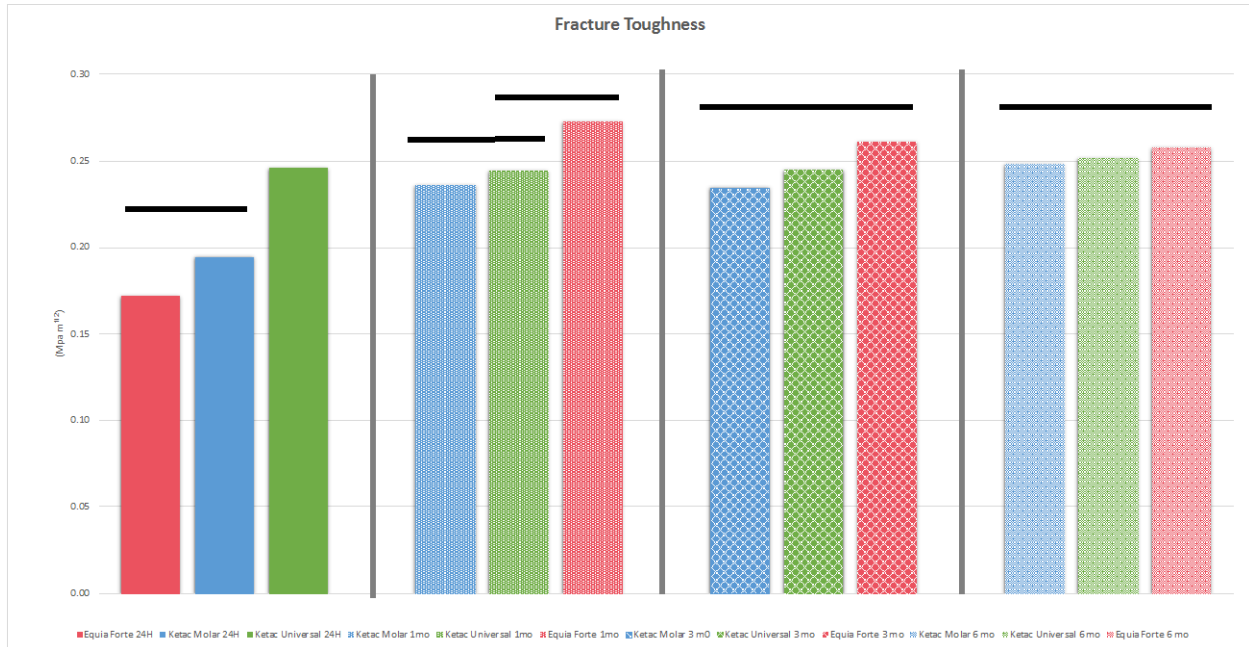
n=12; horizontal lines indicate statistically similar groups per row (p = 0.05)

Figure 9



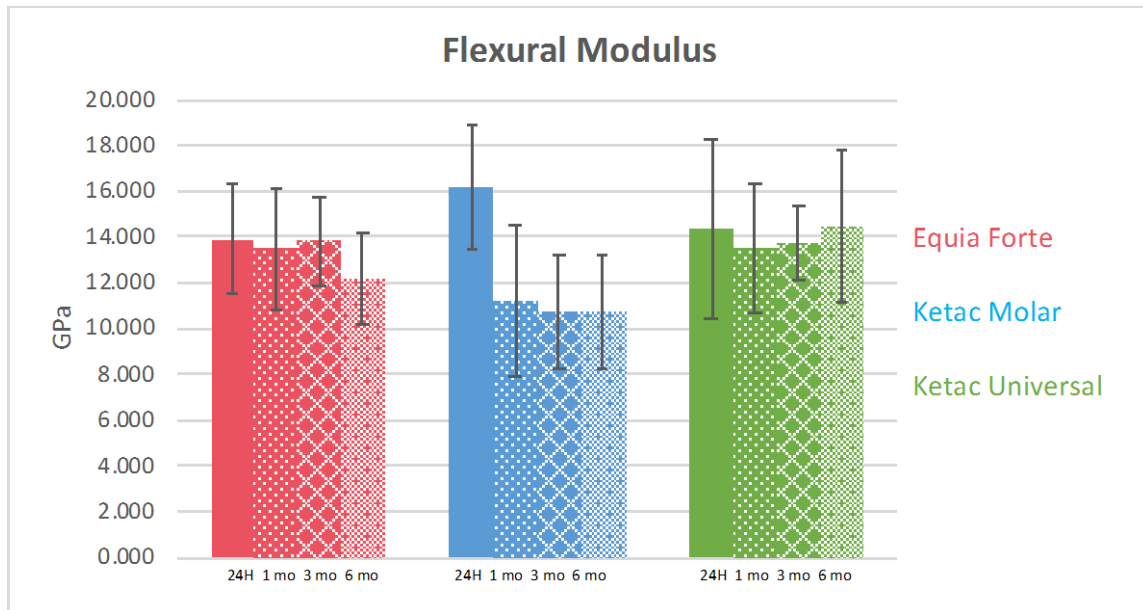
n=12; horizontal lines indicate statistically similar groups per row ( $p = 0.05$ )

Figure 10



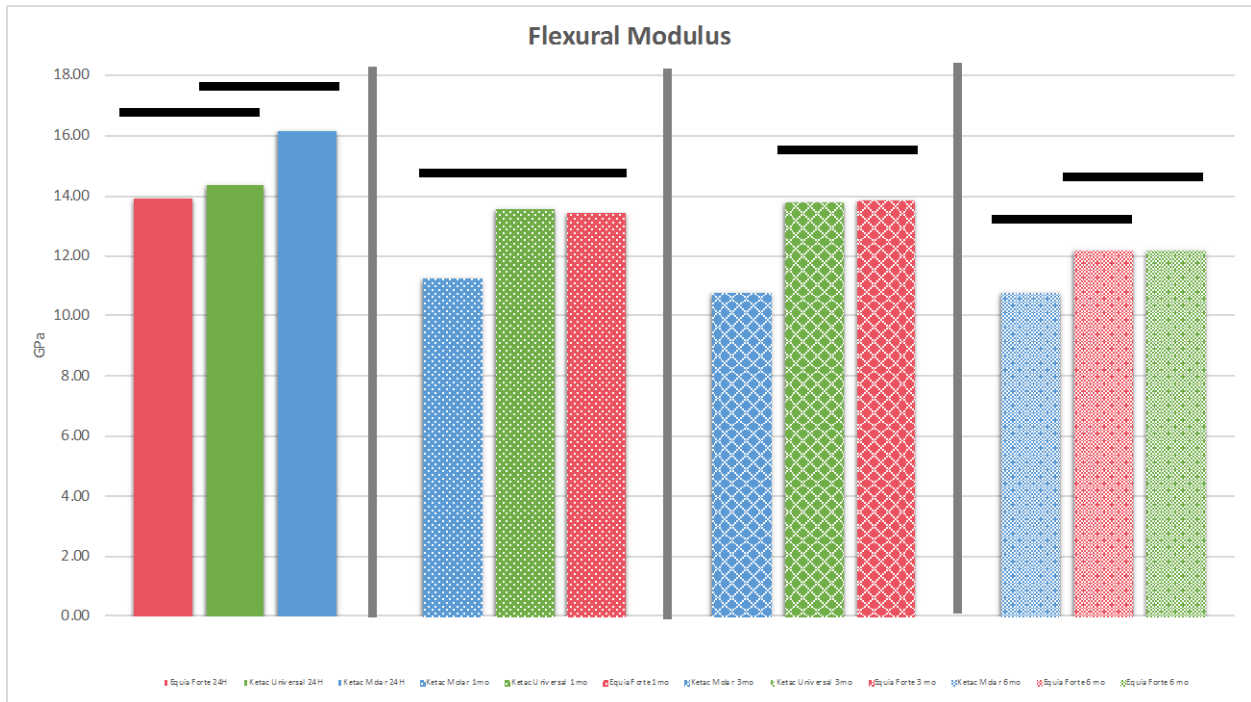
n=12; horizontal lines indicate statistically similar groups per row ( $p = 0.05$ )

Figure 11



n=12; horizontal lines indicate statistically similar groups per row ( $p = 0.05$ )

Figure 12

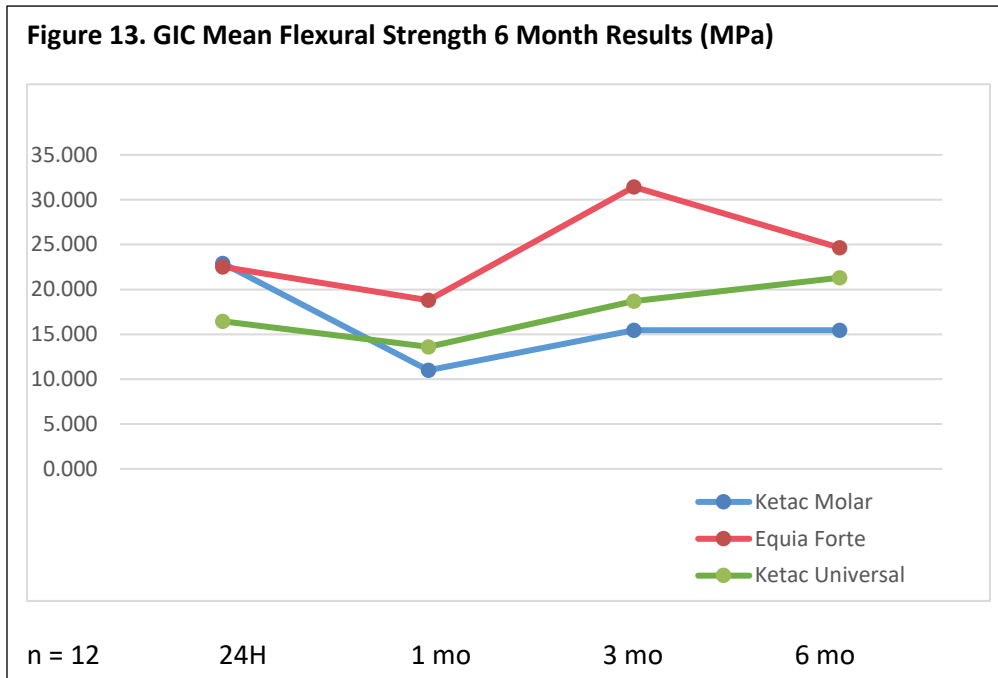


n=12; horizontal lines indicate statistically similar groups per row (p = 0.05)

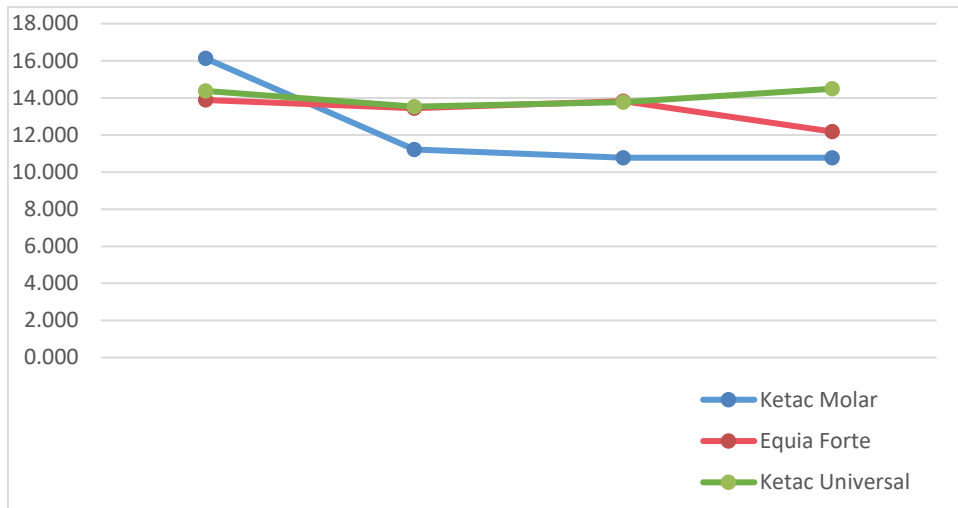
Figures 7-8 shows the flexural strength results for the materials tested over the 6 months of this evaluation.

At 24 hours, there was no statistically significant difference in the flexure strength between Equia Forte, Ketac Molar and Ketac Universal. However, Ketac Molar displayed a flexure strength deterioration over the course of the evaluation that resulted in significantly less flexure strength compared to the others at six months. Ketac Universal and Equia Forte demonstrated showed no significant flexure strength change between 24 hours to 6 months.

Flexural modulus is derived from the linear portion of the flexure strength stress-strain curve. Both Ketac Universal and Equia Forte showed no significant modulus change between 24 hours and 6 months, which is somewhat not surprising as flexural modulus is a function of flexural strength. Mirroring flexure strength results, Ketac Molar was an exception as it was the only GIC product that demonstrated a statistically significant modulus decrease throughout the 6-month evaluation (Figure 11).



**Figure 14. GIC Mean Flexural Modulus 6 Month Results (GPa)**



n = 12

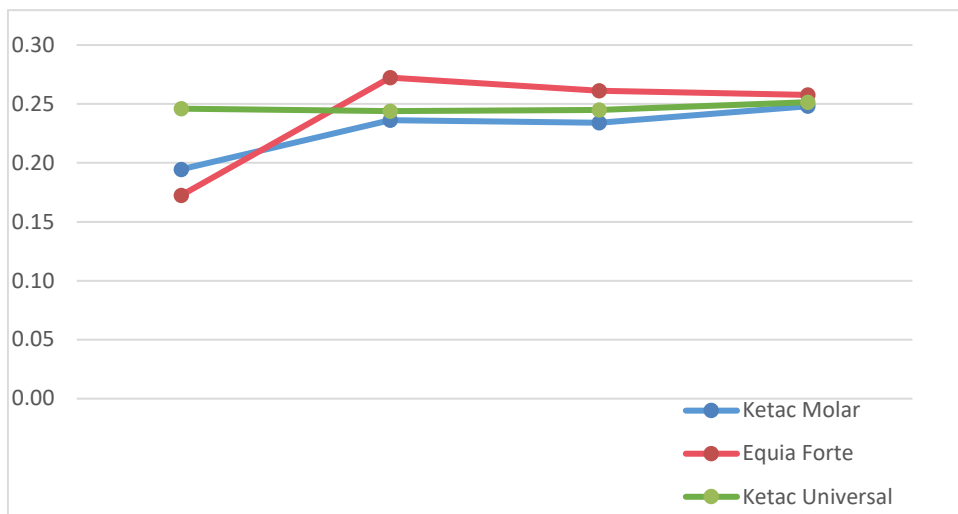
24H

1 mo

3 mo

6 mo

**Figure 15. GIC Mean Fracture Toughness 6 Month Results (mPa m<sup>1/2</sup>)**



n = 12

24H

1 mo

3 mo

6 mo

Fracture toughness has been described as an in vitro test that may correlate with clinical performance, as fracture toughness testing determines a material's ability to resist crack propagation from a pre-existing flaw.<sup>27</sup> Fracture toughness during this evaluation were tested using the single edge notched beam method in accordance with ASTM Standard E399 (Figure 4).

The results in this study approximate results previously reported in the literature. The flexure strength found for Ketac Molar Quick was similar to that reported by Yamazaki et al<sup>29</sup> while almost being identical to that stated by Xie and colleagues.<sup>30</sup> While the flexural strength for Ketac Molar was slightly lower than that reported by Wren et al,<sup>31</sup> the flexural modulus values found in the present study was nearly identical to that reported by the former authors. However, while this study observed diminishing trends for both flexural strength and modulus with Ketac Molar, the same phenomena was not noted by Wren et al.<sup>31</sup> These physical property reductions witnessed with Ketac Molar is presently not understood by the authors. The fracture toughness determined in this study was similar to that reported by Yamazaki and colleagues,<sup>29</sup> but lower than values published by Al-Angari et al<sup>32</sup> and Elie et al.<sup>33</sup> The latter two studies involved a variance to the methodology than the present study that could account for these differences.

Due to the recent market entrance of both Equia Forte and Ketac Universal, little reports in the scientific literature can be found. Due to modifications in the composition the material, the manufacturer states that the physical properties of Ketac Universal are improved compared to previous 3M/ESPE conventional GI restorative materials. Under the conditions of this study significant differences in the physical properties evaluated between Ketac Universal and Ketac Molar were apparent for flexural strength and modulus with no difference being found for fracture toughness at 6 months. Furthermore, the small magnitude of difference observed would most likely not be of clinical significance. Similarly, the physical property results found with Equia Forte does not appear to dramatically differ from that reported for its predecessor product, Equia.<sup>29, 30, 33</sup>

Although the physical properties investigated in this study are unlikely to be clinically significant, manufacture claims of improved handling properties were not evaluated and should be the subject of future studies. To further add support to the ongoing improvement of newly developed glass ionomer

restorative products a direct comparison should be made between Equia Forte and its predecessor Equia.

## Conclusions

Under the conditions of this study manufacturer claims in physical property enhancement with both Equia Forte and Ketac Universal as compared to predecessor products were not largely supported in this evaluation. Although significant changes with some materials evaluated were noted, the small magnitude of these changes would unlikely be of clinical significance.

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## Bibliography

1. Wilson AD, Kent BE. The glass-ionomer cement, a new translucent dental filling material. *J Appl Chem* 1971;21:313.
2. Nicholson JW. Adhesion of glass-ionomer cements to teeth: A review. *Int J Adhes Adhes* 2016; <http://dx.doi.org/10.1016/j.jadhadh.2016.03.012>
3. Frankenberger R, Sindel J, Kramer N. Viscous glass-ionomer cements: a new alternative to amalgam in the primary dentition? *Quintessence Int* 1997;25:667-76
4. Yoshida Y, Van Meerbeek B, Nakayama T, Snauwaert J, Hellemans L, Lambrechts P, *et al.* (2000). Evidence of chemical bonding at biomaterial-hard tissue interfaces. *J Dent Res* 79:709-714
5. Fukuda R, Yoshida Y, Nakayama Y, Okazaki M, Inoue S, Sano H, Suzuki K, Shintani H, Van Meerbeek B. (2003) Bonding efficacy of polyalkenoic acids to hydroxyapatite, enamel, and dentin. *Biomaterials* 2003;24:1861-1867.
6. Nicholson JW. Chemistry of glass-ionomer cements: a review. *Biomaterials* 1998;19:485-94.
7. Young AM. FTIR investigation of polymerization [sic] and polyacid neutralization kinetics in resin-modified glass-ionomer dental cements. *Biomater* 2002;23: 3289-3295.
8. Young A, Sherpa G, Pearson B, Schottlander, Waters DN. Use of Raman Spectroscopy in the Characterisation of the Acid-Base Reaction in Glass-Ionomer Cements. *Biomaterials* 2000;21:1971-9.
9. Stamboulis A, Matsuya S, Hill RG, Law RV, Udoh K, Nakagawa M, Matsuya Y. MAS-NMR spectroscopy studies in the setting reaction of glass ionomer cements. *J Dent* 2006;34:574-581.
10. Wren AW, Kidari A, Cummins NM, Towler MR. A spectroscopic investigation into the setting and mechanical properties of titanium containing glass polyalkenoate cements. *J Mater Sci: Mater Med* 2010;21:2355-2364.
11. Wan ACA, Yap AUJ, Hastings GW. Acid-base complex reactions in resin-modified and conventional glass ionomer cements. *J Biomed Res (Appl Biomater)* 1999;48:700-704.
12. Zainuddin N, Karpukhina N, Hill RG, Law RV. A long-term study on the setting reaction of glass ionomer cements by <sup>27</sup>Al MAS-NMR spectroscopy. *Dent Mater* 2009;25:290-5
13. Baig MS, Fleming GJP. Conventional glass-ionomer materials: A review of the developments in glass powder, polyacid liquid and the strategies of reinforcement. *J Dent* 2015;42:897-912.
14. Khoroushi M, Keshani F. A review of glass-ionomers: From conventional glass-ionomer to bioactive glass-ionomer. *Dent Res J (Isfahan)* 2013;10:411-420.
15. Bonifácio CC, Kleverlaan CJ, Raggio DP, Werner A, de Carvalho RCR, van Amerongen. Physical-mechanical properties of glass ionomer cements indicated for atraumatic restorative treatment. *Aus Dent J* 2009;54:233-237.

16. de Amorim RG, Leal SC, Mulder J, Creugers NHJ, Frencken JE. Amalgam and ART restorations in children: a controlled clinical trial. *Clin Oral Invest* 2014;18:117–124.
17. Cefaly DFG, Tapety CMC, Mondelli RFL, Lauris JRP, Phantumvanit P, Navarro MFL. Three-Year Evaluation of the ART Approach in Class III and V Restorations in Permanent Anterior Teeth. *Caries Res* 2006;40:389-392.
18. Frencken JE, van't Hof MA, van Amerongen WE, Holmgren CJ. Effectiveness of Single-surface ART Restorations in the Permanent Dentition: A Meta-analysis. *J Dent Res* 2004;83:12-123.
19. da Mata C, Allen PF, McKenna G, Cronin C, O'Mahony D, Woods N. Two-year survival of ART restorations placed in elderly patients: A randomised controlled clinical trial. *J Dent* 2015;43:405-411.
20. Faccin ES, Ferreira SH, Kramer PF, Ardenghi TM, Feldens CA. Clinical performance of ART restorations J. Frencken JE. The ART approach using glass-ionomers in relation to global oral health care. *Dent Mater* 2010;26:1-6.
21. Rutar J, Mcallan L, Tyas MJ. Three-year clinical performance of glass ionomer cement in primary molars. *Int J Paediat Dent* 2002;12:146–147.
22. Fagundes TC, Barata THE, Bresciani E, Santiago SL, Franco EB, Lauris JRP, Navarro MF. Seven-year clinical performance of resin composite versus resin-modified glass ionomer restorations in noncarious cervical lesions. *Oper Dent* 2014;39:578-587.
23. Qvist V, Manscherb E, Teglers PT. Resin-modified and conventional glass ionomer restorations in primary teeth: 8-year results. *J Dent* 2004; 32:285–294.
24. ISO 9917-2:2010. Water Based Cements – Part 2: Resin-modified cements. International Organization for Standardization, Geneva, Switzerland.
25. Billington R, Williams J, Pearson GJ. Variation in powder/liquid ratio of a restorative glass-ionomer cement used in general dental practice. *Brit Dent J* 1990;168:164-167.
26. Dowling AH, Fleming GJP. Are encapsulated anterior glass-ionomer restoratives better than their hand-mixed equivalents? *J Dent* 2009;37:133-140.
27. Ferracane JW. Resin-based composite performance: Are there some things we can't predict? *Dent Mater* 2013;29:51-58.
28. Prosser HJ, Powis DR, Brant P, Wilson AD. Characterization of glass-ionomer cements. 7. The physical properties of current materials. *J Dent* 1984;12:231-40.
29. Yamazaki T, Schricker SR, Brantley WA, Culbertson BM, Johnston WJ. Viscoelastic behavior and fracture toughness of six glass-ionomer cements. *J Dent Res* 2005;96:266-72.
30. Xie D, Brantley WA, Culbertson BM, Wang G. Mechanical properties and microstructures of glass-ionomer cements. *Dent Mater* 2000;16:129-38.
31. Wren AW, Coughlan A, Laffir FR, Towler MR. Comparison of a SiO<sub>2</sub>-CaO-ZnO-SrO glass polyalkenoate cement to commercial dental materials: glass structure and physical properties. *J Mater Sci: Mater Med* 2013;27:1-280.

32. Al-Angari SS, Hara AT, Chu T, Platt J, Eckert G, Cook NB. Physicomechanical properties of a zinc-reinforced glass ionomer restorative material. *J Oral Sci* 2014;56:11-16.

33. Ilie N, Hickel R, Valceanu AS, Huth KC. Fracture toughness of dental restorative materials. *Clin Oral Invest* 2012;16:489-498.