



Physical property investigation of contemporary glass ionomer and resin-modified glass ionomer restorative materials

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Received: 24 July 2017 / Accepted: 2 July 2018 / Published online: 11 July 2018
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Abstract

Objectives The objective of this study was to investigate selected physical properties of nine contemporary and recently marketed glass ionomer cement (GIC) and four resin-modified glass ionomer cement (RMGI) dental restorative materials.

Materials and methods Specimens ($n = 12$) were fabricated for fracture toughness and flexure strength using standardized, stainless steel molds. Testing was completed on a universal testing machine until failure. Knoop hardness was obtained using failed fracture toughness specimens on a microhardness tester, while both flexural modulus and flexural toughness was obtained by analysis of the flexure strength results data. Testing was completed at 1 h, 24 h, 1 week, and then at 1, 3, 6, and 12 months. Mean data was analyzed with Kruskal-Wallis and Mann-Whitney ($p = 0.05$).

Results Physical properties results were material dependent. Physical properties of the GIC and RMGI products were inferior at 1 h compared to that at 24 h. Some improvement in selected physical properties were noted over time, but development processes were basically concluded by 24 h. A few materials demonstrated improved physical properties over the course of the evaluation.

Conclusions Under the conditions of this study:

1. GIC and RMGI physical property performance over time was material dependent;
2. Polyalkenoate maturation processes are essentially complete by 24 h;
3. Although differences in GIC physical properties were noted, the small magnitude of the divergences may render such to be unlikely of clinical significance;
4. Modest increases in some GIC physical properties were noted especially flexural modulus and hardness, which lends support to reports of a maturing hydrogel matrix;
5. Overall, GIC product physical properties were more stable than RMGI;
6. A similar modulus reduction at 6 months for both RMGI and GIC produced may suggest a polyalkenoate matrix change; and
7. Globally, RMGI products demonstrated higher values of flexure strength, flexural toughness, and fracture toughness than GIC materials.

Clinical relevance As compared to RMGI materials, conventional glass ionomer restorative materials demonstrate more stability in physical properties.

Keywords Polyalkenoate · Glass ionomer · Resin modified glass ionomer · Hydrogel matrix · Physical property testing

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s00784-018-2554-3>) contains supplementary material, which is available to authorized users.

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Introduction

Glass ionomer cements (GIC) were invented and developed by Wilson and Kent in the early 1970s to overcome shortcomings associated with silicate restorative cements [1, 2]. GIC restorative materials generally consist of a mixture of various polyalkenoate (polyacrylic) acids and tartaric acid that react with a fluoroaluminosilicate glass. The acid-base setting reaction between the acid and the glass surface liberates metal cations that allows crosslinking between the polyalkenoate chains [3, 4], with additional maturation beyond 24 h consisting of continued polymer chain cross linking and hydrogel matrix maturation formation with physical property improvement [5–8]. GICs are self-adhesive materials that bond to tooth hard tissues through chemical bonding, consisting of ionic bonds between polyalkenoate acid carboxyl groups and enamel and dentin hydroxyapatite in enamel and dentin [9, 10]. GIC restorative materials have been improved with formulation changes to enhance physical properties and clinical handling characteristics [4, 11, 12]. These modifications have included the use of alternative polyacids [4, 13, 14], water-activated dehydrated polyacid powders [4, 13, 15], cermets [16], metal additions [17–19], smaller glass particle size [20], antibacterial agents [21, 22], novel glass compositions [13, 23], and most recently aluminum-free glasses [24].

Resin-modified GICs (RMGICs) were first developed as bases and liners but were soon further modified to serve as direct restorative materials, hopefully to overcome early moisture sensitivity and lower mechanical properties associated with the GIC restoratives of that era [10, 25, 26]. Similar to GIC materials, RMGICs contain not only an acid-base reaction but also a resin free radical polymerization [10, 27, 28]. The resin content is added either with a direct monomer addition such as 2-hydroxyethyl methacrylate (HEMA) or uniquely grafted on the polyalkenoate acid chain. These monomers polymerize either by visible light curing (VLC) photo activation or an internal chemical reaction [10, 26]. RMGI materials also demonstrate bonding to tooth structure, as demonstrated by X-ray photoelectron spectroscopy and infrared spectroscopy as well as hybrid layer micromechanical interlocking similar to, but not to the same extent as resin adhesive systems [29–33]. Although the exact composition of each GIC and RMGI material is generally proprietary, the polymerized resin composition in the early RMGI products was earlier estimated to be approximately 4.5–6% [34]. Unfortunately, the resin and polyalkenoate setting reactions compete as the resin retards the polyalkenoate reaction by stereo-chemical distortion of the polyalkenoate acid chains making reaction sites less available. Furthermore, RMGIs contain less water for the polyalkenoate reaction to proceed as resin is added at the expense of water [9, 35–37].

Glass ionomer setting reactions have been investigated by several different methods to include infrared spectroscopy

[38], Raman spectroscopy [39], NMR spectroscopy [40], pH measurements [41], rheology [42, 43], dielectric spectroscopy [44–47], inductively coupled plasma optical emission spectroscopy (ICP-OES) [48], and thermal analysis techniques [49]. Although some laboratory novel GIC formulations have shown the capacity for continuation of the acid-base reaction [27], it has been established by different analysis methods that the GIC polyalkenoate acid-base reaction is essentially complete by 24 h [19, 27, 38, 40, 50]. However, the continued changes in both the organic and inorganic GIC matrix past 24 h remains a source of interest as some GIC products continue to display an increase in physical properties with time [51–54]. The initial setting reaction and subsequent matrix formation is a multifaceted phenomenon, while Nicholson [4] relates the possibility of an intermediary phase that may influence in the timing of these processes. Moreover, Dickey et al. [55] recently reported evidence of a complex intermediary phase that delayed polyalkenoate crosslinking, but this was only observed to be particular to the glasses used. After acid-base reaction completion, both Stamboulis et al. [40] and Zainuddin et al. [56] reported the formation of a network and a hydrated silica gel phase, consisting of either a pure silicate or a mixed silicate phosphate matrix that contributed to physical property improvement with continued matrix maturation [6].

Both GIC and RMGI materials have displayed excellent clinical performance with atraumatic restoration treatment (ART) [57–62], as well as definitive restorations in both primary and permanent teeth [63–71]. Several GIC and RMGI restorative products have been recently marketed but lack independent verification of reported physical properties. The purpose of this study was to evaluate selected physical properties, namely flexural strength, flexural modulus, Knoop hardness, fracture toughness, flexural toughness and resiliency of newer GIC, and RMGI restorative materials compared with materials that have enjoyed marketing tenure. The null hypotheses were that there will be no difference in the physical properties between the tested restorative materials.

Materials and methods

The restorative materials used in this study were comprised of four RMGI products and nine GIC products and are listed in Tables 1 and 2, respectively. Twelve specimens were fabricated for each test. Fracture toughness and flexural strength specimens were fabricated using standardized, stainless steel molds (Sabri Dental Enterprises, Downers Grove, IL, USA) whose exact dimensions are described in each particular test. Materials were placed into respective molds on a mylar strip-covered glass slab with a second mylar strip placed on top of the filled mold. A glass microscope slide was then placed over the top mylar strip and digital pressure was applied to form a uniformly flat surface. GIC materials were allowed to set for

Table 1 RMGI restorative products

Material	Manufacturer	Powder/liquid ratio (g/g)	Powder content	Liquid content
Fuji II LC Capsules	GC America (Alsip, IL, USA)	0.33/0.10	Trade secret	HEMA 25–50% Polybasic carboxylic acid 5–10% UDMA 1–5% Dimethacrylate 1–5%
Ketac Nano Quick Mix Capsules	3 M ESPE (St. Paul, MN, USA)	N/A	Paste A: Silane-treated glass 0–55% Silane-treated zirconia 0–30% PEGDMA 5–15% Silane-treated silica 5–15% HEMA 1–15% BISGMA < 5% TEGDMA < 1%	Paste B: Silane-treated ceramic 40–60% Copolymer of acrylic and Itaconic acids 20–30% Water 10–20% HEMA 1–10%
Riva LC Capsules	SDI Limited (Bayswater, Victoria, AUS)	0.42/0.14	Fluoroaluminosilicate glass powder 95–100%	Polyacrylic acid 15–25% Tartaric acid 1–5% HEMA 20–30% Dimethacrylate cross-linker 10–25% Acidic monomer 10–20%
Riva LC HV Capsules	SDI Limited	0.47/0.14	Fluoroaluminosilicate glass powder 95–100%	Polyacrylic acid 15–25% Tartaric acid 1–5% HEMA 15–25% Dimethacrylate cross-linker 10–25% Acidic monomer 10%

Content information obtained from manufacturer information

BISGMA bisphenol A diglycidyl ether dimethacrylate, *HEMA* 2-hydroxyethyl methacrylate, *PEGDMA* polyethylene glycol dimethacrylate, *TEGDMA* triethylene glycol dimethacrylate, *UDMA* urethane dimethacrylate

the manufacturer recommended setting time in an oven at 35 °C. RMGI materials were polymerized using a light-emitting-diode (LED) visible-light-curing (VLC) unit (Bluephase G2, Ivoclar-Vivadent, Amherst, NY, USA) for 20 s in an overlapping fashion on both sides. The performance of the VLC unit was periodically assessed (~1000 mw/cm²) using a laboratory-grade laser power meter (10A-V1, Ophir-Spiricon, North Logan, UT, USA). Specimens were removed from the respective molds and refined as needed using surgical scalpel blades removing any flash material from the edges. Specimens were then stored under dark conditions in a 0.2 M physiologic phosphate-buffered saline environment at 37 °C and 98 ± 1% humidity until testing. Testing occurred at 1 h, 24 h, 1 week, and then at 1, 6, and 12 months after fabrication.

Flexure strength specimens were formed in a 2 × 2 × 25 mm stainless steel mold (Sabri Dental Enterprises) as formerly described and were tested on a three-point bend apparatus mounted on a universal testing machine (Alliance RT/5, MTS Corporation, Eden Prairie, MN, USA). Specimens were stressed using a cross head speed of 0.5 mm/min until failure with the maximum force recorded. Flexure strength results was determined using the formula $F = 3FI/2bh^2$, where F = maximum load recorded (N), I = distance between supports (mm), b = width of specimen (mm), and h = height of specimen (mm). Flexural modulus was determined using the slope of the linear portion of the flexure strength stress-strain curve while flexural

toughness was determined from the same data by integrating the area under the entire flexural testing stress/strain curve. Fracture toughness specimens were fabricated as described earlier using a stainless steel mold 2 × 5 × 25 mm in accordance with the single edge notch beam method as described in ASTM Standard E399. Each specimen's dimensions were measured in three equally spaced positions along the specimen with the mean recorded. Testing occurred in a three-point bend apparatus with a crosshead speed of 0.5 mm/min in a universal testing machine (Alliance RT/5) until failure. The true notch length was measured post-testing with a digital measuring microscope (Hirox 7700, Hirox USA, Hackensack, NJ, USA). The fracture toughness calculation was accomplished using the following equation: $K_{IC} = (3PLa^{1/2}/2tw^2) \times f(a/w)$ where P = failure load (N), L = distance between the support rollers (mm), a = measured notch length (mm), t = specimen thickness (mm), w = specimen width (mm), and $f(a/w) = 1.93 - 3.07(a/w) + [14.53(a/w)^2 - 25.11(a/w)^3] + 25.80(a/w)^4$. Surface hardness was determined using post-testing fracture toughness specimens ($n = 12$). Eleven Knoop hardness (KH) indentations were made taken in an alternating fashion over a 5.25-mm distance with 0.5 mm spacing between indentations using a microhardness tester (OmniMet MHT, Buehler Manufacturing, Inc., Lake Bluff, IL, USA) using a 100-g load and a dwell time of 10 s. Indentations were measured under 50× magnification with the representative specimen hardness determined by the mean of

Table 2 GIC restorative products

Material	Manufacturer	Powder/liquid ratio (g/g)	Powder content	Liquid content
Chemfil Rock Capsules	Dentsply International, (York, PA, USA)	— ^a	Polycarboxylic acid 10–25%	Polycarboxylic acid 10–25% Tartaric acid 2.5–10%
Equia	GC America (Alsip, IL, USA)	0.40/0.12	Trade secret	Trade secret
Fuji Triage Capsules	GC America	0.30/0.15	Trade secret	Trade secret
Ketac Molar Quick Aplicap	3M ESPE (St. Paul, MN, USA)	— ^a	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%
Ketac Silver Aplicap	3M ESPE	— ^a	Silver 45–55% Oxide glass chemicals 40–50% Titanium dioxide 1–5% Copper < 0.01	Water 40–60% Copolymer of acrylic acid-maleic acid 30–50% Tartaric acid 5–15%
Riva Protect Fast Capsules	SDI Limited, (Bayswater, Victoria, AUS)	0.34/0.19	Fluoro aluminosilicate glass 90% Polyacrylic acid 10%	Polyacrylic acid 25% Tartaric acid 10%
Riva Self Cure Fast Capsules	SDI Limited	0.40/0.15	Fluoro aluminosilicate glass 90–95% Polyacrylic acid 5–10%	Polyacrylic acid 20–30% Tartaric acid 10–15%
Riva Self Cure High Viscosity Capsules	SDI Limited	0.50/0.13	Fluoro aluminosilicate glass 90–95% Polyacrylic acid 5–10%	Polyacrylic acid 20–30% Tartaric acid 10–15%
Riva Silver Capsules	SDI Limited	0.72/0.14	Fluoro aluminosilicate powder 40–60% Polyacrylic acid < 10% Alloy powder 30–50%	Polyacrylic acid 30% Tartaric acid 10% Balance ingredient 60%

Content information obtained from manufacturer information

^a Not available from manufacturer information

the 11 calculated measurements. A total of 12 specimens were tested for each material, with the mean of the samples representing sample mean. All property mean testing results were submitted first to the Shapiro-Wilk and Bartlett's test, which identified irregularities in both the distribution and variance within the mean data. Therefore, the data was analyzed using Kruskal-Wallis with Dunn's post hoc testing performed with a 95% level of confidence ($p = 0.05$). Statistical analysis was performed using SPSS 21 (IBM/SPSS, Chicago, IL, USA).

Results

The GIC physical property testing mean results are listed in Tables 3, 4, 5, 6 and 7. The mean flexure strength results are presented in Table 3. All GIC products gained flexure strength between 1 and 24 h but increases with both Equia and Ketac Molar Quick were not significant. Fuji Triage, Ketac Molar Quick, Riva Self Cure Fast, Riva Self Cure HV, and Riva Silver attained highest flexure strength values at 1 week, while

Table 3 GIC mean flexure strength (MPa)

	1 h	24 h	1 week	1 month	3 months	6 months	12 months
Chemfil Rock Rock	16.5 (4.6) B a	33.6 (6.4) E cd	27.4 (3.1) B b	34.8 (6.3) C cd	33.8 (6.3) C cd	38.6 (5.9) D d	32.1 (5.7) BC bc
Equia	17.4 (5.7) B a	26.8 (4.7) CD ab	19.8 (5.07) A ab	27.16 (3.4) AB ab	31.4 (5.3) BC b	24.0 (3.0) A a	30.7 (5.9) ABC b
Fuji Triage	10.3 (5.3) A a	19.8 (4.9) AB b	26.4 (6.0) B c	24.3 (4.3) A bc	24.5 (5.0) A bc	23.2 (4.3) A bc	26.1 (6.0) AB c
Ketac Molar Quick	18.6 (5.4) B a	21.6 (7.6) ABC a	29.6 (6.6) BC b	32.3 (6.7) C b	31.4 (5.2) BC b	30.5 (6.7) BC b	30.3 (3.5) ABC b
Ketac Silver	9.8 (2.1) A a	26.2 (5.4) BCD bc	25.4 (5.7) AB b	31.2 (3.3) BC d	30.1 (3.3) BC cd	26.4 (3.0) AB bc	29.5 (5.3) ABC bcd
Riva Protect	8.8 (4.2) A a	18.0 (4.4) A b	19.4 (5.4) A bc	24.4 (3.6) A d	23.4 (4.5) A cd	24.2 (4.1) A cd	24.6 (6.0) A d
Riva Self Cure Fast	17.7 (4.2) B a	28.8 (4.0) DE bc	33.7 (5.0) CD d	31.6 (4.4) BC bcd	28.2 (4.2) AB b	32.7 (6.0) C bcd	33.2 (3.3) C cd
Riva Self Cure HV	19.7 (4.4) B a	25.7 (6.3) BCD b	37.5 (5.5) D e	33.8 (3.3) C de	32.5 (3.2) BC cd	29.6 (3.5) BC bcd	28.1 (4.6) ABC bc
Riva Silver	9.4 (3.3) A a	28.9 (6.7) DE b	33.7 (4.0) CD c	33.6 (3.0) C c	34.3 (4.3) C c	32.7 (4.2) C bc	30.9 (4.8) ABC c

$n = 12$; capital letters annotate similar groups by column, small letters by row (Kruskal-Wallis/Dunn's $p = 0.05$)

Table 4 GIC mean flexural modulus (GPa)

	1 h	24 h	1 week	1 month	3 months	6 months	12 months
Chemfil Rock	4.8 (0.4) BC a	9.02 (0.5) CD cd	7.68 (1.05) AB b	8.45 (1.1) B bc	8.53 (1.1) A bc	10.48 (1.8) BC d	9.9 (1.3) A d
Equia	4.8 (1.2) B a	9.7 (1.5) D c	7.5 (1.1) AB b	10.9 (1.9) CDE c	14.67 (1.2) D d	10.3 (1.1) BC c	12.2 (2.2) B d
Fuji Triage	3.1 (0.6) A a	7.8 (0.5) B b	8.4 (1.4) BC b	9.0 (0.9) AB bc	10.0 (2.0) AB c	10.2 (1.0) B c	10.2 (1.6) A c
Ketac Molar Quick	6.9 (0.8) D a	11.1 (0.8) E b	12.5 (1.7) D cd	10.2 (1.7) BC bc	12.2 (1.7) C bc	11.4 (1.2) CD bc	11.4 (1.4) AB bc
Ketac Silver	5.6 (0.6) C a	8.0 (1.7) BC b	9.5 (1.1) C cd	10.6 (0.6) CD d	9.8 (1.1) A cd	8.4 (0.9) A bc	10.9 (2.4) AB d
Riva Protect	2.9 (0.5) A a	5.6 (0.9) A b	6.8 (1.0) A c	8.1 (0.9) A d	8.8 (0.9) A de	8.1 (0.9) A d	9.5 (0.1) A e
Riva Self Cure Fast	6.5 (0.6) D a	9.3 (0.8) D b	11.5 (1.1) D c	12.2 (0.6) E c	11.4 (1.7) BC c	11.9 (0.8) D c	12.2 (1.1) B c
Riva Self Cure HV	8.2 (0.9) D a	11.1 (0.9) E b	12.7 (1.1) D cd	12.2 (1.5) E bc	12.3 (1.2) C bc	13.6 (0.8) E d	12.2 (1.5) B bc
Riva Silver	5.5 (0.9) BC a	9.9 (.7) D b	11.9 (1.0) D c	11.6 (1.0) DE c	11.6 (1.2) BC c	10.0 (0.7) B b	10.0 (0.5) A b

n = 12; capital letters annotate similar groups by column, small letters by row (Kruskal-Wallis/Dunn *p* = 0.05)

Chemfil Rock, Riva Protect, and Ketac Silver required 1 month to attain maximum flexure strength. These flexure strength values, despite some fluctuations, were essentially maintained for the remainder of the evaluation.

All GIC materials demonstrated modulus increase between 1 and 24 h (Table 4). Ketac Molar Quick, Ketac Silver, Riva Self Cure Fast, Riva Self Cure HV, and Riva Silver reached maximum modulus values at 1 week that was maintained at 12 months. Only Chemfil Rock and Riva Protect displayed a continual modulus improvement in which Chemfil Rock attained maximum modulus at 6 months, while Riva Protect demonstrated a slow modulus increase up to 12 months.

All GIC materials except for Equia, Ketac Molar Quick, and Riva Self Cure HV demonstrated a significant flexural toughness increase between 1 and 24 h (Table 5). Thereafter, material performance was individual achieving significant maximum toughness either at 1 week (Fuji Triage; Riva Self Cure Fast) or at 1 month (Chemfil Rock; Ketac Molar Quick; Ketac Silver). Interestingly, Equia displayed no toughness change beyond that observed at 1 h while the toughness of Riva Protect was stable after 24 h. All GIC materials demonstrated significant increase in hardness between 1 and 24 h (Table 6). However, Chemfil Rock, Equia, Riva Self Cure

Fast, Riva Self Cure HV, and Riva Silver did not demonstrate any difference in hardness between the hardness established at 24 h and that observed at 12 months. Only Fuji Triage, Ketac Molar Quick, Ketac Silver, and Riva Protect manifested hardness increases beyond 24 h that was maintained at 12 months. Fracture toughness mean results are presented in Table 7. The fracture toughness of Chemfil Rock, Equia, Ketac Molar Quick, Riva SC Fast, and Riva Self Cure HV did not demonstrate any significant change over 12 months from that seen at 1 h. Fuji Triage, Ketac Silver, Riva Protect, and Riva Silver demonstrated increases in fracture toughness, with both Fuji Triage and Ketac Silver increasing in fracture toughness up to 12 months. Riva Protect achieved maximum fracture toughness at 1 week while Riva Silver fracture toughness reached maximum values at 6 months.

The RMGI restorative mean physical property results are displayed in Tables 8, 9, 10, 11, and 12. All RMGI materials demonstrated significant flexure strength increase between 1 and 24 h (Table 8). However, both Fuji II LC (after 24 h) and Ketac Nano (after 1 week) displayed progressive flexure strength decline over the 12-month evaluation. Both Riva LC and Riva LC HV acquired maximum flexure strength at 1 month that remained stable thereafter. Table 9 reveals that all

Table 5 GIC mean flexural toughness (mJ/mm³)

	1 h	24 h	1 week	1 month	3 months	6 months	12 months
Chemfil Rock	0.034 (0.02) BC a	0.065 (0.02) C bc	0.065 (.03) C bc	0.078 (0.02) C c	0.072 (0.02) C bc	0.075 (0.03) C bc	0.054 (0.02) C ab
Equia	0.039 (0.02) Ca	0.041 (0.02) ABa	0.03 (0.01) Aa	0.036 (0.01) Aa	0.036 (0.02) ABa	0.030 (0.01) A a	0.042 (0.01) ABC a
Fuji Triage	0.022 (0.02) ABC a	0.021 (0.01) AB b	0.042 (0.01) ABC c	0.035 (0.01) A bc	0.033 (0.02) A bc	0.029 (0.02) A bc	0.036 (0.01) AB c
Ketac Molar Quick	0.030 (0.01) BC ab	0.022 (0.01) A a	0.039 (0.02) AB a bc	0.055 (0.02) B c	0.047 (0.02) AB bc	0.047 (0.03) AB bc	0.044 (0.01) ABC bc
Ketac Silver	0.01 (0.001) A a	0.044 (0.01) B bc	0.036 (0.02) AB b	0.047 (0.005) AB c	0.050 (0.01) AB c	0.043 (0.01) AB bc	0.044 (0.01) ABC bc
Riva Protect	0.019 (0.01) ABa	0.032 (0.01) ABb	0.046 (0.04) ABC b	0.039 (0.01) AB ab	0.034 (0.01) AB ab	0.038 (0.009) AB ab	0.036 (0.01) AB ab
Riva Self Cure Fast	0.026 (0.01) ABC a	0.044 (0.01) B bc	0.056 (0.01) BC c	0.048 (0.01) AB bc	0.037 (0.01) AB ab	0.047 (0.02) AB bc	0.051 (0.01) BC bc
Riva Self Cure HV	0.024 (0.01) ABC a	0.030 (0.01) ABa	0.059 (0.02) BC b	0.052 (0.01) B b	0.048 (0.01) ABb	0.03 (0.006) A a	0.033 (0.01) A a
Riva Silver	0.012 (0.006) A a	0.044 (0.02) B b	0.054 (0.01) ABC c	0.050 (0.01) AB c	0.053 (0.01) B c	0.055 (0.02) B c	0.054 (0.01) C c

n = 12; capital letters annotate similar groups by column, small letters by row (Kruskal-Wallis/Dunn’s *p* = 0.05)

Table 6 GIC mean hardness (KHN)

	1 h	24 h	1 week	1 month	3 months	6 months	12 months
Chemfil Rock	12.6 (3.0) A a	37.4 (5.4) B c	31.0 (5.3) A b	39.6 (3.2) A cd	43.5 (7.0) A d	43.7 (7.7) AB d	41.4 (2.5) A cd
Equia	18.7 (5.0) AB a	50.3 (5.7) C c	41.5 (5.4) B b	43.7 (7.7) AB bc	52.2 (5.5) BCD c	53.6 (5.3) BC c	53.2 (4.9) C c
Fuji Triage	17.7 (3.3) A a	29.6 (8.1) A b	40.3 (3.5) B c	47.4 (4.3) ABC de	52.4 (5.4) BCD e	48.1 (6.7) ABC de	44.4 (2.2) AB cd
Ketac Molar Quick	19.6 (6.2) AB a	53.3 (1.8) C bc	57.7 (11.7) C bc	46.8 (11.6) ABC b	53.7 (5.2) CD bc	53.6 (8.5) C bc	59.8 (2.4) D d
Ketac Silver	18.2 (6.0) AB a	33.8 (3.1) AB b	30.4 (3.9) A b	41.5 (8.0) A c	46.9 (4.3) AB cd	48.2 (5.0) ABC d	48.4 (4.7) BC d
Riva Protect	14.0 (3.3) A a	29.0 (2.9) A b	39.4 (2.4) B c	42.8 (4.0) A c	42.1 (5.6) A c	44.9 (5.9) ABC c	41.2 (3.7) A c
Riva Self Cure Fast	25.5 (8.0) B a	52.6 (7.0) C bc	61.4 (3.3) C d	54.4 (5.3) C cd	56.3 (5.2) D cd	45.9 (9.4) ABC b	52.4 (5.1) C bc
Riva Self Cure HV	25.5 (6.3) B a	52.1 (7.5) C b	46.2 (5.7) B b	52.1 (4.5) BC b	50.8 (4.1) BCD b	47.1 (4.0) ABC b	48.5 (4.1) BC b
Riva Silver	18.6 (6.3) AB a	46.7 (6.4) C b	40.4 (12.0) B b	42.5 (7.2) A b	47.8 (3.5) ABC b	40.4 (2.1) A b	42.3 (1.4) A b

$n = 12$; capital letters annotate similar groups by column, small letters by row (Kruskal-Wallis/Dunn's $p = 0.05$)

RMGI materials exhibited significant modulus increase between 1 and 24 h, while Riva Self Cure HV demonstrated significant modulus improvement at 1 week. For flexural toughness (Table 10), both Fuji II LC and Ketac Nano mirrored the flexural modulus results with early maximum values that thereafter declined while Riva LC HV also demonstrated toughness diminution but only after 1 month. Only Riva LC demonstrated toughness increase that was significantly greatest at 6 months and stable afterward. When considering hardness (Table 11), both Fuji II LC and Ketac Nano displayed highest hardness values at 1 h. Subsequently, Fuji II LC subsequently displayed decay of hardness values while Ketac Nano remained stable. Riva LC increased hardness values up to 1 month while Riva LC HV reached its maximum stable hardness at 6 months. RMGI fracture toughness mean values can be seen in Table 12. The fracture toughness of both Fuji II LC and Ketac Nano were greatest at 1 h after which Fuji II LC exhibited declining fracture toughness while Ketac Nano remained stable after 24 h. The fracture toughness of Riva LC HV did not significantly change between 1 h and 12 months, while Riva LC demonstrated a significant increase between 1 and 24 h that was stable thereafter.

Discussion

This study encompassed the physical properties of nine GIC and four RMGI restorative products over a 12-month period. This study not only included products that have had lengthy market tenure but also included newer materials, some of which have not been previously reported in the scientific literature. Only precapsulated materials were chosen for this study in order to eliminate variables introduced by manual hand-mixing of glass ionomer materials [72, 73]. In addition to evaluating recently marketed materials, this study is somewhat novel in that 0.2 M phosphate-buffered saline (PBS) was used as a storage media. PBS represents a physiologic as well as a slightly basic environment that has been suggested to promote hydrolysis of some dental resins [74] as well as being the recommended storage media suggested by ISO 9917 [75]. Also, physical property evaluation started at 1 h after specimen preparation, as the authors maintain that this would represent perhaps a more realistic testing time at when restorative materials might be first subjected to oral forces.

Flexure testing encompasses both compressive and tensile force components and is considered a more discriminating and

Table 7 GIC mean fracture toughness (MPa \sqrt{m})

	1 h	24 h	1 week	1 month	3 months	6 months	12 months
Chemfil Rock	0.26 (0.02) BC a	0.3 (0.03) CD a	0.3 (0.04) D a	0.28 (0.05) DE a	0.27 (0.02) B a	0.26 (0.03) B a	0.28 (0.03) CD a
Fuji IX EXTRA	0.22 (0.04) B a	0.20 (0.04) A a	0.22 (0.03) A a	0.2 (0.02) A a	0.2 (0.04) A a	0.22 (0.03) A a	0.22 (0.03) A a
Fuji Triage	0.15 (0.02) A a	0.18 (0.02) A b	0.21 (0.01) A c	0.22 (0.02) AB cd	0.21 (0.01) A cd	0.22 (0.02) A cd	0.23 (0.02) AB d
Ketac Molar Quick	0.26 (0.03) BC b	0.27 (0.04) BC b	0.26 (0.03) BCD b	0.24 (0.03) C ab	0.21 (0.05) A a	0.22 (0.03) A a	0.26 (0.03) ABC a
Ketac Silver	0.23 (0.04) B a	0.26 (0.02) B b	0.27 (0.03) CD b	0.29 (0.03) CD cd	0.28 (0.02) BC bc	0.27 (0.03) B bc	0.31 (0.03) D d
Riva Protect	0.13 (0.04) A a	0.2 (0.02) A b	0.23 (0.02) AB c	0.22 (0.02) AB bc	0.23 (0.03) A bc	0.22 (0.01) A bc	0.23 (0.02) AB bc
Riva Self Cure Fast	0.25 (0.07) BC a	0.27 (0.03) BC ab	0.28 (0.02) CD ab	0.27 (0.02) CD ab	0.31 (0.02) C b	0.29 (0.02) BC ab	0.27 (0.08) BCD ab
Riva Self Cure HV	0.28 (0.07) C a	0.3 (0.02) D a	0.27 (0.04) CD a	0.3 (0.02) D a	0.3 (0.03) BC a	0.31 (0.02) C a	0.28 (0.05) CD a
Riva Silver	0.21 (0.06) B a	0.28 (0.04) BCD b	0.26 (0.03) BC b	0.26 (0.03) CD b	0.27 (0.03) B b	0.35 (0.04) D c	0.32 (0.04) D bc

$n = 12$; capital letters annotate similar groups by column, small letters by row (Kruskal-Wallis/Dunn's $p = 0.05$)

Table 8 RMGI mean flexure strength (MPa)

	1 h	24 h	1 week	1 month	3 months	6 months	12 months
Fuji II LC	52.08 (6.0) B a	76.2 (5.4) C c	72.5 (8.3) B bc	76.7 (7.7) C c	63.2 (3.8) B b	59.3 (2.5) A b	61.5 (9.4) B b
Ketac Nano	32.0 (6.8) A a	49.3 (7.1) A b	61.3 (10.5) A c	48.5 (12.7) A b	49.2 (13.7) A b	64.7 (7.5) A c	46.3 (10.1) A b
Riva LC	29.1 (3.8) A a	55.5 (7.4) B b	59.2 (5.4) A bc	60.3 (6.5) B bc	60.8 (8.4) B bc	64.4 (6.1) A c	62.4 (4.5) B c
Riva LC HV	27.8 (4.7) A a	53.1 (4.4) AB b	59.6 (7.8) A cd	62.8 (4.2) B d	54.4 (10.3) AB bc	64.5 (4.6) A d	59.3 (5.1) B bcd

n = 12; capital letters annotate similar groups by column, small letters by row (Kruskal-Wallis/Dunn’s *p* = 0.05)

clinically relevant in vitro test [76, 77]. The GIC materials exhibited inferior flexure strength values at 1 h compared to that observed at 24 h at which time Chemfil Rock, Riva Silver, and Riva Self Cure fast demonstrated greater flexure strength than Ketac Molar Quick, Fuji Triage, and Riva Protect, with the other products being intermediary. Between 24 h and 1 week, physical property development significantly improved flexure strength for Fuji Triage, Ketac Molar Quick, Riva Self Cure Fast, Riva Self Cure HV, and Riva Silver. However, as after 24 h, Equia and Chemfil Rock flexure strength remained while up to 1 week the flexure strength of Fuji Triage, Ketac Molar Quick, Ketac Silver, Riva Self Cure Fast, and Riva Silver continued to increase, only Riva Protect, demonstrating further significant improvement to 1 month which subsequently stabilized. It could be reasonable to conjecture that the continued physical property development observed with these materials can be ascribed to matrix maturation. The flexure strength results in this study were similar to that reported by Hu et al. [78], but had higher values for Equia, Chemfil Rock, and Riva Self Cure than that from Zoergibel and Ilie [79], whose methodology differed from the present evaluation. Flexure strength values in this study for Riva Self Cure and Equia were similar to that reported by Bonifácio et al. [80] but lower for Ketac Molar Quick. Moreover, KetacMolar Quick findings were similar as that reported by Yamazaki et al. [81] while that of Ketac Molar and Ketac Silver were almost identical to that reported by Xie et al. [82]. A 1-h glass ionomer material physical properties study by Lucksanasombool et al. [83] reported flexural values higher than that found in this study, but those authors’ method varied from that accomplished in the present study.

RMGI products demonstrated a significant flexure strength increase between 1 and 24 h. Ketac Nano’s 12 month flexure

strength, albeit some variation, was similar to that observed at 24 h. Fuji II LC’s flexure strength displayed a reduction after 1 month that stabilized while only Riva LC and Riva LC HV demonstrated increased flexure strength behavior that did not deteriorate. The flexure strength trend noted in this evaluation is similar to that reported by Azillah et al. [53] who likewise reported a decline in Fuji II LC flexure strength after 100 days. However, it must be noted that the data are not directly comparable, as Azillah and colleagues used four-point-bend testing methodology [53]. Furthermore, this study’s results are greater than reported by Xie et al. [84] and Weng et al. [85], who used higher loading rates. Moreover, this study’s RMGI flexure strength values are similar to that reported by Yamazaki et al. [81] and nearly identical to that reported for Fuji II LC by Xie et al. [82] as well as Culbertson [86]. The graphical flexure strength results for both GIC and RMGI products are available in Supplemental Figs. 1 and 2, respectively.

The GIC products mean modulus results graphically can be viewed in Supplemental Fig. 3. Under the conditions of this study, flexural modulus was determined from the linear portion of the flexure strength stress-strain curve. GIC products demonstrated significant modulus increase up to 1 and 3 months (Chemfil Rock 6 months) that overall remained stable. Although the group variance was small, results would probably not be of clinical significance. This modest modulus increase lends further support of a matrix maturation process [6]. The modulus results for Ketac Molar Quick, Riva Self Cure Fast, Riva Self Cure HV, and Riva Silver agrees with an observation made by Wren et al. [52]. Contrary to the flexural strength trends, RMGI materials demonstrated significant modulus increases (Supplemental Fig. 4). The only exception was Riva LC, of which 24-h modulus values remained stable thereafter. RMGI modulus development deserves

Table 9 RMGI mean flexural modulus (GPa)

	1 h	24 h	1 week	1 month	3 months	6 months	12 months
Fuji II LC	5.0 (0.5) C a	7.2 (0.9) C cd	6.1 (0.3) B bc	8.1 (0.8) C e	6.8 (0.6) B cd	5.7 (0.5) B ab	7.6 (0.8) C de
Ketac Nano	2.8 (0.3) A a	4.0 (0.1) A b	4.6 (0.4) A c	4.4 (0.4) A c	5.0 (0.5) A de	4.7 (0.2) A cd	5.1 (0.4) A e
Riva LC	3.9 (0.1) B a	6.1 (0.5) B b	6.5 (0.3) B b	6.4 (0.6) B b	7.1 (0.7) B c	6.5 (0.6) C b	6.5 (0.9) B b
Riva LC HV	4.0 (0.2) B a	6.9 (0.7) C b	9.0 (0.8) C cd	8.5 (0.7) C c	8.9 (0.9) C cd	9.7 (0.7) D de	10.4 (1.0) D e

n = 12; capital letters annotate similar groups by column, small letters by row (Kruskal-Wallis/Dunn’s *p* = 0.05)

Table 10 RMGI mean flexural toughness (mJ/mm³)

	1 h	24 h	1 week	1 month	3 months	6 months	12 months
Fuji II LC	0.46 (0.2) B ab	0.55 (0.07) C b	0.53 (0.1) B b	0.45 (0.1) B b	0.38 (0.05) C a	0.4 (0.04) B a	0.29 (0.1) BC a
Ketac Nano	0.24 (0.1) A a	0.37 (0.1) B ab	0.53 (0.2) B c	0.39 (0.2) AB ab	0.28 (0.1) B a	0.54 (0.1) C c	0.25 (0.12) AB a
Riva LC	0.15 (0.05) A a	0.31 (0.08) AB b	0.30 (0.06) A b	0.33 (0.07) AB bc	0.29 (0.08) BC b	0.38 (0.09) B c	0.36 (0.04) C c
Riva LC HV	0.13 (0.05) A a	0.24 (0.06) A ab	0.21 (0.05) A ab	0.26 (0.04) A b	0.19 (0.07) A a	0.23 (0.04) A ab	0.18 (0.04) A a

$n = 12$; capital letters annotate similar groups by column, small letters by row (Kruskal-Wallis/Dunn's $p = 0.05$)

additional thought. It is well established that the resin content in RMGI impedes the polyalkenoate reaction [35–37]. The resin presence distorts the polyalkenoate polymer chain that reduces available reaction sites as well as slowing the reaction due to less water content [35–37]. In an infrared spectroscopy study involving Fuji II LC, Young [38] reported that the resin free radical polymerization reaction was essentially complete 5 min after VLC exposure. Thereafter, the polyalkenoate acid-base reaction occurred largely supported by water absorption. Therefore, water uptake may compensate for the resin-influenced polyalkenoate reaction rate that may possibly compare to that observed with conventional GIC materials [38]. Also, using infrared spectroscopy, Wan et al. [50] found that the acid-base reaction in Fuji II LC continued for 96 h and thus RMGI water absorption appears to allow the acid-base reaction to occur longer compared with GIC materials, and may partially compensate for the inhibiting properties of the monomer system.

Flexural toughness is a seldom-reported feature in the dental scientific literature. Flexural toughness is determined by integrating the area under the total stress-strain curve, and toughness can be considered to represent a material's ability to resist total catastrophic rupture. Hence, toughness may also reflect the material's matrix organizational level. Toughness could be a function of a material's flexural strength and modulus, as both affect both the length and slope of the stress-strain curve and consequently the area underneath. Curiously, besides some initial increase, the GIC materials did not largely experience great change in toughness over the course of the evaluation (Supplemental Fig. 6). Even with this level of change, under this study's conditions, GIC flexure strength influenced toughness more than modulus for some of the materials (Supplemental Table 1). At 12 months, the

flexural toughness values strongly correlated with the flexure strength of Chemfil Rock ($r^2 = 0.9$), Equia ($r^2 = 0.83$), and Riva SC HV ($r^2 = 0.85$), while Fuji Triage and Riva Self Cure Fast displayed moderate correlation ($r^2 = 0.76$ and 0.66 , respectively). The RMGI flexural toughness values for Riva LC essentially mirrored flexural strength performance, largely demonstrating a significant toughness increase throughout the evaluation. However, Fuji II LC, Ketac Nano, and Riva LC HV exhibited toughness increases that were followed by progressive decline. Similar to GIC materials, both Fuji II LC and Ketac Nano flexure strength was found to exhibit a strong correlation ($r^2 = 0.84$) with toughness (Supplemental Table 2). Review of the literature reveals little research reporting GIC and RMGI flexural toughness results, as this study may be the first to report 12-month results for these materials.

Surface hardness represents a material's localized surface resistance to deformation, which has been suggested to be related to the underlying material matrix [48]. To minimize any RMGI potential surface microhardness irregularities due to the Polywave® LED light curing unit used [87], 11 Knoop hardness indentations spaced 0.5 mm apart in alternating fashion apart were made on each specimen. The mean of the 11 hardness values was then recorded as that specimen's representative KHN value. This was accomplished for a total of 12 specimens. GIC materials demonstrated significant hardness increases compared to that observed at 1 h. Although some materials essentially did not display hardness increase beyond 24 h (Equia, Riva Protect, Riva Self Cure Fast, Riva Self Cure HV, and Riva Silver), other materials continued in surface hardness increase (Supplemental Fig. 7). Hardness results were lower for Chemfil Rock than that reported by Al-Angari et al. [88] but comparable for Equia and Ketac Molar

Table 11 RMGI mean hardness (KHN)

	1 h	24 h	1 week	1 month	3 months	6 months	12 months
Fuji II LC	30.5 (3.5) C d	29.2 (2.6) B cd	28.6 (2.3) A cd	27.7 (2.8) A bcd	26.6 (1.5) A abc	25.1 (0.8) A ab	24.4 (1.2) A a
Ketac Nano	26.2 (2.1) B a	26.3 (1.1) A a	27.7 (1.5) A a	27.3 (5.0) A a	27.1 (1.2) A a	25.9 (2.1) A a	27.6 (1.4) B a
Riva LC	23.1 (1.0) A a	26.1 (1.7) A b	27.0 (0.9) A bc	28.4 (2.1) A c	28.4 (2.1) A c	25.7 (2.0) A b	27.2 (2.2) B bc
Riva LC HV	24.0(1.03) AB a	32.1 (3.5) C b	33.2 (1.8) B b	32.1 (1.2) B b	32.6 (2.3) B b	37.8 (2.8) B c	39.3 (2.1) C c

$n = 12$; capital letters annotate similar groups by column, small letters by row (Kruskal-Wallis/Dunn's $p = 0.05$)

Table 12 RMGI mean fracture toughness (MPa√m)

	1 h	24 h	1 week	1 month	3 months	6 months	12 months
Fuji II LC	0.74 (0.1) C c	0.67 (0.05) B b	0.66 (0.04) C b	0.65 (0.04) B b	0.62 (0.04) B ab	0.58 (0.04) C a	0.68 (0.04) D b
Ketac Nano	0.59 (0.06) B b	0.51 (0.03) A a	0.45 (0.1) A a	0.51 (0.07) A a	0.46 (0.07) A a	0.46 (0.06) A a	0.48 (0.03) B a
Riva LC	0.47 (0.03) A a	0.51 (0.04) A ab	0.54 (0.03) B b	0.5 (0.06) A ab	0.49 (0.09) A ab	0.53 (0.02) B b	0.53 (.004) C b
Riva LC HV	0.43 (0.02) A a	0.49 (0.03) A a	0.48 (0.07) A a	0.47 (0.06) A a	0.43 (0.1) A a	0.47 (0.05) A a	0.42 (0.03) A a

n = 12; capital letters annotate similar groups by column, small letters by row (Kruskal-Wallis/Dunn’s *p* = 0.05)

Quick. Riva SC Fast hardness development mirrored that reported by Shiozawa et al. [51] while Ketac Silver hardness values were very similar to that reported by De Moor and Verbeeck [89]. The continued hardness development for Chemfil Rock, Fuji Triage, Ketac Molar Quick, and Ketac Silver provides further evidence of a maturation process of the hydrogel matrix.

Among the RMGI materials, Ketac Nano did not evidence any hardness changes beyond 1 h. Interestingly, Fuji II LC’s maximum hardness was observed at 1 h and thereafter displayed continued hardness deterioration below that observed initially. Riva LC developed maximum and stable hardness at 24 h, with only Riva LC HV manifested a slow but significant increase in Knoop hardness over the 12-month evaluation. As previously discussed, some RMGI products have been reported to exhibit a delayed acid-base reaction that may slowly progress up to 96 h after preparation [50, 82]. Although this reported delay could provide rationale for hardness improvement between 24 h and 1 week, but under the conditions of this study, no RMGI products demonstrated a hardness increase for this time period. Realistically, any improvement could be due to the continued hydrogel matrix maturation, but explanation for the late Riva LC HV hardness improvement is presently unclear. The only compositional difference between Riva LC HV and Riva LC is that Riva LC HV contains a higher powder/liquid ratio and may contain a slightly smaller amount of HEMA.

Fracture toughness has been described as an in vitro test that may correlate with clinical performance [77]. Fracture toughness is a material’s ability to resist crack propagation

from a pre-existing flaw [90–93] with some correlation reported with Class IV restoration clinical performance [91] as well as resin composite marginal deterioration [92]. The graphical results of the fracture toughness testing for the GIC and RMGI products are shown in Supplemental Figs. 9 and 10, respectively. For the GIC materials, fracture toughness performance was material specific. Only Fuji Triage, Ketac Silver, Riva Protect, and Riva Silver displayed any significant increase in fracture toughness over the evaluation. However, low variance may render any significant results to be unlikely of clinical significance, and essentially GIC fracture toughness values changed very little during this evaluation. These results are somewhat perplexing, as the fracture toughness results did not follow the same trend evidenced by the other GIC physical property results. It may be noteworthy that the two cermets evaluated demonstrated higher fracture toughness values than the other GIC products. Perhaps the cermet microstructure metallic interfaces may afford additional crack deflection ability, but such is conjecture and remains to be seen. The limited GIC fracture toughness findings do seemingly reinforce a recent report by Baig et al. [92] that questions fracture toughness testing’s discriminatory value in GIC physical property evaluation. Nevertheless, fracture toughness results for Ketac Molar Quick were similar to that values reported by Yamazaki et al. [81]. Contrastingly, this study’s fracture toughness results were lower than that reported for Chemfil Rock, Equia, and Ketac Molar Quick by Al-Angari and colleagues [88], lower for Ketac Silver and Ketac Molar Quick reported by Ilie et al. [93], as well as the 1-h results reported for Fuji IX reported by Lucksanasombool et al. [83]. All these studies used different

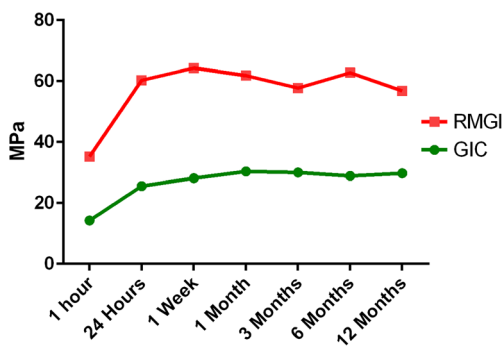


Fig. 1 GIC & RMGI flexure strength global comparison (MPa). GIC *n* = 9; RMGI *n* = 4

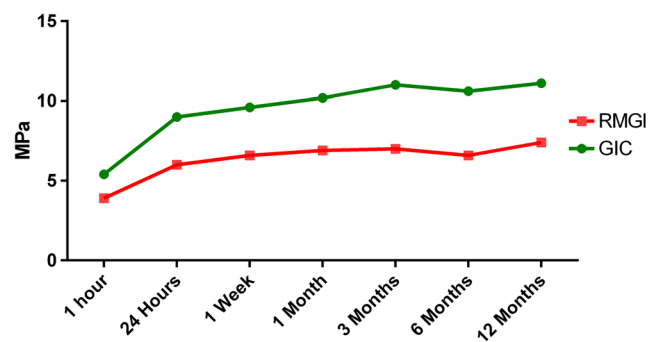
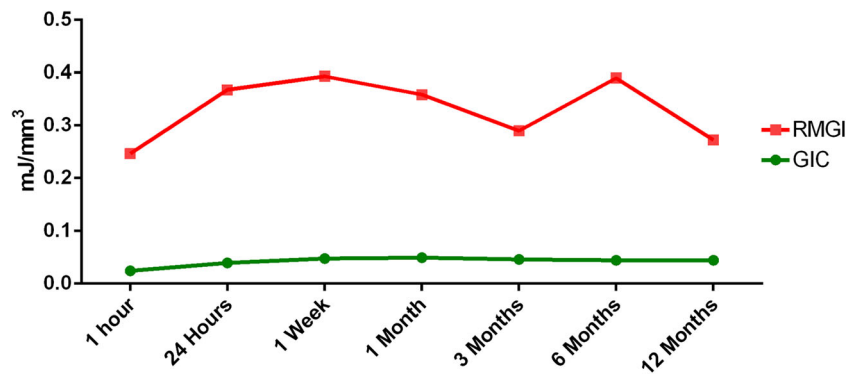


Fig. 2 GIC and RMGI flexural modulus global comparison (GPa). GIC *n* = 9; RMGI *n* = 4

Fig. 3 GIC and RMGI flexural toughness global comparison (mJ/mm^3). GIC $n = 9$; RMGI $n = 4$



methodologies than the present study that could account for these differences. For RMGI materials, both Fuji II LC and Ketac Nano displayed significant decreases in fracture toughness after 1 h that somewhat stabilized for both materials for the remainder of the evaluation. The reason for this deminuation is presently unknown, but could possibly be due to irregularities between the resin and conventional polyalkenoate domains and/or matrix plasticization due to water absorption that has been reported for RMGI materials [94]. Riva LC HV demonstrated no fracture toughness changes from that observed at 1 h but Riva LC was the only material to demonstrate significantly greater fracture toughness development. Nonetheless, variance was small and any noted significant changes are unlikely to be of clinical relevance. RMGI fracture toughness reports are sparsely reported in the dental literature, but this study's findings for Fuji II LC and Ketac Molar were similar to that reported by Yamazaki et al. [81], whereas lower for Fuji II LC, Ketac Molar, and Ketac Silver as reported by Ilie and colleagues [93].

The results of this study suggest that GIC restorative materials typically exhibited more physical property stability than some RMGI products. While global mean RMGI results may depict stability, in real contrast, some individual RMGI products at each observation time generally demonstrated significant declining mean values of flexural modulus and toughness, fracture toughness, and hardness. The deterioration of these RMGI physical properties have been attributed to water

absorption due to the hydrophilic nature of the included resins [94–96]. Accordingly, Kanachanasavita et al. [94] reported that RMGI products absorbed water twice the amount compared to GIC materials. Moreover, these authors found that absorption exponentially increased during 30 days storage in artificial saliva, presumably due to RMGI matrix changes [94]. Small and colleagues [95] observed that RMGI materials displayed greater water absorption as compared to resin composites while Versluis et al. [96] noted that particular RMGI products displayed matrix expansion due to water absorption. Hence, water absorption with ensuing matrix plasticization may be considered as a contributor to RMGI physical property loss over time.

GIC and RMGI material global mean comparisons provide perspective between the two classes of products as well as identify general trends. Understandably, due to the marked disparity between the group sizes as well as the different nature between the two materials, statistical analysis was not pursued. The global flexure strength comparison is shown in Fig. 1. The RMGI restorative materials demonstrated higher flexure strength values than the GIC counterparts. Based on this singular comparison, a RMGI product might be the choice material for restorations exposed to functional forces. Realistically, as discussed earlier GIC performance reported by ART technique studies can attest their functional area suitability [57–63]. Moreover, GIC products largely demonstrated some increasing flexure strength trends, whereas RMGI

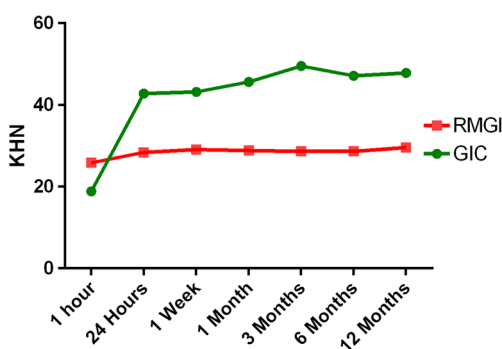


Fig. 4 GIC and RMGI hardness global comparison (KHN). GIC $n = 9$; RMGI $n = 4$

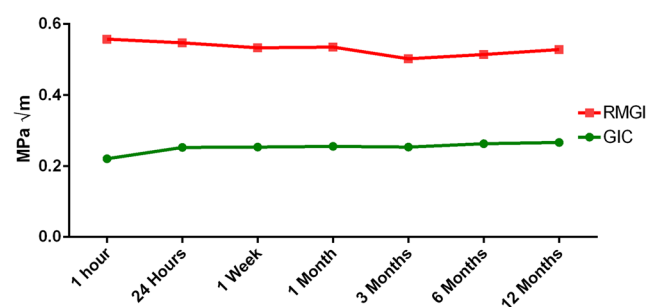


Fig. 5 GIC and RMGI fracture toughness global comparison ($\text{MPa}\sqrt{\text{m}}$). GIC $n = 9$; RMGI $n = 4$

products were noticed to display overall reduced flexure strength trends with time. In contrast to flexure strength, GIC products displayed higher modulus values than the RMGI products (Fig. 2). Yamazaki and colleagues [81] discussed that the RMGI resin matrix network's viscoelastic nature could account for lower RMGI modulus values. Furthermore, the GIC products overall demonstrated increasing modulus trends which again may provide evidence supporting matrix network maturation [6, 7]. Interestingly, both GIC and RMGI materials demonstrated a parallel modulus decrease at 6 months, which might be conjectured to possible polyalkenoate network change at that time period.

When flexural toughness global results are reviewed (Fig. 3), GIC products demonstrate lower but stable flexural toughness. RMGI toughness was observed to decline with time but displayed increasing trends at 6 months. GIC products display greater hardness values as compared to the RMGI materials (Fig. 4) with the GIC products revealing a slight increasing trend up to 3 months. Lower RMGI hardness values have been attributed to the resin content's ability to allow substantial creep under load with resultant recovery and stress relief [81]. Under the conditions of this study, the RMGI products' hardness was stable after 1 week and did not demonstrate a hardness decline after 6 months as observed by Shiozawa et al. [51]. Figure 5 depicts that RMGI products globally demonstrate greater fracture toughness than the GIC restorative materials. The GIC brittle nature may account for this difference, whereas the RMGI viscoelastic nature may require more energy for crack propagation. In conclusion, global comparison overall depicts that RMGI products demonstrate higher flexure strength, flexural toughness, and fracture toughness than the GIC counterparts, and may allow conclusions that RMGI products could afford superior performance in functional areas. However, information is presented in this work that longitudinally GIC materials may exhibit more stability with selected physical properties and should also be considered with recent reports of GIC material longevity in adult functional environments [71, 97].

Conclusions

This study evaluated selected physical properties of nine GIC and four RMGI restorative materials over 12 months. Under the conditions of this study:

1. GIC and RMGI physical property performance over time was material dependent;
2. Polyalkenoate maturation processes are essentially complete by 24 h;
3. Although differences in GIC physical properties were noted, the small magnitude of the divergences may render such to be unlikely of clinical significance;

4. Modest increases in some GIC physical properties were noted especially flexural modulus and hardness, which lends support to reports of a maturing hydrogel matrix;
5. Overall, GIC product physical properties were more stable than RMGI;
6. A similar modulus reduction at 6 months for both RMGI and GIC produced may suggest a polyalkenoate matrix change; and
7. Globally, RMGI products demonstrated higher values of flexure strength, flexural toughness, and fracture toughness than GIC materials.

Acknowledgments The opinions offered in the work are those of the authors only and do not reflect the official opinion of the United States Air Force, Department of Defense, or the United States Government.

Funding This work was supported by 81 Medical Group Protocol FKE20150010N.FI.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

Informed consent For this type of study, formal consent is not required.

References

1. Wilson AD, Kent BE (1971) The glass-ionomer cement, a new translucent dental filling material. *J Appl Chem* 21:313
2. Wilson AD, Batchelor RF (1967) Dental silicate cements I. The chemistry of erosion. *J Dent Res* 46:1078–1085
3. Wilson AD (1989) Developments in glass-ionomer cements. *Int J Prosthodont* 2:438–446
4. Nicholson JW (1998) Chemistry of glass-ionomer cements: a review. *Biomaterials* 19:485–494
5. Hatton PV, Brook IM (1992) Characterization of the ultrastructure of glass-ionomer (poly-alkenoate) cement. *Br Dent J* 173:275–277
6. Cattani-Lovente MA, Godin C, Meyer JM (1994) Mechanical behavior of glass ionomer cements affected by the long-term storage in water. *Dent Mater* 10:37–44
7. Matsuya S, Maeda T, Ohta M (1996) IR and NMR analyses of hardening and maturation of glass-ionomer cement. *J Dent Res* 75:1920–1927
8. Crisp S, Lewis BG, Wilson AD (1976) Characterization of glass-ionomer cements. 1. Long term hardness and compressive strength. *J Dent* 4:162–166
9. Sidhu SK, Nicholson JW (2016) A review of glass ionomer cements for clinical dentistry. *J Funct Biomater* 28. <https://doi.org/10.3390/jfb7030016>
10. Mitra SB (1991) Adhesion to dentin and physical properties of a light-cured glass-ionomer liner/base. *J Dent Res* 70:72–74
11. Baig MS, Fleming GJP (2015) Conventional glass-ionomer materials: a review of the developments in glass powder, polyacid liquid and the strategies of reinforcement. *J Dent* 42:897–912. <https://doi.org/10.1016/j.jdent.2015.04.004>

12. Khoroushi M, Keshani F (2013) A review of glass-ionomers: from conventional glass-ionomer to bioactive glass-ionomer. *Dent Res J (Isfahan)* 10:411–420
13. Baig MS, Dowling AH, Fleming GJ (2013) Hertzian indentation testing of glass-ionomer restoratives: a reliable and clinically relevant testing approach. *J Dent* 41:968–973. <https://doi.org/10.1016/j.jdent.2013.04.004>
14. Moshaverinia A, Roohpour N, Cheea WWL, Schricker SR (2012) A review of polyelectrolyte modifications in conventional glass-ionomer dental cements. *J Mater Chem*. <https://doi.org/10.1039/c2jm14880c>, www.rsc.org/materials
15. Prosser HJ, Powis DR, Brant PJ, Wilson AD (1984) Characterization of glass-ionomer cements. The physical properties of current materials. *J Dent* 12:231–240
16. McLean JW, Gasser O (1985) Glass cermet cements. *Quintessence Int* 16:333–343
17. Simmons JJ (1983) The miracle mixture: glass-ionomer and alloy powder. *Tex Dent J* 100:6–12
18. Williams JA, Billington RW, Pearson GJ (1992) The comparative strengths of commercial glass-ionomer cements with and without metal additions. *Br Dent J* 172:279–282
19. Wren AW, Kidari A, Cummins NM, Towler MR (2010) A spectroscopic investigation into the setting and mechanical properties of titanium containing glass polyalkenoate cements. *J Mater Sci Mater Med* 21:2355–2364. <https://doi.org/10.1007/s10856-010-4089-2>
20. Guggenberger R, May R, Stefan KP (1998) New trends in glass-ionomer chemistry. *Biomaterials* 19:479–483
21. Tüzüner T, Kuşgöz A, Er K, Taşdemir T, Buruk K, Kemer B (2011) Antibacterial activity and physical properties of conventional glass-ionomer cements containing chlorhexidine diacetate/cetrimide mixtures. *J Esthet Restor Dent* 23:46–56. <https://doi.org/10.1111/j.1708-8240.2010.00385.x>
22. Xie D, Weng Y, Guo X, Zhao J, Gregory RL, Zheng C (2011) Preparation and evaluation of a novel glass-ionomer cement with antibacterial functions. *Dent Mater* 27:487–496. <https://doi.org/10.1016/j.dental.2011.02.006>
23. Boyd D, Towler MR, Watts S, Hill RG, Wren AW, Clarkin OM (2008) The role of Sr²⁺ on the structure and reactivity of SrO-CaO-ZnO-SiO₂ ionomer glasses. *J Mater Sci Mater Med* 19:953–957
24. Kiri L, Boyd D (2015) Predicting composition-property relationships for glass ionomer cements: a multifactor central composite approach to material optimization. *J Mech Behav Biomed Mater* 46:285–291. <https://doi.org/10.1016/j.jmbbm.2015.02.007>
25. Sidhu SK, Watson TF (1995) Resin-modified glass ionomer materials. A status report for the American Journal of Dentistry. *Am J Dent* 8:59–67
26. Friedl KH, Powers JM, Hiller KA (1995) Influence of different factors on bond strength of hybrid ionomers. *Oper Dent* 20:74–80
27. Kakaboura A, Eliades G, Palaghias G (1996) An FTIR study on the setting mechanism of resin-modified glass ionomer restoratives. *Dent Mater* 12:173–178
28. Tay FR, Pashley EL, Huang C, Hashimoto M, Sano H, Smales RJ, Pashley DH (2001) The glass-ionomer phase in resin-based restorative materials. *J Dent Res* 80:1808–1812
29. Mitra SB, Lee CY, Bui HT, Tantbirojn D, Rusin RP (2009) Long-term adhesion and mechanism of bonding of a paste-liquid resin-modified glass-ionomer. *Dent Mater* 25:459–466. <https://doi.org/10.1016/j.dental.2008.09.008>
30. Fukuda R, Yoshida Y, Nakayama Y, Okazaki M, Inoue S, Sano H, Suzuki K, Shintani H, Meerbeek BV (2003) Bonding efficacy of polyalkenoic acids to hydroxyapatite, enamel, and dentin. *Biomaterials* 24:1861–1867
31. Yiu CK, Tay FR, King NM, Pashley DH, Sidhu SK, Neo JC et al (2004) Interaction of glass ionomer cements with moist dentin. *J Dent Res* 83:283–289
32. Yip HK, Tay FR, Ngo HC, Smales RJ, Pashley DH (2001) Bonding of contemporary glass ionomer cements to dentin. *Dent Mater* 17:456–470
33. Tay FR, Smales RJ, Ngo H, Wei SH, Pashley DH (2000) Effect of different conditioning protocols on adhesion of a GIC to dentin. *J Adhes Dent* 3:153–167
34. Hammesfahr PD Developments in resinomer systems. In: Hunt P (ed) *Glass ionomers: The next generation*. Proceedings of the 2nd International Symposium on Glass Ionomers, June 1994, Philadelphia, PA. International Symposia in Dentistry, PC, Philadelphia, pp 47–55
35. Berzins DW, Abey S, Costache MC, Wilkie CA, Roberts HW (2010) Resin-modified glass-ionomer setting reaction competition. *J Dent Res* 89:82–86. <https://doi.org/10.1177/0022034509355919>
36. Roberts HW, Berzins DC (2015) Early reaction kinetics of contemporary glass-ionomer restorative materials. *J Adhes Dent* 17:67–75. <https://doi.org/10.3290/j.jad.a33526>
37. Yelamanchili Y, Darvell BW (2008) Network competition in a resin-modified glass-ionomer cement. *Dent Mater* 24:1065–1069. <https://doi.org/10.1016/j.dental.2007.12.005>
38. Young AM (2002) FTIR investigation of polymerization [sic] and polyacid neutralization kinetics in resin-modified glass-ionomer dental cements. *Biomaterials* 23:3289–3295
39. Young A, Sherpa G, Pearson B, Schottlander, Waters DN (2000) Use of Raman spectroscopy in the characterisation of the acid–base reaction in glass-ionomer cements. *Biomaterials* 21:1971–1979
40. Stamboulis A, Matsuya S, Hill RG, Law RV, Udoh K, Nakagawa M, Matsuya Y (2006) MAS-NMR spectroscopy studies in the setting reaction of glass ionomer cements. *J Dent* 34:574–581
41. Wasson EA, Nicholson JW (1993) Change in pH during setting of polyelectrolyte dental cements. *J Dent* 21:122–126
42. Griffin SG, Hill RG (1999) Influence of glass composition on the properties of glass polyalkenoate cements. Part I: influence of aluminium to silicon ratio. *Biomaterials* 20:1579–1586
43. Algera TJ, Kleverlaan CJ, Pahl-Andersen B, Feilzer AJ (2006) The influence of environmental conditions on the material properties of setting glass-ionomer cements. *Dent Mater* 22:852–856
44. Tay M, Braden M (1981) Dielectric properties of glass ionomer cements. *J Dent Res* 60:1311–1314
45. Watts C (1998) Analysis of reactions in glass-polyalkenoate/resin systems by dielectric impedance spectroscopy. *Biomaterials* 19:551–577
46. Babu TA, Ramesh KV, Sastry DL (2012) Studies on electrical and thermal properties of dental glass ionomer cement. *J Biomed Sci Eng* 5:638–638. <https://doi.org/10.4236/jbise.2012.511078>
47. ŠSantić A, Čalogović AM, Pavić L, Gladić J, Vučić Z, Lovrić D, Prskalo K, Janković B, Tarle Z, Mogaš-Milanković A (2015) New insights into the setting processes of glass ionomer cements from analysis of dielectric properties. *J Am Ceram Soc* 98:3869–3876. <https://doi.org/10.1111/jace.13830>
48. Watts DC (1986) The development of surface hardness in visible light cured posterior composites. *J Dent* 14:169–174
49. Roberts HW, Berzins D (2014) Thermal analysis of contemporary glass-ionomer restorative materials. *J Therm Anal Calorim* 115:2099–2106. <https://doi.org/10.1007/s10973-013-3428-1>
50. Wan ACA, Yap AUJ, Hastings GW (1999) Acid-base complex reactions in resin-modified and conventional glass ionomer cements. *J Biomed Mater Res* 48:700–704. <https://doi.org/10.1007/s00784-013-1074-4>
51. Shiozawa M, Takahashi H, Iwasaki N (2014) Fluoride release and mechanical properties after 1-year water storage of recent restorative glass ionomer cements. *Clin Oral Invest* 18:1053–1060. <https://doi.org/10.1007/s00784-013-1074-4>
52. Wren AW, Coughlan A, Laffir FR, Towler MR (2013) Comparison of a SiO₂-CaO-ZnO-SrO glass polyalkenoate cement to commercial dental materials: glass structure and physical properties. *J Mater*

- Sci Mater Med 24:271–280. <https://doi.org/10.1007/s10856-012-4813-1>
53. Azillah MA, Anstice HM, Pearson GJ (1998) Long-term flexural strength of three direct aesthetic restorative materials. *J Dent* 26: 177–182
 54. Wasson EA, Nicholson JW (1993) New aspects of the setting chemistry of glass-ionomer cements. *J Dent Res* 72:481–483
 55. Dickey B, Price R, Boyd D (2016) Evidence of a complex species controlling the setting reaction of glass ionomer cements. *Dent Mater* 32:596–605. <https://doi.org/10.1016/j.dental.2016.01.012>
 56. Zainuddin N, Karpukhina N, Hill RG, Law RV (2009) A long-term study on the setting reaction of glass ionomer cements by ²⁷Al MAS-NMR spectroscopy. *Dent Mater* 25:290–295. <https://doi.org/10.1016/j.dental.2008.07.008>
 57. de Amorim RG, Leal SC, Mulder J, Creugers NHJ, Frencken JE (2014) Amalgam and ART restorations in children: a controlled clinical trial. *Clin Oral Investig* 18:117–124. <https://doi.org/10.1007/s00784-013-0955-x>
 58. Cefaly DFG, Tapety CMC, Mondelli RFL, Lauris JRP, Phantumvanit P, Navarro MFL (2006) Three-year evaluation of the ART approach in class III and V restorations in permanent anterior teeth. *Caries Res* 40:389–392
 59. da Mata C, Allen PF, McKenna G, Cronin C, O'Mahony D, Woods N (2015) Two-year survival of ART restorations placed in elderly patients: a randomized controlled clinical trial. *J Dent* 43:405–411. <https://doi.org/10.1016/j.jdent.2015.01.003>
 60. Faccin ES, Ferreira SH, Kramer PF, Ardenghi TM, Feldens CA (2009) Clinical performance of ART restorations in primary teeth: a survival analysis. *J Clin Pediatr Dent* 33:295–298
 61. Frencken JE (2010) The ART approach using glass-ionomers in relation to global oral health care. *Dent Mater* 26:1–6. <https://doi.org/10.1016/j.dental.2009.08.013>
 62. Frencken JE, van 't Hof MA, van Amerongen WE, Holmgren CJ (2004) Effectiveness of single-surface ART restorations in the permanent dentition: a meta-analysis. *J Dent Res* 83:120–123
 63. Rutar J, Mcallan L, Tyas MJ (2002) Three-year clinical performance of glass ionomer cement in primary molars. *Int J Paediatr Dent* 12:146–147
 64. Burrow MF, Tyas MJ (2007) Clinical evaluation of three adhesive systems for the restoration of non-carious cervical lesions. *Oper Dent* 32:11–15
 65. Fagundes TC, Barata THE, Bresciani E, Santiago SL, Franco EB, Lauris JRP, Navarro MF (2014) Seven-year clinical performance of resin composite versus resin-modified glass ionomer restorations in noncarious cervical lesions. *Oper Dent* 39:578–587. <https://doi.org/10.2341/13-054-C>
 66. McComb D, Erickson RL, Maxymiw WG, Wood RE (2002) A clinical comparison of glass ionomer, resin-modified glass ionomer and resin composite restorations in the treatment of cervical caries in xerostomic head and neck radiation patients. *Oper Dent* 27:430–437
 67. Qvist V, Manscherb E, Teglers PT (2004) Resin-modified and conventional glass ionomer restorations in primary teeth: 8-year results. *J Dent* 32:285–294
 68. van Dijken JWV, Pallesen U (2008) Long-term dentin retention of etch-and-rinse and self-etch adhesives and a resin-modified glass ionomer cement in non-carious cervical lesions. *Dent Mater* 24: 915–922
 69. Friedl K, Hiller KA, Friedl KH (2011) Clinical performance of a new glass ionomer based restoration system: a retrospective cohort study. *Dent Mater* 27:1031–1037. <https://doi.org/10.1016/j.dental.2011.07.004>
 70. Mickenautsch S, Yengopal V, Leal SC, Oliveria LB, Bezerra AC, Bonecker M (2009) Absence of carious lesions of glass-ionomer and amalgam restorations: a meta-analysis. *Eur J Paediatr Dent* 10:41–46
 71. Türkün LS, Kanik Ö (2016) A prospective six-year clinical study evaluating reinforced glass ionomer cements with resin coating on posterior teeth: Quo Vadis? *Oper Dent* 41:587–598. <https://doi.org/10.2341/15-331-C>
 72. Billington R, Williams J, Pearson GJ (1990) Variation in powder/liquid ratio of a restorative glass-ionomer cement used in general dental practice. *Br Dent J* 168:164–167
 73. Dowling AH, Fleming GJP (2009) Are encapsulated anterior glass-ionomer restoratives better than their hand-mixed equivalents? *J Dent* 37:133–140. <https://doi.org/10.1016/j.jdent.2008.10.006>
 74. Gonzalez-Bonet A, Kaufman G, Yang Y, Wong C, Jackson A, Huyang G, Bowen R, Sun J (2015) Preparation of dental resins resistant to enzymatic and hydrolytic degradation in oral environments. *Biomacromolecules* 16:3381–3388. <https://doi.org/10.1021/acs.biomac.5b01069>
 75. ISO 9917-2:2010. Water based cements—Part 2: resin-modified cements. International Organization for Standardization, Geneva
 76. Prosser HJ, Powis DR, Brant P, Wilson AD (1984) Characterization of glass-ionomer cements. 7. The physical properties of current materials. *J Dent* 12:231–240
 77. Ferracane JW (2013) Resin-based composite performance: are there some things we can't predict? *Dent Mater* 29:51–58. <https://doi.org/10.1016/j.dental.2012.06.013>
 78. Hu J, Du X, Huang C, Fu D, Ouyang X, Wang Y (2013) Antibacterial and physical properties of EGCG-containing glass ionomer cements. *J Dent* 41:927–934. <https://doi.org/10.1016/j.jdent.2013.07.014>
 79. Zoergiebel J, Ilie N (2013) Evaluation of a conventional ionomer cement with new zinc formulation: effect of coating, aging and storage agents. *Clin Oral Investig* 17:619–626. <https://doi.org/10.1007/s00784-012-0733-1>
 80. Bonifácio CC, Kleverlaan CJ, Raggio DP, Werner A, de Carvalho RCR, van Amerongen (2009) Physical-mechanical properties of glass ionomer cements indicated for atraumatic restorative treatment. *Aust Dent J* 54:233–237
 81. Yamazaki T, Schrickler SR, Brantley WA, Culbertson BM, Johnston WJ (2005) Viscoelastic behavior and fracture toughness of six glass-ionomer cements. *J Dent Res* 96:266–272
 82. Xie D, Brantley WA, Culbertson BM, Wang G (2000) Mechanical properties and microstructures of glass-ionomer cements. *Dent Mater* 16:129–138
 83. Lucksanasombool P, Higgs WAJ, Higgs RJED, Swain MV (2002) Time dependence of the mechanical properties of GICs in simulated physiologic conditions. *J Mater Sci Mater Med* 13:745–750
 84. Xie D, Yang Y, Zhao J, Park JG, Zhang JT (2007) A novel comonomer-free light-cured glass-ionomer cement for reduced cytotoxicity and enhanced mechanical strength. *Dent Mater* 23:994–1003
 85. Weng Y, Howard L, Xie D (2014) A novel star-shaped poly (carboxylic acid) for resin-modified glass-ionomer restoratives. *J Biomater Sci Polym Ed* 25:1076–1090. <https://doi.org/10.1080/09205063.2014.920169>
 86. Culbertson BM (2006) New polymeric materials for use in glass-ionomer cements. *J Dent* 34:556–565
 87. Price RBT, Labrie D, Rueggeberg FA, Sullivan B, Kostylev I, Fahey J (2014) Correlation between the beam profile from a curing light and the microhardness of four resins. *Dent Mater* 30:1345–1357. <https://doi.org/10.1016/j.dental.2014.10.001>
 88. Al-Angari SS, Hara AT, Chu T, Platt J, Eckert G, Cook NB (2014) Physicomechanical properties of a zinc-reinforced glass ionomer restorative material. *J Oral Sci* 56:11–16. <https://doi.org/10.2334/josnusd.56.11>
 89. De Moor RJG, Verbeeck RMH (1998) Changes in surface hardness of conventional restorative glass ionomer cements. *Biomaterials* 19: 2269–2275
 90. Tyas MJ (1990) Correlation between fracture properties and clinical performance of composite resins in class IV cavities. *Aust Dent J* 35:46–49

91. Ferracane JL, Condon JR (1999) In vitro evaluation of the marginal degradation of dental composites under simulated occlusal loading. *Dent Mater* 15:262–267
92. Baig MS, Lloyd CH, Fleming GJP (2015) Fracture toughness testing: a discriminatory mechanical testing performance indicator for glass-ionomer restoratives? *Dent Mater* 31:877–886. <https://doi.org/10.1016/j.dental.2015.04.014>
93. Ilie N, Hickel R, Valceanu AS, Huth KC (2012) Fracture toughness of dental restorative materials. *Clin Oral Investig* 16:489–498. <https://doi.org/10.1007/s00784-011-0525-z>
94. Kanchanasita W, Anstice HM, Pearson GJ (1997) Water sorption characteristics of resin-modified glass-ionomer cements. *Biomaterials* 18:343–349
95. Small ICB, Watson TF, Chadwick AV, Sidhu SK (1998) Water sorption in resin-modified glass-ionomer cements: an in vitro comparison with other materials. *Biomaterials* 19:545–550
96. Versluis A, Tantbirojn D, Lee MS, Tu LS, DeLong R (2011) Can hygroscopic expansion compensate polymerization shrinkage? Part I. Deformation of restored teeth. *Dent Mater* 27:126–133. <https://doi.org/10.1016/j.dental.2010.09.007>
97. Gurgan S, Kutuk ZB, Ergin E, Oztas SS, Cakir FY (2015) Four-year randomized clinical trial to evaluate the clinical performance of a glass ionomer restorative system. *Oper Dent* 40:134–143. <https://doi.org/10.2341/13-239-C>