Hardness of Three Resin-Modified Glass-Ionomer Restorative Materials as a Function of Depth and Time

HOWARD W. ROBERTS, DMD, MS* DAVID W. BERZINS, PhD[†] DAVID G. CHARLTON, DDS, MSD[‡]

ABSTRACT

Statement of the Problem: The polymerization of bulk-placed resin-modified glass-ionomer (RMGI) restoratives is compromised when penetration of the curing light is limited because of the materials' thickness. It is unknown if additional post light-curing resin polymerization and/or glass-ionomer setting occurs over time to ensure adequate polymerization.

Purpose: The primary objective was to evaluate the depth of cure of various thicknesses of RMGI restorative products over 1 year using Knoop hardness (KH) testing.

Materials and Methods: The materials were placed in Delrin molds having an internal diameter of 5.0 mm and heights of 2, 3, 4, and 5 mm and were photopolymerized with a halogen lightcuring unit. Five specimens of each depth were prepared for each time period evaluated. Specimens were stored in darkness at $37 \pm 2^{\circ}$ C and $98 \pm 2\%$ humidity until being tested at 24 hours, 1 week, and 1, 3, 6, 9, and 12 months after fabrication. Mean KH values were calculated for the bottom and top surfaces of each thickness group and used to determine bottom/ top hardness ratios. Data were compared using two-way analysis of variance (factors of time, thickness) at a 0.05 significance level with Scheffé's post hoc analysis, where required.

Results: The materials had relatively stable top surface KH, which permitted valid assessment of changes in bottom surface KH over time. The bottom surface KH of some RMGIs changed significantly over time (p < 0.001), but degrees of change were material dependent. Certain RMGIs demonstrated a potential for statistically significant post light-activation hardening; however, that too was material dependent. As compared with top surface KH, deeper layers of the thicker RMGI specimens consistently failed to achieve an adequate degree of polymerization.

Conclusion: Although certain RMGI materials demonstrate a potential for post light-activation chemically initiated resin polymerization and/or polyalkenoate acid/base reaction, these reactions may not be sufficient to ensure that the material is adequately polymerized for long-term success. This is particularly true when RMGI materials are placed in thicker layers where curing light penetration may be compromised.

*Director, Dental Biomaterials Evaluations, USAF Dental Evaluation and Consultation Service, Great Lakes, IL, USA [†]Director, Graduate Dental Biomaterials, Marquette University, Milwaukee, WI, USA [‡]Senior Biomaterials Scientist, Naval Institute for Dental and Biomedical Research, General Dynamics Information Technology, Great Lakes, IL, USA

CLINICAL SIGNIFICANCE

RMGI materials should not be placed in bulk but photopolymerized in layers to ensure adequate light activation. The results of this study suggest that Photac-Fil Quick be placed in layers no thicker than 2 mm while Fuji II LC and Vitremer may be placed in layers up to 3 mm in thickness.

(J Esthet Restor Dent 21:262–274, 2009)

INTRODUCTION

D esin-modified glass ionomers **N**(RMGIs) essentially consist of conventional glass-ionomer (GI) components combined with organic photopolymerizable monomers and a visible-light initiation system.¹ RMGIs were developed to improve the mechanical properties and reduce the early moisture sensitivity of conventional GI materials.²⁻⁴ Although exact formulas of commercially available RMGI products are proprietary, the amount of polymerized resin in them has been estimated to be approximately 4.5 to 6%.5 RMGIs exist basically in two forms: one in which part of the water is replaced by water-soluble, photopolymerizable 2-hydroxyethylmethacrylate (HEMA) monomer, and one in which pendant methacrylate groups are present on the polyacrylic acid molecules.^{6,7}

The setting reaction of RMGIs is complex compared with that of conventional GI materials,⁸ especially in terms of the interactions that occur between HEMA and other constituents. While

Andrzejewska and colleagues9 reported that aqueous polyacids enhance HEMA's photopolymerization, others have reported that HEMA lengthens both the working and setting times of GI materials and decreases their compressive strength.^{10,11} HEMA also affects the polyacrylic acid's configuration and has been theorized to induce possible phase separation because components in polymerized HEMA are water insoluble and may precipitate out of solution.12 HEMA also decreases polyacrylic acid solubility, reducing its availability for reacting.¹⁰ The overall effect of adding HEMA to a conventional GI material is a decreased acidbase curing reaction, which may result in a material with inferior physical properties.8,10

Another concern when using RMGIs is the possibility that they will not adequately set when placed in bulk and activated by visible light, because the amount of light that reaches the deeper regions of the restoration may not be sufficient to initiate photopolymerization.⁸ To compensate for this potentially adverse effect, manufacturers have added chemically activated (i.e., auto-cure) components,¹³ which purportedly increase RMGI depth of cure. As a result, some clinicians assume RMGI materials can be placed without regard to depth because the deeper areas of compromised light penetration can polymerize sufficiently because of the presence of chemically polymerizing resins and by the conventional acid-base polyalkenoate reaction.

One of the ways of studying the setting/curing behavior and depth of cure of RMGI materials has been to measure their hardness.^{14–19} Hardness has been used as an indicator of degree of conversion (i.e., extent of polymerization of monomers to polymers) in dental materials.²⁰ In one study, it was found that Knoop hardness (KH) exhibits a strong, significant, positive linear correlation with degree of conversion.²¹ This finding was true for thicknesses from 2 mm to 5 mm for the three resin composites that were studied. Yap¹⁷ measured the top surface hardness of seven materials, three of which were RMGIs. Results over 6 months

indicated that hardness changes were material dependant. He reported that Fuji II LC's (GC America, Alsip, IL, USA) and Photac-Fil's Photac-Fil Quick (3M/ ESPE, St. Paul, MN, USA) topsurface hardness decreased but Vitremer's (3M/ESPE) increased. In a 12-month study of Fuji II LC, Photac-Fil Quick, and Vitremer, Ellakuria and colleagues¹⁸ also reported top surface, materialdependent hardness changes. In another 12-month study, Kanchanavasita and colleagues¹⁹ reported a top-surface hardness increase for Fuji II LC and Vitremer.

Hardness has also been used to assess the depth of cure of RMGI materials.14,15,22,23 Burke and colleagues¹⁴ investigated the depth of cure of a RMGI liner using a scrape technique and reported that in cases where light penetration was compromised, the material showed an increase in depth of cure 12 hours later. In a study of the strength, depth of cure, and translucency of RMGIs, Mount and co-investigators²² also used a scrape test to assess the depth of cure resulting from the irradiation component of the setting reaction. The authors found that depth of cure was dependent upon shade and irradiation time. They also determined that specimens subjected to light activation were stronger than non-irradiated ones. In a study of a RMGI luting agent, Sigemori and colleagues²³ used KH to assess depths of cure at three depths of a RMGI luting product and compared them with those of two resin luting agents. They found that the KH values of the RMGI luting agent at its middle (7.0 mm) and deepest (11.4 mm)third were significantly higher than at its superficial (2.3 mm) third. Swift and colleagues¹⁵ investigated depth of cure of Fuji II LC, Photac-Fil Aplicap, and Vitremer using KH testing. Nine-mm-deep molds were filled and light activated, and hardness was measured at 10 minutes, 24 hours, and 7 days. For all materials, only the top 5 mm of the specimens demonstrated sufficient hardness for testing purposes. At 7 days, no statistically significant difference in hardness was noted between the top surfaces and those at the 5-mm level. However, because hardness tended to decrease as the materials' thickness increased, the authors recommended that RMGI materials be placed and light activated in 2to 3-mm increments. In a review article, McCabe¹³ cited previously reported depths of cure for RMGI liners and restorative materials that ranged from 1.54 to 2.26 mm for lining materials and from 2.68 to 2.97 mm for restorative materials.

One of the ways of using hardness to assess depth of cure of materials is to compute the bottom/top KH ratios of various thicknesses of the material. This has frequently been done for resin composites^{24,25} and has been shown to correlate well with degree of conversion of carbon-carbon bonds measured with Fourier Transform Infrared Spectroscopy.^{21,26} The hardness ratio technique for determining depth of cure of RMGI restorative materials has not received the attention paid to that of resin composites or other versions of RMGIs.^{15,23}

Measuring the hardness changes of different thicknesses and bottom/ top ratios of RMGI restorative products over time is important as a means of confirming or refuting the opinion held by many clinicians that the resin's chemically activated polymerization and the polyalkenoic acid-base reaction compensate for inadequate light photopolymerization.⁸

PURPOSE

The purpose of this study was to investigate the depth of cure of various thicknesses of three commercially available RMGI restorative materials over 12 months using KH testing.

MATERIALS AND METHODS

The RMGI materials used were Fuji II LC, Vitremer, and Photac-Fil Quick (Table 1). All materials were prepared per manufacturer's instructions and placed by one

TABLE 1. RESIN-MODIFIED GLASS-IONOMER RESTORATIVE MATERIALS USED IN THE STUDY.								
Material	Manufacturer	Composition	Shade	Recommended Light Curing Duration and Material Thickness				
Fuji II LC	GC America 3737 W. 127th Street Alsip, IL 60803 800-323-7063 http://www.gcamerica. com	<u>Powder</u> Alumino-silicate glass <u>Liquid</u> polyacrylic acid; HEMA; 2,2,4, TMHEDC; TEGDMA	A2	20 seconds; maximum recommended thickness is 1.8 mm				
Vitremer	3M ESPE Building: 275-2SE-03 3M Center St. Paul, MN 55144 800-634-2249 http://www.3m.com	<u>Powder</u> fluoroaluminosilicate glass; microencapsulated potassium persulfate and ascorbic acid; pigments <u>Liquid</u> aqueous solution of polycarboxylic acid; HEMA; photoinitiators	A3	40 seconds; maximum recommended thickness is 2.5 mm				
Photac-Fil Quick	3M ESPE	Powder Na-Ca-Al-La fluorosilicate glass; amine activator Liquid glass ionomer compatible monomers and oligomers; acrylic- and maleic-acid copolymers; camphorquinone; stabilizers; water	A2	20 seconds; maximum recommended thickness is 2 mm				
dimethacrylate.	C = 2,2,4 trimetnyi nexametnyiene ere purchased in 2005.	cicarbonate; FIEMA = 2-nydroxyetnylmethacryla	te; TEGDMA	a = trietnyiene giycoi				

operator (HWR). To prevent inadvertent material polymerization, all preparation/testing was conducted in a laboratory equipped with gold fluorescent lamps (F40/GO Gold, Sylvania, Danvers, MA, USA), which filtered out wavelengths below 525 nm. Precapsulated materials (Fuji II LC, Photac-Fil Quick) were prepared using a mechanical mixing unit (Automix, Sybron Dental Specialties, Orange,

CA, USA) while the powder/liquid material (Vitremer) was dispensed, manually mixed, placed in a delivery syringe (AccuDose Low Viscosity, Centrix Inc., Shelton, CT, USA), and injected into molds. Delrin molds with an internal diameter of 5.0 mm and heights of 2, 3, 4, and 5 mm were used. Five specimens of each depth were prepared for each time period evaluated. Molds were placed on a mylar-covered glass slide, and the mold was completely filled with the RMGI material, followed by placement of another mylar strip and a glass slide, with pressure manually applied to express excess material and produce a flat surface. Specimens were then photopolymerized as per the manufacturers' recommended exposure times using a halogen visible-light polymerization unit (Optilux 501,

TABLE 2. *A, FUJI II LC MEAN (SD) TOP-SURFACE KNOOP HARDNESS. *B, FUJI II LC MEAN (SD) BOTTOM-SURFACE KNOOP HARDNESS. * ¹ C, FUJI II LC MEAN (SD) BOTTOM/TOP KNOOP HARDNESS RATIOS (%).							
Thickness	24 hours	1 week	1 month	3 months	6 months	9 months	12 months
(mm)							
А							
2	$20.9 (0.3)^{Aa}$	$20.6 (0.9)^{Aa}$	$19.8 (0.8)^{Aa,b}$	$20.6 (1.0)^{Aa}$	17.9 (0.2) ^{Ab,c}	$17.2 \ (0.2)^{Ac}$	18.6 (1.0) ^{Ab,c}
3	20.3 (0.3) ^{Aa,b}	$20.7 (0.5)^{Aa}$	20.2 (0.7) ^{Aa,b}	$20.6 (0.6)^{Aa}$	$17.6 \ (0.1)^{Ac}$	$17.0 \ (0.8)^{Ac}$	$19.0 (0.4)^{Ab}$
4	$20.2 (0.4)^{Aa,b}$	21.2 $(0.6)^{Aa}$	19.6 $(0.7)^{Ab,c}$	21.3 $(0.6)^{Aa}$	17.5 (0.3) ^{Ad,e}	$16.3 (0.5)^{A,Bd,e}$	18.4 $(0.5)^{Ac,d}$
5	20.4 $(0.4)^{Aa}$	21.2 $(0.9)^{Aa}$	$20.2 (0.5)^{Aa}$	21.1 $(0.6)^{Aa}$	$17.4 \ (0.5)^{Ab}$	$15.6 (0.5)^{Bc}$	$18.6 (0.2)^{Ab}$
В							
2	18.4 $(0.3)^{Aa}$	19.1 $(1.2)^{Aa}$	$18.1 \ (0.5)^{Aa,b}$	$18.8 (0.7)^{Aa}$	$16.9 (0.2)^{Ab,c}$	$15.9 (0.4)^{Ac}$	16.9 (0.5) ^{Ab,c}
3	$15.1 (0.3)^{Ba}$	18.3 (0.6) ^{Ad}	$16.8 (0.6)^{Ac}$	19.4 $(0.2)^{Ad}$	16.4 $(0.4)^{Ab,c}$	$15.5 (0.5)^{Aa,b}$	$16.6 (0.2)^{Ac}$
4	11.3 (1.2) ^{Ca}	$15.3 (0.4)^{Bc}$	$12.3 (1.1)^{Ba,b}$	$13.2 (1.6)^{Ba,b,c}$	$11.5 (0.4)^{Ba}$	$13.3 (0.3)^{Ba,b,c}$	14.2 $(0.8)^{Bb,c}$
5	9.7 $(0.4)^{Da}$	12.7 (0.5) ^{Cb,c}	$10.6 (1.0)^{Ba,b}$	$10.8 (0.6)^{Ca,b}$	9.8 $(1.4)^{Ca}$	$10.8 (1.1)^{Ca,b}$	12.9 (0.4) ^{Cc}
С							
2	88.3 $(1.9)^{Aa}$	92.7 $(9.2)^{Aa}$	91.1 $(2.7)^{Aa}$	91.3 (4.2) ^{Aa}	94.4 $(1.1)^{Aa}$	92.1 $(1.5)^{Aa}$	91.8 (5.2) ^{Aa}
3	74.7 $(1.4)^{Ba}$	88.5 (2.3) ^{Ab,c,d}	82.8 (3.8) ^{Bb}	93.9 (1.7) ^{Ac,d}	92.9 (1.6) ^{Ac,d}	91.5 (3.7) ^{Ac,d}	87.3 (1.8) ^{Ab,c}
4	55.8 (6.1) ^{Ca}	72.1 (2.0) ^{Bb,c}	62.5 (5.8) ^{Ca,b}	62.2 (6.2) ^{Ba,b}	65.8 (2.7) ^{Ba,b}	$81.5 (4.0)^{Bc}$	77.2 (3.5) ^{Bb,c}
5	47.6 (1.5) ^{Da}	60.1 (3.9) ^{Cb,c}	52.9 (5.7) ^{Da,b}	51.4 (3.8) ^{Ca,b}	56.3 (7.6) ^{Ca,b}	68.9 (6.4) ^{Cc}	69.3 (1.8) ^{Cb,c}

SD = standard deviation.

*Within a column, values with the same upper-case superscript letter are not significantly different (p > 0.05, Scheffé's test). Within a row, values with the same lower-case superscript letter are not significantly different (p > 0.05, Scheffé's test).

[†]Values expressed are Knoop hardness ratios × 100.

Sybron Dental Specialties). During light curing, the tip of the light guide was in contact with the mylar on the mold's top surface. The illuminance level of the light unit was periodically assessed using a properly calibrated laboratory laser power meter (PowerMax 5200 with PM10 Probe, Molectron, Portland, OR, USA), which ensured accuracy of the measurements. Light output was consistently 875 mw/cm². After light exposure, specimens were stored in darkness to prevent ambient light from causing additional post light-curing polymerization. Specimens were stored in a

 $98 \pm 2\%$ humidity environment in a humidor at 37 ± 2 °C until being tested at 24 hours, 1 week, and 1, 3, 6, 9, and 12 months after fabrication.

At each testing time, KH was measured with a microhardness tester (M-400-G2, LECO, St Joseph, MI, USA) using a 100-g load and a 10-second dwell time. For each specimen, three hardness measurements were made near the centers of the top and bottom surfaces, and the mean of the three values was calculated for each surface and designated as the surface mean. Means were then calculated for the bottom and top surfaces of each thickness group and used to determine bottom/top hardness ratios. Data were compared using two-way analysis of variance (ANOVA) (factors of time, thickness) at a 0.05 significance level with Scheffé's post hoc analysis, where required. Statistical analysis was performed using SPSS software (12.0, SPSS Inc., Chicago, IL, USA).

RESULTS

For Fuji II LC (Table 2A–C), twoway ANOVA identified a significant time effect (p < 0.001) for the top surface KH with a significant interaction (p = 0.004) between the

RATIOS (%).							
Thickness	24 hours	1 week	1 month	3 months	6 months	9 months	12 months
(mm)							
А							
2	$11.5 (0.4)^{Aa}$	$13.7 (0.4)^{Ab}$	17.6 (0.5) ^{Ac,d}	$17.0 \ (0.4)^{Ac}$	$17.8 (0.1)^{Ac,d}$	17.6 (0.2) ^{Ac,d}	$18.1 \ (0.6)^{\text{Ad}}$
3	$11.7 (0.9)^{Aa}$	13.5 (0.4) ^{A,Bb}	$17.9 (0.6)^{Ac}$	16.8 (0.3) ^{Ac}	$17.6 \ (0.1)^{Ac}$	$17.5 (0.1)^{Ac}$	$18.2 (1.1)^{Ac}$
4	$12.1 \ (0.8)^{Aa}$	$12.9 (0.5)^{A,Ba}$	$18.2 (0.2)^{Ab}$	16.8 (0.3) ^{Ac}	17.4 (0.2) ^{Ab,c}	17.6 (0.3) ^{Ab,c}	17.6 (0.2) ^{Ab,c}
5	$11.6 (0.8)^{Aa}$	$12.7 (0.3)^{Ba}$	$17.6 \ (1.0)^{Ab}$	$17.4 \ (0.4)^{Ab}$	17.5 (0.2) ^{Ab}	17.5 (0.3) ^{Ab}	17.5 (0.3) ^{Ab}
В							
2	9.5 $(0.8)^{Aa}$	12.0 (0.4) ^{Ab}	$16.2 (0.4)^{Ac,d}$	15.6 (0.3) ^{Ac}	$16.9 (0.1)^{Ad}$	$16.8 (0.1)^{Ad}$	$16.6 (0.1)^{\text{Ad}}$
3	9.3 (0.3) ^{Aa}	11.3 (0.4) ^{A,Bb}	$15.5 (0.5)^{Ad}$	$13.5 (0.4)^{Bc}$	$15.3 (0.7)^{\text{Bd}}$	$15.4 (0.3)^{Bd}$	15.6 (1.4) ^{A,Bd}
4	8.5 $(0.6)^{Aa}$	$10.5 (0.2)^{B,Cb}$	14.6 $(0.8)^{Ac,d}$	11.0 (0.5) ^{Cb}	$13.5 (0.3)^{Cc}$	14.1 (0.4) ^{Cc,d}	14.8 $(0.3)^{Bd}$
5	8.7 $(0.8)^{Aa}$	9.9 $(0.7)^{Ca}$	$10.9 (1.4)^{Ba,b}$	$10.8 (0.9)^{Ca,b}$	12.5 (1.1) ^{Cb,c}	13.4 (0.6) ^{Cc}	14.0 $(0.5)^{Bc}$
С							
2	82.8 (5.9) ^{Aa}	87.9 (4.7) ^{Aa,b}	92.1 (4.3) ^{Ab}	91.6 (2.9) ^{Ab}	95.2 (0.7) ^{Ab}	95.1 (0.6) ^{Ab}	92.0 (2.4) ^{Ab}
3	78.8 $(5.4)^{Aa}$	83.6 (4.7) ^{A,Ba}	86.3 (4.2) ^{A,Ba}	$80.9 (2.5)^{Ba}$	86.9 $(4.2)^{Ba}$	$88.2 (2.0)^{Ba}$	$85.5 (3.9)^{Ba}$
4	70.8 (2.6) ^{Aa,b}	81.3 (2.9) ^{A,Bc}	80.6 (4.6) ^{Bc}	65.6 (4.0) ^{Ca}	77.5 (1.3) ^{Cb,c}	80.2 (1.9) ^{Cc}	83.9 (1.6) ^{Bc}
5	75.4 (10.5) ^{Aa,b}	77.8 (6.3) ^{Bb}	61.6 (4.0) ^{Ca}	$62.6 (6.0)^{Ca}$	71.4 (5.9) ^{Ca,b}	76.4 (2.8) ^{Ca,b}	80.1 (4.0) ^{Bb}

TABLE 3. *A, PHOTAC-FIL QUICK MEAN (SD) TOP-SURFACE KNOOP HARDNESS. *B, PHOTAC-FIL QUICK MEAN (SD) BOTTOM-SURFACE KNOOP HARDNESS. *¹C, PHOTAC-FIL QUICK MEAN (SD) BOTTOM/TOP KNOOP HARDNESS

SD = standard deviation.

*Within a column, values with the same upper-case superscript letter are not significantly different (p > 0.05, Scheffé's test). Within a row, values with the same lower-case superscript letter are not significantly different (p > 0.05, Scheffé's test). *Values expressed are Knoop hardness ratios × 100.

main effects. Subsequent one-way ANOVA indicated that the top surface hardness significantly decreased at 6 months for all thickness groups; however, with the exception of the 9-month groups, no significant differences were noted among thickness groups at other time periods. For the Fuji II LC bottom surface KH, two-way ANOVA revealed significant differences for time and depth (p < 0.0001) along with significant interaction between the factors (p < 0.0001). Subsequent one-way ANOVA found that bottom surface hardness significantly increased for the 3-, 4-, and 5-mm groups over

12 months. The 4- and 5-mm groups were significantly softer than the 2- and 3-mm groups at all time periods. Two-way ANOVA of bottom/top KH ratios identified significant main effects (p < 0.0001) and significant interaction (p < 0.0001) between them. One-way ANOVA found no significant differences in the 2-mm groups over time but revealed significant increases over 12 months for the 3-, 4-, and 5-mm groups. At 24 hours, significant differences in the ratios existed among all thicknesses (p < 0.001), but after 3 months there was no difference between the 2- and 3-mm groups.

The 4- and 5-mm thickness ratios were significantly different from each other, and were less than the 2- and 3-mm ratios at all time periods.

Photac-Fil Quick results can be seen in Table 3A–C. Two-way ANOVA of top surface KH data identified a significant time effect with no significant interaction (p = 0.111). One-way ANOVA indicated a significant increase in top surface hardness after 1 month that largely remained for the duration of the evaluation. With the exception of the 1-week groups, top surface hardness was not

TABLE 4. *A, VITREMER MEAN (SD) TOP-SURFACE KNOOP HARDNESS. *B, VITREMER MEAN (SD) Bottom-Surface knoop hardness. * [†] C, vitremer mean (SD) Bottom/top knoop hardness ratios (%).							
Thickness	24 hours	1 week	1 month	3 months	6 months	9 months	12 months
(mm)							
А							
2	25.3 (1.9) ^{Aa,b,c}	22.5 (0.3) ^{A,Bd}	26.8 (0.8) ^{A,Ba,b}	27.1 $(0.8)^{Aa}$	23.4 (0.3) ^{Ac,d}	23.9 (0.6) ^{Ab,c,d}	24.6 (0.4) ^{Ab,c,d}
3	25.2 (1.0) ^{Aa,b}	22.5 $(0.3)^{A,Bc}$	$26.8 (0.4)^{Aa}$	24.1 (1.9) ^{A,Bb,c}	23.1 (0.4) ^{Ab,c}	24.3 (0.2) ^{Ab,c}	24.7 (0.3) ^{Aa,b}
4	24.3 (1.3) ^{Aa,b}	22.1 (0.2) ^{Bb}	27.7 $(0.5)^{A,Ba}$	21.9 (3.3) ^{Bb}	23.0 (0.4) ^{Ab}	23.8 (0.3) ^{Ab}	$23.9 (0.7)^{Ab}$
5	24.2 $(1.1)^{Aa}$	22.7 $(0.1)^{Aa}$	27.8 (0.3) ^{Bb}	24.6 (1.1) ^{A,Ba}	22.5 (1.3) ^{Aa}	$23.6 (1.1)^{Aa}$	24.3 (0.5) ^{Aa}
В							
2	23.5 (1.3) ^{Aa,b}	$19.9 (0.2)^{Ac}$	24.1 (0.8) ^{Aa,b}	$25.2 (1.2)^{Aa}$	$20.0 (0.9)^{Ac}$	22.0 (1.2) ^{Ab,c}	22.5 (0.4) ^{Ab}
3	22.8 (0.7) ^{Aa,b}	$17.9 (0.4)^{Bd}$	24.0 $(0.7)^{Aa}$	20.8 (1.8) ^{Bb,c}	$18.7 (0.7)^{Ac,d}$	21.1 (0.5) ^{A,Bb}	22.4 (0.4) ^{Aa,b}
4	20.5 (1.6) ^{A,Ba}	$17.2 \ (0.4)^{Cb}$	21.4 $(0.4)^{Ba}$	17.4 (2.2) ^{Cb}	$18.4 (1.1)^{Aa,b}$	19.5 (1.2) ^{Ba,b}	19.4 $(0.5)^{Ba,b}$
5	17.4 (2.9) ^{Ba,b}	$15.3 (0.2)^{Da}$	18.4 (0.3) ^{Cb}	16.5 (0.8) ^{Ca,b}	$15.7 (0.3)^{Ba,b}$	16.8 (0.3) ^{Ca,b}	$16.5 (1.1)^{Ca,b}$
С							
2	93.0 (4.1) ^{Aa}	88.8 $(1.3)^{Aa}$	89.8 $(1.1)^{Aa}$	93.5 (6.5) ^{Aa}	85.2 (3.3) ^{Aa}	91.7 (2.7) ^{Aa}	91.6 $(1.1)^{Aa}$
3	90.5 $(1.7)^{Aa}$	79.8 (1.4) ^{Bb}	89.6 (2.4) ^{Aa}	86.4 (3.4) ^{A,Ba}	80.7 (2.1) ^{Ab}	86.6 (2.4) ^{A,Ba}	90.4 $(1.1)^{Aa}$
4	84.7 (5.8) ^{Aa}	77.7 $(1.8)^{Ba}$	77.2 $(1.8)^{Ba}$	80.1 (9.8) ^{B,Ca}	80.1 (5.3) ^{Aa}	81.9 (4.3) ^{Ba}	$80.9 (3.8)^{Ba}$
5	71.5 (9.8) ^{Ba}	$67.5 (1.2)^{Ca}$	66.3 (1.3) ^{Ca}	66.9 $(5.5)^{Ca}$	$69.8 (4.5)^{Ba}$	71.6 (3.6) ^{Ca}	$68.0 (4.7)^{Ca}$

SD = standard deviation.

*Within a column, values with the same upper-case superscript letter are not significantly different (p > 0.05, Scheffé's test). Within a row, values with the same lower-case superscript letter are not significantly different (p > 0.05, Scheffé's test).

[†]Values expressed are Knoop hardness ratios × 100.

significantly different among the thicknesses. Two-way ANOVA of the Photac-Fil Quick bottom surface hardness data identified significant time and thickness effects (p < 0.0001) with a significant interaction (p < 0.0001) between the two factors. Further one-way ANOVA revealed that bottom surface hardness at 24 hours for all groups was similar. Hardness then significantly increased for each thickness group and became largely stable after 6 months. With one exception, the 4- and 5-mm groups were significantly softer than the 2- and 3-mm groups after 3 months. Two-way

ANOVA of Photac-Fil Quick's bottom/top hardness ratios identified significant main effects (p < 0.0001) and a significant interaction (p < 0.0001). Subsequent one-way ANOVA revealed that, although the thickness groups' ratios numerically increased over time, only the 2and 4-mm groups were significantly harder at 12 months than at 24 hours. The ratios of the thickness groups were not significantly different at 24 hours, but significant differences were found at each subsequent test period. With one exception (12 months), the 4and 5-mm groups had significantly

lower ratios than the 2- and 3-mm groups after 3 months.

Results of the Vitremer KH evaluation are provided in Table 4A–C. Two-way ANOVA of the top surface data identified significant main effects (p < 0.001) with significant interaction (p < 0.0001). Follow-up one-way ANOVA identified significant top surface hardness changes for all thickness groups at various times during the 12-month test; however, no significant changes were noted between 24 hours and 12 months for any groups. Some significant differences were periodically found among thickness groups; however, this was infrequent. For the Vitremer bottom surface KH values, two-way ANOVA identified significant main effects (p < 0.0001) with significant interaction (p < 0.0001). One-way ANOVA indicated significant hardness changes for all thicknesses over time; however, at 12 months, the KH for each bottom surface thickness was not significantly different from its 24-hour value. For four of the seven time groups, the 4- and 5-mm thicknesses were significantly softer than the other two groups. Two-way ANOVA of Vitremer's bottom/top KH ratios indicated significant main effects (p < 0.0001) but no significant interaction (p = 0.055). No significant difference was found between the 24-hour and 12-month ratios for any of the thickness groups. One-way ANOVA identified significant differences among the thickness groups, but after 1 month there was no difference between the 2- and 3-mm groups' ratios. With the exception of the 3-month group, the hardness ratios of the 5-mm thickness group were significantly lower than those of the other groups at all time periods.

DISCUSSION

The results of this study are comparable with those reported earlier for RMGI materials,^{17–19} in that top-surface hardness changes were material dependent. Compared with the results reported by Yap,¹⁷ this study found a similar topsurface KH change for Fuji II LC (decrease), but different results for Vitremer (increase) and Photac-Fil (decrease). Unlike the findings of a 12-month study by Ellakuria et al.,¹⁸ our work reported different overall top-surface hardness changes between 24 hours and 12 months. The current study was similar, however, to a 12-month study by Kanchanavasita et al.,¹⁹ in that top-surface hardness values for Fuji II LC and Vitremer were relatively stable over time.

A number of studies have evaluated the depth of cure of RMGI materials.^{13–15,22,23} Most of these studies assessed the adequacy of polymerization at various depths from the surface of the tested RMGI materials. Because a 2-mm depth is often the recommended maximum thickness for clinical placement of these products prior to light activation, it is suggested that when tests for adequacy of polymerization are performed, this thickness be used. This is particularly prudent when using materials susceptible to light attenuation such as those of a dark shade and/or ones containing organic pigments.

Studies of RMGI depth of cure have used a number of different methodologies. None of the studies used the methodology employed in this study, which measured hardness changes over 12 months. The results of our study are very similar to those reported for Vitremer and Fuji II LC in a review article by McCabe;¹³ however, they are in stark contrast to the results for 5-mm-thick specimens reported by Swift et al.¹⁵ Greater values for RMGI depth of cure have been reported by Mount et al.,²² but those authors used a scrape technique, unlike the microhardness technique used in this study. The conclusions reached by Mount et al.²² for Fuji II LC and Vitremer, however, are similar to those of this report.

Using the KH methodology as an indicator of changes occurring in the RMGI materials was believed to be a valid method in this study for two reasons. First, with minor exceptions, all specimens within each specific RMGI material exhibited similar top surface KH values. Also, in cases where each material exhibited a time-dependent top surface hardness change, the effect was similar in all specimens. The relative stability of the top surface hardness values allowed the establishment of a durable platform to base the comparative evaluation of hardness changes in the deeper RMGI regions. Accordingly, the stable top surface hardness platform allowed and justified, under the experimental conditions, using

bottom/top KH ratios as a relative indicator of RMGI change within each material group. The authors do caution overgeneralization of the use of the KH ratios reported in this study to that established for resin composites. Additional research is required with RMGIs, especially correlated with infrared spectroscopy results, before a specific KH ratio can be used as an indicator of RMGI adequacy of cure.

Each material's bottom/top KH ratios (Tables 2C, 3C, 4C) generally decreased with time and then increased. This was particularly true for the 4- and 5-mm specimens. Fuji II LC exhibited significant differences among the various thicknesses at 24 hours, whereas Vitremer showed a significant difference only for the 5-mm specimen group. Interestingly, no significant difference among sample thickness ratios was noted for Photac-Fil at 24 hours. With increased time, all materials displayed KH ratio stratification according to specimen thickness. This stratification was less apparent, however, for the 2- and 3-mm thickness groups of Fuji II LC and Vitremer, as each demonstrated similar KH ratios for their 2- and 3-mm specimens after 1 and 3 months, respectively.

Evaluating differences between 24-hour and 12-month bottom/top

KH ratios for the 4- and 5-mm specimen groups indicates what, if any effect, the chemically activated resin polymerization and ongoing polyalkenoate reaction had on each material's hardness. For Fuji II LC, the 4- and 5-mm groups both showed a significant increase in hardness. With Photac-Fil, only the 4-mm group exhibited a significant increase. Although the hardness change in the deeper levels could be indicative of a slow but ongoing polyalkenoic acid/base reaction, the hardness increase never approached statistical similarity with the 2-mm groups. Vitremer's 4- and 5-mm groups showed no significant change in hardness over 12 months, which suggests that little, if any, additional chemically activated resin polymerization or polyalkenoate acid/base reaction occurs in Vitremer when it is inadequately light activated.

Although in this study we have attributed the changes in post light-activation hardness to the presence of chemically polymerizing resins and a conventional polyalkenoate reaction, other factors may also play a role. For example, hardness may be affected by the imbibition of water by the materials, which may result in softening from plasticization. Also, RMGI hardness could be affected by ion exchange reactions or dissolution of phases that may form on the material's surface. Future research should attempt to determine what roles these post light-activation factors may play. Future research should also address the possible difference between surface and subsurface hardness of RMGI materials. As specimen fabrication involves compressing the surface of the materials just prior to light activation, it is possible that a resin-rich layer forms on the surface. If so, the hardness measured on the exposed surface may not be a true reflection of the materials' actual hardness. In future work, microscopic analysis should be employed to determine if, in fact, this layer forms.

In research, study design is both an art and a science. Researchers should always question their design and seek ways to improve future work. In this study, a source of variability that may have affected the results was the use of different shades for the tested RMGI products. Although A2 was used for Photac-Fil Quick and Fuji II LC, A3 was used for Vitremer. This was because of the fact that no A2 shade is available for Vitremer. In designing the study today, we would use a shade common to all three materials to eliminate the effect that shade differences may have on the results. Specific batch and lot numbers would also have been recorded for future reference should that have been deemed necessary based on the results.

CONCLUSION

Under the conditions of this study, it was observed that RMGI KH changes over time, but specific degrees of change are material dependent. It also suggests that certain RMGI materials demonstrate a potential for post lightactivation chemically initiated resin polymerization and/or polyalkenoate acid/base reaction; however, this is also material dependent. Based on the conditions of this study, it is recommended that Fuji II LC and Vitremer be placed and photopolymerized in layers no thicker than 3 mm to ensure that setting from light activation is maximized. Photac-Fil Quick should be limited to layers of 2-mm thickness to ensure adequate light-cure photopolymerization. The nature and extent of post light-activation reactions require further research.

ACKNOWLEDGMENTS

We would like to thank GC America and 3M/ESPE for donating the materials used in this study.

DISCLAIMER

The opinions expressed within are those of the authors only and do not constitute the official opinion of the US Air Force, US Navy, Department of Defense, or the US Government. No commercial product endorsement is implied. The authors do not have any financial interest in the companies whose materials are included in this article.

REFERENCES

- McLean JW, Nicholson JW, Wilson AD. Proposed nomenclature for glass-ionomer cements and related materials. Quintessence Int 1994;25:587–9.
- Davidson CL, Mjör IA. Advances in glass-ionomer cements. Chicago (IL): Quintessence Publishing; 1999.
- Wilson AD. Resin-modified glass-ionomer cements. Int J Prosthodont 1990;3:425–9.
- Ilie N, Hickel R. Mechanical behavior of glass ionomer cements as a function of loading condition and mixing procedure. Dent Mater J 2007;26:526–33.
- Sidhu SK, Watson TF. Resin-modified glass ionomer materials. A status report for the American Journal of Dentistry. Am J Dent 1995;8:59–67.
- de Gee AJ, Leloup G, Werner A, et al. Structural integrity of resin-modified glass ionomers as affected by the delay or omission of light activation. J Dent Res 1998;77:1658–63.
- Hammesfahr PD. Developments in resin ionomer systems. In: Hunt P, editor. Glass ionomers: The next generation. Proceedings of the Second International Symposium on Glass Ionomers. Philadelphia (PA): International Symposia in Dentistry, PC; 1994. pp. 47–55.
- Nicholson JW. Chemistry of glassionomer cements: a review. Biomaterials 1998;19:485–94.
- Andrzejewska A, Andrzejewska M, Socha E, Zych-Tomkowiak D. Effect of polyacid aqueous solutions on photocuring of polymerizable components of resinmodified glass ionomer cements. Dent Mater 2003;19:501–9.
- Anstice HM, Nicholson JW. Studies in the setting of polyelectrolyte materials. Part II: the effect of organic compounds on a glass poly (alkenoate) cement. J Mater Sci Mater Med 1994;5:299– 302.

- Nicholson JW, Anstice HM. The physical chemistry of light-curable glass-ionomers. J Mater Sci Mater Med 1994;5:119–22.
- Culbertson BM. Glass-ionomer dental restoratives. Prog Polym Sci 2001;26:577–604.
- 13. McCabe JF. Resin-modified glass ionomers. Biomaterials 1998;19:521–7.
- Burke FM, Hamlin PD, Lynch EJ. Depth of cure of light-cured glass-ionomer cements. Quintessence Int 1990;21:977– 81.
- Swift EJ, Pawlus MA, Vargas MA, Fortin D. Depth of cure of resin-modified glass ionomers. Dent Mater 1995;11:196–200.
- Gladys S, Van Meerbeek B, Braem M, et al. Comparative physico-mechanical characterization of new hybrid restorative materials with conventional glassionomer and resin composite restorative materials. J Dent Res 1997;76:883–94.
- Yap AU. Post-irradiation hardness of resin-modified glass ionomer cements and a polyacid-modified composite resin. J Mater Sci Mater Med 1997;8:413–6.
- Ellakuria J, Triana R, Minguez N, et al. Effect of one-year water storage on the surface microhardness of resin-modified versus conventional glass-ionomer cements. Dent Mater 2003;19:286–90.
- Kanchanavasita W, Anstice HM, Pearson GJ. Long-term surface micro-hardness of resin-modified glass ionomers. J Dent 1998;26:707–12.
- Asmussen E. Restorative resins: hardness and strength vs. quantity of remaining double bonds. Scand J Dent Res 1982;90:484–9.
- 21. Dewald JP, Ferracane JL. A comparison of four modes of evaluating depth of cure of light-activated composites. J Dent Res 1987;66:727–30.
- Mount GJ, Patel C, Makinson OF. Resin modified glass-ionomers: strength, cure depth and translucency. Aust Dent J 2002;47:339–43.
- Sigemori RM, Reis AF, Giannini M, Paulillo LA. Curing depth of a resinmodified glass ionomer and two resinbased luting agents. Oper Dent 2005;30:185–9.

- 24. Leonard DL, Charlton DG, Roberts HW, et al. Determination of the minimum irradiance required for adequate polymerization of a hybrid and a microfill composite. Oper Dent 2001;26:176–80.
- 25. Polydorou O, Manolakis A, Hellwig E, Hahn P. Evaluation of the curing depth

of two translucent composite materials using a halogen and two LED curing units. Clin Oral Investig 2008;12:45–51.

 Rueggeberg FA, Craig RG. Correlation of parameters used to estimate monomer conversion in a light-cured composite. J Dent Res 1988;67:932–7. Reprint requests: David G. Charlton, DDS, MSD, Naval Institute for Dental and Biomedical Research, General Dynamics Information Technology, 310A B Street, Bldg 1-H, Great Lakes, IL, USA 60088; e-mail: david.charlton@med.navy.mil Copyright of Journal of Esthetic & Restorative Dentistry is the property of Blackwell Publishing Limited and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.