The properties of experimental resin-modified glass-ionomer luting cements (RMGICs) containing novel monomers.

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Abstract:

Objectives. To investigate working and setting times, compressive fracture strength (CFS), compressive modulus (CM), three-point flexure strength (TFS) and tensile flexure modulus (TFM) of commercial, control and experimental RMGICs.

Methods. RelyX Luting (RX, 3M-ESPE) and Fuji Plus (FP, GC), two control home liquids and eight new liquid compositions (F1-F4 and R1-R4) comprising different percentages of the monomer HPM (hydroxypropyl-methacrylate) and/or THFM (tetrahydrofurfuryl-methacrylate) with the original monomer HEMA (2-hydroxyethyl-methacrylate) were used in this study. The polymerization was initiated chemically (using benzene sulfonic acid sodium-salt in FP powder and potassium persulfate/ascorbic acid in RX powder). Home and experimental liquids were mixed with the corresponding commercial powder. An oscillating rheometer was used to measure the working and setting times (n=6). 20 cylinders per material (6.0±0.1 mm height, 4.0±0.1 mm diameter) were fabricated for CFS and CM testing, 20 bars per material (25.0±0.1 mm length, 2.0±0.1mm width, 2.0±0.1 mm thickness) were made for TFS and TFM testing.

Results. All RX compositions showed longer setting times ($p\leq 0.0001$) and lower CFS values compared to their FP counterparts ($p\leq 0.0001$). The TFS testing showed that commercial and home RMGICs behaved as brittle materials with linear load/deflection curve while experimental materials showed plastic ductile deformation before fracture. F3, F4 and F2 showed significantly higher CFS values compared to the corresponding home material ($p\leq 0.0001$).

Significance. All new experimental compositions demonstrated working and setting times that are clinically acceptable. The new experimental FP compositions containing THFM (especially F3 and F4) demonstrated improved mechanical properties compared to their corresponding home material.

Keywords: Resin modified glass ionomer; mechanical properties; working times; setting times; compressive strength; compressive modulus; flexure strength; flexure modulus.

1 Introduction:

Luting cements play an important role in determining the long-term clinical success of fixed prosthodontic restorations [1]. However, selecting an appropriate material for a particular clinical situation may be challenging due to the wide range available, resulting from recent improvements [2]. Ideally they should have adequate biological, physicomechanical and handling properties [3], and can also be classified according to their bonding durability to, i) low, e.g. zinc phosphate cements, ii) medium, e.g. poly(carboxylate) cements, iii) high, e.g. glass ionomer cements (GICs), resin-modified glass ionomer cements (RMGICs) and resin composites [2].

GICs were first developed by Wilson and Kent at the Laboratory of the Government Chemist in London, United Kingdom and current cements are derived from the first clinically acceptable dental cement (G-200) [4]. GICs generally contain a degradable glass and a polymeric acid [poly(alkenoic acid), e.g. poly(acrylic acid)] in powder and liquid form, but they can also be encapsulated [5]. Despite the various advantages associated with GICs, such as chemical adhesion to tooth structure [6], fluoride release and subsequently caries inhibition [7], they possess disadvantages in relation to their sensitivity to moisture, they are prone to wear and present low flexural strength [8, 9].

Resin cements were introduced in the 1960s, consisting of a resin matrix, filler and coupling agent, which can be chemical, light or dual-cured. They are recommended for restorations lacking retention, such as Maryland bridges and, for aesthetic restorations, due to the availability of different shades (e.g. bonding veneers) [10]. However, they lack the advantages of fluoride release and chemical adhesion to teeth associated with GICs [10].

In order to produce a material that has the advantages of both a resin (e.g. improved strength) and a GIC, a resin system was incorporated into a GIC [11].This was first mentioned in a patent application in 1988 [12] and it was introduced as a new development by Mitra in 1992 [13]. Resin modified glass ionomers (RMGICs) include the same components of GICs with the addition of a suitable resin (usually HEMA) [11, 14]. Compared to GICs, it has been reported that this led to improvements in their mechanical properties including compressive strength [15], modulus of elasticity [16] diametrical indirect tensile strength and flexural strength [16, 17]. However, there are disadvantages associated with the addition of HEMA, such as water uptake and swelling, as a result of the hydrophilic nature of this component [18-20, 44], and also the reduced biocompatibility associated with this monomer [21].

Therefore, it was suggested that it may be beneficial to replace HEMA in RMGIC with monomers that are known to have lower water uptake and may demonstrate improved biocompatibility [22]. Tetrahydrofurfuryl-methacrylate (THFM) and/or hydroxpropyl-methacrylate (HPM) are two monomers proposed to replace HEMA in this study for the formation of experimental RMGICs.

The THFM is a heterocyclic, hydrophobic monomer that has been studied with polyethyl methacrylate (PEM) for potential use as temporary crown and bridge materials [23], fluoride releasing biomaterials [24], and as a tissue repair material [25], where it was reported to be biocompatible in the oral cavity as well as in bone. This monomer was also mentioned in patents concerning RMGICs [26, 27]. Room-temperature polymerizing PEM/THFM has been studied with respect to its water uptake, mechanical properties and potential clinical uses [28-

30]. It was shown to have a low polymerization exotherm [28], and low water uptake (about 1.5% by weight) when measured in a different solutions [31].

HPM is also a hydrogel, just above HEMA in the homologous series, with an extra CH_2 group between the hydroxyl and the methacrylate groups. It has a lower setting exotherm and reduced water uptake compared to HEMA [32]. It can be assumed that it may have similar, or improved, biocompatibility compared to HEMA, since it has a higher molecular weight and its diffusion through the dentinal tubules to the pulp may be more difficult than HEMA [33]. Limited literature was found regarding the use of HPM in the dental applications.

It is essential to test the working and setting times of these new cements to ensure that they demonstrate clinically acceptable features. Also, it is crucial to test the mechanical properties of RMGICs incorporating alternative monomers to HEMA (THFM and HPM) to make sure that their strength is not adversely affected.

The oscillating rheometer has proved useful in the determination of working and setting times of GICs [34]. Using this method, the working and setting times are determined by the change in viscosity and this is directly related to the handling properties and ease of use of each material. All materials should be manipulated within the working time and adjusted and finished inside the mouth within the initial setting time. Any modification beyond the setting time might jeopardize the material's physical properties, and on the other hand, the material requiring a long time to set leads to longer chair-side time. Therefore, the preferred material property is longer working time and 'rapid' setting times [34].

Strength testing of RMGICs is usually carried out following ISO 9917-1 for GICs (CFS), ISO 4049 for resin cements and ISO 9917-2 for RMGICs (TFS). According to Baig *et al.* (2015), CFS was the most reliable mechanical test for hand-mixed GICs compared to TFS, biaxial flexural strength (BFS) and Hertzian indentation (HI) [35]. For resin cements, TFS is usually the test of choice as described in ISO 4049 [36]. As stated by Chung *et al.* (2004), TFS results were more reliable compared to results obtained from BFS, which showed higher CoV compared to TFS [36].Therefore the aims of this study were to:

1. Develop new experimental RMGICs liquids incorporating different percentages of two monomers, HPM and/or THFM, partially/fully replacing HEMA.
2. Test the working and setting times of all materials (commercial, homemade liquids with their corresponding commercial powders and experimental).
3. Investigate CFS, CM, TFS, TFM of home and experimental compositions and compare with available commercial materials.

2 Materials and methods:

2.1 Materials:

This study included two commercial chemically cured RMGICs, Fuji Plus (FP, GC Corporation, Tokyo, Japan) and RelyX Luting (RX, 3M-ESPE, St Paul, MN, USA). They set by an acid-base GIC setting reaction plus the polymerisation of the resin that is initiated chemically; in RelyX Luting the redox system consisted of potassium persulfate and ascorbic acid, that are included in the cement powders [37]. In Fuji Plus, according to manufacturer (GC, Japan), the polymerization takes place using a benzene sulfonic acid sodium salt. The liquid consisted mainly of water, 2-hydroxyethyl methacrylate (HEMA), tartaric acid, poly(acrylic acid) in Fuji Plus and a copolymer of acrylic and itaconic acids in RelyX Luting (Table 1).

RMGIC	Composition	CAS	% by weight	Mixing ratio (g)
FP powder	Fluoroalumino-silicate glass	Not listed	95-100	2
FP liquid	Distilled water	7732-18-5	20-30	1
	Poly (acrylic) acid	9003-01-4	20-30	
	HEMA	868-77-9	25-35	
	Urethanedimethacrylate (UDMA)	72869-86-4	<10	
	Tartaric acid	87-69-4	5-7	
RX powder	Fluoroalumino-silicate glass	Not listed	>98	1.6
	Potassium persulfate	7727-21-1	≤0.2	
RX liquid	Water	7732-18-5	30-40	1
	Copolymer of acrylic and itaconic acids	25948-33-8	30-40	
	HEMA	868-77-9	25-35	
	Ethyl acetate	141-78-6	<2	
	Tartaric acid	Not listed	Not listed	

Table 1 The components and amounts of the two commercial materials investigated with their corresponding CAS number and manufacturers recommended powder: liquid mixing ratio.

Two additional control (home) liquids were prepared in-house, based on the formulations of the commercial liquids as given in the manufacturer's safety data sheets (MSDS). Home liquids were formulated and characterized using Fourier Transform Infrared Spectroscopy (FTIR) and compared with the commercial liquids. The final compositions of the home liquids are presented in Table 2. These home liquids were mixed with the corresponding commercial powders.

RMGIC	Composition	CAS	%
FP in-house liquid	Distilled water	7732-18-5	30
	Poly (acrylic acid)	9003-01-4	30
	HEMA	868-77-9	31
	Urethanedimethacrylate (UDMA)	72869-86-4	4
	Tartaric acid	87-69-4	5
RX in-house liquid	Water	7732-18-5	35
	Poly (acrylic acid)	9003-01-4	30
	HEMA	868-77-9	29
	Ethyl acetate	141-78-6	1
	Tartaric acid	87-69-4	5

Table 2 Home liquid components and amount with their corresponding CAS number.

Eight experimental liquid formulations were prepared, two based on each of the commercial products (RX, FP), where HEMA was replaced with either 100% HPM, 70%/30% HPM/THFM, 70%/30% THFM/HEMA in F2 and R2 or 50%/50% THFM/HEMA in F1 and R1. Attempts were made to replace all the HEMA in the liquid composition with 100% THFM but, as THFM is a hydrophobic monomer, it showed phase separation on mixing with water; thus there was a need for the THFM to be combined with HEMA or HPM to avoid separation.

2.2 Methods:

2.2.1 Working and setting times:

An oscillating rheometer was used to measure working and setting times of commercial, home and novel RMGICs. The oscillating rheometer employed was developed and reported by Bovis *et al.* (1971), consisting of a lower platen with a diameter of 10 mm, and a distance of 1.5 mm between the two platens. The lower platen rotates in an oscillatory movement driven by an electric motor. Amplitude was recorded as displacement of the rod in relation to the center of the lower platen using a 'differential transformer'. The upper platen temperature was controlled using a temperature controlled water bath [38].

The materials were mixed at room temperature (23 ± 1°C) according to the manufacturers powder: liquid mixing ratio (2:1 g:g for FP and 1.6:1 g:g for RX). Immediately following mixing, the mixture was placed on the lower platen and the upper platen, which had a controlled temperature of 37°C, was fixed in place with a 1.5 mm gap from the lower platen [34]. The oscillations were recorded from the start of mixing until the amplitude was zero, using a chart recorder (L200E, Linseis GmbH, Selb, Germany). The rheometer trace decreased with increased viscosity and with time, which was translated into working time when the amplitude reached a 5% decrease in the trace, and setting time when a 95% decrease in the first recorded amplitude trace. Figure 1 is a schematic diagram of an amplitude trace obtained using the oscillating rheometer, showing the working and setting times (decrease by 5% and by 95% respectively) recorded [34, 39].

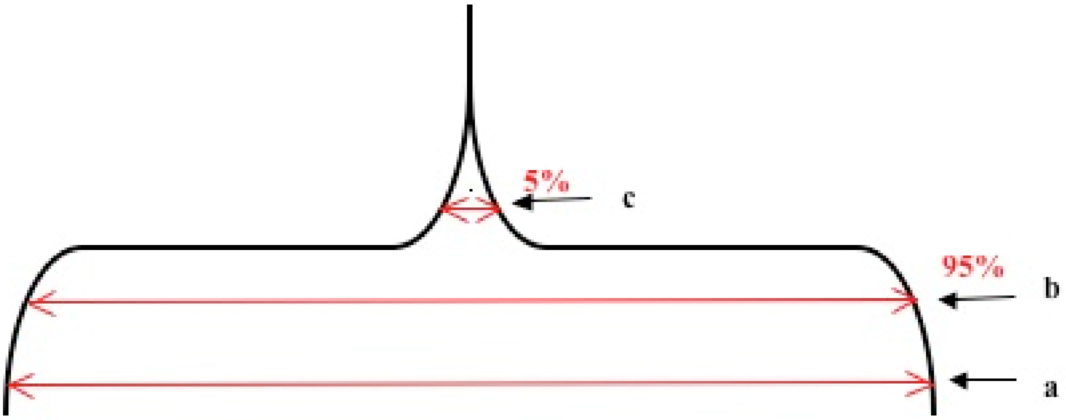

Figure 1 Schematic diagram of amplitude trace of oscillating rheometer which includes, a: start of trace, b: decrease of the trace by 5% corresponding to the working time of the material, c: amplitude decrease by 95% corresponding to setting time of material. Redrawn from Ogawa *et al.* (2001).

2.2.2 CFS and CM:

2.2.2.1 Sample preparation:

A total of 240 RMGICs cylindrical samples (n=20) of commercial, home and novel, experimental RMGICs (6.0 ± 0.1 mm height and 4.0 ± 0.1 mm diameter) were prepared for CFS tests following ISO 9917-1:2007, using a stainless-steel split-mould. Powder and liquid were weighed and mixed following the manufacturer's recommended powder: liquid ratio (2:1 g:g for FP and 1.6:1 g:g for RX). The mix was transferred to the mould and clamped before transferring to an oven (Carbolite, Camlab, Cambridge, UK) maintained at 37 ± 1°C and 100% humidity to set for 1 hour.

After 1 hour, samples were de-moulded and visually inspected for any defects or impurities (e.g. bubbles or chipped edges). The selected samples were then hand-lapped using P600 silicon carbide abrasive paper (Buehler, IL, USA) to remove any residual flash, numbered according to the order that they were made and then stored in 100 mL glass screw-top bottles filled with 50 mL of DW and transferred to an incubator (LTE Qualicool, Scientific

Laboratory Supplies, Yorkshire, UK), maintained at 37 ± 1°C, for a further 23 hours before testing.

2.2.2.2 Compressive fracture testing procedure:

Samples were removed from the test tubes after 24 h from the start of mixing, dried on filter paper and their thickness and diameter were measured using a digital micrometer, accurate to 1μm (Mitutoyo, Kawasaki, Japan). Two pieces of wet filter paper were placed on the two loading platens of the universal testing machine (Instron model 5567, High Wycombe, England) in accordance with ISO 9917-1:2007, in order to test the specimens in a wet environment. The specimen was then placed on the wet filter paper on the loading platen of the testing machine and a compressive load was applied vertically at a loading rate of 1 mm/min. The maximum load-to-failure was recorded and CFS was calculated for each specimen using Equation 1

$$\mathrm{CFS} = \frac{4\mathrm{P}}{(\pi \mathrm{d}^2)} \qquad \text{Equation 1}$$

where P was the load-to-failure in Newton and d the mean specimen diameter in mm.

CFS value is dependent on the specimen dimensions because the height and diameter of each sample have an effect on the load-to-failure and hence can influence the CFS value calculated. However, Ritter (1995) reported that the probability of samples containing defects and impurities was positively affected by increasing the specimen dimensions (height or diameter) and this will therefore negatively affect the CFS value recorded [40]. Therefore, it was suggested that determining the compressive modulus (CM) value for each material is advantageous since CM is considered ‘an intrinsic material property’ and it is not influenced by the sample’s dimensions [41, 42]. CM was calculated by measuring the slope of the initial linear segment of the stress-strain plot for each specimen tested for compressive strength using Equation 2.

$$\mathrm{CM\ (GPa)} = \frac{\mathrm{Stress\ (MPa)}}{\mathrm{Strain\ (\%)}} / 1000 \qquad \text{Equation 2}$$

2.2.3 TFS and TFM:

2.2.3.1 Sample preparation:

The RMGIC control materials (FP and RX) and their experimental variants were chosen using a randomization method whereby selection bias was avoided. Each of the twelve groups, which consisted of twenty specimens (four batches of five) were prepared for each material (n=20). Every batch was assigned a number and prior to cement mixing the material under investigation was chosen at random. The powder and liquid were mixed as described in 2.2.2.1. Polytetrafluoroethylene (PTFE) bar-shaped moulds with internal dimensions of 25.0 ± 0.1 mm (length), 2.0 ± 0.1 mm (thickness), 2.0 ± 0.1 mm (width) were used to manufacture the samples. A mould was placed on a glass microscope slide, covered with an acetate strip and filled with the mixed material from left to right. A second acetate strip was placed on the mould followed by a glass microscope slide and the mould assembly was clamped using two bulldog clips. The mould assembly was transferred to a water-bath maintained at 37 ± 1°C for 1 h. The samples were removed from the water-bath, de-moulded and checked for any defects; those with defects or impurities (e.g. bubbles or chipped edges) were discarded. Flash was removed by hand-lapping the sample using P600 silicon carbide abrasive paper. Samples were then numbered and transferred into 100 mL glass screw-top bottles filled with 50 mL deionized water for a further 23 hours (each batch of samples which included five of the same material prepared at the same time were immersed in individual glass tubes).

2.2.3.2 Three-point flexure strength testing (TFS) procedure:

Samples were removed from the glass tubes after 24 hours from the start of mixing, dried on filter paper and loaded, in accordance with ISO 4049:2009, on a three-point flexure testing assembly, in a universal testing machine (Instron model 5565, High Wycombe, England). The three-point flexure apparatus included a central loading indenter and two point supports of 2 mm diameter each, separated by a fixed loading span of 20 mm. The bars were placed horizontally in the centre of the test apparatus supported by the two point support at each end.

A 100 N load cell was used at a cross-head speed of 1mm/min and the maximum load-to-failure (N) was recorded. The TFS was calculated using Equation (3).

$$\mathrm{TFS} = \frac{3\mathrm{PL}}{2\mathrm{bh}^2} \qquad \text{Equation 3}$$

where P was the load to failure (N), L was the span which was constant (20 mm), b and h were the mean specimen thickness and mean specimen width (mm) which were measured using a digital micrometre accurate to 10 μm.

Similar to CM, tensile flexure modulus (TFM) is an 'intrinsic material property' that can better highlight the structure of the material compared to the strength data. TFM takes into account both the specimen deflection following loading in the three-point flexure test and the load-to-failure. Therefore, TFM was calculated using Equation 4 for each specimen.

$$\mathrm{TFM} = \left(\frac{\Delta\mathrm{P}}{\Delta\mathrm{D}}\right)\frac{\mathrm{L}^3}{4\mathrm{bh}^3} \qquad \text{Equation 4}$$

where $\Delta P/\Delta D$ was calculated as the slope of the steepest initial linear part of the load-deflection curve generated for each specimen.

2.2.4 Statistical methods:

Where appropriate, data were analyzed using one way ANOVA followed by post-hoc Tukey test at significance level of $p=0.05$ using SPSS (IBM SPSS statistics version 22) under the assumptions of normally distributed measurements using Shapiro-Wilk test ($p<0.05$) and equal variances between groups using Levene's test.

3 Results:

3.1.1 Working and setting times:

Table 3 presents the mean working and setting times (± SD) for all materials tested.

Material	**Working time (sec)(SD)**	**Setting times (sec)(SD)**
FP	137 (7.97)^{d,e,f}	207 (9.86)
FP-Home	135 (6.29)^{d,e,f}	339 (21.38)^{d,e}
FI	191 (11.64)^{a,b}	363 (14.07)^{d}
F2	162 (17.80)^{c}	310 (14.03)^{e,f}
F3	113 (4.52)^{f}	273 (11.22)^{f}
F4	125 (8.83)^{f}	286 (12.96)^{f}
RX	206 (19.22)^{a}	465 (31.23)^{a,b,c}
RX-Home	151 (11.01)^{c,d,e}	476 (27.80)^{a,b}
R1	157 (7.01)^{c,d}	497 (34.24)^{a}
R2	134 (6.20)^{d,e,f}	422 (10.51)^{c}
R3	129 (6.29)^{e,f}	442 (32.57)^{b,c}
R4	173 (23.21)^{b,c}	472 (22.34)^{a,b}

Table 3 Mean ± SD of working and setting times for all materials in both groups (FP and RX) measured in seconds. Groups sharing same superscript letter indicates no statistical significant difference ($p<0.05$).

In the FP group, F1 showed a significantly longer working time compared to all other materials (191 ± 11 seconds; $p \leq 0.007$) followed by F2 (162 ± 17 seconds; $p \leq 0.036$). FP, FP-Home, F4 and F3 presented statistically comparable working times ($p \geq 0.052$).

There was a significant difference in the RX group between the commercial, home and novel materials; commercial RX showed a significantly longer working time compared to all other cements (206 ± 19; $p \leq 0.001$). R3 presented with the shortest working time compared to all materials in that group although it was not statistically different from, R2 and RX-Home ($p \geq 0.106$).

The two commercial materials (FP and RX) presented significantly different working times ($p < 0.0001$), with RX showing a longer working time than FP, by about 69 seconds (approximately 50% of the total working time of FP). This indicates a clinically significant difference between the two materials. However, there was no significant difference between the two home materials when comparing their working times ($p = 0.518$).

The setting time for commercial FP was significantly lower than all other materials in the group (207 ± 9 seconds; $p < 0.0001$). This was followed by F3, F4 and F2 (273 ± 11 seconds, 286 ± 12 seconds and 339 ± 21 seconds). Composition F1 had the longest setting time in the FP group (363 ± 14 seconds) although it was not statistically significant from FP-Home ($p = 0.763$).

In the RX group, RX commercial showed comparable setting times (465 ± 31 seconds) compared to all materials in the same group ($p \geq 0.053$). Although the setting time of R2 (422 ± 10 seconds) was not significantly different from RX and R3 (442 ± 32 seconds; $p \geq 0.053$), it was shorter than R4, RX-Home and R1 (472 ± 22 seconds, 476 ± 27 seconds and 497 ± 34 seconds; $p \leq 0.011$).

All FP compositions (commercial, home and novel materials) demonstrated significantly shorter setting times compared to all materials in the RX group ($p \leq 0.0001$).

3.1.2 Compressive fracture strength (CFS) and compressive modulus (CM):

Mean CFS and CM for twenty samples of each material ($n=20$; commercial, home and novel) in both groups (FP and RX) are presented in Table 4.

Material	CFS (SD) (MPa)	CoV	CM (SD) (GPa)	CoV
FP	131.75 (8.97)	0.07	1.18 (0.22)	0.19
FP-Home	77.38 (5.26)	0.07	0.59 (0.12)^{d,e}	0.20
F1	87.09 (9.97)^{b}	0.11	0.70 (0.21)^{c,d}	0.30
F2	96.81 (7.21)^{a}	0.07	0.87 (0.13)^{a}	0.15
F3	103.25 (10.46)^{a}	0.10	0.85 (0.15)^{a,b}	0.18
F4	101.83 (7.39)^{a}	0.07	0.84 (0.12)^{a,b,c}	0.14
RX	88.27 (7.41)^{b}	0.08	0.70 (0.21)^{b,c,d}	0.30
RX-Home	54.06 (2.80)^{c}	0.05	0.43 (0.07)^{f}	0.16
R1	53.72 (1.94)^{c}	0.03	0.41 (0.07)^{f}	0.18
R2	52.24 (2.93)^{c}	0.06	0.43 (0.10)^{f}	0.22
R3	57.54 (3.87)^{c}	0.07	0.43 (0.11)^{f}	0.25
R4	66.46 (4.06)	0.06	0.53 (0.09)^{e,f}	0.16

Table 4 Mean CFS, CM, standard deviations (SD) and coefficient of variation (CoV) for all materials tested (commercial, home and novel). Groups sharing same superscript letter indicates no statistical significant difference ($p<0.05$).

FP presented the highest CFS value compared to all materials in both groups ($p<0.0001$), followed by F3, F4 and F2 between which there were no statistically significant differences ($p \geq 0.097$). F1 containing 100% HPM showed the lowest CFS compared to all novel materials ($p<0.0001$).

The mean CFS for R4 was the highest compared to home and novel materials in the same group ($p \leq 0.002$), but it was lower than commercial RX ($p<0.0001$).

When comparing the CFS between the two groups, RX compositions showed lower values compared to their FP counterparts, in particular the home and novel materials ($p \leq 0.0001$).

The CoV (SD divided by the mean), for FP materials ranged from 0.7 to 0.11, whilst in the RX group it ranged from 0.3 to 0.8; this indicates good reproducibility of the CFS data.

Table 4 highlights mean CM values for all materials. FP showed the highest compressive modulus compared to all other materials ($p<0.001$) similar to the CFS (Table 8). Also similar to the CFS data, CM of RX novel and home materials were lower than all FP compositions (commercial, home and novel) ($p \leq 0.032$). Commercial RX had comparable CM to FP-Home, F1 and F4.

3.1.3 Three-point Flexure strength (TFS) and tensile flexure modulus (TFM):

For all materials investigated in both groups (FP and RX) the TFS and TFM are presented in Table 5.

Material	TFS (SD) (MPa)	CoV	TFM (SD) (GPa)	CoV
FP	17.20 (3.85)	0.22	4.77 (0.53)	0.11
FP-Home	7.75 (1.59)^{d,e}	0.21	2.39 (0.34)^{b}	0.14
F1	7.19 (2.73)	0.38	2.28 (0.96)^{b,c}	0.42
F2	8.03 (1.99)^{c,d,e}	0.25	2.73 (0.92)^{a,b}	0.34
F3	10.37 (1.29)^{a,b}	0.12	2.98 (0.50)^{a}	0.17
F4	10.28 (0.92)^{a,b,c}	0.09	2.58 (0.66)^{a,b}	0.25
RX	20.85 (3.86)	0.19	2.32 (0.24)^{b,c}	0.10
RX-Home	8.40 (1.65)^{b,c,d,e}	0.20	1.67 (0.22)^{d,e}	0.13
R1	9.48 (1.19)^{a,b,c,d}	0.13	1.48 (0.36)^{d,e}	0.24
R2	9.91 (1.81)^{a,b,c,d}	0.18	1.79 (0.19)^{c,d}	0.11
R3	10.96 (1.35)^{a}	0.12	1.32 (0.16)^{d,e}	0.12
R4	8.87 (1.58)^{a,b,c,d,e}	0.18	1.19 (0.16)^{e}	0.13

Table 5 Mean of three point flexural strength (TFS), standard deviations (SD) and coefficient of variation (CoV) for all materials (commercial, home and novel). Groups sharing same superscript letter indicating no statistical significant difference at (p<0.05).

The one-way ANOVA analyses showed a significant difference between groups ($p<0.0001$); then the post-hoc Tukey's test confirmed that TFS for RX was the highest compared to all materials in both groups ($p<0.0001$), followed by FP commercial ($p<0.0001$). Conversely, the two home materials showed lower TFS results compared to their commercial counterparts and were also lower than some of the corresponding novel compositions. As an example, F3 and F4 showed higher TFS compared to the home material ($p\leq 0.017$), whilst only R3 in the RX group presented with a higher value compared to the home material in the same group ($p=0.014$).

During testing it was noted that some materials demonstrated different load/deflection curves. Commercial (FP and RX) and home materials showed a linear load/deflection curve typically associated with brittle materials, whilst novel materials showed plastic deformation (deviation from linearity) before fracture; this is indicative of the material being ductile rather than brittle. Differences between the brittle and ductile materials curves are presented in Figure 2. Therefore, the load at fracture value needed for the measurement of TFM of ductile materials was determined from the initial linear region of the curve (up to the elastic limit) rather than the load at fracture, and moreover the deflection of the sample was taken at the same point.

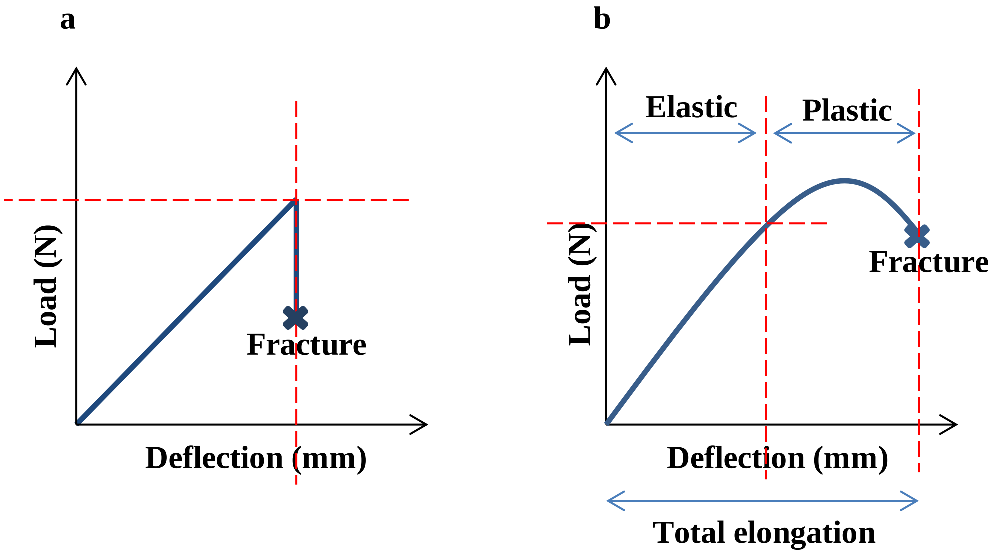

Figure 2 Schematic diagram of load/deflection curve in TFS test used to calculate TFM where a: is a typical load/deflection curve for brittle materials and b: represents the curve associated with ductile materials.

Table 5 represents the TFM data for all materials. One-way ANOVA confirmed a significant difference of $p<0.0001$ between groups, which was then followed by Post hoc Tukey test to demonstrate the significant difference between materials at $p<0.05$. According to Tukey test, FP showed the highest TFM compared to all materials in both groups ($p<0.0001$).

4 Discussion:

The presence of HEMA in RMGICs has been known to cause problems. The latter are associated with HEMA's high water uptake, which leads to swelling of the matrix [43, 44]. This increases the incidence of the all-ceramic fracture when cemented with RMGIC [45, 46]. Agha *et al.* (2016) reported that replacing HEMA partially with THFM resulted in the formulations having lower volume changes and absorbing less water from distilled water and artificial saliva, compared with commercial FP and RX materials [44]. Hence, this study focused on developing experimental RMGICS with HPM and THFM replacing HEMA. In dentistry, HEMA is highly effective due to it being a bifunctional monomer with one end of its structure being hydrophilic and the other hydrophobic [47]. Its hydrophilic nature is desirable when bonding to dentine as it increases the wettability of the adhesive material, and as a result, increases the bond strength [48]. Therefore, in this study, HEMA was replaced only partially when using THFM; since THFM is more hydrophobic than HEMA, and so the benefits of HEMA's hydrophilicity would be lost if it was replaced completely. Eight different experimental compositions were formulated and their mechanical properties were tested; four were based on FP and the other four on RX formulations. Two further home liquids were prepared as controls. THFM and HPM are known for their low water uptake [29] and THFM for its improved biocompatibility compared to HEMA; the latter is conventionally used in commercial RMGICs [22].

The oscillating rheometer method was used to determine the working and setting times although it was not advocated in the ISO standards 4049:2009 and was criticized by some dental researchers [49-52]. The sensitivity of the oscillating rheometer can be influenced by the strength of the spring that controls the oscillation of the lower platen. Weak springs would emphasize the initial changes and strong springs would emphasize the final changes on setting, therefore, Bovis *et al.* (1971) reported using a tension that falls between the two [38]. Additionally, Vermilyea *et al.* (1977) found that the measured setting times of zinc phosphate cements were longer if measured using a method that stirred the cement compared to a method that did not. It was suggested that the continuous motion inhibited matrix formation resulting in lower viscosity and prolonged working and setting time [52]. Despite all previously mentioned criticism, the oscillating rheometer gives a good indication of the clinical and handling properties of the material since it is directly linked to the change in viscosity of the tested cement [34].

F1 and F2 had longer working times compared to all other compositions, which indicates a slower reaction. The explanation for this is that these two compositions contained HPM instead of HEMA and, as HPM includes an additional CH_2 compared to HEMA, it therefore has a higher molecular weight, which may contribute to the increase in viscosity and movement of the monomers within the matrix, resulting in longer working times [53, 54]. This was also confirmed in an article where THFM was partially replaced with either HEMA or HPM; the system employing HPM showed reduced reactivity compared to that containing HEMA [32]. It was difficult to correlate the results of the novel compositions with existing literature since there were neither similar products, nor similar experimental compositions available in literature. However, these results agreed with commercial FP instruction leaflet, which quotes the working time of the cement as 2.30 minutes.

Setting time behavior for all materials did not follow the same trend as the working times therefore these two parameters could not be correlated and should be studied separately for each product, as was stated in literature [34].

RX group showed longer working times and they took a longer time to set (8.29 for R1 and 7.03 for R2; all other compositions times fell between these two). The working and setting times could be influenced by the powder: liquid ratio of each material. FP group had a higher powder: liquid ratio compared to RX and thus higher viscosity, which subsequently affected the working and setting times, and these were shorter than those of the RX group. Therefore, the FP group demonstrated better handling properties, despite their shorter working times compared to RX, as they also showed shorter setting times. However, although shorter setting times are preferable to reduce chairside time, it might not be the choice for inexperienced clinicians who may need more time to manipulate and finish the restoration.

Since RMGICs include both the components of the GICs and resin cements, the choice of strength tests was the one recommended in the ISO 4049:2009 for resin cements, ISO 9917-2:2010 for RMGICs and the one advocated to be used when testing the strength of GICs (CFS) in ISO 9917-1:2010. CM and TFM were moreover studied since they demonstrate intrinsic materials properties and are not affected by specimen's dimension [35].

All novel compositions and home materials presented with lower CFS compared to commercial FP, which may have been a result of the lower molecular weight poly(acrylic acid) used to formulate the home and novel cements liquid (~2000). Cements with higher molecular weights are expected to have more cross-linked polyacrylate chains and therefore a higher strength [55, 56]. Wilson *et al.* (1989) reported the improvement in the GICs performance when increasing the poly(acrylic acid) molecular weight, which corresponds to longer polymer chains [57]. This also agrees with published literature on the relationship between molecular weight of poly(acrylic acid) and CFS [55, 58]. Although the molecular weight of poly(acrylic acid) used in the commercial liquids could not be identified, it was speculated to be in the range of 2000 or more. However, although using a high molecular weight poly(acrylic acid) could enhance the physical properties of the cements, it also causes an increase in viscosity [59], which in turn makes it difficult to manipulate especially when used as a luting cement.

All materials in the RX group showed lower CFS than the FP group. This may be due to the higher water content and lower powder: liquid ratio in RX compared to FP. Some of this water was lost in the immersion solution during storage prior to testing, and this was confirmed by the solubility results where RX had higher solubility compared to FP [44]. The higher the solubility of the cement, the higher the percentage of pores and porosity [60], which in turn contributes to the reduced strength of the material [61]. CM values were generally in agreement with CFS as FP showed significantly higher values compared to all materials in both groups. The study showed promising results for compositions containing THFM especially (F3 and F4), when comparing their CFS and CM with the home material; as such these systems are worthy of further research.

As mentioned earlier, TFS was the selected test for strength of polymer based materials according to ISO 4049:2009 and ISO 9917-2:2010. However, this test was questioned for its reliability due to the stresses developing in the specimen during the test. A compressive stress occurs in the top surface of the specimen and a tensile stress at the bottom, while the stress is equal to zero in the central region [62]. Hence, the effect of surface finishing could affect the values obtained from TFS test [63]. Thus, samples in this study were all treated in the same way and the two surfaces that were exposed to stresses (top and bottom) were the ones that were in contact with the acetate sheet during the setting of the sample. However, the possibility of different surface textures in all samples could not be ruled out and could have played a role in the values obtained. Therefore, TFM was calculated to give a better idea of the strength of the material, as similar to CM, it is considered an intrinsic material property.

Similar to CFS, TFS of the two commercial materials were higher than for the home and novel cements, which again could be related to the higher molecular weight poly(acrylic acid) used in the commercial products. Promising results were obtained for F3 and F4 as similar to CFS and CM presented with higher value than the home material and moreover pass the ISO 9917-2:2010 requirement of a minimum 10 MPa for TFS. The latter also applies to R3, which also passed the ISO 9917-2:2010 requirements.

The load/deflection curves for the novel materials showed ductile behavior compared to brittle behaviour, as presented by the home and commercial cements. The former materials did not fracture immediately after reaching the maximum stress point, but rather underwent some plastic deformation prior to fracture. This could be due to a lower degree of conversion in compositions containing HPM (F1, F2, R1 and R2). Also in compositions where THFM was employed (F3, F4, R3 and R4), this may have been a result of the increased molecular weight of this monomer (compared to HEMA) and also the ductility of THFM, which was confirmed by Patel and Braden when studied with PEM [28, 64].

TFM data generally showed similar trends to CM where FP had a higher value compared to all materials in both groups. Moreover, FP compositions presented with higher TFM compared to their RX counterparts. However, CoV was relatively high reaching 42% in F1, which might have been a result of the subjectivity in choosing the end of the initial linear region in order to calculate the TFM. CoV of CFS data were considerably low, ranging between 3-11%, compared to higher CoV calculated of TFS data reaching 38% in F1, which makes the CFS test more reliable in determining the strength of the materials tested. This is in agreement with Baig *et al.* (2015) as the authors concluded that the CFS is ‘the only discriminatory performance indicator of hand-mixed GICs’ [35].

Conclusion:

1- Although times varied between materials in each group, all new experimental compositions demonstrated working and setting times that are clinically acceptable and, more importantly, satisfactory working times (not lower than the commercial). The latter will enable clinicians to manipulate the cement and the seating of the crowns or bridges [65].

2- All novel materials passed the ISO 9917-1:2010 requirements for a minimum of 50 MPa for CFS, and moreover, F3, F4 and R3 passed the ISO 9917-2:2010 requirement for a minimum of 10 MPa for TFS.

3- The new experimental FP compositions containing THFM (especially F3 and F4) demonstrated improved mechanical properties compared to their corresponding home materials, which emphasize the need for more research on these compositions.

4- The novel formulations have potential to fully or partially replace HEMA in RMGICs in order to improve the problems associated with HEMA containing RMGICs.

5 References:

[1] Ladha K, Verma M. Conventional and contemporary luting cements: an overview. J Indian Prosthodont Soc 2010;10:79-88.

[2] Pameijer CH. A review of luting agents. Int J Dent 2012; 2012:752861. https://doi:10.1155/2012/752861.

[3] Rosenstiel SF, Land MF, Crispin BJ. Dental luting agents: A review of the current literature. J Prosthet Dent 1998;80:280-301.

[4] Wilson AD. A Hard Decade's Work: Steps in the Invention of the Glass-ionomer Cement. J Dent Res 1996;75:1723-7.

[5] McLean JW. Evolution of glass-ionomer cements: a personal view. J Esthet Dent 1994;6:195-206.

[6] Wilson AD, McLean JW. Glass-ionomer cement. Michigan: Quintessence Pub. Co.; 1988.

[7] Mount GJ. Glass ionomer cements and future research. Am J Dent 1994;7:286-92.

[8] Cho SY, Cheng AC. A review of glass ionomer restorations in the primary dentition. J Can Dent Assoc 1999;65:491-5.

[9] Lohbauer U. Dental Glass Ionomer Cements as Permanent Filling Materials? – Properties, Limitations and Future Trends. Materials 2009;3:76-96.

[10] Diaz-Arnold AM, Vargas MA, Haselton DR. Current status of luting agents for fixed prosthodontics. J Prosthet Dent 1999;81:135-41.

[11] Mathis RS, Ferracane JL. Properties of a glass-ionomer/resin-composite hybrid material. Dent Mater 1989;5:355-8.

[12] Antonucci JM, McKinney JE, Stansbury JW. Resin-modified glass ionomer cement. US Patent 1988; 7,160,856.

[13] Mitra S.B., Photocurable ionomer cement systems. US Patent 1992; 5,130,347.

[14] Nicholson JW, Anstice HM. The Physical-Chemistry of Light-Curable Glass-Ionomers. J Mater Sci Mater Med 1994;5:119-22.

[15] Mallmann A, Ataide JC, Amoedo R, Rocha PV, Jacques LB. Compressive strength of glass ionomer cements using different specimen dimensions. Braz Oral Res 2007;21:204-8.

[16] Yamazaki T, Schricker SR, Brantley WA, Culbertson BM, Johnston W. Viscoelastic behavior and fracture toughness of six glass-ionomer cements. J Prosthet Dent 2006;96:266-72.

[17] Xie D, Brantley WA, Culbertson BM, Wang G. Mechanical properties and microstructures of glass-ionomer cements. Dent Mater 2000;16:129-38.

[18] Yap AUJ. Resin-modified glass ionomer cements: a comparison of water sorption characteristics. Biomaterials 1996;17:1897-900.

[19] Meyer JM, Cattani-Lorente MA, Dupuis V. Compomers: between glass-ionomer cements and composites. Biomaterials 1998;19:529-39.

[20] Karaoglanoglu S, Akg, Uuml, L N, Ouml, Zdabak HN, et al. Effectiveness of surface protection for glass-ionomer, resin-modified glass-ionomer and polyacid-modified composite resins. Dent Mater 2009;28:96-101.

[21] Nicholson JW, Czarnecka B. The biocompatibility of resin-modified glass-ionomer cements for dentistry. Dent Mater 2008;24:1702-8.

[22] Pearson GJ, Picton DC, Braden M, Longman C. The effects of two temporary crown materials on the dental pulp of monkeys (Macaca fascicularis). Int Endod J 1986;19:121-4.

[23] Ibsen R, Glace W. Provisional crown-and-bridge resin. US Patent 1981; 4,264,489.

[24] Patel MP, Braden M, Pearson GJ. Fluoride releasing biomaterial. UK Patent application 1995; 95,011,839.

[25] Braden M, Downes S, Patel MP, Davy K. The use of biomaterials for tissue repair. A polymeric system for the intra-oral delivery of an anti-fungal agent. UK Patent 1991;91,244,871.

[26] Mitra SB, Mitra S. Universal water-based medical and dental cement. US Patent 1992; 5,154,762

[27] Anstice HM, Kanchanavasita W, Pearson GJ, Schottlander BD, Sherpa AL. Polymerizable cement compositions. US Patent 2001; 6,313,192.

[28] Patel MP, Braden M. Heterocyclic methacrylates for clinical applications. I. Mechanical properties. Biomaterials 1991;12:645-8.

[29] Patel MP, Braden M. Heterocyclic methacrylates for clinical applications. III. Water absorption characteristics. Biomaterials 1991;12:653-7.

[30] Patel MP, Braden M. Heterocyclic methacrylates for clinical applications. II. Room temperature polymerizing systems for potential clinical use. Biomaterials 1991;12:649-52.

[31] Sawtell RM, Downes S, Patel MP, Clarke RL, Braden M. Heterocyclic methacrylates for clinical applications-further studies of water sorption. J Mater Sci Mater Med 1997;8:667-74.

[32] Patel MP, Johnstone MB, Hughes FJ, Braden M. The effect of two hydrophilic monomers on the water uptake of a heterocyclic methacrylate system. Biomaterials 2001;22:81-6.

[33] Dantas RV, Conde MC, Sarmento HR, Zanchi CH, Tarquinio SB, Ogliari FA, et al. Novel experimental cements for use on the dentin-pulp complex. Braz Dent J 2012;23:344-50.

[34] Ogawa T, Tanaka M, Matsuya S, Aizawa S, Koyano K. Setting characteristics of five autopolymerizing resins measured by an oscillating rheometer. J Prosthet Dent 2001;85:170-6.

[35] Baig MS, Dowling AH, Cao X, Fleming GJ. A discriminatory mechanical testing performance indicator protocol for hand-mixed glass-ionomer restoratives. Dent Mater 2015;31:273-83.

[36] Chung SM, Yap AU, Chandra SP, Lim CT. Flexural strength of dental composite restoratives: comparison of biaxial and three-point bending test. J Biomed Mater Res B Appl Biomater 2004;71:278-83.

[37] RelyX Luting Cement and RelyX Luting Plus Cement-technical product profile. http://multimedia.3m.com/mws/media/250363O/relyxtm-luting-luting-plus-cement.pdf; 2009 [accessed 06.06.17].

[38] Bovis SC, Harrington E, Wilson HJ. Setting characteristics of composite filling materials. Br Dent J 1971;131:352-6.

[39] Pearson GJ, Atkinson AS. Effects of temperature change on the working and setting characteristics of water-based dental cements. Dent Mater 1987;3:275-9.

[40] Ritter JE. Predicting lifetimes of materials and material structures. Dent Mater 1995;11:142-6.

[41] Dowling AH, Fleming GJP. Is encapsulation of posterior glass-ionomer restoratives the solution to clinically induced variability introduced on mixing? Dent Mater 2008;24:957-66.

[42] Dowling AH, Fleming GJP. Are encapsulated anterior glass-ionomer restoratives better than their hand-mixed equivalents?. J Dent 2009;37:133-40.

[43] Braden M, Causton EE, Clarke RL. Diffusion of water in composite filling materials. J Dent Res 1976;55:730-2.

[44] Agha A, Parker S, Patel MP. Development of experimental resin modified glass ionomer cements (RMGICs) with reduced water uptake and dimensional change. Dent Mater 2016;32:713-22.

[45] Sindel J, Frankenberger R, Kramer N, Petschelt A. Crack formation of all-ceramic crowns dependent on different core build-up and luting materials. J Dent 1999;27:175-81.

[46] Federlin M, Schmidt S, Hiller KA, Thonemann B, Schmalz G. Partial ceramic crowns: influence of preparation design and luting material on internal adaptation. Oper Dent 2004;29:560-70.

[47] Bakopoulou A, Papadopoulos T, Garefis P. Molecular toxicology of substances released from resin-based dental restorative materials. Int J Mol Sci 2009;10:3861-99.

[48] Hasegawa T, Manabe A, Itoh K, Wakumoto S. Investigation of self-etching dentin primers. Dent Mater 1989;5:408-10.

[49] Plant CG, Jones IH, Wilson HJ. Setting characteristics of lining and cementing materials. Br Dent J 1972;133:21-4.

[50] Jacobsen PH. Working time of polymeric restorative materials. J Dent Res 1976;55:244-51.

[51] Cook WD, Brockhurst P. The oscillating rheometer--what does it measure?. J Dent Res 1980;59:795-9.

[52] Vermilyea S, Powers JM, Craig RG. Rotational viscometry of a zinc phosphate and a zinc polyacrylate cement. J Dent Res 1977;56:762-7.

[53] Abed YA, Sabry HA, Alrobeigy NA. Degree of conversion and surface hardness of bulk-fill composite versus incremental-fill composite. Tanta Dent J 2015;12:71-80.

[54] Atai M, Watts DC, Atai Z. Shrinkage strain-rates of dental resin-monomer and composite systems. Biomaterials 2005;26:5015-20.

[55] Griffin S, Hill R. Influence of poly(acrylic acid) molar mass on the fracture properties of glass polyalkenoate cements. J Mater Sci 1998;33:5383-96.

[56] Wilson AD, Crisp S, Abel G. Characterization of glass-ionomer cements 4. Effect of molecular weight on physical properties. J Dent 1977;5:117-20.

[57] Wilson AD, Hill RG, Warrens CP, Lewis BG. The influence of polyacid molecular weight on some properties of glass-ionomer cements. J Dent Res 1989;68:89-94.

[58] Fennell B, Hill RG. The influence of poly(acrylic acid) molar mass and concentration on the properties of polyalkenoate cements Part III Fracture toughness and toughness. J Mater Sci 2001;36:5185-92.

[59] Dowling AH, Fleming GJP. The influence of poly(acrylic) acid number average molecular weight and concentration in solution on the compressive fracture strength and modulus of a glass-ionomer restorative. Dent Mater 2011;27:535-43.

[60] Bertenshaw BW, Piddock V. Porosity in water-based dental luting cements. J Mater Sci Mater Med 1993;4:415-7.

[61] Nomoto R, Komoriyama M, McCabe JF, Hirano S. Effect of mixing method on the porosity of encapsulated glass ionomer cement. Dent Mater 2004;20:972-8.

[62] Kumar N. Inconsistency in the strength testing of dental resin-based composites among researchers. Pak J Med Sci 2013;29:205-10.

[63] Berenbaum R, Brodie I. Measurement of tensile strength of brittle materials. Br J Appl Phys 1959;10:281-7.

[64] Moore DR, Turner S. 8 - Strength, ductility and toughness: general principles. In: Mechanical Evaluation Strategies for Plastics, Cambridge: Woodhead Publishing; 2001. p. 169-200.

[65] Lad PP, Kamath M, Tarale K, Kusugal PB. Practical clinical considerations of luting cements: A review. J Int Oral Health : JIOH 2014;6:116-20.