



Original Article

Improving flexural strength of resin modified glass-ionomer cement by poly(alkenoic acid) modifications

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Abstract

Poly(alkenoic acid)s based on copolymers of acrylic acid and itaconic acid were synthesized and further modified with glutamic acid (Glu) and glycidyl methacrylate (GMA). The resultant polymers were characterized by means of proton nuclear magnetic resonance, gel permeation chromatography, and elemental analysis. Specimens of resin modified glass-ionomer cement (RMGIC) prepared from the cement-forming reactions between the synthesized polymers and a commercially reactive glass were fabricated and investigated for flexural strength using three-point bending test. The effects of different amounts of Glu and GMA on the flexural strength were evaluated. The results showed significantly improved cement strength due to the incorporation of Glu into the copolymer with an optimal feed of Glu and GMA at 0.1-0.2 and 0.4 per mole of copolymer, respectively. The addition of 2-hydroxyethyl methacrylate (HEMA) to the RMGIC formulations tremendously increased the cement strength. In this study, a formulation containing 20%-wt. of HEMA and 45%-wt. of polymer concentration gave the highest flexural strength with 62.7 ± 3.4 MPa.

Keywords: flexural strength, poly(alkenoic acid), glutamic acid, glycidyl methacrylate, resin modified glass-ionomer cement

1. Introduction

Since it was invented 40 years ago, glass-ionomer cements (GICs) - a cement set by acid-base reaction between the basic fluoro-aluminosilicate glass and the aqueous poly(alkenoic acid) - have been considerably changed in compositions in order to eliminate their disadvantages. The first cement forming acid is poly(acrylic acid), which undergoes gelation after a period of time due to intermolecular hydrogen bonding (Crisp, 1975). The gelation of poly(acrylic acid) is then prevented by copolymerization of acrylic acid with other unsaturated carboxylic acids that are less regular than acrylic acid and so less liable to form intermolecular

hydrogen bonds. Those copolyacids, particularly copolymers of acrylic and itaconic acids or maleic acids have been the most important ones of the poly(alkenoic acid)s used to date. A major advancement in GIC technology occurred in the late 1980s when the combined GIC with light-cured resin, the so-called resin modified glass-ionomer cement (RMGIC) was introduced (Wilson, 1989; 1990). The original RMGIC was simply produced by the addition of 2-hydroxyethyl methacrylate (HEMA) to GIC (Wilson, 1989; 1990; Mitra, 1991; Momoi *et al.*, 1995) which then led to the addition of other methacrylate substances, usually those used in dental composite resin. RMGIC that contains polymerizable double bonds undergoes dual setting reactions by further polymerization of poly(alkenoic acid), besides the conventional acid-base reaction. There have been various studies (Kao *et al.*, 1996; Xie *et al.*, 1998; Culbertson, 2001; 2006) showing that the main cause of the poor cement strength was the chemical

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structures of poly(alkenoic acid)s in GIC. During the course of acid-base reaction, not all the carboxylic acid groups of poly(alkenoic acid) are converted to carboxylate groups to form a complex with the metal ion released from the glass. When most of the carboxylic groups have been ionized, the negative charge on the polymer chain increase to such an extent that the positively charged hydrogen ions become very strongly bound to the remaining un-ionized carboxylic acid groups and are not easily replaced by metal ions. Moreover, the close attachment of carboxylic groups to the polyacid backbone and to each other resulted in a very rigid polymeric structure. This lessened mobility of the polymeric chain also reduced the ability of ion-carboxylate complex formation, hence weakening the set cement. In order to overcome this problem, recent studies have incorporated different monomers such as N-vinylpyrrolidone (Xie *et al.*, 1998; Culbertson, 2006), N-vinylcaprolactam (Moshaverinia *et al.*, 2009a) and amino acid derivatives (Kao *et al.*, 1996; Wu *et al.*, 2003; Xie *et al.*, 2004a;b; Moshaverinia *et al.*, 2009b) as spacers between the carboxylic groups. Terpolymers with these spacer-monomers rendered the polymeric backbone more flexible with less steric hindrance, allowing greater access for acid-base reaction. This method of modification was proved to be a promising way to enhance the mechanical properties of cements.

In this study, an attempt was made to improve the flexural strength of RMGIC by following the promising route of introducing spacers between carboxylic groups. Instead of the synthesis of terpolymer, the random attachment of an amino acid onto the copolymer was chosen as a new method to introduce spacers. The copolymers of acrylic acid and itaconic acid (CAI) were synthesized and then randomly attached with glutamic acid (Glu) to get chemical structures different from those of the terpolymers. These Glu incorporating copolymers (CAI-Glu) were further reacted with glycidyl methacrylate (GMA) to obtain active sites for light-initiated polymerization. The synthesized polymers (CAI-Glu-GMA) were characterized and their formed cements were investigated. The effects of adding Glu and GMA to the copolymer as well as the amount of added HEMA and polymer concentration on flexural strength were evaluated.

2. Experimental

2.1 Materials

Acrylic acid (AA) and N-(3-dimethylaminoethyl)-N'-ethylcarbodiimide hydrochloride (EDAC) were obtained from Acros Organics Co. Itaconic acid (IA), glycidyl methacrylate (GMA) and pyridine were purchased from Aldrich Chemical Co. L-glutamic acid (Glu), N-hydroxysuccinimide (NHS), 2-hydroxyethyl methacrylate (HEMA), butylated hydroxytoluene (BHT) and potassium persulfate ($K_2S_2O_8$) were purchased from Fluka Chemicals. Solvents were reagent grade and obtained from Lab-scans Ltd. All chemicals were used as received.

2.2 Polymer synthesis

2.2.1 Synthesis of copolymer

Copolymers of AA and IA having different AA/IA molar ratios were prepared in an aqueous solution with $K_2S_2O_8$ as an initiator and isopropanol as a chain transfer agent. The reaction was carried out at 80°C for 4 hrs under nitrogen atmosphere. The synthesized copolymer (CAI) was concentrated by rotary evaporator (Büchi Rotavapor R-114, Büchi Lab., Switzerland), and dried using a lyophilizer (Supermodulyo-230, Thermo Electron Corp., U.S.A.).

2.2.2 Modification of CAI with Glu

CAI was modified with Glu in an aqueous solution using EDAC/NHS as catalysts. The mixture of CAI with catalysts was heated at 80°C for 30 minutes under nitrogen atmosphere. Then, a certain amount of Glu was slowly added into the mixture. The reaction was kept at 80 °C for 24 hrs. The purification of the product (CAI-Glu) was performed by dialysis technique in deionized water for 48 hrs, following by dehydration using freeze-drying method.

2.2.3 Modification of CAI-Glu with GMA

CAI-Glu was reacted with various amounts of GMA in THF using pyridine as a catalyst and BHT as an inhibitor. The reaction was carried out under nitrogen atmosphere at 60°C for 5 hrs and then kept at room temperature overnight. The resulting product (CAI-Glu-GMA) was precipitated in diethyl ether and dried in a vacuum oven at room temperature.

2.3 Characterization

All modified CAIs were characterized by proton nuclear magnetic resonance (1H NMR, Bruker DPX-300 spectrometer, Bruker BioSpin AG, Switzerland) using D_2O as a solvent. The molar mass of CAI was determined by Gel Permeation Chromatography (GPC, Water 600E, Waters Corp., U.S.A.). The analytical column was an ultrahydrogel linear with 0.05 M sodium bicarbonate buffer at 30°C as effluent at a flow rate of 0.6 ml/min. Calibration was with a series of poly(ethylene oxide) samples of known molecular weight. The nitrogen content in the modified CAIs was analyzed by Elemental Analysis (EA, Leco TruSpec[®] CHNS (micro) Analyzer, Leco Corp., U.S.A.).

2.4 Flexural strength test

2.4.1 Specimen preparation

The CAI-Glu-GMA polymers were formulated with water and HEMA using different weight proportions of CAI-Glu-GMA/water/HEMA. Tartaric acid, camphorquinone and

N,N'-dimethylaminoethyl methacrylate were added to each polymer solution at 2, 0.7 and 1.4 %, respectively. The viscosity values of some formulations were measured at 20°C using Brookfield RV (Brookfield Engineering Labs, Inc., U.S.A.) at 10 rpm with spindle no. 21. Specimens were prepared by mixing the commercial glass powder, Fuji II LC (GC Corporation, Japan), with the polymer solution. Five rectangular specimens with a dimension of 2 mm in width x 2 mm in height x 25 mm in length were fabricated using PMMA moulds. The top and bottom of the specimens that were covered with transparent polyester films and glass plates were exposed to visible light at wavelength of 470 nm (3M ESPE device, 3M ESPE Dental Supplies, U.S.A.) for 20 s each. After being clamped in the moulds at 37°C for 1 hr, the specimens were gently removed from the moulds and immersed in deionized water at 37°C for 23 hrs prior to testing.

2.4.2 Determination of flexural strength

Flexural strength (FS) test was performed in three-point bending with a span of 20 mm between two supports using Universal Testing Machine (Instron model 55R4502, Instron Corp., U.S.A.) at a crosshead speed of 0.75 mm/min. The FS (in MPa) was calculated using the following equation;

$$FS = 3PL/2bh^2 \quad (1)$$

where P is the maximum load (N), L is the distance between two supports (mm), b is the width of the specimen (mm), and h is the height of the specimen (mm). Data obtained from the test was subjected to statistical analysis using one-way ANOVA, followed by Scheffe test at the 0.05 significance level.

3. Results and Discussion

3.1 Synthesis and characterization

The scheme for synthesis of CAI-Glu-GMA is illustrated in Figure 1. First, the CAI copolymer was obtained by free-radical polymerization of AA and IA. Then, the reaction between CAI and Glu was performed, resulting in the formation of amide linkages between amino groups of Glu and carboxylic groups of CAI, either from AA or IA units. This new approach of polymer preparation allowed for the random attachment of Glu onto the CAI chain giving the CAI-Glu polymer a different chemical structure from those previously reported terpolymers (Wu *et al.*, 2003; Xie *et al.*, 2004a;b; Moshaverinia *et al.*, 2009b). The resultant CAI-Glu polymers were then further methacrylated by GMA. The reaction

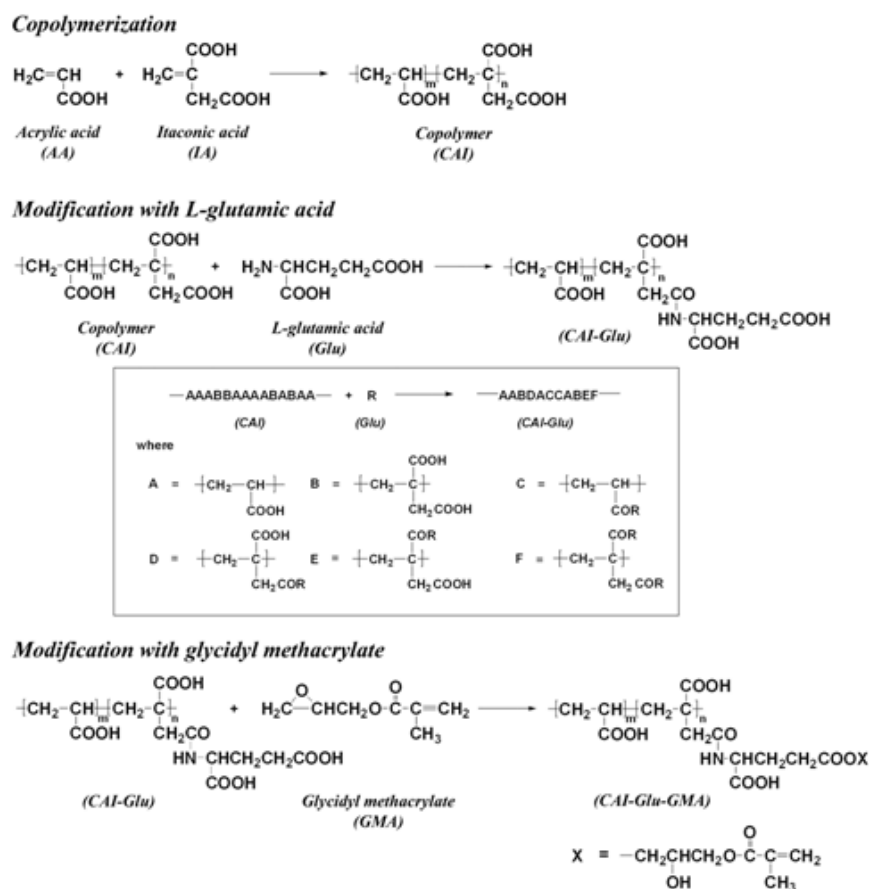


Figure 1. Scheme for CAI-Glu-GMA synthesis.

between carboxylic groups of CAI-Glu and epoxy groups of GMA generated the polymer with active sites for light-initiated polymerization.

The products of each reaction were examined by $^1\text{H-NMR}$, as shown in Figure 2. The results indicated the successful synthesis of CAI-Glu-GMA. In the spectrum of CAI-Glu, there should appear two distinct peaks from its original CAI, belonging to the amide proton and the methine proton of Glu. However, only a new $^1\text{H-NMR}$ chemical shift of the methine proton of Glu at 2.87-2.98 ppm was observed, which has confirmed the amide formation between CAI and Glu. This peak was found to increase significantly as a greater amount of Glu was incorporated onto the CAI chains (results not shown). The disappearance of amide proton

(-NH(CO)-) signal at ~ 8 ppm is due to hydrogen-deuterium exchange which commonly occurs when D_2O is used as a solvent.

The $^1\text{H-NMR}$ spectrum of methacrylated CAI-Glu (CAI-Glu-GMA) showed new chemical shifts as expected at 5.96 and 5.53 as well as 1.71 ppm designated for $\text{C}=\text{CH}_2$ and CH_3 from GMA, respectively. There was also the appearance of signals at the region of 3.49-4.67 belonging to glyceryl ester protons of GMA (Reis *et al.*, 2009).

Table 1 shows the results of the analysis of CAI copolymers by NMR and GPC. Two batches of CAI; C1 and C2, were obtained with different co-monomer ratio, but same approximate molecular weight. C1 was used as a starting material to study the effect of varying GMA while C2 was

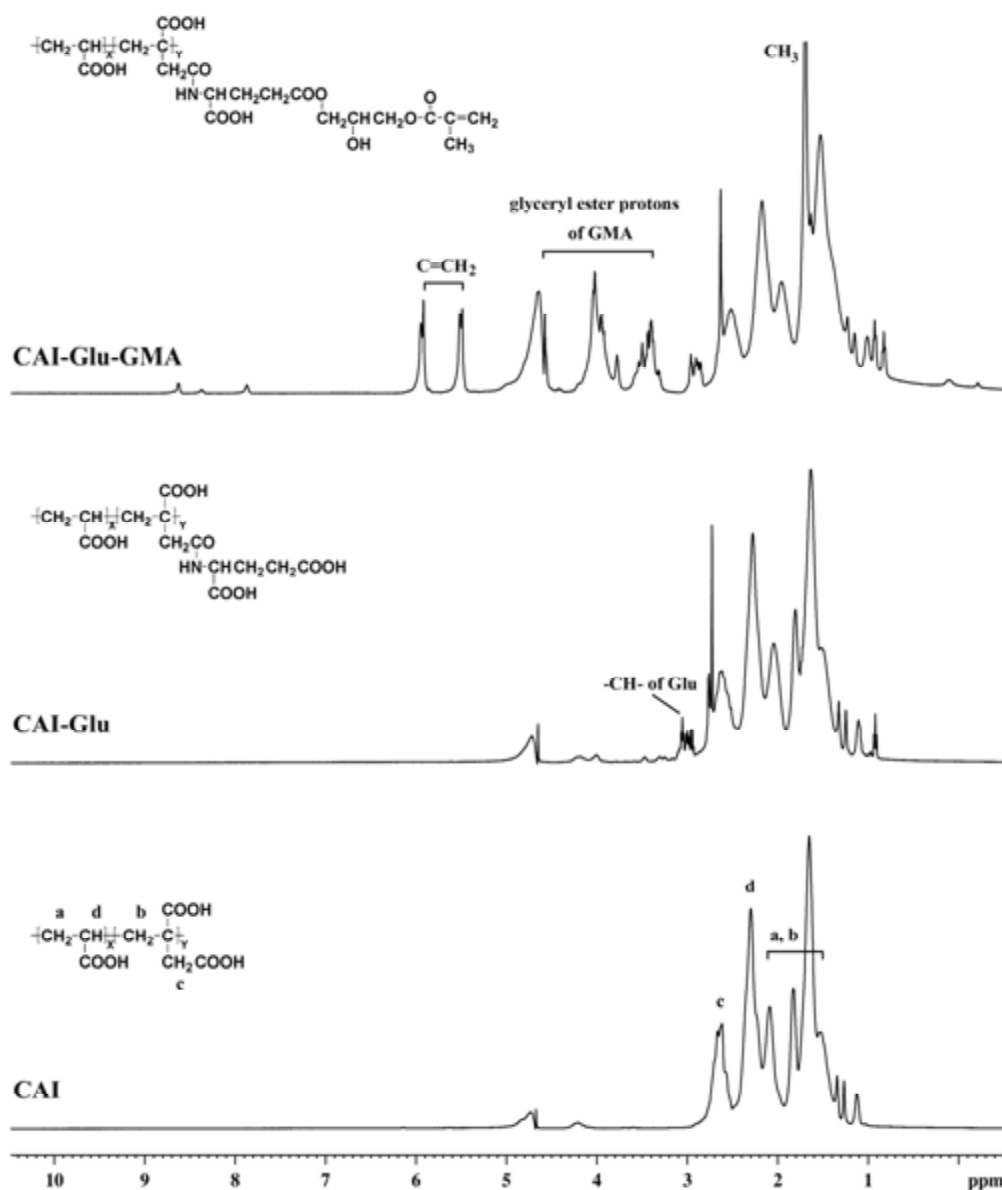


Figure 2. $^1\text{H-NMR}$ spectra for CAI, CAI-Glu and CAI-Glu-GMA.

Table 1. Characterization of CAI copolymers by NMR and GPC.

CAI	¹ H-NMR	GPC	
	AA/IA (mole ratio)	Mw (Dalton)	Mw/Mn
C1	1.7	44600	1.93
C2	2.5	43700	1.99

used to study the effect of varying Glu. The synthesized CAI-Glu-GMA polymers are described in Table 2, including their codes, their CAI parents, and amounts of incorporated Glu and GMA as calculated from the elemental analysis. Some values of incorporated amounts of Glu were found slightly greater than those of the feed amount. This was partly a result of a loss of short chain polymers during dialysis. However, the obtained Glu per mole of CAI unit was close to that expected from feed. It indicated the successful incorporation of Glu onto the CAI chain by obtaining almost 100% yield of the amide linkage.

In contrast, the methacrylation of CAI-Glu with GMA was not successful when comparing the observed one from the lower incorporated amount of GMA to the feed one. The CAI-Glu polymer became more hydrophilic as a greater amount of Glu was incorporated, resulting in a poorer miscibility between CAI-Glu and GMA in the methacrylation reaction. This mixture immiscibility was clearly observed for

the highest feed amount of Glu used in this study i.e. 0.4 mole ratio of Glu to CAI (C2-G4-MA2). The mixture immiscibility likely obstructed the methacrylation of CAI-Glu with GMA, resulting in a low degree of methacrylation.

3.2 Flexural strength test

The polymer solutions formulated at various weight proportions of CAI-Glu-GMA/water/HEMA were mixed with Fuji II LC glass powder to obtain cements. The cement formulations exhibited different values of viscosity which made manipulation difficult in some formulations if powder to liquid ratios (P/L) were kept constant. Therefore P/L ratio in this study was varied in the range of 3.0/1-3.2/1 by bearing in mind the handling consistency for each cement formulation.

The 24-hr flexural strengths of the cements prepared from the synthesized polymers are given in Table 3 to 6. For

Table 2. Composition of the synthesized CAI-Glu-GMA.

Code	CAI	Amount of Glu (per mole of CAI unit)		Amount of GMA (per mole of CAI unit)	
		Feed	Incorporation ^{a)}	Feed	Incorporation ^{a)}
C1-G1-MA1	C1	0.04	0.05	0.23	0.01
C1-G1-MA2	C1	0.04	0.05	0.38	0.11
C1-G1-MA3	C1	0.04	0.05	0.54	0.33
C2-G0-MA2	C2	0	n/a	0.37	n/a
C2-G2-MA2	C2	0.10	0.09	0.36	0.11
C2-G3-MA2	C2	0.21	0.25	0.35	0.31
C2-G4-MA2	C2	0.43	0.37	0.36	0.13

a) determined by elemental analysis.

Table 3. Effect of glutamic acid content on the flexural strength of cements.

Polymer	formulation *	P/L ratio	FS (MPa) (SD) **
C2-G0-MA2	50/50/0	3.1/1	11.0 (1.9) ^a
C2-G2-MA2	50/50/0	3.1/1	30.0 (2.5) ^b
C2-G3-MA2	50/50/0	3.1/1	29.6 (4.9) ^b
C2-G4-MA2	50/50/0	3.0/1	20.1 (2.2) ^c

* Ratio by weight of CAI-Glu-GMA/water /HEMA.

** Values with the same superscript letter are not significantly different ($p > 0.05$).

Table 4. Effect of glycidyl methacrylate content on the flexural strength of cements.

Polymer	formulation *	P/L ratio	FS (MPa) (SD) **
C1-G1-MA1	50/50/0	3.0/1	21.8 (2.4) ^d
C1-G1-MA2	50/50/0	3.0/1	28.6 (6.0) ^{d,e}
C1-G1-MA3	50/50/0	3.0/1	30.3 (1.5) ^e

* Ratio by weight of CAI-Glu-GMA/water /HEMA.

** Values with the same superscript letter are not significantly different ($p>0.05$).

Table 5. Effect of HEMA content on the flexural strength of cements.

Polymer	formulation *	P/L ratio	FS (MPa) (SD)**
C2-G2-MA2	45/50/5	3.2/1	35.5 (4.8) ^f
C2-G2-MA2	45/45/10	3.2/1	36.8 (2.7) ^f
C2-G2-MA2	45/40/15	3.1/1	52.5 (3.6) ^g

* Ratio by weight of CAI-Glu-GMA/water /HEMA.

** Values with the same superscript letter are not significantly different ($p>0.05$).

Table 6. Effect of polymer concentration on the flexural strength of cements.

Polymer	formulation *	P/L ratio	FS (MPa) (SD) **	Viscosity (cP)
C2-G3-MA2	40/40/20	3.2/1	32.6 (4.5) ^h	505
C2-G3-MA2	45/35/20	3.2/1	62.7 (3.4) ⁱ	1325
C2-G3-MA2	50/30/20	3.1/1	60.8 (5.0) ⁱ	3485

* Ratio by weight of CAI-Glu-GMA/water /HEMA.

** Values with the same superscript letter are not significantly different ($p>0.05$).

the effect of Glu incorporation (Table 3), there was no significant difference between C2-G2-MA2 and C2-G3-MA2, and both were found strongest, followed by C2-G4-MA2 and C2-G0-MA2, respectively. It was clear that the incorporation of Glu into the polymer significantly increased flexural strength ($p<0.05$). The flexural strength of Glu incorporated polymers increased almost three times from 11 MPa of the polymer without Glu (C2-G0-MA2). This indicated the effectiveness of the new method for preparing an amino acid containing polymer to improve the flexural strength of cement.

Amino acid containing polymers have been reported to improve the mechanical properties of GIC (Kao *et al.*, 1996; Wu *et al.*, 2003; Moshaverinia *et al.*, 2009b) and RMGIC (Xie *et al.*, 2004a;b). The amino acids, for example glutamic acid, alanine, and aspartic acid were first prepared as amino acid derivatives and were then used in a polymerization with acrylic acid (AA) and itaconic (IA) or maleic acid (MA) monomers to obtain terpolymers. These amino acid derivatives allowed for attaching of carboxylic groups at certain distances away from the main backbone, resulting in

greater ionic complex formation between carboxylic groups and Al^{3+} ions from the glass, thereby strengthening the set cement. In this study, the amino acid containing polymers were synthesized using a method different from that mentioned above, giving the resultant polymers different chemical structures from those of the terpolymers, but similar capability in lengthening the space between the carboxylic group and polymeric backbone. Randomly incorporating Glu disordered the structure of CAI resulting in decreasing the degree of steric hindrance and increasing the ability of ionic-crosslink. The incorporation of Glu into CAI copolymer not only induced a disordered structure but also increased the molecular weight of the polymer as well as the number of carboxylic groups. The higher Mw of the polymer strengthened the cement matrix whereas the more carboxylic groups coupled with the greater disordered structure allowed for greater ionic crosslinks. From Table 3, a high flexural strength was obtained when using the feed mole of Glu to CAI at 0.1-0.2. At the highest feed ratio (C2-G4-MA2), the CAI-Glu polymer was found to dissolve less in GMA as mentioned

earlier, leading to poor methacrylation which in turn weakened the strength of the cement.

In respect of GMA incorporation (Table 4), the cement of C1-G1-MA3 exhibited the highest strength followed respectively by C1-G1-MA2 and C1-G1-MA1, but was not statistically significant. A statistical difference, however, was observed between C1-G1-MA1 and C1-G1-MA3. These results suggested that an increased GMA amount was promising for increasing strength. A higher amount of GMA implied a greater amount of active double bond for photocrosslinking. Thus, higher strength was expected for cement containing a higher amount of GMA. However, too much GMA might result in poor cement strength. As the amount of GMA increased, the synthesized polymer became less soluble in water leading to the poorer ionic forming reaction, hence lowering the strength of the cement. In this study, the optimal feed mole of GMA for high cement strength was found at 0.4 per mole of CAI (C1-G1-MA2).

For the effect of HEMA (Table 5), a significant increase in strength ($p < 0.05$) was observed when the HEMA content was raised to 15% (52.5 MPa). HEMA is a component that is commonly used in RMGIC. HEMA not only helped dissolve the synthesized polymer in water, but also acted as a comonomer, which underwent polymerization under light exposure. Therefore, the greater amount of HEMA added, the more cured polymer would be incorporated into the cement matrix resulting in the higher cement strength. Unreacted HEMA, on the other hand, has been documented regarding its cytotoxicity to dental pulp (Stanislawski *et al.*, 1999; de Souza Costa *et al.*, 2003). Accordingly, the lowest amount of HEMA that was enough to contribute effectively to high cement strength was preferred, which in this study should not be less than 15%-wt.

Flexural strength was also affected by polymer content. The increasing concentration of polymer resulted in increased cement strength as seen from the significantly greater strengths ($p < 0.05$) for 45% (62.7 MPa) and 50% (60.8 MPa) than for 40% (32.6 MPa) polymer contents (Table 6). An increase in viscosity of the polymer solution was also observed as the polymer concentration increased. As a result, C2-G3-MA2 at the highest polymer concentration (50/30/20) exhibited difficulty in mixing. Its P/L ratio was then reduced to ease mixing which limited the increased strength as the polymer concentration increased. In this study, the optimal polymer concentrations observed for high strength were at 45-50%-wt. With our best formulation observed in this study, the formulation of C2-G3-MA2/water/HEMA at 45/35/20, its strength was less than those of the previous studies which reported flexural strength of the optimal experimental cement at 71.7 ± 5.4 MPa (Xie *et al.*, 2004a;b). However, the flexural strength was higher than 25 MPa, which is the minimum strength requirement for restorative resin-modified cement as recommended by the International Organization for Standardization (ISO9917-2). This result suggested that the new method used in this study to reduce

rigidity of the polymer structure was a promising approach in improving the strength of RMGIC.

4. Conclusion

The random attachment of Glu onto the CAI chain was reported, which offered a new method to improve the strength of cement. The amount of Glu and GMA contained in the polymer affected the cement strength, which was found to be optimal at 0.1-0.2 and 0.4 feed ratios per mole of CAI, respectively. The effects of HEMA and polymer concentration on flexural strength were studied and the highest strength value at 62.7 ± 3.4 MPa was obtained for the formulation that contained 20%-wt. HEMA and 45%-wt. polymer concentration.

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