

Synthesis and Evaluation of Novel Light-Curable Amino Acid-Constructed Glass-Ionomer Cements

Dong Xie, Jong-Gu Park, Mona Faddah

Department of Biomedical Engineering, Purdue School of Engineering and Technology, Indiana University-Purdue University at Indianapolis, Indianapolis 46202

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ABSTRACT: Poly(alkenoic acid)s constructed with β -alanine and glutamic acid were synthesized and grafted with glycidyl methacrylate (GM). The purified polymers were further formulated with water, acrylic acid (AA), and Fuji II LC glass filler to form photocurable dental cements. Compressive strength (CS) and flexural strength (FS) of the cement, and viscosity of the resin liquid were used as screening tools to find the optimal formulation. The specimens were conditioned in distilled water at 37°C for 24 h, prior to testing. The results show that the effects of grafting ratio, polymer content, powder liquid (P/L) ratio, initiator concentration, and light exposure time were significant, but the effect of molecular weight was not. Aging study shows that the experimental cement showed a con-

stant increase in mechanical strength for up to 1 week and then kept constant over 1 month. The formulation with 50/25/25 (liquid composition of polymer/AA/water), 70% (grafting ratio of GM), 3.2/1 (P/L ratio) as well as 0.9% (camphorquinone) and 1-min light exposure time were found to be the optimal. The experimental cement was 19% higher in CS, 47% higher in diametral tensile strength and 176% higher in FS, compared to Fuji II LC. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1587–1595, 2007

Key words: amino acid-constructed polyacid; glycidyl methacrylate; light-cured glass-ionomer cements; synthesis; formulation; compressive strength; flexural strength; viscosity

INTRODUCTION

Among dental restoratives, glass-ionomer cements (GICs) are one of the most promising polymer-ceramic composites.¹ These materials show a great potential to be considered as an alternative for replacement of traditional dental amalgam.^{1–3} They are superior in many properties including direct adhesion to tooth and base metals, anticariogenic properties, thermal compatibility with tooth, self-healing, and repairing, and the least microleakage to the other existing materials.^{1–6} Resin-modified glass-ionomer cements (RMGICs) are hybrid materials of glass-ionomer and composite resin, which not only undergo an acid-base reaction but also participate in an onsite free-radical polymerization, because they contain polymerizable methacrylate groups either on polyacid backbone or grafted as side chains.^{6–8} These cements have gained more popularity in restorative dental community, because they have more attractive properties compared to conventional glass-ionomer cements (CGICs). RMGICs reduce the prob-

lems of moisture sensitivity and low early mechanical strength associated with CGICs.^{7,8} They are easier to be handled clinically,⁸ exhibit extended working time, and have significant improvement on some of the mechanical strengths, such as flexural (FS) and diametral tensile strengths (DTS).^{6,9} The FS and DTS of RMGICs were reported to be 2–3 times higher than those for CGICs.⁶

So far, there are three major types of RMGICs on the market. One is made of a fluoroaluminosilicate glass powder and an aqueous solution of a copolymer of acrylic acid (AA) and maleic acid, 2-hydroxyethyl methacrylate (HEMA), mixed dimethacrylates, water, and initiators.¹⁰ Another is composed of sodium lanthanum calcium aluminum fluorosilicate glass combined with a copolymer of AA and maleic acid in dry form and a solution of polymerizable monomers as well as oligomers, HEMA, water, and initiators.¹⁰ The third is composed of a calcium fluoroaluminosilicate glass powder and an aqueous solution of a copolymer of AA and itaconic acid with pendant methacrylate groups, HEMA, water, and initiators.¹¹ Different commercial RMGICs may vary in compositions.

More efforts have been made to further improve the mechanical strengths of these existing cements.^{12,13} Two factors have been identified to be closely related to mechanical strength enhancement influenced by the polymer in the cement: polymer backbone compositions and pendant methacrylate

Correspondence to: D. Xie (dxie@iupui.edu).

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groups.^{9,11–13} Xie and coworkers found that modification of conventional poly(acrylic acid) homopolymer or poly(acrylic acid-*co*-itaconic acid) copolymer backbone using amino acid residues could significantly improve the mechanical^{14,15} and bonding strengths.¹⁶ This idea has been found valid in dentistry.^{14–16} For the grafting of pendant carbon–carbon double bond, direct grafting of methacrylate functional groups onto a polyacid backbone, using 2-isocyanatoethyl methacrylate (IEM), is still one of the most promising methods for commercial light-cured GICs up to date, because of its simplicity and the resultant strong semi-interpenetrating polymer network formation.^{9,10,12,17} However, owing to the highly hydrophobic nature of IEM, the carbon–carbon double bonds on IEM can only be grafted up to 50% by mole at maximum, without interfering with polymer solubility in water.^{18,19} Further, 25% grafting ratio was reported to be the best to a strength increase.^{18,19} As we know, carbon–carbon double bonds play a key role in improving mechanical performance of RMGIC.^{6,10} Therefore, there is a need to find an alternative way to graft more pendant carbon–carbon double bonds onto the polyacid backbone for improved mechanical strengths, without reducing the solubility of the grafted polymer. In this article, we proposed to construct the polyacid backbone by solely using amino acid followed by grafting polymerizable methacrylate onto the polyacids, using glycidyl methacrylate (GM).

The objective of this study was to synthesize and characterize amino acid-constructed polymers grafted with GM, use them to formulate light-cured GICs, and evaluate the mechanical strengths of the formed cements.

EXPERIMENTAL

Materials

Methacryloyl chloride (MC), acryloyl chloride (AC), L-glutamic acid, β-alanine, acrylic acid (AA), potassium persulfate (K₂S₂O₈), *dl*-camphorquinone (CQ), diphenyliodonium chloride (DC), hydroquinone (HQ), butylated hydroxytoluene (BHT), pyridine, anhydrous magnesium sulfate (MgSO₄), sodium hydroxide (NaOH), hydrochloric acid (HCl, 37%), diethyl ether, tetrahydrofuran (THF), and ethyl acetate were used as received from Acros/Fisher Scientific (Pittsburgh, PA) without further purifications. GC Fuji II[™] LC glass powders were supplied by GC America (Alsip, IL).

Synthesis and characterization

Synthesis of amino acid derivatives

Methacryloyl glutamic acid (MGA) and acryloyl β-alanine (ABA) were synthesized using the Schotten-

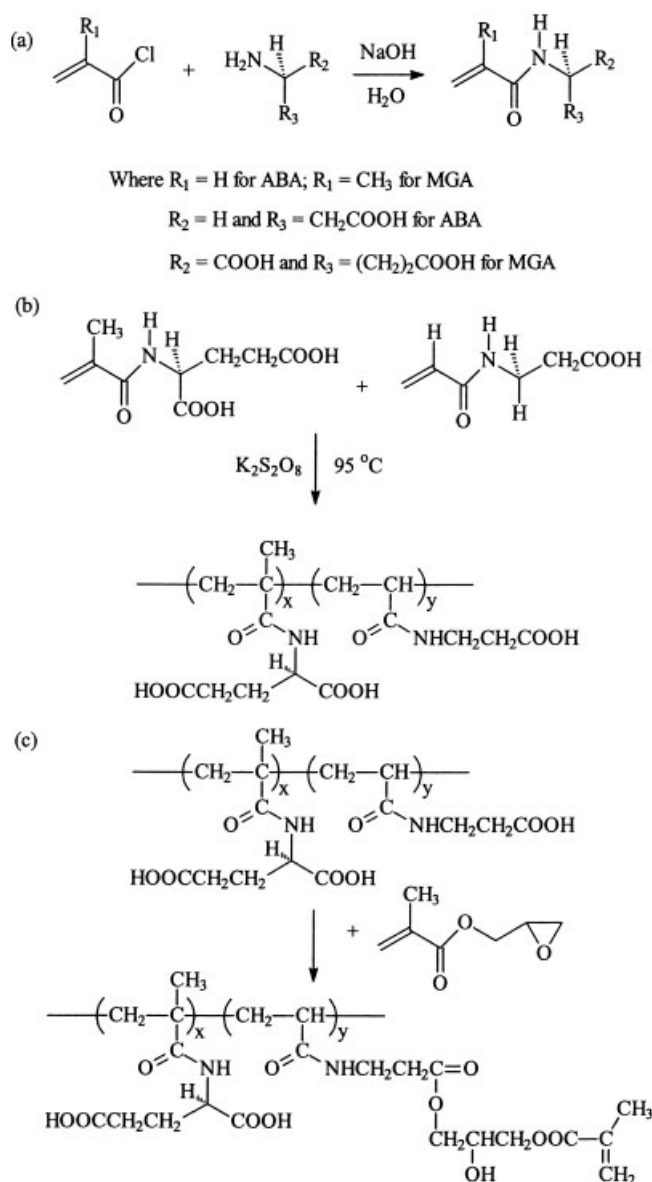


Figure 1 Schematic diagram for synthesis: (a) Synthesis of MGA and ABA; (b) Synthesis of poly(MGA-*co*-ABA) copolymer; (c) Grafting reaction of GM onto poly(MGA-*co*-ABA) copolymer.

Baumann reaction.²⁰ Briefly, to a three-neck flask containing amino acid and NaOH (moles changing with the number of carboxylic acid) aqueous solution, MC or AC equivalent to the amino group on the amino acid was added with stirring at the temperature below 5°C. After addition was complete, additional 1 h was added to complete the reaction. The solution was acidified to pH = 2 with HCl (37%), and extracted three times with ethyl acetate. The extract was dried with anhydrous MgSO₄ and concentrated using a rotary evaporator, to obtain white crystals. The crystals were recrystallized from ethyl acetate. The schematic diagram for monomer synthesis is shown in Figure 1(a).

Synthesis of amino acid-constructed copolymer

The copolymers composed of MGA and ABA were synthesized using free-radical polymerization. Briefly, to a three-neck flask, equipped with a thermometer, a nitrogen inlet, and a magnetic stirrer, containing distilled water, a mixture of MGA, ABA, $K_2S_2O_8$, and distilled water was added dropwise. The reaction was run under a nitrogen blanket at 93–95°C for 3 h. The molar feed ratio for the copolymer was 8:2. The polymers with different molecular weights (MW) were prepared by changing the amount of initiator. The final products were freeze-dried, ground, and stored prior to use. The scheme for copolymer synthesis is described in Figure 1(b).

Synthesis of copolymer having pendant methacrylate group

To a three-neck flask containing amino acid-constructed copolymer, THF, and BHT (1%), a mixture of GM (ratios were varied by mole), THF, and puridine (1%) was added dropwise. Under a nitrogen blanket, the reaction was initiated and run at 60°C for 6 h and then kept at room temperature overnight. Fourier transform-infrared (FT-IR) spectroscopy was used to monitor the reaction. The polymer grafted with GM was recovered by precipitation from diethyl ether, followed by drying in a vacuum oven at 23°C. The scheme for synthesis of the copolymer with pendant methacrylate groups is described in Figure 1(c).

Characterization of amino acid derivatives and the polymers

The synthesized derivatives were characterized using a melting point test apparatus (Mel-Temp II, Laboratory Devices, Holliston, MA), FT-IR, and nuclear magnetic resonance (NMR) spectrophotometers. The polymer was identified by FT-IR, NMR, and gel permeation chromatography (GPC). The FT-IR spectra were obtained with a FT-IR spectrophotometer (Mattson Research Series FT/IR 1000, Madison, WI). The proton nuclear magnetic resonance (1H NMR) spectra were obtained on a FT-300 MHz Bruker ARX-300 spectrophotometer, using deuterated methyl sulfoxide as solvent. MW was estimated on the Waters GPC unit (model 410 differential refractometer, Waters, Milford, MA), using standard GPC techniques, with polystyrene as a standard. THF was used as a solvent.

Evaluations of light-cured GICs

Viscosity determination

The viscosity of the liquid formulated with the polymer containing pendant methacrylate, AA, and dis-

tilled water was determined at 23°C using a programmable cone/plate viscometer (RVDV-II + CP, Brookfield Eng. Lab., Middleboro, MA). About 5.5 g of polymer and 2.5 g of AA were dissolved in 2.5 g water. After the viscometer was calibrated, the solution was placed into the sample cup. The cup was then attached to the viscometer, followed by allowing sufficient time for temperature equilibrium for the sample, cone, and cup. Once the equilibrium was reached, the viscometer was run under certain revolution per minute (rpm) to obtain the viscosity value. The mean value was obtained by averaging three readings.

Preparation of specimens for strength tests

The formulated liquid was further mixed with 0.7% CQ, 1.4% DC, and 0.05% HQ for photoinitiation. Fuji II LC glass powder was used to formulate the cements with a powder/liquid (*P/L*) ratio of 3.0/1. Fuji II LC kit with the *P/L* ratio of 3.2/1 (recommended by manufacturer) was used as control. Specimens were fabricated at room temperature according to the published protocol.²¹ Briefly, the cylindrical specimens were prepared in glass tubing with dimensions of 4 mm diameter by 8 mm length for compressive strength (CS) and 4 mm diameter by 2 mm length for DTS tests. A split Teflon mold with a glass window for light exposure was used to make the specimens with 3 mm width 3 mm thickness, and 25 mm length for FS test. All specimens were exposed to blue light (EXAKT 520 Blue Light Polymerization Unit, 9W/71, wavelength = 450 nm, GmbH, Germany) for 1 min,^{5,9,10} removed from the mold after 15 min in 100% humidity, and conditioned in distilled water at 37°C for 24 h,^{9,10} unless specified.

Strength measurement

Testing of specimens was performed on a hydraulic mechanical testing machine (model 858 Mini Bionix, MTS Systems, Eden Prairie, MN), with a crosshead speed of 1 mm/min for CS, DTS, and FS measurements. The FS test was performed in three-point bending, with a span of 20 mm between supports. The sample sizes were $n = 6-8$ for each test.

CS was calculated using an equation of $CS = P / \pi r^2$, where P is the load at fracture and r the radius of the cylinder, and DTS was determined from the relationship $DTS = 2P / \pi dt$, where P is the load at fracture, d the diameter of the cylinder, and t is the thickness of the cylinder. FS was obtained using the expression $FS = 3Pl / 2bd^2$, where P is the load at fracture, l the distance between the two supports, b the breadth of the specimen, and d is the depth of the specimen.

Statistical analysis

One-way analysis of variance with the *post hoc* Tukey-Kramer multiple range test was used to determine significant differences of strengths among the materials in each group. A level of $\alpha = 0.05$ was used for statistical significance.

RESULTS AND DISCUSSION

Synthesis and characterization

In this study, we have synthesized amino acid-constructed polymer backbone and successfully tethered the carbon-carbon double bond onto the polycarboxylic acid backbone using GM, to make the amino acid-constructed polyacid photocurable.

The synthesis for MGA and ABA was discussed in our previous studies.^{14,17} The synthesis of poly(MGA-co-ABA) copolymer and selection of the molar ratios were discussed elsewhere.²² Successful synthesis of the amino acid-constructed copolymer was confirmed by obtaining 98% yield of the copolymer after freeze-drying. For grafting of GM, we achieved almost 100% grafting, by using pyridine as a catalyst. In fact, the *in situ* disappearance of the characteristic (epoxy) peak from GM at around 761 cm^{-1} and formation of the carbon-carbon double bond at 1636 cm^{-1} on GM-grafted polymer backbone confirmed the completion of the reaction.

The measured melting points and yields of MGA and ABA were $120.8\text{--}121.5^\circ\text{C}$ and $95.0\text{--}96.0^\circ\text{C}$, and 91 and 70%, respectively. The yields for poly(MGA-co-ABA) copolymer and GM grafted poly(MGA-co-ABA) were 98 and 92%, respectively.

Figure 2 shows the FT-IR spectra of MGA, ABA, poly(MGA-co-ABA) copolymer, GM, and poly(MGA-

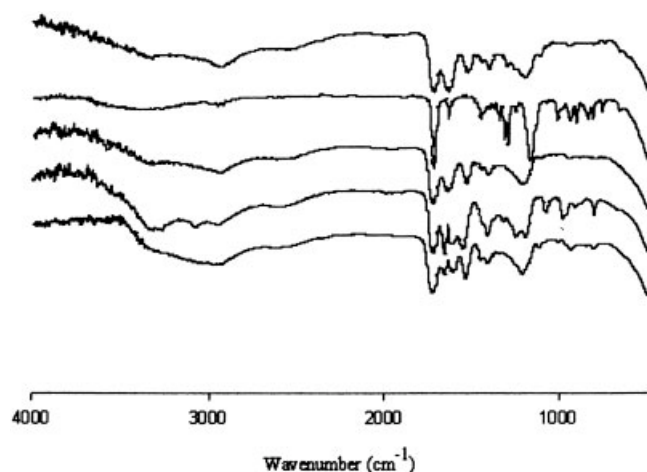


Figure 2 FT-IR spectra for MGA, ABA, GM, poly(MGA-co-ABA), and GM grafted poly(MGA-co-ABA): A = MGA; B = ABA; C = poly(MGA-co-ABA); D = GM; E = GM grafted poly(MGA-co-ABA).

co-ABA) grafted with GM. The spectra A for MGA and B for ABA showed strong FT-IR peaks at 1722 and 1719 ($\text{C}=\text{O}$ stretching), 1656 and 1655 ($\text{C}=\text{C}$ stretching conjugated with $\text{C}=\text{O}$) as well as 936 and 983 ($\text{C}=\text{C}$ out-of-plane bending), 1607 and 1621 ($\text{C}=\text{O}$ stretching), and 1534 and 1553 cm^{-1} ($\text{N}-\text{H}$ bending) associated with carbonyl, carbon-carbon double, amide I, and amide II bonds, respectively. Both monomers also showed strong and broad bands ranging from $3600\text{ to }2400\text{ cm}^{-1}$ ($\text{O}-\text{H}$ stretching at $3300\text{--}2500$, $\text{N}-\text{H}$ stretching at $3100\text{--}2070$ and $\text{C}-\text{H}$ stretching at $2960\text{--}2930$) for hydroxyl group on carboxyl groups, $\text{N}-\text{H}$ from amide groups and $\text{C}-\text{H}$ from CH_3 .

The spectrum C in Figure 2 was FT-IR for poly(MGA-co-ABA) copolymer. Three typical peaks were found at 1722, 1640, and 1531 cm^{-1} for carbonyl, amide I and amide II bonds, in addition to the broad peaks ranging from $3600\text{ to }2400\text{ cm}^{-1}$ for OH, NH, and CH_3 . No carbon-carbon double bond ($1655\text{--}1657\text{ cm}^{-1}$) was found in the spectrum. The FT-IR spectrum for GM is shown as D in Figure 2. Three typical peaks at 1720, 1637, and 761 cm^{-1} were found for carbonyl, carbon-carbon double bond, and epoxy functional groups, respectively. The spectrum for poly(MGA-co-ABA) grafted with GM (E in Fig. 2) was very similar to that for poly(MGA-co-ABA) copolymer, i.e., bands appear at 1721, 1636, and 1530 cm^{-1} for carbonyl, amide I as well as amide II bonds, in addition to the broad peaks ranging from $3600\text{ to }2400\text{ cm}^{-1}$ for OH, NH, and CH_3 . It is apparent that the peak at round $1637\text{--}1640\text{ cm}^{-1}$ was stronger and larger than the one shown for C, which means that the peak for carbon-carbon double bond actually overlapped with that for amide I.

For ^1H NMR, MGA exhibited typical chemical shifts at around 5.75 and 5.42 ppm for carbon-carbon double bonds, whereas ABA showed multiple chemical shifts at 6.25 and 5.75 ppm for carbon-carbon double bonds. They also showed peaks at 8.60 ppm for amide and at around 12.40 ppm for carboxyl group, as shown in Figure 3(a). The peak at 12.40 ppm for MGA was weaker but broader than that for ABA.

Figure 3(b) shows the ^1H NMR spectra for poly(MGA-co-ABA) copolymer, GM, and poly(MGA-co-ABA) grafted with GM. For poly(MGA-co-ABA), strong chemical shifts at around 12.0 and 7.6 ppm were observed for protons on carboxyl and amide groups. For GM, typical chemical shifts at 6.10 and 5.72 ppm were those for carbon-carbon double bonds. In contrast, two typical chemical shifts were also observed for the polymer grafted with GM at exactly the same location as those for GM. The protons from two amide bonds (MGA and ABA) were observed at around 8.2 and 7.05 as well.

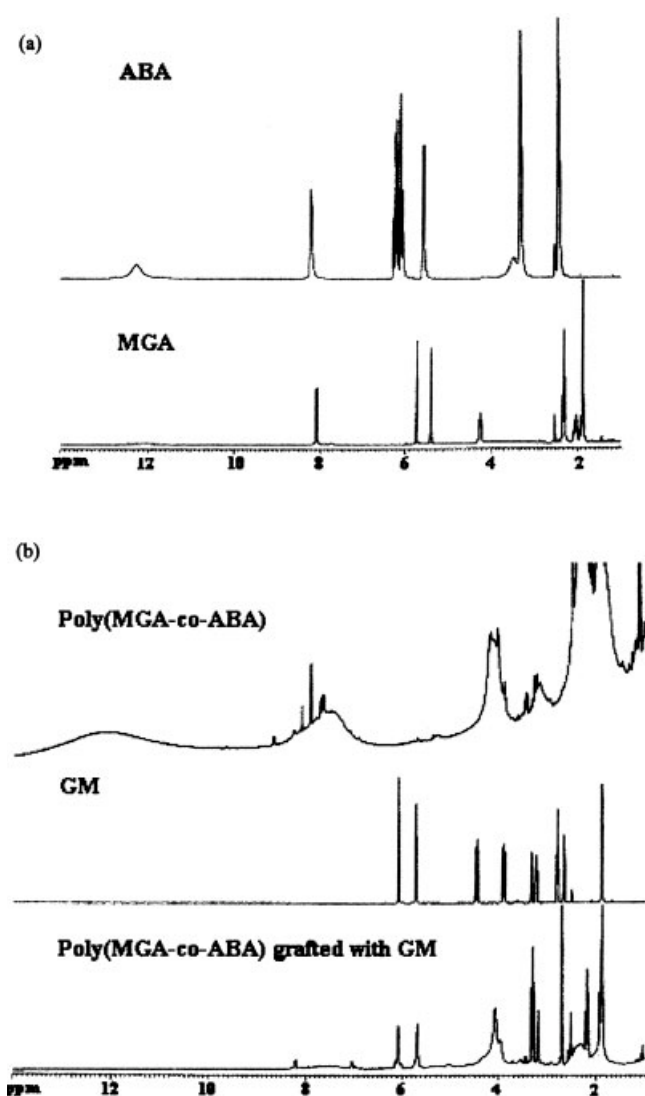


Figure 3 ^1H NMR spectra for MGA, ABA, poly(MGA-co-ABA), GM, and GM grafted poly(MGA-co-ABA): (a) MGA and ABA; (b) poly(MGA-co-ABA), GM, and GM grafted poly(MGA-co-ABA).

Evaluation of cements

To develop a desired light-cured dental GIC, several important parameters need to be considered. These parameters include MW of the polymer, grafting ratio of carbon-carbon double bond, ratio of polymer/comonomer/water, glass powder/polymer resin liquid (P/L) ratio, concentrations of initiators, light-exposure time, aging, etc.^{12,17} Among them, grafting ratio, MW of polymer, ratio of polymer/comonomer/water, and P/L ratio are the most important parameters which determine the ultimate mechanical strengths and working properties.

In this study, CS, FS, and viscosity were used as tools to evaluate the experimental cements. CS is the maximal stress required to fracture a structure under a load, which tends to compress or shorten it. CS

test is very important for evaluation of dental materials, because it reflects the resistance of the material to occlusion forces frequently occurring during mastication, which is very clinically relevant. FS measures three types of stresses simultaneously, i.e., tensile (at the lower surface of the specimen beam), compressive (at the upper surface of the beam), and shear (in the direction which is parallel to the load) stresses.²³ Prosser et al. commented that the most appropriate measure of the strength of GICs was FS, because a material could fail by the separation of planes of atoms (tensile failure) or by the slipping of the planes of atoms (shear failure).²⁴ Viscosity was used to determine which formulation would be workable for dental clinics,²⁵ if the CS values are given much the same.

During the study, we have found that FS and CS were almost equivalent to measurement of our materials, except for the value difference. In other words, they both demonstrated the same trends for the strength evaluation, i.e., if CS is higher, FS is higher and *vice versa*. Therefore, CS and FS can be exchangeably used to evaluate the formulations.

Effect of MW

MW is very important to polymer-containing biomaterials. Generally speaking, the higher the MW, the higher the mechanical strengths of the polymers.² On the other hand, a polymer with a higher MW also makes handling or mixing difficult.¹² From Table I, there were no significant differences in CS between the cements with MWs of 21,300 and 10,200, between the cements with 33,800 and 10,200, and between the cements with 33,800 and 25,200 ($P > 0.05$). There were no significant differences in FS between the cements with 21,300 and 10,200 and between the cements with 33,800 and 10,200. The viscosity (cp) of the liquid was in the decreasing

TABLE I
Effect of Molecular Weight on CS, FS, and Viscosity

M_w/M_n ¹	CS (MPa)	FS (MPa)	Viscosity (cp)
33.8/15.2	196.6 (7.8) ^{a,b,2}	41.3 (9.2) ^d	2891 (23)
25.2/11.2	187.7 (3.7) ^a	42.1 (4.5) ^d	1468 (34)
21.3/9.83	210.3 (5.7) ^c	54.9 (6.7) ^e	342 (12)
10.2/4.30	200.9 (2.9) ^{b,c}	49.3 (3.5) ^e	291 (11)

¹ M_w = weight-average MW (Da) and M_n = number-average MW (Da). The GM-grafted polymer had a grafting ratio of 25%; Polymer : AA : H₂O = 50 : 25 : 25; P/L = 3.0/1; CQ concentration = 0.7%. The cements were conditioned in distilled water at 37°C for 24 h, before testing.

² Entries are mean values with standard deviations in parentheses; the mean values with the same superscript letter were not significantly different ($P > 0.05$).

order: 33,800 (2891) > 25,200 (1468) > 21,300 (342) > 10,200 (291). It is apparent that the cements composed of polymers with lower MWs and viscosity values showed higher CS and FS. In fact, we did experience difficulties in mixing the cements with higher MWs. It is believed that manipulation difficulties in the specimen preparations due to higher viscosities led to a lower strength.¹²

Effect of grafting ratio

In this study, we tethered *in situ* polymerizable methacrylate functionality onto the polyacid, by using GM instead of IEM.^{12,18} Table II shows the effect of grafting ratio of GM on CS and FS along with the viscosity. Unlike IEM grafting, the grafting ratio of GM could be increased up to 70%, without reducing the solubility of the grafted polymer in water, which is a very important discovery. Our previous experience with IEM grafting indicated that 50% grafting led to a reduction of mechanical strengths and 25% was the best.^{12,18} However, it is evident from Figure 5 that both CS and FS were increased with the increase of GM grafting from 15 to 70%. The grafting ratio at 70% actually showed the highest CS (258.0 MPa) and FS (90.5 MPa) but a lower viscosity (620 cp).

Effect of polymer content

In formulating the liquid for LCGICs, three components often need to be considered: grafted polymer, comonomer, and water. A suitable balance among them is very critical to both strength and workability. Usually, higher content of the polymer leads to higher strengths.²⁶ In this study, we compared four formulations (grafted polymer:AA:H₂O), i.e., 30/35/35, 40/30/30, 50/25/25, and 55/20/25. The ratio that was higher than 55/20/25 could not be pre-

TABLE II
Effect of Grafting Ratio on CS, FS, and Viscosity

Grafting ratio ¹ (mol %)	CS (MPa)	FS (MPa)	Viscosity (cp)
15	157.5 (3.0) ²	43.1 (6.1)	896 (31)
25	210.3 (5.7) ^a	54.9 (6.7) ^b	342 (12)
35	213.4 (7.2) ^a	57.1 (5.6) ^b	1130 (56)
55	230.1 (4.9)	64.2 (11) ^b	1400 (32)
70	258.0 (8.1)	90.5 (10)	620 (8.1)

¹ The GM-grafted polymer had a weight-average molecular weight (M_w) of 21,300 Da; Polymer : AA : H₂O = 50 : 25 : 25; $P/L = 3.0/1$; CQ concentration = 0.7%. The cements were conditioned in distilled water at 37°C for 24 h, before testing.

² Entries are mean values with standard deviations in parentheses; the mean values with the same superscript letter were not significantly different ($P > 0.05$).

TABLE III

Effect of Liquid Formulation on CS, FS, and Viscosity

Liquid ratio ¹	CS (MPa)	FS (MPa)	Viscosity (cp)
30/35/35	238.7 (12) ^{a,2}	72.4 (8.2) ^c	20.1 (1.1)
40/30/30	255.4 (11) ^b	80.1 (11) ^{c,d}	53.4 (1.4)
50/25/25	258.0 (8.1) ^b	90.5 (12) ^d	620 (8.1)
55/20/25	248.9 (7.5) ^{a,b}	78.3 (9.2) ^c	783 (12)

¹ The GM-grafted polymer had a grafting ratio of 70% and a weight-average molecular weight (M_w) of 21,300 Da; $P/L = 3.0/1$; CQ concentration = 0.7%. The cements were conditioned in distilled water at 37°C for 24 h, before testing.

² Entries are mean values with standard deviations in parentheses; the mean values with the same superscript letter were not significantly different ($P > 0.05$).

pared due to extremely high viscosity of the formed solution. From Table III, the formulations with 40/30/30 and 50/25/25 showed higher and similar CS as well as FS, but quite a different viscosity. However, we prefer the latter, because we found that the viscosity for the former was a little too low, which might easily cause artificial defects such as pores and entrapped air bubbles during the specimen preparation.²⁷ Both 30/30/35 and 55/20/25 showed lower CS and FS. The reason for the former may be attributed to its extremely low viscosity leading to pore and defect formation, whereas the explanation for the latter may be due to handling difficulties during mixing because of its relatively high viscosity. The formulation with 50:25:25, therefore, was selected as the best, with high CS (258.0 MPa) as well as FS (90.5 MPa) and good handling properties.

Effect of P/L ratio

In creating composites, synergetic properties are often anticipated when the two components are combined. In general, the proportion or ratio of these components in the mix is very important. Figure 4 shows the effect of P/L ratio on CS and FS. It is clear that both CS and FS increased with the powder/liquid (P/L) ratio up to 3.2/1, and the FS increased even more significantly, although there were no statistically significant differences among some of them. It is true that more glass powder in the system often results in higher compression resistance,²⁸ but not necessarily higher FS. Too much glass can lead to difficult handling. During the mixing, we found that the cements with P/L ratios of 2.2/1, 2.5/1, 2.7/1, 3.0/1, and 3.2/1 could be easily mixed. However, we experienced difficulty in mixing the cement with 3.5/1, which may explain why the high ratio at 3.5/1 resulted in reduction of strengths. The P/L ratio at 3.2/1 was believed to be the optimal, because it demonstrated both good mechanical strengths and acceptable handling characteristics.

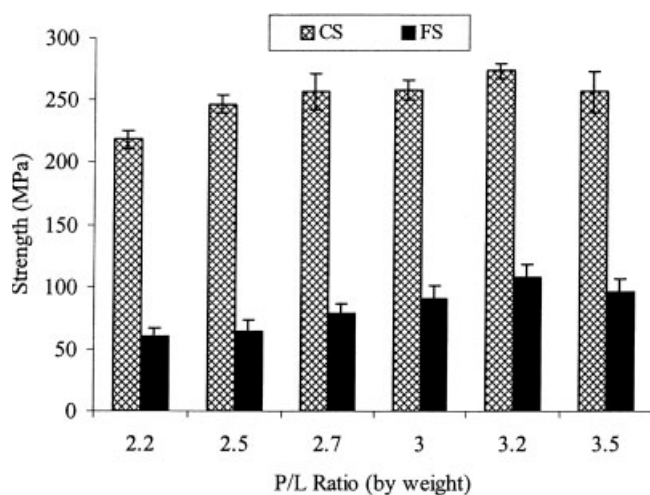


Figure 4 Effect of *P/L* ratio on CS and FS. The GM grafted polymer had a grafting ratio of 70% and a weight-average molecular weight (M_w) of 21,300 Da; liquid formulation = 50/25/25; CQ concentration = 0.7%; viscosity of liquid = 620 cp. The cements were conditioned in distilled water at 37°C for 24 h. The *P/L* ratios with the same superscript letter were not significantly different from each other in strengths ($P > 0.05$): CS: (3.5/1)^{a,b}, (3.2/1)^a, (3.0/1)^{a,b}, (2.7/1)^{a,b}, (2.5/1)^b, and (2.2/1) and FS: (3.5/1)^{a,b}, (3.2/1)^a, (3.0/1)^{b,c}, (2.7/1)^c, (2.5/1)^d, and (2.2/1)^d.

Effects of initiator concentration and light exposure time

CQ and DC is a pair of *in situ* photopolymerization initiators in which CQ is a photosensitizer and DC is an initiator that provides free radicals.⁵ The ratio of CQ/DC is generally 1:2, because one molecule of CQ generates two DC radicals.⁵ Therefore, whenever the amount of CQ is changed the amount of DC will be correspondingly changed twofolds. As we know, the use of a suitable amount of initiator or initiator concentration can improve the mechanical strengths of the cements more or less.¹⁸ Either high or low concentration will result in a reduced strength. From Table IV, the CS was increased as CQ increased up to 0.9% and then decreased. The CQ at 0.9% was the best among all the concentrations studied. This may be explained as the reason that polymerization was not completed when insufficient amount of the initiator was used. On the other hand, we assume that excessive amount of initiator may lead to sudden gel (highly crosslinked network) formation over a very short time, thus limiting the ability of both carboxyl groups and metal ions released from glass particles to reach each other and form ionic crosslinks. Thus, the concentration of CQ at 0.9% was believed the most appropriate for the current experimental cements.

Light exposure time is also very crucial to mechanical strengths, because it affects the degree of conversion. As shown in Table IV, the CS of the specimens

increased significantly with the light exposure time within the first minute. This may be interpreted as the fact that insufficient light exposure leads to incomplete initiation of the polymerization, and thus a reduced strength. It seems that longer light exposure did not affect the CS much. The 1-min light exposure was very acceptable clinically, because most currently used light-curable dental cements and composites are cured within 1–3 min.^{5,23}

Effect of aging

Figure 5 shows the effect of aging on CS. It is known that GICs usually increase their strengths with time.^{3,29,30} To examine the effect of aging on our novel experimental cements, we conditioned the cements in distilled water at 37°C for 1 h, 1 day, 1 week, and 1 month and then tested their CS. As shown in Figure 5, the CS significantly increased with the time, especially within 24-h period. After conditioning in water for 1 week, the strength kept constant over a month. The reason for this behavior is attributed to gradual salt-bridge formation, after initial covalent crosslinks were formed by photopolymerization. Post salt-bridges usually take awhile to form due to slow water penetration and polyacid network reorganizations.³¹ After 1 week, ionic bond formation between metal ions and polyacids reached

TABLE IV
Effects of Initiator Concentration and Light Exposure Time

	CS (MPa)
Concentration ¹ (wt %)	
0.4	240.0 (4.9) ^{a,2}
0.7	254.2 (6.1) ^{b,c}
0.9	262.0 (3.9) ^b
1.0	250.1 (7.1) ^c
1.2	239.5 (3.6) ^a
Time ³ (min)	
0.33	207.9 (11) ^d
0.67	225.6 (15) ^d
1.00	261.9 (13) ^e
3.00	258.1 (14) ^e
5.00	260.6 (6.6) ^e
7.00	261.0 (8.9) ^e
10.0	266.5 (8.6) ^e
15.0	273.2 (5.9) ^e

¹ Effect of initiator concentration. The grafting ratio of GM = 70%; liquid formulation = 50/25/25; *P/L* ratio = 3.2/1.

² Entries are mean values of CS with standard deviations in parentheses; mean values with the same superscript letter were not significantly different ($P > 0.05$).

³ Effect of light exposure time. The grafting ratio of GM = 70%; liquid formulation = 50/25/25; *P/L* ratio = 3.2/1; CQ concentration = 0.9%. All the cements were conditioned in distilled water at 37°C for 24 h, prior to testing.

equilibrium, and thus no significant strength changes were observed.

Comparison between the experimental cement and Fuji II LC

Finally, we measured DTS and FS of the experimental cement and compared them with those for Fuji II LC (Fig. 6). Significantly higher CS, DTS, and FS of the experimental cement were found after conditioning in distilled water for 1 week, as compared to Fuji II LC ($P < 0.05$). The experimental cement was 19%, 47%, and 176% higher in CS, DTS, and FS than Fuji II LC. Fuji II LC is a commercially available LCGIC, which is composed of a fluoroaluminosilicate glass powder and an aqueous solution of a copolymer of AA and maleic acid, HEMA, mixed dimethacrylates, water, and initiators.^{10,32} In Fuji II LC cement formulation, a substantial amount of HEMA (20–35%) and mixed low MW dimethacrylate oligomers exist.^{10,32} These monomers and oligomers cannot contribute any salt-bridges, because they do not contain any carboxylic acids, except for carbon–carbon double bonds. In contrast, both amino acid-composed polyacid and AA in the experimental cement can provide a significant amount of carboxylic acids for salt-bridge formation, except for carbon–carbon double bonds for covalent crosslinking. That may be why the experimental cement was significantly higher in CS, DTS, and FS than Fuji II LC. Therefore, developing these novel amino acid-composed cements may allow GICs to be used for those high stress-bearing sites

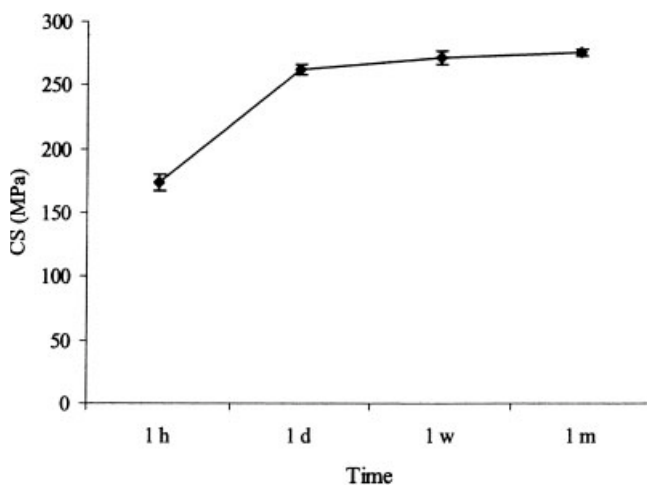


Figure 5 Effect of aging on CS. The grafting ratio of GM = 70%; liquid formulation = 50/25/25; viscosity of liquid = 620 cp; P/L ratio = 3.2/1; CQ concentration = 0.9%. The cements were conditioned in distilled water at 37°C prior to testing. The times with the same superscript letter were not significantly different from each other in CS ($P > 0.05$): CS: (1 m)^a, (1 w)^a, (1 d), and (1 h).

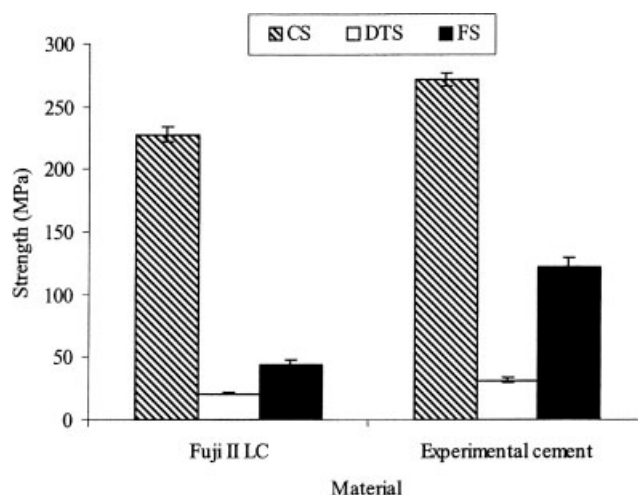


Figure 6 CS, DTS, and FS of the optimal experimental cement and Fuji II LC. The cements were conditioned in distilled water at 37°C for 7 days prior to testing. For experimental cement, the grafting ratio of GM = 70%, liquid formulation = 50/25/25, viscosity of liquid = 620 cp, P/L ratio = 3.2/1, and CQ concentration = 0.9%. For Fuji II LC, P/L = 3.2/1. The CS, DTS, and FS values of the experimental and Fuji II LC cements were significantly different from each other ($P < 0.05$), respectively.

such as Class I and II.⁵ Impressively, the high FS value (122 MPa) of the experimental cement is actually equivalent to those for high-strength dental composite resins.^{33,34}

CONCLUSIONS

We have developed a novel amino acid-constructed photocured glass-ionomer system. The amino acid-constructed polymers were grafted with GM. It is the grafting with GM that makes the cements with a higher grafting ratio, and thus provides a higher FS which is equivalent to those for composite resins. Effects of grafting ratio, polymer content, P/L ratio, initiator concentration, and light exposure time were significant. It is found that an appropriate ratio balance between these parameters is very important. Effect of MW was not significant. Aging study shows that the experimental cement showed a constant increase in mechanical strength over a month period, which is of great clinical importance. The experimental cement exhibited significantly higher CS (271.4 MPa), DTS (31.2 MPa), and FS (122.0 MPa), compared to commercial Fuji II LC cement with corresponding 228.2, 21.2, and 44.2 MPa after conditioning in water for 7 days. Future studies will focus on evaluation of adhesion to tooth, biocompatibility, and other properties of these novel amino acid-constructed cements.

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