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Novel resin modified glass-ionomer cements with improved flexural strength and ease of handling

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Abstract

Poly(acrylic acid-co-itaconic acid) copolymers containing pendent methacrylates were synthesized and used to formulate redox-initiated in situ cured glass-ionomer cements (GICs) by mixing with reactive glass fillers (Fuji II LC). Various formulations for the redox initiator were studied, and flexural strength (FS) was used as a screening tool for optimization. Effects of molecular weight (MW), grafting ratio, comonomer, polymer content in the liquid composition, powder/liquid (P/L) ratio, and aging on FS were investigated. The results show that the in situ cured GICs demonstrated higher FS (89.6–123.2 MPa), as compared to commercial Fuji II LC GIC (57.1 MPa). The optimal concentrations for redox initiators were found to be 0.15% (by weight) for $K_2S_2O_8$ and 0.2% for ascorbic acid (or 0.6% for microencapsulated ascorbic acid), respectively. Effects of MW, grafting ratio, P/L ratio and polymer content in the liquid formulation were significant. During aging, the cement showed an increase in strength over 24 h and then no change for time periods up to six months. SEM analysis supports the strength data associated with the formulations. The exotherm and setting time suggest that novel redox-initiated resin-modified GICs hold promise as biocompatible and workable cement for orthopedic applications.

Keywords: Redox; Resin-modified glass-ionomer cement; Polyacids containing pendent methacrylates; Evaluation; Flexural strength

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1. Introduction

Glass-ionomer cement (GIC) is a water-based material that hardens following an acid–base reaction between calcium fluoroaluminosilicate glass powder and an aqueous solution of polyacid [1]. GIC has been widely used as dental restorative and adhesive material for more than twenty-five years, due to its numerous clinically attractive properties, such as direct adhesion to tooth and base metals due to salt-bridge formation, anticariogenic properties due to constant fluoride release, and thermal compatibility with tooth due to low thermal expansion coefficient [2–9].

When polyacids in GICs are modified with pendant methacrylate groups, the GICs not only undergo an acid–base reaction but also participate in an in situ free-radical polymerization [10]. These cements are called resin-modified glass-ionomer cements (RMGICs) [10]. RMGICs have gained popularity in the restorative dentistry community, since they demonstrate more attractive properties, as compared to conventional glass-ionomer cements (CGICs). In addition to maintaining the clinical advantages of CGICs, RMGICs reduce the problems of moisture sensitivity and low early mechanical strength associated with CGICs [11,12], are easier to handle clinically [12], exhibit

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extended working time and have significantly improved mechanical strengths, such as higher flexural strength (FS) and diametral tensile strength (DTS) [10,13]. The strengths of these RMGICs are increased as much as 2–3 times as compared to their conventional counterparts [10].

Due to the similarity between tooth (especially dentin) and bone, glass-ionomer cement has shown great potential to be used as an orthopedic restorative as well [14,15]. However, so far only CGICs, but not RMGICs, have been extensively studied for orthopedic applications. Photocurable RMGICs that have been popular in dentistry are not suitable for orthopedic applications, because the depth of light penetration in translucent composites is very limited (only 2–3 mm) [6]. Such limited light penetration makes it impossible to use these materials in hip replacement surgery. In order to apply RMGICs for orthopedics, suitable redox-initiator systems have to be developed. In this paper, we introduce a novel water-soluble redox initiation system for in situ polymerization of RMGICs. This exploratory system has made it possible to develop water-based RMGICs with potential applications in orthopedic surgery.

The objectives of this study were to synthesize and characterize polyacid copolymers containing pendent methacrylates, to formulate the redox-initiated RMGICs while varying different parameters, such as MW of the polyacids, grafting ratios of pendent methacrylate, comonomers, powder/liquid (P/L) ratios and liquid compositions of the cements, and to evaluate the flexural strengths of the formed cements. The effects of the amount of initiator used and aging of the cement on strength were also studied. The exotherm and setting time of the cements were determined.

2. Experimental

2.1. Materials

Diethyl ether, ethyl acetate, *n*-hexane, tetrahydrofuran (THF), sodium hydroxide, sodium chloride, hydrochloric acid (37%), anhydrous magnesium sulfate ($MgSO_4$), acryloyl chloride (AC), butylated hydroxy toluene (BHT), and cellulose acetate butyrate (CAB) were used as received from Acros Chemical Co. Acrylic acid (AA), itaconic acid (IA), β-alanine (BA), potassium persulfate ($K_2S_2O_8$), 2,2′-azobisisobutyronitrile (AIBN), dibutyltin dilaurate (DBTL), triphenylstibine (TPS), ascorbic acid, 2-hydroxyethyl methacrylate (HEMA), and 2-isocyanatoethyl methacrylate (IEM) were used as received from Aldrich Chemical Co. Fuji II LC glass powder was supplied by GC American Dental Corp.

2.2. Synthesis of acryloyl β-alanine (ABA) and polyalkenoate with pendant methacrylate

ABA was synthesized using the Schotten–Baumann reaction, and details were described previously [16]. Briefly, to a three-neck flask containing BA (one mole) and NaOH (two moles) aqueous solution, AC (one mole) was added with stirring at temperature below 5 °C [17]. After the reaction was completed, the mixture was acidified to $pH = 2$ with HCl and extracted with ethyl acetate. The extract containing acryloyl BA (ABA) was dried with $MgSO_4$ and concentrated via a rotary evaporator to afford white crystals having a melting point of 85 ± 2 °C.

For synthesis of polyacids with pendant methacrylate groups, a simple one-pot synthesis technique was used. Briefly, to a three-neck flask, equipped with a thermometer, a nitrogen inlet and a mechanical stirrer, containing a solution of distilled THF, a mixture of AA, IA and AIBN was added. The reaction was run under N_2 purging at 60 °C for 18 h. The molar feed ratio for the polymers was 4:1 (AA:IA). Polymers with different molecular weights were prepared by using different amounts of AIBN. After the polymerization was completed, the solution was cooled down to 40 °C followed by a slow addition of a solution containing IEM, DBTL, TPS, BHT and distilled THF. An additional one hour was used to complete the reaction after the addition was finished. The IEM grafted polymers were recovered by precipitation from diethyl ether, followed by drying in a vacuum oven at room temperature. Fourier transform-infrared (FT-IR) and proton nuclear magnetic resonance (^{1}HNMR) spectroscopic techniques were used to monitor the reactions. The schematic diagrams for synthesizing both ABA and polyacid with pendent methacrylate are shown in Fig. 1(A and B).

2.3. Characterization of monomer and polymer

The synthesized monomer was characterized using a melting point test apparatus (Mel-Temp II, Laboratory Devices, Inc., Holliston, MA) for melting point determination, a FT-IR spectroscopy (Mattson Research Series FT/IR 1000, Madison, WI), 400 MHz NMR (Bruker AM 400), and gel permeation chromatography (GPC). Deuterated methyl sulfoxide was used as a solvent for ^{1}H-NMR characterization. Molecular weight was estimated on a Waters GPC unit (Model 410 differential refractometer, Waters Inc., Milford, MA), using standard GPC techniques and polystyrene standards. THF was used as a solvent.

2.4. Microencapsulation of ascorbic acid

To a flask containing 3.0 g of CAB and 300 ml of ethyl acetate, 1.0 g of ascorbic acid was added and

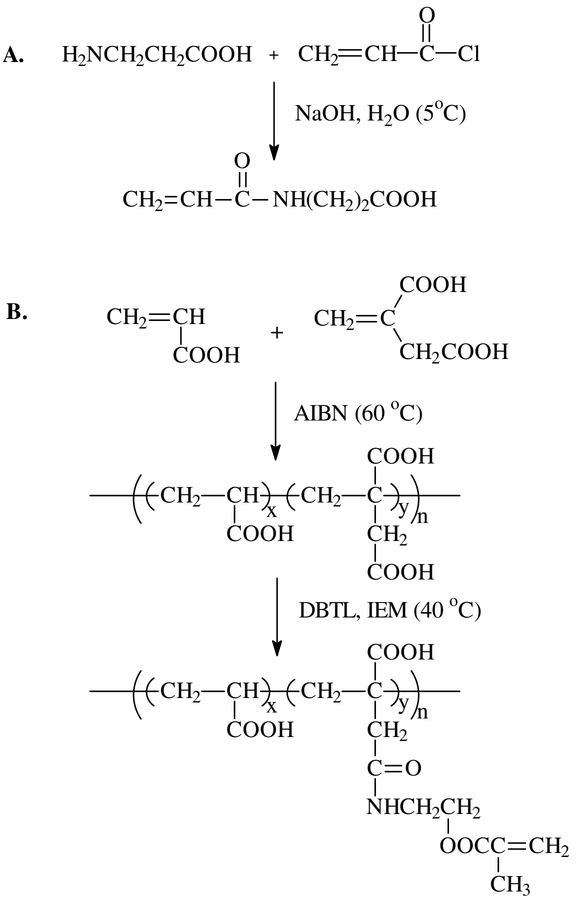

Fig. 1. Scheme for syntheses of ABA and copolymer containing pendent methacrylate.

suspended in the solution by stirring. Then 150 ml of *n*-hexane was added. After completing the addition, the flask was cooled with cold water to harden the formed microcapsules. The microcapsules were recovered by decantation and air-drying and stored prior to use.

2.5. Formulation of cements

A two-component system (liquid and powder) was used to formulate the cements. The liquid component was made by mixing the polymer with $K_2S_2O_8$, comonomer and distilled water. The powder component was prepared by mixing Fuji II LC glass powders with encapsulated ascorbic acid, using a vortex vibrator. Specimens were prepared under the same conditions unless specified (by weight): powder/liquid ratio (P/L) = 2.7/1, glass powder = Fuji II LC glass, liquid formulation = 50:20:30 (polymer:HEMA:H_2O), $K_2S_2O_8 = 0.15\%$, and encapsulated ascorbic acid = 0.6%. The polyacids with pendent methacrylate groups had a grafting ratio of 25% and a weight-average molecular weight (M_w) of 15,800 g/mol or number-average (M_n) of 5700 g/mol unless specified.

2.6. Strength determination

Specimens were fabricated at room temperature, according to the published protocol [16,18,19]. Briefly, the cylindrical specimens were prepared using a rectangular Teflon mold with dimensions of 3 mm in width by 3 mm in depth by 25 mm in length. The specimens were removed from molds after 15–30 min and conditioned in distilled water at 37 ± 2 °C for 7 days, prior to testing.

Testing of specimens was performed on a hydraulic mechanical testing machine (Model 858 Mini Bionix, MTS Systems Corp., Eden Prairie, MN), with a cross-head speed of 1 mm/min. The test was performed in three-point bending, with a span of 20 mm between the two supports. The sample sizes were $n = 6$ for each test. The flexural strength (FS) was obtained using the expression $FS = 3Pl/2bd^2$, where P = the load at fracture, l = the distance between the two supports, b = the breadth of the specimen, and d = the depth of the specimen.

2.7. Exotherm and setting time measurements

The heat generated from the setting reaction of the cement was determined using a slightly modified ASTM F-451 or ISO 5833 procedure. Briefly, the cement paste was placed in a cylindrical Teflon mold with dimensions of 30 mm in diameter by 6 mm in height, and covered with a Teflon plunger having holes for allowing the excess cement to escape. A digital thermocouple (Fisher Scientific, Springfield, NJ) was inserted in the center of the cement and used to record the temperature change. The setting curve (temperature/time) was recorded and used to determine the exotherm and setting time. The maximum temperature was defined as the exotherm and the setting time was determined from the turning point of the curve in the range of the steepest ascent.

2.8. Statistical analysis

One-way analysis of variance (ANOVA) 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.

2.9. Scanning electron microscopic (SEM) analysis

The fracture surface of one representative specimen from selected materials was observed under a magnification of 3000× with a scanning electron microscope (Model 515, Philips Electronics N.V., Eindhowen, The

Netherlands) to investigate the effects of microstructure on the mechanical strengths. The specimens were vacuum sputter-coated with gold–palladium (Au–Pd), and a high vacuum (5.5×10^{-5} Torr) was used for dehydration of the coated specimens before SEM analysis.

3. Results and discussion

3.1. Characterization

The yield and measured melting point for ABA were 52% and 85 ± 2 °C. ABA exhibited strong FT-IR peaks at around 1720, 1620, 1540 and 1655 cm^{-1} associated with carbonyl, amide I (C═O stretching vibration), amide II (NH_2 deformation) and carbon–carbon double bonds, respectively. For ^{1}HNMR, ABA exhibited typical chemical shifts at around 12.62, 8.60, and 5.76 as well as 6.58 ppm for carboxyl, amide, and carbon–carbon double bonds, respectively. The yield for the polymer was 95%. Three typical peaks at 1715, 1649 and 1638 cm^{-1} on FT-IR were observed for carbonyl, amide and double bonds for the polymer. The ^{1}HNMR spectra of IEM, poly(AA–IA) copolymer, and copolymer grafted with methacrylate groups are shown in Fig. 2. The ^{1}HNMR chemical shifts of carboxyl, amide, and double bonds were found at 12.25, 8.05, and 5.67 as well as 6.12 ppm, respectively.

3.2. Flexural strength as a screening tool

A flexural strength test is a test on a beam supported at each end under a static load, and it reflects a combination of tensile, compressive and shear strengths. It can be assumed that the principal stresses on the upper surface (or the load bearing side) are compressive, those on the lower surface (or away from the loading bearing site) are tensile, and those at the surface parallel to the load are shear [6,20]. Prosser et al. [21] suggested that the most appropriate measure of the strength of GICs is obtained with a flexural test. They pointed out that many brittle materials, such as cements and ceramics, have strengths under tension that are markedly lower than the corresponding strengths under compression, since these materials often have many microcracks, defects, and voids inside or on the surface. If standard tensile testing were used, tremendous variations and erroneous values would be easily obtained. It is believed that the measurement of flexural strength offers the best practical and reliable estimate of tensile strength [18]. Therefore, FS was used as a screening tool for evaluation of the cements in this study. Basic formulations were selected based on previous research [19].

3.3. Determination of initiator system

In this study, we have introduced a novel redox initiation system to the water-based resin cements for potential orthopedic applications. As mentioned earlier, popular photo-initiator systems used in dental RMGICs cannot be applied to orthopedics because of the limited depth of light illumination. In hip fixation, restoration requires a large quantity of material, which is something that the photo-initiator system is unable to accomplish. Benzoyl peroxide and *N,N*′-dimethyl-*p*-toluidine are

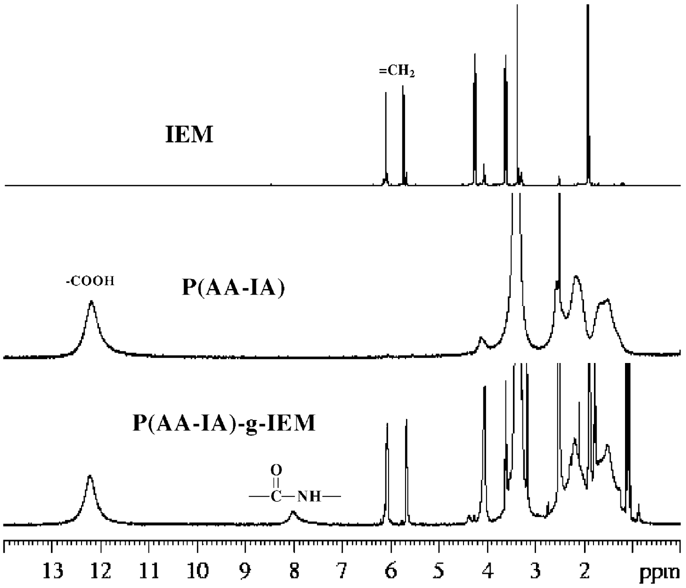

Fig. 2. ^{1}HNMR spectra for IEM, copolymer and copolymer containing pendent methacrylate.

known hydrophobic redox initiators for either PMMA [23] or bioactive resin composites [24]. In the case of water-based resin cements, such as RMGICs, so far little work on redox-initiator systems has been reported. In our research, it was impossible to initiate in situ polymerization just by simply mixing water-soluble redox-initiators with water-soluble polymer resin system because setting was too fast to allow one to mix the cement well. The setting often occurred in seconds. To overcome the difficulty in manipulation, ascorbic acid (activator) was microencapsulated to allow an extended working or curing time. We have studied the effect of concentration of redox-initiator pair on FS of the cements. By studying the concentration range from 0.1% to 0.25% (percentage by weight) for $K_2S_2O_8$ and 0.05–2.0% for ascorbic acid (or 0.15–0.6% for microencapsulated ascorbic acid), we found that the working time was in the range of 3–4.5 min and the FS in the range of 66.9–96.3 MPa. The best concentrations for $K_2S_2O_8$ and ascorbic acid (or microencapsulated ascorbic acid) were 0.15% and 0.2% (or 0.6%), respectively. The FS and working time for this initiator pair were 96.3 MPa and 3 min, respectively. It is concluded that microencapsulation extends the working time and makes the water-soluble initiator system workable.

3.4. *Effect of molecular weight*

Table 1 illustrates the effect of molecular weight of the polymers on FS of the cements. It is apparent that neither low nor high MW polymers gave the highest FS. Instead, the formulation based on polymer of intermediate MW exhibited the highest FS. Generally speaking, the higher the MW the higher the mechanical strengths of the resin [9]. It is believed that manipulation difficulties for the specimens with high MW of 28,300 (M_w) led to a lower FS.

Table 1
Effects of MW and grafting ratio

M_w/M_n $(10^{-3}/10^{-3})$	FS (MPa)*
Effect of MW	
28.3/9.9	63.0 (9.7)^a
15.8/5.7	96.3 (8.8)
8.3/2.9	60.7 (7.5)^a
Grafting ratio	
Effect of grafting ratio	
10	81.6 (8.8)^{b,c}
25	96.3 (8.8)^b
50	73.5 (4.7)^c

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

3.5. *Effect of grafting ratio*

The effect of grafting ratio is also shown in Table 1. Polymer grafted with 25% of IEM exhibited the highest FS, which means that the optimal grafting ratio is also important to mechanical strength. Both high and low grafting ratios led to lower FS. The role of grafting is actually to add more resin component into the brittle GIC system, which enhances plastic deformation of the material. Excessive grafting, however, can lead to lower strengths due to a decreased capacity for the acid–base reaction in GICs, causing glass particles to only play a role as filler instead of as a reactive species. On the other hand, insufficient grafting also caused a lower strength because there were not enough double bonds to lead to effective covalent crosslinking. In this situation, the RMGICs behaved like CGICs. As a result, the grafting ratio of 25% gave resins of higher FS, as compared to those grafted with 10% and 50% methacrylate groups. SEM photomicrographs supported the above results. As one can see (Fig. 3), smooth and homogeneous surface was found in Fig. 3(a) for the cement with 10%, as compared to the cement with 25% (Fig. 3(b)). On the other hand, Fig. 3(c) shows numerous small and large pores that were responsible for a lower FS, although large resin fragments exist.

3.6. *Effect of comonomer*

Three comonomers, HEMA, ABA and AA were investigated. It is known that HEMA is one of the major components in RMGICs [19]. It acts as both cosolvent and comonomer in the system. Vinyl-containing polyacids require the addition of an amphiphilic difunctional monomer like HEMA to help them dissolve in water because of their relatively limited water solubility. Unfortunately, HEMA has been reported to have certain cytotoxity to soft tissue such as pulp in tooth [25] and osteoblasts in bone [22,26]. Unreacted HEMA can cause inflammatory reaction to dental pulp if the dentin barrier is not thick enough [25]. ABA is a newly synthesized amino acid derivative and has great potential as an alternative to replace HEMA because of its biocompatibility. AA was used as control because it has lower MW and is considered more acidic, as compared to the others. From the strength data in Table 2, there was no significant difference between ABA-(B) and HEMA-(C) containing cements but there was a significant difference between AA-containing cement (A) and either ABA-(B) or HEMA-(C) containing cements.

The differences between B and C can be interpreted by the reactivity of the comonomers (acidity) with metal ions and the amount of the comonomer added. AA and ABA both carry acidic carboxyl groups but HEMA does not. AA may be more acidic than ABA because a stronger electron donating effect to the carboxylic acid

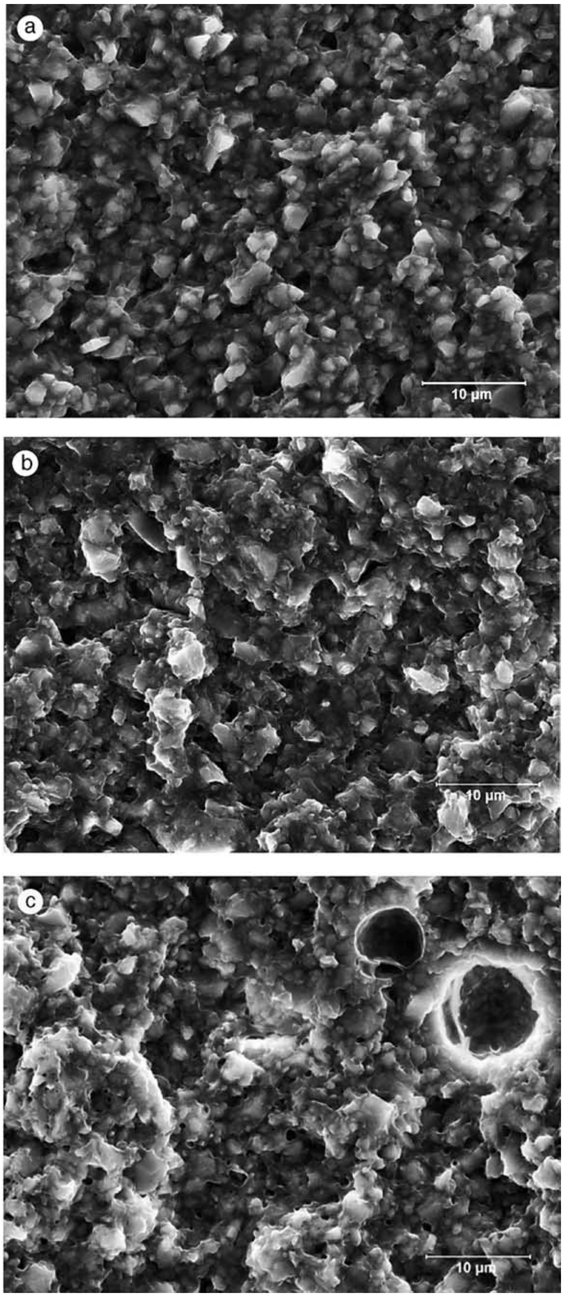

Fig. 3. Fracture surface photomicrographs at a magnification of 3000× after three-point bending: (a) cement having a 10% grafting ratio, (b) cement having a 25% grafting ratio and (c) cement having 50% grafting ratio.

in ABA, as compared to AA. The more acidic the comonomer, the stronger the acid–base reaction and thus the more salt-bridge formations are anticipated. In addition, the moles used for each comonomer were very different even though the weight ratios were the same. Assuming 100 g of liquid, we actually added 0.28, 0.14 and 0.15 mol for AA, ABA and HEMA into the formulation, respectively, based on adding 20 g of comonomer. Considering the reactivity of the double bond, AA is the most reactive, followed by ABA and HEMA, based on the stability of the formed free radical [27]. The reason why ABA did not exhibit higher FS than HEMA may be attributed to the existence of less double bonds and higher viscosity in ABA-containing cements, because ABA was added less in mole (0.14) than HEMA (0.15) and it is also a crystalline material.

From SEM photomicrographs (Fig. 4), the SEM with AA (Fig. 4(b)) exhibited a tougher fracture surface having less particles exposed, as compared to those with HEMA (Fig. 3(b)) and ABA (Fig. 4(a)). The fracture surface on the SEM with ABA (Fig. 4(a)) was tougher than that with HEMA (Fig. 3(b)). More exposed particles and homogeneous fracture surface was observed for the SEM with HEMA. The SEM photomicrographs show why AA-containing cement was the strongest.

3.7. Effect of polymer content

In formulating the liquid, three components need to be considered. They are the grafted copolymer, comonomer and water. A suitable balance among them is very critical. Usually, higher content of the polymer leads to higher strengths [16]. In this study, we compared three formulations (polymer:HEMA:H_2O), i.e., 60:20:20 (D), 50:20:30 (C) and 40:40:20 (E). From the results (Table 2), the formulation with 60:20:20 showed almost the same FS (65.0 MPa) as the one with 40:40:20 (62.5 MPa) and neither gave the highest FS. The reason for the former can be attributed to handling difficulties during mixing because of the high viscosity. In fact, we did experience a very high viscosity with the liquid of 60:20:20 and a difficulty in mixing with the glass powder during cement preparation. The reason for the poor properties of the formulation with 40:40:20 can be attributed to low content of polymer. The formulation with 50:20:30 was the best among three cements, with high FS (96.3 MPa) and good handling properties.

3.8. 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. From Table 2, we can see that the FS increased with the powder/liquid (P/L) ratio, although there was no statistically significant difference between the cement with 3.2/1 (F) and 2.7/1 (C). 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, like the effect of very high polymer content. We have

Table 2
Effect of formulations of the cements on FS

Code	Comonomer	Polymer:comonomer:water	P/L	FS (MPa)*
A	AA	50:20:30	2.7/1	123.2 (15.6)
B	ABA	50:20:30	2.7/1	89.6 (9.8)^{a}
C	HEMA	50:20:30	2.7/1	96.3 (8.8)^{a,b}
D	HEMA	60:20:20	2.7/1	65.0 (9.9)^{c}
E	HEMA	40:40:20	2.7/1	62.5 (6.0)^{c}
F	HEMA	50:20:30	3.2/1	111.1 (13.5)^{b}
G	HEMA	50:20:30	2.2/1	79.1 (11.3)^{a}
H	Fuji II LC			37.1 (6.2)

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

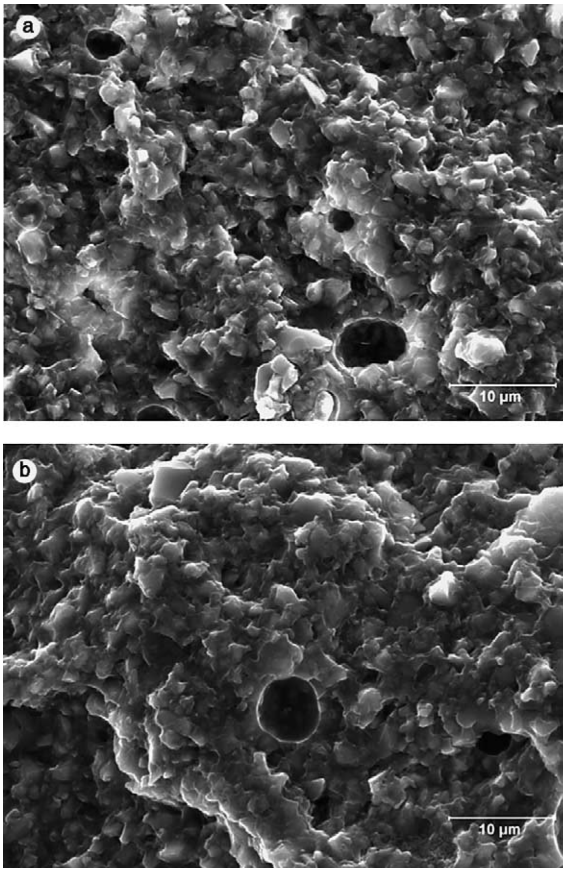

Fig. 4. Fracture surface photomicrographs at a magnification of 3000× after three-point bending: (a) cement having ABA as comonomer and (b) cement having AA as comonomer.

experienced difficulties in mixing the cements when a high P/L ratio (3.2/1) was used. It was found that the P/L ratio of 2.7/1 was optimal because it demonstrated both good mechanical strength and acceptable handling characteristics.

3.9. Effect of aging

It is well known that GICs increase their strengths with time due to constant salt-bridge formations [1]. The cements with the optimal formulation were conditioned for 1 h, 1 day, 1 week, 1 month and 6 months, followed by FS determinations. As shown in Fig. 5, FS was significantly increased from 1 h to 1 day and then kept constant up to 6 months. The result was quite consistent with previous reports in the dental literature [1,29].

3.10. Exotherm and setting time

One problem with traditional PMMA cements has been their high exotherms, which may cause the death of surrounding tissues. The results of exotherm measurements (Table 3) on the experimental GICs were rather low with a peak temperature ranging from 33.4 to 39.7 °C, as compared to PMMA cement (86.8 °C). This is very encouraging because body temperature is around 37 °C. Such low exotherms can be attributed to the presence of both filler and water, because it is known

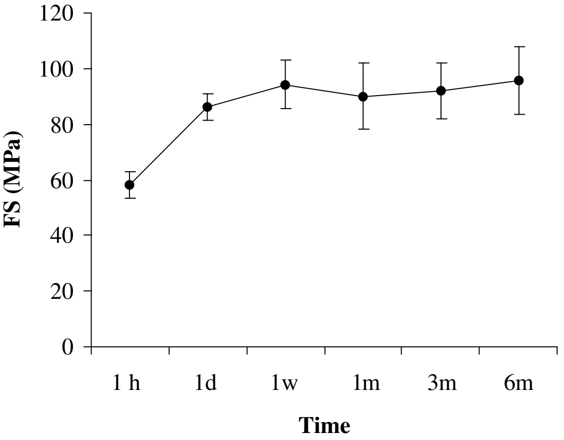

Fig. 5. Effect of aging on FS.

Table 3
Effects of P/L ratio and grafting ratio on exotherm and setting time

Grafting ratio	T_{peak} (°C)	Setting time (Time)
Effect of grafting ratio		
10	33.4	3.3
25	35.2	3.2
50	39.7	2.8
P/L ratio		
Effect of P/L ratio		
2.2	37.2	3.3
2.7	35.2	3.2
3.2	33.9	3.15

that ceramic or glass fillers are usually considered as heat insulators and water as a heat sink. This low exotherm would be likely to improve biocompatibility.

The effects of both grafting ratio and P/L ratio on the exotherm were also determined. As one can see from Table 3, the peak temperature was directly proportional to the grafting ratio and inversely proportional to the P/L ratio. This can be explained because higher content of double bonds in the cements having a higher grafting ratio contributed to higher exotherm, whereas higher glass content in the cement with a higher P/L ratio contributed to better heat insulation. On the other hand, the setting time showed the opposite trends, meaning that both higher double bond content and P/L ratio reduced the setting time.

4. Conclusions

We have developed a water-based redox-initiated RMGIC system. The cement demonstrated much higher FS (89.6–123.2 MPa), as compared to commercial light-cured Fuji II LC GIC (57.1 MPa). The optimal concentrations for redox initiators were 0.15% (by weight) for $K_2S_2O_8$ and 0.2% for ascorbic acid (or 0.6% for microcapsulated ascorbic acid), respectively. Effects of MW, grafting ratio, P/L ratio and polymer contents in the liquid formulation were significant. The highest strengths were found at the optimal formulations where the MW was 15,800 (in M_w), grafting ratio 25% (in mole), P/L ratio 2.7 (in weight) and liquid composition 50:20:30 (in weight). During aging, the cement showed an increase in strength over the 24 h and then no change for time periods up to six months. SEM analysis supports strength data associated with the formulations. The exotherm and setting time suggest that redox-initiated RMGICs show promise as biocompatible and workable cements for orthopedic applications.

Acknowledgements

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