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Original Article

Effect of glass and polyacid preparations on the strength of glass ionomer cements for dental applications

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Abstract

Glass ionomer cements (GICs), widely used as restorative materials in dentistry, are principally composed of fluoroaluminosilicate glass powder combined with a water-soluble polyacid. The investigation of new glass compositions and polyacid components are very important to improve the mechanical properties of these cements. The objective of this work was to prepare glass ionomers and polyacids for the use as GICs. The effects of spherical bodies, Al_2O_3:SiO_2 ratios, replacing CaO by SrO, and ZrO_2 adding in glass powder in combination with the variation of acidic copolymer concentration on the compressive strength were investigated and discussed.

Key words: glass ionomer, ionomer cements, silicate cement, dental materials

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1. Introduction

Glass-ionomer cements (GICs) are restorative materials, firstly described by Wilson and Kent in 1969 (Wilson *et al.*, 1969; Wilson *et al.*, 1972). These materials consist of a powder and liquid, which are mixed to produce a plastic mass, and subsequently changes to a rigid solid. Typically, a GI-liquid is derived from an aqueous polyalkenoic acid such as polyacrylic acid and the GI-powder is usually composed of fluoroaluminosilicate glass. When the powder and liquid are mixed together, an acid-base reaction appears (Nicholson, 1998). GICs have been extensively used in dentistry for over 30 years as an alternative of amalgam for restoring primary dentition because of their excellent biocompatibility (Hübel *et al.*, 2003; Nourmohammadi *et al.*, 2007). Advantages of these cements are translucent and adhesive to tooth structure due to the similar coefficient of thermal expansion of glass ionomer to tooth structure (Moshaverinia *et al.*, 2008). However, the shortcoming of the conventional GICs is probably their lack of strength and toughness. Therefore, this research is aimed at the preparation of glass powder and polyacid to improve the mechanical strength of GICs. It is well documented that cement strength associates with glass composition, especially the Al_2O_3:SiO_2 ratio, where a value of 0.5 or more is being required for the formation of cement (Kent *et al.*, 1979; Wilson *et al.*, 1980). In this study, several efforts for strength improvement have been made regarding in the glass component. The Al_2O_3:SiO_2 ratio was raised to a value of 1-1.6 in combination with the replacement of CaO by SrO and the addition of ZrO_2. The formation of spherical particle of glass powder by using the spray drying method (Vehring *et al.*, 2007) was also applied to increase the cement strength. In the liquid component, the characteristics of polyacid such as molecular mass and monomer unit ratio, as well as the concentration of liquid component were investigated for their influences on the cement strength.

2. Materials and Methods

2.1 Glass preparation and characterization

The glass compositions of GI2-8 represent modifications from the original composition reported by Hurrell-

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Gillingham *et al.* (Hurrell-Gillingham *et al.,* 2003) with an approximate Al_2O_3:SiO_2 weight ratio of 1.13 (GI1) as shown in Table 1. The Al_2O_3:SiO_2 ratio was increased to improve the mechanical strength, CaO was replaced by SrO for a natural color aspect, and ZrO_2 was added to the glass formula to induce higher mechanical properties. The glass batches were melted at 1450°C for 2 hrs to make glass frits. The frits were then ground to achieve the mean particle size of ~4-6 µm. Spherical powder was produced through a spray dryer (Büchi Mini Spray Dryer, B-290) using an inlet temperature of drying air of 200°C. Phase and composition analyses of glasses were performed by X-ray diffraction (XRD, JEOL JDX 3530) and X-ray fluorescence (XRF, Philips PW 2404). Cement surface was also viewed by scanning electron microscopy (SEM, JEOL JSM-6301F). The commercial GIC, Fuji II, was used as a control throughout the study.

2.2 Copolyacid preparation and characterization

Copolymers of acrylic acid (AA) and itaconic acid (IA) were prepared by free radical polymerization in aqueous solution using potassium persulphate as the initiator and isopropyl alcohol as the chain transfer agent. The polymerization was carried out at 90°C for 4 hrs under nitrogen atmosphere using different monomer feed ratio of AA:IA. The molecular mass and AA/IA molar ratio of the copolymers were determined using gel permeation chromatography (GPC, Waters 600E) and nuclear magnetic resonance spectroscopy (NMR, Bruker DPX-300 spectrometer), respectively.

2.3 Cement fabrication and characterization

2.3.1 Compressive testing

The glass powders were mixed with copolymer solutions, using the weight ratio of 8:3. Specimens were prepared and tested according to the method described in ISO 9917. The cylindrical specimens (6 mm height x 4 mm diameter) were made by placing the mixed materials into stainless steel molds. After being stored in an incubator at 37°C ± 2°C for 1 hr, the specimens were gently removed from the molds, immersed in deionized water and incubated at 37°C ± 2°C for 23 hrs. The compressive strength (CS) was tested using a Universal Testing Machine (Instron Model 55R4502) at a cross-head speed of 0.75 mm/min. The CS was calculated using the following equation: $CS = \Delta F/\pi d^2$, where F is the maximum applied load (N) and d is a diameter of the specimen (mm) according to ISO 9917.

2.3.2 Working time and setting time test method

Working and setting times were determined using the methods described in British standard specification for dental glass ionomer cements; BS 6039. Cements were mixed at room temperature using a powder to liquid weight ratio of 8:3, and then filled into an acrylic mold (10 mm x 10 mm x 6.5 mm) within 2 min after start of the mixing. A Gilmore apparatus (Humboldt MFG, Model H-3150F) equipped with an indentor of 113.4 g mass and with a flat-end diameter of ~ 2.12 mm was employed to measure working time at ambient temperature. Five minutes after starting the mixing, the indentor was carefully lowered vertically onto the surface of the cement and allowed to remain there for 5 s. The testing was repeated at 10 s intervals until the needle failed to make a complete circular indentation in the cement. In case of setting time measurement, the testing method is almost the same as measuring working time except an indentor of 453.6 g mass with a diameter of ~1.06 mm was used and the experiment was carried out in an oven at 37°C ± 1°C with a relative humidity of at least 90% after cement mixing. The working and setting times were recorded as the time elapsed between the start of mixing to the time, when the needle failed to make a complete circular indentation in the cement. At least three repeats were done to evaluate the working and setting times.

3. Results and Discussion

3.1 Glass ionomer powder

3.1.1 Phase and composition analyses

Figure 1 shows the XRD patterns of all glasses. The presence of amorphous structure appeared in the XRD patterns of all glasses. It seems from Figure 1 only in GI4, a slightly white opaque observed, which was determined as corundum, (Al_2O_3, JCPDS No. 46-1212).

Table 1 presents the glass compositions and Al_2O_3:SiO_2 ratios determined by XRF after melting. XRF results demonstrated a close similarity in molar composition between the pre-melt glass and the frit, apart from a minute increment of SiO_2 and Al_2O_3 observed in post-melting due to the contamination of alumina and silica contents from alumina crucible during melting.

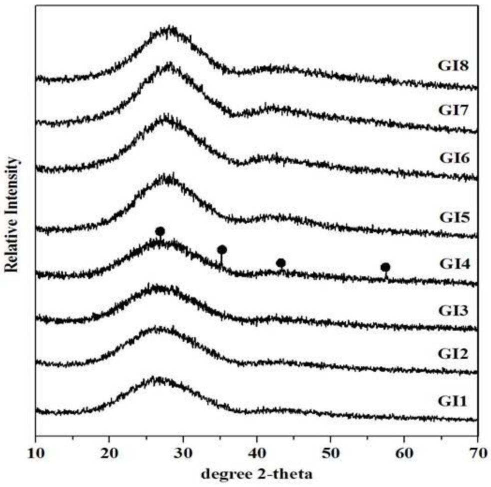

Figure 1. XRD patterns of all glasses, ● Corundum.

Table 1. Glass compositions after melting coupled with Al_2O_3:SiO_2.

Oxides	Post-melt glass composition (%wt)							
	GI1	GI2	GI3	GI4	GI5	GI6	GI7	GI8
SiO_2	24.60	23.10	23.04	21.06	21.96	23.29	23.16	22.11
Al_2O_3	27.94	29.64	32.81	33.66	28.35	26.50	25.46	25.25
P_2O_5	18.55	18.30	17.52	17.77	16.31	15.05	12.02	12.67
CaO	22.55	22.16	18.56	20.06	5.73	5.11	1.05	3.29
SrO	-	-	-	-	21.27	18.01	19.71	19.83
CaF_2	4.76	6.32	6.20	5.67	4.93	7.70	11.56	8.72
ZrO_2	-	-	-	-	-	2.53	4.45	6.10
Total	98.40	99.52	98.13	98.22	98.55	98.19	97.41	97.97
Al_2O_3:S iO_2	1.14	1.28	1.42	1.60	1.29	1.14	1.10	1.14

3.1.2 Spray drying of glass ionomer powder

Figure 2 shows the morphologies of the synthesized glass ionomer powders (GI4 and GI7) after spray drying. The synthesized glass powders (size ~4-6 µm), which appeared irregular in shape before spray drying were agglomerated to form spherical particles after spray drying. The particle sizes of spherical powders were around 20-25 µm. Other synthesized glass powders were also investigated for the morphology and particle size after spray drying. The results were found similar and are not shown here.

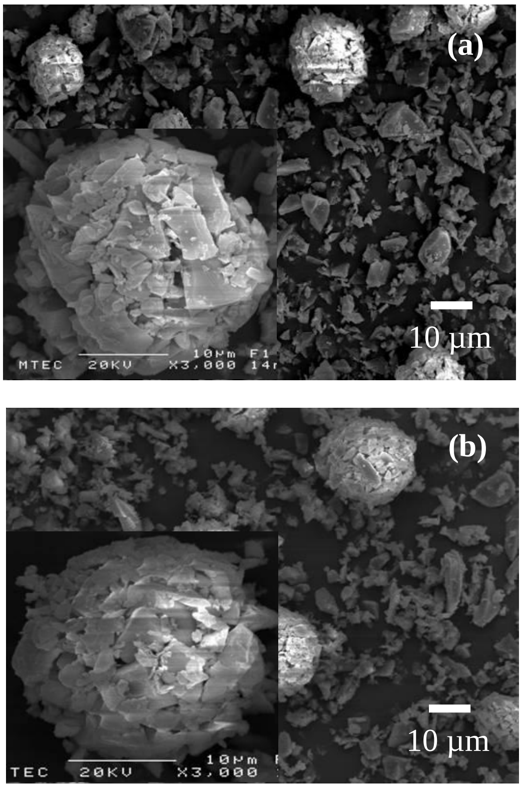

Figure 2. Morphology of glass ionomer powders after spray drying process a) GI4 powder and b) GI7 powder.

3.2 Glass ionomer liquid

3.2.1 Characterization of copolymer

The AA/IA copolymers (CAI), which were a major component in GI-liquids were synthesized. A ^{1}H-NMR spectrum of CAI and the peak assignments are presented in Figure 3. The molar ratio of AA/IA was calculated from the ratio of peak integral between CH in AA unit to CH_2COOH in IA unit, which was equal to 2(b/d). The results are given in Table 2, as well as the results of the molecular weight determined by GPC.

3.2.2 Influences of AA/IA ratio and molecular weight on cement strength

To investigate the influences of AA/IA ratio and molecular weight of the copolymer on cement strength, CAI solutions were mixed with the commercial glass (Fuji II powder) and tested for compressive strength. The results are exhibited in Table 3. It was demonstrated that the AA/IA ratio seemed not significantly affecting the cement strength. CAI#3 and CAI#2 at 50% concentration yielded cements having

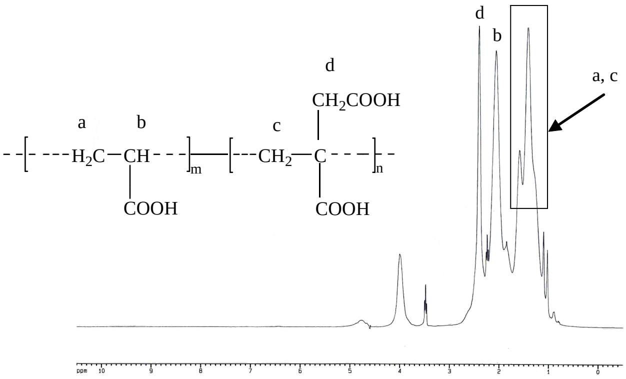

Figure 3. ^{1}H-NMR spectrum of acrylic acid and itaconic acid copolymer.

Table 2. Molar ratio and molar mass of acrylic acid and itaconic acid copolymers (CAI).

Sample	NMR	GPC	
	AA/IA* (mole ratio)	molar mass (Dalton)	polydispersity
CAI#1	3.6	55600	2.41
CAI#2	2.6	48900	2.18
CAI#3	1.8	34700	1.85

* AA: acrylic acid, IA: itaconic acid.

Table 3. Compressive strengths of cements made of Fuji II glass and CAI solutions.

CAI solutions	Compressive strength (MPa)
CAI#1 (40%wt)	71.88±15.72
CAI#2 (50%wt)	140.07±7.27
CAI#3 (50%wt)	147.67±11.56
CAI#3 (55%wt)	89.80±21.87

similar compressive strength. CAI#1 showed the poorest mechanical strength, which could be explained by its high molecular weight, and thus high viscosity. In spite of being prepared at low concentration, 40% CAI#1 was found to be more viscous than 50% CAI#3 and CAI#2 and that had limited the good cement forming. The increase in the molecular weight and concentration of the copolymer usually increased the strength of the cement. In this study, however, the cements made from the high molecular weight (40% CAI#1) and the high concentration (55% CAI#3) showed relatively low mechanical strength. The molecular weight and concentration influenced the viscosity of the liquid. By increasing those factors, viscosity increased, which caused the difficulty in mixing and molding the specimens. Specimens were obtained small defects, which are weakening the cement strength. As a result, it seemed that a low molecular weight copolymer having a low viscosity was preferable for cement formation. A liquid component could be prepared at a high concentration, which expectedly resulted in higher cement strength. Accordingly, CAI with the lowest molecular weight (CAI#3) was intensively used for further investigating the cement strength with our synthesized glass.

3.3 Cement samples

3.3.1 Compressive strength

Cements made of Glasses GI1-4 and CAI#3 solutions; 50%wt and 55%wt, were investigated for the effects of Al_2O_3:SiO_2 ratio and copolymer concentration on compressive strength as shown in Figure 4. The results revealed a significant increase of CS as the Al_2O_3:SiO_2 ratio increased for cements made of 55%wt CAI#3. In contrast, cements made of 50%wt CAI#3 showed a rather similar CS for all glasses. It was also found that 55%wt CAI#3 shows a better handling characteristic during mixing of cement than 50%wt CAI#3. The poor mixing of 50%wt CAI#3 could contribute to inferior cement forming, resulting in no increase in CS observed with increasing Al_2O_3:SiO_2 ratio.

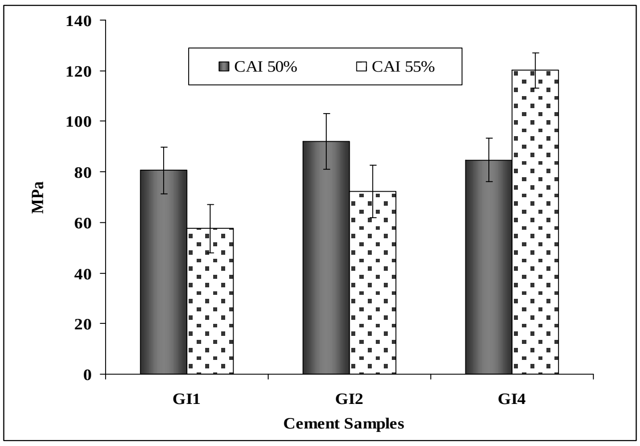

Figure 4. Mean compressive strengths of cements made of GI1, GI2, and GI4 with 50% and 55% CAI#3.

The compressive strengths of cement GI1-4 with 55% CAI#3 are presented in Table 4. The result shows an increase of the strength with an increasing Al_2O_3:SiO_2 ratio, as expected. The highest Al_2O_3:SiO_2 ratio; 1.60, yielded the strongest cement (120.07±6.84 MPa). This could be explained by the partial crystallization of corundum, Al_2O_3, in GI4 that induced the increase of the cement strength.

The effects of replacing CaO by SrO and adding of ZrO_2 were investigated in cements made of Glasses GI5-8. The compressive strengths of cements made of GI5-8 and 55% CAI #3 are presented in Table 4.

Significantly, the color of GI5-8 cements looked more closely to the natural teeth color compared to that of GI1-4 cements, owning to the presence of SrO. However, the compressive strength of cements was lowered when replacing CaO with SrO. Therefore, ZrO_2 was added in glass containing SrO to improve the compressive strength of the cements. The

Table 4. Compressive strengths of cements made of GI1-GI8 and 55% CAI#3.

Cements	Mean Compressive Strength (MPa)
GI1	57.64±9.59
GI2	72.30±10.41
GI3	74.73±9.79
GI4	120.07±6.84
GI5	87.77±7.08
GI6	91.49±3.13
GI7	111.23±8.37
GI8	73.57±4.49

Table 5. Average values of working and setting time of cements.

Samples	Avg. Working Time (min)		Avg. Setting Time (min)	
	Irregular shape	Spherical shape	Irregularshape	Sphericalshape
GI4+55% CAI#3	06:23	06:42	08:20	08:58
GI7+55% CAI#3	03:32	03:45	05:58	06:13
BS 6039 : 1981	> 02 :75		< 05 :00	

highest compressive strength in this series was obtained from cements made of GI7 (111.23±8.37 MPa), which probably contained the ideal compositions of SrO and ZrO_2.

3.3.2 Working and setting times of cements

According to the high CS values found during the previous experiments, GI4 and GI7 were selected for working and setting time testing. Table 5 shows the average working and setting time values of GI4 and GI7 mixed with 55% CAI#3. Typically, all cements had duration for setting time longer than for working time. Referring to BS 6039, the working and setting times for dental glass ionomer cements as a restorative material were required at more than 2.75 and less than 5 mins, respectively.

A longer working and setting time was observed when spherical-shaped powder was used. This could be explained by a larger particle size (20-25 μm) induced by the agglomeration of irregular powder (4-6 μm) during spray drying. A larger particle size resulted in a smaller surface area/ volume, hence retarded the working and setting times of cements. The spherical shape also promoted flow ability during cement mixing. The viscosity of cement could be reduced, leading to the simplicity of mixing and molding cement. These phenomena were observed in both GI4 and GI7 cements. However, the working time and setting time of GI4 cement were longer than that of GI7 cement, which resulted from the presence of CaO and the higher Al_2O_3:SiO_2 ratio in the glass composition.

3.3.3 SEM results

Figure 5 shows the SEM images of cement surfaces. SEM images show a few gaps and cracks on the surface of all cements. This may be due to water loss (dehydration) from cements by exposing to air (ambient temperature) during being kept. Some cracks were observed around the particle (glass powder)-matrix (copolymer) interface, suggesting that the interfacial bonding between the glass powders and the matrix was relatively weak (Gu *et al.*, 2004). In addition, some voids can also be seen on the fracture surface due to air bubbles trapped within the cements during transferring the mixed cement into the mold cavity. The presence of cracks and voids on the surface area of cements indicated that internal defects and weaknesses in the cements were most likely due to the weakness at the glass particle-matrix interface, resulting in the low CS of the cement.

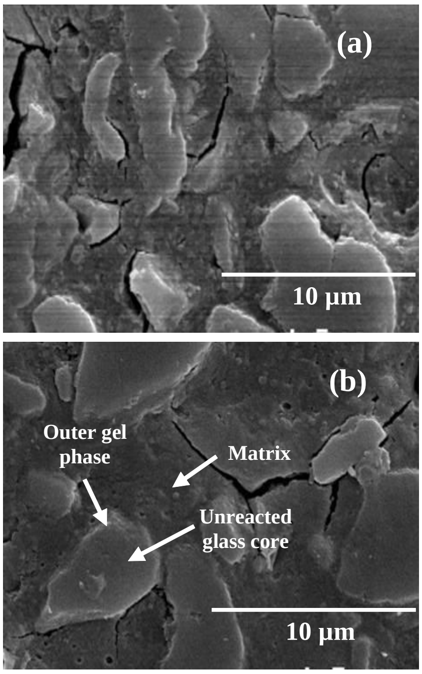

Figure 5. SEM images of cement surfaces after mixing with 55%wt CAI#3 (a) GI4 and (b) GI7.

4. Conclusions

Both, glass and polyacid components have an effect on the mechanical strength of glass ionomer cements. In this study, the optimized cement strength was achieved by increasing the copolymer concentration in combination with using a proper Al_2O_3:SiO_2 ratio. The replacing of CaO by SrO induced a nearly natural teeth color. If SrO contained in the composition, the addition of ZrO_2 could improve the compressive strength of the cements.

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