

Synthesis and Characterization of Diethanolamine-Containing Glass Ionomer Cement

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ABSTRACT: In this study, glycidyl methacrylate (GMA) diethanolamine was synthesized and incorporated into polyacid main chains, which would be used for glass ionomer cements (GICs). The polymer was prepared by the free radical polymerization of acrylic acid and itaconic acid with readily synthesized GMA diethanolamine. Effects of molecular weight, polymer content in the liquid composition, powder/liquid ratio, and aging on compressive strength and diametral tensile strength were investigated. Working and setting time, water sorption and solubility

(Wsl), pH value of the immersed solution, and microhardness were also measured. The experimental GICs had comparable mechanical properties to Fuji II GICs while exhibiting less Wsl and high hydrophilicity. The results suggested that the experimental GICs held promise as biocompatible and workable cement for application. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1330–1338, 2012

Key words: mechanical properties; copolymers; dental polymers; biomaterials

INTRODUCTION

Glass ionomer cements (GICs) have been widely used as dental restorative materials since invented by Wilson and Kent in 1969.¹ Compared to dental composites, there are many advantages for GICs, such as bonding to dentine and enamel through chemical reaction, anticariogenic properties due to release of fluoride,² biological compatibility, and low cytotoxicity. Conventional GICs are formed by the reaction of poly(alkenoic acid)s with a calcium fluoroaluminosilicate glass powder via an approximate acid base reaction. In the presence of water, the polymeric acid reacts with the glass powder, then releases calcium and aluminum cations, and forms a silica gel area.^{3–5} With the released cations, the polyacid chains are crosslinked by chelating the carboxylate groups with the cations and then forming salt bridges.⁶ However, GICs have some disadvantages, such as inferior mechanical properties brittleness and low abrasion resistance compared to composites, and their usage is limited in sealing, luting, and primary teeth restoration. Many studies have been made to overcome drawbacks to widen their usage. The strength of the GICs is influenced by

both the type of glass powder and the chemical composition of the polymer. According to many studies,^{7,8} it is shown that not all the carboxyl groups of poly(acrylic acid) (PAA) are converted to carboxylate groups during the reaction. Because of the very close attachment of the carboxylic acid groups to the polymeric backbone, a very rigid matrix is formed, which causes steric hindrance. In fact, very few salt-bridges are formed in view of steric requirements.

Using PAA alone to formulate glass-ionomers is unstable in aqueous solutions. As the molecular weights increase, the polymer solution forms a gel because of the strong intermolecular hydrogen bonds. Conventionally, itaconic or maleic acid was added into the polymer backbone to provide disorder, forming stable aqueous solutions at high concentration. Many efforts have been made to solve this problem, such as *N*-vinylpyrrolidone and amino acid derivatives used as spacer to hinder the close attachment of carboxylic acid groups, and then formed more Al³⁺ di- and tricarboxylate salt-bridges in the set cement.^{7,9–12} The results showed an improvement in the mechanical strength of GICs.

The glass-ionomers setting reaction happens in aqueous solutions. With the help of water, the H⁺ from the acid penetrates into the surface layers of the glass particles. It is known that the hardening and maturation process in glass ionomers is a diffusion-controlled process. The water plays an essential and indispensable role during the reaction. Regarding the

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spacer of the polymer backbone, it is necessary to choose a hydrophilic moiety as well as flexible to make more carboxylic acid groups available in the setting process. According to clinical data, a normal oral pH value is 6.8; neither higher nor lower pH value of restorative material is good to maintain a healthy oral environment. At the same time, low pH value might cause pulp allergy,¹³ and so it is reasonable to design more biocompatible and less irritated GICs.

In this study, a glycidyl methacrylate (GMA) diethanolamine derivative was synthesized as a spacer and used to prepare a polymer backbone through free radical polymerization, maintaining water solubility (Wsl) as well as exploring its impact on the performance of GICs. In addition, regarding the presence of less carboxylic acid and more hydroxyl groups, there might be more probability of salt-bridge forming as well as crosslinkage, which resulted in stronger final cement. FTIR and NMR were used to identify the structure of the polymer. The effect of the derivative on mechanical strengths and working properties of GICs were studied. Fuji II GIC was considered as the control group in this study.

MATERIALS AND METHODS

Materials

All the chemicals used in the experiments were of analytical grade. GMA and itaconic acid (IA) were used as received from Shanghai Aladdin Reagent Company. Acrylic acid (AA), diethanolamine (DEA), tartaric acid, potassium peroxydisulfate ($K_2S_2O_8$), dichloromethane, and isopropyl alcohol were used as received from Beijing Chemistry Company without further purification. The glass powders and liquid used in the experiments were of commercial grade and from Fuji II (GC International, Suzhou, China).

Methods

Synthesis of GMA diethanolamine

Glycidyl methacrylate diethanolamine (GMADEA) was synthesized by using modified ring-open reaction, as described previously in a US patent.¹⁴ Briefly, 40 g GMA was put into 250-mL three-necked flask equipped with a thermometer, a dropping funnel, and a mechanical stirrer. The flask was heated to a temperature of 30°C while 30 g DEA was added drop wise into the solution via a dropping funnel for about 1 h. The reaction mixture was stirred at 50°C for 4 h monitored with FTIR (Nicolet Spectra 5700 spectrometer, Nicolet Instrument, Thermo Company, Madison), until the epoxy peak at

910 cm^{-1} disappeared. The crude product was diluted in dichloromethane and extracted with distilled water three times, and then the distilled water residual part was purified by distillation under reduced pressure to obtain pure GMADEA. The yield was about 30%. The final products were identified by using both FTIR and 1H -NMR (Bruker AV 600 spectrometer, Bruker, Rheinstetten, Germany).

Poly(AA-IA-co-GMADEA) synthesis

The polymers composing acrylic acid (AA), itaconic acid (IA), and DEAGMA were synthesized by using a free-radical polymerization. A mixture of AA, IA, DEAGMA, and distilled water was added dropwise to a four-necked flask containing $K_2S_2O_8$ and distilled water. The concentration of the solution was about 25%, the molar feed ratio for the polymers was 8 : 2 : 1 (AA : IA : GMADEA), and polymers with different M_w were prepared by changing the amount of initiator and adding isopropyl alcohol. The solution was stirred with a mechanical stirrer and heated continuously up to 90°C proceeding for 16 h with continuous stirring under the blanket of nitrogen. Then, the heating was switched off and the polymer solution was dialyzed for 2 days following by freeze-dried.

The schematic illustration for the polymer synthesis is shown in Figure 1. The molecular weight of the polyacid was determined by gel permeation chromatography (GPC). GPC was performed by using Waters 1515 (Waters, USA) in conjunction with Waters Ultrahydrogel 250, 500, and 1000 columns. The mobile phase consisted of disodium hydrogen phosphate, potassium dihydrogen phosphate, and sodium azide. A flow rate of 0.8 mL/min was used. Polypropylene sulfonate was used as standards for calibration.

Formulation of GMADEA containing GIC samples

Specimen preparation for strength tests. The polymer was dissolved in distilled water to form the liquid part of GIC system. Fuji II glass powder was used to formulate the cements with a powder/liquid (P/L) ratio of 2.7 unless specified. Samples were prepared at room temperature in accordance with the manufacturer's instructions. For the compressive strength (CS) test, samples were prepared by using polytetrafluoroethylene (PTFE) cylindrical-shaped molds, 10 mm in diameter by 10 mm in length for CS tests, and 10 mm in diameter by 5 mm in length for the diametral tensile strength (DTS) tests. The molds were filled with the material and covered with glass slides, flattened, and gently pressed by hand to remove air bubbles from the uncured cement paste. The samples were removed from the molds after

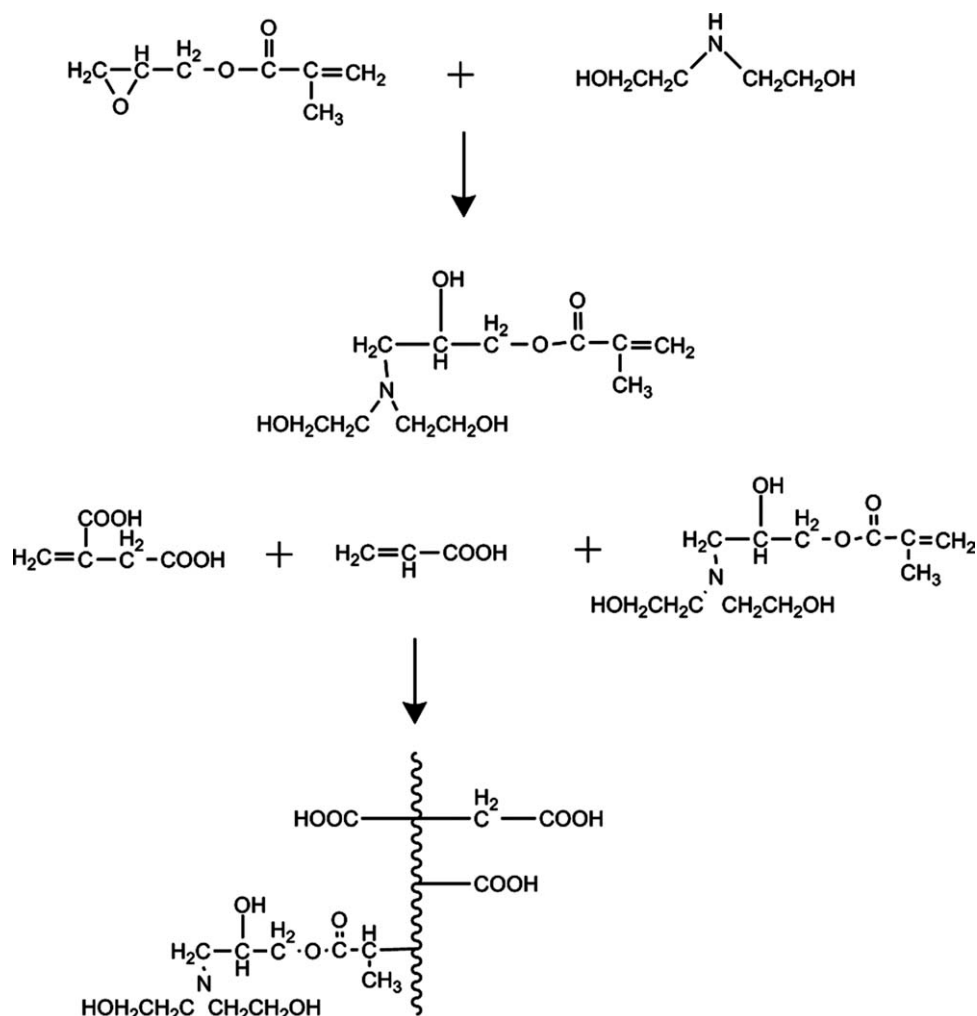


Figure 1 Synthesis process of [poly(AA-IA-GMADEA)].

30 min and conditioned in distilled water at 37°C for 24 h unless specified. A minimum of five samples were prepared for each test.

Strength measurements. Testing of specimens was performed on screw-driven mechanical tester (DOCER WDW-10, Docer Testing Mechanical Co., Jinan, China), with a crosshead speed of 1 mm/min for CS and DTS measurements. CS was calculated by using the equation of $CS = P/\pi r^2$, where P is the load at fracture and r is the radius of the cylinder. DTS was determined according to the equation

$$DTS = 2P/\pi dt,$$

where t is the thickness of the specimen.

Working and setting time. The working and setting times were determined according to the method described by GB 0271-1995 standards for the dental water-based cements. A small amount of the cement was mixed for 30 s and then placed into the PTFE mold to set. After finished mixing for 90 s, put a 300 g pressure head with 1 mm diameter onto the

cement surface carefully, repeated until no indentation could be formed. The time from initially mixing to forming no indentation was taken as the working and setting time. The values reported were the average of three determinations.

Scanning electron microscopy. The fracture surface of the selected specimen was observed at an accelerating voltage of 20 kV using a scanning electron microscope (Hitachi S-4700, Hitachi, Tokyo, Japan). The specimens were vacuumed and sputter-coated with gold.

Water sorption and solubility. The specimens with 15 mm in diameter and 2 mm in thickness were stored in vacuum drying oven to reach constant weight (m_1). Then, the specimens were immersed in water and various pH values buffer solutions and maintained at 37°C for different days. After this time, samples were removed, blotted to remove surface water, dried in air for 30 s, and weighed. The result was recorded as m_2 . Then, the specimens were placed in the vacuum drying oven again until a final constant mass was obtained (m_3). The

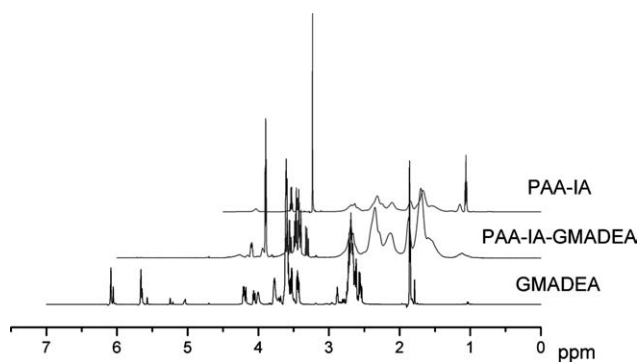


Figure 2 $^1\text{H-NMR}$ spectra of synthesized monomer and polymers.

specimen volumes (V) were also measured. Three specimens were tested to obtain a mean value for each material or formulation.

To calculate the water sorption (w_{sp}) and solubility (w_{sl}), the following equations were used:

$$w_{\text{sp}} = \frac{m_2 - m_3}{V}$$

$$w_{\text{sl}} = \frac{m_1 - m_3}{V}$$

pH value and surface microhardness measurement. pH was measured after the specimen was immersed in various buffer solutions for different times. The values were collected with a standard pH electrode (Hanna pH213, Hanna instruments Corp., Beijing). A vicker's diamond indenter was used in a standard microhardness tester (leco-DM-400, Leco Corp., USA) for specimen indentation. A load of 200 g applied for 20 s was used to make indentations of each group. Each sample was subjected to six indentations at randomly selected areas. The diagonal length impressions were measured, and the hardness number (Hv) was calculated by computer automatically.

Statistical analysis

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

RESULTS AND DISCUSSION

In this study, high hydrophilic and low-carboxyl concentration diethanolamine-derivative poly(carboxylic acid)s were synthesized and used as GIC liquid part. The polymers synthesized via conventional free radical polymerization showed a higher microhardness and lower W_{sl} compared to Fuji II cement, which provided an opportunity for us to further

formulate the cement with relatively high molecular weight to enhance mechanical strengths and biocompatibility. Because more hydroxyls have been incorporated into the synthesized polymer, the W_{sp} of the GICs increased that might exert pressure on the restoration.¹⁵

Several formulation parameters, which affected the application of the experimental GICs, were investigated, such as the functional group of the modified polymer, P/L and P/W ratios, molecular weight of the polymer (M_w), aging of the cement in water, and the role of adding tartaric acid into the formulation.

Characterization and mechanical properties

The chemical structure of GMADEA was shown in Figure 1 and had been confirmed by $^1\text{H-NMR}$ and FTIR spectrum.

FTIR (KBr, cm^{-1}) for GMADEA: 3336 cm^{-1} ($-\text{OH}$), 1714 cm^{-1} ($\text{C}=\text{O}$), 1630 cm^{-1} ($=\text{CH}_2$), and 880 cm^{-1} ($\text{C}=\text{C}$); $^1\text{H-NMR}$ for GMADEA (D_2O , δ , ppm): 6.08 (1H), 5.66 (1H), 4.00, 4.05, 4.21 (3H), 3.77 (2H), 3.53 (4H), 2.69, 2.88 (6H), and 1.85 (3H); FTIR (KBr, cm^{-1}) for the polymer: 3092 cm^{-1} ($-\text{OH}$) and 1722 cm^{-1} ($\text{C}=\text{O}$); $^1\text{H-NMR}$ (DMSO , δ , ppm) for the polymer: the polymer exhibited typical chemical shifts at around 3.5 ppm and 2.5 ppm for methylene brought by GMADEA. Besides, two typical carbon–carbon double-bonds peaks at 5.5 and 6 ppm were disappeared because of the polymerization.

As could be seen from Figure 2, GMADEA had carbon–carbon double bonds before polymerization (5.6 and 6.1 ppm), after copolymerized with PAA and IA, the carbon–carbon double bonds disappeared completely, which meant that the polymerization occurred. GMADEA exhibited typical chemical shifts at around 2 ppm for methyl. From Table I, it could be found that as the concentration of potassium peroxydisulfate increased from 0.6 to 2 wt %, the molecular

TABLE I
The Composition of GICs Used in This Study

Sample code	P/W	$\text{K}_2\text{S}_2\text{O}_8$ (wt %)	P/L	M_n	M_w/M_n
Fuji II	1 : 1	N/A	2.7 : 1	23,000	1.52
EGIC A	32 : 68	0.6	2.7 : 1	121,000	1.01
EGIC B	1 : 1	1.0	2.7 : 1	57,000	1.22
EGIC C	1 : 1	1.5	2.7 : 1	74,000	1.14
EGIC D	1 : 1	2.0	2.7 : 1	60,000	1.20
EGIC E	1 : 1	2.0	2.7 : 1	30,600	1.43
				(5% isopropyl alcohol)	
EGIC F	1 : 1	2.0	2.0 : 1	60,000	1.20
EGIC G	1 : 1	2.0	1.5 : 1	60,000	1.2
EGIC H	32 : 68	2.0	2.7 : 1	60,000	1.2
EGIC I	32 : 68	1.5	2.7 : 1	74,000	1.14

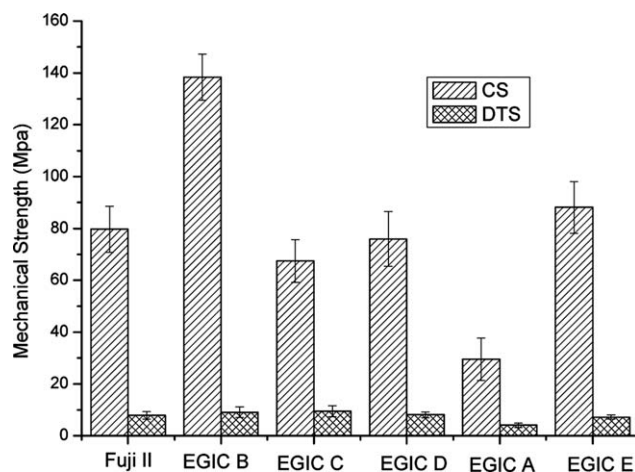


Figure 3 The mechanical strength of Fuji II GIC and experimental GICs.

weight decreased from 121,000 to 60,000 correspondingly. Because of the high viscosity of the large molecular weight, it is difficult to add adequate amount of glass powder into the liquid. The synthesized polyacid initiated by 2% initiator was chosen during the following measurement except mentioned. The polydispersity index of Fuji II was 1.52, which was higher than experimental liquid (about 1.20).

The Fuji II cements were made according to manufacturer recommended, and the experimental cements were made by using the liquid component prepared from the above polymer and then mixing the powder of Fuji II. The powder and liquid ratio (P/L) was 2.7 : 1 by mass, and the polymer and water ratio (P/W) were 50 : 50 by mass except mentioned.

The mechanical strength of Fuji II GIC and experimental GIC after 24 h immersing in distilled water was shown in Figure 3. There was significant difference in CS between Fuji II and EGIC B; the CS for the latter one was about 0.75 times higher than the former. Among other formulations that had the same concentration as EGIC B, there were no statistical differences ($P > 0.05$). When decreasing the polymer concentration from 50 to 30%, both the CS and DTS reduced to less than half of its original results. The formulation added chain transfer agents showed comparable strength with other groups at the same concentration.

The Fuji II, EGIC C, and EGIC D were immersed in distilled water for 18 days, followed by DTS determinations. As shown in Figure 4, only the Fuji II formulation showed an increase from the 1st day to the 7th day and then slightly decreased till the 18th day. On the contrary, the experimental formulations decreased slowly to a constant value at the 7th day and then kept unchanged till the 18th day. We could also see that as the molecular weight increased, the DTS value increased proportionately.

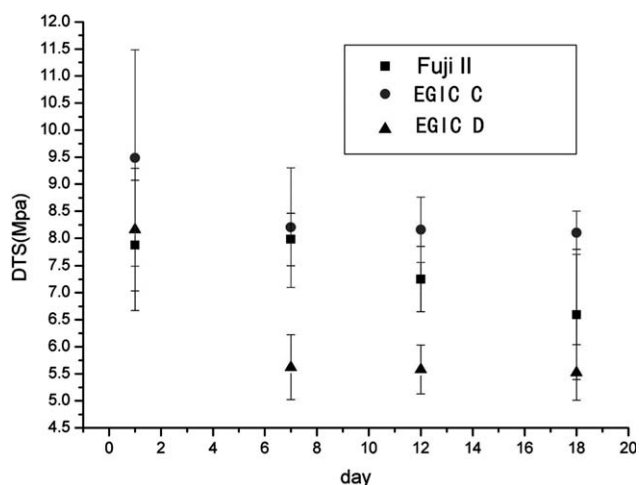


Figure 4 Effect of aging time on DTS.

Table II listed a series of factors that influenced the DTS of GIC. The factors considered were the P/W ratio, the P/L ratio, and the tartaric acid. Commonly, higher content of the polymer leads to higher strengths. With the increase of polymer content from 32 to 50%, the DTS improved from 4.4 to 8.1 MPa. The DTS also increased with the increase of powder/liquid ratio slowly. On the other hand, adding tartaric acid to the formulation could slightly increase the DTS, but there was no statistically significant difference ($P > 0.05$). As the polymer content and the P/L ratio increased, the cements became more difficult to mix.

Effect of the functional group

In this modification of the polyacid, hydroxyl and amino groups were incorporated into the polymer chain, which would result in more hydrophilic and weaker acidic polymer solution. Low pH value could lead to pulp stimulus and consequently reduce the biocompatibility.¹⁶ The data in Table III were the pH, and the Vicker's microhardness changes of the GICs immersed in two different buffer solutions for a series of time. The

TABLE II
Effect of the GIC Formulations on DTS

Formulations	DTS (MPa; SD)
Effect of P/W ratio	
EGIC D	8.16 (1.14)
EGIC H	4.43 (1.12)
Effect of P/L ratio	
EGIC G	5.35 (1.93)
EGIC F	6.03 (1.04)
EGIC D	8.16 (1.14)
Effect of tartaric acid	
EGIC H + 5 wt % tartaric acid	4.65 (0.25)

TABLE III
Vickers Microhardness (HV) and pH Values of Experimental GIC and Fuji II

Formulations	HV (SD)	Immersed in pH 7.12 solution for 7 days			Immersed in pH 4.2 solution for 7 days		
		pH value	Wsp ($\mu\text{g}/\text{mm}^3$)	Wsl ($\mu\text{g}/\text{mm}^3$)	pH value	Wsp ($\mu\text{g}/\text{mm}^3$)	Wsl ($\mu\text{g}/\text{mm}^3$)
Fuji II	102.3 (8.9)	6.75	125.10	50.21	4.27	55.00	50.61
EGIC D	179.2 (15.7)	7.32	182.21	55.75	4.51	154.11	37.52

experimental GICs had much higher microhardness than Fuji II. After 7 days immersion, the pH value of the experimental GICs increased both in the neutral and acidic buffers. On the contrary, the pH value of commercial Fuji II only increased in the acidic buffer. Considering the Wsp, the Fuji II showed better Wsp resistance than the experimental GIC, but the Wsl in the acidic buffer was not as well as the experimental GIC. From Table III, the results showed that the Wsp and Wsl for both Fuji II and experimental cements decreased when immersed in acid buffer solution. The pH value of the experimental cements was higher than the Fuji II cement throughout the measurement period, which might be the lower amount of carboxyl groups and a part of amino group in the polymer. Generally speaking, hydrophobic surfaces are more protein adsorbent than hydrophilic surfaces.¹⁷ Besides, it could be seen that the experimental cement exhibited higher hydrophilic than Fuji II, thus might provide better biocompatibility than the Fuji II one.

The microhardness can be defined as the resistance of a material to indentation. Vicker's microhardness of experimental cement was significantly higher than the Fuji II cement while their mechanical strengths were no statistic difference ($P > 0.05$).

Meanwhile, incorporating hydroxyl groups might reduce the mechanical strength and increase the viscosity. The reason for that was, on one hand,

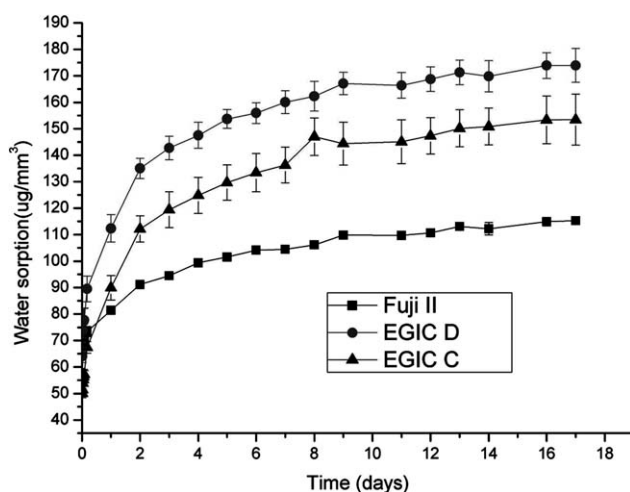


Figure 5 Water sorption of the experimental GICs and Fuji II.

hydroxyl groups could absorb water and serve as a hydrogel, which led to a strength reduction; on the other hand, they could also make a contribution to hydrogen bond formation, which resulted in an increase of viscosity.¹⁸

Wsp and Wsl were recorded at different periods of time during 18 days till reached equilibrium. Results were shown in Figure 5 and Table IV. The results indicated that the commercial Fuji II GIC had much lower Wsp than the experimental GIC, with equilibrium value of $110 \mu\text{g}/\text{mm}^3$, which was half of the experimental GIC. The results also showed that the Wsp increased as the initiator content increased. But the experimental GIC had lower Wsl than the Fuji II GIC and different initiator contents of the experimental GIC impacted on the Wsl greatly. After 18 days immersion (Fig. 5), Wsp for experimental cements was much higher than the Fuji II. However, the Wsl was much lower than latter one. It also showed that EGIC C had lower weight loss than EGIC D. We speculated that the high molecular weight of the experimental polymer formed a tangled network structure, which hindered the outward diffusion of small molecules. From mechanical test results (Fig. 4), the high Wsp did influence the initial mechanical properties (DTS) of the cements.

Effect of molecular weight and tartaric acid

By varying the ratio of initiator concentration and the content of tartaric acid, the working and setting time were listed in Table V. It was observed that the setting and working time of the experimental cements showed an increase from 14.8 to 18.2 min with the decrease of initiator concentration from 2 to 0.6 wt %. It is meant that as the molecular weight increased, the working and setting time increased coordinately. In free radical polymerization, the molecular weight of the polymer increased with the decrease of initiator content. A number of factors

TABLE IV
Equilibrium Water Sorption (W_{sp}) and Weight Loss (W_{sl}) of the Experimental GICs and Fuji II

GIC formulation	Wsp ($\mu\text{g}/\text{mm}^3$)	Wsl ($\mu\text{g}/\text{mm}^3$)
Fuji II	115.24	59.45
EGIC C	153.46	42.04
EGIC D	173.93	56.90

TABLE V
Working and Setting Time of Different Formulations

Formulations	Fuji II	EGIC H	EGIC A	EGIC H 5 wt % TA	EGIC I 5 wt % TA
Time (min)	7.78 ± 0.1	14.83 ± 0.1	18.25 ± 0.1	7.50 ± 0.1	12.12 ± 0.1

TA means tartaric acid.

influenced the speed of the setting reaction and the final strength of the GIC. Among them, the molecular weight (M_w) played an essential role.¹⁹ Through changing the initiator concentration from 0.6 to 2 wt % and adding chain transfer agent, we changed the M_w from 121,000 to 30,600. The mechanical strength showed (Fig. 3) that only 1 wt % initiated 50% solid content polymer had higher CS than other groups, but DTS of all groups with the same solid content had no statistic difference ($P > 0.05$). According to other study,²⁰ increasing the M_w of polymer would not always result in increased CS. Because the polymer viscosity was increased with increasing the M_w , this increase in viscosity would make the powder mixing inconvenience and the acid-base reaction immaturity. For each polymer M_w , there was an optimum concentration that would obtain the maximum mechanical properties. Meanwhile, increasing the polydispersity index could enhance the final cements' strength to a certain extent. It might be concluded that low molecular weight improved the mixing properties of the cement, and the polymer chains had more possibility to be attacked by ions leaked from glass powder, finally formed homogenous cement. At the same

time, too low M_w of the polymer in the matrix would propagate more microcracks after setting, and so it was reasonable to design polymers with a higher polydispersity index, maintaining the homogenous in the matrix as well as decreasing microcracks and bettering the handling ability.

The molecular weight had effect on working and setting time (Table V). Compared to Fuji II GIC, experimental cements with higher molecular weight had much longer working and setting time, which was owing to the less number of carboxylic acid present in the experimental cements exhibited a retarding of the reaction with the basic glass in comparison with the Fuji II formulation. Besides, high molecular weights of the polymers that might have detrimental effects on the setting times have reported in other studies.²¹

Scanning electron micrographs of the fracture surface of the GIC were shown in Figure 6. Smooth and homogeneous fracture surface was observed for high-initiator content GIC. From pictures a–c, it could be found that the higher the molecular weight of polymer, the tougher the fracture surface with less particles exposed. Seen from Figure 6, the cement with higher molecular weight polymer

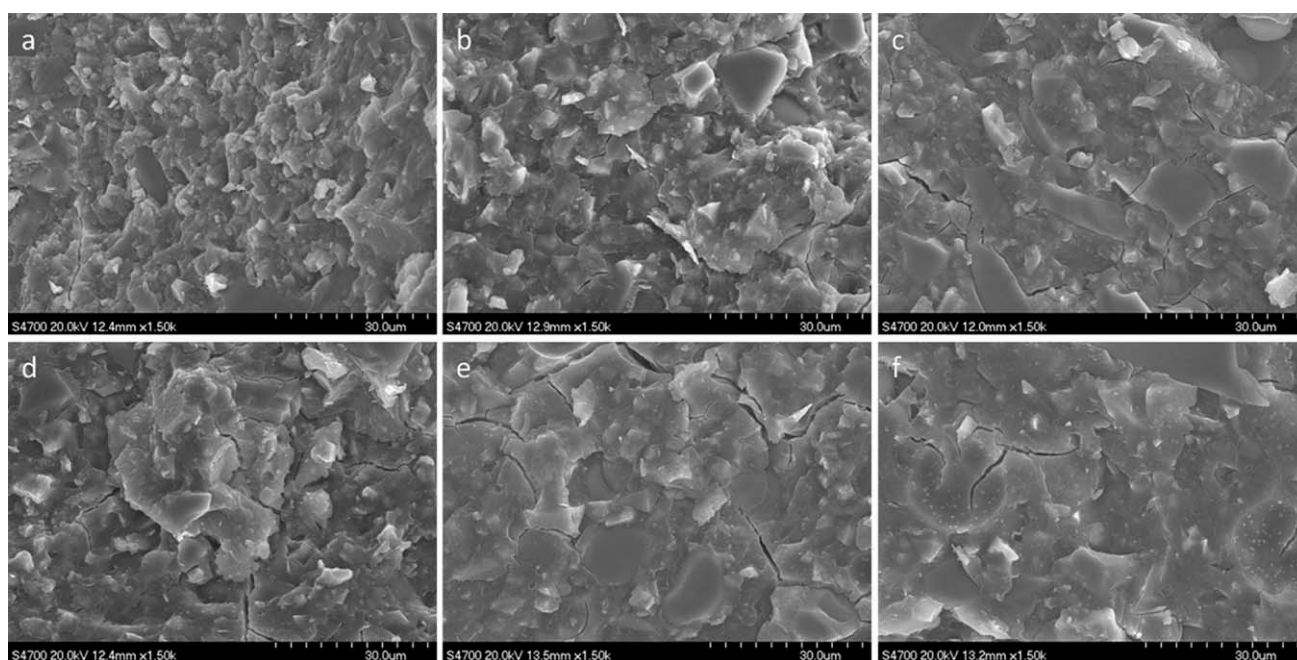


Figure 6 Scanning electron micrographs of fracture surfaces: (a) EGIC B (b, d), EGIC D (c), Fuji II (e), EGIC F, and (f) EGIC G.

[Fig. 6(a)] exhibited much rougher fracture surface with less particles exposed, compared to those with lower molecular weight polymer [Fig. 6(b)]. More microcracks and less structural integrity were observed for the Fuji II cements. Because the low-molecular weight polymer lacked the toughen ability compared to the experiment cement. Some cement has been found to be sensitive to early moisture and desiccate.¹⁹ Too high moisture would influence the setting reaction thus reduce the strength, and desiccation can propagate microcracks making a fragile material.

The results also showed that adding the tartaric acid decreased the setting and working time dramatically. Adding 5 wt % of tartaric acid could make the setting and working time of experimental cements in the range of commercial formulation (about 7.5 min) and increase the concentration of tartaric acid would decrease the working and setting time accordingly. The presence of tartaric acid endowed the reaction with more free and available carboxyl group, consequently higher degrees of salt bridge formation in a very short time. Adding 5% tartaric acid could significantly reduce the working and setting time from 14.8 to 7.5 min (Table V). Nevertheless, tartaric acid had little effect on mechanical strength (Table II). It might be predicted that more small-molecule salt-bridges could be easily hydrolyzed by water, and more microcracks were presented in setting sample thus deteriorated mechanical strength.

Effect of polymer/water and powder/liquid ratio

In Figure 6, pictures d–e exhibited the influence of powder/liquid (P/L) ratio on the fracture surface of GICs. The fracture surface with 1.5 P/L ratio was observed more homogeneous and smoother compared to 2.7 P/L ratio. The P/L and polymer/water (P/W) are important parameters in formulating GICs.²² In general, a higher P/L and P/W ratio results in higher mechanical strengths. In this study, both the CS and DTS significantly increased with the P/L and P/W ratio increase, which were agreed with other former results.²³ It was because that the more polymers in the formulation, the more carboxyl available to form salt-bridges. Although adding the powder content could enhance the strengths, the cement was difficult to mix because of the high viscosity and formed much brittle cement. Figure 6(d–f) demonstrated the effect of different P/L ratio. Increasing the polymer content, there were more free carboxyl groups to undergo reaction, and so the fracture surface exposed less unreacted glass particles, containing a smooth and homogenous surface. The edges of the glass particle appeared to be eroded

for the reason of degradation of the acid base reaction. Meanwhile, less particle-reinforced matrix materials had weaker strength. That is why the low P/L ratio demonstrated low CS and DTS. We noticed that the viscosity increased with the increase of P/W ratio and molecular weight. The carboxyl groups of the PAA and hydroxyl groups on GMADEA form intermolecular hydrogen bonds with water. Therefore, the more polymers in water, the stronger the hydrogen bonds formed, which led to a higher viscosity.¹⁸

Effect of aging time

In former studies, GICs increased their strengths with time in the presence of water owing to constant salt bridge formations.²⁴ From Figure 4, only Fuji II showed a 3.9% increase in DTS from 1 to 7 days, which was very different from the other two experimental cements. On the contrary, higher molecular weight GICs had comparably stronger DTS than lower molecular weight GICs, but the strength of them decreased by 12.6 and 31.2% on the 7th day. When immersing the cement for 18 days, the DTS of Fuji II decreased dramatically, while the experimental cement kept almost unchanged. The results for Fuji II were very consistent with those reported elsewhere.²⁵ The result indicated that the setting reaction lasted at least 7 days for Fuji II GIC, with the immersing time increase, the silicate hydrolysis prevail the reaction than the salt bridge forming,² and so the DTS dropped quickly. Concerning the experimental cements, first, DTS rapidly decreased in the first 7 days, which might be resulted from the W_{sp}, then it kept constant until the 18th day could be attributed to diffusion process of the silicate hydrolysis at first, and then high viscosity and strong hydrogen bond hindered silicate hydrolysis.

CONCLUSIONS

In this study, a diethanolamine derivative polymer was synthesized through free radical polymerization and used in GICs formulation. Incorporation of diethanolamine-derivative into the composition of the experimental polymer resulted in a harder and less brittle cement. In addition, the high hydrophilic and higher pH value might improve the biocompatibility of the final cement. The optimized experimental cement showed comparable CS and DTS to Fuji II GICs. Although after 7 days aging in water, the DTS of experimental cement decreased to 90% of its original data, it kept stable in the following 11 days. The microhardness and working and setting time of the cements were acceptable and meet the requirements of GICs.

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