Alternative Methacrylate-Tethering Methods for Resin-Modified Glass-Ionomer Cements

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ABSTRACT: We have explored two novel methacrylate-tethering methods for resin-modified glass-ionomer cements using 2-hydroxyethyl methacrylate (HEMA) and glycidyl methacrylate (GM) as a tethering agent. Both were compared with the published method using 2-isocyanatoethyl methacrylate (IEM). The tethering reactions were monitored using FTIR spectroscopy. It was found that IEM and HEMA tethering reactions were relatively fast compared with the GM-tethering, even though all three tethering reactions can be completed within 6 h. The cements composed of the IEM-tethered polymer showed the highest CS, DTS, and modulus, followed by the cements composed of the HEMA- and GM-tethered polymers, which was attributed to different chemical bonds introduced. It appears that both alternative tethering methods are quite equivalent to IEM-tethering based on the strength and reaction efficiency. The results suggest that HEMA and GM can be used as promising methacrylate-tethering alternatives for resin-modified glass-ionomer applications. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 869–875, 2009

Key words: tethering; resin-modified glass-ionomer cement; HEMA; GM; IEM; polyacids; FT-IR; strength

INTRODUCTION

Among dental restoratives, glass-ionomer cement (GIC) is one of the most attractive materials. Because of its unique properties, such as direct adhesion to tooth structure and base metals,[1,2] release of fluoride,[3] thermal compatibility with tooth enamel and dentin,[4] minimized microleakage at the tooth-enamel interface,[5] biological compatibility, and low cytotoxicity,[6,7] GIC has been widely used in restorative dentistry for more than 25 years.[1,8,9]

Conventional GIC (CGIC) is a water-based material that hardens following an acid-base reaction between calcium fluoroaluminosilicate glass powder and an aqueous solution of polyacid.[8] When polyacids in CGIC are modified with pendant methacrylate groups, the GIC not only undergoes an acid–base reaction but also participate in an *in situ* free-radical polymerization.[10] These modified cements are called resin-modified glass-ionomer cements (RMGICs).[10] RMGIC has gained popularity in the restorative dentistry community, as it demonstrates more attractive properties including reduced moisture sensitivity, higher early mechanical strength, easier handling clinically, extended working time, and improved mechanical strengths, as compared with CGIC.[11–13]

So far, three major types of RMGIC have been investigated, as described elsewhere.[14] Direct tethering methacrylate functional groups onto a polyacid backbone to form RMGIC has been one of the most promising methods up to date, due to its simplicity and strong network formation.[15,16] Currently the direct tethering is accomplished via a tethering agent, 2-isocyanatoethyl methacrylate (IEM).[15,16] However, due to high toxicity of IEM, the availability of IEM becomes limited and thus its cost becomes outrageously high. Therefore, there is a need to find the alternatives and reasonable ways to make the alternatives. In this article, we introduced two novel alternatives for methacrylate-tethering and described the ways to tether. This study may also provide valuable information for those who need molecular tethering of these reactive functional groups.

The objectives of this study were to synthesize and characterize the polyacids with pendent methacrylates using HEMA, GM, and IEM, to formulate them with reactive glass fillers and to evaluate the mechanical strengths of the formed cements.

EXPERIMENTAL

Materials

Acrylic acid (AA), itaconic acid (IA), 2-hydroxyethyl methacrylate (HEMA), glycidyl methacrylate (GM),

N,N'-dicyclohexylcarbodiimide (DCC), pyridine, N,N'-dimethylaniline, tetrahydrofuran (THF), diethyl ether (anhydrous), DL-camphoroquinone (CQ), and N,N'-dimethylaminoethyl methacrylate (DMAEMA) were used as received from Fisher Scientific Inc. (Pittsburgh, PA) without further purifications. 2,2'-Azobisisobutyronitrile (AIBN), dibutyltin dilaurate (DBTL), triphenylstibine (TPS), Hydroquinone (HQ), and 2-isocyanatoethyl methacrylate (IEM) were received from Aldrich Chemical Co. (Milwaukee, WI). GC Fuji II™ LC glass powders were supplied by GC America Inc. (Alsip, IL).

Synthesis and characterization
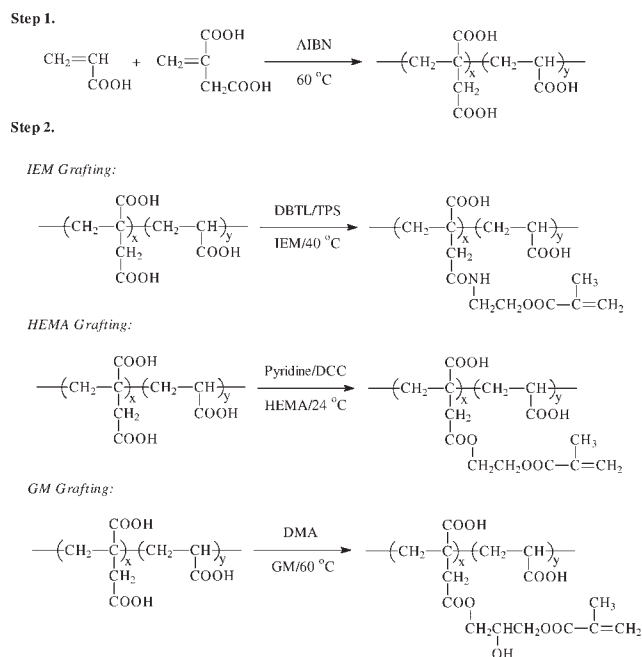
Synthesis

A two-step reaction was used for synthesis of the polymers with pendant methacrylates. In Step 1, the polymers consisting of acrylic acid (AA) and itaconic acid (IA) were synthesized using a free-radical polymerization.[15,17] Step 2 involved tethering of carbon–carbon double bonds onto the polyacid backbone. A chemical reaction scheme is shown in Figure 1.

For Step 1, briefly to a three-neck flask containing a solution of distilled THF, equipped with a thermometer, a nitrogen inlet and a magnetic stirrer, a mixture of AA, IA, and AIBN was added. The reaction was run under N_2 purging at 60°C for 24 h. The formed polymer solution was directly used for tethering of methacrylates. The molar feed ratio for the polymers was 4 : 1 (AA : IA).[17]

For Step 2, three different methacrylate-tethering experiments were conducted. For IEM tethering, the polymer solution was cooled down to 40°C, followed by a slow addition of a solution containing IEM, DBTL, TPS, HQ, and distilled THF. An additional 1 h was used to complete the reaction after the addition was finished. The IEM-tethered polymer was recovered by precipitation from diethyl ether, followed by drying in a vacuum oven at room temperature.[15,16]

For HEMA tethering, the polymer solution was cooled down to room temperature, followed by an addition of a solution containing HEMA, pyridine, HQ, and distilled THF. After the solution became clear, a mixture of DCC and THF was added. The reaction was kept at room temperature for 20 h. The HEMA-tethered polymer was recovered by filtration out the insoluble dicyclohexyl urea (DCHU) and precipitation from diethyl ether, followed by drying in a vacuum oven at room temperature.

For GM tethering, to the polymer solution a small amount of HQ was added, followed by a slow addition of a solution containing GM, pyridine, and distilled THF at 60°C. The reaction was kept at 60°C for 20 h. The GM-tethered polymer was recovered by

Figure 1 Schematic diagrams: (1) Synthesis of poly (AA-IA); (2) Tethering of IEM, HEMA, or GM onto the poly(AA-IA).

precipitation from diethyl ether, followed by drying in a vacuum oven at room temperature.

Characterization

The synthesized polyacid and polyacids with pendant methacrylates were characterized by Fourier transform-infrared (FTIR) and proton nuclear magnetic resonance (¹HNMR) spectroscopy. The FTIR spectra were obtained with a FTIR spectrophotometer (Mattson Research Series FT/IR 1000, Madison, WI). The ¹H NMR spectra were obtained on a FT-300 MHz Bruker ARX-300 spectrophotometer using deuterated methyl sulfoxide as solvent. The molecular weight of the polyacid was determined by gel permeation chromatography (GPC) with a Waters GPC unit (Model 410 differential refractometer, Waters Inc., Milford, MA), using standard GPC techniques and polystyrenes as standards. THF was used as solvent.

Preparation of specimens for strength tests

The cements were formulated with a two-component system (liquid and powder).[16,18] The liquid was formulated with the methacrylate-tethered polymer (50%, by weight), HEMA (25%), distilled water (25%), CQ (0.7%), and DMAEMA (1.4%). Fuji II LC glass powder was used to formulate the cements with a powder/liquid (P/L) ratio of 2.7/1.[18] Specimens were fabricated at room temperature according to the published protocol.[18] 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 diametral tensile strength (DTS) tests. Specimens were exposed to blue light (EXAKT 520 Blue Light Polymerization Unit, 9W/71, GmbH, Germany) for about 2 min, removed from the mold after 15 min in 100% humidity, and conditioned in distilled water at 37°C for 24 h before testing.

Strength measurements

Testing of specimens was performed on a screw-driven mechanical tester (QTest QT/10, MTS Systems Corp., Eden Prairie, MN), with a crosshead speed of 1 mm/min for both CS and DTS measurements. 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. DTS was determined from the relationship $DTS = 2P/\pi dt$, where P, the load at fracture; d, the diameter of the cylinder; and t, the thickness of the cylinder.

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. A level of $\alpha = 0.05$ was used for statistical significance.

RESULTS AND DISCUSSION

Synthesis and characterization

Characterization

The yields for three different methacrylate-tethered polymers were in the range of 82–95%. The molecular weights of the polyacid used for tethering were 16,933 g/mol for weight-average molecular weight (M_w) and 10,995 g/mol for number-average (M_n). Figure 2(a) shows the FT-IR spectra for poly(AA-IA), IEM-tethered poly(AA-IA), HEMA-tethered poly (AA-IA), and GM-tethered poly(AA-IA). Except for a strong peak at 1720 (cm^{-1}) for carbonyl group and a broad and strong peak at 3800–2500 for COOH, all methacrylate-tethered polymers exhibited significant peaks at 1636 and 950 cm^{-1} for carbon–carbon double bonds. Furthermore, two strong peaks at 1638 for amide I and at 1559 for amide II on the IEM-tethered polymer and a strong peak at 3452 for hydroxyl group on the GM-tethered polymer were observed in Figure 2(a). Figure 2(b) shows the ^{1}H NMR spectra for three methacrylate-tethered polymers and poly(AA-IA). All four spectra showed a chemical shift of carboxyl for COOH at around 12.25–12.10 ppm. Three methacrylate-tethered polymers showed
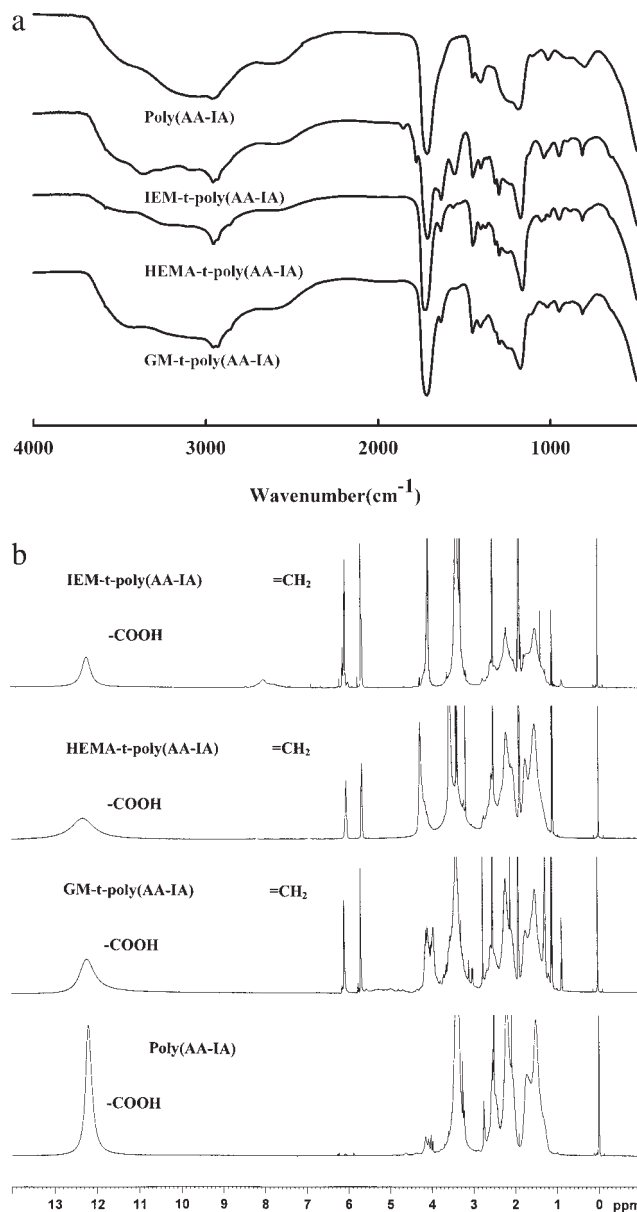

Figure 2 FTIR and ^{1}H NMR spectra: (a) FTIR spectra (from top to bottom): poly(AA-IA), IEM-tethered poly (AA-IA), HEMA-tethered poly(AA-IA), and GM-tethered poly(AA-IA); (b) ^{1}H NMR spectra (from top to bottom): IEM-tethered poly(AA-IA), HEMA-tethered poly(AA-IA), GM-tethered poly(AA-IA), and poly(AA-IA).

strong chemical shifts at around 5.6 and 6.1 for carbon–carbon double bonds. The IEM-tethered poly(AA-IA) also showed a weak chemical shift at 8.1 for amide bond, which was generated by the reaction between isocyanate group from IEM and carboxyl group from polyacid.

Comparison among three methacrylate-tethering reactions

The rates for three methacrylate-tethering reactions were evaluated using FTIR spectra. Figure 3 shows
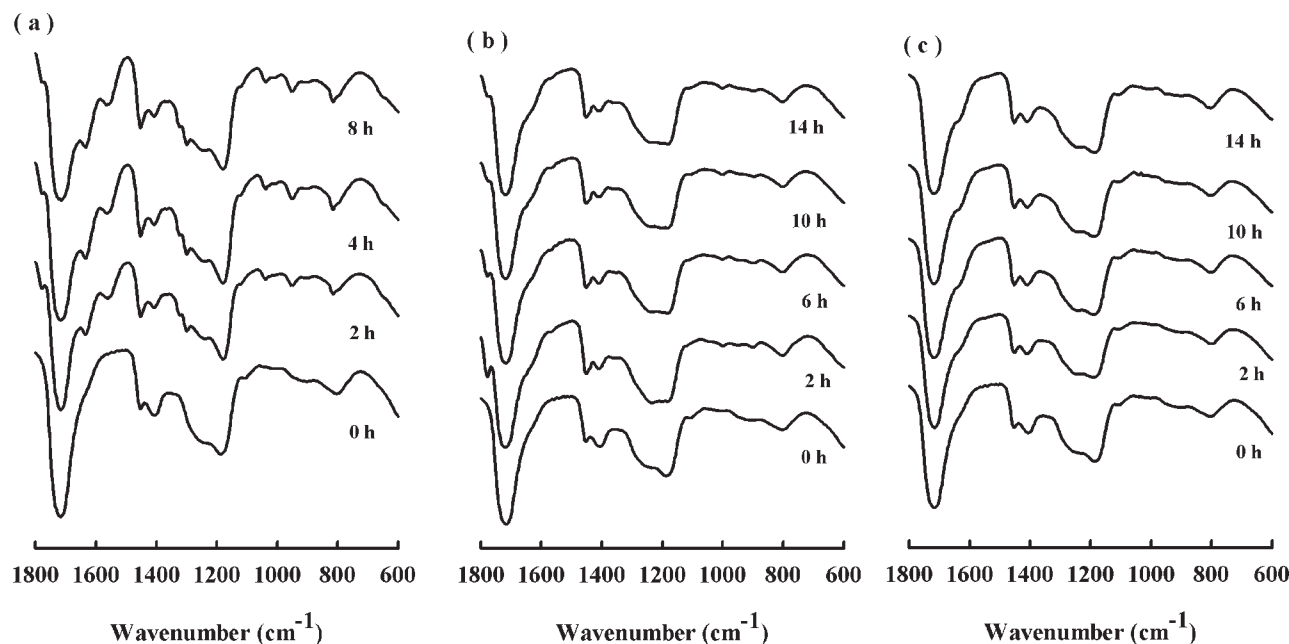
Figure 3 FTIR spectra: (a) conversion of IEM-tethering; (b) conversion of HEMA-tethering; (c) conversion of GM-tethering. Tethering ratio = 20%.

the dynamic spectra of FTIR as a function of reaction time. The reaction for IEM tethering is the reaction between carboxyl group from polyacid and isocyanate group from IEM. The reaction was very fast and it was completed within 2 h. As shown in Figure 3(a), there is nearly no difference in spectra among 2-, 4-, and 8-h reactions. The formation of new peaks at 1638 for amide I, 1559 for amide II, and 1636 as well as 950 for C=C, an increase in the existing peak at 1541 for CH$_3$, and a decrease in the existing peaks at 1404 as well as 1220–1310 for COOH indicate a successful tethering of IEM onto the polymer. During the experiment, we also noticed a significant amount of heat generation. Therefore, the reaction temperature for IEM tethering has to be well controlled (no greater than 40°C).[15,16,18]

HEMA tethering is the reaction between carboxyl group from polyacid and hydroxyl group from HEMA. It depends on how fast and how easily the generated water can be removed. With the help of pyridine (catalyst) and DCC (water scavenger), water can be removed fairly quickly accompanying the formation of insoluble DCHU. From Figure 3(b), it appears that the reaction was completed within 2 or 4 h. No significant changes in spectra were observed between 2, 6, 10 and 14 h. The formation of new peaks at 1636 and 950 for C=C, an increase in the existing peak at 1451 for CH$_3$ and a decrease in the existing peaks at 1404 and 1220–1310 for COOH indicate a successful tethering of HEMA onto the polymer. During the reaction, a significant amount of white DCHU precipitates were observed.

GM tethering is the reaction between carboxyl group from polyacid and epoxy group from GM. No byproduct is generated from this reaction. With the help of pyridine (catalyst), the epoxy group reacts with the carboxyl group, producing an ester with an extra pendant hydroxyl group formation. From Figure 3c, the reaction seems completed at 6 h. No significant changes in spectra were observed between 6, 10, and 14 h. The formation of new peaks at 1636 and 950 (not significant) for C=C, an increase in the existing peak at 1451 for CH$_3$, and a decrease in the existing peaks at 1404 and 1220–1310 for COOH indicate a successful tethering of GM onto the polymer.

Effect of tethering ratio on three different methacrylations was also evaluated using FTIR spectra and the results are shown in Figure 4. For IEM-tethering (Fig. 4a), with tethering ratio increasing, the peak strengths at 1638 for amide I, 1559 for amide II, 1636 as well as 950 for C=C (1636 and 950), and 1541 for CH$_3$ significantly increased but the peak strengths at 1404 and 1200–1310 for COOH decreased correspondingly. Similar trends were observed for both HEMA- and GM-tethering, as shown in Figure 4(b) and Figure 4(c), respectively.
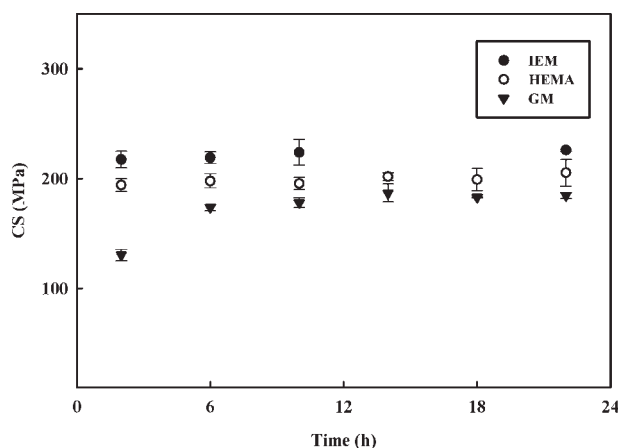
Strength comparison among the cements composed of three methacrylate-tethered polyacids

The methacrylate-tethered polymers were used to formulate resin-modified glass-ionomer cements with HEMA (comonomer), water, photo-initiation
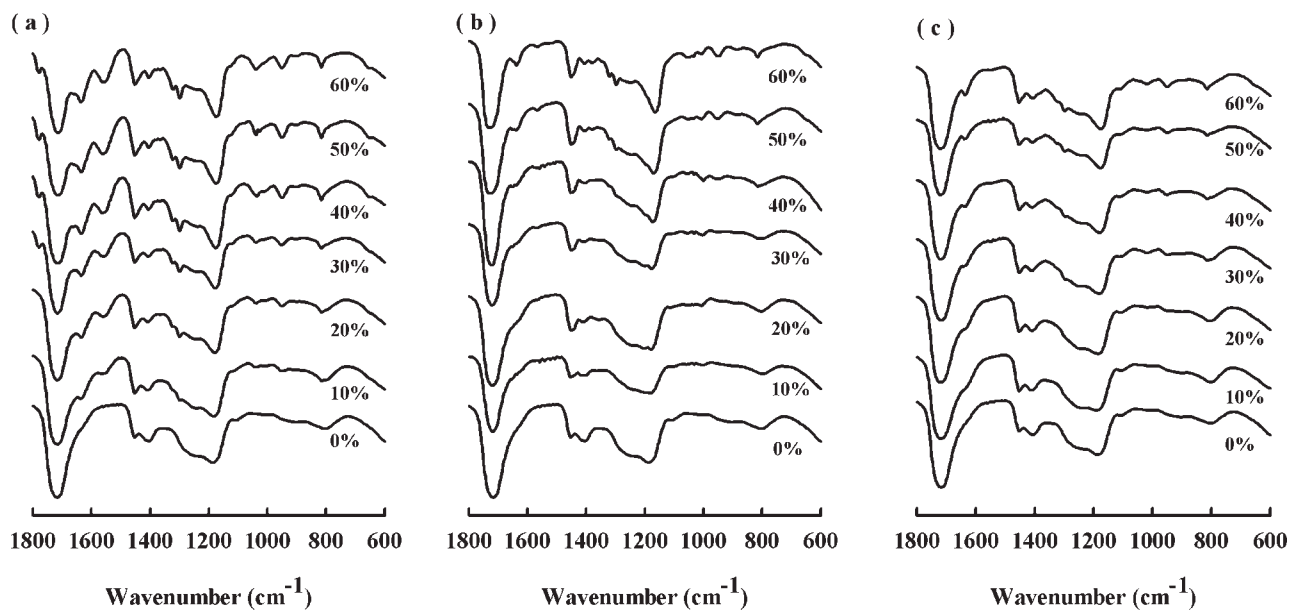
Figure 4 FT-IR spectra: (a) Effect of IEM tethering ratio; (b) Effect of HEMA-tethering ratio; (c) Effect of GM-tethering ratio. Reaction time = 20 h.
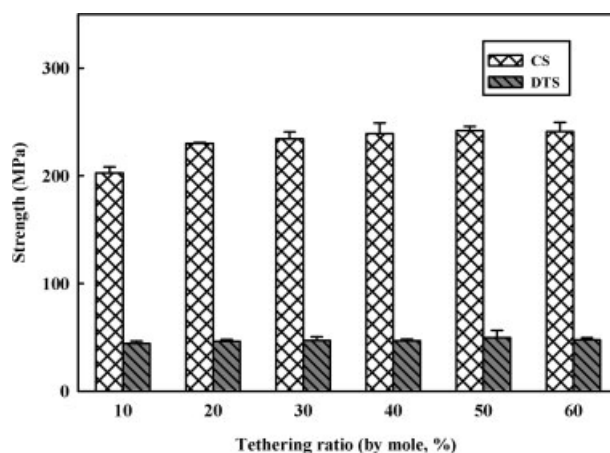
system, and reactive glass filler (Fuji II LC).[19] Both compressive (CS) and diametral tensile (DTS) strengths were used to evaluate the formed cements.[15–19] Figure 5 shows the CS changes of the cements composed of three methacrylate-tethered as a function of reaction time. The cement composed of the IEM-tethered polymer showed the highest CS, followed by the cement composed of the HEMA-tethered polymer. The cement composed of the GM-tethered polymer was the lowest in CS. Furthermore, the cements composed of both IEM- and HEMA-tethered polymers showed a steady CS starting from 2 h, indicating that the 2-h reaction time is probably

long enough for completion of both tethering. However, the cement composed of the GM-tethered polymer showed a lower CS at 2 h (130.4 MPa) and increased to 173.7 MPa at 6 h, indicating that 6 h may be the minimum reaction time required for a successful GM-tethering. This result is somehow consistent with that from FTIR spectra (Fig. 3b).

Figure 6 shows the effect of IEM-tethering ratio on CS and DTS of the cements. The strengths (MPa) were in the decreasing order: (CS) 50% > 60% > 40% > 30% > 20% > 10%, where no significant differences were found among 20%, 30%, 40%, 50 and 60% ($P > 0.05$); (DTS) 50% > 60% > 30% > 40% > 20% > 10%, where they were not significantly different from each other ($P > 0.05$). There were no
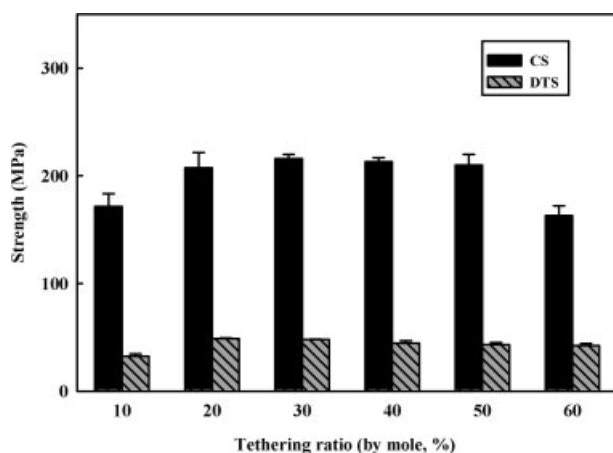

Figure 5 CS values of the formed cements verse the corresponding conversions of IEM, HEMA, and GM tethering: The tethering ratio = 20% (by mole) for all three cements; P/L ratio = 2.7; Polymer/HEMA/H_2O = 50 : 25 : 25; The specimens were conditioned in distilled water at 37°C for 24 h before testing.

Figure 6 Effect of IEM tethering ratio on CS and DTS: P/L ratio = 2.7; polymer/HEMA/H_2O = 50 : 25 : 25; The specimens were conditioned in distilled water at 37°C for 24 h before testing.
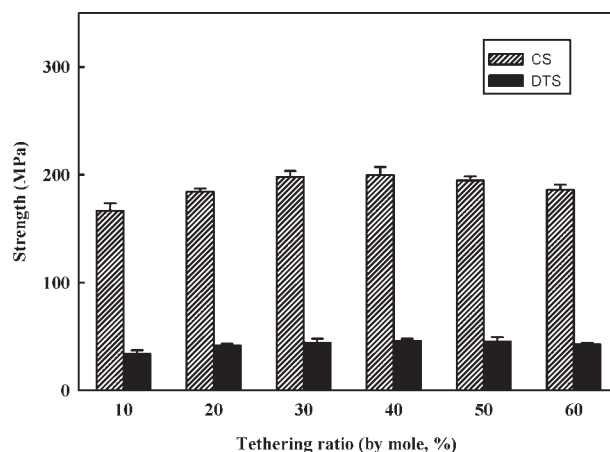
statistically significant differences in CS and DTS among the cements with different IEM-tethering ratio. It seems that the strong interchain hydrogen bonds from the amide linkage pendent on polymer chains (see Fig. 1) can offset the negative effect from the increased resin contents due to increased IEM-tethering

Figure 7 shows the effect of HEMA-tethering ratio on CS and DTS of the cements. The strengths (MPa) were in the decreasing order: (CS) 30% > 40% > 50% > 20% > 10% > 60%, where no significant differences were found between 10 and 60% and among 20%, 30%, 40 and 50% ($P > 0.05$); (DTS) 20% > 30% > 40% > 50% > 60% > 10%, where no significant differences were found among 20%, 30 and 40% and among 40%, 50%, and 60% ($P > 0.05$). It is obvious that the cement composed of 10% HEMA-tethering ratio showed the lowest CS (second to the lowest) and DTS (the lowest) values, which can be attributed to a lower tethering ratio. However, the cement composed of 60% HEMA-tethering ratio also showed very low CS (the lowest) and DTS (second to the lowest), which may be attributed to too much resin introduced. With increasing tethering ratio, the originally brittle cement became less and less brittle. It is known that CGIC is more brittle than RMGIC. That is why the strength reached the maximum value at 30 or 20% and then decreased.

Figure 8 shows the effect of GM-tethering ratio on CS and DTS of the cements. The strengths (MPa) were in the decreasing order: (CS) 40% > 30% > 50% > 60% > 20% > 10%, where no significant differences were found among 20%, 30%, 40%, 50%, and 60% ($P > 0.05$); (DTS) 40% > 50% > 30% > 60% > 20% > 10%, where no significant differences were found between 10 and 20% and among 20%, 30%, 40%, 50%, and 60% ($P > 0.05$). There appears a simi-
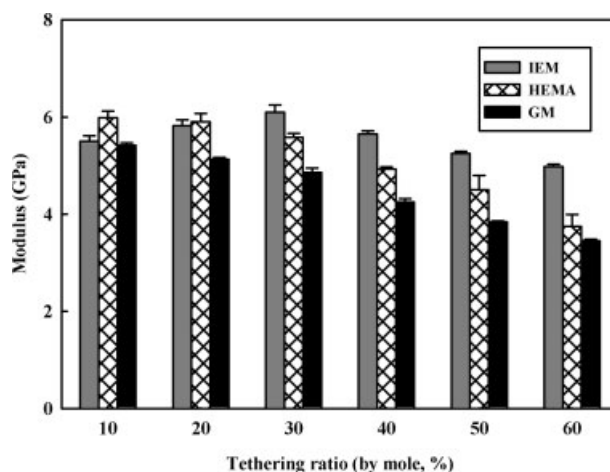

Figure 8 Effect of GM tethering ratio on CS and DTS: P/L ratio = 2.7; polymer/HEMA/H$_2$O = 50 : 25 : 25; The specimens were conditioned in distilled water at 37°C for 24 h before testing.

lar trend in CS and DTS to those for the cements composed of the HEMA-tethered polymers, i.e., increasing a tethering ratio increased CS and DTS. However, after reaching the maximum, the strength went down due to the increased resin contents.

Figure 9 shows the measured moduli for the cements composed of all three methacrylate-tethered polymers at different tethering ratios. First, with increasing tethering ratio, all the moduli showed a decrease trend, especially for the cements composed of HEMA- and GM-tethered polymers. The cement composed of the IEM-tethered polymer showed the maximum modulus at a tethered ratio of 30%. Second, the cements composed of the GM-tethered polymer showed the lowest moduli whereas the cements composed of the IEM-tethered polymer

Figure 7 Effect of HEMA tethering ratio on CS and DTS: P/L ratio = 2.7; polymer/HEMA/H$_2$O = 50 : 25 : 25; The specimens were conditioned in distilled water at 37°C for 24 h before testing.

Figure 9 Effect of tethering ratio on moduli of the IEM-, HEMA-, and GM-tethered poly(AA-IA) formed cements: P/L ratio = 2.7; polymer/HEMA/H$_2$O = 50 : 25 : 25; The specimens were conditioned in distilled water at 37°C for 24 h before testing.

showed the highest moduli. The reason can be explained as the fact that the IEM-tethered polymer can form strong hydrogen bonds provided by amides between the polymer chains (see Fig. 1). With increasing IEM-tethering, the number of amide bond increased and thus the number of hydrogen bond increased, leading to a modulus increase. The HEMA-tethered polymers can only form dipole–dipole interactions provided by esters between the polymer chains. It is known that dipole–dipole interaction is weaker than hydrogen bond. The GM-tethered polymers may partially provide hydrogen bonds provided by the extra hydroxyl groups (see Fig. 1) but meanwhile these pendant hydroxyl groups can absorb surrounding water (water often acts as a plasticizer), leading to a reduced strength. That is why the cements composed of the GM-tethered polymer showed lower CS, DTS, and modulus (Figs. 5, 8 and 9) as compared to both cements composed of the IEM-and HEMA-tethered polymers.

CONCLUSIONS

We have explored two novel methacrylate-tethering methods using HEMA and GM as a tethering agent for resin-modified glass-ionomer cements. Both IEM and HEMA tethering reactions were relatively fast as compared with GM-tethering, even though all three tethering reactions can be accomplished within 6 h. The cements composed of the IEM-tethered polymer showed the highest CS, DTS, and modulus, followed by the cements composed of the HEMA-and GM-tethered polymers. With increasing tethering ratio, the cement became less and less brittle and

thus the strength went down. It seems that both alternative tethering methods are quite equivalent to IEM-tethering based on the strengths and reaction efficiency. This study provides two valuable alternative tethering routes for improved resin-modified glass-ionomer restoratives.

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