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PREPARATION AND EVALUATION OF ACRYLIC ACID, ITACONIC ACID, AND N-METHACRYLOYLGLUTAMIC ACID COPOLYMERS FOR USE IN GLASS-IONOMER TYPE DENTAL RESTORATIVES

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Key Words: Polyelectrolytes, Acrylic Acid, Itaconic Acid, N-Methacryloylglutamic Acid, Copolymers, Glass Polyalkenoates, Glass-Ionomers, Dental Restoratives, Mechanical Properties

ABSTRACT

A series of copolymers containing various molar ratios of acrylic acid, itaconic acid and N-methacryloylglutamic acid were prepared in aqueous solution, using standard free-radical polymerization conditions. Specimens for mechanical property studies were prepared by mixing water solutions of the copolymers (50:50, wt:wt) with a commercial, calcium-fluoroaluminosilicate glass powder, with curing or hardening achieved by salt-bridge formation. The glass powder used in the formulation(s) was the same as that used in Fuji II (GC America) glass-ionomer. The working and setting times of the various formulations were evaluated. The compressive strength was used as the basic screening property to find the optimum molar ratio of the three monomers. The diametral tensile strength, flexural strength and Knoop sur-

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face hardness of the cured materials were also determined. All mechanical properties were measured after the specimens were conditioned in distilled water for 7 days at 37°C. Based on the compressive strength (CS), poly (AA-co-IA-co-MGA) with a monomers ratio of 8:1:1, respectively, showed the highest CS (269.9 MPa). The 8:1:1 copolymer with different molecular weights were also prepared to evaluate the effect of MW on the compressive strength. The optimum MW copolymer gave a glass-ionomer having the compressive strength improved by 30%, compared to Fuji II (293.9 MPa vs. 224.9 MPa). The same polymer solution was also mixed with glass powders used in other commercial glass-ionomers, i. e., Ketac-Molar (ESPE, Seefeld, Germany), α-Fil and α-Silver (DMG, Hamburg, Germany) to produce conventional glass-ionomers test specimens. The mechanical properties of these materials were also obtained and compared to the Fuji II, Ketac-Molar, α-Fil and α-Silver controls.

INTRODUCTION

Glass polyalkeonates (glass-ionomers) are inorganic-organic based dental composites/restoratives, exhibiting anticaries capability, due to fluoride release [1-3], good biocompatibility and/or low cytotoxicity [4], excellent adhesion to tooth structures, via the $Ca^{++}(CO_2^-)_2$ salt-bridge formation and hydrogen bonding [5, 6], as well as having a coefficient of thermal expansion (α) similar to the tooth structure [7, 8]. Even though they were introduced back in 1971 [9], glass-ionomer (GI) restoratives still suffer from having their modulus of elasticity too low or exhibiting brittle failure.

Copolymers currently used in conventional GIs are water soluble polyelectrolytes having carboxylic acid groups directly or very closely attached to the polymer backbone, such as poly(acrylic acid-co-itaconic acid) or poly(acrylic acid-co-maleic acid). Aqueous solutions of the copolymers mixed with basic glass powders, such as calcium fluoro-alumino-silicate (CaFAlSi), produce restoratives hardened by carboxylate salt-bridge formation, due to acid-base neutralization reactions. In the process of hardening, not all carboxylic acid groups are converted to carboxylate groups. When a certain number of carboxylic acid groups are ionized, the negative charge on the polymer chain has increased to such a degree that the remaining unionized carboxylic acid groups are not replaced easily by metal ions from the glass powders [10]. Also, when the density of the crosslinks increases to a certain level, diffusion of the metal ions decreases [11].

Believing that hindered salt-bridge formation, especially the limited formation of aluminum di- and tricarboxylates in the set cement, acts to prevent the modulus development, our research has been focused on finding ways to enhance salt-bridge formation in cured GIs. As part of our study, we have been looking at ways to tether carboxylic acid groups various distances off the copolymer backbone, which would reduce steric hindrance and facilitate salt-bridge formation. Our original hypothesis was that the latter arrangement would foster more Al-carboxylate salt-bridge formation, supported by a recent publication [12].

The preparation and use of amino acid modified, water-soluble acrylic acid copolymers, having the carboxylic acid groups tethered various distances off the copolymer backbone has been an ongoing study in our laboratory. Several N-acryloyl and N-methacryloyl substituted amino acids have been prepared and copolymerized with acrylic acid and itaconic acid to produce new polyelectrolytes, having various molar ratios of the three monomers in the backbone, different molecular weights, and different types of acid groups attached to the copolymer backbone [13-15]. Following up on these studies, the monomer N-methacryloylglutamic acid (MGA) was selected as the most economically attractive monomer to use for further study, since MGA could be prepared in good yield. Previously, we hypothesized that MGA could be particularly useful in the design of improved GIs, for both conventional (chemically cured) as well as visible light-cured (VLC) formulations. Preliminary work with the MGA monomer, to produce a poly(AA-co-IA-co-MGA) having a monomers ratio, respectively, of 7:3:3, showed our concept was valid [15,16]. For example, it was found that the 7:3:3 poly(AA-co-IA-co-MGA) material could significantly improve the mechanical properties of both conventional as well as VLC glass-ionomers [15, 16]. Given this result, we hypothesized that the 7:3:3 terpolymer and the molecular weight of the terpolymer used may not be optimum for conventional GIs. This led us to prepare a family of poly(AA-co-IA-co-MGA) materials (Tables 1-3) to see what monomers ratio in the copolymer backbone, as well as MW, would work best. To our surprise, we found that we did not need to incorporate a great amount of IA and MGA monomers into the copolymer backbone to achieve significantly improved mechanical properties, for formulation of both conventional and VLC glass-ionomer materials. In this paper we focus only on the use of MGA to mod-

TABLE 1. Molar Ratios, Working Times, Setting Times, and Viscosities of Fuji II and Experimental Copolymers

System	Molar Ratio AA-IA-MGA	WT (SD) min	ST (SD) min	Viscosity cP
Fuji II		3.0 (0.2)	3.5 (0.1)	540
A	1:1:1	7.1 (0.3)	9.2 (0.3)	680
B	6:1:1	4.5 (0.1)	6.5 (0.2)	1350
C	7:1:1	4.4 (0.2)	6.3 (0.3)	1410
D	7:1:3	4.4 (0.2)	6.5 (0.3)	1300
E	7:2:3	7.0 (0.3)	8.4 (0.4)	570
F	7:2:2	5.1 (0.1)	7.1 (0.4)	1420
G	7:3:3	7.2 (0.2)	10.0 (0.4)	910
H	8:1:1	5.4 (0.3)	7.3 (0.3)	1520
I	8:3:3	6.4 (0.4)	8.3 (0.3)	790
J	9:1:1	5.2 (0.3)	6.4 (0.2)	1750
K	10:1:1	5.0 (0.1)	7.0 (0.3)	1760

ify AA-IA copolymers for use in conventional GI system, with our results on MGA in preparation of VLC GIs to be reported later.

EXPERIMENTAL

Materials

Acrylic acid (AA), itaconic acid (IA), L-glutamic acid, potassium pesulfate ($K_2S_2O_8$), hydrochloric acid, anhydrous magnesium sulfate (Mg_2SO_4), sodium chloride, isopropanol, ethyl acetate and methanol were used as received from Aldrich Chemical Co. Methacryloyl chloride, also from Aldrich, was distilled prior to use. The CaFAlSi glass powders, used in the formulations were part of commercial glass-ionomer kits supplied by GC America (Fuji II), ESPE, Seefeld, Germany (Ketac-Molar), and DMG, Hamburg, Germany (α-Fil and α-Silver).

Characterization

The ^{1}H-NMR and ^{13}C-NMR spectra of the monomers and polymers were collected on a 300 MHz Bruker AM spectrometer, using deuterated water as solvent, with TMS as internal standard. FT-IR spectra were obtained on a MIDAC spectrophotometer. The monomer melting point was determined by differential

TABLE 2. Mechanical Properties of MGA Based Copolymers

Copolymer	CS (SD) MPa	DTS (SD) MPa	KHN (SD)
Fuji II	224.9 (25.8)	11.0 (0.5)	36.5 (1.4)
A	175.3 (16.5)	9.4 (0.5)	37.0 (2.1)
B	212.8 (19.0)	13.8 (.05)	40.5 (2.5)
C	232.4 (22.6)	15.7 (1.1)	35.8 (1.0)
D	188.8 (18.9)	10.2 (1.0)	35.2 (1.9)
E	177.5 (15.4)	9.7 (0.8)	28.3 (0.2)
F	164.0 (18.6)	8.6 (0.8)	42.8 (2.6)
G	208.7 (18.1)	11.4 (1.0)	41.2 (1.8)
H	269.9 (24.8)	14.1 (1.1)	36.7 (1.3)
I	197.1 (23.5)	9.4 (1.4)	37.7 (1.3)
J	136.2 (10.2)	13.3 (1.1)	36.8 (1.1)
K	101.9 (11.5)	14.8 (1.7)	44.3 (2.8)

scanning calorimetry (TA Instruments, DSC 910). Viscosities of the aqueous copolymer solutions (50:50, wt:wt) were measured on a cone and plate viscometer, using a Cap 2000 Viscometer (Brookfield Engineering Laboratories, Inc., Stoughton, MA), at 30°C.

Monomer Synthesis

N-Methacryloylglutamic Acid (MGA) Synthesis

Methacryloyl chloride (52.27 g, 0.5 mol) was added slowly over 1 hour to an ice-salt cooled and vigorously stirred solution of L-glutamic acid (73.57 g, 0.5 mol) and sodium hydroxide (60.00 g, 1.5 mol) in 150 ml of distilled water (17). After stirring at 0°C for an additional 1.5 hours, a solution of concentrated hydrochloric acid and water (1:1, v:v) was slowly added until pH~2 was

TABLE 3. Properties of Poly(AA-IA-MGA), 8:1:1, Copolymer Based on Various Viscosities

System	Initiator (%)	WT (SD) min.	ST (SD) min.	Vis (SD) cP	CS (SD) MPa	DTS (SD) MPa
Ha	4	5.4 (0.3)	7.3 (0.1)	1520	269.9 (24.8)	14.1 (1.1)
Hb	3	5.4 (0.2)	7.6 (0.3)	2960	287.1 (10.4)	18.8 (1.5)
Hc	2	5.3 (0.1)	7.5 (0.3)	3340	293.9 (8.4)	19.3 (1.6)
Hd	1	6.0 (.02)	8.1 (0.5)	6020	246.6 (11.0)	21.0 (1.5)

reached. The mixture was further stirred for 30 minutes and saturated with sodium chloride. After several extractions of the solution with warm ethyl acetate, the combined extracts were dried over anhydrous magnesium sulfate. The ethyl acetate solvent was removed under reduced pressure, giving a 75 g (70%) yield of crystalline monomer, m.p. 130-132°C. The MGA structure was confirmed by FT-IR and NMR (^{1}H and ^{13}C) [13]. For all polymerizations, MGA was recrystallized from ethyl acetate.

Polymer Synthesis

Terpolymer Synthesis (System H)

A mixture of potassium persulfate (0.20 g) in 20 ml of distilled water was stirred under a nitrogen sparge for 30 minutes to remove dissolved oxygen. A solution of acrylic acid (6.57 g, 91.2 mmol) and MGA (2.45 g, 11.4 mmol) in 2 ml of isopropanol and 10 ml of distilled water, along with a solution of $K_2S_2O_8$ (0.2 g) in 6 ml of distilled water and solid itaconic acid (1.48 g, 11.4 mmol) were each subdivided into 15 equal portions and added every 5 minutes to the polymerization solution, which was at 95^{o}C. The polymerization reaction was carried out for 6 hours and the terpolymer was isolated by a standard freeze drying technique, using Edwards High Vacuum International (Sussex, UK) equipment, similar to reported procedures [18]. With stirring, a concentrated methanol solution of the polymer was combined with a large excess of ethyl acetate to precipitate and obtain the purified terpolymer(s) in high yields, as white powders. The structure of the copolymers was confirmed by FT-IR and NMR (^{1}H and ^{13}C).

Test Methods

All terpolymers (Table 1) were dissolved in distilled water (50:50, wt:wt) to form the viscous solutions used in the formulation of GIs. The Fuji II glass powder was selected for blending with the terpolymer solutions, providing a control material/system to determine CS. The powder/liquid (P/L) ratio used in the experimental formulation was 2.7/1, the same as recommended for commercial Fuji II.

Compressive Strength and Diametral Tensile Strength

Six cylindrical test specimens (4 mm in diameter by 8 mm in length for CS and 4 mm in diameter by 2 mm in thickness for DTS), were prepared for each experimental and control material, using glass tubing with the help of a pressure fixture to remove air bubbles from the uncured paste. All samples were kept at 37°C in 100% relative humidity for 1 hour in the glass tubing. After removal from the glass tubing, the specimens were stored in distilled water at 37°C for 7 days. The CS of each material was determined by loading the flat ends of the specimen and the DTS by loading the sides of the specimens using an Instron universal testing machine (Model 4204, Instron Corp., Canton, MA, USA) at a crosshead speed of 0.5 mm/min (Table 2).

$$\mathrm{CS} = \mathrm{P}/\pi\mathrm{R}$$

$$\mathrm{DTS} = 2\mathrm{P}/\pi\mathrm{DT}$$

where P = the load at fracture, R = the radius of the sample cylinder, D = the diameter of the cylinder, and T = the thickness of the cylinder.

Flexural Strength

The FS test specimens (25 mm in length × 2 mm in width × 2 mm in depth) were prepared in a mold made from Durel plastic. Six test samples for each experimental and control material were made and left to set in a humidor for 15 minutes before being removed and stored in distilled water at 37°C for 7 days. The FS test was performed with the help of a three-point bending assembly using an Instron testing machine. Test specimens were placed between two horizontal, parallel knife edges placed 20 mm apart, followed by progressively applying an increasing load at a crosshead speed of 0.5 mm/min (Table 4).

TABLE 4. Properties of Poly(AA-IA-MGA), 8:1:1, Copolymer Hc, Formulated with Different Glass Powders

System	P/L Ratio	CS (SD) MPa	DTS (SD) MPa	FS (SD) MPa
Fuji II	2.7:1	224.9 (25.8)	11.0 (0.5)	16.3 (1.2)
Hc/Fuji II	2.7:1	293.9 (8.4)	19.3 (1.6)	19.6 (0.9)
Ketac-Molar	2.9:1	313.9 (24.2)	17.1 (1.5)	21.0 (2.5)
Hc/KM	2.9:1	176.9 (5.0)	19.5 (2.4)	14.6 (3.0)
α-Fil	2.7:1	201.0 (8.6)	16.4 (3.0)	17.3 (3.0)
Hc/α-Fil	2.7:1	199.1 (10.3)	17.7 (0.9)	40.1 (2.3)
α-Silver	4.2:1	191.0 (6.5)	20.2 (1.2)	25.6 (3.5)
Hc/α-Silver	4.2:1	209.0 (7.2)	19.4 (0.6)	42.0 (1.1)

$$FS = 3PL/2WD^2$$

where P = the load at fracture, L = the length between two supports, W = the width of the specimen, and D = the depth of the specimen.

Knoop Surface Hardness

Four specimens (6 mm in diameter × 2 mm in thickness) were prepared in glass molds for each experimental and control material. The mold was overfilled slightly with uncured paste and compressed with a glass plate. The partially cured test specimens were removed from the mold after 15 minutes, followed by conditioning in distilled water for 7 days at 37°C. The Knoop hardness (KHN) test was carried out by using a microhardness tester (Model MVK-E, M 400, Leco Co., MI, USA), with the diamond indenter set at 25 g of force for 30 seconds and the length of the crack on the surface subsequently measured. Seven readings taken for each specimen, with averaged obtained to calculate the hardness values (Table 2).

$$KHN = (4P/7.028A^2)10^5$$

where P = the force and A = the length of the crack

Working Time

A 28 g indenter with a flat end of 2.0 mm diameter was lowered vertically onto a flat block specimen of each formulation, beginning 2 minutes from the start of mixing at 25°C. The indenter was allowed to remain for 5 seconds. This was repeated until the needle failed to make a complete circular indentation in the cement, when viewed using a low magnification lens. The mean working times (WT) is an average for three specimens, per ADA specifications (Table 1).

Setting Time

A 400 g indenter with a flat end of 1.0 mm in diameter was lowered vertically onto a flat block specimen of each glass-ionomer formulation, beginning 2 minutes p from the start of mixing at 25°C. The indenter was allowed to remain for 5 seconds. This was repeated until the needle failed to make a complete circular indentation, when viewed using a low magnification lens. The mean setting times (ST) is an average of three specimens, per ADA specifications (Table 1).

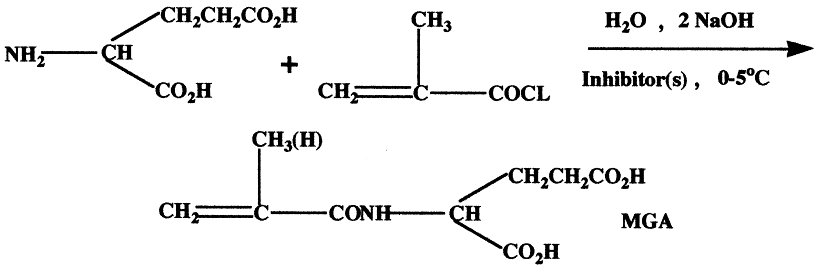

Figure 1. Synthesis of N-Methacryloylglutamic Acid (MGA).

Statistical Analysis

One-way analysis of variance (ANOVA) with subsequent multiple comparisons using Tukey's studentized (HSD) test was then utilized to evaluate the results about strengths.

RESULTS AND DISCUSSION

The MGA monomer was prepared as previously described [16], via modification of a known procedure [17], where glutamic acid was reacted with methacryloyl choride (Figure 1) in an alkaline medium. Various ratios of purified MGA, AA and IA were copolymerized in aqueous solution, using known free radical polymerization techniques [13-16, 18]. Potassium persulfate was used as the initiator and isopropanol as a chain transfer agent, providing high yields of the poly (AA-co-IA-co-MGA) materials (Figure 2).

Molar feed ratios for the copolymers were varied from 1 to 10 for the AA monomer and 1 to 3 for both the IA and MGA monomers (Table 1). The molar

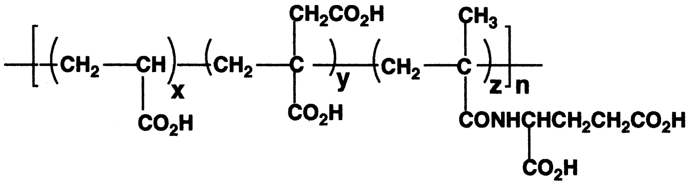

Figure 2. Poly(Acrylic Acid-co-itaconic Acid-co-N-methacryloylglutamic Acid).

ratios, working times, setting times and viscosities of the experimental copolymers and the Fuji II control liquid component are also reported in Table 1. Working times ranged from 4.1 to 7.2 minutes, setting times from 6.4 to 10.0 minutes, and viscosities from 570-1760 cP (Table 1). Copolymer C (7:1:1) showed the fastest WT and ST while G (7:3:3) the slowest WT and ST, with the viscosities of C and G being 1410 and 910 cP, respectively. These results suggest that formation of inter- and intramolecular salt-bridges, via acid-base reaction between the carboxylic acid functionalized polymers and calcium fluoro-alumino-silicate (CaFAlSi) glass powders, was somehow independent of the length of the copolymers with different molar feed ratios for the monomer components. Although a statistical design of experiment (DOE) was not employed in this study to predict the optimal molar ration of AA, IA, and MGA monomers needed to prepare a copolymer which would give the highest CS, the results showed that poly (AA-co-IA-co-MGA) with the molar ratio of 8:1:1 was the best material. It indicated that the CS increase was more dependent on the AA amount incorporated into the copolymer backbone. However, at a certain level of AA incorporated into the copolymer backbone, the decline of CS was observed. It could be that the AA segment length might play a roll in salt-bridge formulation in GIs. Copolymers A (1:1:1), B (6:1:1), C (7:1:1), H (8:1:1) proved the concept with increasing CS of 175.3, 212.8, 232.4, 269.9, then decreasing CS of 136.2 and 101.9 MPa for J (9:1:1) and K(10:1:1), respectively. The effect of the IA monomer ratio was inconclusive in our study. While AA and MGA amounts were kept the same and the IA amount was varied from 1 to 3, CS values were fluctuating: D (7:1:3), E (7:2:3), and G(7:3:3) with CS of 188.8, 177.5, and 208.7 MPa. We have postulated that proper tethering of various types of carboxylic acid groups along the polymer backbones would allow more freedom and less steric hindrance in salt-bridge formation and hence improve the mechanical properties of the materials. Unexpectedly, we have found that tethered acid groups, other than those found on the poly(AA) component, had to be kept in the low range, when using MGA to achieve the best CS. Copolymers C (7:1:1) and D (7:1:3) gave CS of 232.4 and 188.8 MPa, showing that significantly increasing the tethered acid groups, associated with MGA, in the copolymer backbone did not result in an improved CS. Diamentral tensile strengths of copolymers ranged from 9.4 to 15.7 MPa with copolymers A and I having the lowest and copolymer C the highest DTS. No unusual value was recorded for the Knoop hardness properties, compared to the Fuji II control. The CS, DTS, and KHN properties of GIs formulated with poly (AA-co-IA-co-MGA) copolymers are summarized in Table 2.

Copolymer H (8:1:1) had CS = 269.9 MPa, DTS = 14.1 MPa and KHN = 36.8, compared to Fuji II having CS = 224.9 MPa, DTS = 11.0 MPa and KHN = 36.5, was the best material in this series of MGA based copolymers prepared under the same conditions (Table 2). To evaluate the effect of viscosities (molecular weights) of the copolymer having the 8:1:1 monomers ratio, three additional terpolymers (Hb, Hc and Hd) were prepared by varying the initiator concentrations. In a given family of polymers, the compressive strengths usually increase with higher molecular weight of polymer used in the formulations, due to the longer polymer chains improving the bonding between glass particles and the polymer matrix whose strength is reinforced by stronger intermolecular interactions between the polymer backbones. Viscosities or MW of the four polymers prepared (Ha-Hd), by varying the amount of potassium persulfate from 4% to 1%, ranged from 1520 to 6020 cP (Table 3). The series Ha, Hb and Hc showed that increasing the copolymer viscosity or MW would improve CS, with the Hc copolymer having the best CS of 293.9 MPa. But, beyond a certain molecular weight range the CS would be negatively impacted, as shown with Hd having both the highest viscosity (6020 cP) and the lowest CS, due to difficulty of mixing the very viscous polymer solution with the glass powder in the recommended P/L ratios. The effect of viscosity on improving the DTS is also shown in Table 3.

Copolymer Hc, having a viscosity of 3340 cP, was also formulated with glass powders used in Ketac-Molar, α-Fil and α-Silver in a powder/liquid (P/L) ratio recommended by the manufacturers to produce their conventional glass-ionomers. The results were compared to the formulations prepared with the Fuji II glass powder. The properties were compared to the controls, which were commercial GIs (Table 4). The results indicated that the experimental formulation, using Fuji II glass powder, had better properties than commercial Fuji II. Copolymer Hc had CS = 293.9 MPa, DTS = 19.3 MPa and FS = 19.6 MPa while Fuji II had CS = 224.9 MPa, DTS = 11.0 MPa and FS = 16.3 MPa. The glass powder used in Ketac-Molar was not suitable for the MGA based copolymers, resulting in a much lower CS, FS and somehow higher DTS. CS and DTS of the copolymer Hc formulated with glass powders used in α-Fil and α-Silver and the controls were almost the same but FS showed an unexpectedly high value, with improvement of 64% compared to α-Silver and 132% compared to α-Fil.

CONCLUSION

A series of poly (AA-co-IA-co-MGA) were prepared by varying the molar feed ratios for monomer AA from 1 to 10, and monomers IA and MGA from 1 to 3, using the same polymerization conditions. While design of experiment (DOE) methods were not employed in this study, it was shown that polymer H (Tables 1-3), with a molar ratio of 8:1:1, was the best polymer based on the CS property. The effect of viscosities (molecular weights) on the MGA modified AA-IA copolymers were also studied. Copolymers with different viscosities were prepared by varying the initiator concentrations. Copolymer Hc, with a molar ratio of 8:1:1 and a viscosity of 3340 cP, was the best material in the series of MGA based copolymers prepared. The copolymer showed an improvement in CS, DTS, KHN, and FS compared to the highly used Fuji II system. At this point, it is useful to note that the copolymer used in the Fuji II formulation is a poly(AA-co-IA), having a monomers ratio, respectively, of about 2:1. A significantly increased FS compared to the α-Fil and α-Silver controls were achieved, 132% and 64%, respectively, while CS, DTS revealed no improvement. For some reason, the glass powder used in Ketac-Molar was not suitable for the MGA based formulations. Clearly, for the most part, the experimental 8:1:1 poly(AA-co-IA-co-MGA) may be used with many available glass-powders to produce improved conventional GIs.

Based on this work, MGA based copolymer with the 8:1:1 molar ratio of monomers was chosen as a polymer backbone for additional study in preparing VLC materials. The exceptional results achieved for the VLC formulations based on the MGA modification will be reported in the near future.

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