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NEW MATRIX RESINS FOR GLASS POLYALKENOATES OR GLASS-IONOMERS WITH PENDANT AMINO ACID RESIDUES

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Key Words: N-acryloylglutamic Acid, N-methacryloylglutamic Acid, Acrylic Acid, Itaconic Acid, Copolymers, Polyelectrolytes, Glass Polyalkenoates, Glass-ionomers, Visible Light Polymerization, Mechanical Properties

ABSTRACT

The monomers N-acryloyl (AGA) and N-methacryloylglutamic acid (MGA) have been prepared and copolymerized with acrylic acid (AA) and itaconic acid (IA) to make polyelectrolytes for evaluation in glass polyalkenoates or glass-ionomers. It was shown that poly(AA-co-IA-co-AGA) and poly(AA-co-IA-co-MGA), having a monomers ratio, respectively, of 7:3:3 could be formulated with glass powders used in Fuji II (GC America), α-Silver (DMG-Hamburg), α-Fil (DMG-Hamburg) and Ketac-Molar (ESPE, Seefeld, Germany) to produce conventional glass-ionomers with improved compressive strength (CS), flexural strength (FS) and fracture toughness (FT), compared to Fuji II, α-Silver, α-Fil and Ketac-Molar controls. Since MGA is much easier to produce in high yields than AGA, it was important to show that MGA could be used as well as AGA to produce new matrix resins for glass-ionomers. Furthermore, we demonstrated that both the 7:3:3 AGA and MGA copolymers could be reacted with 2-isocyanatoethyl methacrylate (IEM) to produce interme-

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diates useful for formulating visible light-curable (VLC) glass-ionomers with improved CS, FS and FT, compared to two commercial VLC materials Fuji II™ LC and Vitremer™ Tricure. Here again, it was found that MGA could be used as well as AGA to prepare improved materials. We also demonstrated that poly(AA-co-MGA) could be used to formulate glass-ionomers with improved properties. Further, we demonstrated that small amounts of MGA could be used as a reactive diluent in VLC formulations such as Fuji II™ LC, Vitremer™ Tricure, and an experimental VLC formulation to improve their mechanical properties, adhesion to tooth structure, and fluoride release.

INTRODUCTION

The chemistry of conventional type glass polyalkenoates, commonly called glass-ionomers, may be briefly explained as follows: Aqueous solutions (ca. 50% solids) of carboxylic acid functionalized polymers (polyelectrolytes) are blended with glass powders containing varying ratios of Si, Ca, Al and F, i. e., calcium fluoro-alumino-silicate (CaFAlSi) glass powders, with the reaction between the mixed materials producing composites which are very useful in dentistry [1]. These mixtures harden or cure by an acid-base reaction, where the reaction occurring produces inter- and intramolecular salt-bridges, or ionic type crosslinking, along with slow release of fluoride to the oral cavity. In the reaction, the salt-bridges formed are Ca or Al carboxylates, with the Al carboxylates being most desirable but slower to form. The latter is a diffusion controlled process, facilitated by controlled amounts of water present in the starting formulation. In the described chemistry, very few Al tricarboxylates are formed. Furthermore, there are considerable numbers of carboxylic acid groups not tied up in salt-bridges, due to a variety of factors, including steric hindrance. These acid groups are needed to maintain water solubility and stability for the starting polymers. The early glass-ionomers employed acrylic acid (AA) polymer. But, poly(acrylic acid) was found to be unstable in aqueous solutions at elevated molecular weights, i.e., the polymer forms a stiff and rubbery gel on standing in aqueous solutions [2]. Thus, a monomer such as itaconic (IA) or maleic acid (MA) was incorporated into the copolymer backbone to provide disorder, enabling formulators to have stabile, aqueous solutions of the copolymers with high solids content [2, 3].

Poly(AA-co-IA), used extensively for glass-ionomer formulations, has the acid groups very close or directly attached to the copolymer backbone. It was

our concept that tethering some of the acid groups further off the backbone could lessen steric hindrance and possibly facilitate additional Ca or Al carboxylate formation, resulting in improved mechanical properties. The procedure could establish the presence of additional primary and secondary carboxylic acid groups on the copolymer backbone, along with possibly broadening the pKa range of the polyelectrolyte. This procedure might also bring about enhanced Ca or Al carboxylate formation, resulting in improved properties. To check out the validity of our hypothesis, we explored the concept of using N-acryloyl substituted amino acids to modify AA-IA copolymers, i.e., producing copolymers with N-acryloyl-substituted amino acids residues along the backbone of the copolymers (Figure 1) [4, 5]. It is important to note here, any attempt to develop new monomers for use in the oral cavity must consider bioacceptability. With this in mind, we reasoned that any free amino acid, such as glutamic, aspartic, etc., acids, which might appear at some very low level in the oral cavity, from a degrading matrix resin, would not present any hazard to a patient. The latter knowledge makes this approach to generate improved matrix resins for dental restoratives very attractive.

In an earlier paper on this subject, related only to conventional glass-ionomers, we reported on the use of monomers such as N-acryloylglutamic (AGA) and N-acryloyl-6-aminocaproic acid (AACA) for development of improved glass-ionomer formulations [5] In the latter work, we showed that a poly(AA-co-IA-co-AGA) with a monomers ratio, respectively, of 10:1:4, when mixed with a commercial glass powder had a compressive strength (CS) of 212 (± 9.2) MPa, flexural strength (FS) of 34.1 (± 3.3) MPa, and fracture toughness (FT) of 0.39 (± 0.05) $MPam^{0.5}$, with all testing done by standard ASTM methods. The AACA based terpolymer with the same monomers ratio, formulated with the same glass powder, cured, conditioned, and tested in the same fashion had CS = 183.0 (± 10.7) MPa, FS = 31.0 (± 3.1) MPa, and FT = 0.30 (± 0.03) $MPam^{0.5}$.

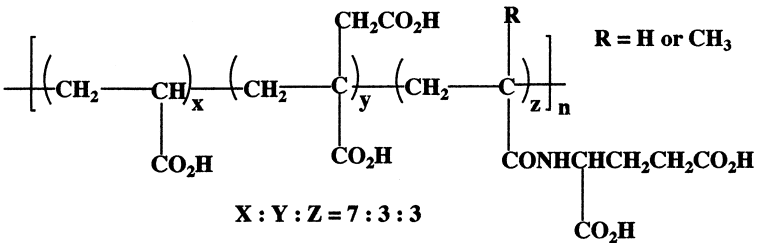

Figure 1. Poly(AA-co-IA-co-AGA) or Poly(AA-co-IA-co-MGA).

Fuji II (GC America) commercial glass-ionomer, which employs a poly(AA-co-IA) with ca. a 7:3 ratio of monomers, was used both as a control and the source of the glass powder used in the experimental formulations. Both the experimental and control samples were prepared and conditioned in water (37ºC/1 w) and tested in the same fashion. The Fuji II had CS = 168.2 (± 11.0) MPa, FS = 8.8 (± 2.03) MPa, and FT = 0.20 (± 0.04) $MPam^{0.5}$ [5, 6]. In addition, we showed that the presence of amino acid residues substantially enhanced the bond strength of the matrix resins to tooth surfaces [6], for example a 10:1:1 poly(AA-IA-AGA) glass-ionomer formulation, using Fuji II glass powder at P/L = 2.7/1, had bonding to enamel of 7.8 MPa and to dentin of 6.6 MPa, versus Fuji II control having 4.5 MPa bonding to enamel and 3.8 MPa bonding to dentin. In addition, the presence of the amino acid residues enhanced fluoride release to the oral cavity [7]. Clearly, we showed that tethering an amino acid, such as glutamic acid, to the backbone of the commonly used polyelectrolyte could make available formulations with improved mechanical properties [4-6]. Later studies by Kao *et al.* [8] showed that the tethered acid groups bring about more salt-bridge (Al carboxylate) formation.

One of the major difficulties of using AGA or AACA type monomers, as described above, resides in the fact that the N-acryloyl substituted amino acids are difficult to prepare in yields attractive for commercial uses. In contrast, N-methacryloyl substituted amino acids are more readily prepared in good yields, making these monomers much more attractive to try and design new resins to exploit commercially. In this paper, we describe some of our preliminary work on the preparation and evaluation of N-methacryloylglutamic acid (MGA) as a monomer to prepare polyelectrolytes for use in glass-ionomers. Our main goal is to show that MGA monomer, as well as N-acryloyl substituted amino acid (AGA, AACA, etc.) monomers, could also provide a path to improve the toughness or mechanical properties of both conventional as well as VLC glass-ionomers. In this preliminary study, properties such as CS, FS, DTS and FT are focused on as the areas needing improvement in both conventional as well as VLC formulations. However, we give the VLC systems the most attention, since this is the major class of glass-ionomer restoratives currently marketed.

Several techniques may be utilized to prepare VLC type glass-ionomers, with chemistry and structures described by Anstice and Nicholson [9]. We employed the technique patented by 3M Dental Products, a Division of 3M Corp. [10, 11], which takes advantage of the fact that carboxylic acid functionalized copolymers may be treated in dry tetrahydrofuran with 2-isocyanatoethyl methacrylate (IEM) to produce copolymers with pendant methacrylate residues

(Figure 2) [11, 12]. These copolymers, with pendant methacrylate residues, in the presence of a reactive diluent in the aqueous solution, such as 2-hydroxyethyl methacrylate (HEMA), and a certain level of visible light triggered initiators, may be mixed with basic glass powders to produce VLC type glass-ionomers. This procedure substantially improves the mechanical properties of the glass-ionomers, due to the level of covalent crosslinking achieved by free radical initiated carbon-carbon bond formation. Using the 3M techniques [10-12], we prepared new VLC glass-ionomer matrix materials, using copolymers prepared from acrylic acid, itaconic acid and N-acryloyl- (AGA) or N-meth-acryloyl (MGA) substituted glutamic acid.

EXPERIMENTAL

Materials

Glutamic acid, acryloyl and methacryloyl chloride, 2-hydroxyethyl methacrylate (HEMA), solvents, inhibitors (triphenylstibine), antioxidant (butylated hydroxytoluene, BHT), initiators (potassium persulfate and camphoroquinone,CQ), and p-tolylsulfonylmethylnitrosamide (Diazald, a diazomethane source) [13] were obtained from Aldrich Chemical Co. The 2-isocyanatoethyl methacrylate (IEM) was used as received from Monomer-Polymer Laboratories, Inc. The acryloyl and methacryloyl chlorides were distilled prior to use. The CaFAlSi glass powders and commercial glass ionomer kits for controls were supplied by GC America (Fuji II and Fuji II^{TM} LC), 3M Dental Products (Vitremer^{TM} Tricure), DMG, Hamburg,Germany (α-Silver and α- Fil), and ESPE GmbH, Seefeld, Germany (Ketac-Molar).

Synthesis of Monomers

The N-acryloyl (AGA) and N-methacryloylglutamic acid (MGA) monomers were prepared by slight modification of previously reported [5, 14] procedures. A solution of 0.3 mol of NaOH and 0.1 mol of glutamic acid in 30 ml of distilled water was vigorously stirred and cooled to –10˚C, using an ice-salt bath. To this solution, 0.1 mol of methacryloyl chloride was added slowly with vigorous stirring over a 30 minute period. The reaction mixture was stirred at –10˚C for an additional 1.5 hour. Concentrated HCl was slowly added to the reaction mixture, until about pH = 2.0 was reached. At this point, stirring was done for an additional 30 minutes. The resulting mixture was extracted

several times with hot ethyl acetate. The combined ethyl acetate extracts were dried over anhydrous magnesium sulfate. After filtration and removal of the ethyl acetate from the product, under reduced pressure, the crude product was obtained as a white solid in good yields. The product was recrystallized from ethyl acetate. The yields of recrystallized MGA monomer from several trials averaged ca 75%. In contrast, recrystallized yields of AGA by the same procedure were ≤45%. The AGA and MGA compounds, with melting points, respectively, of 120-121 (reported 120-122) and 130-131˚C (reported 130-132) [4, 14], were additionally confirmed by FT IR and NMR (^{1}H and ^{13}C).

Copolymer Synthesis and Characterization

Copolymerization to prepare poly(AA-co-IA-co-AGA) and poly(AA-co-IA-co-MGA), Tables 1 and 2, were run in water, under nitrogen, with 2.0 wt % ammonium persulfate initiator at 95-100˚C for 6-7 hours, as previously reported [4-6], following techniques described by Crisp *et al.* [3]. Copolymer recovery was achieved by freeze-drying, a commonly used procedure. The copolymers were dissolved in a minimum amount of methyl alcohol, solution filtered, and the alcohol solutions combined with diethyl ether to precipitate the copolymers, with purity checked by thin layer chromatography. The materials were collected by filtration and dried for extended periods of time at ambient temperature, under hard vacuum. The copolymers were characterized by FT IR, ^{1}H and ^{13}C NMR, elemental (N %) analysis, and gel permeation chromatography (GPC, Waters GPC equipment, with THF solvent and with PS standard). Viscosities (50% solids in water) measurements were made on a CarriMed CSL^{2} Controlled Stress Rheometer (TA Instruments) at 25˚C. To perform GPC, it was necessary to treat the copolymers with diazomethane, generated from Diazald decomposition [13]. The diazomethane converted some of the acid groups to ester moieties, making the copolymer(s) soluble in THF.

Copolymer IEM Grafting Reactions

The dry AGA or MGA copolymers were dissolved in tetrahydrofuran (THF), containing 0.5 wt% dibutyltin dilaurate, 0.2 wt% triphenylstibine (TPS) and 0.2 wt% butylated hydroxytoluene (BHT), followed by IEM addition at a controlled rate to the stirred solution [10, 11]. The reaction was run under nitrogen, while keeping the temperature ≤ 40˚C. IEM grafting or conversion of 5-15 molar % of the carboxylic acid residues to methacrylate-amide moieties was achieved as shown in Figure 2. The grafted copolymers were recovered from the

THF, by combining the concentrated polymer solutions with a large excess of diethyl ether. The precipitated polymer was collected, washed with ether, dried under vacuum, and checked by TLC to insure no free IEM was present. Elemental (N %) analysis, FT IR and ^{1}H or ^{13}C NMR was used to confirm copolymer structures and the level of IEM grafting or modification.

Conventional and VLC Liquid Formulations

For conventional or chemical cured systems, the AGA or MGA terpolymers were dissolved in water at 50% solids**,** providing the liquid component. For the VLC formulations, a typical liquid component consisted of 2.5 g of IEM grafted AGA or MGA copolymer, 1.05 g of HEMA, 1.70 g of water, 0.021 g of camphoroquinone (CQ), and 0.135 g of diphenyliodonium hexafluorophosphate (DPHP), akin to a patented procedure [10, 11]. For the VLC formulations using MGA as a reactive diluent/modifier (Table 4), MGA was added to the aqueous components used in the formulations at the 5 wt% level.

Conventional Sample Preparations

The curing reaction for the conventional glass-ionomers was activated by thoroughly mixing the GA or MGA copolymer liquid with glass powder used in Fuji II, per procedure and powder/liquid (P/L) ratio (2.7:1) recommended for the Fuji II control. The mixtures were placed in suitable glass or Teflon molds, allowed to cure for 0.5-1 hour at 100% RH, removed from the molds and conditioned in water at 37 ± 2˚C for 24 hours or 7 days prior to testing. As a control, the Fuji II was mixed, placed in molds, cured, and conditioned in the same fashion.

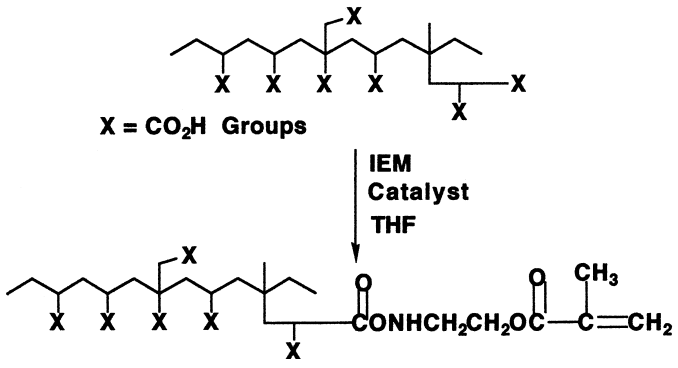

Figure 2. IEM grafting scheme for AGA and MGA polyelectrolytes.

Visible Light Cured Sample Preparations

For the VLC formulations, the experimental liquid component was thoroughly mixed with the Vitremer™ Tricure glass powder, using the recommended P/L ratios called for by Vitremer (Tables 1, 3, and 4). After mixing and placing the formulation in glass or Teflon molds, the specimens were exposed to visible light for 2 minutes, using an Elipar (ESPE GmbH Premier, Seefeld, Germany) light source. The specimens were allowed to remain in the molds for ca. 0.5-1 hour at 100% RH, removed from the molds and conditioned in distilled water at 37 $\pm$ 2˚C for 24 hours or 7 days prior to testing. As controls, the commercial Fuji II™ LC and Vitremer™ Tricure glass-ionomers (Tables 1, 3, and 4) were mixed, placed in molds, cured, and conditioned in the same fashion as the experimental specimens.

Working (WT) and Setting (ST) Times

These variables were evaluated by standard techniques, using a 400 gram indenter having a flat head of 1.0 mm for ST and a 28 g indenter with a flat head of 20 mm for WT. Starting 1 minute from start of mixing at 23˚C, for WT determination, the indenter was lowered vertically onto the surface of a flat specimen and allowed to remain for 5 s. This was repeated every 10 s until the needle failed to make a complete circular indentation in the cement when viewed using a low magnification hand lens. For ST, the indenter was lowered vertically onto the flat disc of each specimen, 2.0 minutes from start of mixing at 23˚C. The indenter was allowed to remain for 5 s. This was repeated every 10 s until the indenter failed to make a circular indentation when view with a low magnification lens.

Test Methods

For compressive (CS) and diametral tensile (DTS) strength tests, cylindrical specimens measuring 6 mm diameter x 12 mm length were prepared in glass tubing. For flexural strength (FS) testing specimens 25 mm long x 3 mm width x 3 mm thick were prepared in Teflon molds. For fracture toughness testing, compact disc specimens were prepared according to ASTM Standard E399-83 (l984). After the glass-ionomer mixture was placed in the mold, a precrack was formed by placing a razor blade into the specimen.

All testing for CS, DTS, FS and FT were done on a universal testing machine (Instron Model 4204, Instron Corp., Canton, MA). The CS was determined by loading the flat ends of the specimens, which were machined parallel, at a crosshead speed of 0.5 mm/min. For DTS determinations, the side of the

specimen were loaded at 0.5 mm/min. For FS testing, a three-point loading apparatus was utilized. The conditioned beams (specimens) were laid horizontally between two parallel knife edges placed 20 mm apart. A progressively increasing load was applied at the midpoint between the knife edge supports, at a crosshead speed of 0.1 mm/min. For FT testing the specimens were tested in tension with the direction of the force perpendicular to the plane of the performed notch in the specimen, at a crosshead speed of 0.5 mm/min. The formulas used to calculate CS, DTS and FS were as follows: $CS = P/\pi r^2$, $DTS = P/2\pi rh$, and $FS = 3PL/ 2bd^2$, with values reported in MPa, where P = load at fracture, r = radius of cylinder, h = height of cylinder. L= distance between the two knife edges, b = width of specimen, and d = thickness of specimen. For FT, the compact disc formula used was $K = P_c /BW^{0.5}$ x f(a/W), where P_c = maximum load prior to catastrophic crack advance (K), B = mean specimen thickness (cm), a = crack length (cm), and $f(a/W) = [2 +a/W] [0.866 + 4.64a/W - 13.32a^2/W^2 + 14.72a^3/W^3 - 5.6a^4/W^4]$.

RESULTS AND DISCUSSION

In earlier studies, we prepared several poly(AA-co-IA-co-AGA), one poly(AA-co-AGA), and one poly(AA-co-IA) copolymers (Table 1), seeking to discover what effect the variation of AGA ratio in the copolymer backbone would have on the final CS, FS, FT, etc., properties of the formulated materials. Also, we wanted to discover what was the best monomers ratio of AA-IA-AGA to use in the VLC copolymers, as well as what was the optimum molecular weight. The reason for the main focus on VLC glass-ionomers centered on the fact that VLC is the area of most market interest. Also, we wanted to know if there was a chance that IA could be eliminated from the copolymers and this would still allow for possible development of a cured VLC glass-ionomer with good properties (Table 1). While this was not a statistical design of experiment (DOE) type study to find the optimum AGA ratio for the best CS, DTS, FS, FT, etc., type properties (Table 1), the results still adequately show that a poly(AA-co-IA-co-AGA), with the monomer ratio 7:3:3, has very good mechanical properties (CS and DTS). This holds true for both conventional (Table 2 and 3) as well as VLC glass-ionomer (Tables 1 and 3) formulations. Furthermore, it appears that a poly(AA-co-AGA) having a monomers ratio, respectively, of 7:3, and treated with IEM, also has potential for formulating VLC glass-ionomers with very good mechanical properties (Table 1).

TABLE 1. Mechanical Properties of AGA Based Copolymers for VLC Glass-Ionomers[a,b,c]

Copolymer	CS, MPa (SD)	FS, MPa (SD)	FT, $Mn/m^{1./5}$ (SD)
AA-IA (7:3)	225.4 (10.3)	63.5 (11.3)	1.08 (0.21)
AA-IA-AGA (7:3:1)	227.9 (8.6)	87.1 (14.6)	1.07 (0.33)
AA-IA-AGA (7:3:2)	235.6 (10.5)	81.0 (12.5)	0.99 (0.50)
AA-IA-AGA (7:3:3)	247.2 (9.10)	88.5 (12.5)	1.13 (0.40)
AA-AGA (7:3)	245.3 (10.5)	67.5 (12.5)	0.98 (0.45)
AA-MGA (7:3)[d]	231.0 (10.4)	59.5 (12.7)	0.83 (0.18)

[a] The copolymers were made by the same synthesis method, using the same level of ammonium persulfate initiator to try and keep molecular weights close to each other. Aqueous viscosities of the copolymers (50 % solids) were ca 3500-5000 cp, with the 7:3:3 copolymer being at the upper viscosity, i. e., 5000 cp, level.

[b] The copolymers were all treated with IEM to achieve methacrylate grafting to 10 % of the carboxylic acid groups.

[c] All copolymers were combined with water, HEMA, CQ, etc., and the liquid mixed with the glass powder used in the Vitremer™ Tricure system, at the same P/L (2.5:1) ratio as Vitremer. After visible light curing for 2 min, setting in the molds for 0.5 h at 100 % RH, and conditioning in water for 7 d at 37 °C, the composites were tested for CS, FS and FT.

[d] The 7:3 AA-MGA copolymer, prepared with the same level of initiator and grafted with the same IEM level as the AGA copolymers, was formulated, cured, conditioned and tested in the same fashion as the AGA copolymers. In all cases 5 specimens were tested for each formulation.

We further evaluated the 7:3:3 poly(AA-co-IA-co-AGA) copolymer in Table 2 with glass powders used in other commercial, conventional glass-ionomers, i. e., α–Silver, α-Fil, and Ketac-Molar, versus the latter glass-ionomers as controls (Table 2) [15]. In all cases, we found that currently used glass powders from other formulations also worked very well with our 7:3:3 copolymer. In fact, it is apparent from the results in Table 2 that the tethering of amino acid groups on the backbone of polyelectrolytes used in glass ionomers generally improves mechanical properties compared to the currently used AA-IA and AA-MA copolymers. It is known that Fuji II and Ketac-Molar copolymers, respectively , use poly(AA-IA) and poly(AA-MA) in their formulations.

Having to prepare more and more AGA for doing the type of experiments shown in Table 1 and 2, and thinking of the need or desire to do a study of statistical design experiments to ascertain optimum molar ratios, optimum molecu-

TABLE 2. Poly(AA-IA-AGA), 7:3:3, Copolymer Formulated into Glass-Ionomers Using Different Glass Powders

Material	P/L	Manufacturer	CS, MPa(SD)	FS, MPa(SD)
α-Silver	4.2/1	DMG-Hamburg	187.4 (10.9)	29.43 (4.7)
[a]AGA/α-Silver	4.2/1		198.0 (9.0)	40.4 (3.5)
α-Fil	2.7/1	DMG-Hamburg	145.1 (15.2)	25.2 (3.5)
[a]AGA/α-Fil	2.7/1		167.2 (9.5)	32.0 (1.5)
Ketac-Molar	3.1/1	ESPE	213.2 (23.7)	25.2 (1.38)
[a]AGA/Ketac -Molar	3.1/1		218.2 (23.0)	28.1 (6.0)

[a] The AGA (AA-IA-AGA copolymer) used in all three formulations was the same as that in Table 3. However these three experiments employed the glass powders used in α-Silver, α-Fil and Ketac-Molar, at the P/L ratios shown, rather than using the Fuji II glass powder shown in Table 3. The working and setting times for the experimental formulations were close to the WT and ST for the controls.

lar weight(s), level of IEM grafting, formulation variables, etc., to achieve the most improved conventional or VLC glass-ionomer, we became concerned that we had not been able to discover a good synthetic route for the preparation of AGA in crystallized yields ≥ 40-45%. It was evident we would need larger and larger quantities of purified AGA. Thus, we decided to refocus our project on MGA, since the same synthetic technique used to prepare AGA would allow MGA to be prepared in recrystallized yields ≥ 70%. In making the switch, stopping our focus on AGA, we wanted to find out if MGA could be used just as well as AGA to design polyelectrolytes for improving both conventional and VLC glass-ionomers. There were some doubts, since MGA would make the copolymers more hydrophobic, have greater steric hindrance, etc., along the copolymer backbone. Further, if the aforesaid factors presented problems for formulating improved conventional glass-ionomers, we felt the problem would be magnified in VLC systems, since reactions of the copolymers with IEM would make the polyelectrolytes have even more hydrophobicity and steric hindrance. However, with MGA containing 42% carboxylic acid residues, versus AGA hav-

ing 44%, we felt there was a good chance that MGA could also be useful for design of the desired new polyelectrolytes.

Table 3 shows the poly(AA-co-IA-co-AGA) and poly(AA-co-IA-co-MGA) copolymers made for this preliminary MGA based study, with both copolymers having a monomers ratio, respectively, of 7:3:3. FT IR and NMR (^{1}H and ^{13}C) confirmed the copolymer structures. Elemental analysis showed that AGA and MGA had copolymerized very well with the AA and IA, with the AGA copolymer having N = 2.72% (theory, N = 2.80%) and the MGA copolymer having N = 2.65% (theory, N = 2.73%). The AGA and MGA copolymers in Table 3 had comparable molecular weights, as shown by aqueous (50% solids) viscosities and GPC curves for the partially esterified samples. Copolymers in Table 3 had lower molecular weights than those in Table 1, since we felt that the MGA copolymer would be more difficult to mix with glass powders and this called for a lower MW. The lower MW is possibly why the AA-IA-AGA (7:3:3) copolymer used in Table 3 has a lower CS value than the same 7:3:3 copolymer evaluated in Table 1. The viscosities (50% solids) of the two 7:3:3 AA-IA-AGA copolymers in water in Tables 1 and 3 were, respectively, 5000 and 2500 cp.

The 7:3:3 monomers ratio for the MGA terpolymer was selected for this initial study since the AGA based copolymer with the same ratio looked most attractive for possible development of both a conventional and a VLC glass-ionomer (Tables 1 and 2). As previously stated, the goal was to see if MGA could be used as a replacement for AGA. As shown in Table 3, the CS, DTS, FS and FT for the MGA based conventional glass-ionomer formulation performed as well as the AGA based formulation, at the same 7:3:3 monomers ratio. Also, both the conventional AGA and MGA based formulations performed slightly better than the commercial Fuji II formulation, especially for FS. It is to be remembered that the Fuji II glass powder was used in the experimental specimens. In all probability, a glass powder specifically designed for the AGA or MGA based copolymers could make improvements even more significant.

Based on our preliminary evaluation of AGA and MGA amino acid based copolymers, along with knowing that Itou *et al.* [16] had shown that N-acryloylaspartic acid was a useful adhesion promoter for the tooth surface, we decided to briefly evaluate MGA addition to VLC formulations [17], as a reactive diluent/modifier to improve properties (Table 4). In a VLC formulations such a Vitremer, the polyelectrolyte chains are both covalently crosslinked by poly(HEMA), as well as some of the HEMA polymer being part of an interpenetrating polymer network (IPN). The crosslinking poly(HEMA) and the IPN poly(HEMA) segments have only hydroxyl residues. It was our hypothesis that

TABLE 3. Mechanical Properties of Experimental Glass-Ionomer Formulations, Based on AGA and MGA, Compared to Commercial Controls

System	P/L Ratio	CS, MPa (SD)	DTS, MPA (SD)	FS, MPA (SD)	FT. Mn/ $m^{1.5}$ (SD)
Fuji II	2.7:1	184.50 (8.60)	9.92 (0.59	14.65 (0.70)	0.48 (0.08)
[a,c] AA-IA-AGA 7:3:3	2.7:1	207.80 (17.80)	-----	40.60 (4.70)	0.50 (0.05)
[a,c] AA-IA-MGA 7:3:3	2.7:1	223.55 (8.43)	20.00 (3.90)	34.60 (6.98)	0.64 (0.13)
Fuji II LC	3:1	241.38 (6.60)	46.39 (0.40)	74.05 (4.90)	0.73 (0.05)
Vitremer Tricure	2.5:1	224.30 (4.60)	46.70 (0.80)	63.00 (11.00)	0.86 (0.03)
[b] AA-IA-AGA LC 7:3:3	2.5:1	227.40 (8.50)	45.50 (6.50)	87.00 (14.60)	1.07 (0.33)
[b,d] AA-IA-MGA LC 7:3:3	2.5:1	247.70 (14.70)	42.60 (6.90)	81.40 (9.00)	1.06 (0.13)

[a] The AGA and MGA based copolymers had aqueous viscositie (50 % solids), respectively, of 2200 and 2500 cp, versus Fuji II having a viscosity ca. 700 cp. Both the experimental AGA and MGA glass-ionomer formulations used Fuji II glass powder.

[b] Both the VLC AGA and MGA copolymers were grafted at the 15 % level with IEM, using Vitremer™ Tricure glass powder in their formulations.

[c] Elemental (N) analysis showed the AGA copolymers had N = 2.70% and the MGA copolymer had N = 2.61 %, reasonably close to theory for AGA copolymer having N = 2.80 % and MGA copolymer having N= 2.73 %.

[d] GPC estimated molecular weight for AA-co-IA-co-MGA copolymer (7:3:3) was 44,000 ,with a dispersivity of 2.4.

some level of carboxylic acid groups pendant on the poly(HEMA) segments within the VLC glass-ionomer organic matrix would also foster salt-bridge formation. Also, this would assist in tying the poly(HEMA) segment in the matrix more tightly to the inorganic phase via ionic bonding. Thus, we reasoned, at some level, this type of incorporation of carboxylic acid groups within the organ-

TABLE 4. Physical Properties of MGA Modified VLC Glass-Ionomer Cements[a]

Cement	P/L	CS, MPa[b] (SD)	DTS, MPa[b] (SD)	FS, Mpa[b] (SD)	FT, MPam$^{0.5}$ (SD)
Fuji II LC	3:1	241.4 (6.6)	46.4 (0.4)	74.0 (4.9)	0.74 (0.04)
Fuji II LC/ 5 % MGA	3.1	261.7 (2.1)	48.1 (1.5)	86.6 (3.1)	0.85 (0.07)
Vitremer Tricure	2.5:1	220.3 (4.6)	46.7 (0.8)	63.7 (11.0)	0.68 (0.09)
Vitremer Tricure/ 5 % MGA	2.5:1	260.2 (6.3)	40.1 (0.7)	94.6 (4.8)	1.04 (0.18
AA-IA-MGA 7:3:3 LC[c] 5 % MGA[d]	2.5:1	253.6 (14.4)	46.6 (4.9)	88.4 (9.5)	1.13 (0.26)
AA-MGA 7:3, with 5 % MGA	2.5:1	240.0 (10.4)	36.2 (5.7)	57.4 (12.$)	0.94 (0.17)

[a] The Fuji II™ LC and Vitremer™ Tricure liquid components were modified by addition of MGA, at the 5 % by wt of the starting liquid [16].Crystalline MGA, which was readily soluble in the aqueous liquid mixtures of the visible light-curable compositions, lowered viscosity to some small degree. After mixing with the glass powders and placing in the molds, the samples (10 for each formulation) were cured with an Elipar {ESPE (Seefeld, Germany)} lamp for 2 min. After light exposure, the samples were allowed to set in the molds at 25 °C and 100 % RH.

[b] After removal from the molds, the samples were conditioned for 24 h in distilled water at 37 °C, followed by CS, FS and FT determinations.

[c] This is the same VLC formulation used in Table 3 for AA-IA-MGA LC, with exception liquid component contained 5 % by wt free MGA.

[d] This copolymer at 50 % solids, had a viscosity of 5500 cp, before addition of 5 % by wt of MGA free monomer.

ic matrix would also improve the properties of VLC glass-ionomers. The results in Table 1 for the VLC AA:MGA formulation and Table 4 for the other experimental MGA containing VLC systems support this hypothesis.

CONCLUSION

Preliminary studies demonstrate that MGA is as valuable as AGA for the synthesis of polyelectrolytes for use in the design of both conventional as well as VLC type glass-ionomers. This is very significant in view of the fact that N-methacryloyl substituted amino acids, such as MGA, are much more readily prepared than N-acryloyl substituted amino acids, making MGA based copolymers have much greater commercial interest. It is also important to note that MGA is a very good reactive diluent or modifier to combine with VLC glass-ionomers, possibly at some low level, to improve various properties, including fluoride release to the oral cavity [7].

In future studies, focusing only on VLC systems, we intend to concentrate on discovering answers to the following type questions: 1) what is the optimum AA:IA:MGA, and possibly AA:MGA, copolymer molar ratios needed to maximize various mechanical properties, such as FS and FT? 2) What is the maximum molecular weight permissible for use in the aqueous (50% solids) components, to allow for adequate working and setting times, along with achieving the best mechanical properties profile, for the formulation(s)? 3) What level of IEM grafting is needed or permissible for maximum properties? 4) What type and level of modification of N-methacryloyl substituted amino acid as a reactive diluent, with major focus on MGA, is needed or allowed to maximize the mechanical properties of both the current commercial VLC formulations, as well as the best MGA based VLC system discovered in our study.

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