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## VISIBLE LIGHT-CURABLE N-METHACRYLOYL-GLUTAMIC ACID MODIFIED POLYELECTROLYTES FOR USE IN DENTAL APPLICATIONS

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Key Words: Acrylic Acid, Itaconic Acid, N-Methacryloylglutamic Acid, Terpolymers, Design of Experiments, Visible Light-Curing, Glass-Ionomers, Dental Restoratives, Mechanical Properties

### ABSTRACT

The visible light-curable N-methacryloylglutamic acid (MGA) modified polymers (VLC MGA MPs), with the optimal molar ratio of 8:1:1 (acrylic acid: itaconic acid: MGA) in the copolymer backbone, were synthesized by a one pot reaction. The compressive strength (CS) was used as the initial basic screening property to determine the best graft ratio. A statistical design of experiment (DOE) technique was utilized to predict the optimal formulation for the VLC MGA MP with the best graft ratio based on the CS. The VLC MGA MPs were synthesized under the same reaction conditions, using a free-radical polymerization process to produce the copolymers, followed by grafting 2-isocyanatoethyl methacrylate (IEM) onto the copolymer backbone to form the VLC materials. Specimens were prepared by mixing the polymer solutions with the basic glass powders and their strength values were measured after the test specimens were conditioned in distilled water at 37°C for 7 days.

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In this study, polymer solutions containing VLC MGA MPs were formulated with the glass powder used in the commercial Fuji II LC (GC America) material to determine the CS. Diametral tensile strengths (DTS) of the produced materials were also determined. Based only on the CS value, the VLC MGA MP with 15 molar % of IEM grafting was the best material. The optimal formulation for this copolymer, i. e., the system having the highest CS value, was found to be at the weight ratio of 52.5:18:29.5 (VLC MGA MP:HEMA:water), providing an improvement in CS of 30% compared to the commercial Fuji II LC system. This formulation was also mixed with the glass powder used in the Vitremer<sup>TM</sup> (3M Dental Products) material to determine its mechanical properties. The MGA monomer was also further evaluated as a reactive diluent/modifier for commercial VLC formulations, such as the Fuji II LC and Vitremer<sup>TM</sup>, as well as the optimal experimental VLC formulation. In the latter effort, the MGA monomer was used to partly replace HEMA in the optimal experimental VLC formulation, providing additional evidence that MGA was useful to formulate improved VLC glass-ionomers.

## INTRODUCTION

Glass-ionomers (GIs) are a special class of dental materials which possess unique properties, promoting their use as restorative and adhesive materials. Their attractive properties, such as biocompatibility and low cytotoxicity [1], anticaries capability [2-4], inhibition of bacterial growth [5-7], adhesion [8, 9], and low coefficient of thermal expansion [10, 11] make them valuable for clinical applications [12, 13]. Polymers used in these formulations are water soluble polyelectrolytes with carboxylic acid groups directly or very closely attached to the polymer backbone, which are usually derived from acrylic acid (AA), itaconic acid (IA) and maleic acid (MA), such as poly (AA-co-IA) or poly (AA-co-MA) materials. The strength of GIs is based on organic-inorganic/acid-base reactions between polymer matrixes and fillers. However, the presently available GIs are not suitable for use in high-stress sites due to low moduli of elasticity, low resistance to brittleness and abrasion [14-16]. Considerable efforts have been carried out in our laboratory to improve the strength of GIs, by modifying the polymer backbone, resulting in incorporation of N-vinylpyrrolidone and amino acids into the polymer chains [17-23].

Visible light-curable GIs have received the most attention due to the fact that they are the major class of glass-ionomer restoratives presently mar-

keted. They are polyelectrolytes containing methacrylate side chains grafted onto the polymer backbone to form VLC segments. There are three major types of VLC-GIs: 1) FAISi glass powder and solution containing poly (AA-co-MA), HEMA, water, an initiator and an activator [24]; 2) NaLaCaAlFSi glass powder combined with solid poly (AA-co-MA) and solution of glass-ionomer-compatible monomers and oligomers, HEMA, water, an initiator and an activator [24]; 3) CaFAISi glass powder and solution of poly (AA-co-IA) grafted with methacrylate groups, HEMA, water, initiators and activators [25].

We have previously reported our optimization research on the poly (AA-co-IA-co-MGA) terpolymers with molar feed ratios varied from 1 to 10 for the AA monomer and from 1 to 3 for both the IA and MGA monomers [26]. In this paper we selected poly (AA-co-IA-co-MGA) with the optimal molar ratio of 8:1:1 for additional formulation study, since that terpolymer had the highest CS value. This polymer backbone was modified with 2-isocyanatoethyl methacrylate (IEM) to produce VLC materials, utilizing the IEM grafting technique patented by 3M Dental Products [25, 27]. After determining the best graft ratio of the VLC MGA MP, with the help of statistical design of experiment (DOE) techniques [28], we formulated the optimal polymer matrix of the IEM grafted poly (AA-co-IA-co-MGA) to achieve the highest CS. We also investigated the effects of MGA monomer as a reactive diluent/modifier for VLC formulations, such as commercial Fuji II LC and Vitremer<sup>TM</sup> and the optimal experimental formulation, by replacing some of the HEMA with MGA in the identified formulation. For the DOE procedure, an initial set of formulations were prepared and the CS values determined. The data were fit to the models and the response-surface contours were examined to predict optimal values. Additional sets of formulations were made to provide more data to refine predictions, providing an experimentally determined optimal formulation for the system under study.

## EXPERIMENTAL

### Materials

Itaconic acid (IA), acrylic acid (AA), 2,2'-azobisisobutyronitrile (AIBN), hydrochloric acid (HCl), anhydrous magnesium sulfate ( $\text{MgSO}_4$ ), sodium chloride (NaCl), 2-hydroxyethyl methacrylate (HEMA), triphenylstibine (TBS), potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), dl-camphorquinone (CQ), diphenyliodonium chloride (DC), dibutyltin dilaurate (DBTL), 2, 6-di-tert-butyl-4-methylphe-

nol (BHT), and solvents were used as received from Aldrich Chemical Co. Methacryloyl chloride, also from Aldrich, was distilled prior to use. 2-Isocyanatoethyl methacrylate (IEM), obtained from the Monomer-Polymer Laboratories, Inc., was used as received. The CaFAlSi glass powders, used in the formulations were part of commercial glass-ionomer kits supplied by GC America (Fuji II LC) and 3M Dental Products (Vitremer<sup>TM</sup>). The N-methacryloylglutamic acid (MGA) monomer used in the study was prepared by previously published procedures [26].

### Characterization

FT-IR spectra were obtained on a MIDAC spectrophotometer. Melting points were determined by differential scanning calorimetry (TA Instruments, DSC 910). The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were obtained on a 300 MHz Bruker AM spectrometer, using deuterated water as a solvent and trimethylsilane (TMS) as an internal standard.

### Polymer Synthesis

Tetrahydrofuran (THF, 45 ml) was stirred under a nitrogen atmosphere and heated up to 60°C. A solution of acrylic acid (17.19 g; 24 mmol), itaconic acid (3.90 g, 3 mmol), MGA (6.46 g, 3 mmol) in 55 ml of THF, and a solution of 0.1 wt% AIBN in 30 ml THF were subdivided into 15 equal portions and added every 5 minutes to the hot THF solvent. The reaction was followed by FT-IR, determining the point in time where the carbon-carbon double bond (C=C) peak of the three monomers disappeared. Next, the reaction temperature was lowered to 40°C, followed by the addition of a mixture of 0.3 wt% butylated hydroxytoluene (BHT), 0.3 wt% triphenylstibine (TPS) and 0.6 wt% dibutyltin dilaurate (DBTL) in 5 ml of THF. A solution of 2-isocyanatoethyl methacrylate (IEM) in 25 ml of THF, with the IEM ranging from 10-20% mole fraction of the polymer carboxylic acid groups, was added over a 1 hour period. After an additional hour at 40°C, the stirred reaction mixture was continued at room temperature until FT-IR showed the absence of the IEM isocyanate (NCO) peak. The reaction mixture was then combined with a large excess of diethyl ether to precipitate the polymer, which was collected, washed several times with ether and dried overnight under vacuum at 30°C.

### Test Methods

The VLC polymer solutions were formulated through dissolution of the VLC MGA MP, 1.4% (wt/wt) of DC (activator), 0.5% (wt/wt) of CQ (photoinitiator) and 0.1% (wt/wt) of  $K_2S_2O_8$  (initiator for a redox system) in a HEMA/distilled water mixture. GC Fuji II LC glass powder was used in this study as a control glass, with a powder/liquid (P/L) ratio of 3/1 as recommended by GC America, for the CS and DTS determinations. Six cylindrical specimens measuring 4 mm in diameter by 8 mm in length for CS testing and 4 mm in diameter by 2 mm in thickness for DTS testing were prepared in glass tubing, using the help of a pressure fixture to remove air bubbles from the uncured paste. A COE-Lite (Model 4000, Imperial Chemical Industries PLC, Macclesfield, Cheshire, UK), was used as the visible light source to cure all specimens. Due to the size of the specimens, the curing light was moved about the surface of the glass molds for a total of 4 minutes, to ensure all test samples were fully cured. After 1 hour in 100% humidity at 37°C, the test specimens were removed from the glass tubing and conditioned in distilled water at 37°C for 7 days, prior to testing. The compressive strength of each specimen was determined by loading the flat ends of the specimen and the diametral tensile strength by loading the sides of the specimens, using a universal testing machine (Instron Model 4204, Instron Corp., Canton, MA, USA) at a crosshead speed of 0.5 mm/min.

$$CS = P/\pi r^2$$

$$DTS = 2P/\pi DT$$

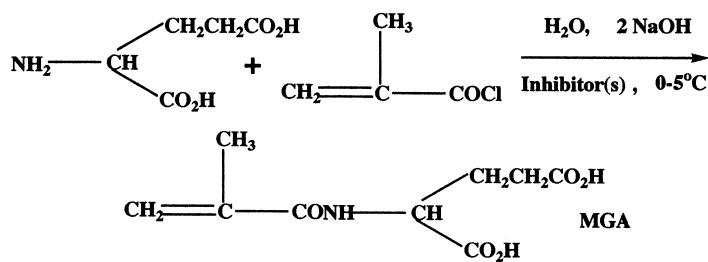
where P = the load at fracture, r = the radius of the sample cylinder, D = the diameter of the cylinder, and T = the thickness of the cylinder.

## RESULTS AND DISCUSSION

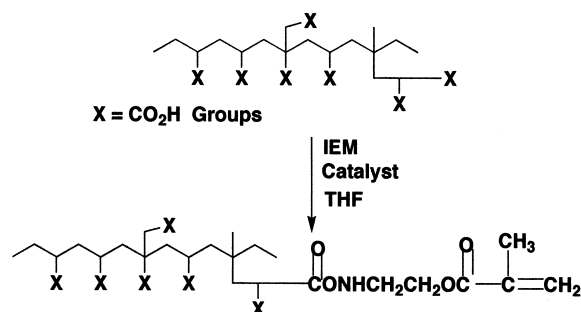
We previously reported that the MGA monomer could be incorporated into poly(AA-co-IA) to produce the poly(AA-co-IA-co-MGA) terpolymers useful for formulating improved glass-ionomers. Furthermore, these terpolymers could be modified or grafted with IEM, producing VLC materials with pendant methacrylate residues. Also, we showed this approach could be used to improve some of the mechanical properties of VLC GIs [23]. Based on the earlier studies, we selected the poly(AA-co-IA-co-MGA) copolymer with a monomers ratio of 8:1:1, respectively, as the polymer backbone for this VLC copolymers study, since that material gave the highest CS value [26].

The MGA monomer was synthesized according to our modified procedure, in which methacryloyl chloride is reacted with glutamic acid in an alkaline medium at low temperature (Figure 1) [26]. The VLC copolymers were prepared by utilizing the 3M patented technique, in which the poly(AA-co-IA-co-MGA) was first formed by free radical polymerization, followed by treatment with IEM to produce copolymers with pendant methacrylate residues (Figure 2) [25]. The FT-IR spectrum of the VLC MGA MP showed the disappearance of the isocyanate ( $\text{-N=C=O}$ ) peak at  $2270\text{ cm}^{-1}$  and formation of the carbon-carbon double bond ( $\text{C=C}$ ) peak at  $1634\text{ cm}^{-1}$ , indicating completion of the grafting reaction. The structure of the VLC MGA MP was also confirmed by NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ).

Since IEM grafting onto the copolymer backbone produces polyelectrolytes having more hydrophobicity and steric hindrance, selection of the graft ratios is based on the concept that salt-bridge formation between carboxylic acid functionalized polymers and calcium-fluoro-alumino-silicate (CaFAISi) glass powder should not be reduced. Further, the correct ratio of the carbon-carbon double bonds pendant on the copolymer must improve the properties of the photocurable GIs. VLC MGA MPs with molar graft ratios ranging from 10% to 20% were prepared, formulated, processed into test samples, conditioned, and tested, to find the best IEM modification/graft ratio. The VLC polymers were formulated with HEMA, water, initiator and activator at the same weight ratio to produce aqueous polymer solutions I, II and III, which were subsequently mixed with the glass powder used in Fuji II LC to determine the CS and DTS values. Polymer solution II, with 15% IEM grafting, exhibited the highest CS (318.7 MPa), while polymer solutions I (10% graft ratio) and III (20% graft ratio) resulted in lower CS values of 206.1 and 273.7 MPa, respectively. Clearly, there can be too little or too much IEM grafting, causing a decrease of the CS values. In contrast, the DTS values changed only slightly, ranging from 45.8 to 48.4



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



**Figure 2.** IEM Grafting Scheme for MGA Polyelectrolyte.

MPa (Table 1). The VLC MGA MP with 15% IEM graft ratio was chosen as the best material for continuing the study to determine the optimal formulation with the highest CS. The VLC GI formulation consists of three major components: VLC polymer (poly), HEMA and water. With the help of a statistical design of experiments (DOE) techniques, the three component ratios were varied to give the optimal proportion in order to achieve the highest CS. For DOE, after determining CS for an initial set of formulations, the CS values are fit, by standard linear regression, to the most basic of models which may be used to relate the CS to concentrations of the three components. The minimum number of formulations for which CS has already been determined is the numbers of parameters, which are in the model to be fit [28]. For this study, the three components contained in the formulations were varied in order to achieve the maximum CS. For the study, the linear model relating the CS to the ratio of components for each formulation studied is given by the equation:

$$P = C_{\text{poly}} f_{\text{poly}} + C_{\text{HEMA}} f_{\text{HEMA}} + C_{\text{water}} f_{\text{water}}$$

where  $P = \text{CS}$ ,  $f_{\text{poly}}$  = fraction of poly,  $f_{\text{HEMA}}$  = fraction of HEMA,  $f_{\text{water}}$  = fraction of water in the formulation,  $C_{\text{poly}}$  = linear coefficient relating CS to  $f_{\text{poly}}$ ,  $C_{\text{HEMA}}$  = linear coefficient relating CS to  $f_{\text{HEMA}}$ ,  $C_{\text{water}}$  = linear coefficient relating CS to  $f_{\text{water}}$ . For any formulation, the condition  $f_{\text{poly}} + f_{\text{HEMA}} + f_{\text{water}} = 1$ , has to be fulfilled.

Four formulations/systems were prepared for Step 1 and their CS were determined and fit to the linear model to determine  $C_{\text{poly}}$ ,  $C_{\text{HEMA}}$ , and  $C_{\text{water}}$ . The linear coefficients were used to calculate the composition of the formulation. The VLC MGA MP concentration was limited to 53% to maintain a working vis-



TABLE 1. Effect of Graft Ratio on Compressive Strengths of Poly (AA-co-IA-co-MGA), 8:1:1, Copolymer

Polymer Solution	IEM (%)	Formulation Poly : Hema : Water			CS (SD) MPa	DTS (SD) MPa
I	10	45	21	34	206.1 (18.7)	48.4 (2.2)
II	15	45	21	34	318.7 (5.5)	45.8 (5.5)
III	20	45	21	34	273.7 (20.1)	46.3 (2.9)

cosity. The four systems A, B, C, and D gave CS values of 318.7, 232.7, 156.6, and 285.9 MPa, respectively (Table 2). The prediction of the maximum CS using these data to fit to the linear model revealed a formulation of 50:21:29 (poly:HEMA:water) with the CS of 329.8 MPa (Table 3). Six additional formulations including the predicted one for Step 2 were also arbitrarily selected which would provide CS values for a more widely dispersed set of mixture compositions, making a total of ten formulations. Their CS values were determined and fit again to the linear model and also fit to the other higher order models. The quadratic model is given by the equation:

$$P = C_{\text{poly}}f_{\text{poly}} + C_{\text{HEMA}}f_{\text{HEMA}} + C_{\text{water}}f_{\text{water}} + C_{\text{PH}}f_{\text{poly}}f_{\text{HEMA}} + C_{\text{PW}}f_{\text{poly}}f_{\text{water}} + C_{\text{HW}}f_{\text{HEMA}}f_{\text{water}}$$

where  $C_{\text{PH}}$  = coefficient relating the CS to the product of fractions of poly and HEMA, and so on for the remaining coefficients,  $C_{\text{PW}}$  and  $C_{\text{HW}}$ .

At least six formulations are required for the quadratic model. The special cubic model containing one additional cubic term requires at least seven mixtures. The six additional systems E, F, G, H, I and J were made and their CS values were determined (Table 2). Although the linear model in Step 1 predicted the maximum CS of 329.5 MPa for a 50:21:29 formulation, the experimental CS of the same system (J) was measured at 344.1 MPa, somewhat higher than predicted.

The surface of the special cubic model as a function of composition at Step 2 is a two-dimensional projection of the three dimensional surface, illustrating the solution of this model (Figure 3). In Step 2, the predicted formulations were 52.5: 21: 26.5 for the linear and the quadratic model with CS of 335.9

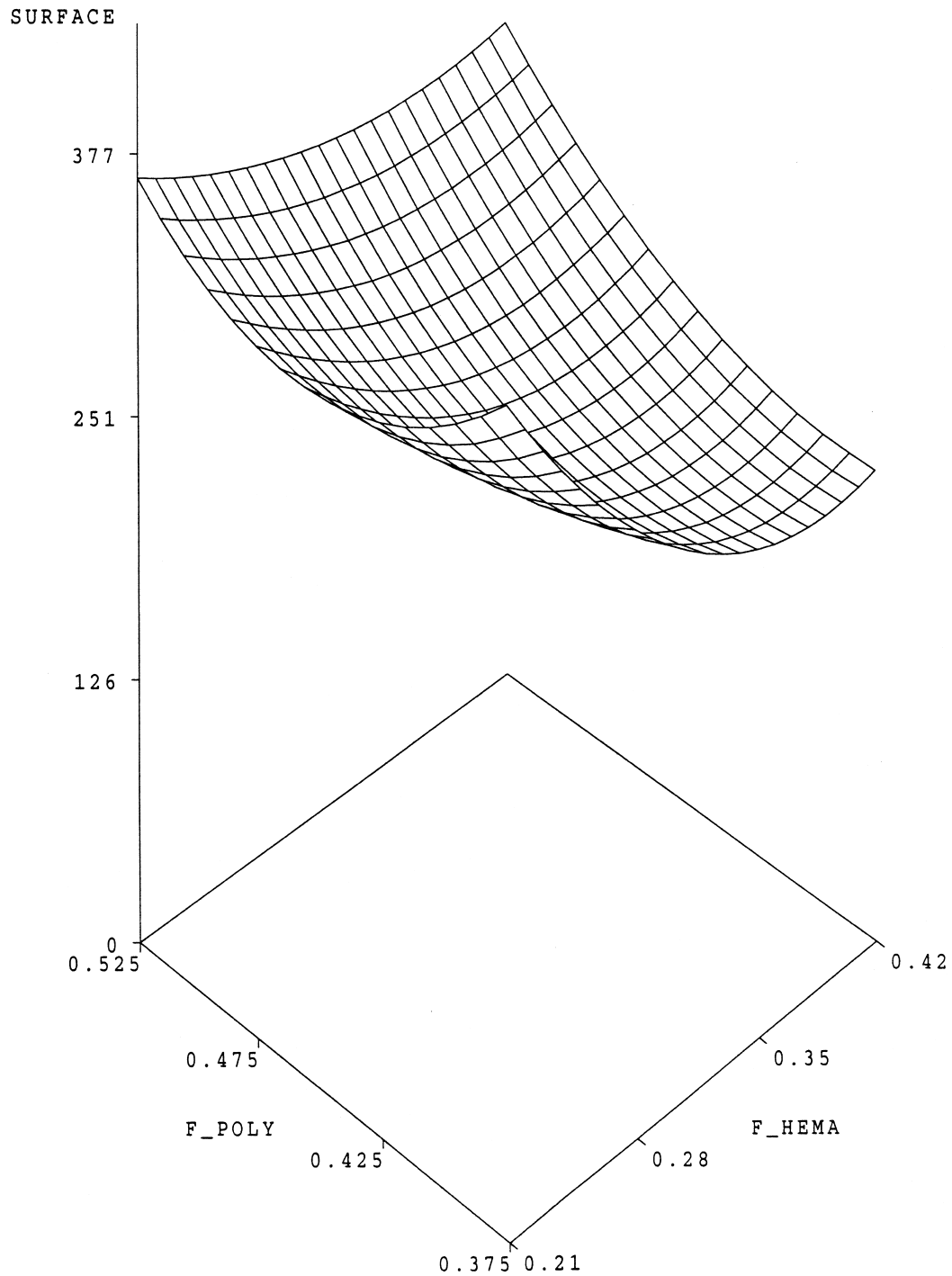
TABLE 2. Compositions of Copolymer Solutions and Mechanical Properties

System	Formulation Poly:HEMA:Water			CS (SD) MPa	DTS (SD) MPa	Modeling Step
A	45	21	34	318.7 (5.5)	45.8 (5.5)	1
B	45	40	15	232.7 (10.2)	40.2 (3.8)	1
C	40	30	30	256.6 (12.6)	43.6 (3.4)	1
D	50	30	20	285.9 (13.5)	43.1 (3.6)	1
E	40	42.5	17.5	234.4 (15.2)	37.3 (3.8)	2
F	37.5	37.5	25	216.9 (9.8)	39.9 (1.5)	2
G	47.5	35	17.5	279.1 (7.1)	45.4 (2.9)	2
H	45	25.5	29.5	279.7 (16.2)	47.3 (3.5)	2
I	45	30	25	249.0 (22.0)	44.3 (3.9)	2
J	50	21	29	344.1 (4.8)	53.9 (3.4)	2
K	35	45	20	183.5 (12.7)	36.6 (2.2)	3
L	50	27.5	22.5	316.0 (6.4)	47.6 (2.4)	3
M	52.5	22.5	25	333.2 (23.3)	52.0 (1.8)	3
N	52.5	18	29.5	370.3 (8.8)	55.4 (5.3)	3
O	35	21	44	196.2 (7.8)	27.5 (2.0)	3

and 363.8 MPa, indicating greater polymer concentration at the expense of water. The special cubic model surprisingly indicated a lower polymer concentration and more water in the (37.5:21:41.5) formulation, to give a predicted CS of 377.2 MPa (Table 3).

TABLE 3. Predicted Formulations Using Design of Experiment (DOE) Based on Compressive Strengths

Model	Predicted Formulation Poly : HEMA : Water			Expected CS (MPa)	Step
Linear	50	21	29	329.8	1
Linear	52.5	21	26.5	335.9	2
Quadratic	52.5	21	26.5	363.8	2
Special Cubic	37.5	21	41.5	377.2	2
Linear	53	15	32	361.5	3
Quadratic	53	15	32	391.6	3
Special Cubic	53	15	32	406.3	3
Full Cubic	53	15	32	412.6	3

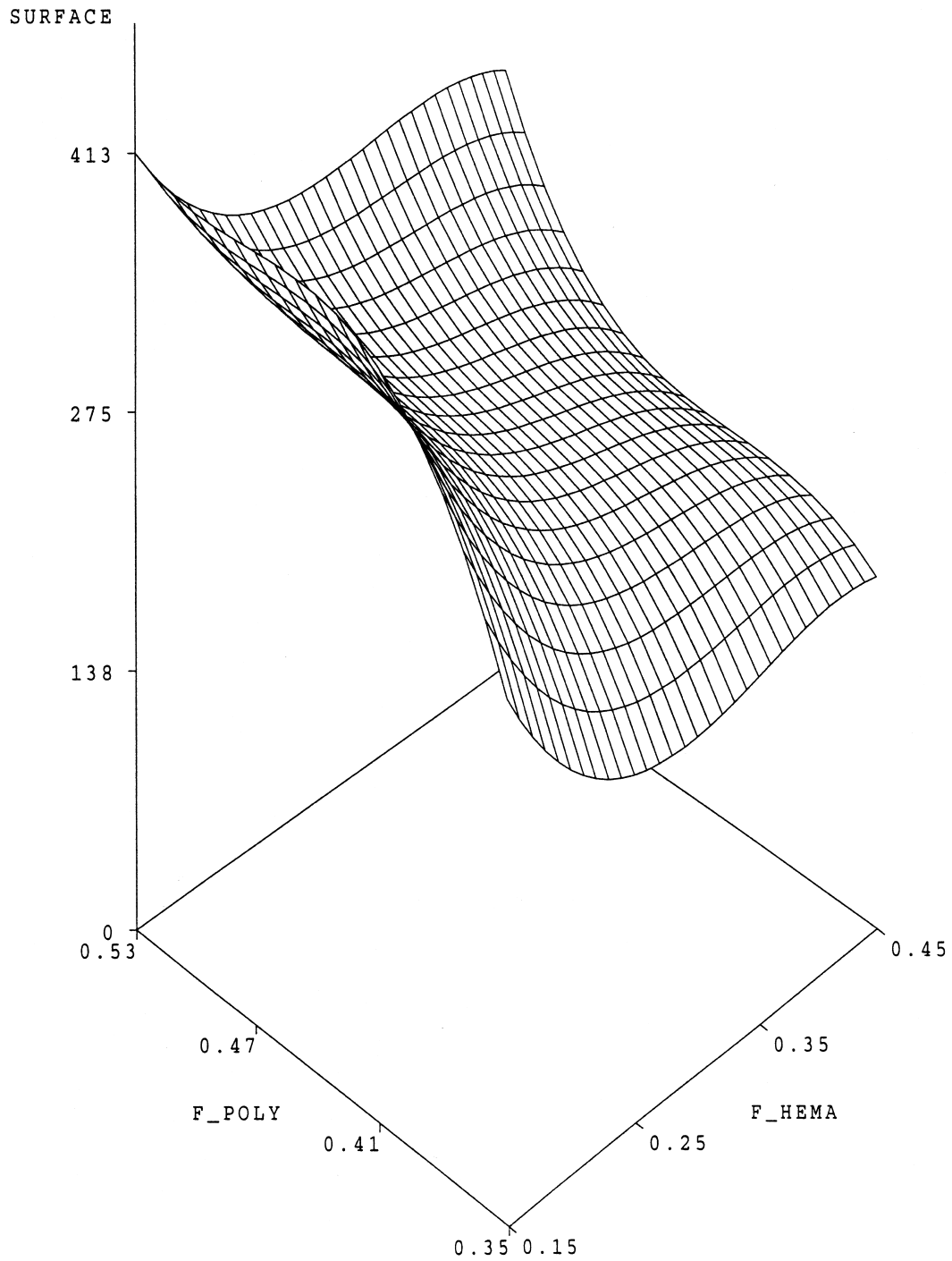


**Figure 3.** The two-dimensional projection of the surface of compressive strength (Mpa) defined by the special cubic model at Step 2, where F-POLY is the fraction  $f_{\text{poly}}$  and F-HEMA is the fraction  $f_{\text{HEMA}}$ . The fraction  $f_{\text{water}}$  is determined by  $f_{\text{water}} = 1 - (f_{\text{poly}} + f_{\text{HEMA}})$ .

Five more systems K, L, M, N, and O were made for Step 3 and tested to obtain additional CS values, since the full cubic model requires a minimum of 10 formulations for which the CS has been determined. All fifteen CS values of the formulations could be fit to four models: the linear, the quadratic, the special and the full cubic model. Based on the linear and quadratic model, the predicted CS of 335.9 and 363.8 MPa for a 52.5:21:26.5 formulation were very close compared to the experimental system M with a CS value of 333.2 MPa for a 52.5:22.5:25 formulation (Table 3). In contrast, the predicted CS of 377.2 MPa for the formulation of 37.5:21:41.5 indicated by the special cubic model (Table 3), system O with a 35:21:44 ratio showed a very low CS of 196.2 MPa. For the third and last step, all the four models predicted that the optimal formulation of 53:15:32 could give the highest CS. The predicted CS were 361.5 (linear), 391.6 (quadratic), 406.3 (special cubic), and 412.6 MPa (full cubic) (Table 3). No more formulations were prepared, since system N with the 52.5:18:29.5 ratio revealed the highest CS of 370.3 MPa, from the fifteen formulations which was comparable with the predicted ones, and due to the limitation of the material used in this study. The DTS values of the fifteen systems were also recorded, with system O giving the lowest of 27.5 and system N the highest DTS of 55.4 MPa (Table 2). The two-dimensional projection of the surfaces of the solution to the full cubic model at Step 3 is also illustrated (Figure 4). The properties of the Fuji II LC control were determined and they showed a decrease of 30% in CS and 33% in DTS compared to system N. The optimal experimental formulation N was mixed with glass powder used in Vitremer<sup>TM</sup> and its properties were compared to the Vitremer<sup>TM</sup> control. The CS value of the system N was slightly higher than Vitremer<sup>TM</sup>, 239.3 compared to 234.3 MPa, while the DTS of Vitremer<sup>TM</sup> was higher (Table 4).

The effects of MGA monomer as a reactive diluent/modifier were investigated by adding the monomer to experimental system N, as well as the Fuji II LC and Vitremer<sup>TM</sup> formulations. With 2% MGA added to the two commercial VLC systems, a slightly improved CS for both Fuji II LC and Vitremer<sup>TM</sup> was obtained. System N mixed with glass powder used in Vitremer<sup>TM</sup> had a slightly increased CS. But, system N mixed with glass powder used in Fuji II LC had a slightly decreased CS. DTS values for all formulations were also determined (Table 4).

The replacement of HEMA with MGA monomer in the optimal formulation N ranged from 1 to 2%. A slightly decreased CS was noted for the system Na with 1% replacement, with the cause no yet known. However, an



**Figure 4.** The two-dimensional projection of the surface of compressive strength (Mpa) defined by the special cubic model at Step 3, , where F-POLY is the fraction  $f_{poly}$  and F-HEMA is the fraction  $f_{HEMA}$ . The fraction  $f_{water}$  is determined by  $f_{water} = 1 - (f_{poly} + f_{HEMA})$ .

TABLE 4. Mechanical Properties of Copolymer N Formulations Compared to Commercial Controls

System	P/L Ratio	CS (SD) MPa	DTS (SD) MPa
Fuji II LC	3.0:1	283.0 (16.9)	41.7 (2.5)
Fuji II LC + 2% MGA	3.0:1	293.3 (12.3)	40.5 (3.5)
Sys N/Fuji II LC	3.0:1	370.3 (8.8)	55.4 (5.3)
Sys N + 2% MGA/Fuji II LC	3.0:1	362.2 (10.6)	59.6 (3.8)
Vitremer <sup>TM</sup>	2.5:1	234.3 (3.4)	43.0 (1.2)
Vitremer <sup>TM</sup> + 2% MGA	2.5:1	239.4 (7.8)	40.1 (2.2)
Sys N/Vitremer <sup>TM</sup>	2.5:1	239.8 (10.0)	38.5 (4.2)
Sys N + 2% MGA/Vitremer <sup>TM</sup>	2.5:1	245.2 (6.4)	46.7 (2.6)

increase of CS could possibly be attributed to the fact that too small a number of pendant acid residues had been incorporated into the poly(HEMA) crosslinking segments, between the main polyelectrolyte chains, to make a significant difference in salt-bridge formation. System Nb, with 1.5% and Nc with 2% showed slightly higher CS values. The increase may indicate that starting from 1.5% replacement of HEMA, the carboxylic acid group of MGA may compensate for the dilute effect on viscosity and foster more salt-bridge formation compared to HEMA. The effect of MGA monomer on the DTS values was inclusive, with system N still showing the best DTS (Table 5).

TABLE 5. Mechanical Properties of Modified Copolymer N Formulations

System	Compositions				CS (SD) MPa	DTS (SD) MPa
	Poly : HEMA : MGA : Water					
N	52.5	18	0	29.5	370.3 (8.8)	55.4 (5.3)
Na	52.5	17	1	29.5	365.1 (7.1)	49.6 (5.5)
Nb	52.5	16.5	1.5	29.5	372.5 (15.0)	46.2 (2.1)
Nc	52.5	16	2	29.5	377.7 (9.4)	49.1 (5.0)

## CONCLUSION

In this study, glass powder used in commercial Fuji II LC glass-ionomer was employed to determine the CS value of experimental VLC polymer formulations. Based on our previous studies, poly (AA-co-IA-co-MGA) with the optimal ratio of 8:1:1 was chosen as the polymer backbone for the VLC research. VLC polymers were prepared under the same conditions reported in a patent by 3M Dental Products [25]. The polymer backbone was synthesized by free radical polymerization, then reacted with IEM to produce VLC copolymers having pendant methacrylate residues. From three copolymers with graft ratios ranging from 10% to 20%, the polymer with 15% IEM grafting showed the highest CS value, which was subsequently used in this study to find the optimal formulation. Design of experiment (DOE) methods were employed to find the best formulation with the highest CS. System N with the formulation of 52.3:18:29.5 (poly:HEMA:water) was the best, showing an improvement of 30% in CS and 33% in DTS, compared to the commercial Fuji II LC. System N was also mixed with glass powder used in Vitremer<sup>TM</sup> to produce specimens for testing. In this case, the CS was slightly higher, while the DTS was slightly lower than the one for Vitremer<sup>TM</sup>.

The effects of MGA monomer were evaluated in two ways: 1) MGA was combined with two commercial VLC formulations, and 2) MGA was used to partly replace HEMA in the optimal experimental formulation. MGA addition (2% ) as a diluent/modified in the Fuji II LC and Vitremer<sup>TM</sup> liquid components, as well as the N system, showed a slightly improved CS value for Fuji II LC and Vitremer<sup>TM</sup>, but a slightly decreased CS for system N. Using MGA to replaced HEMA in the range of 1% to 2% in system N resulted in lower CS for the 1% and a higher CS value starting at the 1.5% concentration

Based on this research, we will attempt to discover answers for the following type questions: 1) Are we still able to improve CS by trying to enhance the working viscosity, meaning to increase the polymer concentration in the optimal experimental formulation to more than 52.5% by using a lower molecular weight polymer? 2) What happens if concentrations of MGA monomer used are >2% or completely replaces HEMA? For the optimal system N, with the Fuji II glass and with MGA modification (Table 2), we need to determine other properties, such as flexural strength, hardness, fracture toughness, adhesion to tooth surface, fluoride release, etc., compared to commercial VLC systems.

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