Improved Flexural Strength of N-Vinyl-Pyrrolidone Modified Acrylic Acid Copolymers for Glass-Ionomers

Dong Xie[a]; Bill M. Culbertson[a]; William M. Johnston[a]

[a] College of Dentistry, The Ohio State University, Columbus, Ohio

PLEASE SCROLL DOWN FOR ARTICLE

IMPROVED FLEXURAL STRENGTH OF N-VINYL-PYRROLIDONE MODIFIED ACRYLIC ACID COPOLYMERS FOR GLASS-IONOMERS

Dong Xie, Bill M. Culbertson *, and William M. Johnston
College of Dentistry
The Ohio State University
305 West 12th Avenue
Columbus, Ohio 43210

Key Words: N-Vinylpyrrolidone Modified Copolymers, Optimal Molar Ratio, Molecular Weight, Flexural Strength, Viscosity

ABSTRACT

The flexural strengths of N-vinylpyrrolidone modified glass-ionomer cements were investigated. The optimal molar ratio of the monomers in copolymers, composed of the three components acrylic acid, itaconic acid and N-vinylpyrrolidone, was determined using a SAS statistical program. The copolymers were prepared using a free-radical polymerization process. The viscosities of aqueous solutions of these polymers were determined. Cements were formed by the reaction of these solutions with glass particles. Flexural strength (FS) was used as the basic screening property to find the optimum molar ratio. Statistical models were applied to predict the optimum molar ratios. All strength values were recorded on the specimens conditioned in distilled water at 37°C for 7 days. The optimal molar ratio for these copolymers was 7:1:3 for poly(acrylic acid-co-itaconic acid-co-N-vinylpyrrolidone), based on flexural strength and viscosity. The effect of molecular weight (MW) on FS was also evaluated. Copolymer with a MW of 10,800 (M_n) showed 85% higher FS than the Ketac-Molar (KM) system, along with a reasonable working viscosity.

INTRODUCTION

Since glass-ionomer cements were introduced to the dental community in 1971 by Wilson, *et al.* [1], they have gained considerable attention and popularity [2-5]. Their attractive properties [2, 6] such as direct adhesion to moist tooth structure and base metals, anticariogenic properties due to release of fluoride, thermal compatibility with tooth enamel because of low coefficients of thermal expansion similar to those of tooth structure, biocompatibility and low cytotoxicity, make them more promising as a restorative filling material than other restoratives. Unfortunately, the low tensile and flexural strengths, or brittleness, of the existing formulations make the cements unsuitable for use in high-stress sites. These cements must be improved in strength and brittleness in order to find a wider range of applications.

With the present glass-ionomer formulation, the major problem resides in that the acrylic acid homo- or copolymers have -COOH groups which are directly attached to the backbone and are closely oriented to each other. Not all the carboxyl groups of polyacids are converted to carboxylate groups during the course of the reaction. Some free COOH groups remain unreacted because they are inaccessible for steric reasons, and also due to the fact that the polyacrylate chain is largely ionized, the remaining hydrogen becomes firmly bound by electrostatic forces; as a result, the metal ions are increasingly hindered in their movements to react at carboxyl sites [7, 8]. It is presumed that the strength and fracture resistance of the material are therefore, weakened due to this steric hindrance, which brings about significantly reduced -COO$^-$ $^{+++}$Al interaction (cluster or salt bridge formation) in the cement.

Polymers containing a flexible spacer linking the main chain to the pendant functionality allow greater mobility of both the main chain and/or spacer linked functionality to assume desired configurations, resulting in improved fracture toughness in the cement [9, 10].

In addition to solely introducing tough polymer structures, mechanical strengths can also be enhanced by improving the working properties [11, 12].

N-vinylpyrrolidone (NVP)-containing polymers have very unique water retention characteristics and have been widely applied [13] in medicine as a blood plasma substitute for prolonging the action of drugs and for detoxification of the organism, due to their hydrophilicity, non-toxicity and high proclivity to complexation. Thus, NVP is potentially useful for improving the working properties. Our preliminary studies [11, 12] showed that the NVP modified glass-ionomer cements (NVPM GICs) improved both mechanical strengths and working properties.

A significant problem in evaluating copolymerization reactions involving three or more monomers is that many molar ratios may need to be prepared and evaluated in order to determine which is the optimum copolymer for some property. With the help of computer-aided statistical programs, design of experiment (DOE) techniques [14, 15] can be remarkably effective in arriving at the optimal formulation. Simply speaking, a DOE methodology consists of four basic steps [14] as follows:

1. Initial data are generated using a pre-planned experimental design.

2. One or more mathematical models (usually polynomials) are fit to the data by statistical curve-fitting techniques.

3. The response-surface contours are examined to determine the composition regions where the optimal values of the response are predicted by the model or models.

4. Additional blends are made in the selected region to provide additional data for refined predictions or to verify experimentally that the optimum composition has been reached.

This may be an efficient tool to design the experiment with multicomponent systems, such as proportions in a mixture, molar ratios in copolymers, etc.

In formulating dental polymers, polymer and materials scientists often deal with research efforts focused on what mixtures can provide the best mechanical performance and what molar ratio in the copolymers results in the optimum properties. Considering our previous studies [11, 12], we do know that the NVP modified dental glass-ionomer cement with the molar ratio of 7:3:1 showed some improved mechanical properties compared to some standard products. Questions remain about which is the optimum molar ratio and how we can reach this.

The objective of the study was to improve the flexural strength of current glass-ionomer cements by introducing NVP into the backbone of the water soluble copolymer, focusing on finding the optimal molar ratio in a three component [acrylic acid (AA), itaconic acid (IA), NVP] copolymer system. Statistical analysis methods, using flexural strength (FS) as the primary screening tool and viscosity as the auxiliary tool, was used to determine the optimal AA:IA:NVP ratio. The effect of molecular weight on FS for an optimized terpolymer was also explored.

EXPERIMENTAL

Materials

N-vinylpyrrolidone (NVP), acrylic acid (AA) and itaconic acid (IA) were used as received from Aldrich Chemical Co. without further purification. Potas-

sium persulfate ($K_2S_2O_8$), methanol, diethyl ether, and diazald (diazomethane pre-cursor) were also used as received from Aldrich.

Synthesis and Characterization

 Three monomers, AA, IA and NVP were utilized in this experiment to form copolymers and terpolymers, based on our experimental design. To a three-neck reactor containing 0.2 g of $K_2S_2O_8$ (2% of total monomer weight), 80% moles of N-vinylpyrrolidone added and 15 ml of water, a mixture of 0.2 g of $K_2S_2O_8$ (2% of total monomer weight), stoichiometric amount of AA, IA, 20% moles of NVP added and 21 ml of water was added dropwise within one hour. Before the reaction was initiated, the system was purged with N_2 for 30 minutes to displace dissolved oxygen and then the temperature was raised to 95-100°C. After completion of the additions, the polymerization was run for an additional 10 hours at 95°C. The feed molar ratios for the copolymer were varied (AA : IA : NVP), as shown in Table 1.

 The copolymer was recovered by freeze drying (Edwards High Vacuum International). The crude yield was 80-97%. The polymer was purified by dissolving in methanol and precipitation from diethyl ether, followed by drying in a vacuum oven.

 The copolymers were identified by Fourier transform-infrared spectroscopy (FT-IR) and nuclear magnetic resonance (NMR). The FT-IR spectra of the copolymers were obtained with a FT-IR Spectrometer (MIDAC Co.), where the sample film was cast on the NaCl crystal. ^{1}H and ^{13}C NMR spectra of the copolymers were conducted on a Bruker AM 250 MHz NMR analyzer using deuterated methyl sulfoxide as a solvent and trimethylsilane (TMS) as a reference. The copolymer was treated with diazomethane, generated from the diazald reaction with potassium hydroxide in water/ethanol solution at 65°C, to obtain partially esterified products, which were soluble in THF for molecular weight estimations. Molecular weights were estimated by Ashland Chem. Co., using a Waters GPC unit, with standard GPC techniques. Elemental Nitrogen percent for the copolymer was obtained by Desert Analytics, Inc. (Tucson, AZ).

Property Determinations

 All copolymer solutions were made by mixing with distilled water, with the proportion of copolymer: water = 50/50 (wt/wt). Glass powder used in this study was the one used in the Ketac-Molar cement [ESPE GmbH (Seefeld, Germany)], with a powder/liquid ratio (P/L) of 3.1/1, as recommended by ESPE. The sample sizes were n = 6 for each material. Specimens were fabricated as described previously [11, 12]. Specimens from each material were prepared, using a Teflon

TABLE 1. Molar Ratios and Average Flexural Strength Values

Code	Molar Ratio			Flexural Strength (MPa) (S.D.)	Modeling Step
	AA	IA	NVP		
A	1	1	1	12.68 (2.048)	Step 1
B	5.5	4.5	1	13.76 (1.899)	Step 1
C	3	7	1	14.58 (2.326)	Step 1
D	7	3	0	16.85 (1.108)	Step 1
E	7	3	1	19.47 (1.147)	Step 1
F	8.5	1.5	1	26.60 (3.312)	Step 1
G	7	1	3	31.40 (2.705)	Step 1
H	7	0	3	35.75 (4.118)	Step 1
I	6	2.7	2	29.86 (6.035)	Step 2
J	8	1	2.5	16.79 (2.909)	Step 2
K	5	0	2	21.25 (3.367)	Step 2
L	3	0	2	37.86 (5.469)	Step 2
M	6	0	1	-	Step 2
N	16	0	1	-	Step 2
O	6	1	4.5	15.82 (2.822)	Step 3
P	6	1	3.4	17.92 (3.945)	Step 3
Q	1.4	2.6	1	10.16 (1.383)	Step 3
R	2.2	1.9	1	9.301 (2.024)	Step 3

mold (2 mm wide x 2 mm deep x 25 mm long), removed from the split mold after 10-15 minutes, and stored in distilled water at $37 \pm 2°C$ for 7 days.

Testing of specimens was performed on a Universal Testing Machine (Instron, Model 4202) with a loading rate of 1 mm/min, with the help of a three-point bending assembly, with a span of 20 mm between supports.

Viscosities of the copolymer solutions were determined using a cone and plate viscometer (Rheometrics, Model: RMS - 800). The concentration of each copolymer solution was 50% (wt/wt).

Design of Experiment

A *SAS* statistical program was used in this study for selection of the optimal molar ratio based on FS. Four models (linear, quadratic, special cubic and full cubic) were used for predicting which new molar ratios should be evaluated in order to establish the optimum molar ratio. First eight copolymers were synthesized, tested for average FS, and the data were fit to the statistical models. Based on the models, several new copolymers with different molar ratios were made, characterized, tested for FS and combined with the previous FS determinations for refitting to the models. A total of eighteen copolymers (see Table 1) were prepared and characterized, and used to select the molar ratio which provided the optimum value of FS.
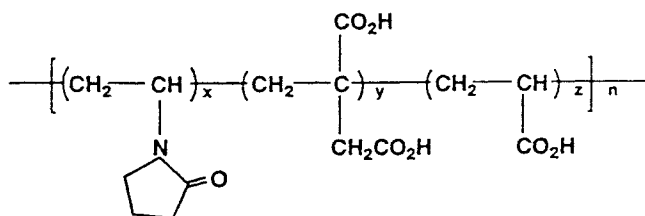
Poly(IA-co-AA) Copolymer:
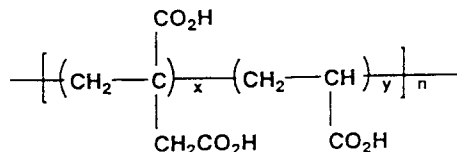
Poly(NVP-co-AA) Copolymer:
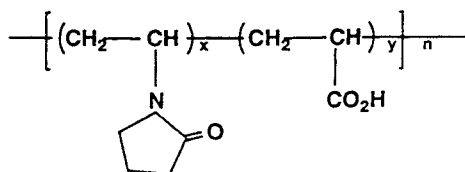
Poly(NVP-co-IA-co-AA) Terpolymer:

Figure 1.   Schematic Structures for Copolymers Used in the Study.

RESULTS AND DISCUSSION

Three types of copolymers were synthesized in this study, which include poly(acrylic-co-itaconic acid) or (AA-co-IA) copolymers, poly(acrylic acid-co-N-vinylpyrrolidone) or (AA-co-NVP) copolymers and poly(acrylic acid-co-itaconic acid-co-N-vinylpyrrolidone) (AA-co-IA-co-NVP) terpolymers, along with varied molar ratios. Their structures are shown in Figure 1.

Characterization

The ^{13}C and ^{1}H NMR chemical shifts of these copolymers are shown in Table 2. The typical ^{1}H and ^{13}C NMR chemical shifts for the carboxyl group were at 12.15 ppm and 176.0 ppm. The typical ^{1}H and ^{13}C NMR chemical shifts for the amide group located at 8.30 ppm and 172.0 ppm. As shown in Table 2, poly(AA-

TABLE 2. Characterization of Selected Copolymers

Code	Copolymer	FT-IR (cm⁻¹)	¹H NMR (ppm)	¹³C NMR (ppm)
D	poly(AA-co-IA)	1726 (carboxyl on AA)	12.15 (carboxyl)	176.0 (^{13}COOH)
		1782 (carboxyl on IA)		
G	poly(AA-co-IA-co-NVP)	1720 (carboxyl on AA)	12.20 (carboxyl)	176.0 (^{13}COOH)
		1785 (carboxyl on IA)	8.32 (amide)	172.0 (^{13}CONR$_2$)
		1649 (amide on NVP)		
H	poly(AA-co-NVP)	1714 (carboxyl on AA)	12.20 (carboxyl)	176.0 (^{13}COOH)
		1645 (amide on NVP)	8.30 (amide)	172.0 (^{13}CONR$_2$)
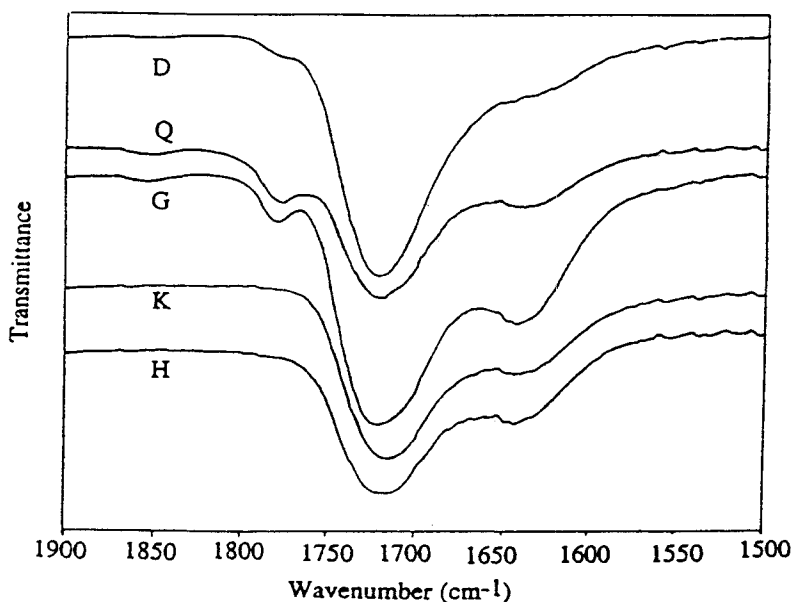
Figure 2.   FT-IR Spectra for Selected Copolymers Synthesized in the Study.

co-IA) copolymer only had the chemical shifts for carboxyl groups, whereas both poly(AA-co-IA-co-NVP) terpolymer and poly(AA-co-NVP) copolymer showed chemical shifts for carboxyl and amide groups. The FT-IR spectra for selected copolymers are shown in Figure 2 and Table 2. For poly(AA-co-IA) copolymers, there is an evident absorption peak at 1784 cm⁻¹ for one of the carboxyl group on the itaconic acid, in addition to a strong peak at 1726 cm⁻¹ for the acrylic acid. For poly(AA-NVP) copolymers, there exists a broad peak at 1647 cm⁻¹ for the amide group on the pyrrolidone ring, except for one at 1726 cm⁻¹ for the acrylic acid. For

TABLE 3. Number of Coefficients in Models as Function of Number of Components (adapted from [14])

Number of components	Model			
	Linear	Quadratic	Special cubic	Full cubic
2	2	3	-	-
3	3	6	7	10
4	4	10	14	20

poly(AA-co-IA-co-NVP) terpolymers, the above three peaks exist. With the change of molar ratio, the absorption peaks changed. As illustrated in Figure 2, Copolymer D had no NVP in it, so there was no band at 1647 cm^{-1}. Copolymer Q contained more IA and less NVP, resulting in a weaker peak at 1647 cm^{-1} and a stronger band at 1784 cm^{-1} than Copolymer G. Both Copolymer K and H had no IA in their backbone, leading to no absorption peak at 1784 cm^{-1}.

Selection of the Optimal Molar Ratio

Flexural strength (FS) was used as a tool to evaluate the mechanical prop-erties of our experimental dental glass-ionomers, composed of the synthesized copolymers and glass powders. Prosser et al. [16] proposed that the most approp-riate measure of the strength of glass-ionomer cements was FS, because a material could fail by the separation of the planes of atoms (i.e., tensile failure), or by the slipping of the planes of atoms (i.e., shear failure). The FS test is a collective measurement of three types of stresses simultaneously, i.e., tensile (at one surface of the specimen beam), compressive (at the other surface) and shear (in the direction which is parallel to the load) stresses [17]. Williams et al. [18] also suggested that, from the clinical viewpoint, the FS test would be more appropriate. Hence we chose FS as the primary property used to determine the optimum molar ratio.

Statistical design of experiment is an efficient way to find the optimum molar ratio for the copolymers. Based on the ideas of response-surface method-ology developed by Box and Wilson [19], there are four models which may be used in our studies. For three components, in general, if there are seven to nine experi-mental data points, the linear, quadratic, and special cubic models will be applicable for use in prediction. If there are ten or more data points, the full cubic model will also be applicable, as shown in Table 3.

Looking at our systems from a very basic standpoint, if three monomers AA, IA, and NVP are combined statistically, only seven combinations exist, i.e.,

three homopolymers (poly(AA), poly(IA) and poly(NVP)), three copolymers (poly(AA-co-IA), poly(IA-co-NVP) and poly(AA-co-NVP)), and one terpolymer (poly(AA-co-IA-co-NVP)). In fact, as we know, only four polymers (poly(AA), poly(AA-co-IA), poly(AA-co-NVP) and poly(AA-co-IA-co-NVP)) are practically useful, whereas poly(IA), poly(NVP) and poly(IA-co-NVP) are not considered useful. Poly(AA) is used only under molecular weight of 40,000. Above this range, the polymer solution is unstable and polyacids will precipitate [20, 21]. Itaconic acid (IA) tends to copolymerize with other monomers but does not like to polymerize with itself. Homopolymerization of itaconic acid causes production of polymers with low molecular weight, leading to poor mechanical properties. Since there is no acid on the poly(NVP) backbone, poly(NVP) cannot react with basic glass powders to produce glass-ionomers. Poly(AA-co-IA) is being used in commercial Fuji II glass-ionomer formulations. Poly(IA-co-NVP) is theoretically not good, due to the same reason as explained for poly(NVP). Poly(AA-co-NVP) showed some good mechanical properties [22]. Our previous studies [11, 12] showed that poly(AA-co-IA-co-NVP) terpolymer had very good feasibility for improved glass-ionomer formulations.

To start our experiments, we chose eight molar ratios in the first step (Step 1), as shown in Table 1 (A-H). The eight starting molar ratios were selected based on both our previous studies [11, 12] as well as studies by others [20, 21], and the concepts that copolymer forming glass-ionomers must contain carboxylic acids. After synthesis and purification of copolymer and formation of glass-ionomer, the FS was measured, with the results shown in Table 1 and Figure 3. Only three models (specific cubic, quadratic and linear) could be used in Step 1, since only eight data points were collected. The special cubic model told us that molar ratios should be selected at those compositions which contain more NVP and/or AA mole fractions, as shown in Table 4. The special cubic model of Step 1 indicated that the next predicted point (AA, IA, NVP) should be taken at (0.663, 0.007, 0.33) with the expected FS of 37.3 MPa. The quadratic model predicted the point at (0.773, 0.007, 0.22) to give a strength of 37.5 MPa. The linear model indicated exactly the same point as the special cubic model, with the predicted strength of 31.6 MPa. Based on these models, we chose the following six points, which were around the points predicted by the models: I (0.5643, 0.25075, 0.185), J (0.6895, 0.0885, 0.222), K (0.7173, 0, 0.2827), L (0.606, 0, 0.394), M (0.8571, 0, 0.1429) and N (0.9412, 0, 0.0588).

After completion of the second step of syntheses and evaluations, a new set of strength data were obtained, as shown in Table 1 and Figure 3 (A-L).
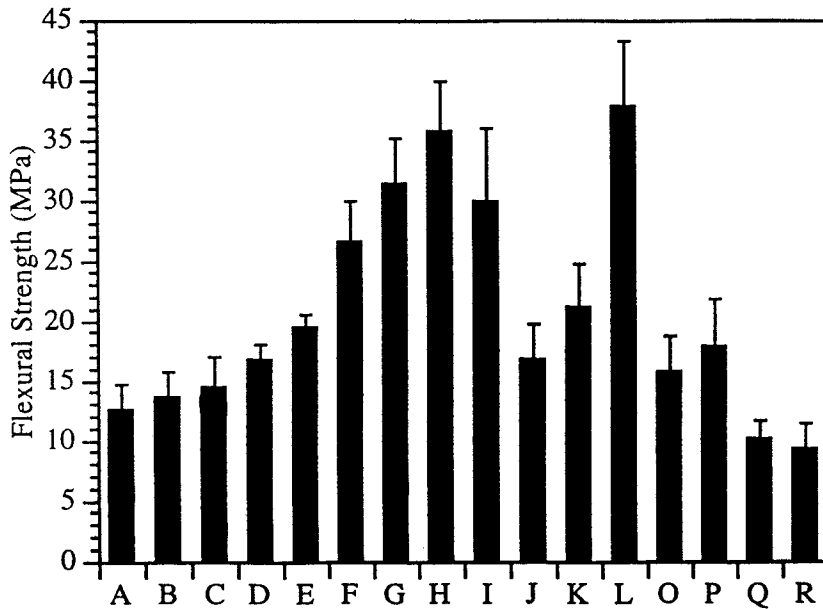
Figure 3. Flexural Strengths for Glass-Ionomers by the Copolymers Used in the Study. The error bars represent the standard deviation (S.D.). Table 2 gives the molar ratios of the compositions A- R.

TABLE 4. Predicted Molar Ratios for Each Modeling Step

Model	Predicted Point			Expected FS (MPa)	Step
	AA	IA	NVP		
Linear	0.663	0.007	0.330	31.60	1
Quadratic	0.773	0.007	0.220	37.50	1
Special Cubic	0.663	0.007	0.330	37.30	1
Full Cubic	-	-	-	-	1
Linear	0.603	0.007	0.390	30.70	2
Quadratic	0.603	0.007	0.390	34.60	2
Special Cubic	0.523	0.087	0.390	42.70	2
Full Cubic	0.273	0.527	0.200	73.60	2
Linear	0.773	0.007	0.220	28.00	3
Quadratic	0.733	0.007	0.260	29.70	3
Special Cubic	0.723	0.007	0.270	29.80	3
Full Cubic	0.603	0.007	0.390	31.50	3

Unfortunately, the copolymers with the molar ratios at M and N could not be evaluated because the aqueous polymer solutions were not stable. In this case, hydrogel formation occurred in the water solutions. It has been noticed that a high amount of acrylic acid in the system would cause unstable aqueous solution formation [21, 23]. As we can see from Table 4, the special cubic model from Step 2 still directed us to go towards more NVP and a little more IA were involved, i.e., at (0.523, 0.087, 0.39), with the expected strength of 42.7 MPa. The full cubic model directed us to select compositions of more 1A, less AA and less NVP, i.e., at (0.273, 0.527, 0.2), with the expected strength of 73.6 MPa. At the same time, linear and quadratic models also indicated the similar trend to the direction that the special cubic asked, i.e., both at (0.603, 0.007, 0.39), with expected strengths of 30.7 and 34.6 MPa, respectively. We chose four data points at O (0.523, 0.087, 0.39) and P (0.690, 0.088, 0.222), based on the special cubic, linear, and quadratic models, and at Q (0.273, 0.527, 0.20) and R (0.430, 0.370, 0.20), based on the full cubic model.

At Step 3, the flexural strengths did not show any improvements, with the results shown in Table 1 and Figure 3. The new directions predicted by the four models all pointed towards more AA or NVP, with the expected strengths of 28.0 to 31.5 MPa, as shown in Table 4. Since there were no significant improvements in flexural strengths of the materials when the molar ratios were taken at the points towards more NVP or AA, we stopped the optimization process using FS and further evaluated the compositions that had been obtained. At this point, we have synthesized a total of eighteen copolymers in this study and all these molar ratios were concentrated at the regions close to the corner of most AA, as illustrated in Figure 4.

In dental glass-ionomer applications, we need to consider the working properties in addition to the mechanical strengths. In order to know the basic working property of our experimental copolymers, we measured the viscosity of the copolymers using a cone and plate viscometer. The values are illustrated in Figure 5.

Copolymers L and H had the highest flexural strengths (37.86 MPa and 35.75 MPa) but also had the second highest viscosities (108.8 poise and 80.22 poise), which may not be applicable for clinical use. Copolymers A, B, C, J, Q, and R showed lower flexural strengths, even though they had very low viscosities. Copolymers D, P and O had fairly reasonable viscosities but showed still a little low flexural strength values. Copolymer K showed highest viscosity value (114.3
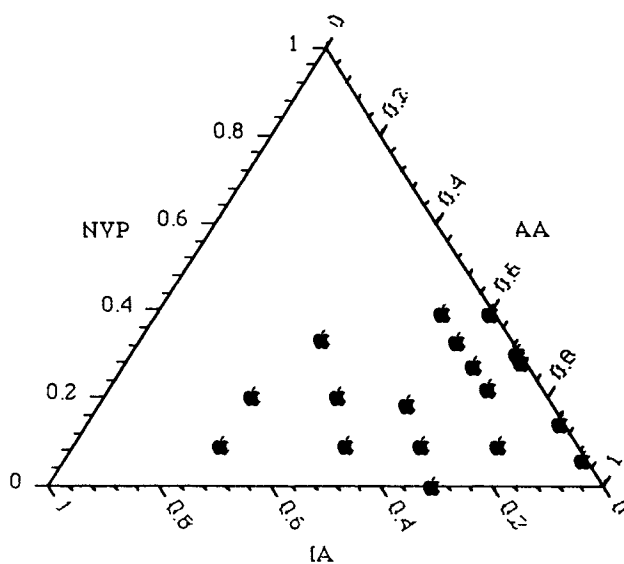
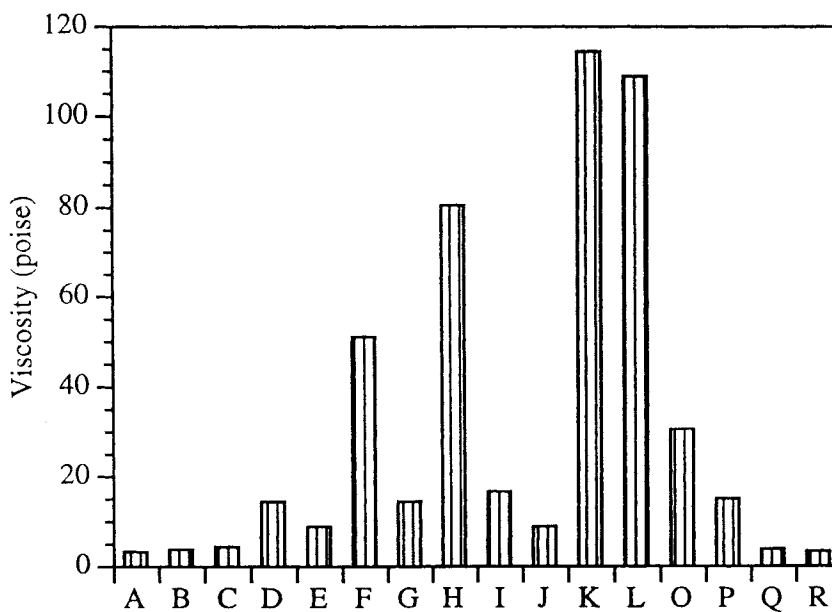**Figure 4.**   Ternary Diagram for Experimental Design.

Figure 5.   Viscosities for Glass-Ionomers Formed by the Copolymers Used in the Study.

TABLE 5. Characterization and Effect of MW of the NVPM TP on the FS of the Cement*

Code	Initiator (%)	Viscosity (poise)	M_n	M_w	PDi	FS (MPa) (S.D.)
a	4	14.27	5510	18700	3.40	31.40 (3.705)
b	1.5	31.78	10800	49200	4.52	39.26 (2.454)
c	0.5	172.0	28800	115000	3.98	51.70 (5.578)

*The concentrations for the initiator were used as a weight percentage of total monomers. M_n, M_w, and PDi represent number average molecular weight (MW), weight average MW, and polydispersity index, respectively.

poise) although its FS value was not too bad (21.25 MPa). Among the rest of the copolymers (E, F, G, and I), copolymer G (7:1:3) had the highest FS value (31.40 MPa) and lower viscosity value (14.27 poise), while the others also showed fairly good FS values (19.47-29.86 MPa) and reasonable viscosities (14.27-50.90 poise). From the above discussion, we concluded that the optimal molar ratio is in the range of 7:1:3 (AA:IA:NVP), based on the flexural strength and viscosity evaluations.

Molecular Weight Consideration and Comparison with the Control

In order to find out the appropriate molecular weight for the NVPM TP with the optimal molar ratio, several concentrations of initiator were used and the effect of MW of the NVPM TP on FS are shown in Table 5 and Figure 6. The results revealed that the FS increased significantly with the molecular weight of the NVPM TP. The higher the MW, the higher the FS. Compared to the commercial control, Ketac-Molar (KM), the NVPM GICs were 47.8%, 84.8% and 143% higher in FS than the KM. Strength is usually increased by increasing the molecular weight of the polyacids [24, 25], since an increase in the molecular weight of the polymer will result in an increase in the matrix strength which results from the increase of the polymer chain length. There exist stronger intermolecular interactions between the longer molecule chains, thus resulting in an increase of strength. Increase in polymer chain length will increase the bonding between filler particles and the polymer matrix. Increases in molecular weight will also increase fracture toughness and resistance to erosion [25]. Combined with the viscosity (Table 5), the NVPM TP b was considered the terpolymer with the best FS, since the Code b terpolymer not only showed higher FS but also exhibited a reasonable viscosity to work with.
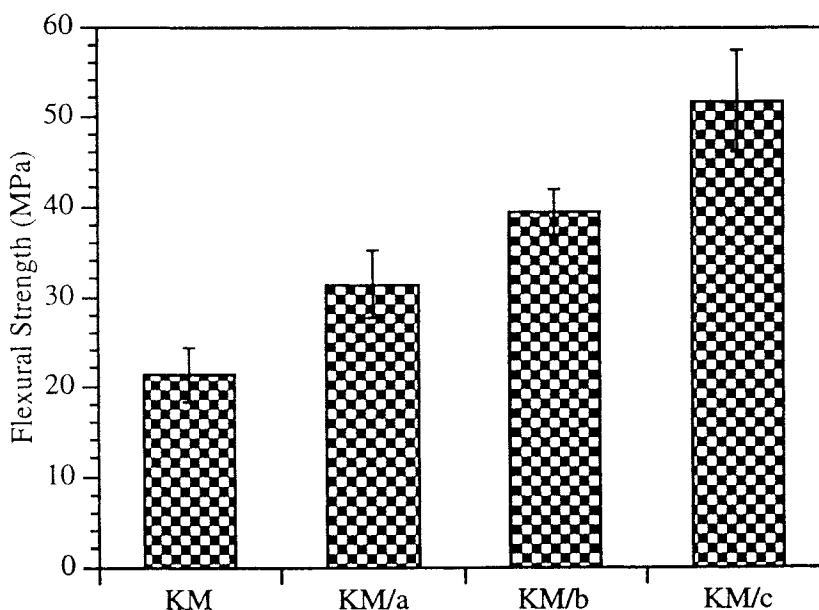
Figure 6. Effect of MW on the FS of the NVPM GICs (Conditioned for 7 days).

CONCLUSION

The N-vinylpyrrolidone modified glass-ionomer cements (NVPM GICs) significantly improved the flexural strength for current commercial GIC, Ketac-Molar (KM). The optimal molar ratio of the copolymers composed of the three monomers AA, IA and NVP was 7:1:3 for poly(AA-co-IA-co-NVP), based on the FS test, using a *SAS* statistical program. The NVPM GICs with different molecular weight (MW) showed improved FS with increasing MW. The experimental copolymer with the MW of 10,800 (M_n) showed 85% higher FS than the commercial KM system, along with a reasonable working viscosity.

Future work in this area of NVP modified AA copolymers for glass-ionomers will involve evaluation of other properties, and formation of the best formulation for their visible light-curable (VLC) versions.

REFERENCES

[1]   A. D. Wilson and B. E. Kent, *J. Appl. Chem. Biotechnol.*, *21*, 313, (1971).

[2]   G. J. Christensen, *JADA, 125*, 1257-8, (1994).

[3]   S. K. Sidhu and T. F. Watson, *Am. J. Dent., 8(1)*, 59-67, (1995).

[4]   A. D. Wilson, *Int. J. Prosthodont., 2*, 438-446, (1989).

[5]   A. D. Wilson, *Int. J. Prosthodont., 3*, 425-429, (1990).

[6]   J. W. McLean, *Dent. Clin. North. Am., 36(3)*, 693-711, (1992).

[7]   S. Crisp, M. A. Pringuer, D. Wardleworth, and A. D. Wilson, *J. Dent. Res., 53(6)*, 1414-1419, (1974).

[8]   S. Matsuya and Y. Matsuya, *Dent. Mater. J.*, *3*, 210-219, (1984).

[9]   E. C. Kao, B. M. Culbertson, and D. Xie, *Dent. Mater., 12*, 44-51, (1996).

[10]   D. Xie, B. M. Culbertson, and E. C. Kao, *J. Dent. Res., 72*, 385, (1993).

[11]   D. Xie and B. M. Culbertson, *J. Dent. Res., 75*, 298 (1996).

[12]   D. Xie and B. M. Culbertson, *J. Dent. Res., 76*, 74 (1997).

[13]   E. A. Bekturov, and Z. Kh. Bakauova, in *Synthetic Water-Soluble Polymers in Solution*, Basel, Huethig & Wepf, 1986, pp. 117-126.

[14]   R. D. Snee, *Chemtech.*, 702-710, Nov. (1979).

[15]   J. N. Cawse and N. Izadi, *Today's Chemist at Work*, 24-28, Jun. (1992).

[16]   H. J. Prosser, D. R. Powis, and A. D. Wilson, *J. Dent. Res., 65(2)*, 146-148 (1986).

[17]   R. W. Phillips, in *Science of Dental Materials*, 9th Ed., W. B. Saunders Co., 1991.

[18]   J. A. Williams, R. W. Billington, and G. J. Pearson, *Br. Dent. J., 172*, 279-282, 1992.

[19]   G. E. P. Box and K. B. Wilson, *Journal of the Royal Statistical Society, Series B, 13*, 1-45 (1951).

[20]   B. E. Kent, B. G. Lewis, and A. D. Wilson, *J. Dent. Res., 58(6)*, 1607-1619 (1979).

[21]   S. Crisp, B. E. Kent, B. G. Lewis, A. J. Ferner, and A. D. Wilson, *J. Dent. Res., 59(6)*, 1055-1063 (1980).

[22]   A. Thakur, Y. Xue, and B. M. Culbertson, *Polym. Prepr., 36(2)*, 400-1 (1995).

[23]   A. D. Wilson and J. W. McLean, in *Glass-Ionomer Cement*, Chicago, Quintessence Publ. Co., 1988.

[24]   A. D. Wilson, S. Crisp, and G. Abel, *J. Dent., 5(2)*, 117-120 (1977).

[25]   A. D. Wilson, R. G. Hill, C. P. Warrens, and B. G. Lewis, *J. Dent. Res., 68(2)*, 89-94, (1989).