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FORMULATION OF VISIBLE LIGHT-CURABLE GLASS-IONOMER CEMENTS CONTAINING N-VINYLPYRROLIDONE

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Key Words: Light-Curable N-vinylpyrrolidone Modified Glass-Ionomer Cements, Graft Ratio, Optimal Formulation, Statistical Design of Experiment, Compressive Strength, Stress-Strain Curve

ABSTRACT

The best graft ratio of the light-curable N-vinylpyrrolidone (NVP) modified terpolymers (LC NVPM TPs) with the molar ratio of 8:2:1 (acrylic acid:itaconic acid:NVP) and the optimal formulation for this light-curable glass-ionomer cement, based on the best graft ratio, were determined. Statistical models were utilized to predict the optimal formulations. The terpolymer was prepared using a free-radical polymerization reaction. The LC NVPM TPs were produced by grafting 2-isocyanatoethyl methacrylate (IEM) onto the terpolymer. Cements were formed by both light-curing and the reaction with glass particles. Compressive strength was used as the basic screening property to find the optimal formulation. Diametral tensile and flexural strengths were also used to evaluate the mechanical properties. The strength values were recorded on the specimens conditioned in distilled water at 37°C for 24 hours or 7 days. The best graft ratio for IEM in this system was 15% of the terpolymer by a molar ratio. The optimal formulation was found to be at the weight ratio of 55:15:30 [LC NVPM TP:2-hydroxyethyl methacrylate (HEMA): H_2O]. Stress-strain curves showed that a

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relatively high amount of water in the formulation led to higher elastic modulus and proportional limit and lower malleability, whereas a relatively high amount of HEMA gave the opposite results. The light-curable NVP modified glass-ionomer cements showed statistically significantly higher values in compressive, diametral tensile, and flexural strengths than the commercial Vitremer™.

INTRODUCTION

Glass-ionomer cements (GICs) are newer generation dental materials that consist of a basic glass and an acidic polymer which set by an acid-base neutralization reaction between these components [1, 2]. Their attractive properties, such as fluoride release [3], thermal compatibility because of a coefficient of thermal expansion similar to that of tooth structure [4], biocompatibility and low cytotoxicity [5], make them useful as luting, lining, and filling materials in clinical applications [6, 7]. However, the low tensile and flexural strengths and brittleness of the existing formulations make the cements unsuitable for use in high-stress sites, particularly where there is lack of support from the cavity wall [8]. Efforts for improvement have been made in several aspects, involving water hardening versions [9], resin-modified GICs (RM GICs) [10-12] and recent formulations of amino acid residue-modified GICs [13, 14] and N-vinylpyrrolidone modified GICs (NVPM GICs) [15, 16].

RM GICs are glass-ionomer hybrid materials, which not only undergo an acid-base reaction, but also contain some methacrylate side chains grafted onto the main polyacid molecules to participate in polymerization [2]. These RM GICs have gained more popularity in restorative dental community since they have more attractive properties compared to conventional (C) GICs. Except for maintaining the clinical advantages of C GICs, these RM GICs reduce the problems of moisture sensitivity and low early mechanical strength associated with C GICs [7, 17], are easier to handle clinically [17] and have significant improvement of some mechanical strengths, such as flexural strength (FS) and diametral tensile strength (DTS) [18, 19]. So far, there have been three major types of RM GICs around the market. One is made of a fluoroaluminosilicate glass powder and an aqueous solution of a copolymer of acrylic and maleic acid, HEMA, water, an initiator and an activator [20]; another is composed of sodium lanthanum calcium aluminum fluorosilicate glass combined with a copolymer of acrylic and maleic acid in dry form and a solution of glass-ionomer-compatible monomers and oligomers, HEMA, water, an initiator and an activator [20]; the third is composed of a calcium fluoroaluminosilicate glass powder and an aqueous solution of a copolymer of a copolymer of acrylic and itaconic acid with pendant methacrylate groups, HEMA, water, initiators and activators [11]. Different commercial RM GICs may vary around these three types. Recently, efforts are being made to further improve the mechanical properties [21].

In this context, we are trying to explore the method to formulate the light-curable (LC) NVPM GICs and find the optimal formulation using a statistical design of experiment. With the help of computer-aided statistical programs, design of experiment (DOE) techniques [22-24] can be remarkably effective in obtaining the best molar ratio in copolymers, the optimal formulation in the mixture, etc., and avoiding unnecessary experiments. A DOE methodology, called response-surface experimentation, consists of four basic steps [22] 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.

The possible models used for a three-component system have been described [22] and used to optimize the FS of a terpolymer [25].

The objective of this study was to determine the best graft ratio of the LC NVPM terpolymers (TPs) and the optimal formulation for the cements made of them, with the help of DOE techniques, using compressive strength (CS) as the primary screening tool. Further, the DTS and mechanical behavior of these LC NVPM GICs were investigated.

EXPERIMENTAL

Materials

NVP, acrylic acid (AA), itaconic acid (IA) and 2-hydroxyethyl methacrylate (HEMA) were used as received from Aldrich Chemical Co. 2-Isocyanatoethyl methacrylate (IEM) was received from Polysciences, Inc. Potassium persulfate ($K_2S_2O_8$), dl-camphoroquinone (CQ), diphenyliodonium chloride (DC), dibutyltin dilaurate (DBTL), triphenylstibine (TPS), butylated hydroxy toluene (BHT), N,N-dimethylformamide (DMF) (anhydrous), methanol and diethyl ether were also used as received from Aldrich Chemical Co. Vitremer™ glass powders were supplied by 3M Dental Products.

Synthesis and Characterization

To a three-neck reactor, containing 0.0788 g of $K_2S_2O_8$, 0.246 g (0.002 mol) of NVP, and 15 ml of water, a mixture of 0.0788 g of $K_2S_2O_8$, 6.387 g (0.088 mol) of AA, 2.883 g (0.022 mol) of IA, 0.984 g (0.008 mol) of NVP 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 around 100°C. After completion of the additions, the polymerization was run for an additional 6 hours at 100°C. The molar feed ratio for the terpolymer was 8:2:1 (AA:IA:NVP).

The terpolymer was recovered by freeze drying (Edwards High Vacuum International). The crude yield was 92%. The terpolymer was purified by dissolving in methanol and precipitation from diethyl ether, followed by drying in a vacuum oven.

The purified terpolymer (10 g) was dissolved in 40 g of anhydrous DMF. The solution was purged with N_2. Inhibitor BHT (0.02 g), catalyst DBTL (0.12 g) and cocatalyst TPS (0.02 g) were added to the solution with constant stirring. After the temperature was raised and maintained at 35-40°C, a solution of IEM (varied from 15-25% mole fraction of the copolymer) in 10 g of DMF was added dropwise to the terpolymer solution. The addition was finished in 45 minutes with stirring. The reaction was completed in a total of three hours. The reaction process was monitored by a Fourier transform-infrared (FT-IR) Spectrometer (MIDAC Co.). The grafted terpolymer was precipitated from the DMF solution by combining it with 500 ml of stirred diethyl ether. The precipitates were washed three times with diethyl ether, collected and dried *in vacuo* below 40°C.

The terpolymer and LC NVPM TPs were identified by FT-IR and nuclear magnetic resonance (NMR). The FT-IR spectra were obtained with a FT-IR Spectrometer, where the sample film was cast on the NaCl crystal. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM 250 MHz NMR analyzer using deuterated methyl sulfoxide as a solvent and trimethylsilane (TMS) as a reference. For determination of molecular weight, the terpolymer was treated with diazomethane, which was generated from diazald reacted with potassium hydroxide in the water/ethanol solution at 65°C, to obtain partially esterified products, having solubility in THF for molecular weight estimation. Molecular weight was estimated by Ashland Chem. Co., using a Waters GPC unit, with standard GPC techniques.

Property Determinations

The formulations for light-curable polymer solutions were made by mixing the LC NVPM TPs with 0.5% (wt/wt) of CQ (photoinitiator), 1% (wt/wt) of DC (activator), 0.1% (wt/wt) of $K_2S_2O_8$ (initiator for redox system), HEMA and distilled water [11]. Glass powder used in this study was the one used in the Vitremer™ tri-cure glass-ionomer system (3M Dental Products), with a powder/liquid ratio (P/L) of 2.5/1, as recommended by 3M Dental Products. Twelve specimens for each formulation were prepared for CS and DTS tests (six for each test). Six specimens for each material were also prepared for the FS test. Specimens were fabricated similar to the procedures used for the conventional glass-ionomers, as described previously [15, 16], except that the curing process was completed by using a COE-Lite (Model 4000, Imperial Chemical Industries PLC, Macclesfield, Cheshire, UK) light source. Glass tubing was used to make the specimens with 4 mm in diameter x 8 mm in height for CS, and 4 mm in diameter x 2 mm in thick-ness for DTS, with the help of a pressure fixture to remove air bubbles from the uncured paste. A split Teflon mold, with a glass window for light exposure, was used to make the specimens with 2 mm in width x 2 mm in thickness x 25 mm in length for FS. Specimens were exposed to the visible light for about 4 minutes using a COE-Lite light source. Specimens were then removed from the glass tubing after one hour and the split mold after 10-15 minutes in 100% humidity. The specimens were finally stored in distilled water at 37 ± 2°C for 24 hours, for all formulation tests, and 7 days, for stress-strain curves and final comparison tests.

Testing of specimens was performed on a Universal Testing Machine (Instron, Model 4202) with a loading rate of 1 mm/min for all CS, DTS and FS tests. The FS test was performed with the help of a three-point bending assembly, with a span of 20 mm between supports. For some selected specimens, the compressive stress-strain curves were obtained. In order to accurately obtain the strain of the specimens, a piece of extremely thin rigid stainless steel (thickness = 0.08 mm, diameter = 4 mm) was used to obtain the displacement of the loading frame as a function of applied force. This loading frame displacement was subtracted from the observed displacement of the glass ionomer specimens and, therefore, the strains for these specimens were corrected.

One-way analysis of variance (ANOVA) with post-hoc multiple comparison using Tukey-Kramer test, was used to determine the significant differences in CS, DTS and FS, between the experimental cements and Vitremer™. A level of 0.05 was considered as not significant.

Statistical Design of Experiment

A *SAS* statistical program was used in this study for selection of the optimal formulation (weight ratios for LC NVPM TP, HEMA and water), based on CS. Four models (linear, quadratic, special cubic and full cubic [22, 25]) were used for predicting which new formulations should be evaluated in order to establish the optimum formulation. Ten formulations were first produced, tested for average CS, and the data fit to the statistical models. Based on the models, the new formulations with different weight ratios were made and tested for CS and combined with the previous CS test results for refitting to the models. A total of fifteen formulations were ultimately prepared and used to select the formulation which provided the optimum value of CS.

RESULTS AND DISCUSSION

The copolymer used in this study was a poly(AA-co-IA-co-NVP) terpolymer with the optimal molar ratio of 8:2:1, which exhibited an optimal CS [25]. The grafting reactions were conducted on this terpolymer with the optimal molar ratio. The reaction scheme for forming light-curable polymers is illustrated in Figure 1A. Basically, 2-isocyanatoethyl methacrylate (IEM) containing both carbon-carbon double bond (C=C) and isocyanate (-N=C=O) reacts with the carboxylic acid groups on the terpolymer, forming an amide bond and leaving the double bond untouched. During formation of glass-ionomers, the terpolymer with pendant double bonds forms dual curing networks by producing salt-bridges and covalent crosslinks, resulting in strengthening the glass-ionomer cements, as shown in Figure 1B. This type of glass-ionomers is named resin modified glass-ionomer cements (RM GICs) [18].

Characterization

The FT-IR spectra for the terpolymer (Curve I), IEM (Curve II) and IEM grafted terpolymer (Curve III) are illustrated in Figure 2 and the peak values are shown in Table 1. Curve I gives three typical bands at 1721, 1781 and 1646 cm^{-1} for carboxyl group on AA, carboxyl group on IA and amide on NVP. Curve II

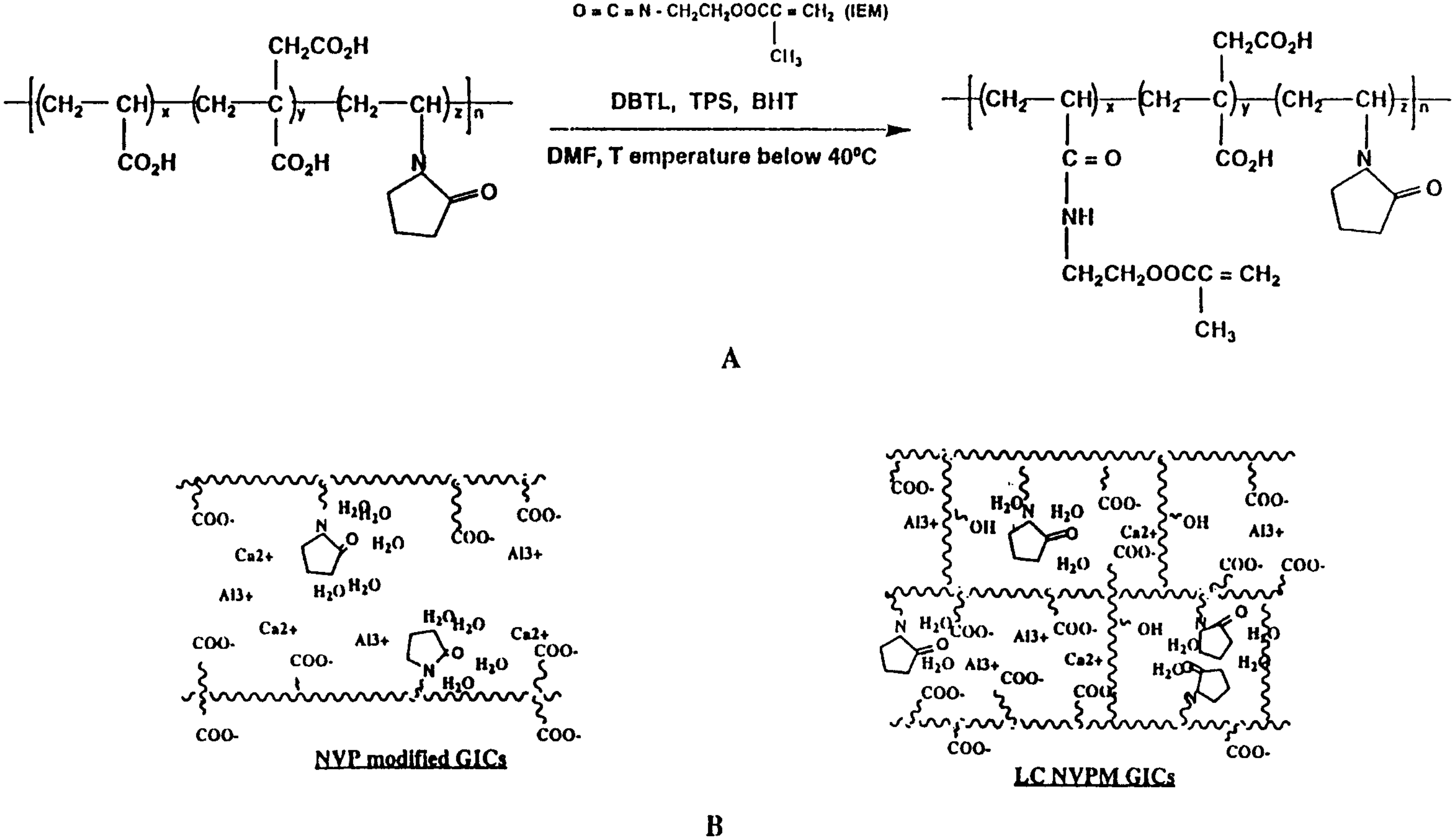

Figure 1. A. Reaction scheme for formation of light-curable terpolymer. B. Scheme for descriptive microstructure of both NVP modified glass-ionomer and its light-cured version.

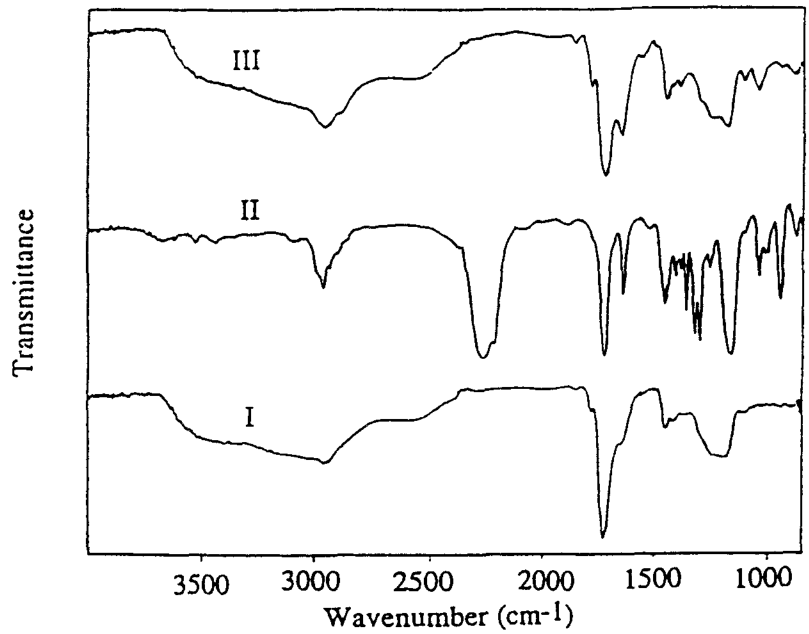

Figure 2. FT-IR spectra for description of light-curable terpolymer formation. Curves I, II and III represent the FT-IR spectra for poly(AA-co-IA-co-NVP) terpolymer, IEM, and IEM Grafted NVP modified terpolymer (LC NVPM GICs), respectively.

TABLE 1. Characterization of NVP Modified Terpolymer and LC NVPM TP*

opolymer	FT-IR (cm^{-1})	^{1}H NMR (ppm)	^{13}C NMR (ppm)	MW
oly(AA-co-A-co-NVP)	1721 (carboxyl on AA) 1781 (carboxyl on IA) 1646 (amide on NVP)	12.20 (COOH) 8.32 (CONR$_2$)	176.0 (^{13}COOH) 172.0 (^{13}CONR$_2$)	14800 (M$_n$) 45200 (M$_w$) 3.05 (PD$_i$)
C NVPM TP	1721 (carboxyl on AA) 1781 (carboxyl on IA) 1646 (CONR$_2$ and CONHR) 1644 (C=C double bond)	12.20 (COOH) 8.00 (CONR$_2$) 7.50 (CONHR) 5.70 and 6.10 (=CH$_2$) 7.95 (=C-H)	176.7 (^{13}COOH) 172.0 (^{13}CONR$_2$) 162.4 and 166.6 (^{13}CONHR) 126.9 and 127.0 (=^{13}CH$_2$) 136.8 (=^{13}C-H)	

LC NVPM TP is an abbreviation of the light-curable NVP modified terpolymer.

shows a strong peak at around 2271 cm^{-1}, which represents the isocyanate (NCO) group, and a sharp peak at 1644 cm^{-1} for the carbon-carbon double bond (C=C). Disappearance of the isocyanate (NCO) peak at around 2271 cm^{-1} and formation of the carbon-carbon double bond (C=C) peak at 1646 cm^{-1} confirmed the completion of the grafting reaction. Curve III clearly shows the disappearance of the NCO peak and appearance of the double bond, compared to Curves I and II. The ^{1}H and ^{13}C NMR chemical shifts of the poly(AA-co-IA-co-NVP) terpolymer and LC NVPM TP are shown in Table 1. For poly(AA-co-IA-co-NVP), the typical ^{1}H and ^{13}C NMR chemical shifts for the carboxyl group were at 12.20 and 176.0 ppm, while the typical ^{1}H and ^{13}C NMR chemical shifts for the amide ($CONR_2$) group on NVP located at 8.32 and 172.0 ppm. For the LC NVPM TP, except those peaks for the terpolymer, the ^{1}H and ^{13}C NMR chemical shifts for newly formed amide (CONHR) group from the grafted IEM were observed at 7.50 ppm, and 164.4 and 166.6 ppm. The carbon-carbon double bond was observed at 5.70 and 6.10 ppm ($=CH_2$) and 7.95 ppm (=C-H) for ^{1}H NMR chemical shifts, and 126.9 and 127.0 ppm ($=^{13}CH_2$) and 136.8 ppm ($=^{13}C$-H) for ^{13}C NMR chemical shifts. The number average molecular weight (M_n) and the weight average molecular weight (M_w) of the terpolymer with the optimal molar ratio were 14800 and 45200, as shown in Table 1.

Selection of the Best Graft Ratio

Selection of the graft ratio was conducted based on the concept that the amount of graft molecules would not reduce the basic reaction units (carboxylic acid) to react with cations (Ca^{++} and Al^{+++}) from the glass powders. Therefore, an insufficient or excessive grafting will result in lower strengths. In this study, four graft ratios were utilized to find the best graft ratio, as shown in Table 2. Based on the CS and DTS, the LC NVPM TP with a graft molar ratio of 15% exhibited the highest values in both CS and DTS. The polymer with 20% graft ratio showed the second highest next to the one with 15%. The one with 25% was the lowest among the group. The reason why an excessive grafting led to lower strengths may be attributed to decrease of capacity of acid-base reaction in glass-ionomers. An insufficient grafting also brought about lower strengths. The possible explanation is that there is not enough double bond to make strengths to jump to certain high values. By selection, the terpolymer with 15% graft ratio was used as our optimal light-curable terpolymer in this study.

Statistical Design of Experiment for Determination of the Optimal Formulation

After the terpolymer with optimal graft ratio was selected, the next step would be determining the optimal formulation. In the light-curable glass-ionomer

TABLE 2. Effects of Graft Ratio on Strength of Copolymer*

Code	Graft Ratio (mole %)	CS (MPa) (S.D.)	DTS (MPa) (S.D.)
A	10	175.8 (5.600)	34.32 (2.067)
B	15	210.3 (5.189)	38.92 (2.206)
C	20	198.3 (10.62)	36.80 (3.053)
D	25	171.3 (2.843)	32.73 (1.027)

*The molar ratio of the terpolymer was 8:2:1. The formulation was used as follows: 0.45:0.21:0.34 (LC NVPM TP : HEMA : H_2O). The specimens were conditioned in distilled water at 37 °C for 24 hours.

formulation [11, 21], there exist three major components, i.e., light-curable polymer (LCP), 2-hydroxyethyl methacrylate (HEMA) and water (H_2O). Consid-ering the polymer matrix, the light-curable polymer may be a major component to produce high strengths, since it not only contains the component for forming salt bridges but also has the component for covalent bond formations. HEMA is used not only as a comonomer but also as a compatibilizer to bring the LCP into water [7, 18]. Water acts as a reaction medium for formation of the salt-bridges [1, 18]. Each component has its own role in the formulation. The question is how to bring them together and to make the optimal proportion in order to give the optimal mechanical performances.

Statistical design of experiment (DOE) is an efficient way to find the optimum formulation for the mixture [22, 23, 25]. Based on the ideas of response-surface methodology developed by Box and Wilson [26], there are four models which may be used in our studies. For three components, in general, if there are less than ten experimental 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.

Before using DOE, we considered several things which might be related to the experiments. According to our observations and experience, the weight ratio of our LC NVPM TP was not allowed to be taken above 0.60, the ratio of HEMA had to be used above 0.10, and water should always exist, in this three-component formulation. Above 0.60, the solution was too viscous to be manipulated, which would not be useful in clinics. If the weight ratio for HEMA was less than 0.10, the initiator (dl-camphoroquinone (CQ)) was not able to dissolve in solution. Further, without water this material would not function as a glass-ionomer.

TABLE 3. Formulations and Average Compressive Strength Values*

Code	Formulation (Weight Ratio) LC NVPM TP	HEMA	Water	CS (MPa) (S.D.)	Modelling Step
a	0.50	0.10	0.40	193.2 (3.012)	Step 1
b	0.50	0.20	0.30	215.4 (3.849)	Step 1
c	0.50	0.30	0.20	197.6 (4.892)	Step 1
d	0.50	0.40	0.10	201.6 (5.393)	Step 1
e	0.40	0.30	0.30	171.0 (5.371)	Step 1
f	0.40	0.20	0.40	151.0 (1.980)	Step 1
g	0.40	0.40	0.20	180.8 (2.877)	Step 1
h	0.60	0.20	0.20	208.9 (2.713)	Step 1
i	0.30	0.50	0.20	150.0 (4.847)	Step 1
j	0.30	0.40	0.30	134.7 (3.993)	Step 1
k	0.50	0.25	0.25	225.3 (4.458)	Step 2
l	0.55	0.15	0.30	257.7 (4.208)	Step 2
m	0.55	0.30	0.15	220.7 (3.747)	Step 2
n	0.45	0.20	0.35	210.3 (5.189)	Step 2
o	0.45	0.40	0.15	214.4 (2.775)	Step 2

*The specimens were conditioned in distilled water at 37 °C for 24 hours.

In the first step (Step 1) of our experiments, ten preliminary formulations were made. Ten formulations were selected based on the concepts discussed above and previous studies [11, 21]. After the materials were conditioned, the specimens were tested for CS, with the results shown in Table 3 (a-j) and Figure 5. The highest CS value (215.5 MPa) was presented by the formulation with 0.50:0.20:0.30 (LC NVPM TP : HEMA : water). Four models (full cubic, specific cubic, quadratic and linear) were used to predict the next, since ten data points were collected. Three of them indicated that formulations should be selected at those compositions which contain more LC NVPM TP and more water weight fractions, whereas one of them more LC NVPM TP and more HEMA, as shown in Table 4. The full cubic model of Step 1 indicated that the next predicted point (LC NVPM TP, HEMA, H_2O) should be taken at (0.60, 0.05, 0.35) with the expected CS of 287.8 MPa. The special cubic model predicted the point at (0.60, 0.01, 0.39) with the expected strength of 239.5 MPa. The surface contour diagrams of both special and full cubic models are shown in Figure 3. The quadratic model predicted the point at (0.60, 0.03, 0.37) to give a strength of 222.9 MPa. The linear model predicted the point at (0.60, 0.30, 0.10) to give a strength of 228.4 MPa. Based on these models and the concepts discussed above, we chose the following five points:

TABLE 4. Predicted Formulations for Each Modelling Step

Model	Predicted Weight Ratio			Expected CS [MPa]	Step
	LC NVPM TP	HEMA	Water		
Linear	0.60	0.30	0.10	228.4	1
Quadratic	0.60	0.03	0.37	222.9	1
Special Cubic	0.60	0.01	0.39	239.5	1
Full Cubic	0.60	0.05	0.35	287.8	1
Linear	0.60	0.30	0.10	242.5	2
Quadratic	0.60	0.04	0.36	244.5	2
Special Cubic	0.60	0.01	0.39	268.4	2
Full Cubic	0.60	0.08	0.32	256.1	2

k (0.50, 0.25, 0.25), l (0.55, 0.15, 0.30), m (0.55, 0.30, 0.15), n (0.45, 0.20, 0.35) and o (0.45, 0.40, 0.15).

After the second step of formulations (Step 2) were evaluated, a new set of strength data were obtained, as shown in Table 3 (k-o) and Figure 5. The formulation with 0.55:0.15:0.30 (LC NVPM TP : HEMA : water) presented the highest CS value (257.7 MPa), which was also the highest value among all fifteen data points. By fitting all data (Step 1 and 2) to the models, the new predicted weight ratios were given. As we can see from Table 4, three high levels of models still directed us to go towards more LC NVPM TP and more water, i.e., (0.60, 0.08, 0.32) by the full cubic model, with the CS of 256.1 MPa; (0.60, 0.01, 0.39) by the special cubic model, with the CS of 268.4 MPa; and (0.60, 0.04, 0.36) by the quadratic model, with the CS of 244.5 MPa. The linear model indicated exactly the same point as predicted in Step 1, with the expected CS of 242.5 MPa. Considering the concepts and limitations discussed previously and the experimental results, we think that this formulation (LC NVPM·TP : HEMA : H_2O = 0.55:0.15:0.30) is the optimal one for the 15% IEM grafted terpolymer with the molar ratio of 8:2:1, as shown in Table 6. In fact, the result from this optimal formulation (0.55:0.15:0.30) satisfied all three high levels of models.

In order to look at the strengths under tension, we measured the diametral tensile strength (DTS) of those formulations. Results showed that the formulation (0.55:0.15:0.30) with highest CS (257.7 MPa) was also the highest in DTS (43.26 MPa). The order of DTS was pretty similar to the order of CS for most formulations used in this study.

Mechanical Behavior of Light-Curable NVP Modified Glass-Ionomers

It is very important to know mechanical and deformation behavior of newly formed dental materials. In order to mimic real mechanical behavior of the natural

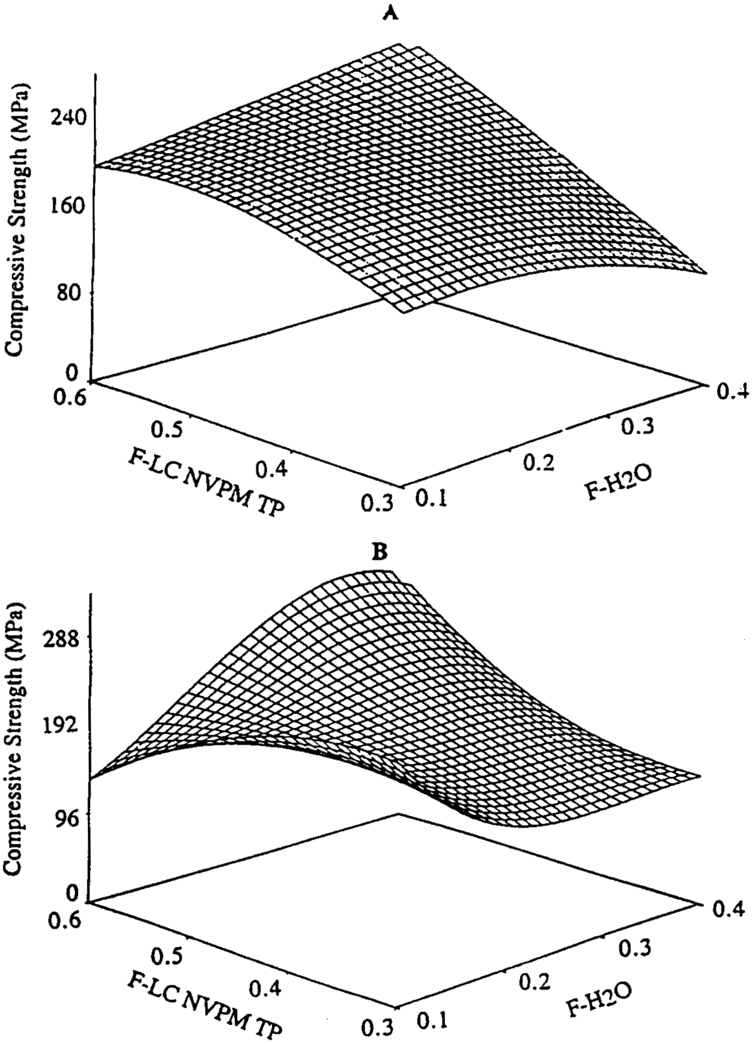

Figure 3. Surface contour diagrams from Modeling Step 1. The x-axis (F-LC NVPM TP) and y-axis (F-H_2O) represent the weight fractions LC NVPM TP and H_2O, respectively, while the weight fraction HEMA is equal to 1-(F-LC NVPM TP + F-H_2O). The z-axis represents compressive strength. A. Surface contour diagram produced by the special cubic model. B. Diagram produced by the full cubic model.

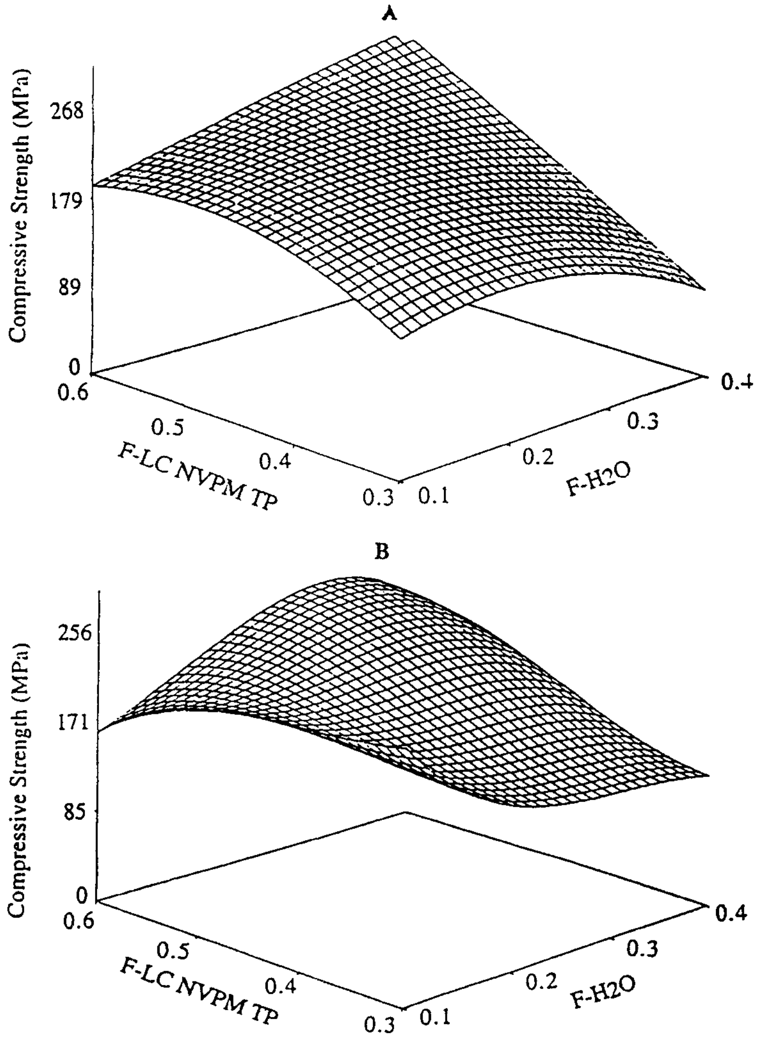

Figure 4. Surface contour diagrams from Modelling Step 2. The x-axis (F-LC NVPM TP) and y-axis (F-H_2O) represent the weight fractions LC NVPM TP and H_2O, respectively, while the weight fraction HEMA is equal to 1-(F-LC NVPM TP + F-H_2O). The z-axis represents compressive strength. A. Surface contour diagram produced by the special cubic model. B. Diagram produced by the full cubic model.

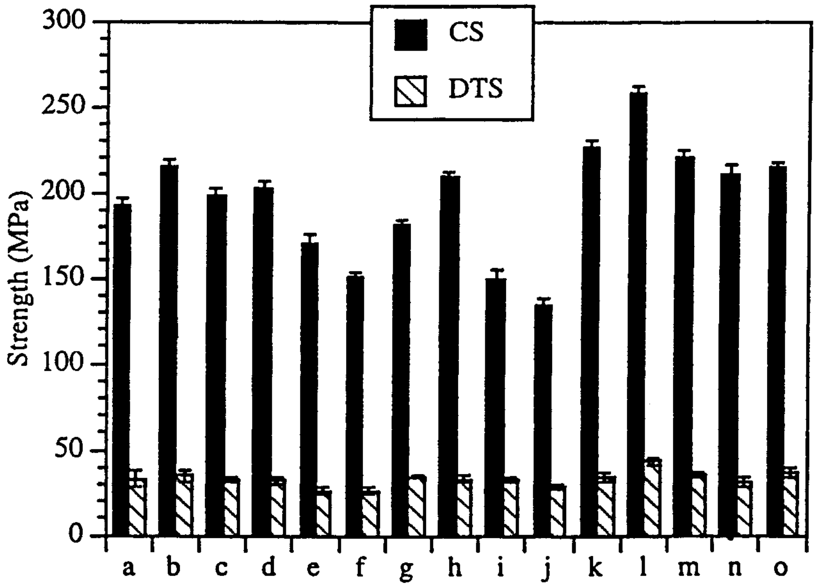

Figure 5. Compressive and diametral tensile strengths for LC NVPM GICs formed by the IEM grafted terpolymers with various formulations in Step 1 and 2. Table 4 gives the weight ratios of the formulations a - o.

TABLE 5. Comparison of Parameters from Stress-Stain Curves in Fig.6 for Various Graft Ratios and Selected Formulations*

	E (MPa)	Malleability	PL (MPa)	CS (MPa)
Graft Ratio (mole %)**				
10	5000	0.087	63	184.0
15	6250	0.067	76	235.0
20	5747	0.057	76	225.5
25	5263	0.073	63	188.6
Formulation***				
50/10/40	6667	0.054	85	210.5
50/40/10	4167	0.078	63	249.0
50/25/25	5714	0.075	68	253.6

*E, PL and CS represent elastic modulus, proportional limit and compressive strength, respectively.

**The formulation was used as follows:
0.45:0.21:0.34 (LC NVPM TP : HEMA : H_2O). The specimens were conditioned in distilled water at 37 °C for 7 days.

***15% (mole fraction) of IEM was grafted onto the terpolymer. The specimens were conditioned in distilled water at 37 °C for 7 days.

TABLE 6. Final Formulation of Liquid Component

Component	Quantity (wt %)	Function
LC NVPM TP*	54.1	formation of both salt bridges and covalent bonds.
HEMA	14.8	comonomers and compatibilizer.
H_2O	29.5	reaction medium for salt bridge formations.
CQ	0.5	photoinitiator.
DC	1.0	activator.
$K_2S_2O_8$	0.1	initiator for redox.

*LC NVPM TP is an abbreviation of the light-curable NVP modified terpolymer.

tooth [4], dental materials scientists are usually required to make strong but brittle restorative materials such as dental cements, composite resins, dental ceramics, etc. [4, 27]. Most of the current dental restorative materials are brittle, but some are still resinous. The reason may be attributed to different types of setting, different types and amount of glasses and polymers (resins) used, and so on. In our study, there are several factors that need to be considered, including graft ratio, formulations, powder/liquid ratio, and molecular weight of the polymers. In this study, we compared the effects of graft ratio and three selected formulations on the mechanical behavior of the cements.

Figure 6 illustrates the stress-strain relationship of the materials used in the study. Curve A represents a stress-strain behavior conducted by four graft ratios. Curve B illustrates a stress-strain behavior conducted by three formulations. The possible effects from the loading frame as a function of applied force were corrected by subtracting the displacement from a piece of extremely thin rigid stainless steel. All these stress-strain curves exhibited more or less plastic behavior [28-30]. The parameters obtained from the stress-strain curves are shown in Table 5. For the effect of graft ratio, the terpolymers with 15% and 20% graft ratios showed higher elastic modulus (E), higher proportional limit (PL), higher CS, and lower malleability (M), compared to the ones with 10% and 25%. This means that the cements with 15% and 20% graft ratios are stiffer and brittle than the ones with 10% and 25% graft ratios. Higher E, higher PL and lower M mean that the material is stronger, stiffer and more brittle [27]. In the case of different formulations, the formulation with 50/10/40 showed the highest E and PL and lowest M and CS. The formulation with 50/40/10 exhibited the lowest E and PL but highest M. The formulation with 50/25/25 showed the E, PL and M values between the other two formulations except the CS being the highest. From these numbers, we can say

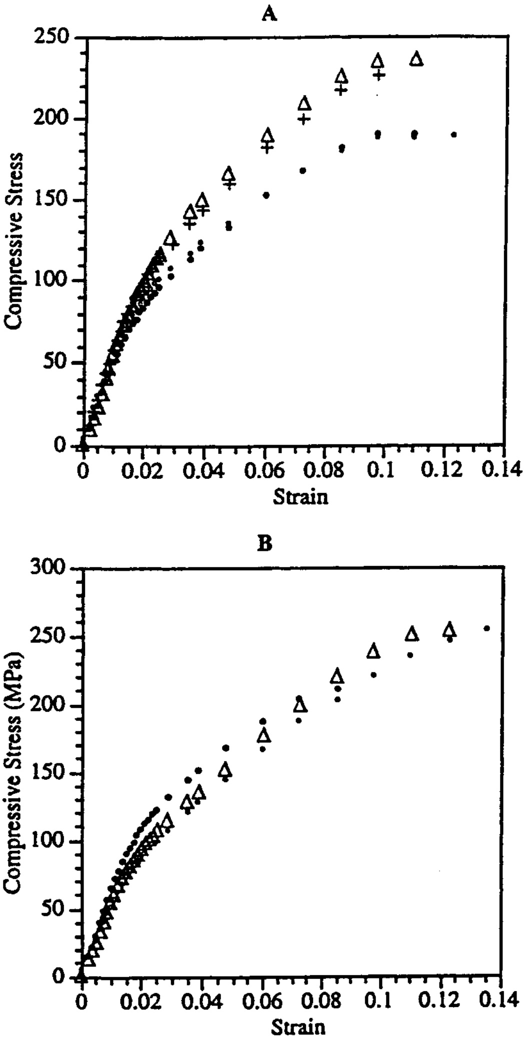

Figure 6. Stress-strain curves for comparisons between various grafting ratios and between several selected formulations under compression. A. Stress-strain curve for various graft ratios (mole %): Δ 15%, + 20%, • 25%, o 10%. B. Stress-strain curve for selected formulations: Δ 50/25/25, • 50/10/40, o 50/40/10.

TABLE 7. Comparison* between the Optimal Formulated LC NVPM GIC and Vitremer™

Material	P/L Ratio	CS (MPa) (S.D.)	DTS (MPa) (S.D.)	FS (MPa) (S.D.)
Vitremer™	2.5/1	265.3 (7.478)	47.50 (0.939)	82.06 (3.279)
LC NVPM GIC	2.5/1	276.2 (4.646)	49.97 (2.171)	88.43 (3.090)

*The LC NVPM GIC was grafted with 15% IEM and formulated with 0.55/0.15/0.30. All specimens for both experimental and commercial cements were conditioned in distilled water at 37 °C for 7 days.

TABLE 8. Student's t-Test Comparing Strengths of Optimal Formulation and Commercial Control

Type of Strength	t-Value	DF	Prob > | t |
CS	3.016	10	0.013
DTS	2.556	10	0.028
FS	3.464	10	0.006

that, at the same amount of polymer used, more water in the formulation leads to an increase of the E and PL values and a decrease of M, showing the material is more brittle and rigid or less plastic. The reason may be explained as that in the formulation containing more water more salt-bridges formed since the C GICs are brittle in nature. More HEMA produces lower E and PL but higher M, which means that the material is more resinous and plastic. Introduction of more HEMA into formulations no doubt increases the resin component in the formulation, thus causing appearance of malleability.

Comparison between Our Optimal Formulation and the Commercial Control

The optimal formulation for our LC NVPM GICs was compared in mechanical strengths with the commercial control Vitremer™ and these results are shown in Table 7. All specimens had been conditioned in distilled water at 37°C for 7 days. Statistically significant differences were found between these two cements for each of CS, DTS and FS, with the statistical tests shown in Table 8.

CONCLUSION

The best graft ratio of the LC NVPM TPs with the molar ratio of 8:2:1(AA: IA : NVP) and the optimal formulation for this LC NVPM GICs based on the best graft ratio were determined. The best graft ratio for IEM in this system was 15% of the terpolymer by a molar ratio. The optimal formulation was found to be at the weight ratio of 55:15:30 (LC NVPM TP: HEMA: H_2O), determined using a statis-tical design of experiment (DOE), with the help of a computer-aid *SAS* program. From the stress-strain curves, it is concluded that a relatively high amount of water in the formulation leads to higher elastic modulus and proportional limit and lower malleability, or the material behaves more brittle. On the contrary, relatively high amount of HEMA produces higher malleability and lower E and PL, or in other words, the material is more plastic. Compared to the commercial Vitremer™, the LC NVPM GICs showed statistically significantly higher values in compressive, diametral tensile and flexural strengths.

Future research will focus on looking for the optimal powder/liquid (P/L) ratio and glass compositions, optimal molecular weight and other properties for these LC NVPM GIC systems.

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