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Mechanical properties and rheology of polyalkenoate cements using various low-cost fillers

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Abstract Low-cost polyalkenoate cements analogous to dental cements, i.e., cements based on polymers of acrylic acid crosslinked via bridging metal cations, were developed with a goal of producing a more flexible alternative to Portland cement. Economic constraints necessitated the replacement of the acid-degradable glass normally used in dental cements; the purpose of the glass is to provide both a source of polyvalent cations for crosslinking and solid filler for a composite material. The dual functionality of the powdered glass was accomplished via the use of manganese tetraoxide as the filler and aluminum chloride as the cation source for the ionic crosslinks. Unlike dental cements that have a gel-like consistency before setting, low viscosity cements were produced by using acrylic acid monomer rather than low-molecular weight poly(acrylic acid). Mechanical and rheological properties were used to monitor cement characteristics. Because of the large number of formulation variables, a design of experiments (DOE) approach was used. DOE helped narrow the search for formulations that would result in hardened cements and find the optimal set of ingredients that led to cements with the best properties given the economic constraints on the ingredients. Rheology was adjusted to match that of Portland cement by altering the filler volume fraction, which was very effective since the rheology depended strongly on that variable. The most pertinent independent variables for the mechanical properties were the curing time and monomer/cation ratio in the ranges tested; however, the monomer/water ratio was fixed at the minimum level possible and not increased because of economic considerations. The best materials produced in terms of mechanical properties resulted when acrylic acid monomer was partially replaced by *N,N′*-methylenebisacrylamide; this substitution resulted in a stronger and tougher cement.

Background

A composite is a material made of filler particles surrounded by a matrix of a second material that binds the filler particles together. In many composites, the purpose of the filler is to impart the composite with improved mechanical properties. In order for this improvement to occur, external stresses are transferred from the continuous phase (polymer) to the discontinuous phase (filler). Glass-ionomer cements, used as dental fillings, consist of finely ground glass powder mixed into a matrix that is usually an acrylic acid polymer, or a copolymer with at least one monomer having acid functionality [1–6]. This special glass degrades in the presence of the acid, slowly releasing multivalent metal cations. These types of dental cements fall under the broader classification of polyalkenoate cements; similar polyalkenoate cements have been made using non-glass fillers such as zinc oxide [7]. These cements have either one or two separate hardening mechanisms. One hardening process is due to crosslinking between carboxylic acid groups by

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cations leached from the glass. Some cements have additional covalent crosslinking through free-radical polymerization of pendant reactive sites extending out from the main chain. The latter types of cements are termed resin-modified glass ionomer cements. The effect of curing time, glass powder/polymer liquid ratio, polymer molecular weight and concentration, conditions of pretreatment of the glass powder, etc., on the properties of the cement have been studied extensively [7–14]. As a point of reference to this work, dental cements can withstand compressive stresses of a magnitude 35–70 MPa [14, 15].

Experimental

Materials

Tech grade 99.25% wt. acrylic acid containing phenothiazine as an inhibitor was purchased from Celanese (Clear Lake, TX) and was used as received, i.e., without inhibitor removal. Aluminum chloride hexahydrate 98% wt. was purchased from Sigma Aldrich (Saint Louis, MO). Hausmannite (Mn_3O_4) was obtained from Elkem (Pittsburgh, PA). 2,2′-Azobis(2-amidinopropane) dihydrochloride (V-50, WAKO Chemicals USA) was used as the initiator. Class F fly ash was supplied by ISG Resources (Tatum, TX). Kelco (Okmulgee, Oklahoma) supplied the stabilizer xanthan gum. *N,N′*-methylenebisacrylamide was obtained from Cyanamid and used as received. Milled glass fibers (731 ED) were obtained from Owens Corning (Anderson, SC).

Methods

Factorial design of experiments and multivariable regression analysis

Due to the large number of independent variables [16–20], the most efficient approach, in our opinion, was to use a factorial design of experiments along with targeted searches to find the most useful ranges for the independent variables. In other words, a series of experiments was done according to a design of experiments methodology and the results examined. Then, a new series of experiments was performed, with the type and range of variables studied based on the results of previous experiments. For reasons that will become clear, dependent variables were also targeted. First we studied the rheology most closely, then compressive properties and finally mechanical properties in tension. Of course, there was some iteration back and forth. A similar approach with Portland cement has been applied: Changes in formulations have been seen to affect its mechanical properties, setting time and rheology [21–25]. This iterative approach allowed us to most efficiently achieve the goal of developing a replacement for Portland cement with high strength and flexibility at the most reasonable cost. Factorial design of experiments (DOE) is a powerful tool for scientific research that has been used to tackle similar problems in cement composition determination [26, 27].

Design of experiments aims to investigate the effect of a given set of independent variables (factors) on a set of dependent variables (response variables). In a complete factorial design of experiments, all possible factor combinations are included. Thus, if p factors are investigated at q values (levels) each, q^p experimental trials are required. In this project, the designs of experiments were conducted so that no more than four factors ($p \leq 4$) and two levels ($q = 2$) were studied per design of experiment. Two-level DOE use coded variables for the factors that take values of –1 and +1 for the low and high levels, respectively. After data treatment the results are fitted and presented in a mathematical equation of the form:

$$y = \bar{y} + F_1 f_1 + F_2 f_2 + \cdots + F_{12} f_1 f_2 + \cdots + \varepsilon \tag{1}$$

where y is a dependent variable (e.g., plastic viscosity, yield point, maximum compressive strength etc.), ε is the error that can be estimated as having the order of three standard deviations (i.e., $\varepsilon = 3S_T$), f subscripted represents the factors (filler volume percentage, initiator ratio, cation ratio etc.) and F subscripted are numerical coefficients bearing the same units as the dependent variable. A coefficient accompanying a single independent variable is termed *effect* (e.g., F_1, F_2, etc.) and a coefficient accompanying a product of two or more independent variables is called *interaction* (e.g., F_{12}, F_{123}, etc.). Not all coefficients are statistically significant; coefficients smaller than three standard deviations were deemed insignificant and discarded. Two methods were used to estimate the error of the statistical samples: with replicates of runs and by neglecting interactions of three or more factors [28]. For the first method, the standard deviation S_T^2 was determined by first calculating the variance s_i^2 for the set of conditions i as shown in formula (2).

$$s_i^2 = \frac{(y_{i_1} - \bar{y}_i)^2 + \cdots + (y_{i_r} - \bar{y}_i)^2}{r_i - 1} \tag{2}$$

where r_i is the number of replicates run for that particular set of conditions i and $\bar{y}_i$ is the average value calculated from:

$$\bar{y}_i = \frac{\sum_{j=1}^{r_i} y_{i_j}}{r_i} \tag{3}$$

The variance for a design of experiments is determined by averaging the calculated standard deviations, weighted appropriately. The weighting factors are the degrees of freedom on each run given by the formula:

$$v_i = r_i - 1 \tag{4}$$

So that the variance for the DOE is:

$$S_T^2 = \frac{\sum_{i=1}^{N} v_i s_i^2}{\sum_{i=1}^{N} v_i} \tag{5}$$

N represents the total number of i conditions, each having r_i replicates.

When there are no replicates in a DOE, a direct measure of the variance is not possible. However, the variance can be estimated if the assumption is made that high order interactions are insignificant. In particular, if all three-variable (F_{123}, F_{124}, F_{234}, etc.) and higher number of variable interactions are assumed to be negligible, these coefficients would quantitatively be related to the experimental error. This set of interactions could provide an appropriate reference set for the remaining effects as shown by Box et al. [28], although this procedure has a tendency to overestimate the actual standard deviation because it uses the predicted value by the model of the dependent variable to calculate the standard deviation instead of the average value of a run (i.e., the estimate depends largely on how good is the fit provided by the model). Formula (6) shows the calculation of the variance with no replicates:

$$S_T^2 = \frac{\sum [\text{COEFFICIENT}]_i^2}{N_{\text{COEFFICIENTS}}} \tag{6}$$

One limitation of factorial DOE is that the conclusions are applicable only to conditions set for the experiment and neither extrapolations nor interpolations are acceptable from the statistical point of view. Looking at this issue from another direction, the model will be accurate only if the dependent variables are linearly dependent on factors and two-variable interactions. As stated earlier, our approach to this problem was to use a DOE to identify useful areas for experimentation and then conduct new DOEs to either fill in regions that were within the range of the previous experiment(s) or go outside the range to investigate promising areas of variable space. Economic considerations were extremely important when deciding which areas to study. With this approach, each DOE has its own model equations. In order to draw more universal conclusions, all data was combined into one data set, the independent variables recoded and the set was then subjected to a multivariable regression analysis for each dependent variable.

Each ingredient amount (i.e., filler, initiator, cation source, water etc.) can be considered an independent variable. However, working with relative amounts means that the results do not depend on the overall amount of the formulation. The key issue is defining a normalizing factor; we chose the monomer amount because this component binds the composite matrix. Time was also included among the factors to be studied. All factors and dependent variables are found in Table 1. Plastic viscosity and yield point were used assuming that the rheological response is well described by the Bingham model. Aluminum chloride was selected because aluminum is multivalent and $AlCl_3$ is relatively inexpensive and soluble in water. It was initially thought that the type of filler would not be crucial to the hardening of the cement. Iron (III) oxide, hausmannite, quartz, fly ash and acid-degradable glass were tested. Of these fillers, only hausmannite (Mn_3O_4) and acid-degradable glass produced hardened materials. The reason for only these two materials producing hardened cements is not clear at the present time; we are currently investigating why only these two materials produced hardened cements. In order to help reduce the cost of the final formulation, the low-cost filler fly ash was mixed with hausmannite and its properties investigated as well.

Table 1 Factors and dependent variables for design of experiments (DOE) and multivariable regressions

Factors	Symbol
Cation ratio (mol acrylic acid monomer/mol cation)	C
Monomers ratio (g acrylic acid/g MBA)	M
Fiber ratio (vol. fibers/(vol. hausmannite + vol. fly ash))	F
Filler type ratio (vol. hausmannite/vol. fly ash)	FR
Filler ratio (vol. acrylic acid/vol. filler)	G
Filler volume percentage (vol. filler(s)/vol. total)	FVP
Initiator ratio (mol monomer (total)/mol initiator)	I
Water ratio (vol. acrylic acid/vol. water)	W
Time (hours)	T
Dependent variables	Symbol
Plastic viscosity (mPa s)	PV
Yield point (dyn/cm^2)	YP
Maximum compressive stress (MPa)	y_1
Compressive modulus (MPa)	y_2
Compressive failure strain (%)	y_3
Maximum tensile stress (MPa)	y_4

Mixing

Solid materials were placed in a variable speed laboratory blender from Waring Laboratory Equipment (Torrington, CT) and mixed together dry at 1,000 rpm. The stabilizer dose was adjusted at 0.01 g Xanthan gum/g fillers to keep all solids suspended. The azo initiator was dissolved with tap water at room temperature. After dissolution, the initiator was added with the aluminum chloride solution, water and acrylic acid to the premixed dry ingredients and mixed for 5 min, or until no lumps of solid material were detected in the slurry, at 3,000 rpm. About 100 ml of monomer was used for most formulations, resulting in a wet basis formulation size of approximately 300 ml, depending on the exact amount of ingredients used as determined by the DOE model being tested.

Rheology

The yield point and plastic viscosity were measured per API recommended practice 10B using a Fann 35A rotational viscometer (Houston, TX) immediately after mixing.

Mechanical properties

Cement substitute slurries were poured in plastic cylindrical moulds with 1″ of diameter or into dog-bone shaped moulds, depending on the test to be run. These samples were placed in an autoclave pressure regulated with nitrogen and allowed to harden at 60 °C and 7 MPa. Compressive and tensile strength were measured in the hardened cylindrical and dog-bone shaped samples per ASTM standards C109 and C190-85, respectively using a Tinius Olsen CMH 496 press (Horsham, PA).

Results and discussion

Rheology

To successfully place the cement in a desired location often requires control of the cement slurry viscosity. One of our first experiments was a DOE, shown in Table 2, geared at determining the effect of the filler, cation and initiator on the yield point and the plastic viscosity for those conditions that yielded hardened samples. Formulas (7) and (8) show how to calculate the plastic viscosity (PV) and yield point (YP):

$$\mathrm{PV(mPa\,s)} = 1.5(\mathrm{READING}_{300\,\mathrm{rpm}} - \mathrm{READING}_{100\,\mathrm{rpm}} \tag{7}$$

$$\mathrm{YP(dyn/cm^2)} = 4.788\left[\mathrm{READING}_{300\,\mathrm{rpm}} - \mathrm{PV(mPa\,s)}\right] \tag{8}$$

Simple inspection by comparing even numbered runs with odd numbered runs on Table 2 shows that the rheology of the cement slurries depends primarily on the filler volume percentage; a similar result has been reported for Portland cement slurries [29]. Experiments were performed to better bracket this dependence for hausmannite. The result of this study was the observation that a filler volume percentage of 22% yields values for PV and YP required for oil-well

Table 2 2^3 DOE for rheology dependance on filler, cation and initiator ratios and on the filler volume percentage

Experimental conditions						
Variables				–	+	
Filler ratio (*G*)				2	4	vol. monomer/vol. filler
Cation ratio (*C*)				10	100	mol monomer/mol cation
Initiator ratio (*I*)				1,000	1,500	mol monomer/mol initiator
Fixed parameters						
Water ratio (*W*)				1	vol. monomer/vol. water	
Run	*G*	*C*	*I*	Filler volume percentage (%)	PV (mPa s)	YP (dyn/cm^2)
8	–	–	–	19.76	11.42	79.15
9	+	–	–	10.96	10.73	18.53
10	–	+	–	19.98	11.25	80.53
11	+	+	–	11.10	10.72	19.25
12	–	–	+	19.76	11.51	82.40
13	+	–	+	10.96	10.80	17.57
14	–	+	+	19.98	11.55	80.20
15	+	+	+	11.10	10.51	20.11
Averages				$\overline{\mathrm{FVP}}$ (%)	$\overline{\mathrm{PV}}$ (mPa s)	$\overline{\mathrm{YP}}$ (dyn/cm^2)
Even numbered runs				19.87 ± 0.13	11.43 ± 0.13	80.57 ± 1.36
Odd numbered runs				11.03 ± 0.08	10.69 ± 0.13	18.86 ± 1.08

cementing at the average values of the parameters listed in Table 2.

The values of the parameters used in Table 2 were not those that yielded the best product. To better test the premise that only filler volume percentage affects the rheological properties of the cement slurry in the operating range of interest, the filler volume percentage was fixed at 22% and the initiator and cation ratios were changed as shown in Table 3. Note that $r^2 = 1$ for the models shown in Table 3, as expected since there were four factors and four trials. Although the other variables do affect the rheology, the filler volume percentage has a much stronger effect on the rheology than either the initiator or cation ratio. As will be shown, none of the other dependent variables, i.e., the mechanical properties, have such a strong dependence on filler volume percentage. Hence, a design strategy is to formulate for rheology by adjusting the filler volume percentage and manipulate the remaining variables to obtain cements with desired mechanical properties.

What effect does the identity of the filler have on the rheological properties? Table 4 shows that PV and YP depend heavily on the hausmannite/fly ash volume ratio. The dependence is probably due to the different particle size distribution of the fly ash and the manganese tetraoxide [30, 31]. This DOE also showed that the filler volume percentage to attain PV and YP required for oil-well cementing is 26% at a 50/50 hausmannite/fly ash volume ratio.

Mechanical properties

Compressive properties

Materials made according to the DOE shown in Table 4 were also used to gather mechanical properties data in compression. Some samples with a water ratio of 0.6 vol. monomer/vol. water did not harden, indicating the lower bound of the water ratio. Mechanical properties results from hardened samples are shown in Table 5 along with a complete description of the experimental conditions. The water ratio was fixed at the minimum level required for consistent hardening, i.e., 0.8 vol. monomer/vol. water. As shown in Eqs. 5-1, 5-2 and 5-3, all effects have the same order of magnitude for the maximum compressive strength and compressive modulus. For the next set of experiments shown in Table 6, the filler volume percentage was set at 26% to be within rheological constraints and the water ratio set at 0.8 vol. acrylic acid/vol. water. For the maximum compressive stress, monomer/cation ratio is the most relevant factor. Increasing the monomer/cation ratio (i.e., diminishing the amount of cation) results in samples with lower compressive strength, but higher flexibilities, consistent with observations made previously [32]. Interpreting compressive moduli results was not straightforward because of the wide range of values. The DOE procedure inherently assumes the same absolute standard deviation for all runs; a large variation in average values means that the absolute standard deviations are almost certainly not constant. A simple expedient is to use the logarithm of the compressive modulus, i.e., calculate the logarithm of each individual value, then average the logarithmic values. Since the standard deviation of this variable is $S_T = 0.084$ and all of the effects and interactions are larger than three standard deviations, none of them can be discarded and no firm conclusion can be established about compressive modulus.

A more elaborate design of experiments than the previous ones is shown in Table 7. Since the monomer/cation ratio effect on some of the mechanical

Table 3 2^2 DOE to test rheology dependence on cation and initiator ratios

Experimental conditions						
Variables			–1	+1		
Cation ratio (*C*)			10	20	mol monomer/mol cation	
Initiator ratio (*I*)			2,000	5,000	mol monomer/mol initiator	
Fixed parameters						
Water ratio (*W*)				0.8	vol. monomer/vol. water	
Filler volume percentage (FVP)				22	vol. filler/vol. total	
Run	*C*	*I*	Yield point (dyn/cm^2)		Plastic viscosity (mPa s)	
1	–1	–1	76.61		22.50	
2	+1	–1	142.44		26.25	
3	–1	+1	146.03		36.00	
4	+1	+1	260.95		54.00	
Rheology			*DOE model equation*			
Plastic viscosity (mPa s)			$PV = 34.69 + 5.44C + 10.31I + 3.56CI$		$r^2 = 1$	3-1
Yield point (dyn/cm^2)			$YP = 156.51 + 45.19C + 46.98I + 12.27CI$		$r^2 = 1$	3-2

Table 4 2^3 DOE using fly ash to verify filler rheology dependance on the filler volume percentage

Experimental conditions							
Variables					–1	+1	
Water ratio (*W*)					0.6	0.8	vol. monomer/vol. water
Filler volume percentage (FVP)					0.2	0.3	vol. filler(s)/vol. total
MM/MFA vol. ratio (FR)					0.3	0.5	vol. hausmannite/vol. fly ash
Fixed parameters							
Cation Ratio (C)					50	mol monomer/mol cation	
Initiator ratio (*I*)					5000	mol monomer/mol initiator	
Time (*T*)					22	hours	
Run	*W*	FVP	FR	Plastic viscosity (mPa s)	Yield point (dyn/cm^2)		
1	–1	–1	–1	11.25	10.77		
2	+1	–1	–1	10.5	19.15		
3	–1	+1	–1	13.5	11.97		
4	+1	+1	–1	12	19.15		
5	–1	–1	+1	30	50.27		
6	+1	–1	+1	50.25	89.78		
7	–1	+1	+1	33	81.40		
8	+1	+1	+1	29.25	73.02		
Rheology				*DOE model equation*			
Plastic viscosity (mPa s)				$\mathrm{PV} = 23.72 + 11.9\mathrm{FR} \pm 6$		$r^2 = 0.9528$	4-1
Yield point (dyn/cm^2)				$\mathrm{YP} = 44.44 + 29.18\mathrm{FR} \pm 34$		$r^2 = 0.9648$	4-2

Table 5 2^2 DOE using fly ash to study mechanical properties under compression dependance on the filler volume percentage and filler ratio

Experimental conditions					
Variables			–1	+1	
Filler volume percentage (FVP)			0.2	0.3	vol. filler(s)/vol. total
MM/MFA vol. ratio (FR)			0.3	0.5	vol. hausmannite/vol. fly ash
Fixed parameters					
Water ratio (*W*)			0.8	vol. monomer/vol. water	
Cation ratio (*C*)			50	mol monomer/mol cation	
Initiator ratio (*I*)			5,000	mol monomer/mol initiator	
Time (*T*)			22	hours	
Run	FVP	FR	Max. comp. stress (MPa)	Comp. mod. (MPa)	Failure strain (%)
2	–1	–1	0.78	1.48	52.68
4	+1	–1	1.06	11.16	17.07
6	–1	+1	5.38	9.62	51.22
8	+1	+1	0.93	17.67	8.05
Properties modeling			*DOE model equation*		
Max. compressive stress (MPa)			$y_1 = 2.04 - 1.04\mathrm{FVP} + 1.12\mathrm{FR} - 1.18\mathrm{FR} \cdot \mathrm{FVP}$	$r^2 = 1$	5-1
Compressive modulus (MPa)			$y_2 = 9.98 + 4.44\mathrm{FVP} + 3.66\mathrm{FR} - 0.41\mathrm{FR} \cdot \mathrm{FVP}$	$r^2 = 1$	5-2
Failure strain (%)			$y_3 = 32.26 - 19.7\mathrm{FVP} - 2.62\mathrm{FR} - 1.89\mathrm{FR} \cdot \mathrm{FVP}$	$r^2 = 1$	5-3

properties can be explained by crosslinking of the polymeric matrix, the ratios were increased (i.e., the amount of cation reduced) to increase the flexibility of the cement matrix. The levels of the initiator remained unchanged because the relative effect of this variable is negligible compared to the remaining variables. Hardening times were arbitrarily chosen to be 20 and 44 h under pressure for the low and high levels of the DOE, respectively. The variance was determined using the values of the coefficients of the three- and four-variable interactions.

Consistent with the previous DOE, a linear model for the compressive modulus does not fit the data very well, while the other dependent variables are well fit by linear models. Time is clearly the most important variable in describing the compressive strength, i.e., the compressive strength builds slowly over time. Figure 1a shows that despite having a single factor (i.e., time) the data is modeled adequately by Eq. 7-1. The increase in maximum compressive strength with time is accompanied by a decrease in failure strain, also well described by the model as shown in Fig. 1b. As before,

Table 6 2^2 DOE for mechanical properties models under compression dependance on the cation and initiator ratios

Experimental conditions								
Variables						–1	+1	
Initiator ratio (I)						2000	5000	mol monomer/mol initiator
Cation ratio (C)						10	20	mol monomer/mol cation
Fixed parameters								
Water ratio (W)							0.8	vol. monomer/vol. water
MM/MFA vol. ratio (FR)							0.5	vol. hausmannite/vol. fly ash
Filler volume percentage (FVP)							26%	vol. filler(s)/vol. total
Time (T)							17	hours
Run	*C*	*I*	*Maximum comp. stress (MPa)*				$\bar{y}_i$ (MPa)	s_i^2
1	–1	–1	3.92	3.87	4.50	4.32	4.15	0.09
2	+1	–1	8.64	12.13			10.39	6.11
3	–1	+1	9.54	9.92	9.09		9.52	0.17
4	+1	+1	13.75	13.52			13.63	0.03
							$s_T^2 =$	0.91
Run	*C*	*I*	*Compressive modulus (MPa)*				$\bar{y}_i$ (MPa)	s_i^2
1	–1	–1	193.68	182.61	236.72	206.17	204.80	545.49
2	+1	–1	243.48	241.45			242.47	2.05
3	–1	+1	639.14	568.13	613.63		606.97	1294.13
4	+1	+1	338.17	306.34			322.26	506.67
							$s_T^2 =$	335.48
Run	*C*	*I*	*Compressive failure strain (%)*				$\bar{y}_i$ (%)	s_i^2
1	–1	–1	3.00	3.25	3.00	3.25	3.13	0.0209
2	+1	–1	7.00	8.00			7.50	0.5
3	–1	+1	2.50	3.38	8.50		4.79	10.50
4	+1	+1	9.50	10.00			9.75	0.125
							$s_T^2 =$	3.08
Properties modeling			*DOE model equation*					
Maximum compressive stress (MPa)			$y_1 = 9.42 - 2.585C + 2.15I \pm 2.73$				$r^2 = 0.8747$	6-1
Compressive modulus (MPa)			$y_2 = 344.12 - 61.76C + 120.49I - 80.59CI \pm 54.95$				$r^2 = 0.7528$	6-2
			$\ln y_2 = 5.75 - 0.12C + 0.35I - 0.2CI \pm 0.16$				$r^2 = 0.7305$	6-3
Failure strain (%)			$y_3\ (\%) = 6.29 + 2.33C \pm 5.2$				$r^2 = 0.7512$	6-4

increasing the monomer/cation ratio increases the failure strain of the samples while the initiator has no impact on the failure strain of the samples. Finally, increasing the amount of monomer by increasing the water ratio does not yield significant improvements in mechanical properties, which is encouraging since increasing monomer increases the cost of the cement. Figure 1c and d shows the modeling for the compressive modulus using linear and logarithmic models. Not only does the logarithmic model better predict the compressive modulus, but only positive values result. However, the logarithmic model for the compressive modulus cannot be fully established on the basis of 16 data runs and no replicates.

The maximum tensile stress of the samples was still not acceptable and for this reason a non-ionic, organic crosslinking comonomer, *N,N′*-methylenebisacrylamide (MBA) and glass fibers were added to the formulations and the results of tests involving those variables are shown in Table 8. Glass fibers reduced the maximum compressive stress and the compressive failure strain and since glass fibers are more expensive than manganese tetraoxide, glass fibers were not added to the formulations hereafter. On the other hand, MBA comonomer increased significantly the maximum compressive stress and the compressive modulus without a significant change in failure strain.

Table 9 shows the results of tensile tests after eliminating glass fibers from the testing. The reason for studying tensile mechanical properties only after determining the best properties from compression is that we were sample limited in the former case; only two dog-bone samples could be fit in the autoclave, while eight cylindrical compression samples would fit. For the same reason, the standard deviation of tensile strength was not estimated as with other properties due to lack of replicates. Cation amount was also added as a variable. Cation amount was added as a test variable because both cation and comonomer cause crosslinking. The fact that the interaction CM is of the same order of magnitude of the effect M in Eq. 9-1 indicates that CM can’t be discarded and is evidence of

Table 7 2^4 DOE for mechanical properties under compression

Experimental conditions							
Variables					–	+	
Cation ratio (C)					20	50	mol monomer/mol cation
Initiator ratio (I)					2,000	5,000	mol monomer/mol initiator
Water ratio (W)					0.8	1.0	vol. monomer/vol. water
Time (T)					20	44	hours
Fixed parameters							
Hausmannite/fly ash ratio (FR)						0.5	vol. hausmannite/vol. fly ash
Filler volume percentage (FVP)						26	vol. filler(s)/vol. total
Run	*C*	*I*	*W*	*T*	*Max. comp. stress (MPa)*	*Comp. fail. strain (%)*	*Comp. modulus (MPa)*
1	–1	–1	–1	–1	9.54	8.25	139.19
2	+1	–1	–1	–1	6.43	30.58	21.98
3	–1	+1	–1	–1	8.63	8.25	152.17
4	+1	+1	–1	–1	4.89	12.74	16.49
5	–1	–1	+1	–1	18.48	14.20	347.19
6	+1	–1	+1	–1	8.67	28.16	29.39
7	–1	+1	+1	–1	1.60	17.96	40.58
8	+1	+1	+1	–1	8.88	29.13	28.41
9	–1	–1	–1	+1	16.20	3.88	671.10
10	+1	–1	–1	+1	16.00	12.74	227.25
11	–1	+1	–1	+1	15.51	3.40	869.95
12	+1	+1	–1	+1	14.69	17.48	150.39
13	–1	–1	+1	+1	25.65	4.85	958.72
14	+1	–1	+1	+1	16.89	15.05	147.95
15	–1	+1	+1	+1	3.71	2.18	142.03
16	+1	+1	+1	+1	17.10	19.42	112.13
Properties modeling					*DOE model equation*		
Maximum compressive stress (MPa)					$y_1 = 12.05 + 3.66T \pm 3.48$	$r^2 = 0.8286$	7-1
Compressive modulus (MPa)					y_3 (psi) $= 253.43 - 161.68C + 156.51T \pm 147.28$	$r^2 = 0.8618$	7-2
					$\ln y_3 = 4.83 - 0.74C + 0.82T \pm 0.41$	$r^2 = 0.9400$	7-3
Failure Strain (%)					y_2 (%) $= 14.27 + 6.4C - 4.39T \pm 3.94$	$r^2 = 0.8911$	7-4

competition with respect to crosslink sites between MBA and the cation source.

The most interesting result of this set of experiments was that the addition of MBA comonomer significantly increased the tensile strength as it did the compressive strength, without any noticeable change in failure strain. At higher amounts of cation (runs 1 and 3), the addition of MBA changes the tensile strength very little, while at lower amount of cation source (runs 2 and 4) MBA has a large effect on the measured tensile strength. An increase in fracture toughness with the addition of moieties containing pendant double bonds, as found here, is typical for resin-modified glass ionomer dental cements versus conventional glass ionomer cements [4, 33, 34]. The reason for this improvement in toughness is not clear. Since both poly(acrylic acid) and poly(N,N'-dimethylacrylamide) are glasses at room temperature, the behavior is not expected to be the result of increased main-chain flexibility. One complicating factor is that aluminum leads to a minimum of a three-functional crosslink, while the MBA crosslink is two functional. Further, the location of the crosslink relative to the main chain is different as well for the two types of crosslinks.

Multivariable linear regression for mechanical properties

In this section, all runs were gathered together and one mathematical model was fit to all the data for each dependent variable. A total of 59 data points exist for the mechanical properties under compression with the factors defined in Table 10. The linear model in Eq. 9 was used:

$$y = \beta_0 + \beta_1 C + \beta_2 M + \beta_3 \mathrm{FR} + \beta_4 F + \beta_5 \mathrm{FVP} + \beta_6 I + \beta_7 W + \beta_8 T + \varepsilon \qquad (9)$$

In multivariable regression analysis, the adequacy and fitting of the data from the model are very important as this reflects how independent variables affect a dependent variable and how well a regression equation fits the data. In order to assess how well the

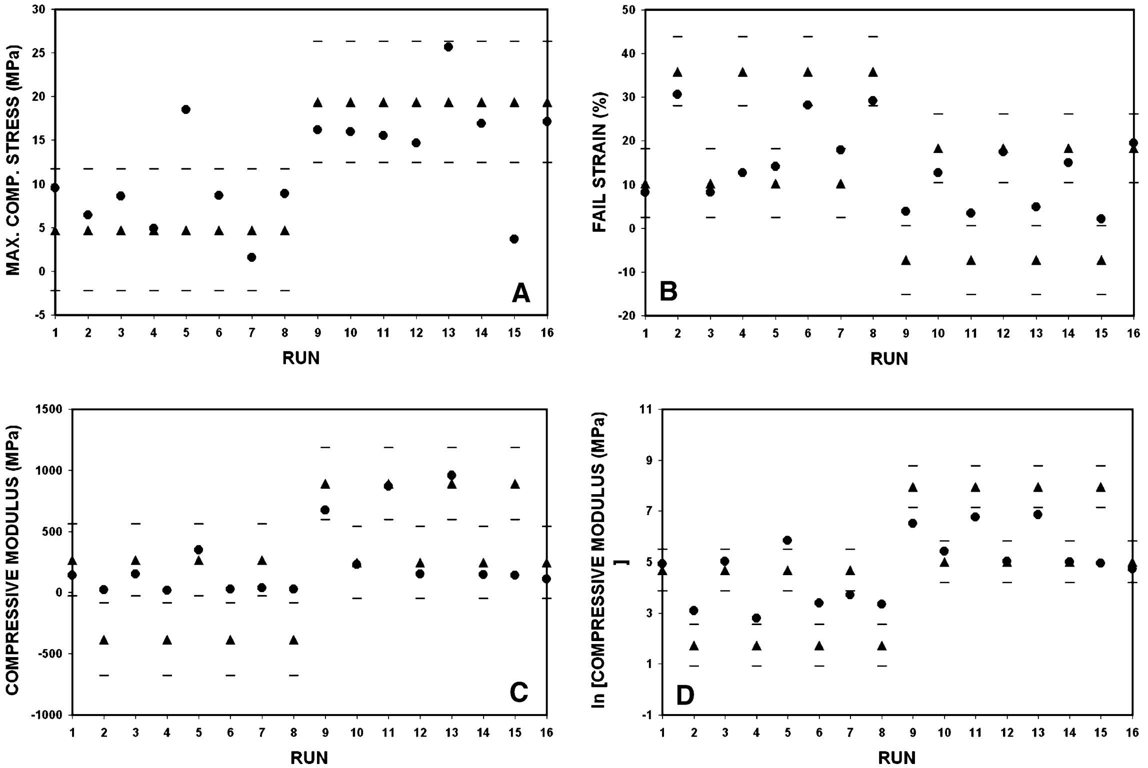

Fig. 1 Graphical representation of experiments shown in Table 7: (**a**) Predicted maximum compressive stress by DOE model and experimental results. (**b**) Predicted failure strain by DOE model and experimental results. (**c**) Predicted compressive modulus by logarithmic DOE model and experimental results. (**d**) Predicted compressive modulus by linear DOE model and experimental results. Triangles represent the predicted value and circles represent the measured value. Error bars represent 3 standard deviations from the predicted value

data is fit by the model the coefficient of determination ($0 < R^2 < 1$) is used. Values of R^2 approaching 1 are desirable as this indicates a good fit of the data. However, it is not enough to have a good fit for the data, because by increasing the number of parameters (by, for example, adding interactions) R^2 can be improved. In order to verify whether an excessive number of independent variables have been used the F statistic given by the formula shown below is used.

$$F = \frac{R^2/v_1}{(1 - R^2)/v_2} \tag{10}$$

v_1 and v_2 are the degrees of freedom given by formulas (11) and (12) below:

$$v_1 = k \tag{11}$$

$$v_2 = N - 1 - k \tag{12}$$

k is the number of predictors (i.e., β coefficients) except for the intercept and N is the number of observations. For the statistical analysis, the calculated value of F has to be compared with the F_α value obtained from the F-distribution tables to assess overall adequacy of the model. For this test we used a confidence coefficient α of 5% and the same degrees of freedom as above.

For example, for the first four equations of Table 10, there are 59 observations ($N = 59$) and 8 coefficients ($k = 8$). With $\alpha = 5\%$ and the specified degrees of freedom we find that $F_\alpha = 2.13$. To address the overall adequacy of the model the condition on formula (13) should be true:

$$|F| > F_\alpha \tag{13}$$

Comparing this value with F for the first four equations in Table 10, it is evident that the predictor variables model well the compressive properties of the cement substitute and that the models are statistically adequate. However, the R^2 value for the compressive modulus are too low and this leads us to conclude that this dependent variable can not be fit using a linear model. The residuals analysis (i.e., $y_i - y_i^P$ versus y_i^P where y_i^P is the predicted value by the model and y_i a

Table 8 2^3 DOE for mechanical properties under compression using glass fibers and methylenebisacrylamide (MBA)

Experimental conditions			
Variables	–1	+1	
Curing time (T)	24	48	hours
Fibers ratio (F)	0.05	0.30	vol. fibers/vol. filler(s)
Monomers ratio (M)	3.33	20	mol acrylic acid/mol MBA
Fixed parameters			
Filler + fibers vol. percentage (FVP)	26	vol. filler(s)/vol. slurry	
Cation ratio (C)	50	mol acrylic acid/mol cation	
Initiator ratio (I)	2000	mol monomers (total)/mol g initiator	
Water ratio (W)	0.8	vol. acrylic acid/l water	
Hausmannite/fly ash ratio (FR)	0.5	vol. hausmannite/vol. fly ash	

Run	*F*	*M*	*T*	*Fail. strain (%)*		*Max. comp. stress (MPa)*		*Comp. modulus (MPa)*	
				Rep. 1	*Rep. 2*	*Rep. 1*	*Rep. 2*	*Rep. 1*	*Rep. 2*
1	–1	+1	–1	23.06	27.43	17.79	14.96	58.21	67.34
2	+1	+1	–1	18.93	19.42	13.04	14.62	64.72	71.02
3	–1	–1	–1	21.84	19.42	40.54	39.44	196.66	189.38
4	+1	–1	–1	13.59	14.08	28.68	27.99	172.47	172.47
5	–1	+1	+1	10.68	11.17	17.79	18.06	142.03	183.81
6	+1	+1	+1	11.89	12.14	17.58	18.06	97.65	97.65
7	–1	–1	+1	15.53	15.05	42.33	39.64	236.72	236.72
8	+1	–1	+1	9.71	11.65	32.27	32.34	224.89	224.89

Properties modeling	*DOE model equation*		
Maximum compressive stress (MPa)	$y_1 = 25.95 - 2.87F - 9.46M \pm 2.57$	r^2 = 0.8912	8-1
Compressive modulus (MPa)	$y_2 = 152.29 - 54.48M + 28.25T \pm 17.1$	r^2 = 0.9198	8-2
	$\ln y_2 = 4.91 - 0.41M + 0.22T \pm 0.14$	r^2 = 0.9268	8-3
Failure strain (%)	$y_3 = 15.97 - 3.75T \pm 2.89$	r^2 = 0.7085	8-4

data point) of the compressive modulus on Fig. 2 shows that these values are not distributed randomly. This particular funneled pattern for the residuals suggests a transformation of the dependent variable into its logarithm to fit the data. The logarithmic model and its improved statistics and R^2 (0.806 vs. 0.485) are also shown.

The next step consists of testing the null hypothesis for each coefficient in the regressions and to determine if there are grounds for considering any of the coefficients to be zero using the t-student distribution. The coefficients fulfilling the condition on formula (14) cannot be neglected.

$$|t| > t_\alpha \tag{14}$$

The value of $t_\alpha = 1.676$ is calculated using $v = N - 1 - k$ degrees of freedom ($v = 50$) and $\alpha = 5\%$. Examining the t-values for each one of the coefficients leads us to propose models with less parameters. As can be seen the F value for the models increase dramatically, while the remaining statistics (i.e., s and R^2) are marginally affected, i.e., the overall adequacy of the models improved.

The final step involves eliminating outliers in the data in order to improve the correlation coefficient. In this analysis, those points that fell outside of two standard deviations for the predicted value of any dependent variable were eliminated. If a sample exceeded 2 standard deviations for any dependent variable, it was eliminated for consideration from *all* dependent variables. The resulting sample still contains 52 data points. Table 9 also shows the resulting models after the elimination of all outliers outside two standard deviations from the predicted values. In general, the models changed minimally in their coefficients but the statistics improved. The predicted values for the failure strain after the elimination of outliers fit accurately within a region of $y_i^P \pm 2.6s$, with five data points that do not fall within two standard deviations from the predicted value. This represents 10% of the data and is very good statistically. However, the resultant formula can give negative failure strain, which does not make physical sense. The predicted values for the maximum compressive stress are very well predicted: Only 11 data points are outside of the $y_i^P \pm s$ interval and all data points can be enclosed in an $y_i^P \pm 1.7s$ interval. Remarkably, two of the points that fall outside of the one standard deviation interval have excellent mechanical properties due to the high comonomer/monomer ratio (maximum compressive stress of

Table 9 2^2 DOE for maximum tensile stress testing

Experimental conditions					
Variables			–1	+1	
Cation ratio (*C*)			20	50	mol acrylic acid/mol cation
Monomer ratio (*M*)			1.67	3.33	mol acrylic acid/mol MBA
Fixed parameters					
Initiator ratio (*I*)			2000		mol monomers (total)/mol initiator
Water ratio (*W*)			0.8		vol. acrylic acid/vol. water
MM/MFA vol. ratio (FR)			50/50		vol. hausmannite/vol. microflyash
Filler volume percentage (FVP)			26%		vol. filler(s)/vol. total
Time (*T*)			72		hours
Run	*C*	*M*	*Maximum tensile stress (MPa)*		
1	–1	+1	1.59		
2	+1	+1	1.36		
3	–1	–1	1.65		
4	+1	–1	2.38		
Mechanical property			*DOE model equation*		
Maximum tensile stress (MPa)			$y_4 = 1.74 + 0.12C - 0.27M - 0.24CM$	$r^2 = 1$	9-1

approximately 40 MPa and a failure strain of 14%). The compressive modulus model had very good results as well. Twelve data points were outside the $y_i^P \pm s$ boundary while almost all data points were enclosed by an $y_i^P \pm 1.5s$ interval. In contrast to the linear model, the logarithmic model did not result in negative values thus making physical sense. Further manipulation of the data did not bring any noticeable improvements.

The conclusions from this model fitting are the following:

(1) Decreasing the amount of aluminum cation increased the compressive failure strain of the samples while reducing the compressive modulus. Cation amount was not a significant factor for the maximum compressive stress.

(2) *N,N′*-Methylenebisacrylamide imparted samples with higher compressive stress and compressive modulus without an appreciable effect on compressive failure strain. Comonomer also significantly raised the tensile strength.

(3) The ratio of hausmannite to fly ash affected all dependent variables: increasing it resulted in higher maximum compressive stress, lower failure strain and higher compressive modulus. Below a filler ratio of 0.5 vol. hausmannite/vol. fly ash the samples do not harden. For economic reasons it is desired to use as little hausmannite as possible and the effect of filler ratio on the mechanical properties is less noticeable than those of the monomer/cation ratio, time and comonomer/monomer ratio.

(4) Increasing the filler volume percentage affected the failure strain and the compressive modulus by making the cement less flexible. However, the largest effect of this variable is on the rheology of the uncured mixture.

(5) Adding glass fibers reduced the mechanical properties of the cements.

(6) Increasing initiator diminished the maximum compressive stress; with no effect on compressive failure strain and compressive modulus. Overall, the effect of initiator amount was small. The range studied did not adequately address this variable; eventually with no initiator the samples would not harden. However, this study showed that initiator amount cannot be used to improve cement properties.

(7) Increased curing time results in less flexible, higher strength samples.

Conclusions

Design of experiments proved to be an excellent way to develop polyalkenoate cement formulations that harden by a combination of free radical polymerization and multivalent cation crosslinking. The independent variables selected for the design of experiments were bound by physical and economical constraints. The first step was to determine approximate operating ranges: among low-cost fillers non-hausmannite containing formulations did not harden, formulations with a monomer/water ratio below 0.8 vol. acrylic acid/vol. water did not harden, formulations with a monomer/cation ratio above 80 mol acrylic acid/mol inorganic cation source did not harden and at 35% by volume solids the slurries had rheological characteristics that prevented measurement by the equipment used to characterize the rheology of cements.

Table 10 Multivariable linear regression with statistical hypotheses analysis

Experimental conditions						
	–1	+1	Definition			
Cation ratio (C)	20	50	mol acrylic acid/mol cation			
Comonomer ratio (M)	3.33	20	mol acrylic acid/mol MBA			
Fiber ratio (F)	0.05	0.3	vol. fibers/vol. filler(S)			
Filler 1/filler 2 (FR)	0.78	1	vol. hausmannite/vol. microflyash			
Filler + fibers volume percentage (FVP)	0.26	0.3	Filler(s) + fibers vol./total vol.			
Initiator ratio (I)	2000	5000	mol monomers (total)/mol initiator			
Water ratio (W)	0.5	1	vol. acrylic acid/vol. water			
Time (T)	24	48	hours			
Model equations and statistics from SAS programs				F	s	R^2
Max. comp. stress (MPa)	$y_1 = 940.43 - 0.20533C + 667.22M - 2.41F + 0.997\mathrm{FR} - 0.42\mathrm{FVP} - 0.92I + 2.42W + 2.78T$			45.38	3.984	0.879
Comp. modulus (MPa)	$y_2 = 3521.07 - 118.48C + 2349.49M - 27.73F + 10.64\mathrm{FR} + 1.85\mathrm{FVP} + 11.79I - 26.1W + 83.37T$			6.12	158.57	0.495
Ln Comp. modulus (MPa)	$\ln y_2 = 38.1 - 0.73C + 23.59M - 0.12F + 0.319\mathrm{FR} + 0.26\mathrm{FVP} - 0.0391I - 0.393W + 0.549T$			26.02	0.6257	0.806
Failure strain (%)	$y_4 = 2.75 + 7.1C + 1.568M - 1.3F - 1.15\mathrm{FR} - 7.86\mathrm{FVP} + 0.16I + 5.93W - 4.07T$			55.64	3.93	0.899
Test of hypotheses	$\alpha = 5\%$	$N = 59$	$k = 8$ $\quad v = N - 1 - k = 50$ $\quad v_1 = k = 8$ $v_2 = N - 1 - k = 50$	$t_\alpha = 1.676$ $F_\alpha = 2.13$		
Improved model equations and statistics from SAS programs				F	s	R^2
Max. comp. stress (MPa)	$y_1 = 963.15 + 682.8M - 2.21F + 1.16\mathrm{FR} + 2.66T$			80.52	4.17	0.856
Ln Comp. modulus (MPa)	$\ln y_2 = 37.9 - 0.76C + 23.45M + 0.31\mathrm{FR} + 0.26\mathrm{FVP} + 0.53T$			41.9	0.62	0.798
Failure strain (%)	$y_1 = 1.63 + 7.01C - 1.27\mathrm{FR} - 7.86\mathrm{FVP} + 6.72W - 4.31T$			85.86	3.98	0.890
Test of hypotheses	$\alpha = 5\%$	$N = 59$	$k = 5$ $\quad v = N - 1 - k = 53$ $\quad v_1 = k = 5$ $v_2 = N - 1 - k = 53$	$t_\alpha = 1.674$ $F_\alpha = 2.389$		
Model equations and statistics after elimination of outliers				F	s	R^2
Max. comp. stress (MPa)	$y_1 = 975 + 691.47M - 2.1F + 1.17\mathrm{FR} + 2.24T$			104.49	3.58	0.899
Ln comp. modulus (MPa)	$\ln y_2 = 33.4 - 0.67C + 20.25M + 0.35\mathrm{FR} + 0.26\mathrm{FVP} + 0.4T$			47.29	0.53	0.837
Failure strain (%)	$y_3 = 1.62 + 6.64C - 1.46\mathrm{FR} - 7.86\mathrm{FVP} + 7.151W - 3.81T$			133.83	3.04	0.936
Test of hypotheses	$\alpha = 5\%$	$N = 52$	$k = 5$ $\quad v = N - 1 - k = 46$ $\quad v_1 = k = 5$ $v_2 = N - 1 - k = 46$	$t_\alpha = 1.679$ $F_\alpha = 2.428$		

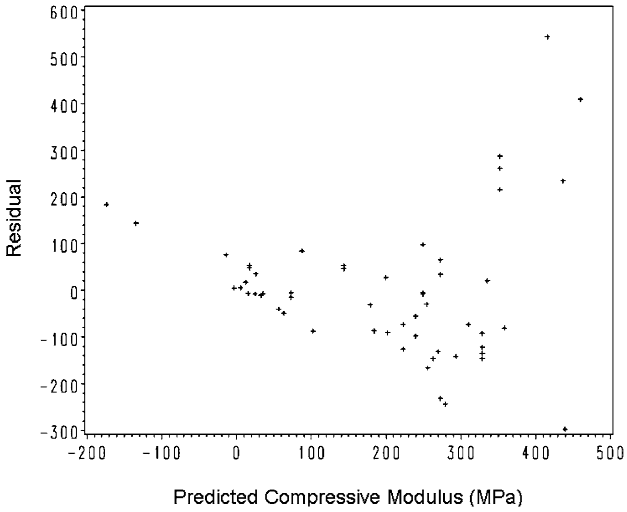

Fig. 2 Residuals plot for compressive modulus

The mechanical properties of the cement were highly affected by hardening time, amount of aluminum cation and *N,N′*-methylenebisacrylamide/acrylic acid (comonomer) mole ratio. Longer curing times and more cation resulted in less flexible, higher strength samples. Higher comonomer/monomer ratios resulted in higher strength samples with little or no change in flexibility. All other variables had an insignificant effect on the mechanical properties. One variable not studied with a large range was monomer/water ratio. Since the economic penalty for changing this variable was high, we found a minimum monomer/water volume ratio that consistently led to hardened samples and fixed this parameter. In the final multivariable analysis of compressive properties, no interactions were needed; while the only interaction needed for the tensile strength was the interaction between the organic and ionic crosslinker.

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