The influence of poly(acrylic acid) molar mass and concentration on the properties of polyalkenoate cements

Part I Compressive strength

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The influence of poly(acrylic acid), PAA molar mass, concentration and glass volume fraction were investigated on the compressive strength of polyalkenoate cements after ageing for 1, 7 and 28 days in water at 37°C. The compressive strength increased with the molar mass of the polyacid. The increase in compressive strength with molar mass was greater at higher PAA concentrations. Increasing the polyacid concentration generally increased the compressive strength, until PAA concentrations greater than 50% m/m were achieved. Increasing the glass volume fraction had liitle influence on the compressive strength increased with low PAA concentrations, however the compressive strength increased with glass volume fraction for cements that had a high PAA concentration. Increasing the ageing time of the cement prior to testing generally resulted in an increase in compressive strength. However the influence of ageing time was greater in cements made with high PAA concentrations. © 2001 Kluwer Academic Publishers

1. Introduction

Glass polyalkenoate (ionomer) cements are formed from ion leachable glasses and aqueous poly(acrylic acid). The acid degrades the glass releasing metal cations, principally Al³⁺ and Ca²⁺, which are chelated by the carboxylate groups of the polymer. The metal cations serve to cross-link the polyacrylate chains, resulting in a hard ceramic like cement. The setting reaction is shown schematically in Fig. 1. The final material consists of residual glass particles embedded in a polysalt matrix. Glass polyalkenoate cements are used widely in dentistry [1] and have also found use in medicine for cementing cochlear implants [2] and as a bone cement and substitute material [3]. Calcium phosphate cements based on apatite [4] and tetracalcium phosphate [5,6] containing poly(acrylic acid) and related polycarboxylic acids have also been studied in recent years. These cements have much higher compressive and flexural strengths than the equivalent polyacid free calcium phosphate cements [7]. Polyalkenoate cements based on bioactive glasses have also been studied [8]. Recently polyalkenoate cements based on waste gasifier slags have also been proposed for use in the









Figure 1 Schematic setting reaction of a glass polyalkenoate cement.

building industry as rapid setting repair cements and moulded products, such as roof tiles [9, 10].

The mechanical properties of current dental glass polyalkenoate cement formulations have improved considerably during the last five years and as a consequence they are increasingly being used as posterior

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dental filling materials. They have many advantages for restoring teeth, including the ability to bond directly to the tooth and the ability to release fluoride ions, which have a cariostatic role.

Most studies have investigated the compressive strength of these cements and have determined the properties of existing commercially available dental compositions [11–17]. Relatively few studies have investigated the influence of the cement formulation or other mechanical properties, such as flexural strength and fracture toughness [18–27].

In recent years poly(acrylic acid) concentration and molar mass were shown to be the most important parameters determining the mechanical properties of these cements [24–27]. In practical cement formulations the viscosity of the cement pastes is determined by the molar mass of the the poly(acrylic acid) and its concentration. Based on the previous studies improved cements with higher compressive strengths could be produced by increasing the molar mass and concentration of the poly(acrylic acid). However such cements would have unacceptably high viscosities, prior to setting and in practical cement formulations polyacid molar mass is "traded off" against polyacid concentration and glass volume fraction.

In order to optimise the mechanical properties of polyalkenoate cements it is important to be able to understand the relationships between polyacid molar mass, polyacid concentration and cement properties. The results of these studies should also be valuable in the development of polyalkenoate cements based on waste gasifier slags for the building industry, as well as the development of medical cements based on calcium phosphate salts, such as tetracalcium phosphate [5, 6], hydroxyapatite and fluorapatite [4].

The present series of papers investigates cement mechanical properties as a simultaneous function of polyacid molar mass, polyacid concentration, glass volume fraction and ageing time. Part I, the present paper deals with compressive strength, whilst part II deals with Young's modulus and flexural strength and part III with fracture toughness and toughness.

2. Experimental

2.1. Materials

2.1.1. Glass

The glass for this study was specially prepared for the purpose. The composition was designed not to lose fluorine from the melt as silicon tetrafluoride during firing [28]. The glass had the following molar composition $4.5\text{SiO}_2 \cdot 1.5\text{P}_2\text{O}_5 \cdot 3\text{Al}_2\text{O}_3 \cdot 4\text{CaO} \cdot \text{CaF}_2$. It was similar to one of the compositions studied by Griffin and Hill [26], except that the glass was melted on a 5 kg scale using aluminium phosphate as a source of phosphorus rather than phosphorus pentoxide. The glass was prepared by a melt quench route and the cross-link density of the glass was 1.33 as calculated according to Ray [29].

2.1.2. Poly(acrylic acid)s

Four poly(acrylic acid)s were obtained from CIBA speciality polymers (PO Box 38 Bradford UK). These four

TABLE I Molar masses determined by gel permeation chromatography

Code	${ar M}_{ m n}$	${ar M}_{ m w}$	PD	
E5	3,030	9,270	3.1	
E7	8,140	25,700	3.2	
E9	26,100	80,800	3.1	
E11	64,400	210,000	3.1	

polyacids have the molar masses given in Table I. The poly(acrylic acid)s were obtained as aqueous solutions which were freeze dried and ground to a particle size $<90 \ \mu m$ prior to use.

2.1.2.1. Cement preparation. Cements were prepared by thoroughly mixing the glass powder ($<45 \ \mu$ m) with the poly(acrylic acid) and mixing this with 10% m/m (+) tartaric acid solution. Cements were allowed to set in split stainless steel moulds measuring 6.0 mm high and 4.0 mm in diameter for one hour at $37 \pm 2^{\circ}$ C then removed from the mould and stored in distilled water at $37 \pm 2^{\circ}$ C prior to testing. Tests were carried out after 1, 7 and 28 days. Cements were prepared with three glass volume fractions; 0.40, 0.45 and 0.50 and with PAA concentrations from 30 to 60% m/m. Cements could not be produced at both high PAA concentrations and high molar masses. The glass volume fraction was calculated based on a glass density of 2.65 g \cdot cm⁻³.

2.1.2.2. Compressive test. The compression tests were performed on the cement cylinders. The testing procedure was based on the ISO standard "ISO 7489 : 1986 Dental Glass Polyalkenoate Cements" [30] An Instron tensometer (Instron High Wycombe Bucks UK) was used for the test at a crosshead displacement rate of $1 \text{ mm} \cdot \text{min}^{-1}$. The test was carried out on 8 samples and the compressive strength was calculated according to:

$$\sigma_{\rm c} = \frac{F}{\pi r^2}$$

Tests were performed in water at $37 \pm 2^{\circ}$ C rather than at room temperature as specified in the ISO standard. This results in most cements exhibiting greater plasticity with generally lower values for compressive strength being obtained.

3. Results and discussion

Table II gives the values obtained for compressive strength of the 0.4 glass volume fraction cements. Fig. 2 shows the influence of number average molar mass (M_n) on compressive strength for 40% PAA cements made with a glass volume fraction of 0.4 at 1, 7 and 28 days. Compressive strength increases, as the molar mass is increased at all three time intervals studied. The highest compressive strength is exhibited by the highest molar mass E11 PAA and the lowest compressive strength by the lowest molar mass E5 PAA. The compressive strength of glass polyalkenoate cements, has previously been shown to increase with the PAA molar mass [31, 32]. The compressive strengths generally

TABLE II Compressive strength (σ_c) for 0.4 glass volume fraction cements

PAA		E5			E7		E9		E11	
[PAA]	Time (days)	$\sigma_{\rm c}$ (MPa)	SD(n = 8)	$\sigma_{\rm c}$ (MPa)	SD(n = 8)	$\sigma_{\rm c}$ (MPa)	SD(n = 8)	$\sigma_{\rm c}$ (MPa)	SD(n=8)	
30%	1	38	5	34	2	43	3	49	3	
30%	7	37	5	69	7	49	3	57	4	
30%	28	39	3	44	4	43	4	48	5	
35%	1	39	7	44	3	55	2	63	4	
35%	7	40	6	57	4	58	5	82	7	
35%	28	37	6	56	5	56	3	75	7	
40%	1	54	5	50	3	76	6	84	7	
40%	7	49	5	69	7	85	3	119	5	
40%	28	65	12	79	18	87	10	129	9	
45%	1	59	5	73	7	86	8	127	13	
45%	7	59	12	80	7	127	6	155	11	
45%	28	65	9	73	3	110	9	156	10	
50%	1	70	8	76	6	118	7	_	-	
50%	7	81	6	84	8	138	13	-	-	
50%	28	80	7	104	9	158	5	-	-	
55%	1	55	5	88	5	112	9	_	-	
55%	7	65	6	89	8	142	15	-	-	
55%	28	68	10	116	6	141	21	_	-	
60%	1	44	2	73	4	_	-	-	-	
60%	7	71	11	97	7	_	_	_	-	
60%	28	56	7	95	13	_	_	-	_	



Figure 2 The influence of number average molar mass (M_n) on compressive strength for 40% PAA cements made with a glass volume fraction of 0.4 at 1, 7 and 28 days. $\blacklozenge = 1$ day $\blacksquare = 7$ days $\triangle = 28$ days.

increases with cement storage time, however the influence of the PAA molar mass is still significant even at 28 days, suggesting that the properties of the polysalt matrix dominate the fracture behaviour. This contrasts with the view of Wasson and Nicholson [33] that the PAA is only important in the early stages of the setting process and that the formation of a silicate phase dominates the long term properties.

Fig. 3 shows the compressive strength of hardened polyalkenoate cement pastes as a function of poly(acrylic acid) concentration for the four poly(acrylic acid)s at 1 day for a glass volume fraction of 0.4. It can be seen that generally the compressive strength increases with PAA concentration. Crisp *et al.* [34] also showed the compressive strength to increase with PAA concentration in a small number of cements. The influence of PAA concentration is greatest for the highest molar mass E11 polyacid. As the polymer molar mass of the cement is increased the influence of the polymer concentration on compressive strength increases and is reflected by a rise in slope of the compressive strength against PAA concentration plot. The greatest increase in compressive strength with PAA concentration occurs with the E11 data, where at the lowest PAA concentration of 30% a compressive strength of 49 MPa is recorded rising to 127 MPa at the highest PAA concentration of 45%. The E5 cement exhibits a rise in compressive strength with PAA concentration, but the increase is not as marked as that seen with the E11 cements. At a PAA concentration of 30%



Figure 3 Compressive strength of hardened polyalkenoate cement pastes as a function of poly(acrylic acid) concentration for four poly(acrylic acid) molar masses at 1 day for a glass volume fraction of 0.4. $\blacklozenge = E5 \blacksquare = E7 \triangle = E9 X = E11$.

for the E5 cement the compressive strength is 38 MPa increasing to 44 MPa at a PAA concentration of 60%. The very small increase in compressive strength with PAA concentration exhibited by the lowest E5 molar mass cement supports the view proposed in part III [35] of this series of papers that most of the molar mass distribution of the E5 polymer lies below the critical molar mass required to form chain entanglements.

There is a slight fall in compressive strength for the E7 data at the 55% PAA concentration and for the E9 data above 50% PAA concentration. This is probably caused by a deficiency of metal cations in the polysalt matrix. It is unlikely that the fall in compressive strength is due to an over cross-linking effect, particularly at such a short ageing times.

Many of the compressive strength values compare well with the values quoted for the new ISO standard [36]. However it must be noted that in the new ISO test method samples uses smaller speciments and testing is performed at room temperature, rather than at 37° C. Testing at 37° C generally enhances the plasticity of the cement and results in lower values for compressive strength being obtained. The minimum acceptable compressive strength of glass ionomer cements is 50 MPa for a Type I luting cement and for a Type II restorative material 100 MPa.

Fig. 4 shows the compressive strength plotted against PAA concentration for cements made from E5, E7, E9 and E11 poly(acrylic acid)s for the 0.4 glass volume fraction cements at an ageing time of 7 days. The E11 linear regression line predicts a compressive strength value of approximately 250 MPa for a cement composition formulated at a PAA concentration of 60%. The use of predosed capsules and a mixing apparatus would make it possible to mix cement pastes at this high polymer molar mass and concentration. At higher PAA concentrations the cement could show a fall compressive strength due to a weakening effect, which is thought to arise from incomplete dissolution of the polyacid particles. Cements studied by Guggenberger *et al.* [16] exhibited such effects. This might also explain the fall in compressive strength for the E7 and E5 0.4 glass volume fraction cements tested at 1 day (Fig. 3) at the high PAA concentrations, but could equally be a result of too few ions being present for crosslinking.

The effect of ageing time on the compressive strength data is noticeable. A value of 118 MPa at an ageing time of one day is recorded for the E9 50% PAA concentration cement. At 7 days, the compressive strength rises to 138 MPa and increases further to 158 MPa at 28 days. Crisp et al. [34] have also observed the compressive strength to increase slowly with time in these materials up to 1 year. The reaction rate probably decreases with ageing time reflecting the decrease in the rate of diffusion of metal cations into the matrix, as the cement becomes more rigid and cross-linked with reaction time. This effect was also seen in the modulus data of part II of this series of papers [35]. Griffin and Hill [26] noticed an increase in compressive strength with ageing time and report that the most significant increase in strength with time occurred from 1 to 7 days. The cements then showed a marginal increase in strength after 7 days, which suggested that either the majority of cross-linking had occurred within the polysalt matrix or the reaction rate falls with ageing time. A recent study of a polyvinyphosphonic acid based cement [21] showed significant increases in compressive strength up to an ageing time of three months.

There is a fall in compressive strength for the E7 data at a PAA concentration of 55% and for the E9 data at 50% at 7 and 28 days. This trend was also seen with the daily data. However, the source of the fall in compressive strength evident in this data may to be due to a a lack of metal cations in the polysalt cement matrix. An incomplete dissolution of the poly(acrylic acid) particles is also a possible explanation for the fall in compressive strength.



Figure 4 Compressive strength of hardened polyalkenoate cement pastes as a function of poly(acrylic acid) concentration for four poly(acrylic acid) molar masses at 7 days for a glass volume fraction of 0.4. $\blacklozenge = E5 \blacksquare = E7 \triangle = E9 X = E11$.

Table III gives the compressive strength for the 0.45 glass volume fraction cements. In Fig. 5 the compressive strength is plotted against PAA concentration for cements made from E5, E7, E9 and E11 poly(acrylic acid)s at a glass volume fraction of 0.45 and an ageing time of one day. An increase in compressive strength with polymer molar mass at almost all PAA concentrations can be seen. A decrease in strength is observed for the E7 data at a PAA concentration above 50%, which was also seen for the 0.4 glass volume fraction data.

Figs 6 and 7 show the compressive strength plotted against PAA concentration for cements made from E5, E7, E9 and E11 poly(acrylic acid)s at a glass volume fraction of 0.45 and an ageing time of 7 and 28 days respectively. The slopes of the compressive strength PAA plots for the 0.45 1, 7 and 28 day series are listed in Table VI. The influence of PAA concentration on compressive strength continues to increase as the molar mass is raised up to a number average molar mass of 6.44×10^3 corresponding to the E11 PAA at both ageing times. At a number average molar mass of 6.44×10^3 a fall in the dependence of compressive strength on PAA concentration is seen. No significant conclusions can be drawn from this as there were only two cement compositions tested with cements formulated from the highest polymer molar mass. There is a significant fall in compressive strength for the E11 monthly data with PAA concentration. The compressive strength shows a decrease in strength from 156 MPa to 79 MPa, representing almost a two-fold

TABLE III Compressive strength (σ_c) for 0.45 glass volume fraction cements

PAA		E5			E7		E9		E11	
[PAA]	Time (days)	$\sigma_{\rm c}$ (MPa)	SD(n = 8)							
30%	1	29	4	36	4	48	7	50	3	
30%	7	38	5	31	10	50	5	70	4	
30%	28	25	8	45	8	42	6	79	4	
35%	1	37	5	68	5	56	5	76	9	
35%	7	43	6	55	5	49	11	82	9	
35%	28	28	4	66	4	69	3	62	5	
40%	1	57	4	62	8	85	5	_	-	
40%	7	67	6	81	12	116	15	_	_	
40%	28	64	4	88	10	65	4	-	-	
45%	1	65	16	79	6	100	11	_	_	
45%	7	86	14	98	11	126	17	_	-	
45%	28	86	7	115	11	124	18	_	_	
50%	1	81	10	115	8	_	_	_	-	
50%	7	68	15	108	21	_	_	_	_	
50%	28	88	9	136	7	_	_	_	-	
55%	1	80	12	114	3	_	_	_	_	
55%	7	93	13	140	9	_	_	_	-	
55%	28	69	13	123	16	_	_	_	_	
60%	1	80	12	100	6	_	_	_	-	
60%	7	85	9	107	6	_	_	_	_	
60%	28	84	4	123	8	-	-	-	-	



Figure 5 Compressive strength plotted against PAA concentration for cements made from E5, E7, E9 and E11 poly(acrylic acid) for the 0.45 glass volume fraction data at an ageing time of 1 day. $\blacklozenge = E5 \blacksquare = E7 \triangle = E9 X = E11$.



Figure 6 Compressive strength plotted against PAA concentration for cements made from E5, E7, E9 and E11 poly(acrylic acid) for the 0.45 glass volume fraction data at an ageing time of 7 days. $\blacklozenge = E5 \blacksquare = E7 \triangle = E9 X = E11$.

decrease in strength. It is difficult to know if this effect is real because there was no fall in other mechanical properties for the same cement formulation. A possible explanation may be the increase in the viscosity of the cement mix. A much smaller quantity of cement mix was required to produce specimens for compression testing compared to samples that were required for the double torsion and flexural tests. It was found that more homogenous cement pastes could be obtained when the quantity of cement mix/powders was increased. This resulted in greater standard deviation on the data for compressive strength and might explain why there was an apparent decrease in strength for the above composition. Fig. 8 shows the compressive strength plotted against PAA concentration for the E5, E7, E9 and E11 polyacids for the 0.5 glass volume fraction cements at an ageing time of one day. There is a further increase in compressive strength with glass volume fraction. The E11 daily data shows an increase in strength as the glass volume fraction is increased from 0.4 to 0.45 to 0.5 with values of 49, 50 and 78 MPa, respectively.

Table VII lists the slopes of the linear regression lines obtained when compressive strength was plotted against PAA concentration for the E5 and E7 ployacid cements for the three glass volume fractions at an ageing time of one day. The slopes all rise with glass volume fraction. The PAA concentration exerts a

TABLE IV Compressive strength (σ_c) for 0.5 glass volume fraction cements

PAA		E5		E7		E9		E11	
[PAA]	Time (days)	$\sigma_{\rm c}$ (MPa)	SD(n=8)	$\sigma_{\rm c}$ (MPa)	SD(n = 8)	$\sigma_{\rm c}$ (MPa)	SD(n = 8)	$\sigma_{\rm c}$ (MPa)	SD(n=8)
30%	1	34	8	54	5	54	7	78	
30%	7	32	7	47	13	40	4	118	14
30%	28	40	6	44	8	59	5	57	4
35%	1	35	8	50	6	46	15	_	_
35%	7	51	10	47	3	73	13	_	_
35%	28	56	5	56	17	66	19	_	_
40%	1	47	11	83	11	_	_	_	_
40%	7	60	13	97	14	_	_	_	_
40%	28	79	6	115	10	_	_	_	_
45%	1	42	6	108	7	_	_	_	_
45%	7	91	9	137	6	_	_	_	_
45%	28	97	9	138	17	_	_	_	_
50%	1	102	8	_	_	_	_	_	_
50%	7	118	9	_	_	_	_	_	_
50%	28	102	19	_	_	_	_	_	_
55%	1	_	_	_	_	_	_	_	_
55%	7	_	_	_	_	_	_	_	_
55%	28	_	_	_	_	_	_	_	_
60%	1	_	_	_	_	_	_	_	_
60%	7	_	_	_	_	_	_	_	_
60%	28	_	_	_	_	_	_	_	_



Figure 7 Compressive strength plotted against PAA concentration for cements made from E5, E7, E9 and E11 poly(acrylic acid) for the 0.45 glass volume fraction data at an ageing time of 28 days. $\blacklozenge = E5 \blacksquare = E7 \Delta = E9 X = E11$.

greater influence on compressive strength as the glass volume fraction is increased for the two lowest molar mass PAAs. The marked dependence of compressive strength on PAA concentration becomes most noticeable as more metal cations become available for crosslinking. If there is a lack of cations present in the matrix to cross-link the poly(acrylate) chains there will only be a small influence of PAA concentration on compressive strength.

A fall in compressive strength with PAA concentration is observed for the E9 data (Fig. 9). This was also observed for the 0.45 glass volume fraction 28 day E11 data (Fig. 7). In this set of results the mag-

TABLE V Slopes of σ_c against PAA conentration plots for 0.4 glass volume fraction cements

Polymer	1 day	7 days	28 days	
E5	0.47	1.31	0.91	
E7	1.65	1.16	2.12	
E9	3.11	4.27	4.68	
E11	5.10	6.62	7.56	

nitude of the decrease is smaller with a compressive strength of 54 MPa recorded at a polymer concentration of 30% and 46 MPa at 35%. Taking into account the standard deviation it can be argued that the drop in



Figure 8 Compressive strength plotted against PAA concentration for cements made from E5, E7, E9 and E11 poly(acrylic acid) for the 0.50 glass volume fraction data at an ageing time of 1 day. $\blacklozenge = E5 \blacksquare = E7 \triangle = E9 X = E11$.



Figure 9 Compressive strength plotted against PAA concentration for cements made from E5, E7, E9 and E11 poly(acrylic acid) for the 0.50 glass volume fraction data at an ageing time of 28 days. $\blacklozenge = E5 \blacksquare = E7 \Delta = E9 X = E11$.

TABLE VI Slopes of the σ_c against PAA concentration plots for 0.45 glass volume fraction cements

TABLE VII Slopes of the σ_c / against PAA concentration plots for the 0.4, 0.45 and 0.5 glass volume fraction data at 1 day

Polymer	1 day	7 days	28 days
E5	1.87	1.72	2.02
E7	2.40	3.03	2.85
E9	4.3	5.9	4.84
E11	5.2	2.4	3.4

Polymer/glass volume fraction	0.4	0.45	0.5
E5	0.47	1.87	2.86
E7	1.65	2.40	3.9

strength can be interpreted as minimal. However, a similar effect was also seen with the fracture toughness and flexural strength data for the same cement formulation [35, 37]. Fig. 9 shows the compressive strength plotted against PAA concentration for cements made from E5, E7, E9 and E11 polyacids for the 0.5 Glass volume fraction data series at an ageing time of 28 days. For most of the data there is a rise in strength with ageing time as

TABLE VIII Slopes of the σ_c / against PAA concentration plots for the 0.4, 0.45 and 0.5 glass volume fraction data at 28 days

Polymer/glass volume fraction	0.4	0.45	0.5
E5	0.91	2.02	3.3
E7	2.12	2.82	6.82

ageing time increases from one day to 7 days. At 28 days the compressive strength does not rise significantly for most of the cements studied. This suggests that after 7 days either the majority of cross-linking in the polysalt matrix has taken place or that the speed at which the cross-links form is hindered by the reduced diffusion of ions in the cement matrix. The strength of the cement matrix will most likely rise beyond an ageing time of 28 days an effect seen in the results obtained from the PVPA based cement system where the compressive continued to increase up to an ageing time of 168 days.

Table VIII lists the slopes obtained when compressive strength is plotted against PAA concentration for the E5 and E7 polyacids at all three glass volume fractions at an ageing time of 28 days. The PAA concentration exerts a greater influence on compressive strength as the glass volume fraction is increased for the E5 and E7 data. This trend was also seen with the data at one day.

Fig. 10 shows the compressive strength plotted against the glass volume fraction of the cement for the E7 polyacid at PAA concentrations of 35 and 45%. There is no consistent increase in compressive strength with glass volume fraction for the 35% PAA cement, however there is a significant increase in compressive strength for the 45% PAA cements. This suggests that in the higher PAA concentration cements at lower glass volume fractions the cations required for cross-linking the PAA chains are in short supply.

There is generally a significant increase in the E5 compressive strength data at all three ageing times as the glass volume fraction is increased from 0.4 to 0.45. As the glass will exhibit a higher Young's modulus than the polysalt matrix, (typically 100 GPa compared to a range of approximately 1 to 4.5 GPa, for the polysalt matrix) it might be expected that the cement samples will become less ductile with this change in glass volume fraction. Brittle materials will generally exhibit higher compressive strengths than ductile materials.

The slopes of compressive strength plotted against PAA concentration rise with glass volume fraction at all three ageing times. The effect of glass volume fraction on the four other mechanical parameters investigated [35, 37], was only significant at the higher end of the molar mass spectrum.

The compressive strengths of these materials are not dominated by polymer concentration and molar mass to the same extent as flexural strength, fracture toughness and toughness. The compressive strength of these materials is as dependent on polymer molar mass and concentration as it is on glass volume fraction. In comparison fracture toughness, flexural strength toughness and Young's modulus were not influenced dramatically by the glass volume fraction. This trend is in good agreement with results obtained by Wilson et al. [24]. While they observed the influence of polymer molar mass on compressive strength they note that the compressive strength was not expected to be markedly molar mass dependent. This is due to the fact that the compressive strength of polymer composites reflects the properties of the filler as well as those of the polymer matrix. Further similarities exist between both these studies. Both studies found that cements formulated from high molar mass polymers tended to exhibit plastic like characteristics compared to cements which were formulated from low molar mass polymers which failed in a more brittle fashion.



Figure 10 Compressive strength plotted against the glass volume fraction of the cement for the E7 PAA for PAA concentrations of $35\%(\clubsuit)$ and $0.45\%(\blacksquare)$.

4. Conclusions

The compressive strength was found to increase as the PAA concentration was increased. The increase in compressive strength with concentration was greater with higher molar mass PAAs. Increasing the molar mass of the PAA increased the compressive strength. The compressive strengths also increased with increasing glass volume fraction. The cements generally exhibited compressive strengths that increased with storage time of the cements in water at 37°C. The increase in strength is attributed to increased cross-linking of the polysalt matrix, rather than the formation of a silicate phase, since even at 28 days the molar mass of the PAA and its concentration have a very dramatic influence on the compressive strength.

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