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

Part III *Fracture toughness and toughness*

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The influence of poly(acrylic acid), PAA molar mass and concentration on fracture toughness and toughness of glass polyalkenoate cements was investigated. Fracture toughness and toughness increased with both the molar mass of the PAA and its concentration. The fracture toughness and toughness increased dramatically with concentration for the highest molar mass PAA studied. However the increase in fracture toughness and toughness with PAA concentration was small for the lowest molar mass PAA. The influence of molar mass was greatest at the highest PAA concentration studied and least for the lowest PAA concentration. The toughness results were analysed with a reptation chain pull-out model. The greater dependance of toughness on PAA concentration for high molar mass cements can be explained by the critical molar mass for chain entanglements to form (M_e) being concentration dependant and M_e decreasing with increasing PAA concentration. *© 2001 Kluwer Academic Publishers*

1. Introduction

Compressive strength has been widely measured for glass polyalkenoate cements and is the subject of the first paper of this series [1] however many other important material properties have not been studied to any great extent. Fracture toughness, toughness and abrasive wear resistance are important properties of any posterior dental filling material. Rabinowich [2] has highlighted how the abrasive wear resistance of materials is often related to their fracture toughness and hardness and proposed:

$$V = CF/K_{\mathrm{IC}}^{0.75}\,H^{0.5}$$

where: C is a constant; V is the loss of material volume, F is the applied load, H is the hardness and K_{IC} is the fracture toughness. Wear measurements are time consuming to perform, however fracture toughness has been shown to correlate strongly with the abrasive wear resistance of model glass polyalkenoate cement compositions [3].

Glass polyalkenoate cements generally lack the strength and fracture toughness required for use as a posterior dental filling material Current commercially available restorative grade glass polyalkenoate cements have fracture toughness values in the range 0.3–0.8 MPa m$^{0.5}$ [4–7]. Despite the low fracture toughness of these materials there have been surprisingly few published studies of their fracture behaviour with view to understanding the parameters controlling the fracture process and improving their fracture toughness.

Previous studies have investigated the influence of molar mass, poly(acid) concentration, glass reactivity and ageing time on the fracture toughness and toughness [3, 8–11].

A reptation chain pull-out model shown schematically in Fig. 1 developed for thermoplastic polymers [12, 13] has been utilised to separately predict the influence of molar mass [8–10] and concentration [11] on toughness of glass polyalkenoate cements. This model envisages fracture taking occurring, exclusively in the polysalt matrix by a disentanglement process with chains being stretched and drawn from their imaginary tubes across the fracture plane. The imaginary tubes are formed from neighbouring chains, which form

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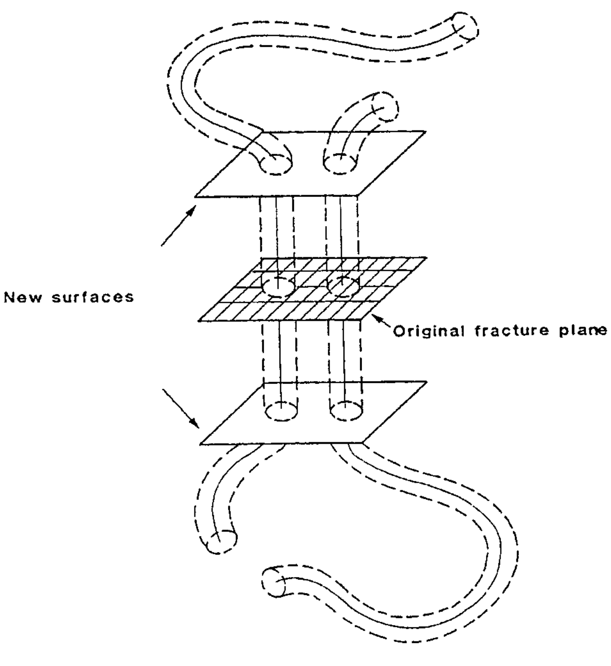

Figure 1 Reptation chain pull-out model for fracture.

entanglements. To form entanglements chains must be above a critical chain length, or molar mass (M_e). The chain pull-out model predicts:

$$\tau = \mu \pi r \, N_s \left(\frac{V}{h} \right)^n L^2$$

where: τ is the energy expended per unit area of crack plane, μ is the coefficient of friction of the chain within its tube, r is the radius of the tube N_s is the number of chain segments crossing a unit area of crack plane, V is the rate of removal of the chain from its tube, h is the spatial gap between the chain and its tube, n is an integer and L is the length of the chain.

The model predicts that cements made with poly(acrylic acid)s below the critical molar molar mass for entanglements to occur should have zero toughness and that above this molar mass the toughness should depend on the molar mass to the power two. In practice above a molar mass of about 10^5 daltons toughness is independent of molar mass. This is because it becomes energetically more favourable for a chain to undergo scission than to undergo chain pull-out.

The model also predicts the toughness to increase with PAA concentration, since the number of chains per unit area crossing the fracture plane, N_s would be expected to be proportional to PAA concentration.

Poly(acrylic acid) concentration and molar mass have been shown to be the most important parameters determining the mechanical properties of polyalkenoate cements [3, 8–11]. 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 fracture toughness values and flexural 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.

TABLE I Molar mass details

Code	$\bar{M}_n$	$\bar{M}_w$	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

In order to optimise the mechanical properties of glass polyalkenoate cements it is important to be able to understand the three way relationship between polyacid molar mass, polyacid concentration and cement properties.

The present series of papers investigates cement mechanical properties as a simultaneous function of polyacid molar mass, polyacid concentration and ageing time. This paper investigates the dependence of toughness and fracture toughness on polyacid molar mass and polyacid concentration at three different glass volume fractions.

2. Experimental

2.1. Materials

2.1.1. Glass

The glass was specially synthesised for the study and has been described previously [10].

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 polyacids have the molar masses given in Table I. The molar mass distributions are shown in Fig. 2.

2.2. Specimen fabrication

Approximately 10 g of glass was mixed with the appropriate amounts of freeze dried PAA and distilled water containing 10% m/m of (+) tartaric acid. The cement paste was placed into stainless steel moulds measuring 65 mm × 25 mm × 3.0 mm. The cements were

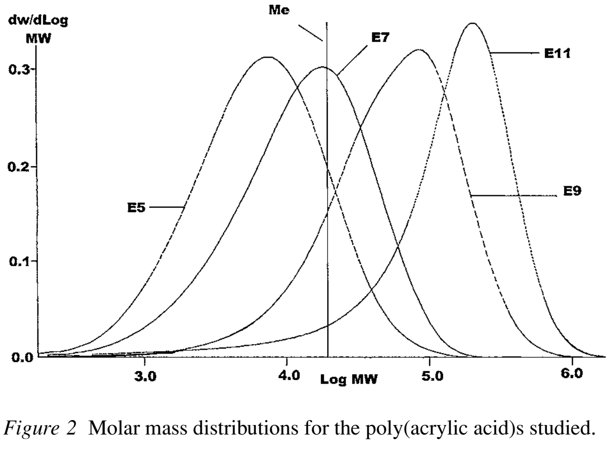

Figure 2 Molar mass distributions for the poly(acrylic acid)s studied.

TABLE II Fracture toughness for 0.4 glass volume fraction cements

		E5		E7		E9		E11	
[PAA]	PAA Time (days)	K_{IC} (MPa m$^{0.5}$)	SD	K_{IC} (MPa m$^{0.5}$)	SD	K_{IC} (MPa m$^{0.5}$)	SD	K_{IC} (MPa m$^{0.5}$)	SD
30%	1	0.17	0.04	0.25	0.03	0.26	0.01	0.41	0.01
30%	7	0.20	0.03	0.29	0.01	0.35	0.05	0.40	0.11
30%	28	0.29	0.02	0.30	0.03	0.35	0.04	0.49	0.05
35%	1	0.19	0.04	0.27	0.1	0.36	0.00	0.61	0.02
35%	7	0.23	0.04	0.35	0.05	0.44	0.04	0.65	0.05
35%	28	0.30	0.06	0.33	0.08	0.47	0.01	0.77	0.07
40%	1	0.19	0.02	0.4	0.05	0.37	0.08	0.91	0.03
40%	7	0.25	0.03	0.4	0.02	0.57	0.05	0.97	0.24
40%	28	0.23	0.02	0.49	0.07	0.62	0.06	1.07	0.02
45%	1	0.27	0.02	0.42	0.08	0.59	0.03	1.06	0.17
45%	7	0.29	0.03	0.49	0.1	0.76	0.06	1.05	0.25
45%	28	0.30	0.05	0.48	0.1	0.74	0.06	–	–
50%	1	0.29	0.05	0.52	0.16	0.91	0.20	–	–
50%	7	0.26	0.01	0.46	0.12	0.82	0.14	–	–
50%	28	0.33	0.06	0.63	0.04	0.94	0.10	–	–
55%	1	0.29	0.09	0.5	0.04	1.00	0.20	–	–
55%	7	0.29	0.02	0.48	0.11	1.17	0.17	–	–
55%	28	0.34	0.03	0.65	0.04	0.97	0.14	–	–
60%	1	0.35	0.06	0.51	0.04	–	–	–	–
60%	7	0.35	0.06	0.56	0.04	–	–	–	–
60%	28	0.36	0.08	0.62	0.14	–	–	–	–

allowed to set in the mould for one hour at 37 ± 2°C then removed from the mould and stored in distilled water at 37 ± 2°C prior to testing. Tests were carried out after 1, 7 and 28 days.

2.3. Double torsion test

The double torsion (DT) test was chosen because of its many advantages. For example the specimens are easy to produce and blunt cracks can readily be detected. The DT test is a linear compliance test where the crack length is not required for the calculation of the fracture toughness. In addition for stable crack propagation the crack propagates at constant load down the specimen. In a recent survey of different fracture toughness geometries [14] the DT test gave the most consistent and reliable results. Finally, after fracturing, the large DT specimens can be cut down to make three-point bend specimens, making economical use of materials and time.

The DT test method has been described previously [8]. A sharp groove 0.5 mm deep was cut down the centre of the moulded cement blanks to form the specimens. A fine slot was cut at one end of the specimen, using a diamond wafer blade to act as a precrack.

The DT test was performed using an Instron electromechanical testing machine. During the test, the specimen was supported on two parallel rollers of 3 mm diameter and spaced 20 mm apart and the load applied at a constant rate (0.1 mm min^{-1}) to the slotted end via two 3 mm diameter ball bearings spaced 10 mm apart. The specimen was therefore subjected to four-point bend loading, during which the crack initiated and propagated, along the centre of the specimen, within the groove. The test was carried out in tap water at 37 ± 2°C. The groove depth and sample dimensions were chosen to eliminate the need for crack shape correction factors [15].

In a DT test the mode I stress intensity factor K_1 is independent of crack length and is given by [16]:

$$K_1 = P_c W_m \left(\frac{3(1+\nu)}{W t^3 t_n} \right)^{1/2} \qquad (1)$$

where: W_m is the moment arm, W the specimen width, t the specimen thickness, t_n is the thickness in the crack plate and ν Poisson's ratio (assumed to be 0.33). Values for K_1, the fracture toughness, were obtained by substituting the appropriate specimen dimensions along with the load at fracture P_c into Equation 1.

3. Results and discussion

Table II shows the fracture toughness values obtained for the 0.4 glass volume fraction cements. Fig. 3 shows the fracture toughness of hardened polyalkenoate

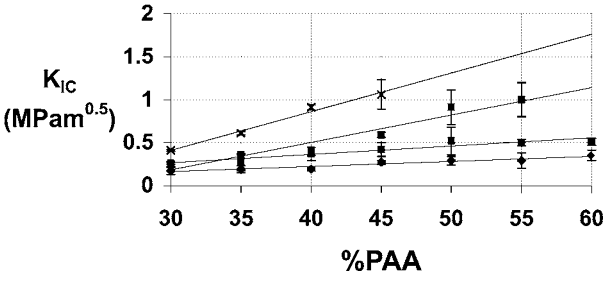

Figure 3 Fracture toughness of hardened polyalkenoate cement pastes as a function of poly(acrylic acid) concentration for four poly(acrylic acid) molar masses at 1 day for a glass volume fraction of 0.4.

TABLE III Fracture toughness for 0.45 glass volume fraction cements

		E5		E7		E9		E11	
[PAA]	PAA Time (days)	K_{IC} (MPa m$^{0.5}$)	SD ($n = 6$)	K_{IC} (MPa m$^{0.5}$)	SD ($n = 6$)	K_{IC} (MPa m$^{0.5}$)	SD ($n = 6$)	K_{IC} (MPa m$^{0.5}$)	SD ($n = 6$)
30%	1	0.17	0.02	0.26	0.00	0.30	0.02	0.40	0.02
30%	7	0.20	0.03	0.39	0.04	0.35	0.03	0.56	0.10
30%	28	0.23	0.03	0.39	0.06	0.33	0.41	0.60	0.03
35%	1	0.20	0.02	0.49	0.03	0.38	0.04	0.70	0.14
35%	7	0.25	0.02	0.42	0.12	0.45	0.09	0.88	0.15
35%	28	0.26	0.01	0.47	0.11	0.51	0.08	0.79	0.08
40%	1	0.23	0.04	0.52	0.09	0.51	0.00	–	–
40%	7	0.31	0.04	0.57	0.01	0.55	0.14	–	–
40%	28	0.27	0.02	0.49	0.07	0.73	0.09	–	–
45%	1	0.37	0.06	0.56	0.05	0.60	0.05	–	–
45%	7	0.41	0.06	0.59	0.11	0.66	0.09	–	–
45%	28	0.46	0.05	0.59	0.03	0.89	0.17	–	–
50%	1	0.41	0.07	0.70	0.03	–	–	–	–
50%	7	0.40	0.08	0.62	0.08	–	–	–	–
50%	28	0.54	0.05	0.76	0.06	–	–	–	–
55%	1	0.45	0.10	0.82	0.03	–	–	–	–
55%	7	0.40	0.07	0.67	0.07	–	–	–	–
55%	28	0.48	0.05	0.72	0.11	–	–	–	–
60%	1	0.51	0.17	0.75	0.03	–	–	–	–
60%	7	0.44	0.06	0.77	0.09	–	–	–	–
60%	28	0.47	0.05	0.35	0.03	–	–	–	–

cement pastes as a function of polyacid concentration for the four PAAs at 1 day for a glass volume fraction of 0.4. It can be seen that the fracture toughness generally increases with PAA concentration. However the increase in fracture toughness with PAA concentration is most marked with the higher molar mass PAAs. Similar results were obtained for cements aged for 7 and 28 days. The fracture toughness declines at high PAA concentrations above 50%. This phenomena was observed by De Barra and Hill [11] and is largely due to a drop in Young's modulus. Increased cement ageing time results in an increase in the fracture toughness and can largely be explained by the increased Young's modulus observed in the previous paper of this series [17]. The increased modulus is a result of continued crosslinking of the polyacrylate chains by metal cations.

Increasing the glass volume fraction from 0.4 to 0.45 has relative little influence on the results obtained and similar trends are found. Table III gives the values for fracture toughness obtained at 1, 7 and 28 days. Fig. 4 shows the influence of PAA concentration on fracture toughness of the cements produced with a a glass volume fraction of 0.45 after ageing for 1 day. Again the influence of concentration is greatest for the highest molar mass PAA studied.

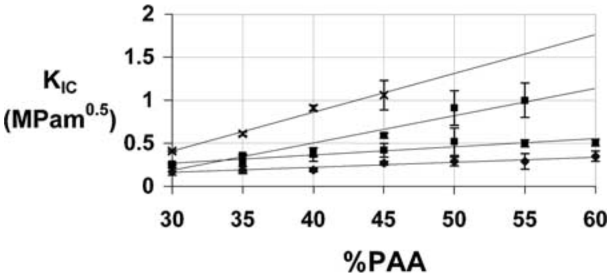

Figure 4 Fracture toughness of hardened polyalkenoate cement pastes as a function of poly(acrylic acid) concentration for four poly(acrylic acid) molar masses at 1 day for a glass volume fraction of 0.45.

The results for the fracture toughness of the 0.5 glass volume fraction cements are shown in Table IV. The range of molar masses and PAA concentrations studied is more limited, since the viscosity of the cement paste becomes too great to mix cements, at both high PAA concentration and high molar masses. In general the experimental scatter is greater on the fracture toughness results for the 0.5 glass volume fraction cements, this probably reflects the problems in obtaining homogenous specimens, as a result of the increased viscosity of the cement pastes. However it can be seen that increasing the molar mass increases the fracture toughness and that the fracture toughness increases with time and with PAA concentration. The lack of data for the two highest molar mass PAAs hinders a detailed analysis. The fracture toughness values for the high molar mass and high PAA concentration cements are typically above 1.0 MPa m$^{0.5}$ and much higher than those found for commercial cements [4–7] including a cement based on polyvinylphosphonic acid [7].

The toughness or critical strain energy release rate (G_{IC}) data for the 0.4, 0.45 and 0.5 glass volume fraction cements are shown in Tables V–VII. Figs 5 and 6 show the toughness of hardened polyalkenoate cement pastes as a function of PAA concentration for the four molar masses studied at an ageing time of 1 day with glass volume fractions of 0.4 and 0.45. In the calculation of the toughness data the Young's moduli data were averaged across the four different molar masses studied. This was done to reduce scatter on the toughness data and is an acceptable approach, since previous studies of glass polyalkenoate cements

TABLE IV Fracture toughness for 0.5 glass volume fraction cements

		E5		E7		E9		E11	
[PAA]	PAA Time (days)	K_{IC} (MPa m$^{0.5}$)	SD	K_{IC} (MPa m$^{0.5}$)	SD	K_{IC} (MPa m$^{0.5}$)	SD	K_{IC} (MPa m$^{0.5}$)	SD
30%	1	0.23	0.00	0.35	0.02	0.56	0.12	0.46	0.04
30%	7	0.18	0.01	0.46	0.01	0.52	0.02	0.62	0.17
30%	28	0.25	0.05	0.37	0.14	0.57	0.07	0.84	0.39
35%	1	0.32	0.03	0.28	0.00	0.50	0.03	–	–
35%	7	0.26	0.02	0.41	0.03	0.40	0.07	–	–
35%	28	0.27	0.05	0.43	0.13	0.71	0.19	–	–
40%	1	0.33	0.04	0.45	0.09	–	–	–	–
40%	7	0.32	0.07	0.67	0.20	–	–	–	–
40%	28	0.29	0.07	0.56	0.09	–	–	–	–
45%	1	0.35	0.05	0.57	0.14	–	–	–	–
45%	7	0.32	0.13	0.69	0.11	–	–	–	–
45%	28	0.36	0.07			–	–	–	–
50%	1	0.53	0.06	–	–	–	–	–	–
50%	7	0.36	0.06	–	–	–	–	–	–
50%	28	0.38	0.05	–	–	–	–	–	–
55%	1	–	–	–	–	–	–	–	–
55%	7	–	–	–	–	–	–	–	–
55%	28	–	–	–	–	–	–	–	–
60%	1	–	–	–	–	–	–	–	–
60%	7	–	–	–	–	–	–	–	–
60%	28	–	–	–	–	–	–	–	–

have demonstrated moduli values that are independent of molar mass [8–10].

The toughness like the fracture toughness again increases with PAA concentration for the 0.4 glass volume fraction data. The toughness is also more dependent on PAA concentration at higher PAA molar masses. For cements based on the lowest molar mass PAAs the toughness is almost independent of PAA concentration. The slopes of the toughness-PAA concentration plots are given in Table VIII.

The reptation chain pull-out model for fracture predicts the toughness to increase with PAA concentration, since the number of PAA chains crossing the fracture plane would be expected to increase with concentration. The toughness would be expected to increase proportionally with concentration. However the increase in toughness is much less than proportional to the PAA concentration for low molar mass PAAs and greater than proportional for the highest molar mass PAAs. One explanation of this phenomena is that

TABLE V Toughness for 0.4 glass volume fraction cements

[PAA]	PAA Time (days)	E5 G_{IC} (J · m^{-2})	E7 G_{IC} (J · m^{-2})	E9 G_{IC} (J · m^{-2})	E11 G_{IC} (J · m^{-2})
30%	1	10	21	23	57
30%	7	10	22	32	41
30%	28	20	21	29	57
35%	1	12	24	42	121
35%	7	12	27	43	95
35%	28	19	23	47	127
40%	1	9	39	34	204
40%	7	12	31	62	181
40%	28	9	40	63	189
45%	1	14	35	69	223
45%	7	12	34	82	156
45%	28	14	36	87	216
50%	1	15	48	146	–
50%	7	9	29	92	–
50%	28	14	49	110	–
55%	1	17	51	204	–
55%	7	11	29	171	–
55%	28	14	50	111	–
60%	1	35	73	–	–
60%	7	18	46	–	–
60%	28	18	53	–	–

TABLE VI Toughness for 0.45 glass volume fraction cements

[PAA]	PAA Time (days)	E5 G_{IC} (J · m^{-2})	E7 G_{IC} (J · m^{-2})	E9 G_{IC} (J · m^{-2})	E11 G_{IC} (J · m^{-2})
30%	1	9	19	28	50
30%	7	8	14	25	64
30%	28	11	31	22	74
35%	1	10	37	36	121
35%	7	12	47	40	153
35%	28	12	32	48	115
40%	1	10	43	51	–
40%	7	15	42	47	–
40%	28	12	53	87	–
45%	1	21	37	56	–
45%	7	23	42	58	–
45%	28	28	45	103	–
50%	1	25	52	–	–
50%	7	19	57	–	–
50%	28	31	40	–	–
55%	1	26	74	–	–
55%	7	17	71	–	–
55%	28	24	46	–	–
60%	1	36	71	–	–
60%	7	24	69	–	–
60%	28	27	72	–	–

TABLE VII Toughness for 0.5 glass volume fraction cements

[PAA]	PAA Time (days)	E5 G_{IC} ($J \cdot m^{-2}$)	E7 G_{IC} ($J \cdot m^{-2}$)	E9 G_{IC} ($J \cdot m^{-2}$)	E11 G_{IC} ($J \cdot m^{-2}$)
30%	1	11	25	65	44
30%	7	7	25	55	78
30%	28	10	35	54	118
35%	1	20	27	50	–
35%	7	13	15	30	–
35%	28	14	31	94	–
40%	1	16	28	–	–
40%	7	14	27	–	–
40%	28	11	61	–	–
45%	1	16	41	–	–
45%	7	11	34	–	–
45%	28	16	60	–	–
50%	1	39	–	–	–
50%	7	14	–	–	–
50%	28	14	–	–	–
55%	1	–	–	–	–
55%	7	–	–	–	–
55%	28	–	–	–	–
60%	1	–	–	–	–
60%	7	–	–	–	–
60%	28	–	–	–	–

the low molar mass PAAs have chain distributions in which the majority of the chains present are below entanglement values and therefore the reptation chain pull- out model does not apply. The entanglement value for PAA is not known, but for most polymer chains it is typically between 100 and 300 monomer units [18], which corresponds to a molar mass of between 7,200 and 21,600 Daltons. From the data and the relatively little influence of polyacid concentration on toughness it can be concluded that a high proportion of the E7 polyacid is below M_e thus M_e must be close to 21,600.

Table VI shows the toughness values for the 0.45 glass volume fraction cements. Fig. 6 shows the toughness-PAA concentration plot at 1 day for the 0.45 glass volume fraction cements. The slopes of the toughness-PAA concentration plots are shown in Table VIII. The influence of PAA concentration is again greatest for the highest PAA molar mass cements and there is again little influence of PAA concentration for the low molar mass PAAs. For the higher molar mass cements, the toughness is greater than proportional to the poly(acrylic acid) concentration. However, the toughness is less than proportional to the PAA concentration for the E5 polymer indicating again that this polyacid may have a molar mass distribution that is largely below the entanglement value and the reptation chain pull-out model is therefore not valid.

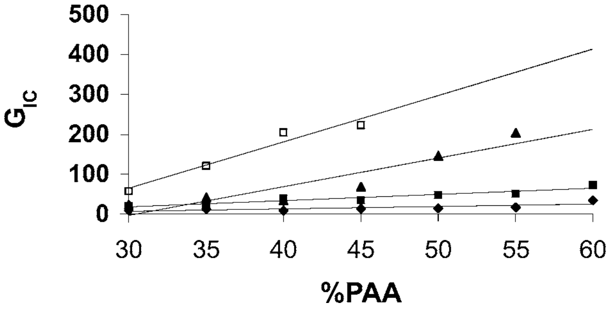

Figure 5 Toughness of hardened polyalkenoate cement pastes as a function of poly(acrylic acid) concentration for four poly(acrylic acid) molar masses at 1 day for a glass volume fraction of 0.4.

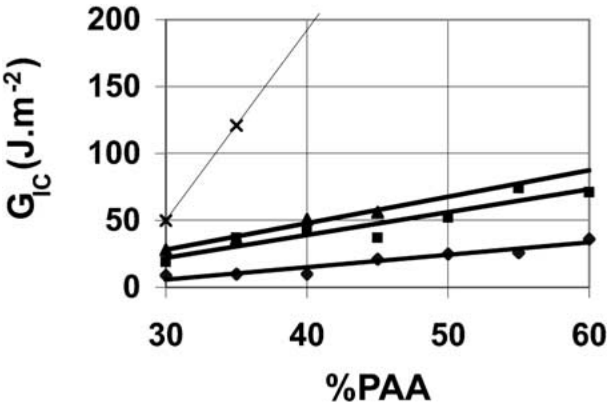

Figure 6 Toughness of hardened polyalkenoate cement pastes as a function of poly(acrylic acid) concentration for four poly(acrylic acid) molar masses at 1 day for a glass volume fraction of 0.45.

Table VII shows the toughness values for the 0.5 glass volume fraction cements. Toughness increases with the molar mass of the PAA and with concentration for the E7 and E9 PAAs, but not for the E5 PAA indicating again that the E5 PAA is probably below the entanglement molar mass.

Fig. 7 plots log toughness against log $\bar{M}_n$ for 1 day old cements made with a glass volume fraction of 0.4. It can be seen that the slope of the log toughness–log $\bar{M}_n$ plot increases at higher PAA concentrations. The increase in the slope can be explained by the molar mass value at which chain entanglements occurr (M_e) being concentration dependent. It is likely that as the concentration of chains increases that the value of M_e will decrease. Since the toughness is given by:

$$\tau \propto (M - M_e)^2$$

the proportion of chains in a given PAA molar mass distribution above the entanglement value will increase

TABLE VIII Slopes of toughness-PAA concentration plots

Polymer molar mass	Glass volume fraction	1 day slope	7 days slope	28 days slope
E5	0.4	0.65	0.13	−0.079
E7	0.4	1.56	0.52	1.14
E9	0.4	7.15	4.92	3.56
E11	0.4	11.62	8.62	10.78
E5	0.45	0.91	0.44	0.65
E7	0.45	1.70	1.62	0.98
E9	0.45	1.98	2.12	5.64
E11	0.45	14.20	17.80	8.20
E5	0.45	0.91	0.44	0.65
E5	0.5	0.012	0.008	0.007
E7	0.5	0.013	0.016	0.019

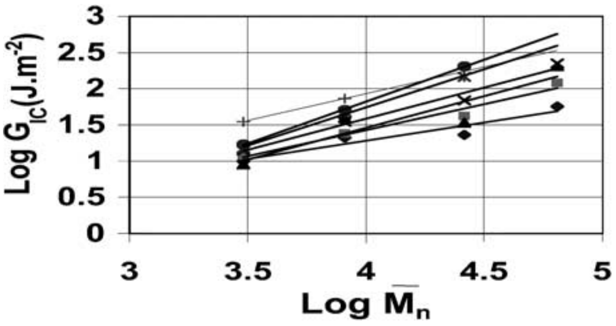

Figure 7 Plot of log toughness against log $\bar{M}_n$ for 1 day old cements made with a glass volume fraction of 0.4.

as M_e decreases. Given the wide distribution of chain lengths or molar masses that are present in each PAA this explanation can account for the general increase in the slopes of the log toughness–log $\bar{M}_n$ plots with PAA concentration shown in Table IX. At high PAA concentrations, where M_e would be expected to be low, the influence of M_e would be small and the slopes of the log toughness–log $\bar{M}_n$ plots would be expected to approach the predicted value of 2.0. Examination of Table IX shows this to be the case. The idea of a concentration dependent value of M_e is supported by viscosity studies that show M_e to decrease with increasing polymer concentration [19].

Another feature of the log toughness–log $\bar{M}_n$ plots is the toughness should extrapolate to zero for chain lengths below M_e. Clearly the plots extrapoloate to molar mass values well below 1000 and well below possible entanglement values. Such behaviour can be accounted for in part by the broad distribution of chain lengths present in each poly(acrylic acid), in part by ionic crosslinking of the polyacrylate chains increasing their effective molar mass and also some residual toughness arising from the possible formation of a silicate phase [20].

TABLE IX Slopes of $\log(G_{IC})$–$\log(\bar{M}_n)$ plots and their linear correlation coefficients

[PAA]	Glass volume fraction	1 day		7 days		28 days	
		Slope	r^2	Slope	r^2	Slope	r^2
30	0.4	0.51	0.84	0.45	0.87	0.36	0.87
35	0.4	0.75	0.95	0.66	0.94	0.67	0.94
40	0.4	0.88	0.86	0.88	0.97	0.93	0.88
45	0.4	0.90	0.95	0.97	0.95	0.91	0.97
50	0.4	1.09	0.94	1.11	0.94	0.95	0.87
55	0.4	1.21	0.97	1.37	0.99	0.96	0.87
60	0.4	1.30	1.00	1.66	1.00	1.91	1.00
30	0.45	0.55	0.93	0.68	1.00	0.49	1.00
35	0.45	0.71	0.78	0.70	1.00	0.70	1.00
40	0.45	0.69	0.62	0.48	1.00	0.88	1.00
45	0.45	0.46	0.90	0.42	0.89	0.64	0.99
50	0.45	1.29	0.94	1.94	0.61	0.45	0.75
55	0.45	1.85	0.78	2.53	0.74	1.15	0.91
60	0.45	1.20	0.95	1.86	0.95	1.73	0.63
30	0.50	0.52	0.89	0.79	0.89	0.76	0.98

4. Conclusions

Fracture toughness and toughness increase with both PAA molar mass and concentration. The increase in fracture toughness and toughness with molar mass is greatest at the higher PAA concentrations studied. The slope of the log toughness–log $\bar{M}_n$ plots increase with PAA concentration. This increase can be accounted for by the broad molar mass distributions of the PAAs studied and a concentration dependant value for M_e. Previous studies attributed the lower dependence of toughness on molar mass to the presence of the ionic crosslinks in the polysalt matrix. It now appears that polydispersity of the PAAs studied and M_e being concentration dependant are more important factors.

Future studies should investigate the toughness of cements produced with more monodisperse PAAs. Such studies could well lead to cements with much improved fracture toughness. The E11 poly(acrylic acid) studied in the present paper has a broad molar mass distribution. Some of the polymer chains present will be too short to give optimum toughness, whilst many of the longer chains will be above the molar mass at which chain scission occurs. The long chains in the molar mass distribution will contribute towards an increased viscosity without contributing towards an increased toughness. The value of molar mass at which chain scission occurs in thermoplastic polymers is typically about 10^5 daltons. This value is marked on the molar mass distributions given in Fig. 2. Approximately 60% of the mass of the E11 PAA is above this value. Furthermore approximately 5% of the mass of the E11 PAA is below a molar mass of 2.16×10^4 corresponding to the upper value for M_e.

The development of polyalkenoate cements, based on high molar mass PAAs, with sharper molar mass distributions, that do not contain chains below M_e (for the PAA concentration chosen), nor contain long chains, which will undergo scission during fracture is likely to result in glass polyalkenoate cements with further improved fracture properties.

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