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

Part II *Young's modulus and flexural strength*

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The Young's modulus and flexural strength were determined for glass polyalkenoate cements as a function of poly(acrylic acid), PAA molar mass, concentration, glass volume fraction and cement ageing time. The Young's modulus was independent of PAA molar mass. The Young's modulus increased dramatically with the PAA concentration of the cement until concentrations greater than 50% m/m were reached. The modulus increased with time for nearly all the cements investigated consistent with a continuing ionic cross-linking process in the cement matrix. The modulus increased with an increase in the volume fraction of the higher modulus glass phase. Increasing the glass volume fraction provides more surface area for acid attack resulting in a more cross-linked polysalt matrix, as well as increasing the volume fraction of residual glass particles. Flexural strength was highly dependent on molar mass of the PAA and its concentration. The molar mass dependence of the flexural strength was greatest at higher PAA concentrations.

1. Introduction

The Young's modulus and flexural strengths of glass polyalkenoate cements are important material properties. The modulus of a restorative dental filling material or luting cement determines how stresses are distributed in the restored tooth structure [1]. Despite this very few measurements of moduli are undertaken. This is largely a result of the difficulties associated with determining moduli of the small test specimens used. In the present study this was largely overcome by using a much larger specimen and in particular a span of 50 mm, rather than the more conventional 20 mm span [2–5].

The flexural strength is also important. Flexural strength of glass polyalkenoate cements is measured infrequently compared to compressive strength. However flexural strength is a more meaningful failure parameter, since analysis of clinical failures indicates that glass polyalkenoate cements fail in a tensile mode. Furthermore compressive strength is not a fundamental material property and failure in compression is complex and may involve a number of failure mechanisms. It has been argued that the inclusion of compressive strength testing in the standards for glass polyalkenoate cements does not provide any useful results on these materials. The mode of failure in compression can occur by plastic yielding, cone failure (secondary shear forces) or by axial splitting (secondary tensile forces). It is often very difficult to compare sets of results from different studies. Because specimen geometry, rate of loading and type of material all effect compressive strength it is important that standard-sized specimens be used under standard conditions of testing. Thus the results of mechanical performance of a cement, based solely on its compressive strength should be viewed with caution. This also highlights the importance of measuring as many mechanical property parameters as possible in order to gain a full insight into structure-property relationships in these materials. Compressive strength is not directly related to other material properties and the over emphasis on compressive strength measurements has been criticised by Kendall [6] and by Darvel [7].

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TABLE I Molar masses determined by gel permeation chromatography

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

TABLE II Young's moduli values

Glass volume fraction		0.40		0.45		0.50	
Fraction [PAA]	Time (days)	E (GPa)	SD ($n = 6$)	E (GPa)	SD ($n = 6$)	E (GPa)	SD ($n = 6$)
30%	1	2.93	0.23	3.22	0.29	4.83	1.48
30%	7	3.86	0.47	4.94	0.33	4.95	0.72
30%	28	4.22	0.39	4.87	0.46	5.97	1.23
35%	1	3.07	0.28	4.06	0.34	5.01	0.44
35%	7	4.47	0.42	5.07	0.50	5.28	0.62
35%	28	4.66	0.40	5.44	0.71	5.35	0.61
40%	1	4.05	0.47	5.11	0.30	6.63	0.94
40%	7	5.21	0.50	6.47	0.60	7.48	0.72
40%	28	6.07	0.40	6.10	1.12	7.34	1.03
45%	1	5.04	0.75	6.43	0.55	7.64	0.18
45%	7	7.09	1.20	7.45	0.69	9.47	0.43
45%	28	6.33	0.48	7.66	1.69	7.88	1.33
50%	1	5.67	0.59	6.72	0.56	7.24	0.53
50%	7	7.28	0.37	8.57	1.30	9.49	0.55
50%	28	8.06	1.25	9.50	0.74	10.18	0.87
55%	1	4.90	0.37	7.78	0.43		
55%	7	7.99	0.69	9.53	1.02		
55%	28	8.44	2.04	9.66	0.27		
60%	1	3.55	0.27	7.30	0.75		
60%	7	6.78	0.45	8.19	0.57		
60%	28	7.28	0.44	8.29	0.72		

2. Experimental

2.1. Materials

2.1.1. Glass

The glass for this study was specially prepared for the purpose. The glass was prepared by a melt quench route as described in Part I [8].

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 poly(acrylic acid)s were obtained as aqueous solutions, which were freeze dried and ground to a particle size <90 μm prior to use.

2.1.3. Cement preparation

Cements were prepared by thoroughly mixing the glass powder (<45 μm) with the poly(acrylic acid) and mixing this with 10% m/m (+) tartaric acid solution. Cements were allowed to set in vaseline coated stainless steel moulds measuring 65.0 × 25.0 × 3.0 mm for one hour at $37 \pm 2°$C then removed from the mould and stored in distilled water at $37 \pm 2°$C prior to testing. These specimens were broken in a double torsion test and the broken halves were ground to make specimens measuring 65.0 × 10.0 × 3.0 mm, which were used for flexural testing. Tests were carried out after 1, 7 and 28 days in water at $37 \pm 2°$C. The cement mixing and testing techniques are based on those used by Fennell and Hill [9] and the ISO standard [10].

2.2. Three point bend test

The Young's modulus, E and un-notched fracture strength, σ_f of each cement were determined at the three time intervals 1, 7 and 28 days using a three point bend test, performed with an Instron tensometer (Instron Ltd High Wycombe Bucks UK). A minimum of six specimens were tested for each test condition. Any specimens that were not visually flaw free were discarded prior to testing. Three ageing times were investigated, since it is known that the cross-linking reaction continues with time [11, 12] and that flexural strengths generally increase with ageing time. The relationship between the applied load, P and the displacement, δ at the centre of a specimen of rectangular cross section is:

$$P = \frac{4\delta E b t^3}{s^3}$$

where t is the specimen thickness, W the width of the specimen and S the distance between the supports. The test was carried out in accordance with ASTMS D790-71 [13] using a span of 50 mm.

The Young's modulus was calculated from the initial slope of the plot of P against δ plot. Moduli were found to be independent of molar mass in agreement with previous studies [5, 11, 14]. Consequently moduli figures were averaged across the four different molar masses investigated. The un-notched fracture strength, σ_f was calculated using:

$$\sigma_f = \frac{3Ps}{2bt^2}$$

where: P is the load at fracture.

3. Results and discussion

The normalised Young's modulus values for the 0.4 glass volume fraction cements as a function of PAA concentration are shown in Table II and Fig. 1. It is known that thermoplastic polymers exhibit moduli that

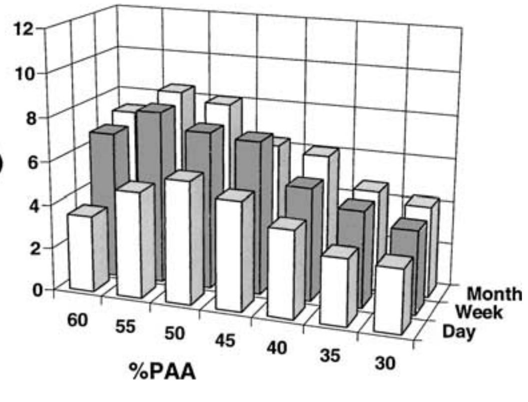

Figure 1 Young's modulus plotted against PAA concentration and time for 0.4 glass volume fraction cements.

are independent of molar mass. Hill [11] plotted the Young's modulus for two glass polyalkenoate cements of different molar mass against log (ageing time). Similar slopes and intercepts were found for both PAAs. The fact that Young's modulus is independent of the molar mass of the PAA indicates that the setting reaction is independent of molar mass. Hill *et al.* [5], and Griffin and Hill [14] have also demonstrated Young's moduli to be independent of molar mass.

The Young's modulus increases with the PAA concentration as might be expected on the basis that a greater concentration of PAA might lead to a greater chain entanglement density, as well as an increased number of carboxyl groups for ionic cross-linking. Simultaneously there will be a reduction in the water content of the cement as the PAA concentration is increased. Water is likely to have a plasticising action and therefore as the water content is reduced there will be fewer loosely bound water molecules and this will contribute to the increased modulus observed. At high PAA concentrations there is a reduction in modulus. This is probably a result of an excess of PAA chains relative to the cross-linking cations from the glass. The increase in modulus with PAA concentration initially followed by a reduction in modulus at high concentrations was also found by de Barra and Hill [16] for a glass polyalkenoate cement based on a sodium containing glass.

On ageing for a further 6 and 27 days in water at 37°C the values for the Young's modulus generally rise. This is consistent with a continuing reaction and increased cross-linking of the polysalt matrix by metal cations, as originally proposed to explain increases in compressive strength observed by Crisp *et al.* [12]. This phenomena of increasing modulus with time has been observed previously in model cements [5, 11, 12, 14, 16]. Increases in Young's modulus have been observed for ageing times up to six months for a commercial glass poly(vinylphosphonate) cement [9]. The increase in Young's modulus is found with most of the cements studied, but is most marked in cements based on a high PAA content, where cations from the glass component are probably in short supply even after one day.

Table II and Fig. 2 show the Young's modulus as a function of PAA concentration and ageing time for cements made with a 0.45 glass volume fraction. Similar trends to those exhibited by the 0.4 glass volume fraction cements are observed. The Young's modulus values for the 0.45 glass volume fraction cements are higher than for the equivalent 0.4 glass volume fraction cements. This increase in modulus probably arises from two sources. Firstly increasing the volume fraction of the higher modulus glass component would be expected to increase the modulus on a simple rule of mixtures basis, since the modulus of the glass phase is at least a factor of ten higher than the polysalt matrix phase. Secondly increasing the glass volume fraction and consequently the number of glass particles will provide more surface area for reaction with the polyacid and would be expected to result in greater ion release and a more cross-linked polysalt matrix. At the highest PAA concentration there is a slight decrease in modulus, indicating that even at the higher glass volume fraction of 0.45 there is still probably a shortage of cross-linking metal cations.

Table II shows the Young's modulus for the 0.5 glass volume fraction cements. It can be seen that there is again an increase in modulus with PAA concentration. The modulus generally increases only slightly with time, the exception being the highest PAA concentration of 50% studied where the increase is more marked.

Fig. 3 shows the Young's modulus as a function of PAA concentration and glass volume fraction for cements aged for one day. There is a general increase in modulus with the acid concentration, however there is a decrease at high concentrations. This decrease is most marked with the lowest glass volume fraction cements studied and occurs at the higher PAA contents and is less marked with the 0.45 glass volume fraction cements. This supports the idea that there is a deficiency of cross-linking cations in the 0.4 glass volume fraction cements produced with PAA concentrations above 50%.

Table III gives the un-notched fracture strength values for the 0.4 glass volume fraction cements. Fig. 4 shows the un-notched fracture strength as a function of PAA molar mass for the 0.4 glass volume fraction cements. It can be seen that in agreement with previous studies [5, 10–12, 14] the un-notched fracture strength is highly dependent on the molar mass of the

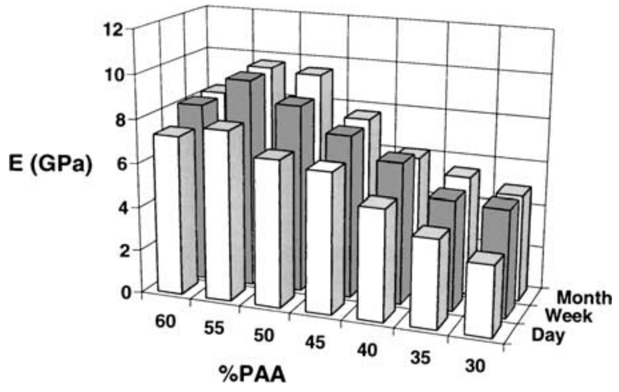

Figure 2 Young's modulus plotted against PAA concentration and time for 0.45 glass volume fraction cements.

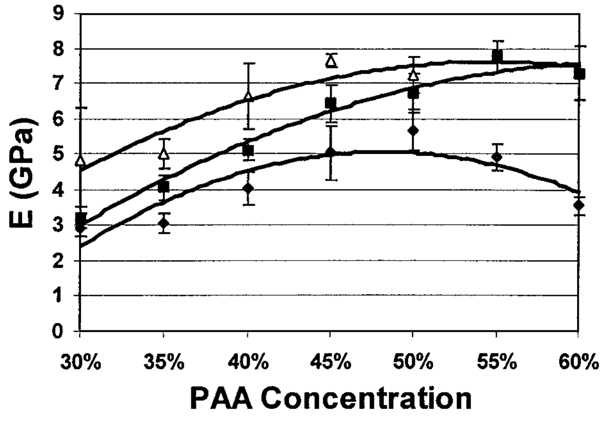

Figure 3 Young's modulus plotted as a function of PAA concentration after ageing for one day for three different glass volume fractions. ◆ = 0.4 , ■ = 0.45 and △ = 0.5.

TABLE III Un-notched fracture strength (σ_f) for 0.4 glass volume fraction cements

		E5		E7		E9		E11	
[PAA]	PAA Time (days)	σ_f (MPa)	SD ($n = 6$)	σ_f (MPa)	SD ($n = 6$)	σ_f (MPa)	SD ($n = 6$)	σ_f (MPa)	SD ($n = 6$)
30%	1	8.20	1.66	5.14	1.28	10.90	1.87	13.25	1.57
30%	7	6.46	1.25	7.53	1.95	13.68	0.02	16.64	1.01
30%	28	4.78	0.44	11.5	3.04	11.77	2.31	17.03	1.25
35%	1	3.90	0.23	5.53	1.14	13.74	2.59	20.17	1.64
35%	7	5.64	0.34	7.73	1.87	16.76	2.53	21.44	1.61
35%	28	4.90	0.89	9.30	1.46	16.32	2.29	23.44	4.24
40%	1	5.23	0.72	8.65	1.31	19.21	2.47	26.19	3.18
40%	7	6.79	0.80	8.49	2.87	19.81	3.75	31.32	3.97
40%	28	6.52	0.47	9.75	1.11	24.61	4.05	34.16	6.14
45%	1	7.23	0.71	10.08	1.83	23.32	6.54	38.62	8.37
45%	7	8.15	3.16	9.47	1.42	29.95	3.38	33.72	7.50
45%	28	6.15	0.64	10.46	1.02	27.38	7.21	34.82	5.02
50%	1	9.95	1.76	11.01	1.38	30.25	6.02		
50%	7	11.35	1.26	15.47	2.93	40.88	4.47		
50%	28	8.87	0.95	20.13	5.55	36.72	3.36		
55%	1	10.04	1.26	19.18	0.65	32.19	4.55		
55%	7	12.41	1.26	17.87	0.63	44.71	3.78		
55%	28	10.77	1.67	25.14	2.95	39.27	4.05		
60%	1	9.57	1.19	18.14	0.72				
60%	7	10.43	0.22	20.94	2.05				
60%	28	9.10	1.6	23.31	2.65				

PAA used to form the cement. For example the strength increases from 7.2 MPa to 38.6 MPa upon increasing the number average molar mass from 3.03×10^3 to 6.44×10^4 for a PAA concentration of 45%. Prosser *et al.* [17] first showed that increasing the PAA molar mass could increase the flexural strength and reported values of 9.7 MPa and 20.4 MPa for two cements made with PAAs of nominal molar masses of 1.3×10^4 and 5.5×10^4 respectively. Fig. 5 shows the un-notched fracture strength at one day as a function of PAA concentration and molar mass. The results show that the influence of PAA molar mass is greater at higher PAA concentrations. This is demonstrated most clearly in Table IV, where the slopes of the un-notched fracture strength- PAA concentration plots are tabulated along with the corresponding values for the linear correlation coefficient values.

Increasing the PAA concentration increases the un-notched fracture strength. Increases in compressive strength with PAA concentration were found by Crisp *et al.* [18] and similar behaviour was found for the compressive strength in part I of this series of papers. Whilst de Barra and Hill [16] on increasing the PAA concentration of the cement observed the un-notched fracture strength to increase. Very similar trends are found for cements aged for 7 and 28 days. The un-notched fracture strength for the cements based on high molar mass PAAs generally increased with time. In contrast there is no significant increase in flexural strength with time for cements based on the lowest molar mass PAA. The increase in strength with time has been found previously, both for commercial cements [2, 4, 9, 19, 20] and also for model cements [5, 11, 14, 16]. However decreases in flexural and compressive strength with time have also been found for some commercial glass polyalkenoate cements [2, 4, 21]. These decreases have been associated hydrolytic instability and a plasticising action of water. Griffin and Hill [14] presented data showing the un-notched fracture strength to increase significantly with time for high molar mass cements, but not to increase significantly with time for low molar mass

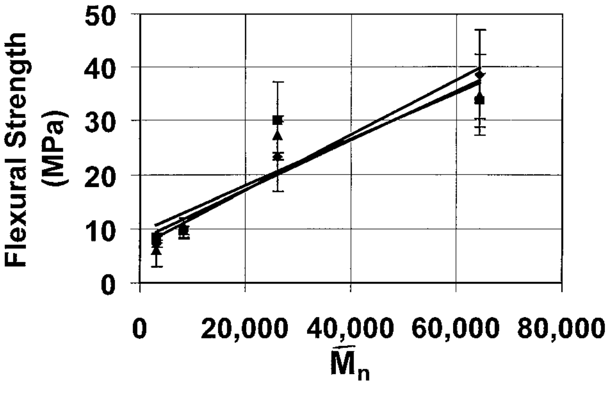

Figure 4 Flexural Strength of 0.4 glass volume fraction cements at a PAA content of 45% as a function of molar mass for three ageing times. ◆ = 1 day, ■ = 7 days and ▲ = 28 days.

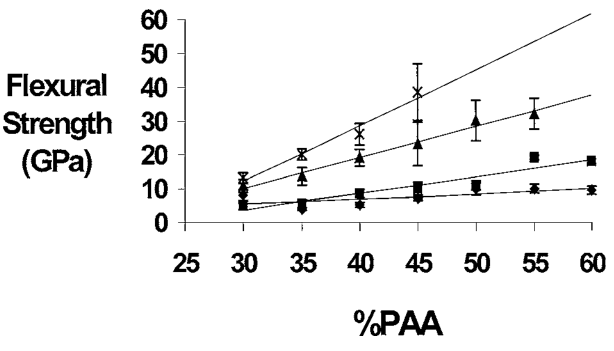

Figure 5 Flexural strength plotted against PAA concentration for 0.4 glass volume fraction cements aged for one day. E5 = ◆, E7 = ■, E9 = ▲ and E11 = X.

TABLE IV Un-notched fracture strength (σ_f) for 0.45 glass volume fraction cements

		E5		E7		E9		E11	
[PAA]	PAA Time (days)	σ_f (MPa)	SD ($n = 6$)	σ_f (MPa)	SD ($n = 6$)	σ_f (MPa)	SD ($n = 6$)	σ_f (MPa)	SD ($n = 6$)
30%	1	3.05	0.50	7.64	0.90	11.05	1.95	14.60	2.50
30%	7	8.71	1.35	10.34	2.65	12.31	2.10	16.30	3.46
30%	28	4.61	1.89	10.27	2.69	12.87	1.01	19.41	1.75
35%	1	4.65	1.12	8.28	1.11	13.89	1.17	19.10	2.07
35%	7	5.84	0.5	7.22	1.32	14.93	3.90	22.69	6.75
35%	28	5.18	1.28	8.49	1.83	16.29	4.27	21.72	5.66
40%	1	4.93	0.32	9.27	0.58	21.74	2.71	–	–
40%	7	5.49	1.22	10.77	0.74	18.07	4.00	–	–
40%	28	5.89	0.93	8.34	0.38	24.05	5.26	–	–
45%	1	6.45	1.10	13.96	1.48	27.11	4.23	–	–
45%	7	6.99	1.44	11.09	1.23	27.57	7.81	–	–
45%	28	7.95	2.13	14.60	0.57	31.05	6.07	–	–
50%	1	8.63	0.88	14.40	1.61	–	–	–	–
50%	7	10.99	1.43	18.02	4.31	–	–	–	–
50%	28	11.96	1.72	18.06	1.63	–	–	–	–
55%	1	12.07	0.90	21.67	4.19	–	–	–	–
55%	7	12.23	3.18	22.74	3.83	–	–	–	–
55%	28	10.27	1.71	31.68	3.24	–	–	–	–
60%	1	11.16	1.59	19.70	1.71	–	–	–	–
60%	7	12.78	2.68	23.70	2.52	–	–	–	–
60%	28	11.46	1.28	20.27	2.70	–	–	–	–

cements, but fail to comment on this aspect in their study.

Fig. 6 shows the results for the 0.45 glass volume fraction cements at one day. The un-notched fracture strength increases with PAA concentration and molar mass and the dependence of flexural strength on molar mass is again greatest at the higher PAA concentrations. Note that because of the high viscosity of the E11 cement paste the PAA concentration was restricted to 35% giving rise to only two data points. In general increases in flexural strength with time are small and not statistically significant.

On comparing the data in Tables III, V and VI it can be seen that the glass volume fraction does not appear to have a significant influence on the flexural strength of the glass polyalkenoate cements studied.

Guggenberger *et al.* [3] examined the influence of polymer concentration and molar mass on experimental glass ionomer cements. They found that the maximum un-notched fracture strength of approximately 30 MPa was independent of the polymer molar mass *if* the "appropriate" polymer concentration was chosen The results of Guggenberger *et al.* are reproduced in Fig. 7. They propose the view that the strength is primarily affected by the concentration of available carboxylic acid groups, rather than by the length of the polymer chain. A high concentration of short polyacid chains, or a low concentration of long chains, will achieve a high concentration of carboxylic acid groups. It can be seen that in the present study that whilst PAA molar mass may be "traded off" against PAA concentration for the higher molar mass PAAs, E9 and E11 to give high strength cements, it is not possible to produce a high strength cement comparable to that achieved with the E9 and E11 PAAs from the E5 PAA by simply increasing the concentration. This difference in behaviour is probably due to the fact that Guggenberger *et al.* [3] used a more reactive glass of lower phosphate content and higher fluorine content, plus a polyacid consisting of a copolymer of maleic and acrylic acid. These two factors together almost certainly result in a much more highly cross-linked polysalt matrix in which plasticity at the crack tip is suppressed. In such cements deformation and flow of the polyacid chains is likely to be restricted and the influence of molar mass is likely to be less important. Griffin and Hill [14] previously found the molar mass to be less important with the more reactive glasses.

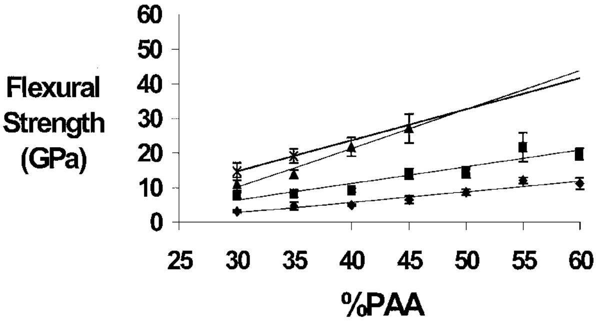

Figure 6 Flexural strength plotted against PAA concentration for 0.45 glass volume fraction cements aged for one day. E5 = ◆, E7 = ■, E9 = ▲ and E11 = X.

Like the cement systems reported on in this study, Guggenberger *et al.* [3] found a limit in the polymer content beyond which a decrease in flexural strength was observed in the studied cements. This decrease is they believe mainly due to viscosity and handling characteristics. Hill *et al.* [5] found that flexural strength increased with the polymer molar mass of the poly(acrylic acid). However, the effect was not as pronounced as that found with a thermoplastic polymer. At very high molar masses ($>5 \times 10^5$), the flexural

TABLE V Un-notched fracture strength (σ_f) for 0.5 glass volume fraction cements

		E5		E7		E9		E11	
[PAA]	PAA Time (days)	σ_f (MPa)	SD ($n = 6$)	σ_f (MPa)	SD ($n = 6$)	σ_f (MPa)	SD ($n = 6$)	σ_f (MPa)	SD ($n = 6$)
30%	1	4.37	0.92	6.06	0.50	13.85	3.22	10.43	3.40
30%	7	4.77	0.88	5.38	0.89	10.88	2.35	17.98	1.94
30%	28	3.13	0.70	8.59	3.23	14.31	3.95	22.11	4.19
35%	1	4.08	0.68	5.15	0.63	12.81	2.87	–	–
35%	7	5.13	0.59	6.26	0.64	12.72	3.43	–	–
35%	28	5.70	0.09	7.91	1.03	12.09	1.53	–	–
40%	1	4.00	0.59	10.11	0.90	–	–	–	–
40%	7	5.54	1.56	9.61	3.32	–	–	–	–
40%	28	6.72	1.17	14.86	4.86	–	–	–	–
45%	1	7.21	0.97	14.36	1.59	–	–	–	–
45%	7	8.57	0.33	16.45	2.50	–	–	–	–
45%	28	8.64	2.18	14.53	2.11	–	–	–	–
50%	1	13.72	1.92	–	–	–	–	–	–
50%	7	9.98	1.68	–	–	–	–	–	–
50%	28	10.68	2.05	–	–	–	–	–	–
55%	1	–	–	–	–	–	–	–	–
55%	7	–	–	–	–	–	–	–	–
55%	28	–	–	–	–	–	–	–	–
60%	1	–	–	–	–	–	–	–	–
60%	7	–	–	–	–	–	–	–	–
60%	28	–	–	–	–	–	–	–	–

TABLE VI Linear regression line slopes and correlation coefficients (r^2) for the σ_f against PAA concentration plots

Time Glass volume fraction	PAA	1 day		7 days		28 days	
		Slope	r^2	Slope	r^2	Slope	r^2
0.40	E5	0.15	0.45	0.21	0.76	0.19	0.82
0.40	E7	0.49	0.89	0.48	0.89	0.55	0.74
0.40	E9	0.91	0.98	1.35	0.95	1.15	0.98
0.40	E11	1.64	0.97	1.20	0.96	1.28	0.91
0.45	E5	0.31	0.92	0.21	0.60	0.26	0.85
0.45	E7	0.49	0.89	0.55	0.84	0.61	0.63
0.45	E9	1.12	0.97	0.97	0.90	1.24	0.98
0.50	E5	0.44	0.68	0.27	0.88	0.36	0.99
0.50	E7	0.60	0.83	0.73	0.88	0.50	0.73

strength of thermoplastics becomes independent of molar mass, a result of reaching a critical stress sufficient to cause chain scission. There was some evidence of this occurring in their cements as the flexural strength ceased to rise above a weight average molar mass of 1.08×10^6 (E13).

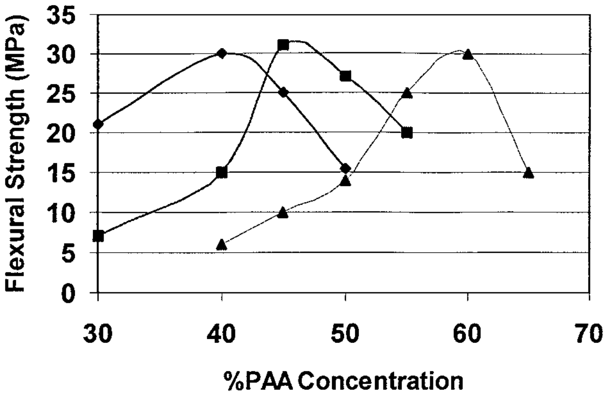

Figure 7 Flexural strength as a function of concentration and molecular weight of the poly(acrylic/maleic acid). Nominal molar masses. ◆ = 80,000, ■ = 30,000 and ▲ = 10,000.

Conclusions

The Young's modulus increases with PAA concentration up to approximately 50% (m/m), above this concentration the modulus falls. The increase in modulus is probably a result of an increased number of chain entanglements plus an increased density of ionic cross-links in the polysalt matrix, plus an increased density of entanglements, a lower water content and less unbound water. Un-bound water is likely to act as a plasticiser. Increasing the glass volume fraction results in a small increase in modulus, which is most likely due to increased glass surface area an a consequential increase in ionic cross-linking of the metal polyacrylate matrix plus an increased volume fraction of the high modulus residual glass phase.

The dominant parameters influencing the flexural strength are the PAA molar mass and PAA concentration. The increase in flexural strength as a function of molar mass is probably brought about by an increase in toughness arising from an increased pull-out energy associated with longer PAA chains. The increase in flexural strength with PAA concentration is also brought about by an increase in toughness arising from the fact that as the PAA concentration increases the number of chains crossing the fracture plane will increase leading to more energy being expended.

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