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Influence of poly(acrylic acid) molar mass on the fracture properties of glass polyalkenoate cements based on waste gasifier slags

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The failure behaviour of glass polyalkenoate cements was investigated using a linear elastic fracture mechanics (LEFM) approach. Cements were based on Drayton gasifier slag and four poly(acrylic acid)s with number average molar masses ranging from 3.03×10^3 to 6.44×10^4. Cement properties were studied at time intervals of one, seven and twenty eight days. Compressive and flexural strengths of the cements increased with increasing molar mass of the poly(acrylic acid)s and time. The Young's modulii increased with time and were independent of poly(acrylic acid) molar mass. Fracture toughness increased with increasing molar mass of the poly(acrylic acid)s. Fracture toughness increases over an ageing time of one week and subsequently decreased over one month. Toughness increased with poly(acrylic acid) molar mass, these increases being most pronounced at higher molar mass. The toughness values decreased with time for the higher molar mass cements, which is consistent with increased crosslinking of the poly(acrylic acid) chains and reducing molecular flow at the crack tip. Plastic zone size increased with poly(acrylic acid) molar mass and decreased with time for lower molar mass cements, remained constant for intermediate molar mass cements and increased with high molar mass cements. © *2000 Kluwer Academic Publishers*

1. Introduction

During the last twenty years there has been considerable interest in the so called "macro defect free cements" (MDF) because of their superior mechanical properties compared to Portland cement produced by conventional techniques [1, 2]. The major problem with these materials however, is their hydrolytic instability [3]. Rodgers *et al.* [4] highlighted the similarities between MDF cements based on polyacrylamide and glass polyalkenoate cements (GPC). Glass polyalkenoate cements, unlike MDF cements retain their strength on exposure to water and are hydrolytically stable. In addition, because of their high compressive and flexural strengths, fast setting characteristics, low porosity and excellent adhesion to a wide range of materials, they have many attractive properties that would be useful to the building industry.

Glass polyalkenoate cements are formed by reacting aqueous poly(acrylic acid)(PAA) with acid degradable calcium aluminosilicate glasses, generally containing fluoride. The polyacid degrades part of the glass network, releasing metal cations, which serve to crosslink the polyacid chains forming a hard cement [5]. The set GPC cement consists of residual glass particles embedded in a polysalt matrix [6], which can be regarded both as a cement and a polymer composite. The setting reactions for the MDF cement and GPC cement are shown schematically in Figs 1 and 2 respectively.

Glass polyalkenoate cements are currently used for dental and biomedical applications [7, 8] where the glass component is specially synthesised and therefore too expensive for large tonnage applications. However, Gasifier Slag (GS), a waste product produced during the manufacture of gas from coal forms a calcium aluminosilicate glass when cooled [9]. The chemical composition of the gasifier slag is similar to the simple model calcium aluminosilicate glasses studied by Wilson *et al.* [10] in the formation of glass polyalkenoate cements.

Sullivan *et al.* [11] carried out a preliminary study of the cement forming ability of four different gasifier slags, termed Drayton, British Gas, Newlands and El Cerrejon. This study has shown that the Si/Al ratio of the glass is an important factor in determining the acid degradability and subsequent reactivity of the gasifier slag. The Si/Al ratio is determined by the type and source of coal used in the gasification process. Drayton slag was found to be the most suitable slag for polyalkenoate cement formation.

Hill [12] has shown that GPC cements exhibit sharp loss peaks by both dynamic mechanical thermal analysis and dielectric thermal analysis that are typical of

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thermoplastics polymers. The molar mass of the poly(acrylic acid) used exerts a significant influence on the mechanical properties of the cement [13–15] and in particular the toughness, indicating that the crosslinks are labile and that these cements have a thermoplastic character. It is therefore worth looking at the fracture behaviour of thermoplastics.

2. Fracture of thermoplastic polymers

Berry's work on poly(methyl methacrylate) and polystyrene [16, 17] demonstrated that the measured fracture surface energy of a thermoplastic polymer was much greater than the energy required to break all the polymer chains crossing the crack plane. The high fracture surface energy was attributed to a localised flow process of polymer chains at the crack tip. The inherent Griffith flaw size found with polymers such as poly(methylmethacrylate) to a plastic zone or craze that formed prior to catastrophic failure.

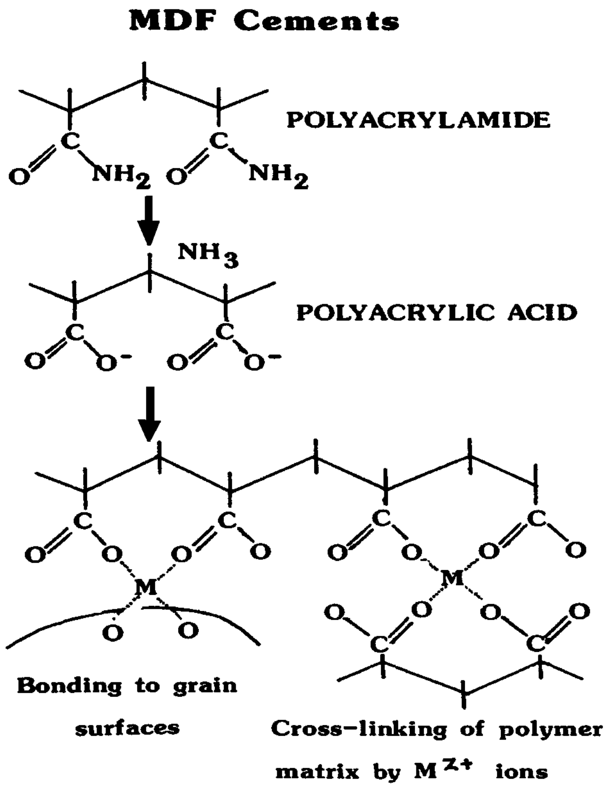

Figure 1 Schematic outline of the setting reaction in MDF cements based on polyacrylamide.

The strength of polymers is related to long range entanglements that serve to restrict chain motion. Originally these long range entanglements were viewed as physical knots. However, most polymer chains are too inflexible to form a physical knot and a model has been developed [18, 19] that views a chain as being trapped in a tube of entanglements formed by neighbouring chains. This model, known as reptation, is shown schematically in Fig. 3.

In the reptation model a chain is viewed as moving along an imaginary "tube" with a snake-like motion. The mobility of the polymer chain is restricted by the presence of entanglements forming its tube. Longitudinal motion is also prevented by the interaction of substituent groups on neighbouring chains that give rise to potential barriers to chain mobility along the tube.

The reptation model/chain pull out model has been used to describe fracture [20, 21] in polymers. This model views polymer chains as being pulled out of hypothetical tubes in the fracture plane during the fracture process. The reptation/chain pull out model is shown schematically in Fig. 4.

This model assumes that a polymer chain only crosses the fracture plane one, which may be questionable, but considerably simplifies the analysis. Prentice [22] derived the following equation

$$\tau = \mu \pi r N_s \left(\frac{V}{h}\right)^n L^2 \qquad (1)$$

where μ is a coefficient of viscosity resulting from the interaction between substituents on the extracted chain and the chains forming the tube, r is the radius of the polymer chain, N_s is the number of segments crossing a unit area of crack plane, L is the total contour length of the tube vacated by the chain, h is the spatial gap

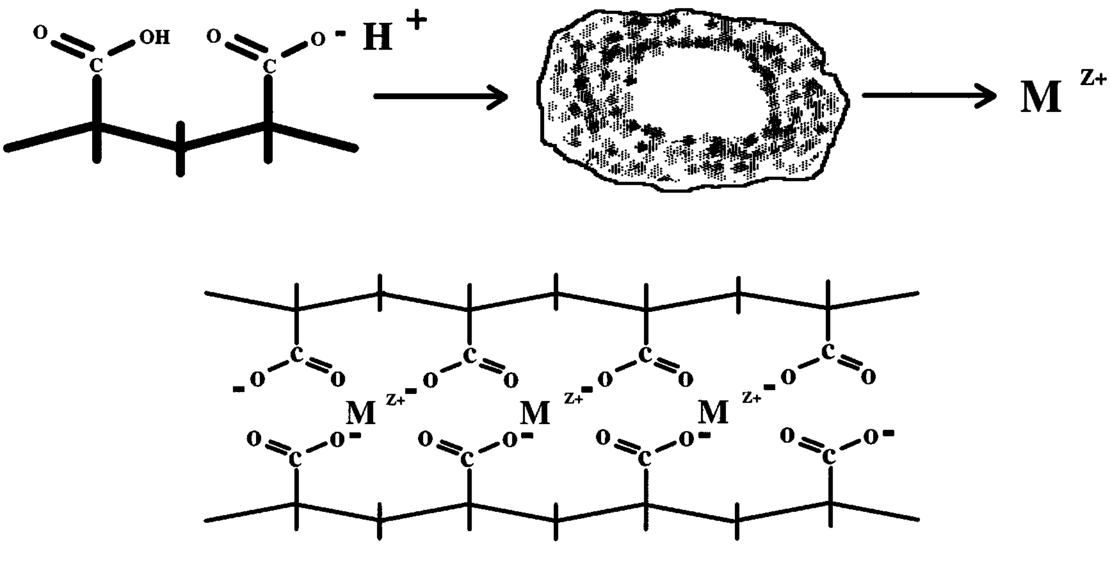

Figure 2 Schematic outline of the setting reaction of glass polyalkenoate cements.

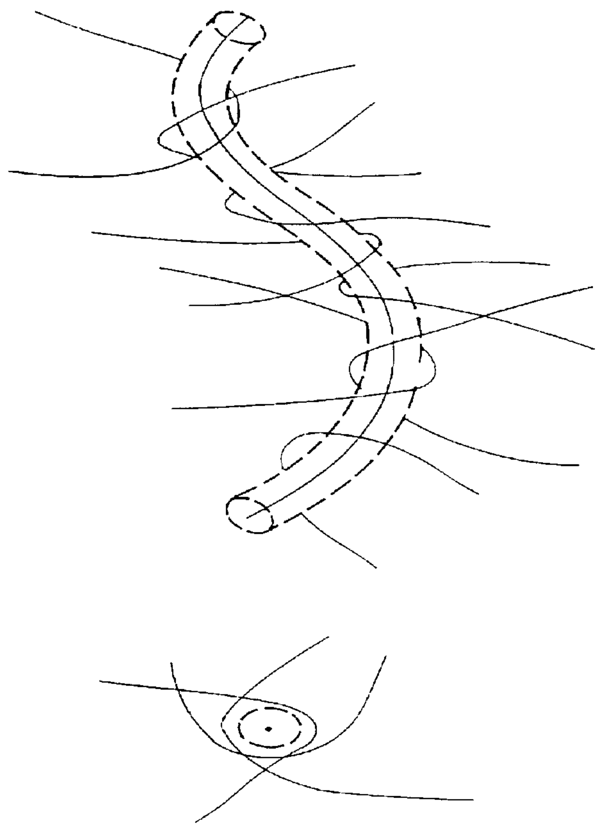

Figure 3 Schematic illustration of an entangled polymer chain.

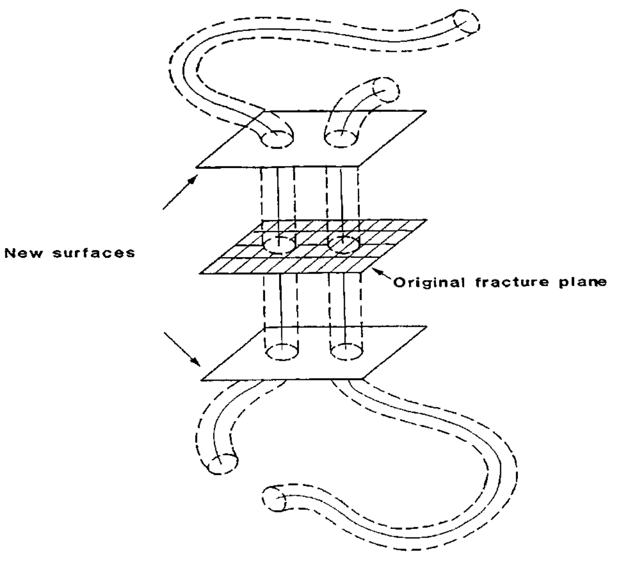

Figure 4 Schematic illustration of the chain pull out model of fracture in polymers.

between the chain and the surface of its imaginary tube, V is the rate of removal of the chain and n is a constant.

The equation implies that at a fixed crack opening velocity (V) the work done in removing chains from a unit area of crack plane is proportional to the molar mass squared.

$$\tau \propto M^2 \qquad (2)$$

At some stage a molar mass will be reached where the stress to extricate a chain from its tube is greater than required for homolytic chain scission of an extended segment. At a constant crack opening velocity a critical value of the force F_c will be reached at a critical chain length l_c. Above this value of l_c the force required to pull chains from their tubes will be greater than that to break the carbon-carbon bonds of the polymer backbone. Below this critical value l_c chain pull out will be the dominant mechanism and the fracture surface energy will be determined by Equation 1. While above l_c chain scission will occur and the fracture energy will then be independent of molar mass.

Equation 2 requires further modification to account for the fact that there is also a critical molar mass, below which chains do not form entanglement. This results in the modification to Equation 2 to

$$\tau \propto (M - M_c)^2 \qquad (3)$$

where M_c is the molar mass required for entanglements to occur.

The critical molar mass is the value above which chain scission occurs and the toughness is no longer dependent on molar mass. The critical molar mass is typically about 10^5, however its value is generally lower, where there are strong inter-molecular interactions between polymer chains [23].

Toughness data is plotted as function of number average molar mass (M_n) for poly(methyl methacrylate) in Fig. 5. At high molar masses above a critical value M_c, toughness is independent of molar mass. This is explained by the force to extricate a chain from its tube being greater than that required to cause chain scission. Polymer chain breakage then occurs and there is no further increase in toughness with molar mass. At low molar masses below approximately 2.7×10^4 the toughness goes to zero, since the chain length is too short to form entanglements and the tube concept no longer applies. At intermediate molar masses the slope of the log(toughness)-log(Mn) plot is about 2.45, slightly higher than the value of two, predicted by the reptation–chain pullout model.

The entanglement molar mass (M_c) again varies from polymer to polymer, but in general corresponds to between 100 and 300 monomer units [26]. The monomer

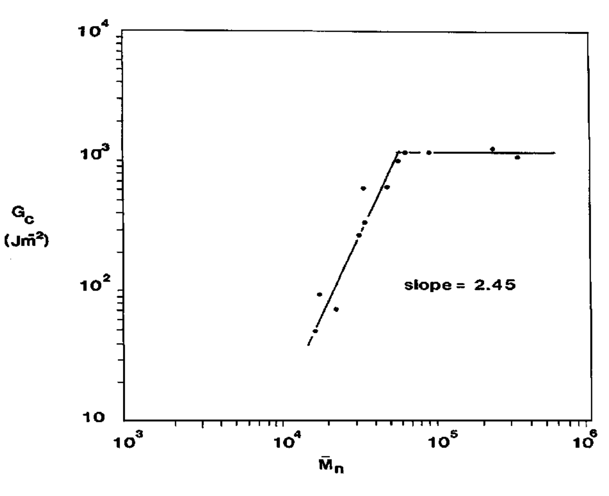

Figure 5 Dependence of toughness on molar mass for the thermoplastic poly(methylmethacrylate). Slope of rising portion = 2.45.

unit molar mass is 72 for PAA which gives a M_c of between 7000 and 21000.

3. Fracture of glass polyalkenoate cements

The mechanical properties of glass polyalkenoate cements change with time as the setting reaction proceeds [15, 25, 26]. Crisp *et al.* [25] studied the compressive strength and modulus of glass polyalkenoate cements as a function of time and concluded that the crosslinking reaction continued up to at least one year after the inital mixing of the cement paste. In some cases the compressive and flexural strengths may also decrease with time [26, 28]. The Young's modulii increase with time [15] and the cements become less viscoelastic with time [29], which is consistent with increased crosslinking of the polyacrylate chains. The toughness may increase, or decrease with time [15] depending on the poly(acrylic acid) molar mass. This suggests that flow of the polyacrylate chains at the crack tip and the extent of the plastic zone formation may be the dominant factors in determining the fracture properties. Decreases in toughness with time may be accounted for by excessive crosslinking, restricting flow of the polyacrylate chains and reducing the plastic zone size at the crack tip. The changes in mechanical properties have generally been ssociated with increased crosslinking of the polyacrylate chains by cations, but recently Nicholson and Wasson [30] have put forward the idea that the changes are due to the formation of a silicate phase, rather than a continuing crosslinking. However, DeBarra and Hill [31] and Matusuya *et al.* [32] have shown that the contribution of the silicate phase is likely to be small.

Furthermore transmission electron microscopy [33] shows that the silicate phase to be located predominantly at the periphery of the reacted glass particles and crack propagation takes place through the polysalt matrix [13].

The objective of the present paper is to gain an under standing of the failure processes in glass polyalkenoate cements based on waste Drayton slag. A Linear Elastic Fracture Mechanics approach is pursued in order to enable the design and optimisation of cement properties in a systematic way. Cements were formed with four poly(acrylic acid)s of varying molar mass and the mechanical properties of the resulting cements were studied as a function of time.

4. Experimental

4.1. Materials

4.1.1. Waste gasifier slag

The chemical composition of the Drayton slag is shown in Table I. The slag was ball milled and sieved to give a maximum particle size of <53 μm.

TABLE I Chemical composition of Drayton slag

SiO_2	Al_2O_3	Fe_2O_3	CaO
0.5	0.16	0.04	0.30

Values in mole fractions.

TABLE II Molar mass details determined by gel permeation chromatography of poly(acrylic acid)s

Code	M_w	M_n	PD	Peak mol wt.
E5	9,270	3,030	3.1	6,810
E7	25,700	8,140	3.2	19,100
E9	80,800	26,100	3.1	83,500
E11	210,000	64,400	3.2	186,000

4.1.2. Poly(acrylic acid)s

The poly(acrylic acid)s were supplied by and Allied Colloids (PO Box 38 Bradford UK.). These are coded, E5, E7, E9 and E11. All the PAAs were supplied as solutions which were freeze dried and ground to a maximum particle size of 90 μm. The relevant code letters and molar mass details in terms of number average molar mass ($\bar{M}_n$) and weight average molar mass ($\bar{M}_w$) and the polydispersity PD all determined by gel permeation chromatography are given in Table II.

4.1.3. Cement preparation

Cement samples were formed by mixing the <53 μm Drayton gasifier slag powder with four different poly(acrylic acid)s) in a weight ratio of 5 : 1 and then adding this mixture to water containing 30% m/v (+) tartaric acid, in a weight ratio of 4 : 1. This represents a glass powder to poly(acrylic acid) solution ratio of 2 : 1 with a polyacid concentration of 40% m/m. Cements were allowed to set in the appropriate 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. The specimen preparation techniques are based on "ISO7489: 1986 Dental Glass Polyalkenoate Cements" [34].

4.2. Cement testing

4.2.1. Compression test

The compression tests were performed on cement cylinders 4.0 mm in diameter by 6.0 mm in height. The testing procedure was based on the ISO ISO7489: "1981 Dental Glass Polyalkenoate Cements" [34]. An Instron Universal tensometer (Instron High Wycombe Bucks UK) was used for the test at a crosshead displacement rate of 2 mm min^{-1}. The test was carried out on 8 samples and the compressive strength calculated according to:

$$\sigma_c = F/\pi r^2 \tag{4}$$

where σ_c is the compressive strength, F is the force in Newtons, r is the diameter. In addition a 1.0% offset yield stress was determined for the compressive tests carried out at 37 ± 2°C in water.

4.2.2. Double torsion test

Double Torsion (DT) specimens 3.5 × 65 × 25 mm, were produced as described previously in the form of rectangular plates. A sharp groove 0.5 mm deep was cut down the centre of the specimen using a microslice cutter. A fine slot was cut at one end of the specimen using a diamond wafer blade. The DT was performed using an Instron Universal tensometer (Instron Ltd., High Wycombe, UK). During the test the specimen was supported on a pair of parallel rollers of 3 mm diameter and spaced 20 mm apart. The load was applied at a constant rate of 0.2 mm min^{-1} to the slotted end of the specimen via two ball bearings spaced 10 mm apart. The specimen was subjected to a four point bend during which the crack initiated and propagated along the groove.

The test was carried out in tap water at 37 ± 2°C. The specimen dimensions and groove depth were selected to eliminate the need for crack shape correction factors to be applied [35].

In the double torsion test the mode I stress intensity factor K_I is independent of crack length and is given by Kies and Clark [36] as:

$$K_1 = P_c W_m \left(\frac{3(1+v)}{W t^3 t_n} \right)^{1/2} \tag{5}$$

where W_m is the moment arm, W is the specimen width, t is the specimen thickness and t_n the thickness in the plane of the crack and v the Poisson's ratio which was assumed to be 0.33. Values for K_{IC} were obtained for continuous fracture by substituting the load P_c and specimen dimensions into Equation 5.

4.2.3. Three point bend test

The Young's modulus, E and un-notched fracture strength, σ_f of each cement at the three time intervals were determined using a three point bend test, performed with the Instron tensometer. The relationship between the applied load, P and the displacement, δ at the centre of a specimen of rectangular cross section is:

$$P = \frac{4\delta E b t^3}{s^3} \tag{6}$$

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 [37]. A span of 50 mm was used with a specimen size of 65 mm × 10 ± 0.03 mm) × 3 ± 0.03 mm. The Young's modulus was calculated from the initial slope of the plot of P against δ plot. The un-notched fracture strength or flexural strength, σ_f is given by:

$$\sigma_f = \frac{3Ps}{2bt^2} \tag{7}$$

where P is the load at fracture.

A minimum of six specimens were tested for each test condition. Any specimens that were not visually flaw free were discarded prior to testing.

4.3. Calculation of the strain energy release rate (G_1) from DT specimens

The strain energy release rate was calculated assuming that pure linear elastic fracture mechanics apply using the following expression:

$$G_1 = \frac{K_1^2(1-v^2)}{E} \tag{8}$$

4.4. Calculation of plastic zone size

The plastic zone size, R_p was calculated from the fracture toughness and the 1.0% offset yield stress determined from the compression test as follows:

$$R_p = K_{IC}^2 / \sigma_{YS} \tag{9}$$

5. Results and discussion

5.1. Compressive strength

Compressive strength data is presented on Table III. Compressive strength increased with poly(acrylic acid) molar mass indicating a strong dependence of this property and furthermore high molar mass cements exhibited a significant plastic character. When the compressive strengths were measured as a function of ageing time lower molar mass cements showed an increase in strength with time. Compressive strength did not show any significant change with ageing time for the higher molar mass cements. Compressive strength although the most frequently quoted cement property in the literature, provides little insight into the mechanisms of failure of cements as it is not a fundamental materials property [38]. However, the extent of crosslinking in the polysalt matrix is reflected in the magnitude of the compressive strength of the cement. Crisp *et al.* [25, 27] measured the compressive strength of glass polyalkenoate cements as a function of time and concluded that the crosslinking reaction continues up to at least one year. However, Williams and Billington [39] have shown the compressive strength of some dental glass polyalkenote cements to decrease after long storage times but could offer no explanation for the observed results. Cattani-Lorenti *et al.* [40] examined the effects of long term ageing in water and found in most cases that the compressive strength of the cement to rise initially and then to remain constant and in some instances demonstrated a reduction in strength. These observations were attributed to hydrolysis of the polymer

TABLE III Compressive strength as a function of poly(acrylic acid) molar mass and time

Polyacid content (40%)	σ_c (MPa)							
	E5	S.D ($n = 4$)	E7	S.D ($n = 4$)	E9	S.D ($n = 4$)	E11	S.D ($n = 4$)
1 Day	13.5	1.0	19.2	1.7	25.2	2.5	29.4	3.10
7 Days	18.2	2.3	25.8	2.5	25.6	2.6	38.7	2.0
28 Days	23.1	1.2	25.6	3.0	27.1	1.9	28.8	1.9

TABLE IV Flexural strength as a function of poly(acrylic acid) molar mass and time

Polyacid content (40%)	σ_f (MPa)							
	E5	SD ($n = 4$)	E7	SD ($n = 4$)	E9	SD ($n = 4$)	E11	SD ($n = 4$)
1 Day	6.3	0.4	6.1	0.3	10.4	1.2	15.3	1.2
7 Days	6.6	0.6	8.8	0.5	10.7	0.3	17.2	0.8
28 Days	7.8	0.4	10.4	0.6	11.8	0.4	18.3	1.2

TABLE V Young's modulus as a function of poly(acrylic acid) molar mass and time

Polyacid content (40%)	E (GPa)							
	E5	S.D ($n = 4$) $\times 10^{-2}$	E7	S.D ($n = 4$) $\times 10^{-2}$	E9	S.D ($n = 4$) $\times 10^{-2}$	E11	S.D ($n = 4$) $\times 10^{-2}$
1 Day	1.3	8.0	1.2	7.0	1.6	2.0	1.2	12.0
7 Days	1.8	8.0	1.5	2.0	1.6	12.0	2.0	11.0
28 Days	1.9	20.0	1.9	5.0	1.6	9.0	1.9	0.2

matrix by water. The results for compressive strength outlined in Table III are consistent with these previous studies.

5.2. Flexural strength

The flexural strength increases with increasing molar mass and time as shown in Table IV. This increase in flexural strength is more pronounced in the cements produced from the polyacid of highest molar mass, termed E11. This may reflect the fact that the cement pastes made from the poly(acrylic acid)s of lower molar mass are more brittle and the sensitivity to inherent flaws on the tensile edge of the sample will be greatly increased. Cements based on the higher molar mass polyacids have a greater degree of plasticity, which reduces the sensitivity of the samples to surface falws and consequently increases the flexural strength. Furthermore as will be seen later, the fracture toughness of the higher molar mass cement is greater, which would be expected to increase the flexural strength.

5.3. Young's modulus

The values for Young's modulii as a function of polyacid and molar mass are presented in Table V. The Young's modulus appears to be independent of poly(acrylic acid) molar mass in the case of cements based on the E5, E7 and E11 polymers. There is a degree of variation in the data for cements based on the E9 polymer which is greater than expected and there is no obvious reason why this is the case. Variations in the homogeneity of the cement during mixing and the inclusion of air bubbles could be the cause. However, in general, the modulus as expected on theoretical grounds appears to be independent of molar mass and therefore consistent with previous results obtained by Hill [15]. The approximate constant modulii of these cements, therefore indicates that the chemistry of the setting process is unaffected by the molar mass of the poly(acrylic acid) used to make the cement. This is expected as Young's modulus is a reflection of the number and strength of crosslinks between the polyacid chains. Irrespective of the molar mass used, there are still the same number of carboxyl groups present for crosslinking. Hill [15] further illustrated the fact that Young's modulus is independent of molar mass by plotting Young's modulus against Log (ageing time) for a low molar mass cement and a high molar mass cement. Hill found similar slopes and correlation coefficients for both cements, providing very strong evidence that the chemistry of the setting reaction is not affected by the poly(acrylic acid) molar mass and only the physics of the failure process changes with molar mass.

TABLE VI Values for the slopes and correlation coefficients of Young's modulus-Log (ageing time) plots

Poly(acrylic acid)	Slope	R^2
E5	0.4565	0.8842
E7	0.4233	0.988
E9	0.0079	0.3328
E11	0.4991	0.6976

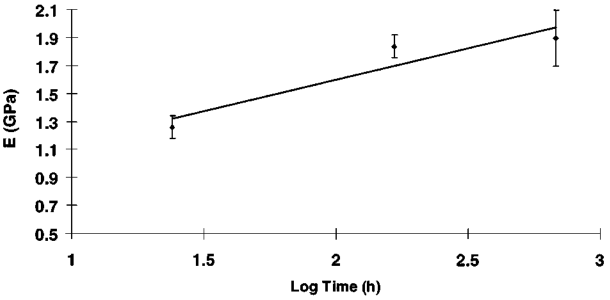

Figure 6 Young's modulus plotted against Log(time) for E5 cement.

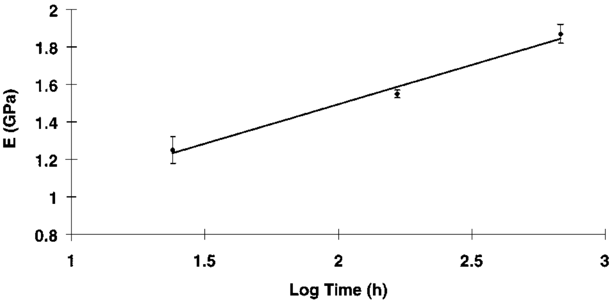

Figure 7 Young's modulus plotted against Log(time) for E7 cement.

Values for Young's modulus obtained in this study were also plotted against Log (ageing time) as shown in Figs 6–8. The results of linear regression analysis for the modulus data is shown in Table VI. Consistent values for the slope and correlation coefficient were obtained for three of the cements based on E5, E7 and E11 and therefore in good agreement with the results obtained by Hill. The values obtained for Young's modulii recorded in this study show an increase in modulus with time for the cements based on the E5 and E7polymers, which is consistent with increased crosslinking in the polysalt matrix. This is consistent with trends in compressive strength outlined in Section 5.1.

TABLE VII Fracture toughness as a function of poly(acrylic acid) molar mass and time

	K_{1C} MPa $(m)^{0.5}$							
Polyacid content (40%)	E5	S.D ($n = 6$) $\times 10^{-2}$	E7	S.D ($n = 6$) $\times 10^{-2}$	E9	S.D ($n = 6$) $\times 10^{-2}$	E11	S.D ($n = 6$) $\times 10^{-2}$
1 Day	0.21	2.0	0.27	1.0	0.54	7.0	0.87	7.0
7 Days	0.36	2.0	0.38	2.0	0.52	5.0	1.09	5.0
28 Days	0.22	1.0	0.33	3.0	0.49	3.0	0.84	5.0

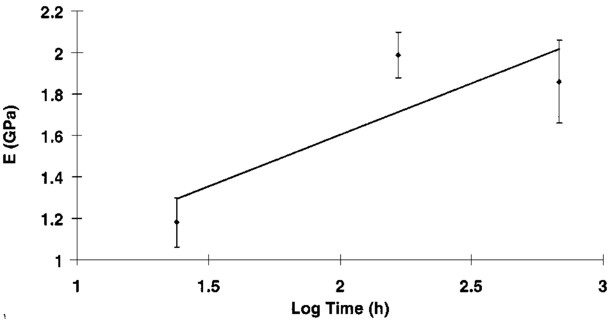

Figure 8 Young's modulus plotted against Log(time) for E11 cement.

5.4. Fracture toughness

The Fracture toughness data are shown in Table VII. From the data it can be seen that increasing the molar mass of the polyacid increases the fracture toughness, the greatest fracture toughness occurs for the highest molar mass cement. There is a slight increase in fracture toughness with an ageing time of one week for all four cement formulations and a subsequent reduction with an ageing time of one month. Overall the fracture toughness remains approximately constant. Changes in fracture toughness with time can be attributed in part to corresponding changes in crosslinking. This can be explained in terms of the following relationship.

$$K_{1C} = (GE)^{0.5}$$

Increasing the degree of crosslinking will increase the Young's modulus of the cement. As a result of the direct relationship between fracture toughness and Young's modulus, it can easily be seen that the increase in crosslinking initally leads to an increase in fracture toughness. Further crosslinking however, will result in a reduction of the toughness (G_{IC}) of the cement, which at a certain degree of crosslinking will cause the decrease in toughness to outweigh the increase from the modulus contribution with the resultant fall in fracture toughness. Values recorded for Young's modulus and toughness in Tables V and VIII respectively are consistent with this theory. In addition it is also important to note that the magnitude of the increase in Young's modulus with time for lower molar mass cement compositions is similar to that of the higher molar mass cements. In contrast however, the magnitude of the decrease in toughness with time for higher molar mass cements is much greater than that of the lower molar mass cements. Therefore this suggests that in lower molar mass cements fracture toughness is dominated by Young's modulus while the higher molar mass cements fracture toughness is dominated by toughness.

TABLE VIII Toughness and as a function of poly(acrylic acid) molar mass (40%) and time

	G_{1C} (J·m^{-2})			
	E5	E7	E9	E11
1 Day	35	60	183	639
7 Days	71	95	164	596
28 Days	26	58	148	377

5.5. Toughness

The results for toughness as a function of polyacid molar mass and time are given in Table VIII. The values given for Young's modulus for the different polyacids were averaged over the three time periods and used to calculate the values for toughness. The toughness values increase with polyacid molar mass, these increases being most pronounced at higher molar mass. The toughness values decrease with time for the higher molar mass cements, which is consistent with increased crosslinking reducing molecular flow at the crack tip.

5.5.1. Log (toughness)-Log (molar mass)

Previous studies of the influence of polyacid molar mass on the toughness of the glass polyalkenoate cement and the related zinc carboxylate cement, have used the chain pull-out model developed for themoplastic materials to analyse the date [13].

The chain pull-out model predicts that the toughness of polyalkenoate cements is dependent on the molar mass squared. However, plots of Log toughness (G_{1C}) against Log number average molar mass ($\bar{M}_n$) plots gave slopes of 0.5 and 1.0 for zinc carboxylate and glass polyalkenoate cements respectively studied previously by Hill *et al.* [41, 13]. This work offers one of the most plausible explanations of the dissimilarities of the data in relation to the chain pull-out model. The reduction in slopes are due to the presence of ionic interactions between chains that act as "labile" crosslinks. At low molar mass these "labile" crosslinks serve to increase the effective molar mass of the cement and therfore increase toughness. At higher molar mass these interchain bonds serves to promote chain scission and consequently the toughness is no longer dependent on molar mass. Hill *et al.* [13] also points out that the reptation model is strictly only valid for monodisperse polymers and cannot take into account polydispersity. The correlations of the slopes are therefore made more complex by the broad distributions of molar mass in any specific polymer which determines the mean molar mass value in the analysis.

Examples of Log (toughness) against Log(molar mass) for the cements used in this study for the three time periods are shown in Figs 9–11. All of the slopes and correlation coefficients are recorded in Table IX. The greatest slope is found for the shortest time period studied at one day, where a value of 0.9291 was

TABLE IX Values for the slopes and correlation coefficients of the Log (toughness)-Log (number average molar mass) plots

Time	Slope	R^2
1 Day	0.9291	0.9737
7 Days	0.6682	0.8832
28 Days	0.9048	0.9920

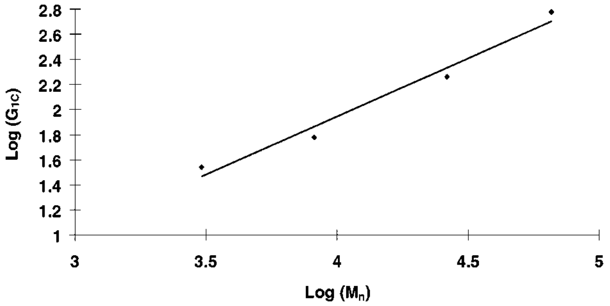

Figure 9 Log(toughness) plotted against Log(molar mass) of cements at 1 day.

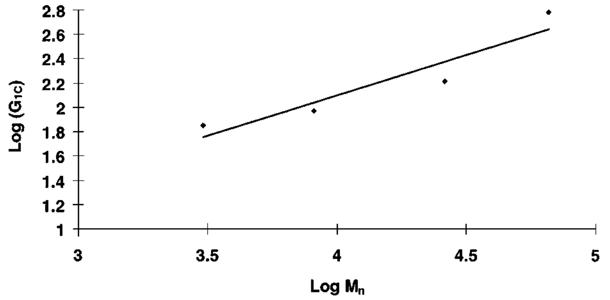

Figure 10 Log(toughness) plotted against Log(molar mass) of cements at 7 days.

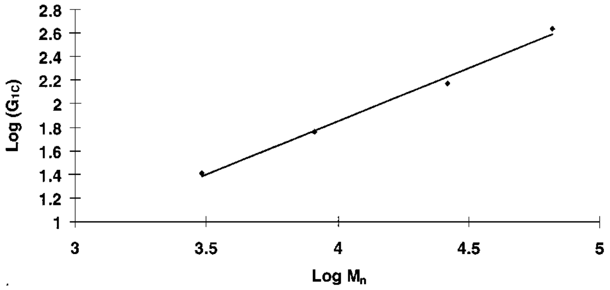

Figure 11 Log(toughness) plotted against Log(molar mass) of cements at 28 days.

obtained. This value is below that for thermoplastic polymers of 2.0 predicted by the reptation chain pull-out model, but consistent with the slope of 1.0 calculated by Hill *et al.* [13] and Griffin [42] for glass polyalkenoate cements. The slope decreases with time from 1 day to 7 days which would be expected on the basis of an increase in the number of ionic crosslinks, which should serve to reduce the molar mass dependence. The slope however, increases again at one month, which is not consistent with, or easily explained by the chain pull out model. In terms of the pull-out model, the extraction of the polyacid chains would be expected to become increasingly difficult, as the degree of crosslinking would be expected to be greater after one month. An increase in slope after one month however, was also observed by Griffin for glass polyalkenoate cements. Griffin suggested that it is possible that the mechanism of chain extraction has changed but was unable to determine what other mechanism may be occuring on the basis of his work.

5.5.2. Toughness and crack opening displacement

In another study Hill [15] examined the influence of ageing time on the toughness of glass polyalkenoate cements. Toughness remained constant for the lower molar mass poly(acrylic acid)s, while marked reductions in this parameter were noted with the higher molar mass poly(acrylic acid)s with time. In addition, the crack opening displacement was found to reduce with time for both cements. Hill [15] takes the view that the number of chains involved in fracture will not be simply the number of single chains crossing the fracture plane, as assumed by the chain pull-out model, but will also include interactions such as chains looping each other and thus chains distant from the fracture plane will be involved in the pull-out process. The number of chains involved in fracture might therefore be expected to be proportional to the size of the crack opening displacement present. The greater the crack opening displacement, the larger will be the number of chains undergoing pull-out and the greater will be the toughness. As the number of ionic linkages between the chain increases, the crack opening displacement will reduce, causing a reduction in toughness. As the cement reaction proceeds with time and there is increased crosslinking of the polyacrylate chains, this would be expected to increase the toughness. However the crosslinking process would decrease the size of the crack opening displacement and hence the number of chains crossing the fracture plane. These two competing process both determine toughness and can give rise to an increase or decrease in toughness depending on which mechanism dominates.

In the case of low molar mass cements, the increase in crosslinking is balanced by the reduction in the size of the crack opening displacement and the overall toughness remains constant. In contrast the increase in crosslinking in the high molar mass serves to promote chain scission and therefore the toughness remains constant, while the number chains crossing the fracture plane decreases due to a decrease in the size of the crack opening displacement with the result that the toughness reduces with increasing cement age.

The values for toughness and crack opening displacement show similar trends to the results obtained by Hill [15]. Looking at Table VIII there is a maximum increase in toughness at 7 days for all cement compositions. However, over the period of 28 days the toughness remains approximately constant for lower molar mass cements whilst the higher molar mass cements exhibit a decline in toughness with increasing sample age.

The 1.0% offset yield stresses were measured in order to calculate the crack opening displacement. The effect of polyacid molar mass and time on the crack

TABLE X Crack opening displacement as a function of poly(acrylic acid) molar mass (40%) and time

	COD (mm) $\times 10^{-3}$			
	E5	E7	E9	E11
1 Day	3.4	4.4	9.0	35.0
7 Days	4.8	5.4	10.0	25.0
28 Days	1.5	3.4	8.0	23.0

TABLE XI Plastic zone size as a function of polyacid molar mass (40%) and time

	PZS (mm) $\times 10^{-2}$			
	E5	E7	E9	E11
1 Day	7.0	6.0	12	36
7 Days	9.0	8.0	17	34
28 Days	2.0	6.0	11	42

opening displacement is shown in Table X. The crack opening displacement increases over a 7 day period and then decreases over a further 21 day period for all four cement compositions.

5.5.3. Plastic zone size

The calculated plastic zone sizes are shown in Table XI. It is important to note that the specimen thickness in this study was approximately 3 mm and therefore the plastic zone size should be less than 0.5 mm in order to maintain plain strain conditions. The largest plastic zone size calculated in this study was 0.42 mm which approaches this maximum value. However, no edge effects, for example, shear lips were observed on any fracture surfaces thus indicating that plain strain conditions were largely maintained. The plastic zone size increased with polyacid molar mass, decreased with time for low molar mass cements, remained constant for intermediate molar mass cements and increased with high molar mass cements. The decrease in plastic zone size with time for cements based on E5 is consistent with further crosslinking of the polyacrylate chains with time and decreased molecular flow at the crack tip. The increase in plastic zone size with cements based on E11 indicates that there is no further crosslinking of polyacrylate chains and increased molecular flow at the crack tip which agrees with the compressive strength and Young's modulus results obtained in Sections 5.1 and 5.3 respectively.

6. Conclusions

Glass polyalkenoate cements based on Drayton slag can be modelled as polymer composites where fracture takes place almost exclusively in the polymer matrix. The results demonstrate the pronounced affect of poly(acrylic acid) molar mass on cement properties. The poly(acrylic acid) molar mass dominated the compressive strength, flexural strength and fracture toughness at all three time intervals. The dependance of toughness on molar mass is not as large as predicted by the chain pull out model, but is however, consistent with results from previous studies on glass polyalkenoate cements. The application of the chain pullout model to glass polyalkenoate cements has been criticised [43, 44], but is currently the only available model for analysing the fracture behaviour that is capable of making quantitative predictions [45]. Despite the fact that the reptation model is quantitively incorrect, it is qualitatively useful in giving an insight into the failure in these materials, allowing the design and optimisation of cement properties to be carried out in a systematic way.

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