

The fracture properties of glass polyalkenoate cements as a function of cement age

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The fracture properties of two glass polyalkenoate cements based on a short chain-length and on a long chain-length poly(acrylic acid) have been studied as a function of the cement age. The stress intensity factor, K_I , increases with cement age for both cements. The un-notched fracture strength σ_f increases with cement age, largely as a result of an increase in the Young's modulus accompanying crosslinking of the polyacrylate chains by metallic ions. The toughness G_I remains approximately constant for the short chain-length cement, but reduces with cement age for the long chain-length cement. Analysis of the toughness data using a chain pull-out model leads to the conclusion that chains distant from the fracture plane are involved in fracture, and that the number of chains that take part in chain pull-out decreases as the crack opening displacement reduces with cement age.

1. Introduction

Glass polyalkenoate cements, or glass-ionomer cements as they are more commonly known, are widely used in dentistry as an anterior restorative tooth filling material and as an adhesive for bonding jacket crowns [1]. Work is currently under way to develop these cements for posterior dental filling materials, an orthopaedic bone cement and a bone substitute material [2–8]. In these three applications of glass polyalkenoate cements, their ability to bond chemically to the apatite phase in dentine, enamel and bone is an important and unique feature. In the case of a posterior dental filling, their ability to wet and bond to teeth conserves healthy tooth material, maintains the structural integrity of the tooth and helps prevent subsequent tooth decay. When used as an orthopaedic bone cement their ability to chemically bond to the alloys used for prostheses, as well as to bone, should result in excellent stress transfer in replacement joints and prevent long-term bone resorption and prosthesis loosening. In addition, because of their high flexural strengths, fast setting characteristics, low porosity and similarity to macro-defect free (MDF) cements [9], glass polyalkenoate cements are also currently being investigated for possible use in the building industry.

In all these applications, the long-term fracture toughness, toughness, Young's modulus and flexural strength of the cement are important. Furthermore, a detailed understanding of the mechanism of fracture in the existing dental materials may enable cements with improved properties to be developed. This is particularly important for the orthopaedic bone cement application, because of the relatively low toughness and fracture toughness of glass polyalkenoate cements compared to the existing acrylic materials. Despite this disadvantage of glass polyalkenoate ce-

ments, their ability to release calcium, phosphate and fluoride ions is a major advantage and Jonck *et al.* [5] claim that glass polyalkenoate cements are bioactive in the bone environment.

Glass polyalkenoate cements are formed by the reaction of aluminosilicate glasses with aqueous polyacids such as poly(acrylic acid). The acid degrades the glass network, releasing cations and forming a siliceous gel. The cations subsequently "crosslink" the polyacid chains causing the cement paste to set. The final hardened cement consists of residual glass particles embedded in a polysalt matrix. The chemistry of the setting process has been extensively studied by Wilson and co-workers [10–12]. The setting reaction is shown schematically in Fig. 1.

Glass polyalkenoate cements have been treated largely as cementitious materials, with the majority of studies concentrating on the chemistry of the glass and the setting reaction. Only Read and Hodd [13, 14] have treated these cements as polymer composites. They assumed that the ionic crosslinks between the polymer chains were permanent so that the polysalt matrix was analogous to a thermoset resin. However, recently [15] the set cements were shown to exhibit sharp loss peaks, by both dielectric thermal analysis and dynamic mechanical thermal analysis, that are typical of thermoplastic polymers. A recent linear elastic fracture mechanics investigation of the role of the poly(acrylic acid) chain length on cement properties [16] has supported the idea that the crosslinks are not permanent in these cements. The toughness, fracture toughness and un-notched fracture strength were all dependent on the length of the polymer chain, whilst the Young's modulus, which is a reflection of the number and strength of chemical interactions within the hardened cement paste, remained constant.

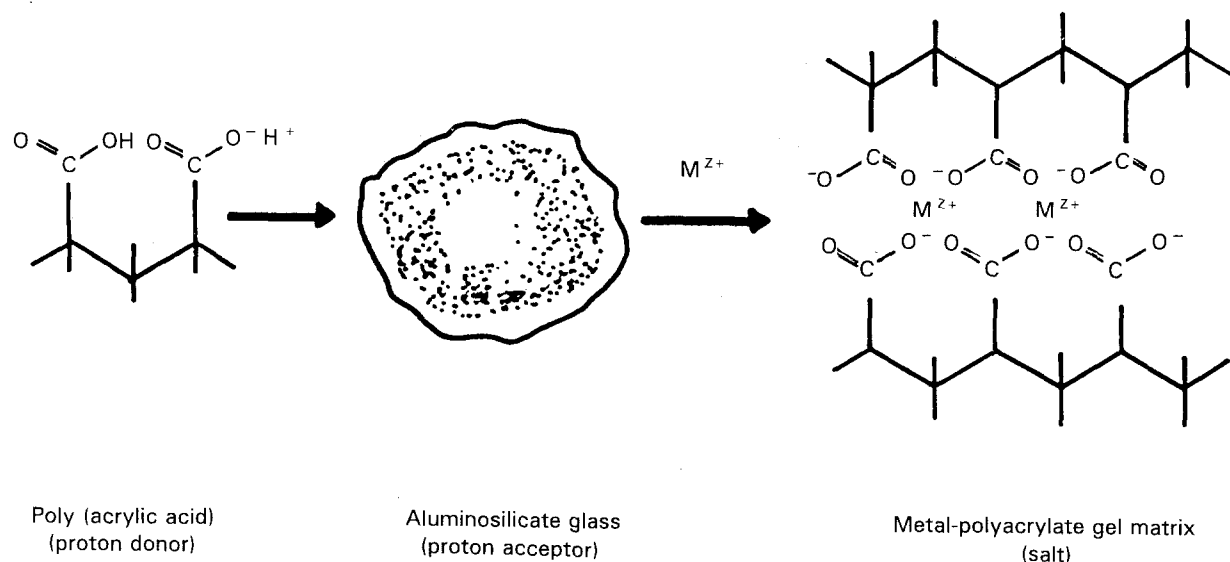


Figure 1 Schematic illustration of the setting reaction in glass polyalkenoate cements.

thus indicating that the chemistry of the setting reaction was unaffected by the chain length. This fracture study also indicated that the inherent Griffith flaw size was attributable to a plastic zone that forms prior to fracture, and that crack propagation takes place through a well-defined process zone at the crack tip. The fracture surfaces of compact tension specimens of glass polyalkenoate cements exhibited “river markings”, providing further evidence for molecular flow of the polymer chains during fracture.

To conclude, the fracture properties of these cementitious materials are surprisingly similar to those of thermoplastic polymers such as poly(methylmethacrylate). The fact that glass polyalkenoate cements exhibit a thermoplastic character suggests that these materials may also exhibit quite marked viscoelasticity. Furthermore, many polymers, especially lightly crosslinked ones, exhibit dramatic changes in their fracture behaviour as the strain rate is increased. For example, with the double torsion test described later in this paper, many epoxy resins exhibit stable fracture at low test rates, but unstable fracture at high test rates [17]. Crisp *et al.* [18] 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 initial mixing of the cement paste. However, recently Williams and Billington [19] have shown the compressive strength of some dental glass polyalkenoate cements to decrease after long storage times. This is a disturbing finding that requires an explanation. Thus, polyalkenoate cements are potentially dynamic materials, exhibiting changes in properties with both the test rate and the time at which the test is conducted.

The present paper attempts to apply some concepts from polymer science to these cementitious materials. For the purpose of the present study, glass polyalkenoate cements can be regarded as a type of polymer composite, where the filler particles have no direct influence on the fracture behaviour, but are simply a source of cations for “crosslinking” the polymer

chains. Thus, fracture of these cements is assumed to be fracture of the polymeric matrix alone. Analysis of fracture surfaces supports this view, as crack propagation takes place almost exclusively through the matrix. The objective of this investigation is to study the long-term properties of model glass polyalkenoate cement compositions. The cements studied have a low glass volume fraction, and poly(acrylic acid) concentration and are not necessarily typical of current restorative materials.

2. Experimental procedure

2.1. Materials

2.1.1. Poly(acrylic acid)s

The poly(acrylic acid)s were obtained from Allied Colloids (Bradford, UK). They were designated E7, E9, E11 and E15. They were supplied as concentrated aqueous solution. The samples were freeze-dried, then ground and sieved below $45\ \mu\text{m}$ prior to use. The manufacturer's batch numbers and their molar mass characteristics, as determined by gel permeation chromatography, are listed in Table I.

2.1.2. Glass powder

The glass was obtained from Dentsply (Weybridge, Surrey, UK). A full chemical analysis of the glass is given in Table II. It was finely ground with a maximum particle size below $45\ \mu\text{m}$. This glass is similar to the glass studied by Barry *et al.* [20]. It has undergone amorphous phase separation to give a matrix phase rich in aluminium and silicon and a dispersed droplet phase rich in calcium and fluorine.

2.2. Preparation of cements

Cement samples were prepared by first blending 7 g of the appropriate poly(acrylic acid) with 50 g of glass

TABLE I Molecular weights determined by gel permeation chromatography of poly(acrylic acid)s

Code	Batch No.	\bar{M}_n	\bar{M}_w	PD ^a	\bar{M}_1
E7	AVS 228	1.13×10^4	2.27×10^4	2.01	5.93×10^4
E9	220	4.04×10^4	1.14×10^5	2.82	2.31×10^5
E11	415	1.12×10^5	3.83×10^5	3.42	6.13×10^5
E15	012	1.30×10^5	1.49×10^6	11.50	2.85×10^6

^a Polydispersity

TABLE II Glass composition

Component	Composition wt %
Si	12.39
Al	16.44
Ca	7.14
F	10.40
Na	7.26
P	4.54

powder. 11 g aliquots of this blend were then hand-mixed with 3.0 ml of 10% (m/m) (+) tartaric acid solution. The (+) tartaric acid was present to retard the set and facilitate handling of the cement paste. The cement mixture was placed in suitably sized moulds consisting of stainless steel formers and plates, which had previously been coated with a mould release agent. The filled moulds were compressed together to eliminate excess cement paste using two G clamps. The filled moulds were then placed in an oven set at $37 \pm 2^\circ\text{C}$ for 1 h. After this period the hardened cement samples were removed from the moulds and then stored in distilled water at $37 \pm 2^\circ\text{C}$ for the appropriate period, prior to testing. All subsequent mechanical tests were carried out in distilled water at $37 \pm 2^\circ\text{C}$.

2.3. Test methods

2.3.1. Double torsion tests

The double torsion (DT) fracture toughness test was used to determine the mode I stress intensity factor K_I . The advantages of this test-piece have been discussed elsewhere. The test-piece (Fig. 2) consists of a flat plate type specimen that is particularly easy to mould. The test-piece is grooved on the underside to ensure crack propagation down the middle of the specimen. During the last ten years this test-piece has been used extensively to study the fracture of thermoset resins. Cracks propagate in DT specimens in one of two modes, with the crack either propagating in a continuous fashion, or proceeding by "stick-slip" where the crack moves along the specimen in a series of jumps. Schematic load deflection records for specimens undergoing stable and "stick-slip" crack growth are shown in Figs 3 and 4, respectively. The testing procedures used have been described in detail previously [16]. The mode I stress intensity factor K_I was calculated by substituting the specimen dimensions and the load at fracture (P_c) into the following equation [21]:

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

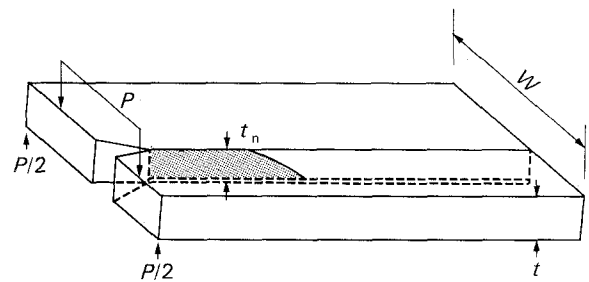


Figure 2 A double torsion test-piece.

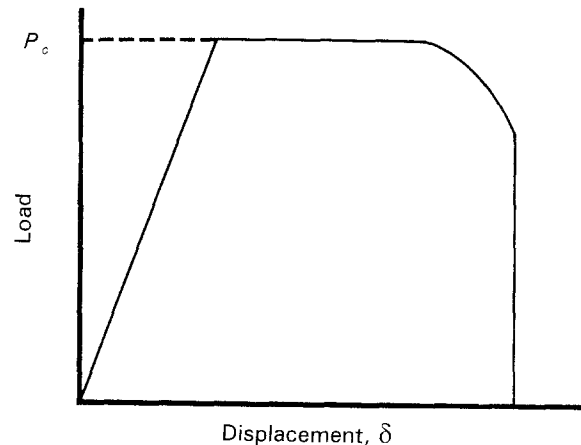


Figure 3 Typical load-displacement record for a double torsion test-piece undergoing stable slow crack growth.

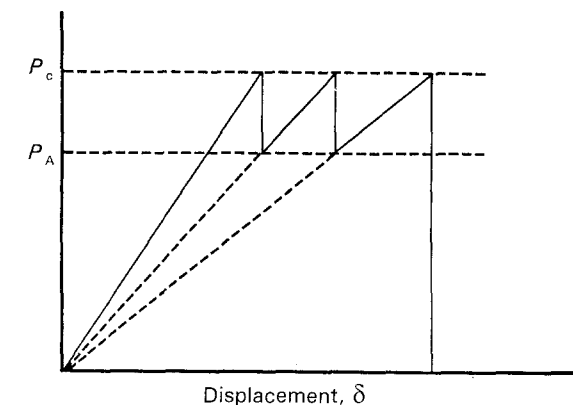


Figure 4 Typical load-displacement record for a double torsion test-piece undergoing unstable stick-slip crack growth.

where: W_m is the moment arm, t the specimen thickness, t_n the specimen thickness in the plane of the groove, W the specimen width and ν the Poisson's ratio (assumed to be 0.33).

2.3.2. Flexural tests

The Young's modulus E and the un-notched fracture strength σ_f were measured using a three-point bend test. Specimens measuring $3.0 \text{ mm} \times 3.5 \text{ mm} \times 30 \text{ mm}$ were used. Frequently the specimens were cut from the broken halves of DT specimens. A span of 20 mm was used for the test. The Young's modulus is given by

$$E = PS^3/4\delta bt^3 \quad (2)$$

where: P is the load, S the span, δ the deflection at the centre of the span, b the breadth of the specimen and t its thickness. The Young's modulus was calculated from the initial slope of the load-deflection plot. The un-notched fracture strength σ_f is defined by

$$\sigma_f = 3PS/2bt^2 \quad (3)$$

Five specimens were tested for each test condition. Specimens that were not visually flaw-free were discarded prior to testing.

2.3.3. The strain energy release rate

The strain energy release rate G_I was calculated from the DT test data, assuming that linear elastic fracture mechanics apply, using

$$G_I = \frac{K_I^2(1 - \nu^2)}{E} \quad (4)$$

This method was less laborious than the compliance calibration method, which gave almost identical results.

2.3.4. Compressive tests

Compressive tests were carried out on 4.0 mm diameter cylinders 6 mm in height. The test was performed in water at $37 \pm 2^\circ\text{C}$ at a test speed of 1 mm min^{-1} . A 0.1 % offset yield stress σ_y was calculated as follows:

$$\sigma_y = 4P/\pi d^2 \quad (5)$$

where: P is the force corresponding to a yield of 0.1 % and d is the diameter of the cylinder.

2.3.5. Calculation of the crack opening displacement

The crack opening displacement δ_c was calculated

using the expression derived by Rice [22].

$$\delta_c = K_{IC}^2/\sigma_y E \quad (6)$$

3. Results and discussion

Table III shows the un-notched fracture strength σ_f and Young's modulus E for cements of identical chemical composition, but of differing molar mass. At all three strain rates studied there is a consistent influence of the poly(acrylic acid) chain length on the un-notched fracture strength of cement. The modulus and strength increase appreciably on increasing the strain rate, exhibiting classic viscoelasticity. The cement made with the highest molar mass poly(acrylic acid) was investigated as a function of time after cement formation. Values for the un-notched fracture strength and Young's modulus after 24, 168 and 672 h are shown in Table IV. The marked viscoelastic behaviour found at 24 h is not so marked at 168 and 672 h, which is consistent with the proposal of Crisp *et al.* [18] that the cross-linking reaction in these cements continues for up to a year after mixing the cement paste.

The two cements made with the E7 and E11 poly(acrylic acid)s were chosen for further study using a linear elastic fracture mechanics approach. The fracture data for the two cements are shown in Tables V and VI. The Young's modulus is plotted against $\log(\text{ageing time})$ in Fig. 5 for both these cements. The results of a linear regression analysis for the modulus data is shown in Table VII; almost identical values for the slope, intercept and correlation coefficient were obtained for the two cements, providing very strong evidence that the chemistry of the setting reaction is unaffected by the poly(acrylic acid) chain length and only the physics of the failure process changes with chain length.

The un-notched fracture strengths for the two cements are plotted against $\log(\text{ageing time})$ in Fig. 6.

TABLE III Strain-rate effect on glass polyalkenoate cements stored prior to testing

Code	\bar{M}_w	0.1 mm min ⁻¹		1.0 mm min ⁻¹		1.0 mm min ⁻¹		0.1 mm min ⁻¹		1.0 mm min ⁻¹	
		σ_f (MN m ⁻²)	SD (n = 5)	σ_f (MN m ⁻²)	SD (n = 5)	σ_f (MN m ⁻²)	SD (n = 5)	E (MN m ⁻²)	SD (n = 5)	E (MN m ⁻²)	SD (n = 5)
E7	2.27×10^4	8.05	0.61	8.78	0.32	9.70	1.42	1754	374	1636	114
E9	1.14×10^5	9.63	0.41	14.45	0.65	13.50	1.80	1220	150	1902	260
E11	3.83×10^5	10.98	0.78	15.40	1.30	16.20	2.32	1313	132	1880	77
E15	1.49×10^6	13.25	1.90	17.01	1.54	20.82	1.48	1580	145	1816	128

TABLE IV Effect of ageing time on the strain-rate effect in glass polyalkenoate cements

Time (h)	0.1 mm min ⁻¹		1.0 mm min ⁻¹		10 mm min ⁻¹	
	σ_f (MN m ⁻²)	SD (n = 5)	σ_f (MN m ⁻²)	SD (n = 5)	σ_f (MN m ⁻²)	SD (n = 5)
24	13.25	1.90	17.01	1.54	20.82	1.48
68	17.55	2.64	20.30	3.04	20.94	1.37
672	17.53	2.52	17.86	1.73	19.60	1.84

TABLE V Influence of ageing time on a low molecular weight (E7) cement

Time (h)	log (time)	K_I (MN m ^{-3/2})	G_I (J m ⁻²)	σ_f (MN m ⁻²)	SD (n = 5)	E (MN m ⁻²)	SD (n = 5)
4.5-5.0	0.7	0.15	16	8.31	0.91	1450	106
24	1.38	0.16	15	8.05	0.61	1754	814
72	1.86	0.18	18	7.61	0.78	1838	262
168	2.22	0.19	17	9.33	0.59	2157	241
264	2.42	-	-	10.40	0.71	2495	390
1832	3.26	0.25	17	11.90	1.01	3659	301
3812	3.58	0.27	19	12.41	1.43	3860	594

TABLE VI Influence of ageing time on a high molecular weight (E11) cement

Time (h)	log (time)	K_I (MN m ^{-3/2})	G_I (J m ⁻²)	σ_f (MN m ⁻²)	SD (n = 5)	E (MN m ⁻²)	SD (n = 5)
4.5-5.0	0.70	0.27	56	10.50	0.92	1355	91
24	1.38	0.27	47	10.98	0.78	1313	132
72	1.86	0.29	45	14.41	0.89	1866	156
168	2.22	0.30	33	15.36	0.81	2729	146
264	2.42	0.31	-	15.41	0.85	2788	318
1536	-	-	-	16.13	1.74	3301	214
1832	3.26	0.32	38	14.28	1.67	1697	194
3812	3.58	0.34	29	19.40	1.84	3954	541

TABLE VII Results of linear regression analysis of ageing study

Data	Gradient	Intercept	Correlation coefficient
Young's modulus-log (time)			
E7 cement	10.197×10^{-4}	- 0.335	0.962
E11 cement	9.608×10^{-4}	- 0.183	0.964
Un-notched fracture strength-log (time)			
E7 cement	0.479	- 2.431	0.898
E11 cement	0.309	- 2.254	0.952

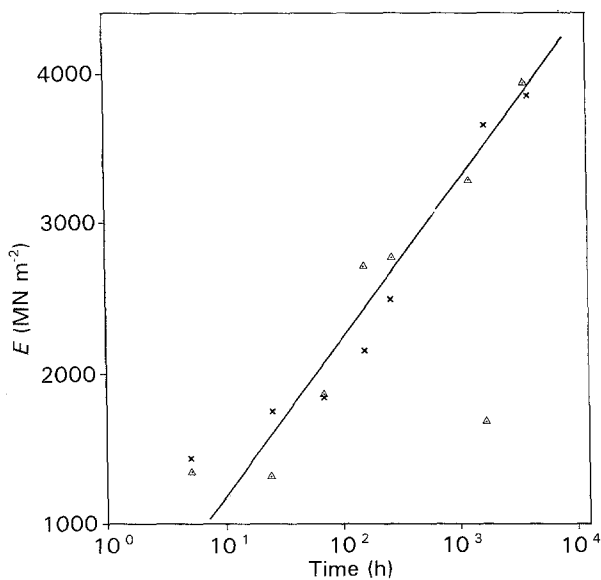


Figure 5 Plot of Young's modulus against log(aging time) for the two cements: (x) E7, (Δ) E11.

Again the slopes are almost identical, suggesting a common process for fracture.

All the cement samples gave slow stable crack growth during the DT test, with no tendency towards

stick-slip behaviour with increased cement age. The validity of the linear elastic fracture mechanics approach has been previously established for the cement samples tested after 24 h. It is reasonable to assume that the increased density of ionic crosslinks and the reduced viscoelasticity of these cements with increasing time will ensure that valid data are being obtained for all the samples tested after 24 h.

The fracture toughness K_I shows a small increase with the age of the cement for both sets of samples. The toughness G_I of the low molecular weight cement remains approximately constant, whilst the high molecular weight cement exhibits a decline in toughness with increasing age of the sample.

In an earlier fracture study of the influence of poly(acrylic acid) chain length on the toughness [16], a chain pull-out model was used to analyse the data. This model views polymer chains as being pulled out of hypothetical tubes formed from entanglements consisting of neighbouring chains, during the fracture process. An entangled chain is shown schematically in Fig. 7, whilst the chain pull-out model is shown in Fig. 8.

The toughness, or fracture surface energy, is a measure of the energy required to pull the chains crossing

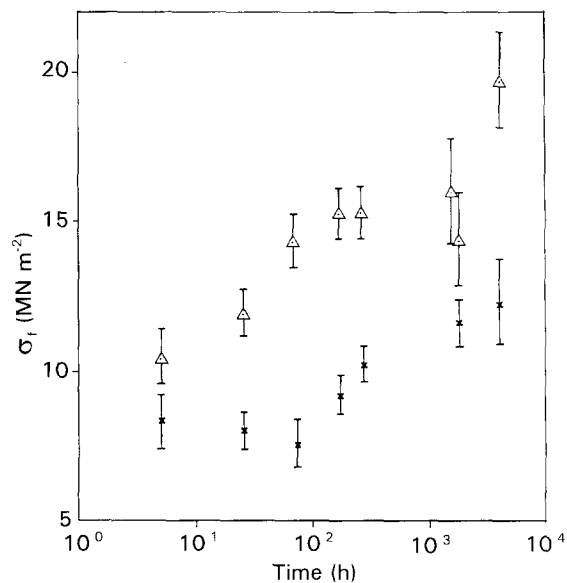


Figure 6 Plot of un-notched fracture strength against log(aging time) for the two cements: (x) E7, (Δ) E11. Bars represent 2 × SD.

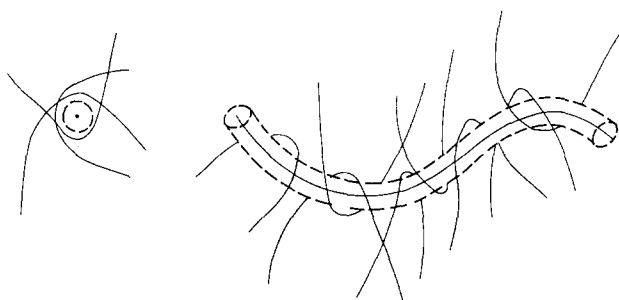


Figure 7 Schematic illustration of an entangled polymer chain.

the fracture plane out of their tubes. The energy required to extricate a chain from its tube (τ_0) is dependent on the length of the chain and the frictional force between the chain and its neighbours forming the tube. Prentice [23] showed that

$$\tau_0 = \int_{l=0}^{l=L} \mu 2\pi r \left(\frac{V}{h}\right)^n dl \quad (7)$$

where: l is the contour length of the tube occupied by the polymer molecule, L the total contour length of the tube vacated, μ the coefficient of friction between the extracted chain and its tube, h the spatial gap between the chain and the surface of its imaginary tube, V the rate of removal of the chain, n the power-law index and r the radius of the polymer chain. For thermoplastics this equation leads to:

$$\tau \propto (MW)^2$$

where: τ is the energy expended in pulling out all the chains crossing the fracture plane from their tubes and MW is the molar mass of the polymer which is directly proportional to its length l . Prentice found experimentally that for poly(methylmethacrylate) the toughness was somewhat more dependent on chain length than predicted, in fact

$$\tau \propto \bar{M}_n^{2.4}$$

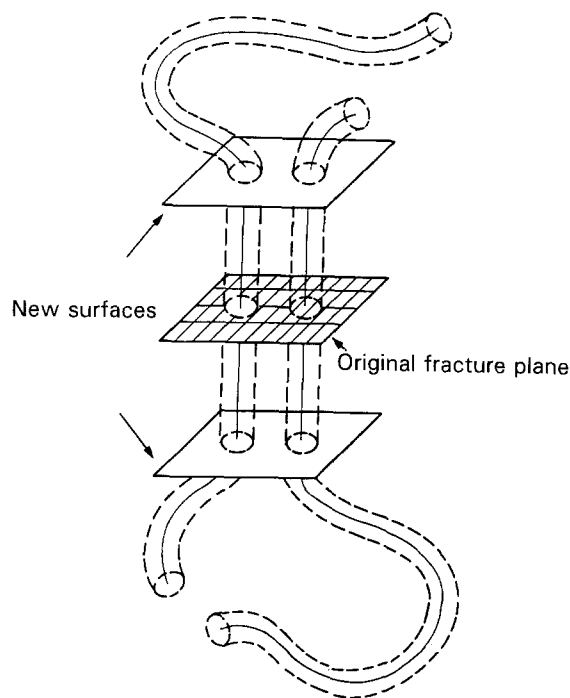


Figure 8 Schematic illustration of the chain pull-out model of fracture in polymers.

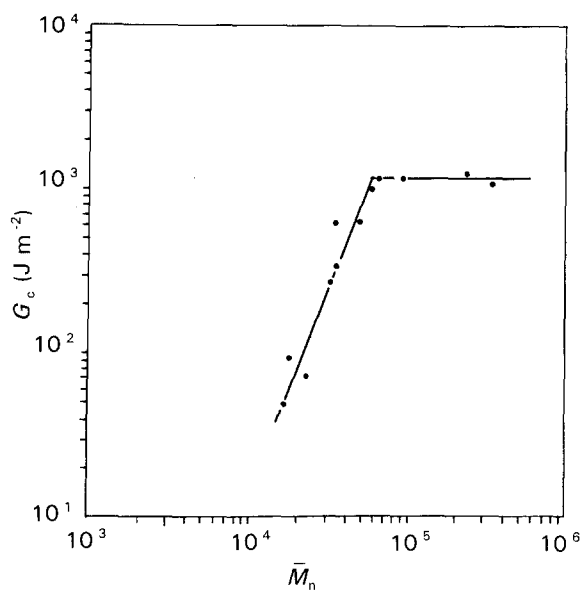


Figure 9 Dependence of toughness on molecular weight for the thermoplastic poly(methylmethacrylate) [23]. Slope of rising portion = 2.45.

where \bar{M}_n is the number-average molecular weight. One explanation for the exponent being greater than 2.0 is that the samples of poly(methylmethacrylate) were polydisperse and that the longer chains in the distribution were contributing more to the toughness than indicated by the number-average molecular weight.

At very high molar masses the toughness was no longer dependent on molecular weight and a plateau was achieved. Prentice's results are shown in Fig. 9. The failure of the toughness to continue to rise with increasing chain length is a result of the force to extricate a long chain from its tube being greater than the force to physically break the carbon-carbon bond

of the polymer backbone. Now in the case of a polymer-based cement we might expect that as the number of ionic linkages between the polymer chains increases, the frictional term μ will increase and the force required to extricate a chain from its tube will, therefore, increase with time; hence chain scission will occur at a lower molar mass or shorter chain length as the cement is aged.

If the polymer chains are all well below the value l_c at which chain scission occurs and assuming μ , the frictional term in Equation 7, to increase with cement age, we would expect the toughness τ to increase. If the chains were all greater than the value at which chain scission occurs, then the toughness would remain constant. However, in the high molecular weight material (E11) the toughness decreases with cement age, whilst the toughness of the low molecular weight cement (E7) remains approximately constant. A third factor is clearly important that is neglected by the chain pull-out model for fracture. Only one chain is envisaged crossing the fracture plane in the chain pull-out model shown in Fig. 9, and elementary calculations show that a single chain even when fully stretched is not sufficiently long to bridge the crack tip that in most polymers has dimensions $> 1 \mu\text{m}$. Thus, chains distant from the fracture plane must undergo flow and pull-out. It is reasonable to assume that the number of chains involved will depend on the crack opening displacement at the crack tip. The greater the crack opening displacement at the crack tip, the larger will be the number of chains undergoing pull-out and slip along their tubes and the greater will be the toughness. In general, highly crosslinked materials such as inorganic glasses and epoxy resins exhibit small crack opening displacements, whilst thermoplastics, which exhibit marked molecular flow during fracture, generally exhibit much larger crack opening displacements. Thus, it would be reasonable to assume that in these cements as the number of ionic linkages between the chains increases, the crack opening displacement will reduce, causing a reduction in toughness.

In the case of the low molar mass E7 cement the reduction in toughness as a result of a reducing crack opening displacement may be balanced by the increase in the pull-out energy of individual chains, and the overall toughness then remains approximately constant. In contrast, the chains in the E11 cement are possibly above the length at which chain scission occurs and the pull-out energy of individual chains remains approximately constant, whilst the number of chains involved during fracture falls with the result that the toughness reduces with increasing age of the cement. It is worth noting here that l_c may well reduce as the crosslinking reaction continues and the pull-out energy of a given chain length increases.

In order to test the hypothesis of the crack opening displacement reducing with the age of the cement, 0.1 % offset yield stresses were measured in order to calculate the crack opening displacement using equation 6. Table VIII shows the experimental yield stress values and the calculated crack opening displacement for the E7 and E11 cements as a function of

the cement age. The crack opening displacement reduces for both cements as the cement ages, as predicted from our chain pull-out model. Prentice [23] in his studies of the toughness of poly(methylmethacrylate) demonstrated that

$$G_c \propto \bar{M}_n^{2.45}$$

rather than

$$G_c \propto \bar{M}_n^{2.0}$$

predicted by the reptation chain pull-out model. As a result of the present data it would be worth investigating the crack opening displacement of poly(methylmethacrylate) as a function of molecular weight in order to see if the greater dependence of the toughness on molecular weight could be accounted for by an increasing crack opening displacement.

The discussion has so far assumed a single chain length in the E7 and E11 cements. The data in Table I clearly show both the E7 and E11 poly(acrylic acid)s to have a wide distribution of chain lengths, which complicates the data analysis. Clearly it is advisable to have chains above l_c , the critical chain length at which chain scission occurs, in order to optimize the toughness. However, it is important to note that chains above l_c will not contribute any further to the toughness, but will continue to contribute towards the viscosity of the cement paste. In practical cement pastes the chain length and the polyacid concentration that can be used are limited by the viscosity. In cement pastes where the chain length is greater than l_c it would be advisable to reduce the chain length and to increase the molecular concentration of chains, thereby increasing the number of chains crossing the fracture plane and increasing the toughness of the final cement. One of the problems of pursuing such a strategy is that we do not know values for l_c ; furthermore, l_c will not be a constant, but is likely to change with cement age and cement composition. The value of l_c is likely to be very dependent on the glass composition and its microstructure, via the number and type of ions released. Thus, the relative proportions of aluminium, calcium, sodium and fluoride ions released by the glass may well be critical to obtaining cements with optimum toughness. Furthermore, the release of these ions by the cement matrix into the aqueous environment surrounding the specimen is also likely to be important in determining final cement properties.

TABLE VIII Influence of ageing time on the yield stress σ_y and calculated opening displacement δ of a low molecular weight (E7) and a high molecular weight (E11) glass polyalkenoate cement

Age (h)	E7		E11	
	σ_y (MPa)	δ_c (μm)	σ_y (MPa)	δ_c (μm)
24	35.75	0.41	46.99	1.18
72	44.44	0.39	50.57	0.89
168	49.60	0.34	52.07	0.63
1832	52.37	—	53.59	—
3812	—	—	—	—

The setting reaction in dental glass polyalkenoate cements is thought [20] to take place primarily with a calcium- and fluorine-rich droplet phase, which results in the formation of a calcium-rich polyacrylate salt gel. The reaction continues over prolonged time periods with the aluminium- and silicon-rich glass matrix phase and the preferential formation of aluminium polyacrylate.

Aluminium ions are known to be more efficient at crosslinking the polyacrylate chains than calcium ions. A cement with a large number of aluminium ions in the matrix may well be highly crosslinked with a very small crack opening displacement and a resultingly low toughness. In contrast, cements based totally on calcium polyacrylate are known to be hydrolytically unstable.

Sodium ions may act to block carboxylate sites, thereby preventing them from chelating aluminium or calcium ions. Fluoride and phosphate ions will complex aluminium and calcium ions and reduce their ability to crosslink polyacrylate chains. For example, in the presence of F^- ions hydrated AlF_2^+ , rather than hydrated Al^{3+} , is likely to exist.

Previous studies of the long-term compressive strength [18, 19] and flexural strength [24] of dental glass polyalkenoate cements have interpreted experimentally observed decreases in strength as a result of long-term hydrolytic instability of the polyalkenoate cement matrix. The results presented here indicate that it is also possible that reductions in strength may be a result of a decreasing toughness and crack opening displacement accompanying long-term crosslinking reactions. Thus, like thermoset resins it may be possible to "over-crosslink" a glass polyalkenoate cement. Such an effect is likely to be observed with restorative materials mixed at a high powder to liquid ratio with a high polyacid concentration. Furthermore, cements based on copolymers of maleic acid, where there is a higher concentration of carboxylic acid functional groups, are most likely to exhibit such an effect. Williams and Billington [19] recently observed a marked decline in the compressive strength of some commercial dental cements based on maleic acid copolymers, and this may be due to over-crosslinking as opposed to hydrolytic instability of the cement matrix.

4. Conclusions

Glass polyalkenoate cements can be modelled as polymer composites where fracture takes place almost exclusively in the polymer matrix. The Young's modulus increases with the age of the cement as crosslinking of the polyacrylate chains continues with time. The fracture toughness and un-notched fracture strength increase with cement age. The toughness does not increase with cement age as predicted from the chain pull-out model, but remains constant for the low molecular weight cement and decreases for the high molecular weight cement.

The crack opening displacement has been shown to decrease with cement age for both low and high molecular weight cements. In the case of the low molecular weight cement the pull-out energy of indi-

vidual chains from their tubes is thought to increase with time as the number of crosslinking ions in the cement matrix increases. In the case of the high molecular weight cement the chain length of the polymer is believed to be close to l_c , the length at which chain scission rather than chain pull-out occurs. In these circumstances there can be little further improvement in toughness with time and the toughness would be expected to remain constant. However, the toughness declines as a result of a reduction in the number of chains undergoing pull-out, caused by the crack opening displacement diminishing with cement age. In the case of the low molecular weight cement, the increase in toughness caused by the increased pull-out energy of individual chains is offset by the decrease in the number of chains involved in fracture.

In summary, glass polyalkenoate cements are complex materials whose properties change with time. The majority of studies carried out on these materials to date have involved only simple measurements of compressive strength and flexural strength in a short time period after mixing the cement. The present study demonstrates that linear elastic fracture mechanics offers a much greater insight into how the strength and toughness of these unusual materials can be improved.

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