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# Influence of poly(acrylic acid) content on the fracture behaviour of glass polyalkenoate cements

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A linear elastic fracture mechanics approach (LEFM) was used to study glass polyalkenoate cements as a function of the poly(acrylic acid) content. Cement specimens were tested at three time intervals after mixing; one, seven and twenty eight days. Two series of cements were investigated one with a glass volume fraction of 0.4 and the other with a glass volume fraction of 0.5. The fracture toughness, toughness, Young's modulus and un-notched fracture strength increased significantly with the percentage polyacid content. The Young's modulus increased with time for all the cement samples studied. In many cases the moduli values at twenty eight days were twice the values at one day. This is consistent with increased ionic crosslinking of the polyacrylate matrix. The toughness increased with the polyacid content as predicted by the chain pull-out model for fracture and did not change significantly on increasing the glass volume fraction from 0.4 to 0.5. Fracture toughness and Young's modulus increased significantly with glass volume fraction consistent with the residual glass particles acting as a reinforcing filler. © *1998 Kluwer Academic Publishers*

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## 1. Introduction

There is a need for a replacement material to mercury based amalgams in dentistry. Glass polyalkenoate cements formed from ion leachable fluoro-alumino-silicate glasses and poly(acrylic acid), Fig. 1 have considerable potential as a posterior filling material for large class I and II cavities if the fracture toughness could be increased and the abrasion resistance improved.

Unlike resin based materials, no polymerisation is involved in the setting process and the materials do not undergo any polymerisation contraction, which is often associated with marginal leakage and ultimately with the development of secondary caries. The release of fluoride ions from these cements is another major benefit, in preventing secondary caries. Furthermore the ability of glass polyalkenoate cements to chemically bond to the apatite phase of enamel and dentine ensures good adaptation and stress transfer in the restored tooth.

The compressive strength of glass polyalkenoate cements has been extensively studied in the literature [1–4], however stress analysis studies and the fractographic analysis of clinical failures of posterior restorations indicates that failure often occurs in a tensile mode [5]. Furthermore there is no theoretical relationship between compressive strength and abrasive wear resistance, which is a key property of a posterior filling material. In contrast fracture toughness in conjunction with hardness is usually one of the dominant factors in determining the abrasive wear rate of a brittle material [5–8].

Wilson *et al.* [9] established a correlation between abrasive wear rate and fracture toughness for glass polyalkenoate cements of fixed composition, but varying polyacid molar mass. The results of this study are reproduced in Fig. 2.

The low fracture toughness of currently available glass polyalkenoate cements [10, 11], compared to amalgams and composite resins is recognised as being a major limitation for their widespread clinical use in class I and II cavities [8]. Attempts have been made to reinforce glass polyalkenoate cements by incorporating metals, notably amalgam alloys and silver. However, these approaches have not resulted in improved toughness and are unlikely to do so in the future, since fractographic analysis of glass polyalkenoate cements indicates that the crack path lies almost exclusively in the polysalt matrix phase [11]. Hill and coworkers [12, 13] have also demonstrated that the molar mass of the poly(acrylic acid) component has a significant influence on toughness, even after one month. This supports the observation that failure takes place predominantly in the polysalt matrix and is dominated by the polymer component. Furthermore the ionic crosslinks between

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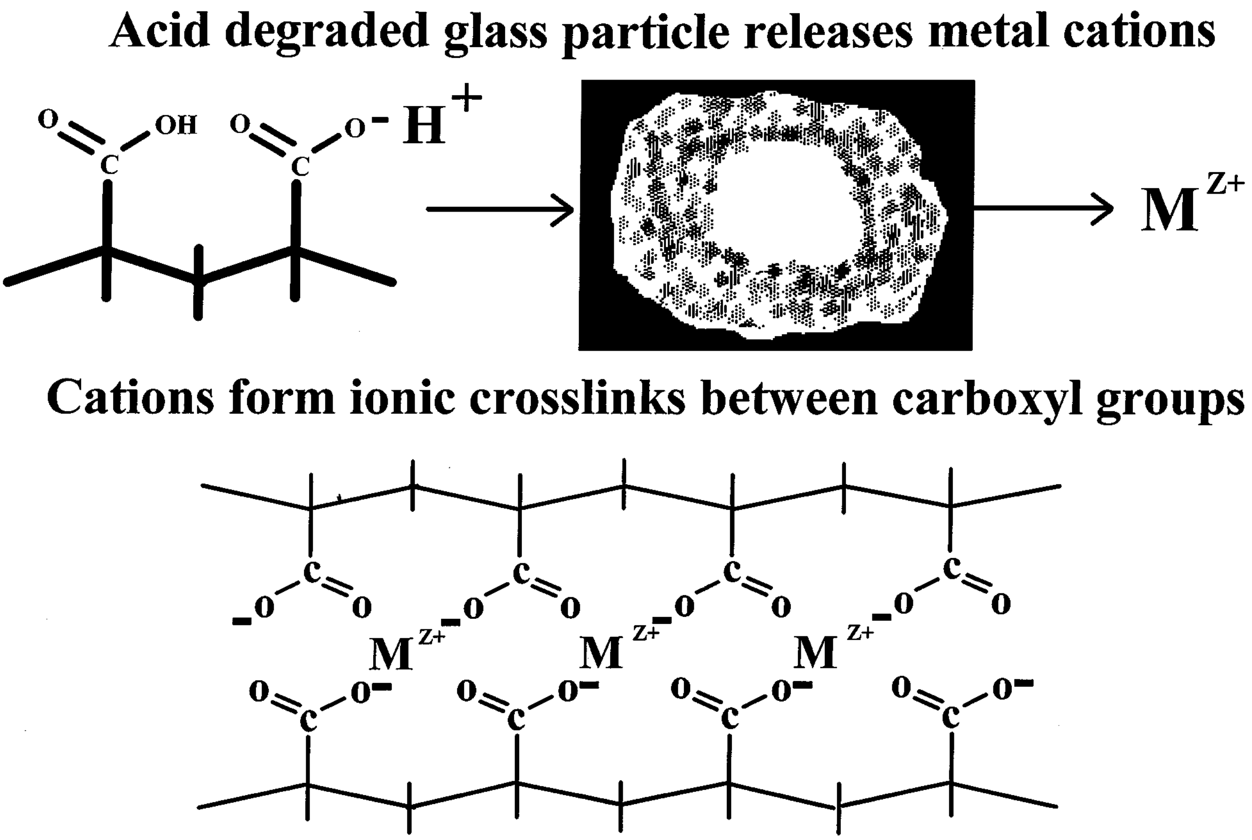


*Figure 1* Schematic setting reaction of a glass polyalkenoate cement.

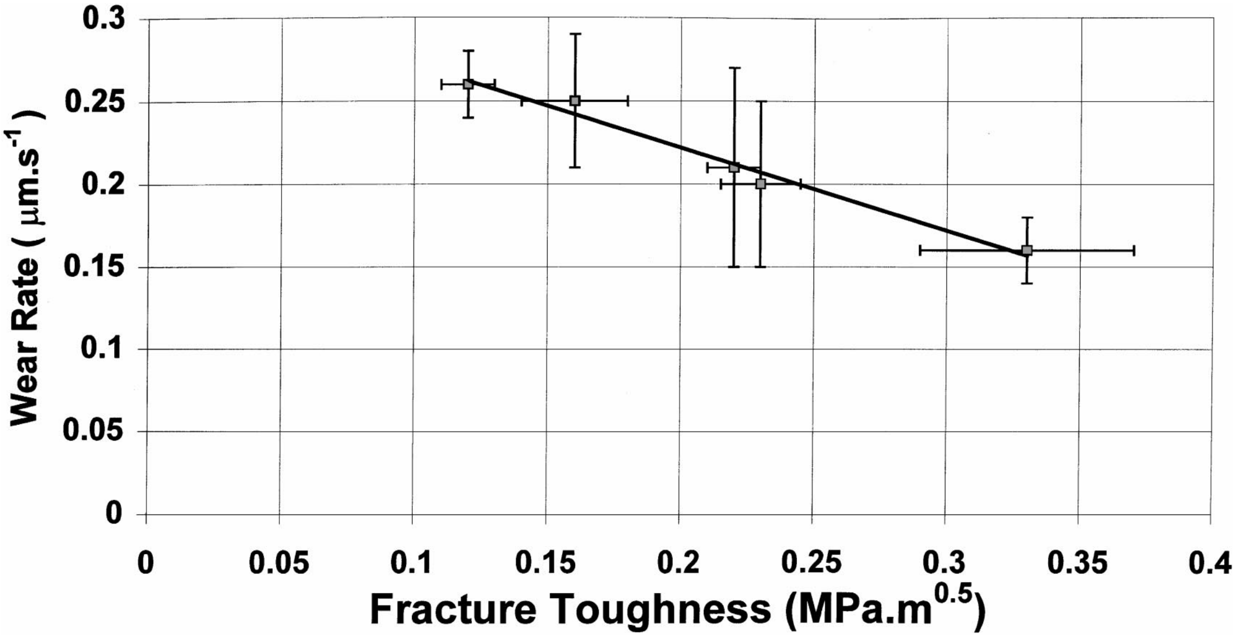


*Figure 2* Plot of abrasive wear rate against fracture toughness.

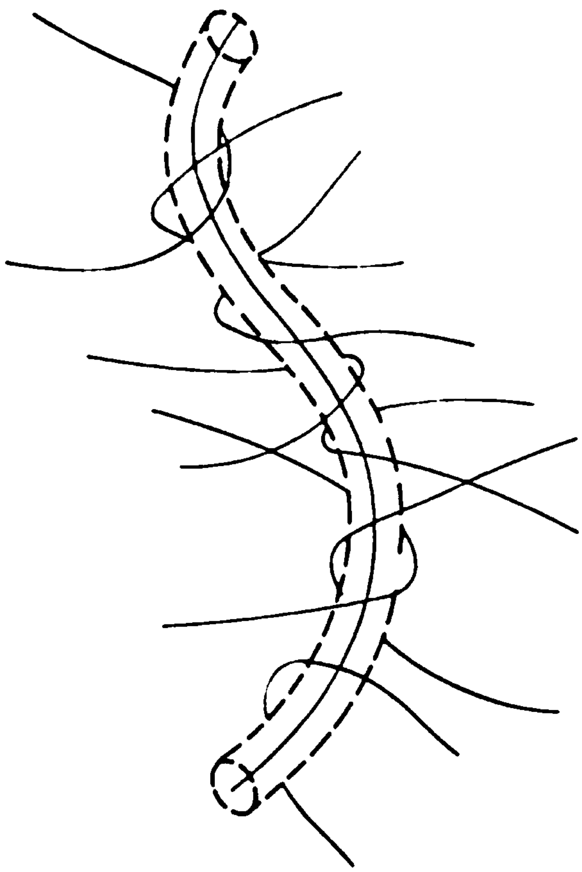
the polyacrylate chains must be labile in order for the toughness to be dependant on molar mass.

Sharp loss peaks have been demonstrated in glass polyalkenoate cements that are typical of thermoplastics [14]. It is therefore worth looking at the fracture behaviour of thermoplastics.

## 2. Fracture of thermoplastic polymers

The fracture surface energy of a thermoplastic polymer is much greater than the energy required to break all the polymer chains crossing the crack plane [15, 16]. The high fracture surface energy is attributed to localized flow of polymer chains at the crack tip. The inherent Griffith flaw size found with polymers, such as poly(methylmethacrylate) is associated with a plastic zone or craze that forms prior to catastrophic failure.

The strength of thermoplastic polymers is related to long range entanglements that serve to restrict chain motion. The early ideas of chain entanglements viewed the entanglement as a physical knot that served to limit chain slippage during fracture. However, polymer



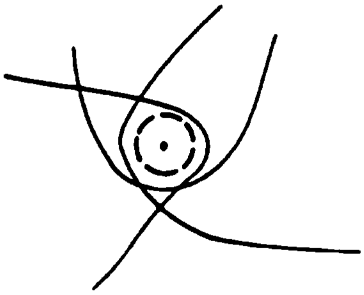


*Figure 3* Polymer chain trapped in a tube of entanglements.

chains are too inflexible to form physical knots and a model has been developed [17] 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, since in moving, one chain may not cross the contour of another. Longitudinal motion is also prevented by the interaction of substituents on neighbouring chains that give rise to potential barriers to chain mobility along the tube.

The dynamics of a polymer chain in a melt, or concentrated solution have been described by the reptation model [18, 19]. This model has also been used to describe fracture [20, 21] in polymers.

The reptation/chain pull out model for fracture is shown schematically in Fig. 4. The model assumes that a polymer chain only crosses the fracture plane once, which may be questionable, but considerably simplifies the analysis. Prentice [22] derived the following equation:

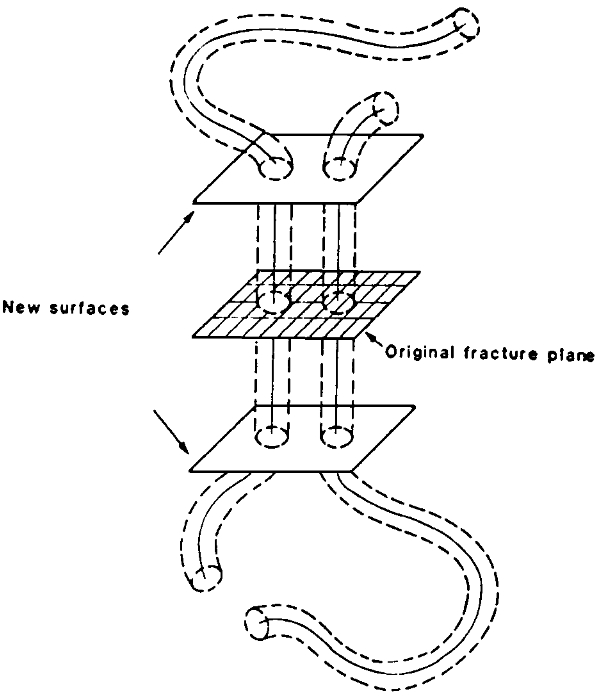


*Figure 4* Reptation chain pull-out model for fracture.

$$\tau = \mu\pi r N_\mathrm{s}\left(\frac{V}{h}\right)^n L^2 \tag{1}$$

where $\mu$ 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, $N_\mathrm{s}$ 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 between the chain and the surface of its imaginary tube, $V$ is the rate of removal of the chain and $n$ is a constant.

In thermoplastic polymers the concentration of chains and thus the number of chains crossing the fracture plane, $N_\mathrm{s}$ and the spatial gap, $h$ are fixed. This is not the case for glass polyalkenoate cements, since the poly(acrylic acid) concentration can be altered. The model predicts the fracture surface energy to increase with increasing polyacid concentration, as $N_\mathrm{s}$ will increase and h will decrease.

In practice since the crack opening displacement is larger than the length of the longest polymer chains present, chains that are close to the fracture plane, but which do not cross the fracture plane also undergo deformation and pull-out. The number of such chains will depend on the extent of plastic zone formation at the crack tip and the critical crack opening displacement.

The Young's modulus would also be expected to increase with the polyacid concentration, since there would be an increased entanglement density and a greater density of carboxylate groups for crosslinking.

## 3. Previous fracture studies of glass polyalkenoate cements

Despite the fact that the composition of a glass polyalkenoate cement is likely to have a significant influence on the mechanical properties only one published study exists in the literature and this is confined to measurements of compressive strength and tensile strengths [3]. This study showed the compressive and tensile strength measured at one day to increase with polyacid concentration.

The molar mass of the poly(acrylic acid) used in the cement would according to the reptation pull-out model for fracture have a pronounced influence on the toughness and fracture toughness of the cement. Experimental studies [9, 12, 13] indicate that molar mass has a significant influence, though the magnitude of the toughness increase with molar mass is not as large as predicted by the model. In practice the initial viscosity of the cement paste limits the concentration and molar mass that can be used in a cement. Thus a higher molar mass poly(acrylic acid) can be only used at a reduced concentration. In designing cements with improved properties it is therefore important to understand how both molar mass and concentration influence fracture toughness and toughness.

The mechanical properties of glass polyalkenoate cements change with time as the setting reaction proceeds [3, 13, 23–26]. Compressive and flexural strengths generally increase with time [3, 13, 24] but in some cases may also decrease with time [25, 26]. The changes in mechanical properties have generally been associated with increased crosslinking of the polyacrylate chains by cations, but recently Wasson and Nicholson [27] have put forward the idea that the changes are due to the formation of a silicate phase. This view has been widely accepted, despite the lack of evidence and the fact that continued ionic crosslinking provides a better explanation of the observed data. For example the Young's moduli increase with time [13] and the cements become less viscoelastic with time [23], which is consistent with increased crosslinking of the polyacrylate chains. The toughness may increase, or decrease with time [13] depending on the poly(acrylic acid) molar mass, which suggests that flow of the polyacrylate chains at the crack tip and the extent of 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. However the best argument against the idea that a silicate phase accounts for significant changes in cement mechanical properties is that cements based on silicate phases, such as Portland cement, or high alumina cement generally have very low toughness values, typically about 5 $\mathrm{J\,m^{-2}}$ compared to glass polyalkenoate cements that have toughness values in the range 30–80 $\mathrm{J\,m^{-2}}$. The contribution of a silicate phase to the toughness is therefore likely to be small. Furthermore transmission electron microscopy [28] shows the silicate phase to be located at the periphery of the reacted glass particles and crack propagation takes place through the polysalt matrix [9, 12, 13].

## 4. Experimental

### 4.1. Materials

#### 4.1.1. Glass

The glass for this study was specially prepared for the purpose in order to have a value for its density. The compositions were designed to eliminate fluorine loss from the melt as silicon tetrafluoride during firing [29]. The glass was produced by mixing the appropriate amounts of silica $>99.99\%$ pure (Tilcon Industrial Minerals Stoke-on -Trent ST7 1TU UK) with GPR grade alumina (BDH Poole BH15 1TD UK), calcium carbonate (E. Merck D-6100 Darmstadt GERMANY) and calcium fluoride (Aldrich Chemical Co Milwaukee WI53233 USA) and ball milling for one hour, whereupon the appropriate amount of GPR grade phosphorous pentoxide (BDH Poole BH15 1TD UK) was added and mixed in. The prefired batch was then placed in a high density sintered mullite crucible (Zedmark Refractories Earlsheaton Dewsbury UK) and fired at the appropriate temperature for two hours. This mixture was then placed in a high density sintered mullite crucible and fired at 1380 °C for two hours. The resulting glass melt was poured into demineralised water to produce granular glass frit. Eight crucible melts giving approximately 4 kg of frit were fired. The frit was mixed and 100 g quantities ground in a Gyro mill (Glen Greston Wembley London UK) with a 120 mm diameter grinding pot for two periods of seven minutes. The resulting glass powder was sieved through a 45 $\mu$m mesh sieve.

#### 4.1.2. Poly(acrylic acid)

The poly(acrylic acid) for this study was a medical grade polymer supplied by AHC (Shofu) (Chiddingstone Causeway, Tonbridge Kent, UK).

Gel permeation chromatography showed this polymer to have a number average molar mass of $2.29 \times 10^4$ and a weight average molar mass of $1.68 \times 10^5$.

#### 4.1.3. Cement preparation

Cements were prepared by thoroughly mixing the glass powder with the poly(acrylic acid) and mixing this with 10% m/v (+) tartaric acid solution. In calculating the glass volume fraction a density of 2.67 $\mathrm{g\,cm^{-3}}$ for the glass was used, which was based on the density of a specially cast sample of the glass.

Cements were allowed to set in the appropriate mould for one hour at $37 \pm 2\,^\circ$C then removed from the mould and stored in distilled water at $37 \pm 2\,^\circ$C prior to testing. Tests were carried out after 1, 7 and 28 days. The specimen preparation techniques are based on British Standard BS6039 [30].

### 4.2. Test methods

#### 4.2.1. Double torsion test

The double torsion (DT) test was selected because of its many advantages. For example the specimens are easy to manufacture and blunt cracks can readily be detected. Finally, after fracturing, the large DT specimens can be cut down to make three-point bend specimens, making economical use of materials and resources.

DT specimens 3.5 × 65 × 25 mm, were produced in the form of rectangular plates. A sharp groove 0.5 mm deep was cut down the centre of the specimen using a miroslice cutter. A fine slot was cut at one end of the specimen, using a diamond wafer blade.

The DT test was performed using and Instron electromechanical testing machine (Instron Ltd., High Wycombe, UK). During the test the specimen was supported on two parallel rollers of 3 mm diameter and spaced 20 mm apart and load applied at a constant rate (0.1 mm $\text{min}^{-1}$) to the slotted end via two 3 mm diameter ball bearings spaced 10 mm apart. The specimen was therefore subjected to four-point bend loading, during which the crack initiated and propagated, along the centre of the specimen, within the groove. The test was carried out in tap water at 37 ± 2 °C. The groove depth was chosen to eliminate the need for crack shape corrections [31].

In a DT test the mode I stress intensity factor $K_1$ is independent of crack length and is given by [32]

$$K_1 = P_c\, W_m \left(\frac{3(1+\nu)}{Wt^3 t_n}\right)^{1/2} \tag{2}$$

where $W_m$ is the moment arm, $W$ the specimen width, $t$ the specimen thickness, $t_n$ is the thickness in the crack plate and $\nu$ Poisson's ratio (assumed to be 0.33). Values for $K_1$, the fracture toughness, were obtained by substituting the appropriate specimen dimensions along with the load at fracture $P_c$ in Equation 2.

### *4.2.2. The flexural test*

Immediately after testing the DT specimens, the broken halves were cut up into three-point bend specimens, measuring 3.0 × 3.5 × 65 mm. The test and method are based on ASTMS D790-1 [33]. In a three-point bend specimen the relationship between the applied load ($P$) and the deflection at the centre of the specimen ($\delta$) for a specimen of rectangular cross section is given by:

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

where $t$ is the beam thickness, $b$ the beam width and $s$ the span. A span of 50 mm was used, with a crosshead displacement rate of 1.4 mm $\text{min}^{-1}$. This gives an almost identical strain rate to that used in the DT tests. The large span of 50 mm relative to the smaller span of 20 mm typically used for restorative dental materials enables the strain to be calculated fairly accurately from the crosshead displacement, following a compliance calibration. All tests were carried out in tap water at 37 ± 2 °C. The Young's modulus was calculated from the initial slope of the load deflection plot. The unnotched fracture strength is defined by:

$$\sigma_f = \frac{3Ps}{2bt^2} \tag{4}$$

A minimum of five 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

$$G_1 = \frac{K_1^2(1-\nu^2)}{E} \tag{5}$$

## 5. Results and discussion

The Young's modulus generally increases with the poly(acrylic acid) content at all three cement ageing times studied (Table I, Figs 5, 6 and 7), however at the highest poly(acrylic acid) content of 60% with a glass volume fraction of 0.40 there is a significant reduction in modulus (Fig. 6). The polymer chains will form the load carrying polysalt matrix phase and the greater chain density would be expected to give rise to an increased Young's modulus. In addition the higher the chain density, the greater the entanglement density and these entanglements will also act as crosslinks and will also serve to increase the Young's modulus. The higher poly(acrylic acid) concentration will also lower the pH and increase the rate of reaction and the extent of reaction. Higher poly(acrylic acid) contents are also synonymous with lower water contents. This factor coupled with increased ionic crosslinks will result in a lower content of unbound water and it is likely that this will also serve to increase the Young's modulus, since it is likely that unbound water will act as a plasticiser. At high poly(acrylic acid) contents the reaction may be suppressed by the lack of water for hydrating the complexes formed [3], or by insufficient metal cations being available from the glass and this may account for the observed reduction in Young's modulus. Examination of Fig. 7 which shows Young's moduli values at seven days, provides support for the view that there is insufficient cations for crosslinking present. At 30 and 40% polymer contents the Young's moduli of the cements made with 0.40 and 0.50 glass volume fractions are approximately equal, suggesting that the polysalt matrix phase is dominating the Young's modulus of the composite. At higher polyacid concentrations the moduli of the 0.5 glass volume fraction cements is significantly higher than the 0.4 volume fraction cements.

TABLE I Young's modulus (GPa) as a function of cement polymer content and storage time in water at 37 °C for cements with 0.4 glass volume fraction

| Polymer concentration | 24 hrs | SD | 1 week | SD | 1 month | SD |
|---|---|---|---|---|---|---|
| 60 | 3.58 | 0.21 | 5.29 | 0.23 | 6.89 | 0.63 |
| 50 | 5.72 | 0.42 | 6.84 | 0.61 | 8.73 | 0.59 |
| 40 | 3.09 | 0.22 | 4.18 | 0.28 | 4.93 | 0.47 |
| 30 | 1.19 | 0.04 | 1.79 | 0.11 | 1.94 | 0.17 |

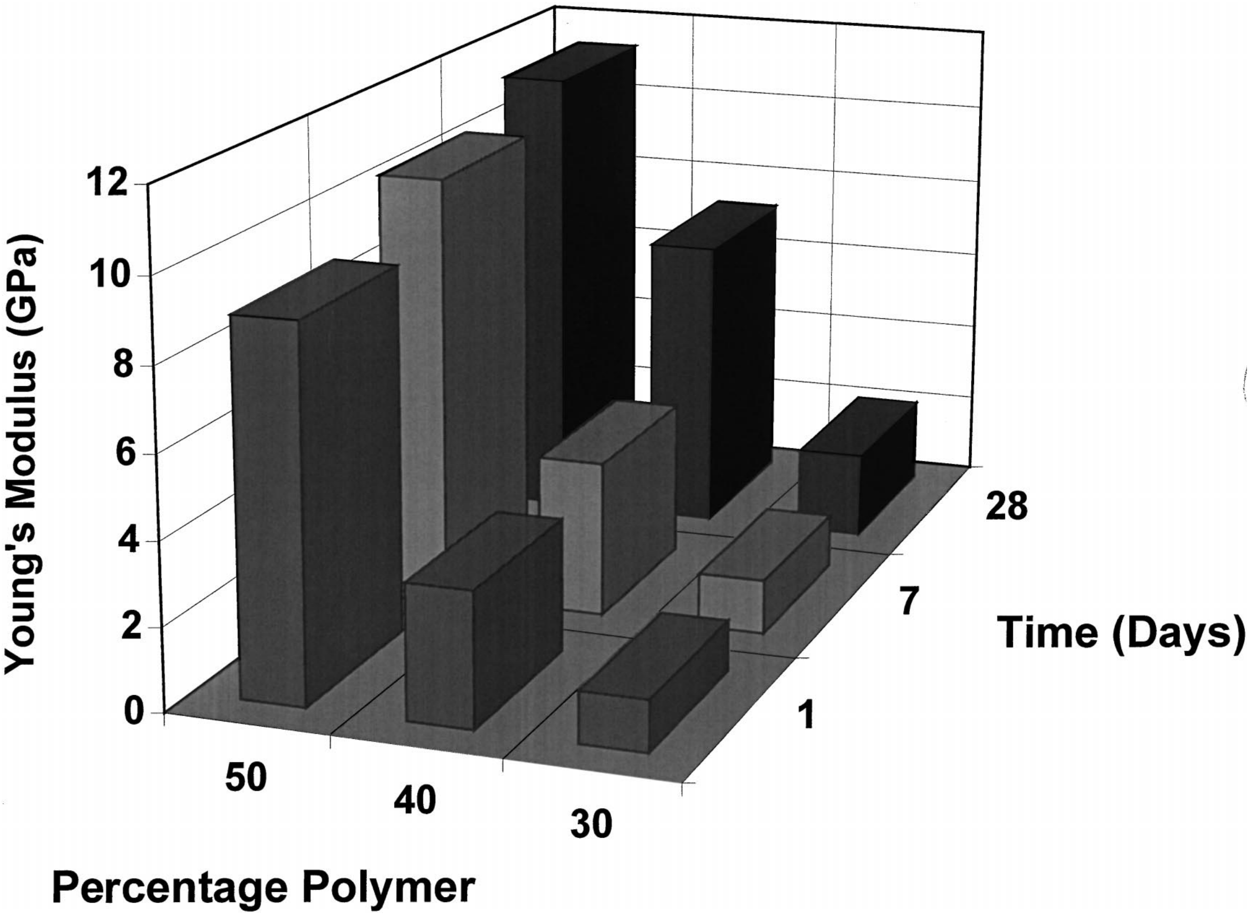


*Figure 5* Young's moduli as a function of percentage PAA content and cement age for cements with a 0.50 glass volume fraction.

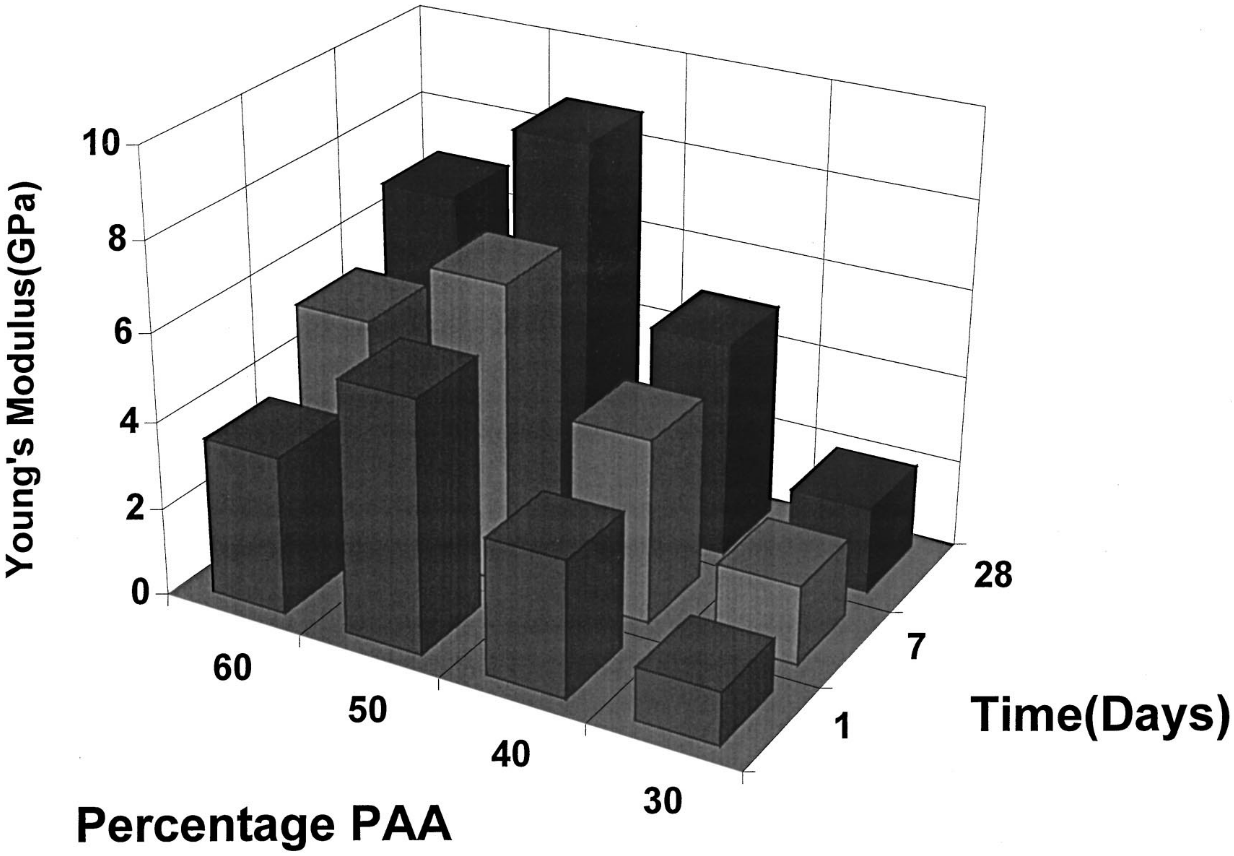


*Figure 6* Young's moduli as a function of percentage PAA content and cement age for cements with a 0.40 glass volume fraction.

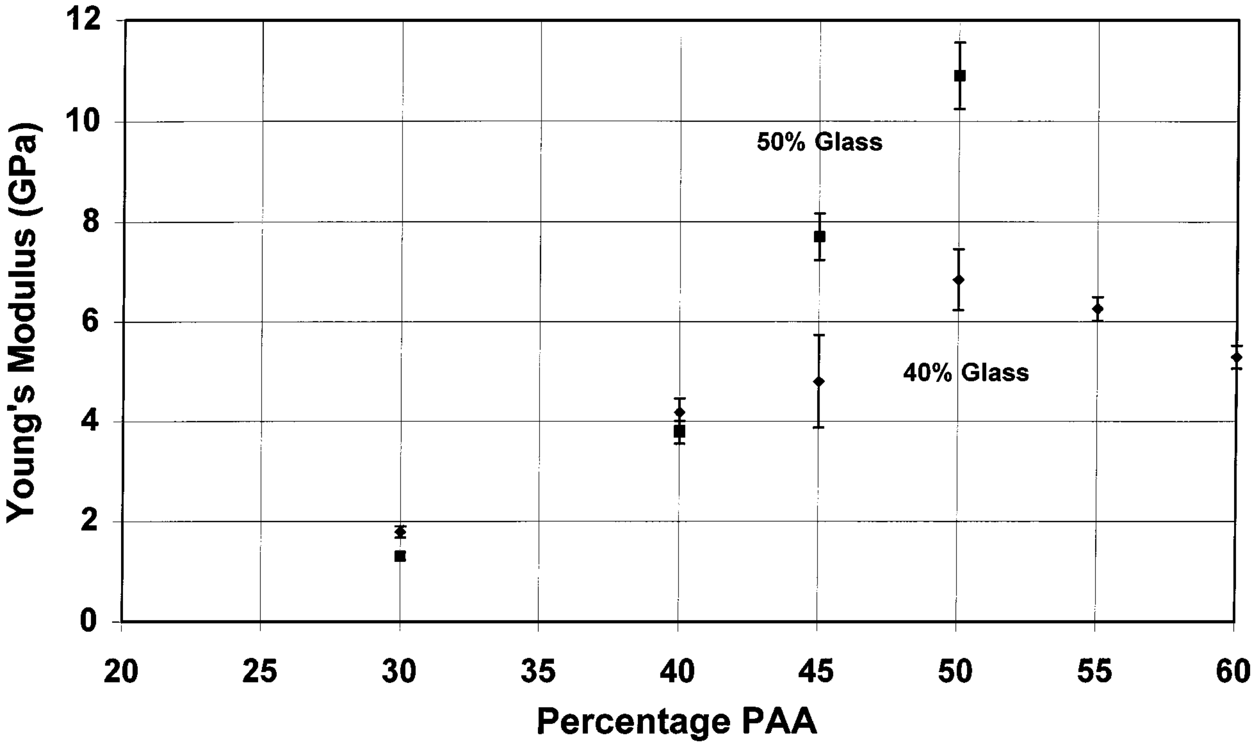


*Figure 7* Young's moduli for cements aged for seven days with 0.4 and 0.5 glass volume fractions as a function of percentage PAA content.

The Young's modulus increases with cement ageing time for all the cements studied which is consistent with increased ionic crosslinking of the polyacrylate chains as proposed by Crisp *et al.* [3] and a reduction in the unbound water content. The increase in modulus is greatest with the highest polymer content cement, which suggests that the reaction may be inhibited by the lack of available crosslinking cations.

The modulus of these cements will also determine how the stresses are distributed in the restored tooth. The ideal restorative material would have a Young's modulus close to that of dentine at between 7 and 12 GPa. The present study demonstrates that cements can be formed with Young's moduli in this range by using high glass volume fractions and high percentage polymer contents.

All the cements exhibited stable fracture with cracks propagating down the DT specimens at constant velocity. The results for the fracture toughness values are generally dominated by the Young's modulus. Note that:

$$K_I = (EG_I)^{0.5}$$

Thus the fracture toughness generally increases with the poly(acrylic acid) content (Table II and Fig. 8). The fact that the fracture toughness does not fall at high poly(acrylic acid) percentages with a glass volume fraction of 0.4, as a result of a reduction in Young's modulus can be attributed to an increase in toughness.

TABLE II Fracture toughness (MPa $m^{0.5}$) as a function of cement polymer content and storage time in water at 37 °C for cements with 0.5 glass volume fraction

| Polymer concentration | 24 hrs | SD | 1 week | SD | 1 month | SD |
|---|---|---|---|---|---|---|
| 50 | 0.82 | 0.03 | 0.89 | 0.07 | 0.82 | 0.06 |
| 40 | 0.42 | 0.02 | 0.43 | 0.06 | 0.58 | 0.03 |
| 30 | 0.17 | 0.01 | 0.21 | 0.02 | 0.27 | 0.03 |

TABLE III Toughness (J $m^{-2}$) as a function of cement polymer content and storage time in water at 37 °C for cements with 0.5 glass volume fraction

| Polymer concentration | 24 hrs | 1 week | 1 month |
|---|---|---|---|
| 50 | 75 | 76 | 60 |
| 40 | 55 | 49 | 47 |
| 30 | 24 | 34 | 35 |

The fracture toughness reduces with cement ageing time for high polymer content cements, remains approximately constant for intermediate polymer contents and increases for low polymer content cements. Reductions in fracture toughness have not been observed before, but have been predicted from previous studies [13].

The toughness increases markedly with the percentage PAA content of both series of cements, as predicted by the reptation chain pull-out model. This is shown in Table III and Figs 9 and 10. There appears to be a limiting toughness being reached at 1 week at about a 55% PAA content (Fig. 10). It is important to note that the reptation chain pull-out model neglects the influence of the ionic crosslinks that will serve to inhibit chain pull-out.

The toughness appears to be relatively independant of glass volume fraction (Fig. 11) with the data for the cements made with 0.4 and 0.5 volume fractions of glass overlapping indicating that the toughness is dominated by polyacid concentration.

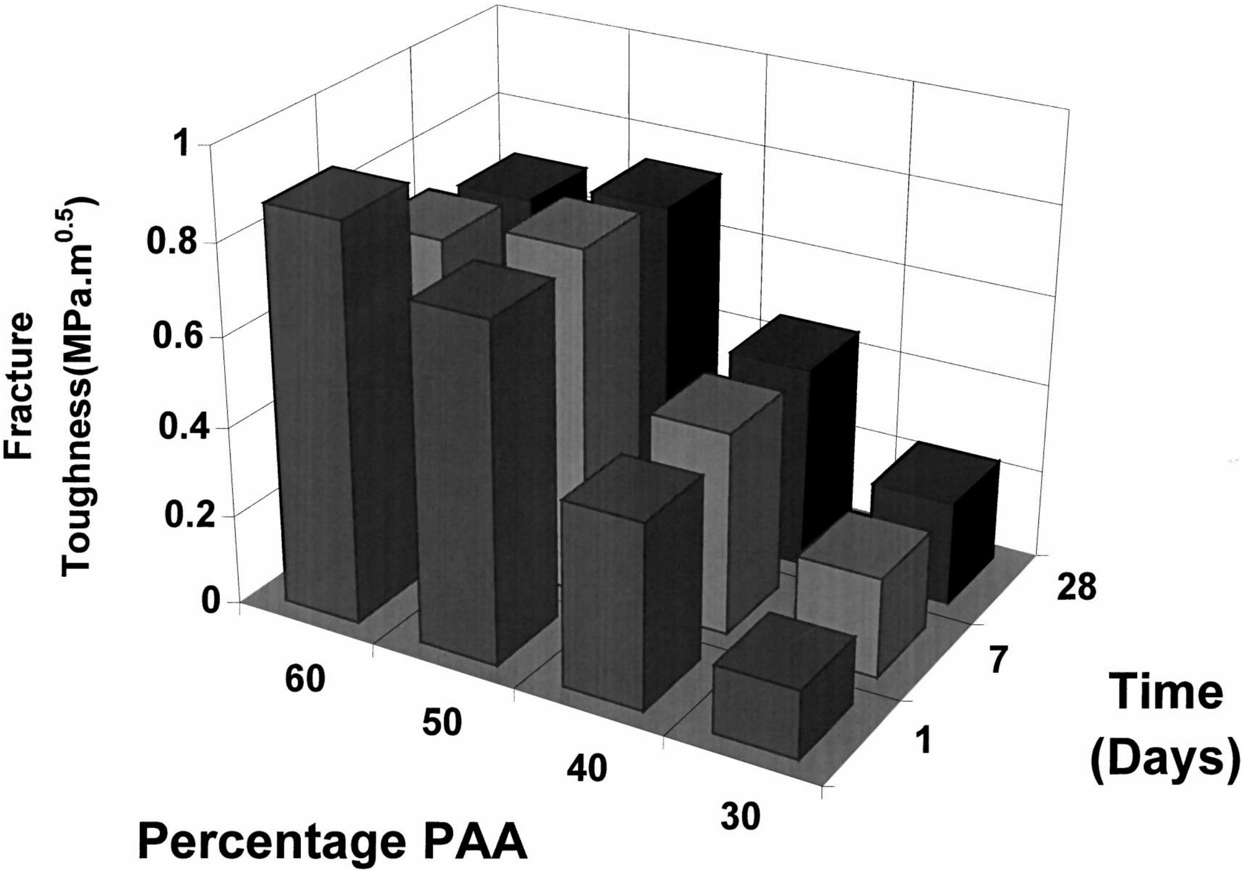


*Figure 8* Fracture toughness ($K_{IC}$) as a function of percentage PAA content and cement age for cements with a 0.40 glass volume fraction.

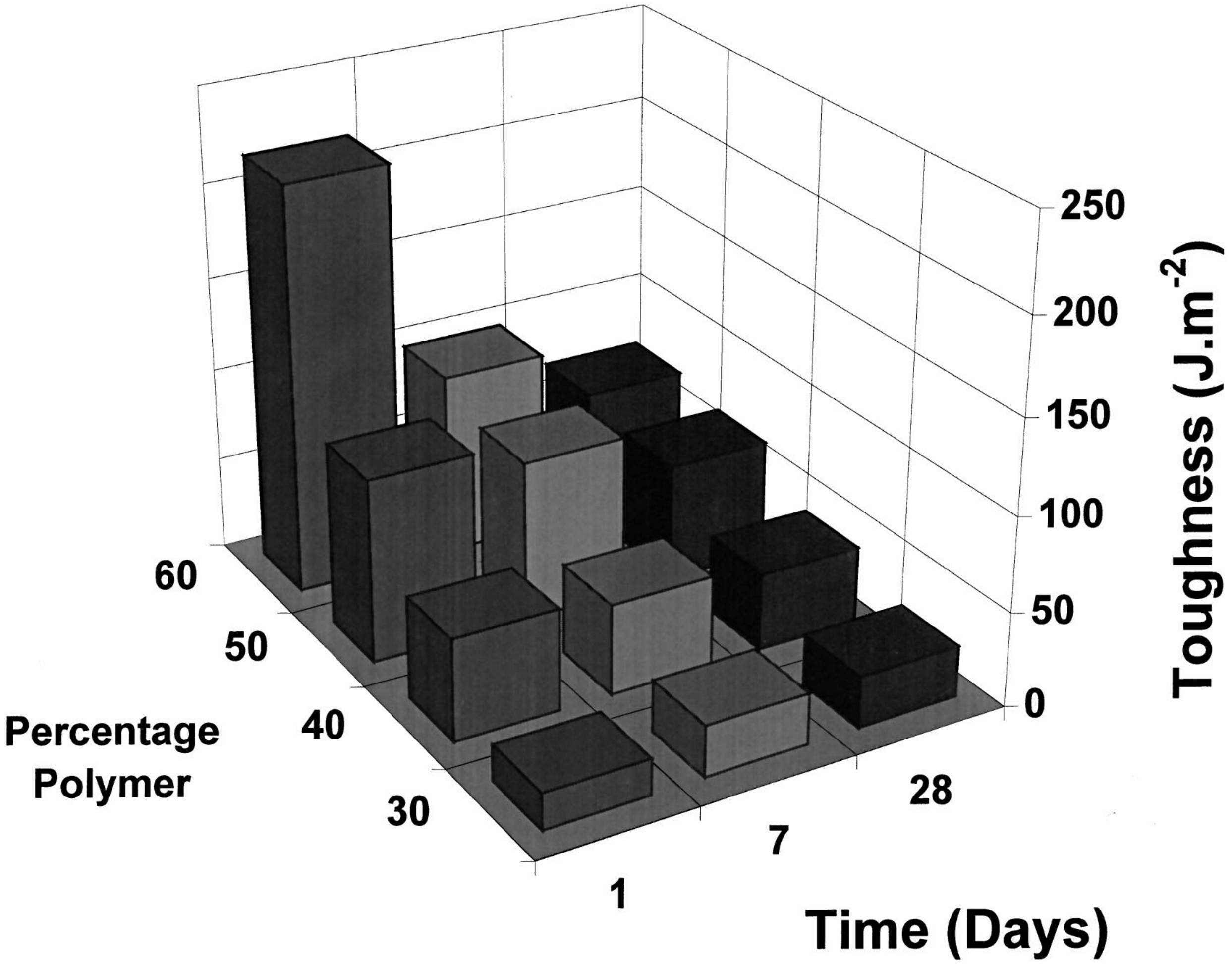


*Figure 9* Toughness ($G_{IC}$) as a function of percentage PAA content and cement age for cements with a 0.40 glass volume fraction.

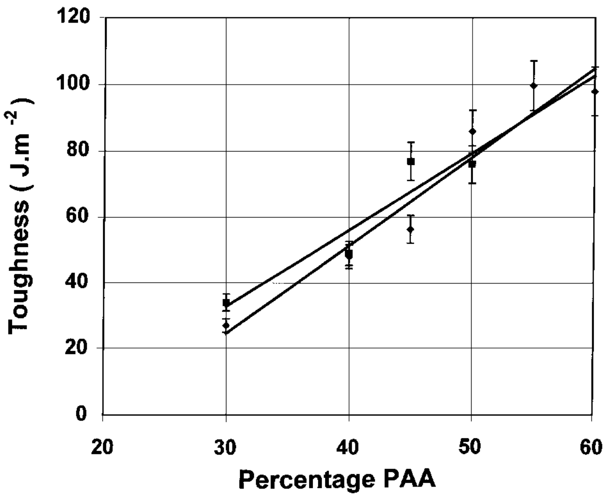


*Figure 10* Toughness as a function of percentage PAA content for cements aged for seven days with a glass volume fraction of 0.4 and 0.5.

The toughness can increase or decrease with time depending on the percentage PAA content of the cement. This is illustrated in Fig. 9 and Table III. The highest PAA content cement has a toughness at 1 day of 216 J m$^{-2}$, which decrease with time to a value of 69 J m$^{-2}$ at 28 days. In contrast the toughness increases with time for the lowest PAA content cement from 19 J m$^{-2}$ at 1 day to 27 J m$^{-2}$ at 28 days. The toughness will be related to the extent of plastic zone formation at the crack tip and the energy expended in this plastic zone. Fracture involves polymer chain pull-out in these cements. The energy to pull-out a polymer chain crossing the fracture plane and hence the toughness will be dependant on the number of ions linking the chain to its neighbours. As the cement reaction proceeds and there is increased crosslinking of the polyacrylate chains the pull-out energy of an individual chain would be expected to increase, however crosslinking would be expected to reduce the amount of molecular motion and plasticity that can occur at the crack tip and hence reduce the number of chains undergoing pull-out. These two competing processes can give rise to an increase, or a decrease in toughness, depending on which mechanism dominates. In the case of low polymer content cements the increase in pull-out energy of individual chains dominates, whilst for high polymer content cements the reduction in the plastic zone size at the crack tip is most likely the dominant factor.

The percentage poly(acrylic acid) content has a dramatic influence on the toughness and the highest toughness values are obtained with the highest poly(acrylic acid) contents. The number of chains crossing the fracture plane will be directly proportional to the poly(acrylic acid) content. However the increase in toughness with PAA content is greater than being proportional to the PAA content. It is likely that an increase in PAA content also decreases the distance between entanglement points, reduces the tube diameter and decreases the spatial gap, h between the chain and its tube, thereby increasing the pull-out energy of a chain. In addition the increased polyacid content will also result in an increased cement reaction, providing more crosslinking cations in the cement matrix and resulting in increased pull-out energies.

It is interesting to try and predict the maximum toughness achievable in a glass polyalkenoate cement assuming the maximum values of Young's modulus and toughness obtained of 11.3 GPa and 216 J m$^{-2}$ are achieved in the same cement. The calculated value is 1.56 MPa m$^{0.5}$. Increasing the molar mass of the polyacid to approximately 100,000 increases the toughness with a related glass to 450 J m$^{-2}$ [34] using this value

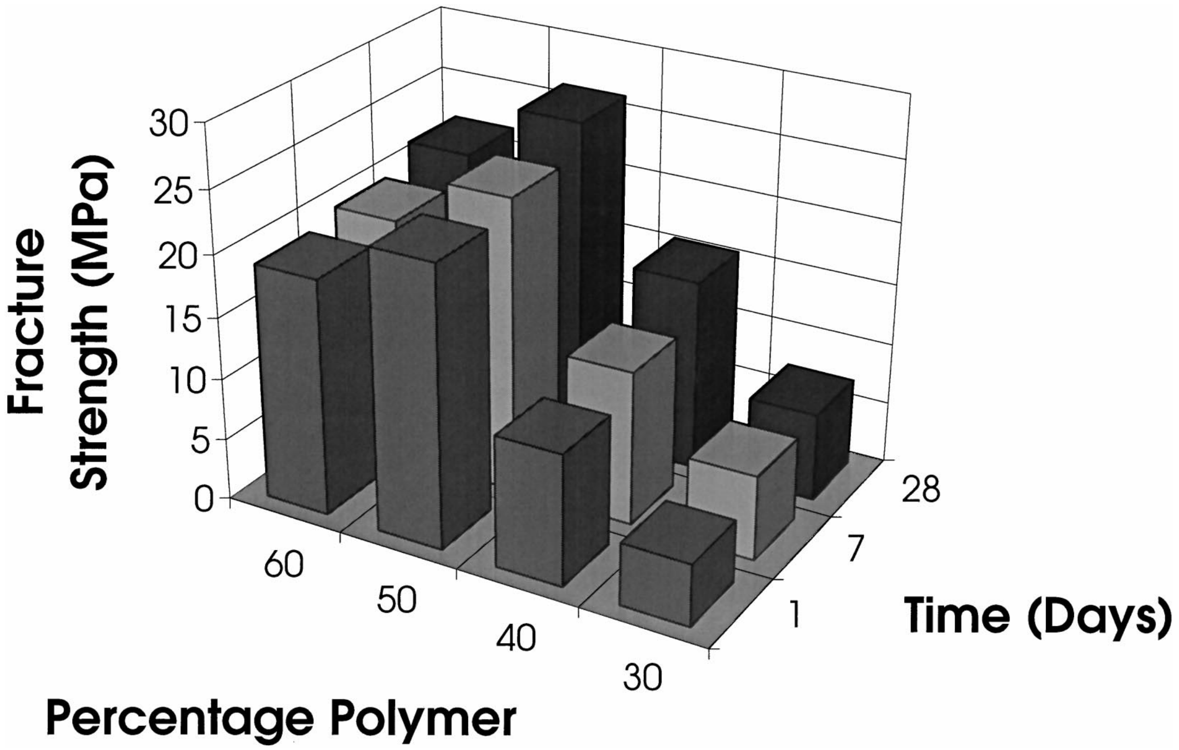


*Figure 11* Un-notched fracture strength as a function of percentage PAA content and cement age for cements with a 0.40 glass volume fraction.

TABLE IV Un-notched fracture strength (MPa) as a function of cement polymer content and storage time in water at 37 °C for cements with 0.5 glass volume fraction

| Polymer concentration | 24 hrs | SD | 1 week | SD | 1 month | SD |
|---|---|---|---|---|---|---|
| 50 | 16.77 | 1.60 | 25.76 | 3.55 | 24.59 | 2.25 |
| 40 | 6.52 | 0.36 | 8.93 | 1.82 | 19.86 | 4.05 |
| 30 | 4.29 | 1.11 | 5.18 | 1.17 | 6.49 | 1.99 |

and the previous moduli value could increase the fracture toughness further to about 2.25 MPa $m^{0.5}$, which is close to that of dentine at approximately 2.4 MPa $m^{0.5}$.

Un-notched fracture strength generally increases with the poly(acrylic acid) content of the cement (Table IV). However at a very high percentage polymer content of 60% in cements with a glass volume fraction of 0.4 there is a decrease in strength (Fig. 11).

The un-notched fracture strengths also increase slightly with cement ageing time. Previous studies have demonstrated increasing compressive and diametral tensile strengths with increasing polyacid concentration [3]. The increase in un-notched fracture strength and tensile strengths found previously can be attributed to the increase in fracture toughness and fundamentally to an increase in toughness and Young's modulus with increasing polyacid concentration. It is worth noting that the highest values of un-notched fracture strength obtained are comparable to the values obtained for the existing commercial materials [25, 26], which have been obtained with much smaller specimens. The larger specimens used in the present study are more likely to contain flaws and defects and consequently use of a smaller test specimen measuring only 3.0 × 3.0 × 20 mm would result in much higher values for the strength being recorded.

## 6. Conclusions

The studies to date show a marked change in cement properties with percentage polymer content. Small changes in polymer content for example increasing the polyacid concentration from 40 to 50% exert a marked influence on cement properties. The polyacid concentration dominates the mechanical properties of the cement at all time intervals. There is no evidence for a silicate phase contributing to the toughness of glass polyalkenoate cements at long cement ageing times and the polyacid becoming less influential as proposed by Wasson and Nicholson [27].

In conclusion to obtain a cement with a high fracture toughness a high polymer content is required, though there does appear to be an optimum content at between 50 and 55% polymer.

It is also important to note that cement properties change quite markedly as a function of time and the changes that do occur are heavily dependant on cement composition and possibly glass composition as well. Relatively few studies have investigated how glass polyalkenoate cement properties change with time. Most studies have involved the study of commercial materials measuring only compressive, or flexural strengths. Considerable controversy exists over whether all glass polyalkenoate cements exhibit compressive and flexural strengths which increase with time, or whether strength can decrease with time. These studies support the view proposed by Hill [13] that it is possible to "overcrosslink" a glass polyalkenoate cement and reduce the toughness. Previous explanations [26, 26] for experimentally observed reductions in strength have included hydrolytic instability of the cement. Given that the commercial materials in which reductions in strength have been experimentally observed have low sodium contents and are based on copolymers with a higher carboxyl content the polyacid chains should be more crosslinked and more hydrolytically stable. The results also point to the limitations of measuring only compressive and flexural strengths of these cements, as these parameters may remain constant, despite major changes in the mechanical behaviour of the cement. It is clear that it is important to measure cement properties over extended time periods. The service life of a posterior dental filling could easily be in excess of 10 years and it is important, to know and be able to predict how cement properties will change.

It is also important to note that even if a cement is over crosslinked with regard to toughness and fracture toughness the increased crosslinking may confer other benefits such as increased hydrolytic stability, hardness and wear resistance.

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