

# The influence of poly(acrylic acid) molar mass on the properties of polyalkenoate cements formed from zinc oxide/apatite mixtures

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The influence of poly(acrylic acid) molar mass was investigated on cements formed from zinc oxide-apatite mixtures at three aging times; one, seven and 28 days. Cements based on both hydroxyapatite and fluorapatite were investigated. The compressive strength, un-notched fracture strength and fracture toughness increased markedly with poly(acrylic acid) molar mass. The fracture toughness and un-notched fracture strength increased with aging time for the two highest molar mass cements, but decreased with time for the two lowest molar mass cements. The greater chain entanglement density present in the higher molar mass cements is thought to contribute significantly to the cement stability in addition to the crosslinking of the polyacrylate chains by calcium and zinc ions.

Substitution of hydroxyapatite by fluorapatite had no significant influence on the mechanical properties of the cements at aging times longer than one day.

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## 1. Introduction

Smith [1] developed the first polyalkenoate cement by reacting modified zinc oxide powder with aqueous poly(acrylic acid). The acid reacts with the basic zinc oxide to form a crosslinked metal polyacrylate salt containing residual zinc oxide particles. Subsequently Wilson *et al.* [2] went on to develop the glass polyalkenoate cements, based on acid degradable fluoro-alumino-silicate glasses and poly(acrylic acid). Both the zinc polyalkenoate cements and the glass polyalkenoate cements are used in dentistry as adhesives and tooth filling materials. However Smith [3] recognized the attractive properties that polyalkenoate cements possessed for orthopaedic applications and suggested their use as a bone cement in orthopaedic surgery. Polyalkenoate cements set at body temperature, without undergoing any polymerization shrinkage and without significant evolution of heat. They can chemically bond to the apatite phase present in bone and the oxide layer on medical grade alloys giving rise to chemical adhesion. Peters *et al.* [4] showed that the zinc polyalkenoate cements were biocompatible in implant studies, but that a fibrous collagen capsular layer was formed adjacent to the cement in a similar manner to acrylic bone cements. This formation of a fibrous capsule at the bone cement interface is the classic response to a bioinert material, which interferes with the ability of the cement to bond directly to bone. In conventional acrylic bone cemented arthroplasties this fibrous capsular layer is a major contributor to aseptic loosening and ultimately to failure.

During the last ten years there has been considerable interest in the development and use of glass polyalkenoate cements for medical applications [5–11]. The glass polyalkenoate cements are claimed to be bioactive in the bone environment [7] as a result of the release of calcium, phosphate and fluoride ions, as well as due to the formation of a silicious gel phase in a similar way to Bioglass [12]. There is evidence for these cements stimulating bone formation and being osteoconductive [10]. However, recent research [13, 14] has shown that the aluminum ions released from glass polyalkenoate cements result in defective bone mineralization and as a consequence the ability of these cements to chemically bond to bone is lost.

Polyalkenoate can also be formed from hydroxyapatite and fluorapatite [15] as well as apatite-zinc oxide mixtures [16]. These cements have been proposed for use as dental filling materials. They would also be attractive for medical use as preset bone substitutes and in situ setting bone cements. Because such cements contain no aluminum, but have the potential to be bioactive, via the release of calcium, phosphate and fluoride ions they should integrate well with bone tissue and should retain the capacity of polyalkenoate cements for direct chemical bonding to bone.

To date there are no thorough studies of such cements in the academic literature and the limited patent literature on this type of cement fails to include any information on the influence of poly(acrylic acid) molar mass on the mechanical properties of such cements. Recent studies have demonstrated that the mechanical properties of

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polyalkenoate cements are highly dependant on molar mass [17–20].

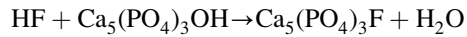
This paper explores the influence of poly(acrylic acid) molar mass on the fracture toughness, toughness, Young's modulus, un-notched fracture strength and compressive strength of polyalkenoate cements formed from zinc oxide-apatite mixtures.

## 2. Experimental

### 2.1. Materials

Medical grade hydroxyapatite was obtained from Howmedica Stryker Osteonics (Raheen Industrial Estate, Dooradoyle, Limerick, Ireland).

Fluorapatite was produced from the hydroxyapatite by heating a two molar excess of ammonium fluoride with the hydroxyapatite slowly to 500 °C and maintaining this temperature. During heating the ammonium fluoride breaks down to give volatile ammonia and hydrofluoric acid. The hydrofluoric acid reacts according to the following reaction:



The fluorapatite produced was analyzed for the presence of hydroxyl groups by Fourier Transform Infra Red Spectroscopy and by X-ray powder diffraction for fluorite which would indicate over reaction. No hydroxyl groups or fluorite were detected.

A modified zinc oxide was supplied by Shofu (AHL) (Chiddingstone Causeway, Tonbridge, Kent, UK). Four poly(acrylic acid)s were obtained from CIBA speciality polymers (PO Box 38, Bradford, UK). These four polyacids had the molar masses given in Table I.

### 2.2. Specimen fabrication

A powder mixture consisting of 3 parts by weight of apatite and 2 parts by weight of zinc oxide was prepared. Cements were then formed by thoroughly mixing this powder mixture with the poly(acrylic acid) in a weight ratio of 3:1 and then mixing this with 10% m/m (+) tartaric acid solution in a weight ratio of 4.3:1 and 3.25:1. These have approximate acid contents of 60% and 50% respectively.

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

### 2.3. Test methods

#### 2.3.1. Compressive 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 standard ‘‘ISO 7489: 1986 Dental Glass Polyalkenoate Cements’’ [21]. An Instron tensometer (Instron, High Wycombe, Bucks, UK) was used for the test at a crosshead displacement rate of 1 mm. min<sup>-1</sup>. The test was carried out on 8 samples and the compressive strength calculated according to:

$$\sigma_c = F/\pi r^2 \quad (\text{I})$$

Tests were performed in water at 37 ± 2 °C.

#### 2.3.2. 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. The test is a linear compliance one and the crack length is not required for the calculation of the fracture toughness. In addition, for stable crack propagation the crack propagates at a constant load down the specimen. Finally, after fracturing, the large DT specimens can be cut down to make three-point bend specimens, making economical use of materials and resources.

The test method has been described previously [17]. DT specimens 25 × 65 × 3.0 mm, were molded in the form of rectangular plates. A sharp groove 1.0 mm deep was cut down the center of the specimen. A fine slot was cut at one end of the specimen, using a diamond wafer blade.

The DT test was performed using an Instron electromechanical testing machine. During the test the specimen was supported on two parallel rollers of 3 mm diameter and spaced 40 mm apart and load applied at a constant rate (0.1 mm min<sup>-1</sup>) 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 center 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 [22].

In a DT test the mode I stress intensity factor  $K_I$  is independent of crack length and is given by [23]:

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

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  $K_I$ , the fracture toughness, were obtained by substituting the appropriate specimen dimensions along with the load at fracture  $P_c$  in Equation II.

#### 2.3.3. The flexural test

Immediately after testing the DT specimens, the broken halves were cut up into three-point bend specimens, measuring 3.0 × 12 × 65 mm. The test and method are based on ASTM D790-1 [24]. In a three-point bend specimen the relationship between the applied load ( $P$ )

TABLE I Molar mass details

Code	$M_n$	$M_w$	PD
E5	3,030	9,270	3.1
E7	8,140	25,700	3.2
E9	26,100	80,800	3.1
E11	64,400	210,000	3.1

and the deflection at the center of the specimen ( $\delta$ ) for a specimen of rectangular cross section is given by:

$$P = \frac{4\delta Ebt^3}{s^3}$$

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 min<sup>-1</sup>. This gives an almost identical strain rate to that used in the DT tests. 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:

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

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

### 2.3.4. Calculation of plastic zone size

The plastic zone size,  $R_p$ , was calculated from the fracture toughness and the 0.5% offset yield stress determined from the compression test as follows:

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

## 2.4. Scanning electron microscopy

Scanning electron microscopy was carried out on the fracture surfaces from DT specimens in order to identify the fracture path and fracture mechanisms. The fracture surfaces were sputter coated with gold prior to examination and viewed using an accelerating voltage of 30 KV and a working distance of 20 mm.

## 3. Results and discussion

The fracture toughness (Tables II and III) increased with poly(acrylic acid) molar mass for the hydroxyapatite based cements formed at polyacid concentrations of 50% and 60% for all three time intervals studied. Fig. 1 shows the fracture toughness as a function of both aging time and molar mass. Increase in fracture toughness with molar mass are expected from previous studies on related glass polyalkenoate cements [17–20]. The fracture toughness generally increases with storage time from 1 to 28 days. The fracture toughness values obtained with the highest molar mass poly(acrylic acid) are much greater than those found previously for zinc polyalkenoate [18] and glass polyalkenoate cements [17, 19, 20, 25, 26] and comparable or higher than existing acrylic bone cements [27]. Increasing the polyacid concentration from 50% to 60% generally increased the fracture toughness. Similar increases in fracture toughness on increasing the polyacid concentration have been found recently for glass polyalkenoate cements [26].

There is appreciable experimental scatter on the Young's moduli data shown in Tables IV and V, which is thought to be due to a small number of randomly distributed air bubbles entrapped during cement mixing. However, the Young's modulus values generally decline with time for the low molar mass cements and increase with time for the high molar mass cement. This is shown graphically for the E7 and E11 cements with 50% PAA in Fig. 2. The reduction in modulus with time for the low molar mass cements is thought to be a result of cement instability during storage in water. It is thought that the greater density of chain entanglements present in the high molar mass cements contributes significantly to cement stability. Previous studies of glass polyalkenoate

TABLE II Fracture toughness for 50% poly(acrylic acid) content cements

	1 $K_{IC}$ (MPa√m)	Day SD ( $n = 9$ )	7 $K_{IC}$ (MPa√m)	Days SD ( $n = 9$ )	28 $K_{IC}$ (MPa√m)	Days SD ( $n = 9$ )
E5	0.05	0.01	0.25	0.06	0.09	0.02
E7	0.48	0.05	0.12	0.03	0.27	0.12
E9	0.61	0.12	0.70	0.27	1.06	0.27
E11	1.39	0.15	1.30	0.19	1.54	0.10

TABLE III Fracture toughness for 60% poly(acrylic acid) content cements

	1 $K_{IC}$ (MPa√m)	Day SD ( $n = 9$ )	7 $K_{IC}$ (MPa√m)	Days SD ( $n = 9$ )	28 $K_{IC}$ (MPa√m)	Days SD ( $n = 9$ )
E5	0.46	0.10	0.47	0.06	0.16	0.02
E7	0.42	0.12	0.38	0.07	0.14	0.01
E9	0.72	0.17	1.03	0.13	1.08	0.27
E11	1.41	0.38	1.73	0.21	1.77	0.21

TABLE IV Young's moduli for 50% poly(acrylic acid) content cements

	1 E (GPa)	Day SD ( $n = 6$ )	7 E (GPa)	Days SD ( $n = 6$ )	28 E (GPa)	Days SD ( $n = 6$ )
E5	3.77	1.12	3.17	0.97	0.54	0.24
E7	2.86	0.45	1.97	0.66	1.19	0.22
E9	2.90	0.43	2.77	0.82	3.46	0.40
E11	2.29	0.67	3.50	1.20	4.34	0.35

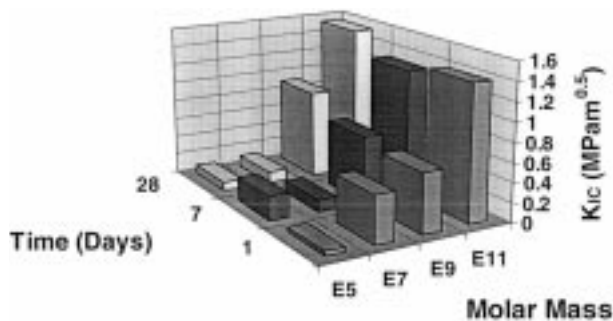


Figure 1 Influence of PAA molar mass and time on fracture toughness of cements with 50% polyacid.

cements have demonstrated an increase in Young's moduli with time [17, 19, 20, 26, 27] and Young's moduli that are independent of molar mass [17, 19, 20]. The increase in Young's moduli with time has previously been attributed to increased crosslinking of the polysalt matrix and this is likely to be the case for the present high molar mass cements.

The flexural strength shown in Tables VI and VII increases with molar mass of the poly(acrylic acid) used to form the cement. This occurs for both polyacid concentrations. Increasing the polyacid concentration from 50% to 60% results in an increase in flexural strength. There is again a difference in behavior with storage time for the two lowest molar mass and two highest molar mass cements. This is shown in Fig. 3. The two lowest molar mass polyacids result in cements whose flexural strength decreases with time. In contrast the two highest molar mass polyacids result in cements whose strength tends to increase or remain constant with time.

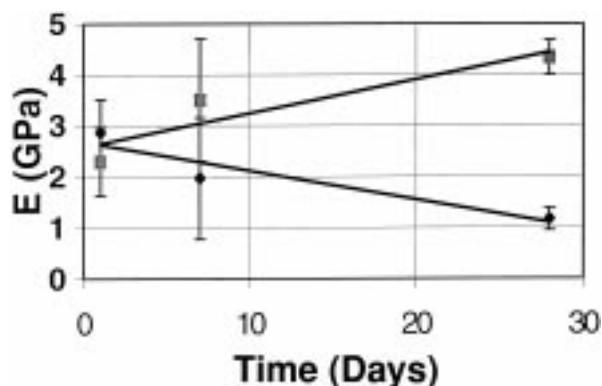


Figure 2 Influence of storage time in water on the Young's modulus of high and low molar mass cements with a 50% PAA content. E11 = ■ E7 = ◆.

An increase in flexural strength is generally found for glass polyalkenoate cements [19, 25, 26] with aging time. Decreases in flexural strength have been associated with hydrolytic instability of the cement [28].

The strength values obtained at 28 days for the highest molar mass cement with the highest polyacid concentration are slightly below those of current acrylic bone cements tested under similar conditions.

Compressive strength given in Tables VIII and IX again increased significantly with the poly(acrylic acid) molar mass rising from 28.9 MPa to 51.3 MPa on increasing the number average molar mass from 3000 to 64,400 for the 50% polyacid cements at one day. The compressive strength for the two highest molar mass cements rises significantly with cement aging time in water at  $37 \pm 2^\circ\text{C}$ , but declines for the two lowest molar

TABLE V Young's moduli for 60% poly(acrylic acid) content cements

	1	Day	7	Days	28	Days
	E (GPa)	SD (n = 6)	E (GPa)	SD (n = 6)	E (GPa)	SD (n = 6)
E5	4.67	1.37	4.36	1.97	0.89	0.31
E7	5.95	4.92	4.16	0.93	1.47	0.37
E9	5.00	1.23	5.23	1.03	5.51	1.24
E11	4.26	0.64	4.61	1.04	3.57	0.60

TABLE VI Un-notched fracture strength for 50% poly(acrylic acid) content cements

	1	Day	7	Days	28	Days
	$\sigma_f$	SD (n = 6)	$\sigma_f$	SD (n = 6)	$\sigma_f$	SD (n = 6)
E5	6.9	2.5	6.0	1.3	0.05	0.02
E7	8.6	1.8	4.1	0.8	2.1	0.9
E9	17.1	1.8	19.2	5.8	17.6	2.5
E11	20.5	3.6	28.8	6.5	28.2	5.3

TABLE VII Un-notched fracture strength for 60% poly(acrylic acid) content cements

	1	Day	7	Days	28	Days
	$\sigma_f$	SD (n = 6)	$\sigma_f$	SD (n = 6)	$\sigma_f$	SD (n = 6)
E5	8.9	2.1	7.5	2.7	1.6	0.03
E7	17.5	4.87	9.58	2.12	2.53	0.42
E9	23.8	7.9	27.5	3.6	29	3.8
E11	32.1	5.6	32.8	5.1	32.9	7.8

TABLE VIII Compressive strength for 50% poly(acrylic acid) content cements

	1	Day	7	Days	28	Days
	$\sigma_c$	SD ( $n = 6$ )	$\sigma_c$	SD ( $n = 6$ )	$\sigma_c$	SD ( $n = 6$ )
E5	28.9	2.2	13.2	0.3	18.2	3.47
E7	32.1	5.6	39.8	2.5	10.1	1.41
E9	42	0.6	43.9	5.6	59.7	1.3
E11	51.3	4.7	59.5	5.7	65.9	4.2

TABLE IX Compressive strength for 60% poly(acrylic acid) content cements

	1	Day	7	Days	28	Days
	$\sigma_c$	SD ( $n = 6$ )	$\sigma_c$	SD ( $n = 6$ )	$\sigma_c$	SD ( $n = 6$ )
E5	46.4	3.03	39.1	3.6	43.7	3.0
E7	43.7	7.8	63.6	5.0	18.2	1.2
E9	71.0	2.6	62.0	3.8	63.3	2.1
E11	79.4	8.9	70.9	1.3	85.1	4.38

TABLE X Plastic zone size for 50% poly(acrylic acid) content cements

	1	Day	7	Days	28	Days
	RP ( $\mu\text{m}$ )	SD	RP ( $\mu\text{m}$ )	SD	RP ( $\mu\text{m}$ )	SD
E5	15	1	7	6	3	5
E7	40	15	18	7	8	3
E9	62	11	45	15	52	20
E11	365	83	100	32	117	11

mass cements. Previous studies [20, 25, 26, 29–31] of glass polyalkenoate cements have shown the compressive strength to increase with time. The explanation for the increase in compressive strength with time has for glass polyalkenoate cements has been attributed to increased crosslinking of the polysalt matrix. The compressive strength for the highest molar mass cements are still lower than those quoted in the patent by Aoki [16]. However, the present compressive strengths were determined in water at  $37 \pm 2^\circ\text{C}$  which would be expected to reduce the compressive strength compared to testing in air at room temperature. The compressive strengths are below the values for acrylic bone cements of approximately 90 MPa, but the compressive strengths would be expected to increase significantly on testing in air at room temperature. The compressive strengths of the highest molar mass cements are equal to the highest

values obtained with the calcium phosphate cements [32] and the flexural strengths are approximately three fold higher.

Tables XI and XII show the calculated plastic zone sizes for the 50% and 60% cements respectively. The plastic zone size of all the cements are much smaller than the specimen thickness of 3.0 mm so all the cement samples are being tested under plain strain conditions. The plastic zone size generally increases with molar mass and with poly(acrylic acid) concentration. Griffin and Hill [20] previously showed the plastic zone size to increase with molar mass. There was no obvious influence of the poly(acrylic acid) concentration on the plastic zone size data. It was expected based on previous studies that the plastic zone size would decrease with aging time as the polysalt matrix became more and more ionic crosslinked. However, this phenomena was only

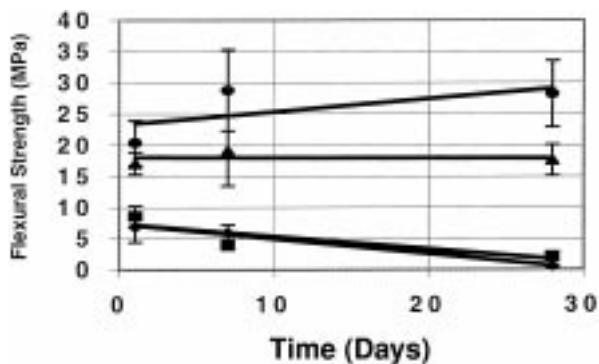


Figure 3 Influence of storage time on the flexural strength of 50% PAA cements of differing molar mass E11 = ●, E9 = ▲, E7 = ■ and E5 = ◆.

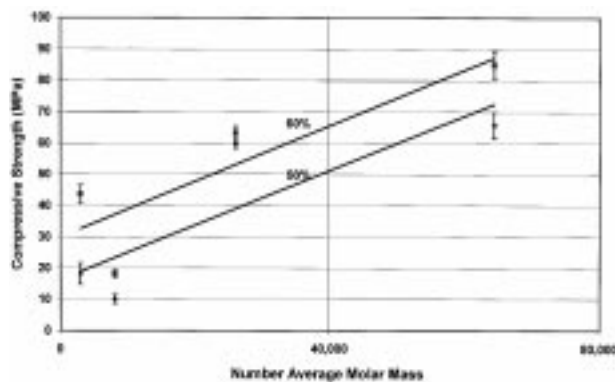


Figure 4 Influence of number average molar mass on compressive strength at 28 days.

TABLE XI Plastic zone size for 60% poly(acrylic acid) content cements

	1 RP( $\mu\text{m}$ )	Day SD	7 RP( $\mu\text{m}$ )	Days SD	28 RP( $\mu\text{m}$ )	Day SD
E5	17	9	16	10	5	4
E7	18	11	6	2	2	1
E9	20	10	26	1	87	16
E11	298	143	145	29	162	25

TABLE XII Comparison of hydroxyapatite and fluorapatite based cements for 50% poly(acrylic acid) content

	HA Mean	1 Day SD	FAP Mean	1 Day SD	HA Mean	7 Days SD	FAP Mean	7 Days SD	HA Mean	28 Days SD	FAP Mean	28 Day SD
$K_{IC}(\text{MPam}^{0.5})$	0.61	0.12	0.33	0.04	0.70	0.27	0.87	0.21	1.06	0.27	0.73	0.16
E (GPa)	2.90	0.43	1.06	0.51	2.77	0.82	4.39	1.23	3.46	0.40	4.85	1.13
$\sigma_f(\text{MPa})$	17.1	1.8	4.51	0.63	19.2	5.8	17.0	4.27	17.6	2.5	15.6	2.89
$\sigma_c(\text{MPa})$	42	0.6	13.6	0.5	43.9	5.6	45.6	3.8	59.7	1.3	44.0	10.0

apparent with the highest molar mass PAA corresponding to the largest plastic zone sizes at between one and seven days.

Fig. 5 shows an SEM of a fracture surface of an E11 cement aged for 7 days with a PAA concentration of 50%. The fracture surface shows evidence of cavitation and voiding around the zinc oxide particles indicative of a plastic deformation mechanism during fracture. This phenomena has not been seen in the related glass polyalkenoate cements and may be a result of reduced crosslinking associated with the absence of aluminum ions in these cements. The voiding around zinc oxide particles was less marked in the lower molar mass cements with lower fracture toughness.

Table XII compares the values for the fracture toughness, Young’s modulus, flexural and compressive strength of the fluorapatite (FAP) based cements made with the E9 poly(acrylic acid) with the equivalent hydroxyapatite (HA) cements. The fracture toughness, Young’s modulus, flexural strength and compressive strength of the FAP cements are all significantly lower than the equivalent HA cements. However, there are no significant differences between the HA and FAP based cements at 7 and 28 days. The lower values of the mechanical properties of the FAP cements at 1 day may reflect the increased stability and decreased reactivity of the FAP compared to the HA.

#### 4. Conclusions

The molar mass and concentration of the poly(acrylic acid) were found to exert a pronounced influence on the fracture toughness, flexural strength and compressive strength of the cements. Fracture toughness, flexural strength and compressive strength all increased with molar mass as has been found previously for cements formed from poly(acrylic acid) with both zinc oxide [18] and ion leachable glasses [17, 19–20]. In contrast to previous studies of polyalkenoate cements the poly(acrylic acid) molar mass also influenced the Young’s moduli of the cements suggesting that chain entanglements contribute to the stability and stiffness of these cements. The Young’s moduli of the high molar mass

cements increased with time indicating a continued crosslinking reaction. Fracture toughness, flexural strength and compressive strength all increased with storage time for the two high molar mass cements. Increasing the poly(acrylic acid) concentration increased the Young’s moduli, fracture toughness, toughness, flexural strength and compressive strength consistent with entanglement density in the polysalt matrix having a dominant role.

Substituting hydroxyapatite for fluorapatite had no significant influence on the mechanical properties of the cements formed. However, the incorporation of fluorapatite may confer the release of fluoride from these cements, which may be an advantage for both medical and dental applications

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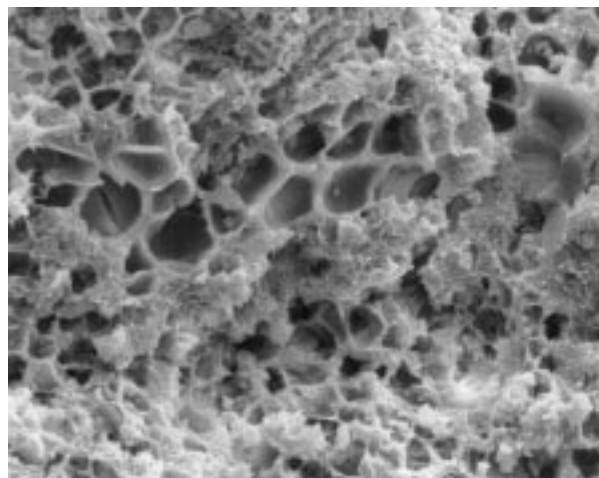


Figure 5 Scanning electron micrograph of a fracture surface from a DT specimen of a 50% E11 HA cement tested after aging for 7 days.

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