A novel acrylic copolymer for a poly(alkenoate) glass-ionomer cement

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The interest in the clinical use of polyalkenoate cements stems mainly from their behavior as bioactive adhesive materials with therapeutic action. Glass-ionomer cements set by an acid-base reaction between a degradable glass and a poly(alkenoic acid) and the therapeutic action is related to the release of fluoride ions which are present in the hardened cement that show a sustained release over years, responsible for caries inhibition in teeth. Conventional glass-ionomers, however, suffer from some disadvantages such as short working time, initial moisture sensitivity and prone to desiccation after setting and are generally brittle. In the present study, a poly(alkenoic acid) copolymer was synthesized based on acrylic acid and 2-hydroxyethylmethacrylate (HEMA) using azobisisobutyronitrile as the initiator and characterized. The acid–base reaction was carried out by reacting aqueous solutions of the new copolymer (40 and 60%) with a commercial aluminofluorosilicate glasses as used in conventional glass-ionomer cements. The results showed that the copolymer of HEMA and acrylic acid was a viable poly(alkenoic) acid for formation of glass-ionomer cements.

Introduction

Polyalkenoate cements were invented by Wilson and Kent as dental restorative [1] cements, commonly referred to as glass-ionomer cements. Commercially available glass-ionomer cements are used in dentistry as restorative materials in the repair of Class V lesions, liners and bases for cavities, as luting agents in the placement of crowns and in the fixation of orthodontic appliances [2]. The interest in the clinical use of polyalkenoate cements stems mainly from their behavior as bioactive adhesive materials with therapeutic action. The therapeutic action is related to the release of fluoride ions, which are present in the hardened cement and show a sustained release over years, responsible for caries inhibition in teeth. Glass–ionomer cements belong to a class of self-hardening cements formed as a result of an acid–base neutralization reaction, often referred to as acid–base cements [3]. Setting occurs when the carboxylic acid groups of the water-soluble polymer is neutralized by the glass powder, which acts as a base. The common polyacids used in glass-ionomer cements, include poly(acrylic acid) and copolymers of acrylic and itaconic or maleic acids. The glass-ionomer cement also contains additives such as tartaric acid to control setting parameters. These dental cements are dispensed as a powder and a liquid or as a powder only, where water needs to be added in recommended amounts to initiate the reaction. On mixing the pastes or with addition of water, the calcium-aluminofluorosilicate glass is attacked by the polyalkenoic acid and decomposes with the liberation of metal ions and silicic acid [4]. The initial setting of the cements are associated with the formation of calcium poly(acrylate) and further maturation occurs with time as aluminum ions become involved in the poly(acrylate) formation. An essential feature is that the reaction requires water, not only for it to progress but it also plays a multifunctional role in the setting chemistry [5]. Conventional glass-ionomers, however suffer from some disadvantages such as a short working time and are generally brittle in nature. Glass-ionomer cements are also sensitive to moisture in the early stages of placement [6] and can lead in either the early washing out of immature cement or desiccation in case of patients who breathe through the mouth. Early desiccation of the cement can cause the arrest of the setting reaction, leading to cracking and softening of the surface and loss of matrix forming ions [2]. Glass-ionomer cements remain susceptible to water loss for approximately 2 weeks after placement and any exposure to air during this time is also detrimental to the cement. Although glass-ionomers cements seem to exhibit mild hydrogel like properties through water absorption, it is still possible to dehydrate the cement restoration anytime during the first 15 days, which is detrimental for the setting and

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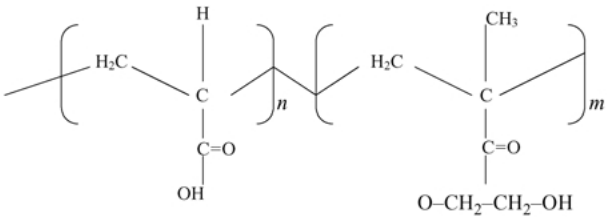

Figure 1 Structure of AA-HEMA copolymer.

maturation process. Although poly(acrylic acid) is a water soluble polymer, the carboxylic acid groups are involved in the neutralization reaction with the glass in a glass-ionomer cement and the system is both prone to desiccation or early dissolution of the poly salt acrylates formed.

The copolymerization of 2-hydroxyethylmethacrylate (HEMA) with other vinyl and acrylic monomers are known to provide biomaterials with controlled hydrophilicity. In the present study the synthesis and characterization of a copolymer based on the reaction of HEMA and acrylic acid (AA) is presented. The efficacy of the new copolymer in the formation glass-ionomer cements was investigated and the preliminary findings are reported in this paper. The copolymer is expected to be a random copolymer with pendant hydroxyl groups, rendering it the ability to retain water due to its molecular structure (Fig. 1).

Materials and methods

Synthesis

A water-soluble copolymer of AA and HEMA was synthesized by reacting HEMA with acrylic acid, using azobisisobutyronitrile (AIBN 1.5 wt %) as the initiator. The monomer feed content for acrylic acid and HEMA was 75% and 25% by weight respectively. The reaction was carried out in a mixture of isopropanol/water (50/50 by volume) and the temperature maintained at 50 °C. At the end of the reaction the solvent was evaporated and the solid polymer was washed with acetone several times to eliminate any residual monomers. The solid was then removed, dissolved in water and the solution lyophilized to yield a white amorphous powder. The copolymer thus obtained was characterized.

Nuclear magnetic resonance spectroscopy

The ^{1}H and ^{13}C nmr (nuclear magnetic resonance) spectra were determined by dissolving the polymer in deuterated dimethylsulfoxide (DMSO-d_6) at 60 °C. A concentration of 5% and 25% wt/vol were used for the ^{1}H and ^{13}C nmr spectra, respectively. A Varian XLR300 spectrometer was used to record the spectra.

Gel permeation chromatography

Sample preparation

A solution was prepared by dissolving an appropriate amount of the polymer to give a concentration of $\sim$ 2 mg/ml, leaving it to stand for 4 h and then warming at 80 °C for 20 min to dissolve completely. After thorough mixing the solution was then filtered through a 0.2 μm PTFE membrane prior to the chromatography.

The equipment used for the determination was a Polymer Laboratories GPC-210 with columns PL gel 2 × mixed bed-B, 30 cm, 10 μm. The solvent used was DMF with lithium bromide. The flow rate maintained was 1.0 ml/min and was detected by a refractive index detector.

Fourier transform infrared spectroscopy

A Nicolet 730 FTIR spectrometer was used to record the infrared spectrum. In each case diffuse reflectance spectra was recorded using the copolymer or cement powder.

Cement preparation

Cements were prepared using two concentrations of the copolymer of acrylic acid and 2-hydroxyethylmethacrylate (AA-HEMA). 40% and 60% solutions were prepared in distilled water and allowed to dissolve completely, the solutions being allowed to stand at room temperature for a further 24 h. The glass component of the commercial glass-ionomer cements, Fuji IX (GC) and Ketac Molar (ESPE) were used to form the cements. Commercial powders are composed of ion leachable calcium aluminofluorosilicate glasses with silicon dioxide, aluminum oxide, aluminum phosphates, calcium fluoride, aluminum fluoride and other components, however it is was difficult to procure exact composition of the commercial glasses. The control cements were mixed in accordance to the manufacturer's instruction. The working and setting times were determined using a Wilson's oscillating rheometer for all cements by a method described in an earlier paper [7]. Working time is defined as the time for the amplitude of oscillation to reach 95% of the initial value; setting time is defined as the time to reach 5% of the initial value. An average of four determinations are reported.

Compressive strength

Compressive strengths of the cements were determined for each of the cements at 24 h according to British Standard Specifications (specification for dental glass-ionomer cements) [8]. Cements were prepared and the pastes introduced into 3 mm diameter × 6 mm long cylindrical stainless steel molds, prewaxed to prevent adhesion of cements to the molds. The cements in the molds were clamped and stored at 37 °C for 1 h. The set cements were then removed and placed in distilled water for a further 23 h. An Instron Universal testing machine was used to determine the compressive strengths at a crosshead speed of 1 mm/min.

Scanning electron microscopy

The fracture surface of compressive strength specimens were analyzed using an environmental scanning electron microscope, ESEM XL30.

Results and discussion

Synthesis and characterization of the copolymer AA-HEMA

The copolymer AA-HEMA, was synthesized using AIBN as the initiator and the residual monomers were eliminated by copious washing with acetone. Both acrylic acid and HEMA are soluble in acetone that enabled the removal of any residual monomers from the copolymer mix. The polymer was then lyophilized to yield an amorphous white powder. The composition of the copolymer was determined from the proton magnetic spectrum (^{1}Hnmr) and details are explained in the following section.

Nuclear magnetic resonance spectroscopy

The ^{1}H and ^{13}C nmr spectra were determined by preparing a solution in DMSO-d_6. Fig. 2(a) shows the ^{1}Hnmr spectrum of the AA-HEMA copolymer, the composition of the copolymer was calculated by taking into consideration the integral of the signal at 4 ppm which arises from the two protons of the HEMA units and the integral of the rest of the protons appearing at a higher field from the three protons of the acrylic acid units and five protons from the HEMA units. The composition of the copolymer was found to be 0.81 mol fraction of acrylic acid and 0.19 mol fraction of HEMA. The ^{1}Hnmr spectrum (Fig. 2(a)) of the AA-HEMA copolymer shows the characteristic resonance from both acrylic acid and 2-hydroxyethylmethacrylate units. The signal at 12 ppm is due to the acidic proton of the acrylic acid units whereas the resonance signals at 3.6 and 4.0 ppm are assigned to $-OCH_2$ and $-CH_2OH$ protons of HEMA units, respectively. The rest of the signals at higher field correspond to the protons of the hydrocarbonated chain of both monomeric units and the signal centered at 1 ppm corresponds to the α-CH_3 of the HEMA unit.

Fig. 2(b) shows the ^{13}C nmr spectrum of the AA-HEMA copolymer. The resonance signal between 174–178 ppm corresponds to the resonance of carbonyl groups of both comonomeric units (carboxylic acid and ester carbonyl), which appear in the same range of chemical shift. The signals at 66.6 and 59.5 ppm correspond to the resonance of the $-OCH_2$ and $-CH_2OH$ carbons, respectively, in the HEMA unit. The signals arising between 42–45 ppm are assigned to the resonance of the quarternary carbons of both monomeric units, these signals being close to resonance signal of the solvent DMSO (40 ppm). The signal between 32–38 ppm is due to the resonance of the β carbon of the acrylic acid unit and finally the signal between 16–20 ppm arises from the resonance of the α-CH_3 group of the HEMA unit. Some signals corresponding to those of β-carbon of AA; α-CH_3 and $-OCH_2$ of HEMA and carbonyl groups of both units appear to split in several peaks due to the sensitivity of these carbon atoms to statistical and

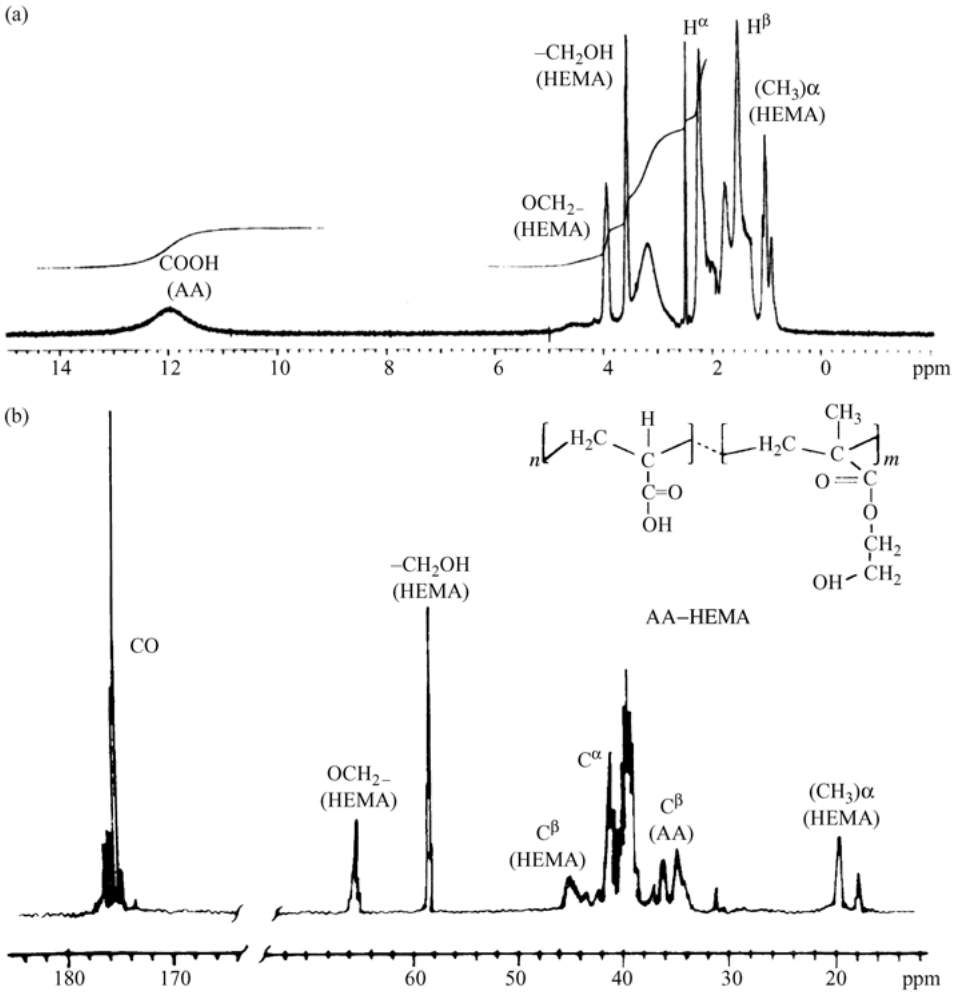

Figure 2 (a) ^{1}H nmr spectrum of AA-HEMA copolymer; (b) ^{13}C nmr spectrum of AA-HEMA copolymer.

TABLE I Working and setting times at 18 °C

Cement	Working time (min)	Setting time (min)
Fuji IX	2.0	5.0
Ketac Molar	3.0	6.5
Fuji IX powder + AA-HEMA (40%)	3.4	10.5
Fuji IX powder + AA-HEMA (60%)	4.0	9.5
Ketac Molar powder + AA-HEMA (40%)	3.2	10.0
Ketac Molar powder + AA-HEMA (60%)	3.8	12.0

sequential distribution of the comonomeric units along the macromolecular chains and tacticity.

Molecular weight determination by gel permeation chromatography

A good detector response was observed for the AA-HEMA copolymer, however, there appeared to be some adsorption despite the addition of the salt and it is difficult to obtain meaningful molecular data unless the adsorption can be suppressed. A progressive increase was observed in the molecular weight for the latter runs which can be presumed to be the blocking of the active sites and hence the decrease in adsorption. As the measured molecular weight distribution approached a steady state, the averages of the runs were taken into consideration. Lithium bromide was added to the dimethylformamide solution to prevent a number of possible non-steric interactions, which appear to have been not fully effective. Ammonium acetate is an alternative salt but as it is not entirely compatible with similar polymers such as poly (HEMA) (communication with Polymer Laboratories), hence it was not used. The calculated molecular weight averages based on the several runs were $Mw = 97\,500$ and $Mn = 20\,600$, $Mw/Mn = 4.7$. The high polydispersity may have resulted from selective adsorption.

Experimental glass-ionomer cements

Cements were prepared using a 40% and 60% aqueous solution of the AA-HEMA copolymer. Two commercial glass powders, Ketac Molar and Fuji IX were used for formulating the acid–base cement with the AA-HEMA copolymer. A powder liquid ratio of 3 : 1 by mass was used which was dispensed as one scoop of powder and one drop of the copolymer solution in water. No variation of powder : liquid ratio was conducted in this study as the first objective was to evaluate the cement forming properties of the aqueous solution of the AA-HEMA copolymer. The polymer strongly influences both setting characteristics and the ultimate mechanical properties. The setting of glass-ionomer cements involves the formation of calcium polyacrylate chains followed by the aluminum polyacrylate chains. Fluoride ions are then released that is free to remain in the matrix while the surface of the glass is involved in the reaction. The set cement contains particles of unreacted glass surrounded and supported by a siliceous hydrogel embedded in a poly salt matrix of cross linked polyalkenoic acid molecules rich in Ca^{2+} and Al^{3+} ions. The set cement contains both bound and free water and in the early stages after mixing the cement can take up further water and be washed out and on the other hand if exposed to air can desiccate which causes a loss in both mechanical strength and physical entity. The presence of the HEMA units with their pendant hydroxyl groups is expected to prevent desiccation due to its ability to retain water according to its molecular structure. In general, decreasing the proportion of the aqueous solution reduces the setting time and accordingly a decrease in the speed of setting was observed with the 60% concentration of AA-HEMA copolymer, however the working times and setting times (Table I) were longer in comparison to the respective Ketac Molar and Fuji IX cements cured with the supplied copolymer which are in effect copolymers of acrylic acid and itaconic acid. It is important to indicate that commercial formulations have tartaric acid present, that functions as a reaction controlling additive, however, no tartaric acid was added in these experimental formulations, in order to study the cement forming ability of the AA-HEMA copolymer. The increase in setting time in the experimental cements may partly be attributed to the absence of tartaric acid in the formulation and additionally the copolymer of acrylic acid contain HEMA units in the polymer chains which can also influence the rate of setting. The solutions of AA-HEMA copolymers exhibited a pH in the range of 1.8–2.2 in comparison with the poly(acrylic acid) and its copolymers that range between 0.9 and 1.6. A longer working time as observed in the Fuji IX + AA-HEMA and Ketac Molar + AA-HEMA formulations (Table I), allows the cements to be mixed thoroughly and also enables the clinician to place the cement with ease. The longer setting time is an indication that the neutralization process is slower in case of AA-HEMA copolymer itself, however it is evident that both concentrations of AA-HEMA solution were able to react with the glass and produce cements, which was further confirmed by FTIR spectroscopy.

The molecular mass of poly(acrylic acid) and its copolymers generally lie in the range of 10 000–75 000. It is known that, the higher the molecular weight of the polyacid, the greater the strength and wear resistance of the cement, however increasing molar mass of poly-(acrylic acid)s decreases the working and setting time, making it difficult to improve cement properties via this route. In this study the experimental glass-ionomer cements were however formulated with AA-HEMA copolymer having an average molecular weight of 97 500 marginally higher than the poly acrylic acid employed commercially. Despite the higher molecular

weight, the setting and working times were greater, thus implying that higher molecular weights of the copolymers may still be used without an adverse effect on the working and time.

FTIR spectroscopy

The infrared spectra of both AA-HEMA copolymer and the cement formed with the glass from Fuji IX are shown in Fig. 3(a) and (b), respectively. The FTIR spectrum of the AA-HEMA copolymer shows representative peaks as expected for the main functional groups. A broad intense peak observed between 3600 and 2500 cm^{-1} with a weak shoulder at 3650--3590 cm^{-1} can be attributed to the free hydroxyl groups arising from the primary alcohol of the HEMA units in the copolymer. The broad intense peak 2600–3200 cm^{-1} is characteristic of the strongly hydrogen bonded –OH of the carboxylic acid group arising from the poly(acrylic acid) units. A strong intense peak centered at 1700 cm^{-1} can be attributed to the carbonyl group of the carboxylic acids of the acrylic acid units and the ester carbonyl group.

The spectrum of the glass-ionomer cement prepared by the reaction of a 60% aqueous solution of AA-HEMA copolymer and a commercial glass powder (Fuji IX) is shown in Fig. 3(b). The two features that can be taken into account is the appearance of the asymmetrical stretching band at between 1550–1610 cm^{-1} and a symmetrical stretch band appearing in the 1440 cm^{-1} region which are characteristic of carboxylate absorptions [7]. A peak centerd around 1620 cm^{-1} appearing as a shoulder can arise from the calcium and Aluminum polyacrylates formed on cement formation by reference to previous results [9, 10]. A broad peak centered at about 1070 cm^{-1} can be assigned to the formation of silicate networks formed after the cement formation. The FTIR spectrum clearly indicates the reaction of the carboxylic acid groups in the block AA-HEMA copolymer.

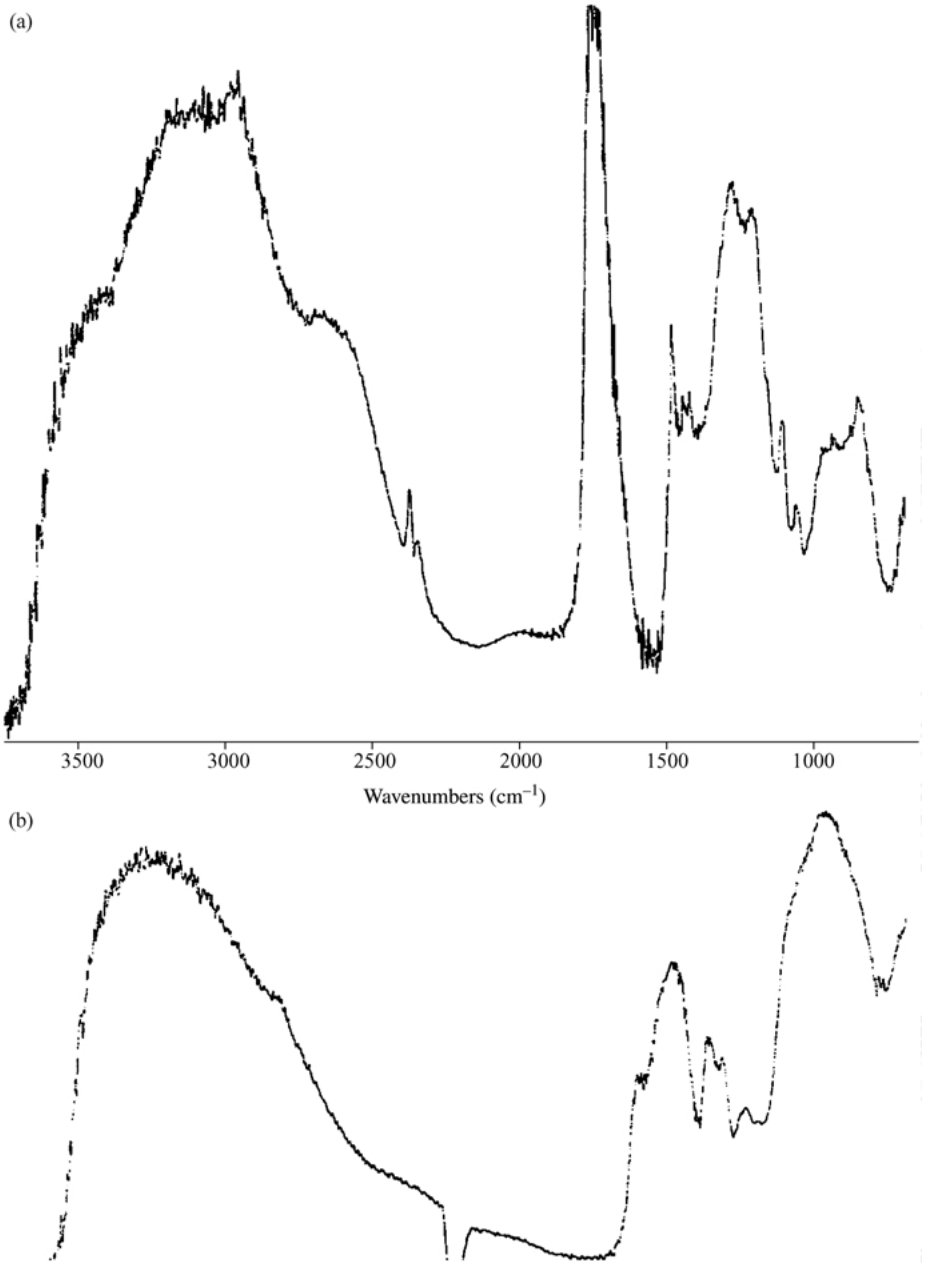

Figure 3 (a) FTIR spectrum of AA-HEMA copolymer. (b) FTIR spectrum of the cement prepared by a 60% solution of AA-HEMA copolymer and glass from Fuji IX.

TABLE II Compressive strength of cements after 24 h in water at 37 °C

Cement	Compressive strength MPa 24 h [SD]
Fuji IX*	148.00 [25.5]
Fuji IX powder + AA-HEMA (40%)	111.51 [14.6]
Fuji IX powder + AA-HEMA (60%)	124.00 [17.3]
Ketac Molar	178.20 [20.5]
Ketac Molar powder + AA-HEMA (40%)	131.51 [14.6]
Ketac Molar powder + AA-HEMA (60%)	144.00 [17.3]

Compressive strength

Compressive strengths of the two groups of cements were determined at 24 h. Cements formulated with the 60% AA-HEMA solution showed higher compressive strength values in comparison to the cements formulated with the 40% solution of AA-HEMA (Table II), however, both cements had lower values than Fuji IX itself. Fuji IX is claimed to have compressive strengths of about 219 MPa, however, mixing using the manufacturer's mixing ratio was difficult as it resulted in extremely dry mixes. As a result, cement mixes were prepared as would be expected in the clinical situation, which explains the lower compressive strength of Fuji IX. It has also been reported [11] earlier that such high compressive strengths are achievable, however it requires great practice and skill. The compressive strength data indicates that cements are formed by the reaction of the AA-HEMA copolymer with the glass, possessing adequate strength which comply with the standard requirements.

Hydration

All the specimens were subjected to two cycles of absorption and desorption and calculations are based on a study reported earlier for acrylic cements [12]. Table III summarizes the water absorption–desorption data for the cement prepared with a 60% solution of AA-HEMA and Fuji IX glass.

The equilibrium hydration data of the new glass-ionomer cements show that they are comparable to conventional glass-ionomer cements [3]. Water plays an important role in the setting of glass-ionomer cements. As the cement sets, water is incorporated within the matrix and is thought to act as both coordinating species to metal ions released from the glass [5]. The water is also believed to be responsible for the hydration of the polyanion and may act as a plasticizer in the bulk polymer structure [13]. A detailed study on the water absorption is being carried out presently, however, from the results obtained, it can be seen that the loss in the second cycles is much less, which indicates that most of the soluble materials are lost in the first stages of equilibration. The net amount of soluble material (Table IV) from the cement is comparable to conventional glass-ionomer cements, however, long-term studies are necessary to comment on the complete water balance studies.

TABLE IV Net amount of soluble material from the cements

Cement	% of soluble material [SD]
[AA-HEMA (60%) + Glass]	4.58 [0.17]

Scanning electron micrographs of the cements Fuji IX, Ketac Molar, Fuji IX-AAHEMA and Ketac Molar-AAHEMA cements are shown in Figs. 4–7, respectively. The glass particles can be clearly distinguished from the matrix by the presence of the angular edges of the areas in the micrograph of Fuji IX (Fig. 4). The edges of the glass particle appear to be eroded as a result of degradation as a result of the acid–base reaction. Fig. 5 shows the Fuji IX-AAHEMA cement that contains the same glass phase as in Fuji IX, however, a more obvious formation of a silica gel layer is observed as the glass particles are generally widely covered and most particles appear to have undergone dissolution. Similarly a comparison of the microstructure of the Ketac Molar

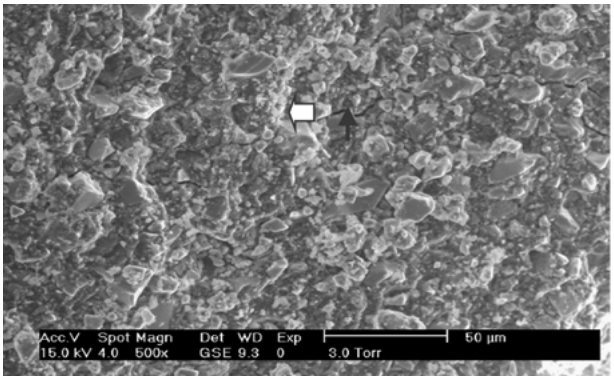

Figure 4 Scanning electron image of Fuji IX cement: white arrows show dissolution a distinct layer on the glass particles; black arrow show cracks due to desiccation.

TABLE III Water absorption data of the cements prepared with a 60% solution of AA–HEMA copolymer and Fuji glass

Cement	Equilibrium[c] (%)		
	Gain [SD]	Loss [SD]	Corrected
[AA–HEMA (60%) + Glass][a]	2.335 [0.310]	4.195 [0.105]	6.53 [0.42]
[AA–HEMA (60%) + Glass][b]	5.685 [0.020]	0.395 [0.02]	6.08 [0.04]

[a] First absorption-desorption cycle.
[b] Second absorption-desorption cycle.
[c] Equilibrium gain (%) $= \dfrac{\text{weight of specimen at equilibrium} - \text{initial weight}}{\text{initial weight}} \times 100$

$$\text{Loss (\%)} = \frac{\text{initial weight} - \text{weight of desorbed specimen}}{\text{initial weight}} \times 100$$

$$\text{Corrected gain} = \text{gain} + \text{loss}$$

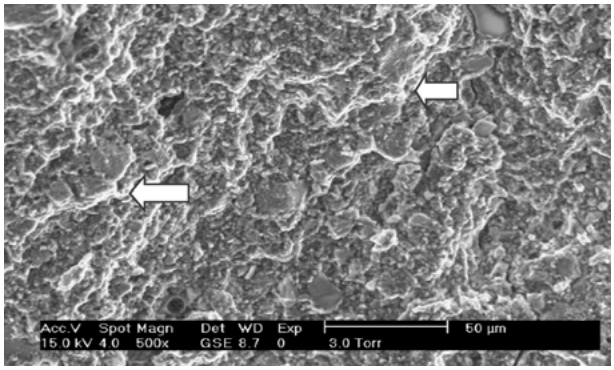

Figure 5 Scanning electron image of AA-HEMA-Fuji IX cement: white arrows show dissolution a distinct layer on the glass particles; no dehydration cracks.

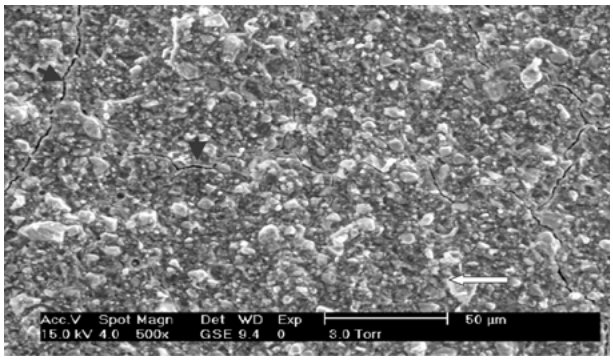

Figure 6 Scanning electron image of Ketac Molar cement: white arrows show dissolution a distinct layer on the glass particles; black arrow show cracks due to desiccation.

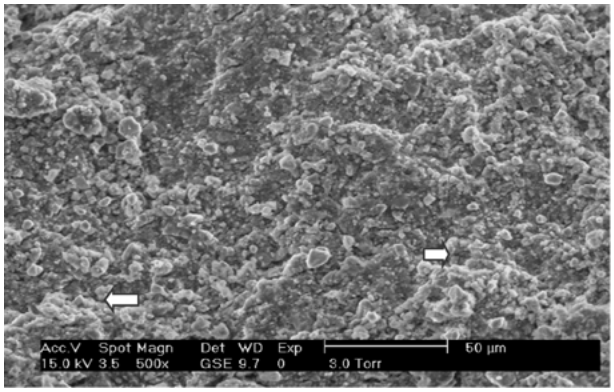

Figure 7 Scanning electron image of AA-HEMA-Ketac Molar cement: white arrows show dissolution a distinct layer on the glass particles; no dehydration cracks.

cement (Fig. 6) and the experimental cement containing Ketac Molar glass phase, show that the glass particles (Fig. 7) are covered by a distinct gel like layer which is more pronounced in the experimental cement. The microstructure shows that partially degraded glass particles are embedded in a matrix of calcium and aluminum polyalkenonates and sheathed in a layer of sileceous gel probably formed on the boundaries of the glass particle. Hatton and Brook [14] have earlier confirmed this model for conventional glass-ionomer cements. No micro-cracks were observed in the cement matrices containing the AA-HEMA copolymer whereas cracks were visible throughout the matrices of the control cements despite similar storage conditions.

Conclusion

A copolymer of acrylic acid and HEMA (AA-HEMA) was synthesized and characterized. The copolymer composition was determined using the ^{1}Hnmr spectrum of the copolymer. The aqueous solutions of the AA-HEMA copolymer (40% and 60%) were able to react with aluminosilicate glasses to form poly alkenoate cements. The cements so produced, compared favorably with conventional glass-ionomer cements. The longer setting times suggest a slower rate of cement formation but the hardening is produced in a period of time that allows the manipulation of the glass-ionomer formulation and its application adequately, with good mechanical properties of the hardened composite and excellent homogeneity.

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