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Characterization of bone cements prepared with functionalized methacrylates and hydroxyapatite

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Abstract—Bone cements prepared with methyl methacrylate and either methacrylic acid or diethyl amino ethyl methacrylate as comonomers were characterized by infrared spectroscopy, nuclear magnetic resonance, gel permeation chromatography, dynamic mechanical thermal analysis, and mechanical testing. Selected formulations containing these functionalized methacrylates were filled with hydroxyapatite and studied in terms of their properties in tension, compression and bending, and X-ray diffraction.

It was found that residual monomer was not greatly affected by the presence of either acid or basic comonomers in the unfilled bone cements. In contrast, molecular weight, curing times, and glass transition temperature were composition dependent. For samples with acidic comonomer, a faster curing time, higher molecular weight, and higher glass transition temperatures were observed with respect to those with the basic comonomer.

X-ray diffraction revealed that the crystalline structure was not affected by the nature of comonomer in the bone cement while scanning electron microscopy showed that hydroxyapatite remained as clusters in the bone cement.The mechanical properties of filled bone cements depended mainly on composition and type of testing. Hydroxyapatite-filled bone cements fullfilled the minimum compressive strength (70 MPa) required for bone cement use. However, the minimum tensile strength (30 MPa) was only fullfilled by cements prepared without comonomer and those containing methacrylic acid. The minimum bending strength requirement (50 MPa) was not satisfied by any of the formulations studied.

Key words: Bone cements; methyl methacrylate; diethyl amino ethyl methacrylate; methacrylic acid; mechanical properties.

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INTRODUCTION

Bone cements have been in the market for almost 40 years since their introduction by Sir John Charnley. Traditional bone cements, primarily made of methyl methacrylate (MMA) and poly(methyl methacrylate) (PMMA), exhibit high exotherm of reaction, various amounts of residual monomer, shrinkage after curing, unsuitable mechanical properties, and cement loosening [1]. Improved formulations include low toxicity activators, low heat of reaction monomers, and bioactive ceramics to improve biocompatibility [2–4].

Hydroxyapatite, HA, is one of the more commonly used fillers in bone cement formulations as it has shown to be biocompatible and osteoconductive. Although the addition of increasing amounts of HA to bone cements is expected to reduce the maximum temperature during polymerization and to increase the setting time, the effect of HA on mechanical properties is not clear as it depends on the type of matrix and concentration of the filler. For example, the addition of increasing amounts of HA (up to 40 wt%) to poly(ethyl methacrylate)-based bone cement is claimed to increase flexural strength and modulus [5]. However, for HA-reinforced PMMA a maximum in Young's modulus and flexural strength has been observed at concentrations as low as 3% HA [6]. Furthermore, Vallo *et al.* [7, 8] have reported an increase in flexural modulus and fracture toughness on PMMA bone cements limited to 15 wt% of HA due to an increase in porosity and pore size.

It is also evident from these studies that a complete mechanical characterization is not generally pursued as bone cement standards only require properties in flexion and compression but not in tension. These studies are justified as bone cements are subjected to tensile stresses in the lateral side of a hip implant due to bending while compressive stresses are found during one-legged stance (medial region). In addition, it has been postulated that the cement mantle can act as a compressive wedge between the femoral stem and the bone tube. Finally, it has been proposed that a combination of shear, tension and compression stresses are found during *in vivo* loading of the artificial joint [9].

In this study, we attempt to provide some information on the mechanical properties in tension, compression and bending of HA-filled bone cements. These bone cements were prepared with functionalized methacrylates as it has been reported that cell adhesion is generally better on hydrophillic surfaces and charged substrata [10]. Because these methacrylates are not commonly used in commercial formulations, a physico-chemical characterization of the unfilled bone cement is also reported.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), methacrylic acid (MAA), diethyl amino ethyl methacrylate (DEAEMA), and *N,N*-dimethyl-*p*-toluidine (DMPT) were purchased from Aldrich and used without further purification. Benzoyl peroxide (BPO) was ob-

tained from Merck and used as-received. A fast curing-transparent acrylic, Nictone (average diameter = 60.6 μm, M_n = 305 150, T_g = 92.5°C), from Manufacturera Dental Continental was used as the solid component of the formulations. (HA) was obtained from Plasma Biotal P81B (average particle size = 9.3 μm).

Methods

Bone cement preparation. Experimental bone cements were prepared with MMA (sample A) as the base monomer and either MAA or DEAEMA as comonomer. The acidic comonomer was incorporated at 0.1 (sample B), 0.2 (sample C), and 0.3 (sample D) molar fractions while the alkaline comonomer was added at 0.04 (sample E), 0.06 (sample F), and 0.08 (sample G) molar fractions. DMPT was added to the monomer mixture at 2.5% v/v while BPO was added to the polymer at 1% w/w. The polymer to liquid ratio used was 2 and both components were hand mixed without vacuum. A commercial bone cement, CMW 3 (sample H) was prepared following manufacturer instructions and used for comparison purposes.

In order to improve biocompatibility, selected bone cement formulations were filled with HA at 5, 10, 15, and 20% w/w. MMA (samples A1–A4), MAA0.3–MMA0.7 (samples D1–D4), and DEAEMA 0.08–MMA0.92 (samples G1–G4) were prepared. A powder to liquid ratio of 2 was kept in all cases and no extra BPO was used.

Characterization of unfilled bone cements.

Spectroscopic analysis. The content of residual monomer was calculated by ^{1}H NMR on a Varian Gemini 200 (0.050 g in 0.6 ml). The monomer was quantified on bone cements plates (3 × 1 × 0.1 cm) after 7 days of preparation. Samples containing DEAEMA and those without comonomer were dissolved in $CDCl_3$ while those containing MAA were dissolved in THF-d_8. The areas for the CH_2=C− at δ 5.6 and 6.1 ppm and for OCH_3 group of the MMA monomer were used to determine the percentage of monomer present in the total sample

Infrared spectra of bone cements as films were obtained with a Nicolet FTIR Protege 460. One hundred scans were recorded for each sample. Additional spectra were recorded for composites containing 20% w/w HA.

Molecular weight distribution. A Perkin-Elmer Gel Permeation Chromatographer LC30 coupled to multiangle light scattering detector (DAWN Wyatt Tech.) was used in order to obtain the molar mass distribution of bone cements. Samples were dissolved in THF and *ca* 0.5 mg were injected. A flow rate of 1 ml mm^{-1} and a wavelength of 632.8 nm for the detector were utilised. A dn/dc of 0.088 cm^3 g^{-1} was used for calculations.

Dynamic mechanical thermal analysis. The glass transition temperature, T_g, of experimental bone cements was determined by means of a DMA-7 (Perkin-Elmer) in the tension mode. Bone cements machined as 20 × 3 × 0.1 mm strips were

deformed under a static force of 60 mN and a dynamic force of 40 mN. Experiments were conducted from −50 to 150°C at a heating rate of 2°C min^{-1}, 1 Hz and under nitrogen flow. The T_g was determined from the peak of the tan δ vs temperature curve.

Determination of maximum temperature and setting time. Peak temperature and curing time were determined in a ISO 5833 (annex C) mould but measured at 15, 20, 25, and 30°C. A water bath was used in order to attain the desired temperature. The change in temperature with time was recorded immediately after mixing the powder and the liquid. An average of at least three measurements for each condition is reported.

Characterization of bioactive bone cements.

Porosity determinations. Porosity was determined in both filled and unfilled composites from density measurements as the complement of the ratio of the observed and theoretical densities. The density was determined by the Arquimides' principle using a density kit attached to a Ohaus Voyager V12130 balance. Water at 20°C was used as the standard of known density. Theoretical densities were calculated following the rule of mixtures with ρ_{HA}, ρ_{PMMA}, $\rho_{PDEAEMA}$, and ρ_{PMAA} is 3.156, 1.2, 1.047, and 1.293 g cm^{-3}, respectively.

Determination of mechanical properties of bone cements. HA-filled and unfilled bone cements were tested on tension, compression, and bending. Tensile tests were conducted using ISO 527 dumbbell specimens. A cross-head speed of 5 mm min^{-1} was used and the final deformation was obtained by means of a contact extensometer. From the load vs displacement curve Young's modulus (E_T), tensile strength (σ_T), and strain (ε) were obtained. Compression tests were carried out according to ISO 5833 (annex E). Cylinders of 12 mm height and 6 mm of diameter were deformed at 20 mm min^{-1} and the compressive strength (σ_C) and modulus (E_C) are reported. Bending modulus (E_B) and bending strength (σ_B) were obtained by means of four-point bending experiments also according to ISO 5833 (annex F). All samples were tested using an Instron 1125 after storing them at 25°C during 1 week. At least five specimens for each type of testing were used.

X-ray difraction (XRD). Because both acidic or basic comonomers were used in the bone cement preparations, XRD was performed in order to determine if HA was modified by the addition of these monomers. XRD was carried out on films of these composites using a Phillips X-ray generator XRG 3100.

Scanning electron microscopy (SEM). Fracture surfaces of unreinforced bone cements (samples A, D, and G) were observed by SEM after tension experiments. Samples were gold-coated and observed with a JEOL JSM 5900-LV at an accelerating voltage of 20 keV. A Cambridge 250 SEM was used for bioactive bone cements (samples A4, D4, and G4) after tensile testing.

RESULTS AND DISCUSSION

NMR characterization

In a free radical polymerization, a wide variety of chemical reactions are expected to occur if the reaction conditions are not properly controlled. In our case, a complete chemical characterization was not feasible not only because of the problems associated with free radical polymerization but also due to secondary reactions. On one hand, as a redox system is utilized to initiate the polymerization, formation of a complex among both DMPT-BPO and DEAEMA-BPO is expected, and aromatic branching units and terminal groups derived from the toluidine free radicals are also expected. On the other hand, it has been shown that tertiary amine can induce deprotonation of carboxylic acid functionalities and this in turn leads to free radical polymerization of acrylic monomers [11, 12]. For the bone cements prepared in this work, a certain extent of stereocontrol can be expected because the principles of template polymerization are involved.

The ^{1}H NMR spectra of bone cements prepared without filler are shown in Fig. 1a and b. An incomplete curing reaction due to vitrification led to residual monomer in all formulations. By ^{1}H NMR, we found that residual monomer ranged from 1.1 to 3.8%. This amount is considered within the range observed for commercial bone cements but care must be taken considering that small specimens were used for determinations. NMR also revealed that Nictone is a 90 : 10 copolymer of MMA and ethyl methacrylate (EMA). A quartet at 4.3 ppm typical of the ethyl moiety can be seen in Fig. 1. NMR did also show that a predominantly syndiotactic copolymer was present as can be inferred from the peak at 0.8 ppm corresponding to the methyl group of the syndiotactic arrangement. Tacticity observed in bone cements derived from DEAEMA has been discussed elsewhere [13].

Average molecular weight

The weight average molecular weight (M_w) and polydispersity (M_w/M_n) of bone cements prepared in this study are presented in Table 1. In general, it was observed that the molecular weight of the newly formed polymer was higher when acidic rather than alkaline comonomers were used. The molecular weight of bone cements prepared with MAA reached 1.4×10^6 g mol^{-1} which was higher than 5.13×10^5 g mol^{-1} obtained for Nictone, the base polymer. When bone cements contained either DEAEMA or MMA alone their molecular weights were comparable to that of Nictone.

Glass transition temperature (T_g)

A single glass transition temperature was observed for DEAEMA–MMA and MMA bone cements whereas MAA containing bone cements exhibited a shoulder for the main transition peak. In general, T_g increased up to 120°C as the con-

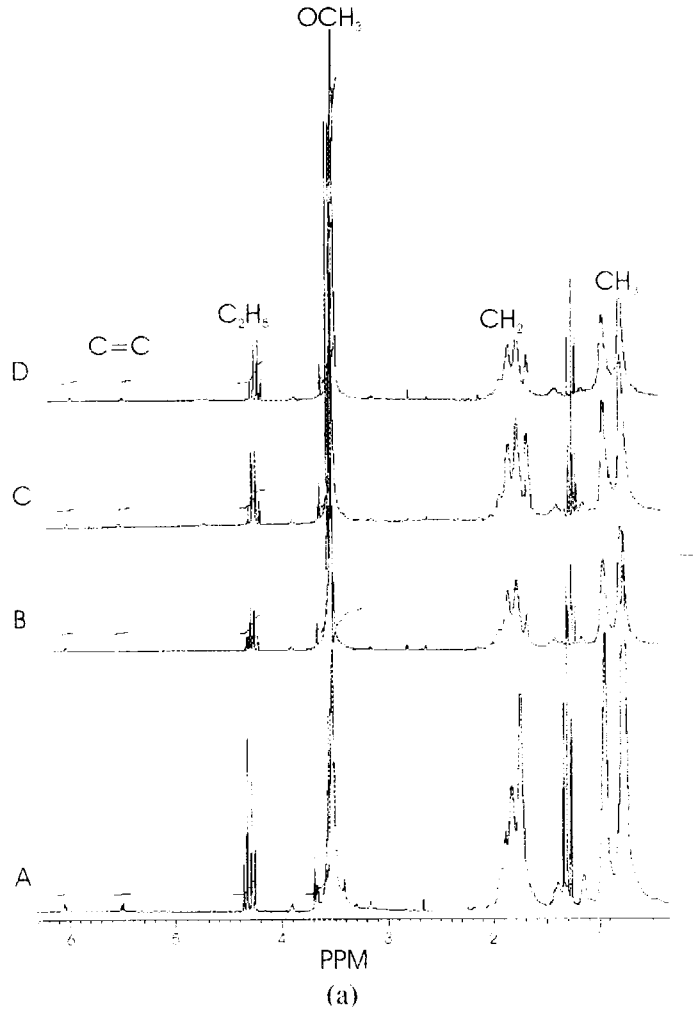


Figure 1. ^{1}H NMR spectra of bone cements prepared with functionalized methacrylates: (a) bone cements containing MAA; and (b) bone cements containing DEAEMA.

tent of MAA reached 0.3 molar fraction (by association of H-bonded acid units) and decreased up to 83.9°C in the presence of DEAEMA. The low T_g detected for the bone cement without comonomer is due to the presence of EMA in the polymer base (Nictone) which exhibits a lower T_g than PMMA. Secondary transition in these formulations were not detected but the shoulder in MAA–MMA bone cements can be explained considering that MAA may undergo dehydration to yield polyanhydrides. Glutaric and succinic anhydrides have been suggested as the main products [14].

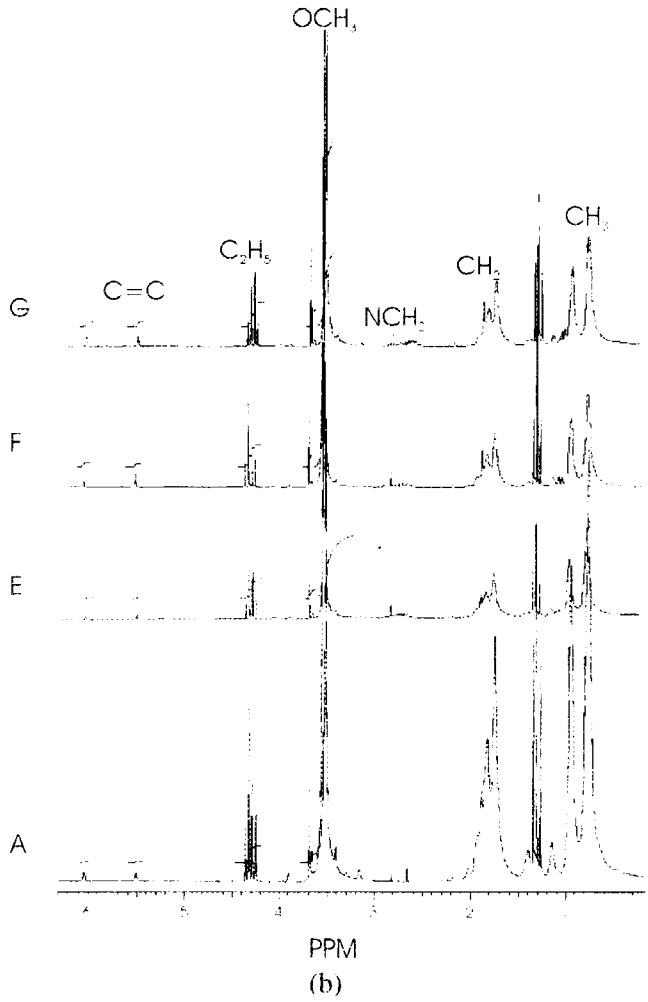


Figure 1. (Continued).

Table 1.
Physical properties of bone cements prepared with functionalized methacrylates

Bone cement	Residual monomer (%)	M_w (g mol^{-1})	(M_w/M_n)	T_g (°C)
Nictone	—	5.1328×10^5	1.68	92.5
A	1.1	4.0614×10^5	24.2	95.2
B	2.7	1.4619×10^6	4.45	104.5
C	2.9	1.4436×10^6	5.9	109.7
D	3.5	6.9763×10^5	2.35	120.0
E	1.6	4.6192×10^5	7.48	88.4
F	3.2	5.3188×10^5	3.99	84.9
G	3.8	5.2707×10^5	18.04	83.9

Table 2.
Curing parameters of bone cements prepared with functionalized methacrylates

Bone cement	Temperature of curing (°C)											
	15			20			25			30		
	T_{max} (°C)	T_{cur} (°C)	t_{cur} (min)	T_{max} (°C)	T_{cur} (°C)	t_{cur} (min)	T_{max} (°C)	T_{cur} (°C)	t_{cur} (min)	T_{max} (°C)	T_{cur} (°C)	t_{cur} (min)
A	55.1 ± 3.9	35.1 ± 1.9	10.3 ± 0.3	60.5 ± 3.8	40.2 ± 1.9	6.7 ± 0.2	61.7 ± 0.6	43.3 ± 0.2	5.3 ± 0.3	69.1 ± 1.3	49.5 ± 0.6	4.1 ± 0.3
B	60.9 ± 2.9	38.0 ± 1.4	6.3 ± 0.1	64.4 ± 1.4	42.2 ± 0.6	5.2 ± 0.2	69.9 ± 1.1	47.4 ± 0.6	3.5 ± 0.5	71.4 ± 3.7	50.7 ± 1.8	2.6 ± 0.1
C	61.3 ± 4.3	38.2 ± 2.2	4.8 ± 0.1	63.0 ± 2.5	41.5 ± 1.2	3.1 ± 0.6	70.9 ± 0.9	48.0 ± 0.4	2.7 ± 0.1	71.5 ± 4.7	50.8 ± 2.2	2.2 ± 0.1
D	59.6 ± 1.4	37.3 ± 0.7	3.1 ± 0.1	72.5 ± 0.1	46.2 ± 0.1	2.6 ± 0.1	76.0 ± 3.0	50.6 ± 1.2	2.5 ± 0.1	69.2 ± 0.5	49.7 ± 0.3	1.8 ± 0.1
E	45.1 ± 2.4	30.1 ± 1.2	10.6 ± 1.3	55.4 ± 0.2	37.7 ± 0.1	8.5 ± 0.2	62.3 ± 0.2	43.7 ± 0.1	6.1 ± 0.1	60.7 ± 0.7	45.2 ± 0.3	4.8 ± 0.1
F	39.8 ± 1.0	27.4 ± 0.5	13.0 ± 1.0	46.6 ± 0.3	33.2 ± 0.2	8.7 ± 0.5	50.3 ± 1.7	37.6 ± 0.9	5.5 ± 0.5	59.0 ± 1.3	44.0 ± 0.2	6.0 ± 0.2
G	32.6 ± 2.5	23.8 ± 1.3	12.8 ± 0.1	37.7 ± 1.8	28.8 ± 0.9	9.1 ± 0.1	46.5 ± 3.4	35.7 ± 1.7	7.6 ± 0.3	54.3 ± 0.7	41.8 ± 0.7	6.2 ± 0.1

Effect of the composition and temperature on setting parameters

Vázquez *et al.* [15] have discussed the influence of the surrounding temperature on curing parameters of bone cements. As in their study, we found that peak temperature increased and that the setting time decreased with increasing temperature. Furthermore, the composition of the monomer mixture played an important role in these parameters. As seen in Table 2, high exotherm temperatures, up to 72°C, and decreased curing times, as low as 2.6 min, were observed when experiments were conducted at 20°C and when MAA was present in the formulation. On the other hand, low exotherm temperatures (37.7°C) and long curing times (9.1 min) were obtained by using DEAEMA in the formulation. The high temperatures reached are enough to cause bone necrosis but in general it is accepted that the temperatures measured *in vitro* do not correspond with the actual values *in vivo* [16]. This is because the actual temperature depends on the cement mantle thickness and heat dissipation by surrounding fluids. The temperatures registered during this study, came from cylindrical specimens (6 × 68 mm) prepared in accordance with ISO 5833 and it is expected that the the maximum temperature reached by bone cements is lower in the final application. Furthermore, when we measured simultaneously the maximum temperature of bone cements without comonomers in four additional places of the ISO 5833 mould (holes for eliminating the excess of cement), we found a difference up to 10°C with respect to the temperature measured in the central hole.

The MAA behaviour has been explained considering that MAA has a higher propagation constant and a lower termination constant than MMA [17]. Therefore, the ratio Kp/Kt is greater for MAA than for MMA. The rate of termination is further reduced by the presence of Nictone (by increasing the viscosity of the medium), which implies that the Kp/Kt ratio is increased even more. To our knowledge, the rate constant for DEAEMA have not been determined but following the aforementioned reasoning we can expect a lower propagation rate constant for DEAEMA and explain their corresponding longer curing times.

Effect of bone cement composition on mechanical properties

Bone cements prepared with MAA as comonomer exhibited improved mechanical properties as compared to bone cements without comonomer. However, the addition of DEAEMA to MMA reduced both modulus and strength. CMW-3 exhibited better mechanical performance than the experimental bone cements except for sample D where properties were comparable. These observations are explained due to the high T_g observed in both MAA and MMA containing bone cements.

It can be observed in Table 3 that the minimum compressive strength (MCS = 70 MPa) and the minimum tensile strength (MTS = 30 MPa) [10, 18] required for bone cement use was fulfilled in all formulations without HA. However, the minimum bending strength (MBS = 50 MPa) [16] was not fulfilled by these experimental formulations. Further reductions in mechanical properties are also expected because of the water absorbing capability of functionalized methacrylates,

leading to low modulus bone cements. The low porosity observed in these bone cements (1.0–2.3% as determined from density measurements) is thought not to affect their mechanical performance and it is concluded that composition is the more important factor.

Table 3.
Mechanical properties of bone cements prepared with functionalized methacrylates

Bone cement	Porosity (%)	Tensile properties			Compressive properties		Bending properties	
		E (GPa)	σ_C (MPa)	ε (%)	E (GPa)	σ_C (MPa)	E (GPa)	σ_B (MPa)
A	2.3	4.5 ± 0.2	44.3 ± 4.7	2.7 ± 1.1	2.1 ± 0.2	104.6 ± 6.1	2.5 ± 0.2	35.4 ± 3.8
B	1.4	4.8 ± 0.6	34.5 ± 2.8	1.7 ± 0.5	2.5 ± 0.2	118.5 ± 5.6	3.0 ± 0.4	41.6 ± 2.6
C	1.1	4.9 ± 0.7	32.5 ± 6.1	2.9 ± 0.9	2.6 ± 0.1	126.4 ± 7.3	3.1 ± 0.2	50.3 ± 7.9
D	0.9	5.4 ± 1.3	33.0 ± 3.6	1.7 ± 0.7	2.8 ± 0.1	131.8 ± 4.8	3.0 ± 0.06	42.9 ± 7.7
E	1.0	2.7 ± 0.3	41.3 ± 6.9	3.1 ± 1.5	2.2 ± 0.1	108.4 ± 1.5	2.6 ± 0.1	59.3 ± 8.7
F	1.0	2.4 ± 0.3	43.4 ± 3.1	5.1 ± 0.8	1.9 ± 0.1	97.7 ± 1.9	2.3 ± 0.1	46.6 ± 3.9
G	1.2	2.2 ± 0.3	33.3 ± 4.4	4.0 ± 2.4	2.0 ± 0.08	86.3 ± 2.8	2.1 ± 0.9	35.6 ± 7.8
H	6–16*	4.1 ± 1.4	35.2 ± 9.5	5.3 ± 0.9	2.3 ± 0.1	113.6 ± 5.5	3.5 ± 0.09	49.7 ± 8.4

*Taken from Ref. [9].

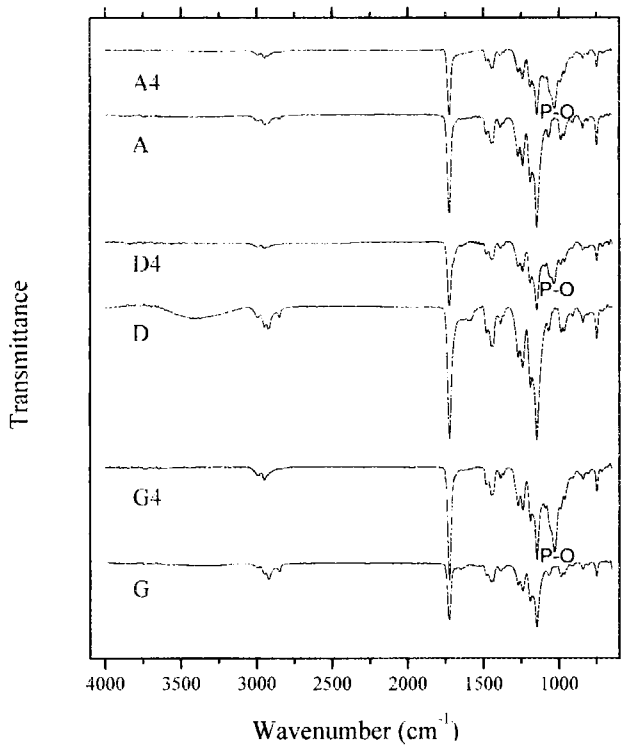


Figure 2. Infrared spectra of unfilled bone cements and 20% HA-filled bone cements.

Effect of the addition of HA on mechanical properties

The presence of HA in bone cements was confirmed by FTIR and X-ray diffraction. Infrared bands corresponding to phosphates were detected at 1097, 1027, and 962 cm^{-1} as seen in Fig. 2. These bands have been reported previously in addition to the 603 and 563 cm^{-1} bands [19]. Furthermore, X-ray diffraction revealed the presence of HA on an amorphous background corresponding to the polymeric matrix, as depicted in Fig. 3. These findings suggest that HA does not show a structural change when in contact with these acidic or basic functionalities so its ability to encourage bone growth is retained.

The minimum compressive strength was fulfilled by all formulations but the minimum tensile strength was only fulfilled by those formulations containing either MAA or just MMA. The minimum bending strength was not satisfied by any of the formulations with HA. A summary of the mechanical properties of HA-filled bone cements is presented in Table 4.

The variation of modulus with HA concentration is shown in Fig. 4a–c for tests in tension, compression, and bending respectively. It is evident that modulus did not change monotonically with composition and mode of testing. By adding HA to MAA bone cements (D–D4) both tensile and compressive modulus tended to reduce although their bending modulus increased. HA-filled DEAEMA-bone cements (G to G4) exhibited reduced tensile and bending modulus but increased

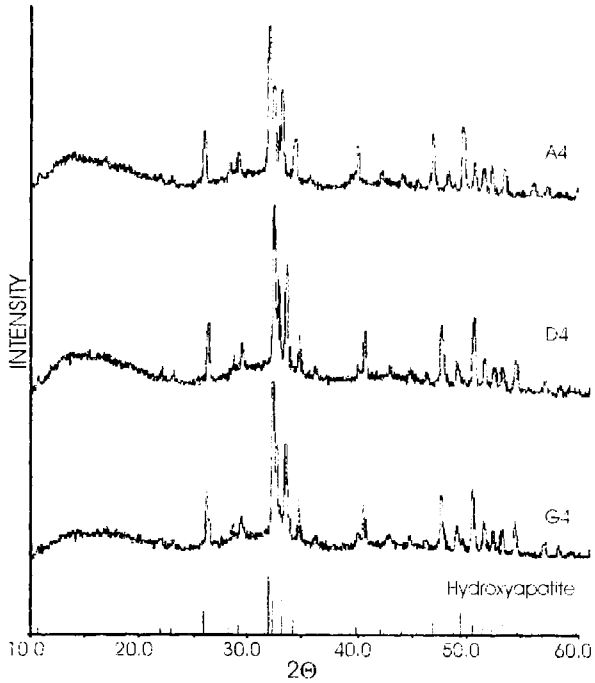
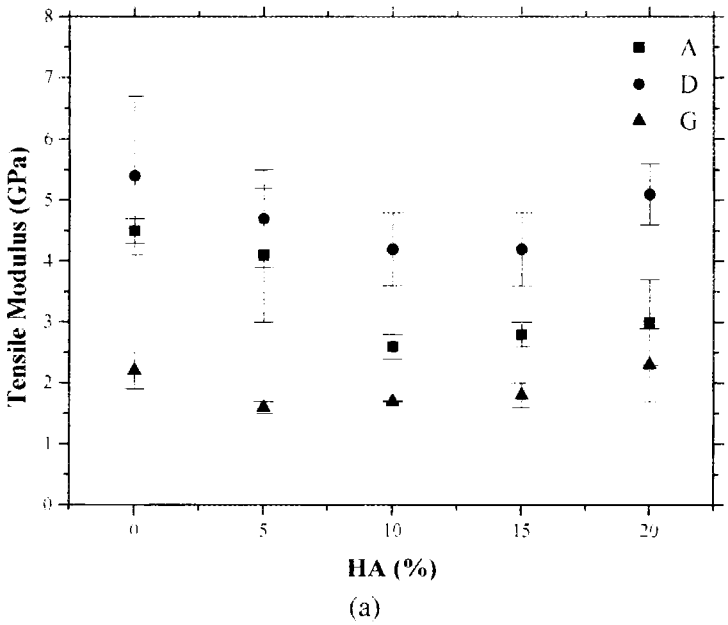


Figure 3. X-ray diffraction of bone cements containing HA as filler.

Table 4.
Mechanical properties of bone cements prepared with functionalized methacrylates and HA

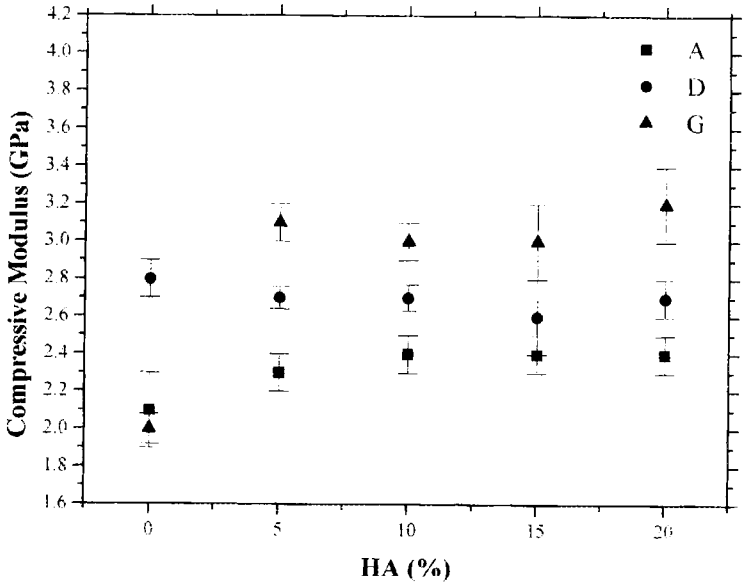
Bone cement	Porosity (%)	Tensile properties			Compressive properties		Bending properties	
		E (GPa)	σ_T (MPa)	ε (%)	E (GPa)	σ_C (MPa)	E (GPa)	σ_B (MPa)
A1	2.0	4.1 ± 1.1	36.4 ± 2.2	1.9 ± 1.2	2.3 ± 0.1	86.7 ± 1.9	2.6 ± 0.1	34.8 ± 4.7
A2	2.1	2.6 ± 0.2	36.6 ± 3.5	2.9 ± 0.4	2.4 ± 0.1	86.0 ± 5.0	2.7 ± 0.1	42.1 ± 3.8
A3	3.6	2.8 ± 0.2	37.2 ± 3.8	2.9 ± 0.6	2.4 ± 0.1	85.6 ± 3.9	2.8 ± 0.1	36.9 ± 2.6
A4	3.7	3.0 ± 0.7	29.4 ± 4.4	2.1 ± 0.8	2.4 ± 0.1	86.2 ± 4.6	3.0 ± 0.09	39.0 ± 3.6
D1	0.8	4.7 ± 0.8	37.2 ± 0.2	2.9 ± 0.6	2.7 ± 0.06	121.4 ± 2.6	3.1 ± 0.1	39.0 ± 5.6
D2	1.3	4.2 ± 0.6	32.7 ± 1.3	1.3 ± 0.5	2.7 ± 0.07	119.9 ± 3.2	3.4 ± 0.1	38.3 ± 5.6
D3	1.9	4.2 ± 0.6	36.7 ± 3.8	2.0 ± 0.6	2.6 ± 0.2	119.6 ± 3.6	3.4 ± 0.2	37.4 ± 3.8
D4	1.9	5.1 ± 0.5	34.3 ± 2.9	1.6 ± 1.1	2.7 ± 0.1	120.1 ± 3.6	3.8 ± 0.3	39.5 ± 3.5
G1	2.0	1.6 ± 0.1	29.7 ± 2.6	9.1 ± 1.8	3.1 ± 0.1	74.5 ± 2.6	1.8 ± 0.2	43.4 ± 8.2
G2	2.0	1.7 ± 0.01	27.2 ± 0.9	4.3 ± 0.9	3.0 ± 0.1	75.7 ± 2.9	1.9 ± 0.1	43.4 ± 6.7
G3	3.6	1.8 ± 0.2	21.2 ± 3.3	2.8 ± 1.1	3.0 ± 0.2	73.3 ± 3.3	1.8 ± 0.1	35.9 ± 4.3
G4	4.0	2.3 ± 0.6	20.0 ± 3.0	2.3 ± 1.4	3.2 ± 0.2	72.7 ± 4.2	1.7 ± 0.1	34.0 ± 3.4



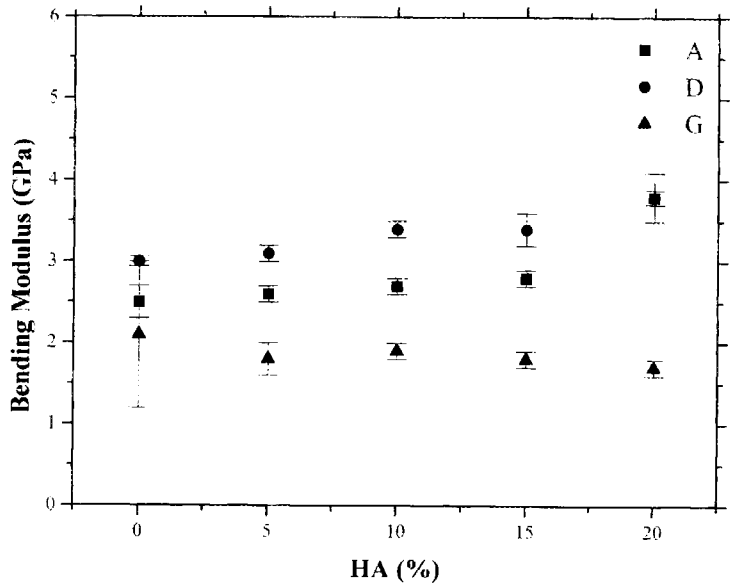
(a)

Figure 4. Variation of modulus with HA concentration: (a) tensile; (b) compressive; and (c) bending.

compressive modulus. Cements prepared without comonomer and HA (A–A4) exhibited low modulus in tension but high modulus in compression and bending. When the different moduli were fitted to Voigt and Reuss models we found a



(b)



(c)

Figure 4. (Continued).

poor agreement with these models, that in general, provide lower and upper limits. However, bone cements A–A4 and D–D4 were fitted by a second order polynomial.

The variation in mechanical properties for the various formulations containing HA can be explained in several ways. The composition of bone cements seems

to be the most important factor as MAA-containing bone cement exhibited the best mechanical properties in agreement with their high T_g. Secondly, the amount of residual monomer depended on the thickness of the actual testing specimen as reported by Vallo *et al.* [20]. Therefore, the amount of residual monomer is expected not to be the same for compressive, tensile or bending specimens. In third place, the speed of testing was not the same as compression test were conducted at higher cross-head speeds (20 mm min^{-1}) than either tension or bending (5 mm min^{-1}). Finally, the presence of HA observed as small clusters within the polymeric matrix suggested not only poor mixing but also a poor adhesion between matrix and filler.

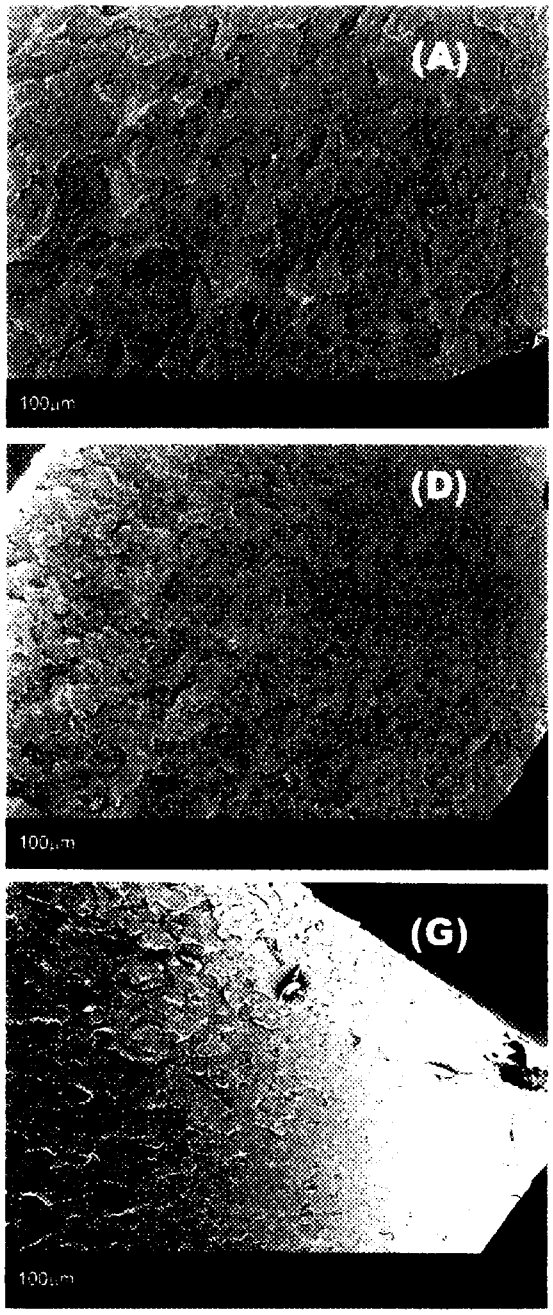
Scanning electron microscopy (SEM)

Fractured surfaces of experimental bone cements revealed many interesting features such as insoluble polymer beads, pores, and HA aggregates, as can be seen in Fig. 5. The presence of insoluble beads in the monomers was more evident in bone cements containing DEAEMA. In low concentration DEAEMA bone cements beads were localized near voids and it was also attributed to mixing problems.

Pores were also seen in all formulations creating defects in the bone cement and they have been related to the places where fracture seems to start. SEM observations revealed pores smaller than 20 μm and macroscopic pores of 500 μm in the crossection under study. However, pores bigger than 1 mm have been reported [10]. In order to clarify this point, at least three bone cements beams (used for the determination of flexural properties) were polished with sand paper and observed with an optical microscope LEICA DMLM (100x) while the pore size were measured with Image Pro Plus software. Figure 6 shows the pore size distribution obtained for the unfilled bone cements (samples A, D, and G). Pores larger than 1 mm were observed in all samples but the pore size distribution of smaller pores depended on the composition. Bone cements prepared without comonomer (sample A) exhibited an average pore size of 505.3 μm and a porosity of 13.7% while when DEAEMA was present in the formulation an average pore size of 421 μm and a 12.6% porosity was observed. For bone cements containing MAA, the average pore size was 281.2 μm and 8.6% porosity. These observations are in agreement with the porosity determined by density measurements, although, it is evident that an optical technique tends to either overestimate porosity or that density measurements tend to underestimate it.

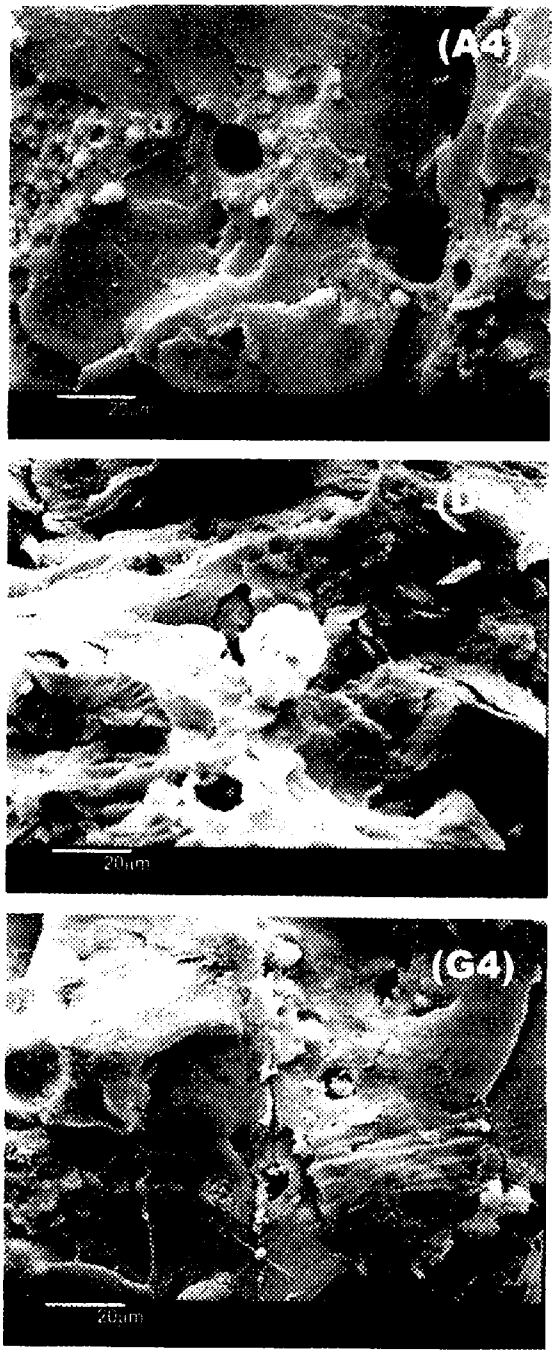
CONCLUSIONS

The main conclusions of this work are the following: (a) Bone cements exhibiting fast curing time, high molecular weight, and high glass transition temperature were obtained when MAA acid was used instead of DEAEMA as the comonomer. (b) Low modulus bone cements were obtained when DEAEMA was present in



(a)

Figure 5. Tensile fracture surfaces of bone cements. (a) Unfilled MMA (A), 0.3 MAA (D), and 0.08 DEAEMA (G). (b) HA-filled MMA (A4), 0.3 MAA (D4), and 0.08 DEAEMA (G4).



(b)

Figure 5. (Continued).

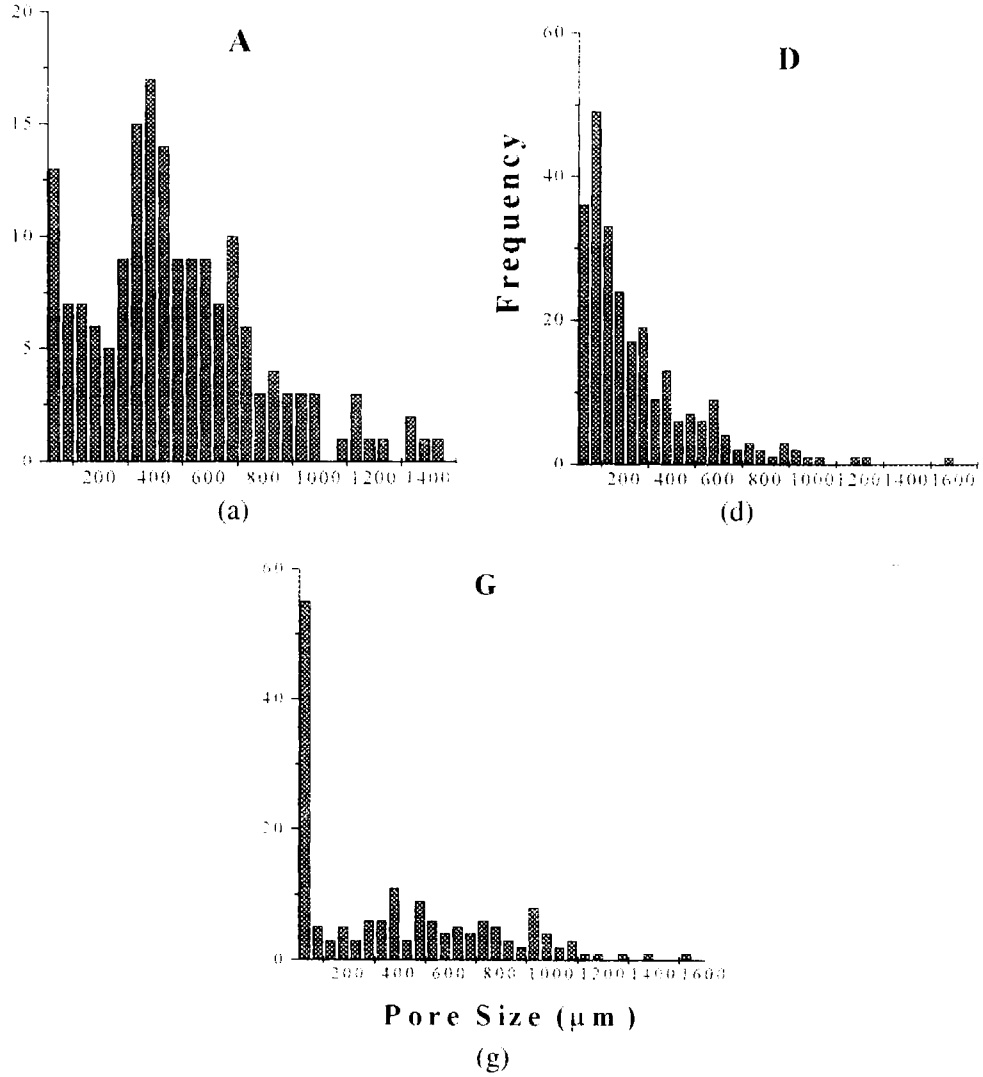


Figure 6. Pore size distribution of bone cements with MMA (A), 0.3 MAA (D), and 0.08 DEAEMA (G).

the formulation while high modulus bone cements were achieved by the addition of MAA. (c) Mechanical properties of HA-filled bone cements depend upon various factors such as matrix chemical composition, HA concentration, and variability of type of testing (i.e. tension, compression, or bending). (d) HA composites prepared solely with MMA and those with MAA fulfilled the minimum compressive strength and the minimum tensile strength required for bone cement use. However, they did not show the minimum bending strength necessary for optimal performance.

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