Acrylic bone cements incorporating polymeric active components derived from salicylic acid: curing parameters and properties

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A methacrylic monomer derived from salicylic acid, 5-hydroxy-2-methacrylamido benzoic acid, 5-HMA, was incorporated with 2-hydroxyethyl methacrylate, (HEMA), in different proportions to the liquid phase of classical bone cement formulations. The monomer 5-HMA shows the ability to form molecular complexes with calcium atoms in order to improve osteointegration in the application of bone cement formulations used for the fixation of joint prostheses such as knee and hip. Kinetic parameters, peak temperature and setting time of the bone cement formulations prepared were determined, obtaining lower peak temperature values when 5-HMA was incorporated, with respect to classical acrylic bone cements based on PMMA. Mechanical and thermal properties as well as surface energy values, have been determined for all cured bone cement formulations. © *1998 Kluwer Academic Publishers*

1. Introduction

Self-curing acrylic bone cements have been widely used in dentistry and orthopaedic surgery as filling agents and for the fixation of prostheses, due to their biostability and good adaptation [1–5]. They are generally obtained by free-radical polymerization of methyl methacrylate monomer (MMA) mixed with a solid phase containing beads of poly(methyl methacrylate) (PMMA) [3]. The polymerization is initiated in the presence of benzoyl peroxide (BPO) which is incorporated in the solid polymer phase. *N*,*N*-dimethyl-*p*-toluidine (DMT) is constituted in the liquid phase which acts as an activator of the reaction. The major function of acrylic bone cement is the stress distribution on the contact area between the bone and the prostheses, therefore their mechanical properties are very important in these applications. One of the major problems of these materials is the fixation into bony structure, so that the most frequent long-term complication is loosening of the prosthetic components, caused by both mechanical and biological factors. In this sense, some research groups have proposed the incorporation of biodegradable components to acrylic bone cement formulations such as carboxymethyl cellulose [6] in order to create a porous cement which could facilitate bone regeneration. Other authors have incorporated bone particles in acrylic bone cements promoting a decrease in the porous number but a better osteointegration [7–9]. Another component which has been added to acrylic bone cement formulations, is hydroxyapatite. It has been incorporated as microparticles, maintaining the mechanical properties, decreasing the maximum curing temperature and accelerating the bone tissue formation in the implant surroundings with respect to classical formulations of PMMA [10–14].

The present work is a study on curing parameters and the most important properties of acrylic bone cement formulations in which the liquid phase has been modified by the incorporation of methacrylic monomers, one derived from salicylic acid, 5-hydroxy-2-methacrylamido benzoic acid, 5-HMA, and 2-hydroxyethyl methacrylate (HEMA). HEMA was also incorporated on its own in order to carry out comparative studies with formulations in which 5-HMA was incorporated into the liquid phase with HEMA. The monomer 5-HMA has the ability to form molecular complexes with calcium atoms [15] and could facilitate osteointegration in the application of these materials.

2. Materials and methods

The experimental solid phase of acrylic bone cements was prepared from commercial PMMA beads obtained by suspension polymerization, kindly supplied

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TABLE I Setting parameters, cross-linked mass and residual monomer content of the acrylic bone cement formulations modified with HEMA and 5-HMA monomers in the liquid phase

Acrylic cement formula	MMA (wt %)	5-HMA (wt %)	HEMA (wt %)	t_{dough} (min)	t_{set} (min)	T_{max} (°C)	Residual monom. (%)	Cross-linked mass (%)
HEMA9	90.50	–	9	2.40	5.75	92	3.5	–
HEMA20	79.50	–	20	1.70	5.25	96	4.0	25.1
HEMA40	59.50	–	40	1.50	3.75	99	4.1	28.0
5-HMA2	88.25	2.25	9	1.60	6.10	89	2.0	–
5-HMA5	74.50	5.00	20	1.00	5.15	84	2.2	24.7
5-HMA10	49.50	10.00	40	1.00	5.00	77	4.4	28.0
PMMA[a]	99.50	–	–	1.75	6.50	86	1.9	–

[a]Control, classical bone cement formulation based on PMMA.

by Industrias Quirúrgicas de Levante. The morphological characteristics were average diameter $\bar{D} = 33.1$ μm, average molecular weight $\bar{M}_n = 64\,000$, polydispersity $\bar{M}_w/\bar{M}_n = 2.02$ and tacticity $\sigma = 0.262$. To the PMMA beads 1.25% (wt/wt) of benzoyl peroxide, BPO (Fluka AG), were added without further purification. The liquid phase of these formulations was prepared from MMA (Fluka AG) stabilized with 100 p.p.m monoethylether of hydroquinone used as-received, 5-HMA synthesized as described elsewhere [16] and HEMA (Fluka AG) which was washed with a $NaHCO_3$ aqueous solution, then washed with hexane, saturated with NaCl and finally washed with diethly ether to be distilled under reduced pressure. Table I shows the weight concentration of monomers present in the liquid phase, for six different formulations prepared. *N*,*N*-dimethyl-*p*-toluidine, (DMT, Merck) was added to the liquid phase, 0.5% (wt/wt) in all formulations, and was used as-received.

2.1. Setting parameters measurements

The preparation of the acrylic bone cement formulations was carried out following the traditional method used for classical bone cements. The activator, DMT, was mixed with the liquid phase (MMA, 5-HMA, HEMA) and the solution was kept at low temperature. The BPO was blended with the PMMA powder. A typical powder–liquid ratio of 2:1 was employed in all preparations. The variation with time of the temperature of the reacting mass was automatically registered using a thermocouple connected to a high-sensitivity thermotester in a Teflon mold designed to obtain significant results at 37 °C [17]. Time and temperature were registered from the moment the powder and liquid were mixed.

2.2. Spectroscopic analysis

Residual monomer content was determined by ^{1}H-NMR spectroscopy using a Varian XL 300 spectrometer. All samples were recorded in deuterated dimethyl sulfoxide DMSO-d_6 (5% wt/wt). The cross-linked mass per cent was determined by gravimetry after selective extraction with *N*,*N*,-dimethylformamide (DMF) as solvent.

2.3. Average molecular weights

Average molecular weights of cured bone cements were determined by GPC using dimethyl formamide (DMF) as eluent in a Waters apparatus equipped with an injector, model 7125, and RI detector Waters 410 differential refractometer. Three columns of μStyragel of 10^3, 10^2 and 50 nm, were used after calibration with PMMA standards supplied by Waters Associates having a narrow molecular weight distribution.

2.4. DMTA analysis

DMTA was carried out in the bending mode from 20–200 °C by means of DMTA MK III (specimen size, 40 mm × 10 mm × 1.5 mm; frequencies used 1, 10, 30 Hz; displacement 0.064 mm; heating rate 3 °C min^{-1}). Glass transition temperatures, T_g, of the cured cements were read off as the temperatures at which the loss factor passed through a maximum [18].

2.5. Tensile mechanical testing

Tensile testing of all specimens was carried out on an MTS Bionix 858 machine with a cell load of 25 kN and at crosshead speed of 1 mm min^{-1}. An extensometer was used to measure displacement. Specimens were prepared by placing the cement dough in Teflon molds and subsequently submitting them to a pressure of 1.4 MPa for approximately 20 min. The specimens then were placed at 60 °C to ensure complete polymerization. Their dimensions were made in accordance to ISO 527-1, and the average cross-section was 10 mm × 5 mm. A maximum of six specimens were tested for each batch. Wet experiments were carried out after immersion of specimens in 0.9% NaCl (wt/vol) aqueous solution at 37 °C for 30 d.

Water sorption studies were carried out on cured cement films of thickness 0.15–0.25 mm and on specimens prepared for tensile tests, immersed in NaCl 0.9% (wt/vol) aqueous solution at 37 °C. Films were weighed several times, previously drying the surface, until sorption equilibrium was attained after weighing three times without changing weight.

2.6. Contact angle measurements

The contact angle between liquid and solid surfaces was measured by means of a Contact Angle

Measuring System G 10 using the following procedure: a drop of a liquid was deposited on the surface to study. The liquids used for the experiments were distilled water and methylene iodide. The quantity of liquid was measured with a syringe monitored by a micrometric screw. The measurements were performed on films of the cured cements at least ten times to average the results.

3. Results and discussion

As is reflected in Table I, the methacrylic monomers 5-HMA and HEMA have been incorporated in the liquid phase with MMA in different weight per cent, as well as HEMA with MMA, to carry out comparative studies between these six formulations. The monomer HEMA has been added to these formulations to dissolve 5-HMA in the liquid phase (being insoluble in MMA solutions), and to increase the hydrophylic character of the formulations in order to absorb small quantities of physiological fluids and increase the cement volume to facilitate adaptation to the bone interface.

3.1. Setting parameters

ASTM specifications (F451-86) [19] were considered to determine the setting parameters of the new formulations which are exhibited in Table I, obtained as described in Section 2. All formulations with only MMA and HEMA in the liquid phase, have peak temperatures higher than the control. However, formulations containing 5-HMA, HEMA and MMA, provide a decrease in the peak temperature and an increase in the setting time with respect to the control based on PMMA, in which polymerization rate is lower and has higher peak temperature than the formulations 5-HMA5 and 5-HMA10. This effect of lowering peak temperature and increasing polymerization rate can be attributed to the lower dissolution of the hydrophobic PMMA beads in a more hydrophylic liquid phase with 5-HMA and HEMA monomers, causing a better heat dissipation in the exothermal polymerization reaction. Figure 1 shows the polymerization exotherms of the acrylic bone cements in which 5-HMA and HEMA have been incorporated to the liquid phase.

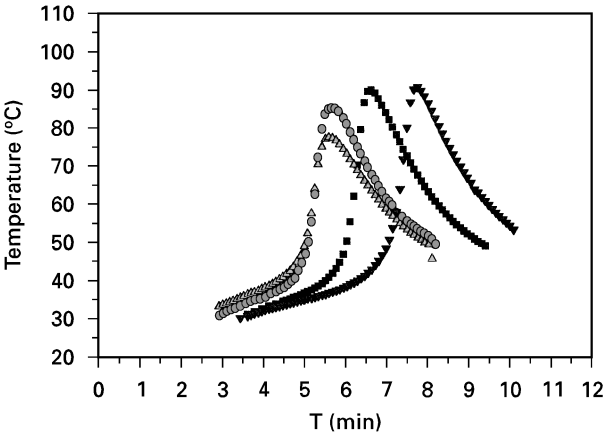

Figure 1 Variation of the temperature profile of the reaction mass with the cutting time for the polymerization of acrylic bone cement formulation modified with the incorporation of monomers 5-HMA and HEMA. [BPO] = 1.25% wt/wt [DMT] = 0.5% vol/vol. (■) 5-HMA2, (●) 5-HMA5, (△) 5-HMA10, (▼) PMMA.

3.2. Spectroscopic analysis

The residual monomer content of the prepared formulations was analyzed by ^{1}H-NMR considering the enlarged vinyl protons signals exhibited in Fig. 2 (5-HMA5 formulation), where it is seen clearly that the spectrum gives accurate information of the fraction of each one of the residual monomers incorporated into the formulation. This allows the comparative analysis of the relative reactivity of each one of the monomeric acrylic derivatives in the curing process of the bone cement. The integral of the signals of the corresponding protons can be determined, giving residual

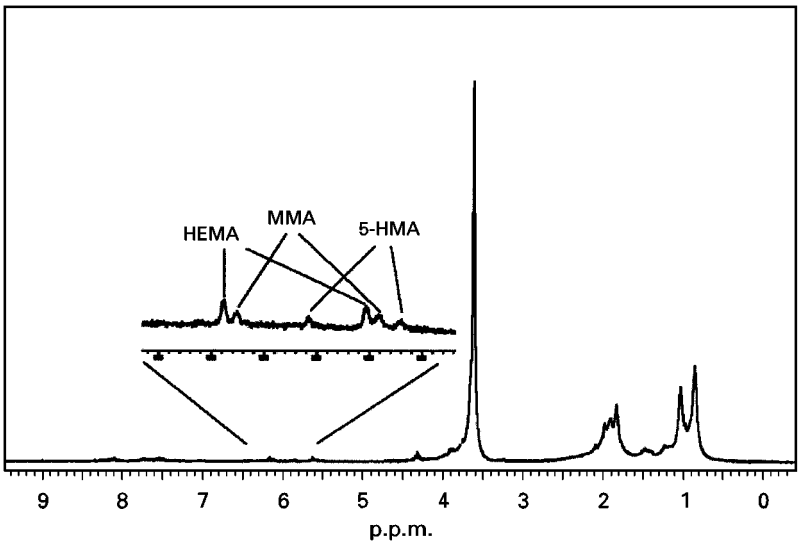

Figure 2 ^{1}H-NMR spectra of the 5-HMA5 acrylic bone cement formulation recorded in DMSO-d_6 solution. The enlarged area corresponds to vinyl protons of the monomers present in these formulations.

monomer percentages of 0.51 of 5-HMA, 0.62 of MMA and 1.14 of HEMA in the 5-HMA5 prepared formulation, which has a total residual monomer content of 2.27%. All formulations of residual monomer content are shown in Table I. It can be observed that, as the concentrations of monomers 5-HMA and HEMA increase, the percentage of residual monomer also increases upto 4% in some cases. This fact is mainly due to the different monomer reactivity in bulk radical polymerization giving rise to a terpolymer which has a higher polymerization rate as a result of the gel effect [20], as the 5-HMA and HEMA concentrations increase.

Some of the prepared formulations, 5-HMA5, 5-HMA10, HEMA20 and HEMA40, were partially insoluble in organic solvents such as DMF, DMSO and chloroform, obtaining cross-linked networks which swell in these solvents. The cross-linking of these formulations is attributed to the HEMA dimerization which gives rise to three-dimensional networks in free radical bulk polymerization [21]. The cross-linked mass percentage of the mentioned formulations was determined gravimetrically by placing samples of 10–15 mg in 2ml DMF under magnetic stirring at 70 °C over 2 d. The insoluble mass was filtered off, dried over P_2O_5 obtaining the cross-linking mass percentages shown in Table I.

3.3. Average molecular weights

Soluble and partially soluble in DMF formulations were analyzed by GPC, and molecular weights $\bar{M}_n$ and $\bar{M}_w$ as well as polydispersity (see Table II), were determined from their molecular distribution curves. As the concentration of the monomers 5-HMA and/or HEMA increases in the prepared formulation, the average molecular weight of the soluble fraction decreases with respect to classical formulations based on PMMA, as a consequence of the partially cross-linked formulations obtained at high concentration of these monomers.

3.4. DMTA analysis

DMTA of all cured samples was carried out. Fig. 3 shows the variation of storage modulus, E, and loss factor versus temperature for the prepared modified acrylic bone cements. It can be seen that E' shows a steep fall as the temperature is raised through T_g (α relaxation), which is usually most clearly identified by the position of the maximum in the tan δ plot. In all cases, the values of T_g increase with increasing the frequency of the experiment. All prepared formulations (see Table III) have higher T_g than PMMA bone cements ($T_g = 111\,^{\circ}C$ at 1 Hz [22]) when adding monomers 4-HMA and HEMA which have chemical groups capable of forming intra- and intermolecular hydrogen bonding, and also amide bonds and aromatic rings which confer major rigidity to the macromolecular chains. Partially cross-linked formulations also exhibit higher T_g due to segmental movement restriction promoted by the cross-linked points.

Taking into consideration an Arrhenius relationship between the α relaxation (T_g) and the frequency applied each DMTA experiment, the activation energy can be determined from the plots ln$f$ versus $1/T$ for each formulation

$$\ln f = \ln A - E_a/RT \quad (1)$$

where A is a constant, E_a is the activation energy, R is the universal gas constant and T the glass transition temperature. The slopes (E_a/R) gave the associated E_a of the glass transition temperatures and are represented in Table IV, obtaining values which are in accordance with classical formulations of PMMA being in the range of 200–300 kJ mol^{-1} [23].

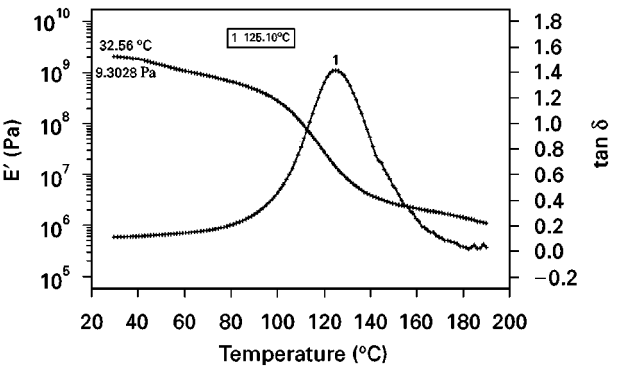

Figure 3 DMTA diagram of the HEMA20 acrylic bone cement formulation.

TABLE II Average molecular weights $\bar{M}_n$, $\bar{M}_w$ and polydispersity of bone cement formulations modified with incorporation of 5-HMA and HEMA

Formulation	$\bar{M}_n$ ($\times 10^3$)	$\bar{M}_w$ ($\times 10^3$)	Polydispersity $\bar{M}_n/\bar{M}_w$
HEMA9	55	127	2.3
HEMA20	44	58	1.3
HEMA40	36	60	1.6
5-HMA2	69	127	1.8
5-HMA5	70	92	1.3
5-HMA10	59	85	1.4
PMMA	69	169	2.4

TABLE III Glass transition temperatures of the prepared acrylic bone cement formulations obtained at different frequencies (1, 10, 30 Hz) by DMTA analysis. Activation energy values associated with the α relaxatioin of the systems, calculated from ln$f$ values $1/T$ Arrehenius plot

Formulation	T_g°C at			Activation energy (kJ mol^{-1})
	1 Hz	10 Hz	30 Hz	
5-HMA2	116	132	138	225
5-HMA5	120	129	136	287
5-HMA10	118	128	141	210
HEMA9	116	127	137	221
HEMA20	116	125	139	287
HEMA40	117	133	138	210

TABLE IV Mechanical tensile properties of the prepared bone cement formulations with monomers 5-HMA and HEMA added to the liquid phase. Ultimate tensile strength, σ, strain to failure, ε, and elastic modulus values E_t

Bone cement	Dry			Wet		
	σ(MPa)	ε(%)	E_t(GPa)	σ(MPA)	ε(%)	E_t(GPa)
5-HMA2	51.0 ± 2.5	2.4 ± 0.1	2.46 ± 0.10	40.0 ± 3.7	4.7 ± 0.1	2.52 ± 0.11
5-HMA5	54.8 ± 3.1	2.4 ± 0.2	2.79 ± 0.14	31.6 ± 4.6	4.7 ± 0.2	2.82 ± 0.32
5-HMA10	62.3 ± 3.4	2.3 ± 0.2	2.92 ± 0.12	28.6 ± 0.9	5.6 ± 0.2	3.10 ± 0.30
HEMA9	50.1 ± 2.0	2.7 ± 0.3	2.39 ± 0.60	36.8 ± 0.4	3.8 ± 0.4	2.42 ± 0.15
HEMA20	52.1 ± 3.5	2.4 ± 0.2	2.50 ± 0.11	40.4 ± 6.5	3.9 ± 0.8	2.53 ± 0.12
HEMA40	60.2 ± 4.2	2.0 ± 0.1	2.83 ± 0.23	36.6 ± 4.6	4.4 ± 0.9	2.93 ± 0.31
PMMA	50.1 ± 1.9	3.1 ± 0.2	2.25 ± 0.13	48.2 ± 3.2	2.6 ± 0.3	2.42 ± 0.16

3.5. Tensile mechanical testing

Mechanical properties of the prepared formulations were evaluated by performing tensile tests. Owing to the hydrophylic character of monomers 5-HMA and HEMA, prior to testing, the specimens were immersed in solutions of 0.9% NaCl at 37 °C for 1 wk in order to determine the influence of water acting as a plasticizer on the mechanical properties. As can be observed in Fig. 4, the swollen films presented a percentage hydration degree ranging between 3.6% and 5.5%, this parameter being defined by the percentage relationship between the weight of the water uptake and the weight of the wet sample at equilibrium.

Ultimate tensile strength, σ, of dry specimens (see Table IV) are higher than that of PMMA bone cements, reaching the highest value of 62 MPa for the 5-HMA10 prepared formulation. The same type of behavior is observed in the elastic modulus. E_i, whereas strain to failure values, ε, decrease as the concentration of monomers 5-HMA and HEMA increases. Incorporation of these monomers into acrylic bone cement formulations confers some elastic character increasing the ultimate tensile strength and elastic modulus values as a consequence of the hydrogen-bonding interactions and cross-linked points.

Tensile strength testing of immersed specimens shows a decrease in ultimate tensile strength, the richest formulations in 5-HMA and HEMA having the poorest values: 28.6 MPa in the case of 5-HMA10. On the other hand, strain to failure, ε, increases in the formulations with respect to dry and PMMA samples, as a consequence of the water plasticization effect. Elastic modulus smoothly increases in all formulations and is in the same range of dry specimens values.

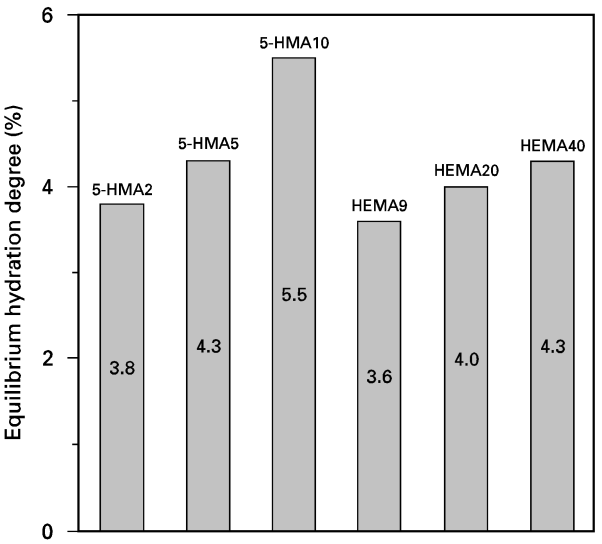

Figure 4 Equilibrium hydration degree of the acrylic bone cement formulations modified with the incorporation of 5-HMA and HEMA monomers.

3.6. Contact angle measurements

Interfacial characteristics of the prepared acrylic bone cement formulations in contact with hydrated media are important in predicting interactions of this kind of material with the surrounding tissues when applied in this type of biomedical application. These parameters are determined, in general, by means of wetting experiments, the sessile drop technique being one of the most usual. In this work, this technique was applied in air and at room temperature to determine the surface energy of the modified acrylic bone cement formulations. The contribution of the dispersion and polar interactions to the surface energy was calculated by considering that the intermolecular attraction which causes surface energy, γ, results from a variety of intermolecular forces according to an additive rule. Most of these forces are functions of the specific chemical nature of a particular material, and the surface energy can be compiled as γ^p (polar interactions), taking into consideration that dispersion forces (γ^d) are always present in all systems, independently of their chemical nature. Thus, the surface energy of every system solid or liquid, can be described as

$$\gamma = \gamma^d + \gamma^p \quad (2)$$

The Fowkes [24] equation is based on the well-known Young–Dupre equation [25] for the contact angle of a liquid on a solid

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta \quad (3)$$

where γ_S is the free interfacial energy of the solid, γ_L is the free interfacial energy of the liquid in equilibrium with its vapor, γ_{SL} is the free interfacial energy of the solid–liquid, and θ is the contact angle. Thus, the

TABLE V Contact angle values measured in air at room temperature. Surface energy values and the respective polar and dispersive contributions (γ_s^p, γ_s^d) to the total surface energy of all formulations prepared. SD = Standard deviation

Bone Cement	Contact angle, θ water (SD)	Contact angle, θ CH_2I_2 (SD)	γ_s (mN/m)	γ_s^d (mN/m)	γ_a^p (nN/m)
5-HMA2	73.7 (3.5)	46.1 (2.3)	43.1	36.4	6.7
5-HMA5	68.0 (1.8)	46.1 (3.3)	45.2	36.4	9.4
5-HMA10	70.0 (2.8)	53.0 (2.8)	42.2	32.6	9.7
HEMA9	71.5 (2.1)	44.7 (2.3)	44.6	37.2	7.4
HEMA20	69.7 (1.9)	48.0 (3.2)	44.8	35.4	9.4
HEMA40	66.3 (4.6)	51.7 (2.7)	44.7	33.3	11.4
PMMA*	80.0	40.0	40.0	36.0	4.0
PHEMA	50.0 (2.7)	38.0 (3.1)	58.4	40.3	18.1
P(5-HMA)	55.0 (3.2)	38.0 (2.6)	55.5	40.6	14.9

*Reference 26

dispersive and polar components of a solid can be determined using liquids with different polarity, such as water and methylene iodide. Owens and Wendt considered that this method is well applicable to polymer surface characterization, and they obtained the surface energy values of some polymeric systems [26].

Table V gives the surface energy values of the prepared acrylic bone cement formulations, as well as those the homopolymers PMMA, PHEMA and P5-HMA. It can be observed that the modified bone cement formulations have higher surface energy values with respect to PMMA bone cements as a result of the contribution of both polar and dispersive components, with the exception of formulations 5-HMA10 and HEMA40, in which the dispersive surface energy contribution is compensated by a considerable increase in the polar component of the surface energy. The polar contribution is higher in all formulations with respect to PMMA bone cements due to the presence of polar and hydrophylic 5-HMA and HEMA monomers. Thus, the amine and carboxylic groups of 5-HMA, as well as the hydroxyl groups of both 5-HMA and HEMA monomers, are able to form hydrogen bonding interactions between these functional groups and with the carbonyl ester group of MMA, either intra- or intermolecularly. The contribution of these functional groups to increase the surface energy was analyzed with respect to PMMA formulations, taking into account the dispersive and the polar components of the corresponding homopolymers by means of an additive rule

$$\gamma^d = \gamma_5^d f(5) + \gamma_{HE}^d f(HE) + \gamma_M^d f(M) \quad (4)$$

$$\gamma^p = \gamma_5^p f(5) + \gamma_{HE}^p f(HE) + \gamma_M^p f(M) \quad (5)$$

where γ_5^d, γ_{HE}^d and γ_M^d are the dispersive components of the surface energy of the homopolymers P5-HMA, PHEMA and PMMA respectively, and γ^p are the polar components of the surface energy of the corresponding homopolymers. $f(5)$, $f(HE)$ and $f(H)$ are the corresponding monomer molar fraction in each formulation. Fig. 5 shows the graphical representations of the surface energies versus the 5-HMA + HEMA and HEMA molar fraction, respectively, for the modified bone cement formulations. The lines correspond to the theoretical polar, dispersive and total surface energy calculated from the above equations, and the points are the experimental data obtained by contact angle measurements. In all cases, the dispersive

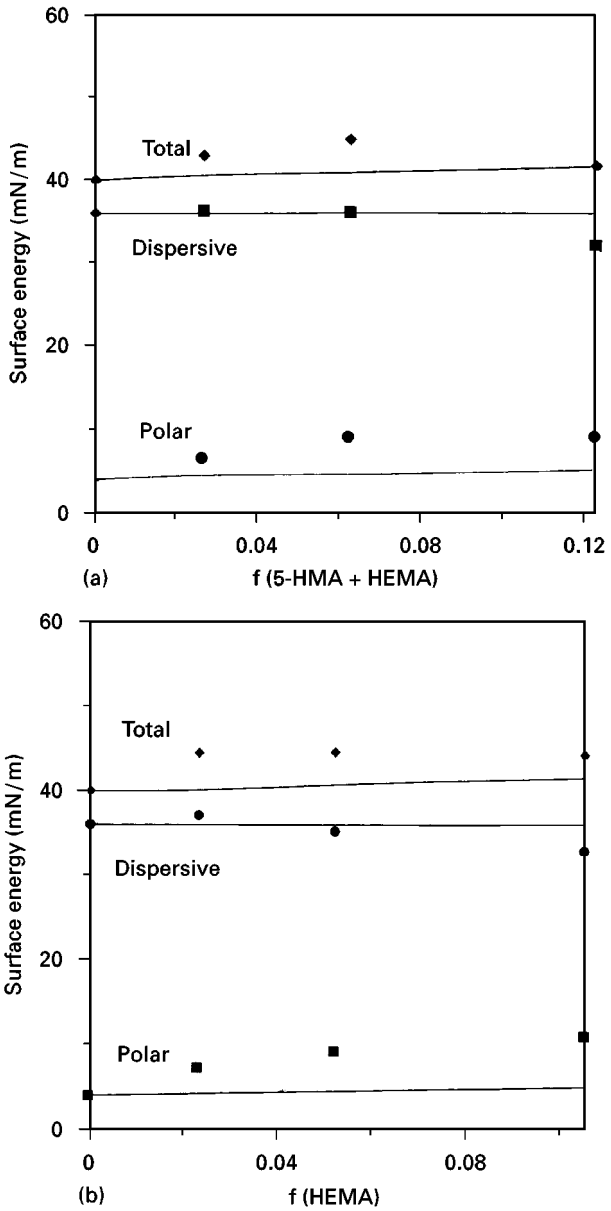

Figure 5 Representation of the dispersive and polar components of the total surface energy of the modified bone cements as a function of the molar fraction of the monomers 5-HMA and (a) HEMA and (b) HEMA

contribution of the surface energy has an additive character, and decreases as the molar fraction of 5-HMA and HEMA increases, whereas the experimental polar component is slightly higher than the theoretical one, and increases with increasing hydrophilic monomers molar fraction. For the 5-HMA10 cement, the experimental surface energy approaches the theoretical one as a consequence of the polar and dispersive components compensation. The deviation between theoretical and experimental results in the polar surface energy reveals a higher hydrophylic character of the modified bone cements than that expected, which means that the modification introduced provided materials of improved biocompatibility.

4. Conclusion

The introduction of polar acrylic monomers such as 5-HMA and HEMA as components of the liquid phase of classical acrylic bone cement formulation provides slightly cross-linked polymeric systems with interesting mechanical properties and changes in the polar character of the surface, with the corresponding effects on the interphase. In addition, the incorporation of the acrylic derivative of salicylic acid, 5-HMA provides the possibility of intermolecular complexes with salts containing calcium ions, as well as the potential pharmacological effect (antiinflammatory and analgesic) associated with the salicylic residue of the acrylic components. The curing parameters (dough time, peak temperature, and setting time) improve the parameters of the classical formulations based on methyl methacrylate monomer and poly (methyl methacrylate) beads.

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