

# PMMA/Ca<sup>2+</sup> BONE CEMENTS. PART I. PHYSICO CHEMICAL AND THERMOANALYTICAL CHARACTERIZATION

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**Abstract**— Acrylic bone cements of poly (methyl methacrylate) (PMMA) have been used for about 40 years to fix artificial prosthesis to bone structure. The objective of this study was to evaluate the thermo analytical properties such as setting time, peak temperature and polymerization enthalpy of PMMA/Ca<sup>2+</sup> bone cements, besides of their physico chemical characterization. Amounts of mineral component were supplied like a mixture of hydroxyapatite (Coralina<sup>®</sup> HAP-200 or HA 3) and calcium carbonate (aragonite from natural sources). Setting time, peak temperature and polymerization enthalpy were performed in all the formulations guiding by a fractional experimental design. The physico chemical characterization showed an expected pattern from the raw materials and matrix composition. The residual monomers were evaluated through <sup>1</sup>H NMR spectroscopy and showed a low value (< 1 mol %). Thermo analytical parameters were determined. The setting time obtained ranged between 3.6 and 8.0 minutes and the peak temperature varied between 62 and 110 °C. Polymerization enthalpy was less than reported for the monomer and the obtained value swinging between 1 and 8 kJ/mol.

**Keywords** — PMMA cements, hydroxyapatite, calcium carbonate, absorption, solubility.

## I. INTRODUCTION

The human skeleton constitutes a novel element in the evolutionary development for its regeneration capacity and the physiologic evolution of tissues formed in embryonic state. Novel synthetic and natural materials have been elaborated to improve regeneration and restoration capacities. The biomaterials before mentioned can be biodegradable and not biodegradable (Bowen *et al.*, 1978).

Bone cements are materials employed in orthopaedic surgery and dental applications for fixation of joints prosthesis. They act as a load distributor between the artificial implant and the bone, as well as filling self-curing materials for bone and dental cavities (Espigares *et al.*, 2002). Since 1960 PMMA has been used in this field (Charnley, 1970), due to its biostability and good mechanical properties (Cameron *et al.*, 1974).

Acrylic bone cements are composed of two parts: A liquid part: formed by methyl methacrylate (MMA), *N,N*-dimethyl-*p*-toluidine (DMpT, as activator) and hydroquinone (HQ, as inhibitor) and a solid part composed by: acrylic beads, usually PMMA beads or their copolymers, benzoyl peroxide (BPO) to initiate the polymerization reaction and frequently they also include a radiopaque agent such as barium sulfate, or zirconium oxide (Morejón *et al.*, 2005).

There are some reports about the influence of the chemical composition, morphology, particle size distribution and molecular weight in the final properties of the bone cements (Brauer *et al.*, 1986 and Pascual *et al.*, 1996). The study of new formulations of cements with better properties is interesting because of its scientific and practical interest.

The setting time of the acrylic bone cements should be between 5-15 min, according to the ASTM or 3-15 min considering the ISO international standards (ASTM, 1999; and ISO, 2002). The polymerization reaction of acrylic bone cements is exothermic and the calculated heat of polymerization for MMA is 54.4 kJ/mol (Meyer *et al.*, 1973). The thermal effects of the polymerization are reflected in a significant temperature peak, ranging between (80-124) °C in the cements (Saha and Pal, 1984) and between (48-105) °C at the bone/cement interface (Brauer *et al.*, 1986). It has been reported that the polymerization temperature of the acrylic bone cements can cause necrosis of the tissues in the surrounding areas of the prosthesis. The international standards established (90±5)°C as a peak temperature in order to minimize the thermal damage of adjacent tissues. The thermal damage in the bone can affect the durability of the implant, because it induces bone reabsorption and produces aseptic loosening of the prosthesis (Morejón *et al.*, 2005).

In this work we analyze the influence of the inorganic load additions such as hydroxyapatite (Coralina<sup>®</sup> HAP-200 or HA 3) and calcium carbonate aragonite (natural source) on the physico chemical and thermo analytical properties (setting time, peak temperature) of the PMMA/Ca<sup>2+</sup> cements. An experimental design and a discussion of the possibility of uses of the PMMA/Ca<sup>2+</sup> bone cements as acrylic resin cement for the orthopedic restoration is carried out.

## II. MATERIALS AND METHODS

### A. Preparation of bone cements

The formulations of bone cements were prepared from a solid and a liquid phase by free radical polymerization. The solid phase was constituted by a commercial PMMA in the form of beads with 1.2 % of BPO as initiator (Autocril, FERSOdental, Cuba), finely grounded and two kinds of hydroxyapatites. The first, named Coralina® HAP-200 (González *et al.*, 1993), was obtained through a flow pass of NH<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> over a mill coral mass and the second, named HA 3 (González and Melo, 1996), from a reaction among CaCO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> under controlled conditions. Both were crushed, milled and particle sized classified and subsequently checked by Fourier transformed infrared spectroscopy (FTIR) and x-ray diffractometry (XRD). Besides, in some formulations according to the experimental design was added calcium carbonate (aragonite from *Porites porites* coral) previously crushed, milled and particle sized classified. Table 1 showed a summary of raw materials characterization.

Methyl methacrylate monomer (Autocril, FERSOdental, Cuba) constituted the liquid phase with 0.4 % of DMpT as activator, was used without further purification. The solid/liquid ratio in all cases was 2:1.

Eight different formulations of the bone cement were developed according to the experimental design 2<sup>4-1</sup> = 2<sup>3</sup> varying load content (A), particle size (B), hydroxyapatite type (C) and the addition or not of calcium carbonate (D). The experimental planning is shown in the Table 2 where D was selected as alias variable (D = A\*B\*C)

The preparation of specimens for subsequent test was carried out following the traditional method. Both phases were mixed and stirred manually until the mixture became paste with a high viscosity.

Table 1. Characterization summary of raw materials

Material	Range (μm)	$\bar{\Phi}$ (μm)	R <sub>Ca/P</sub>
PMMA	---	60 ± 20	---
HAP-200	56-80	66 ± 7	1.69
	100-200	170 ± 30	
HA 3	56-80	67 ± 6	1.71
	100-200	120 ± 20	
CaCO <sub>3</sub>	56-80	67 ± 7	---
	100-200	150 ± 30	

Table 2. Experimental planning

Level	A	B	C	D
-	10 %	56-80	HAP-200	NO
+	30 %	100-200	HA 3	YES
Experiments				
C1	-	-	-	-
C2	+	-	-	+
C3	-	+	-	+
C4	+	+	-	-
C5	-	-	+	+
C6	+	-	+	-
C7	-	+	+	-
C8	+	+	+	+

### B. Physic chemical characterization

The raw materials and the self-cured bone cements were characterized by Fourier transformed infrared spectroscopy (FTIR), x-ray diffractometry (XRD) and proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR).

FTIR spectra were recorded in a Brüker Vector 22 (Germany) in KBr pellets containing 300 mg of samples. The spectra were measured in the wavelength interval from 500 to 4000 cm<sup>-1</sup> in order to study the possible interactions of the main functional groups of all chemical structures present in the sample such as polymers and loads.

XRD patterns was registered at HZG 4 diffractometer (Carl Zeiss, Jena, Germany) from 20 to 60 degrees at 2θ with the K<sub>α</sub>Cu, 1° pass and 3 s of count time. The patterns were processed using a PCPDFWin 2.01 from International Centre for Diffraction Data to analyze the changes in the crystalline structure of the loads after the polymerization process.

In both cases it was previously required samples to be crushed, milled and particle sized classified under 90 μm.

In order to determine the residual monomer content the samples were previously filtered their loads and then analyzed by <sup>1</sup>H NMR in 60 mg/mL of deuterated chloroform solutions. The <sup>1</sup>H spectra were recorded in a Brüker AC 250 F at 250 MHz.

### C. Thermoanalytical studies

A Mettler TA-3000, DSC-30 thermal analysis system was used to perform measurements, in a dynamic program with heat speed of 5°C/min (Peón *et al.*, 2004 a). A portion of solid and liquid parts were mixed according to ratio established for the study and approximately thirty milligrams of the mixture were placed on the aluminum sample pan. The specimens were self-polymerized in a DSC apparatus and the heat output was determined.

The temperature changes, which occurred at the setting reaction, were automatically measured with a precision of ±0.1°C while the room temperature and the relative humidity were kept at (23±1)°C and (48±1)%, respectively.

$$T_{\text{set}} = \frac{T_{\text{max}} + T_{\text{env}}}{2} \quad (1)$$

The temperature was measured every 10 seconds in order to obtain a graphic as shown at Fig. 1. The setting time was calculated as the time at which the temperature reaches the value T<sub>set</sub>, according to the Eq. 1. Five specimens for each composition were prepared and subjected to thermal tests.

## III. RESULTS AND DISCUSSION

### A. Characterization of raw materials

Morphologic analyses of the PMMA beads showed that the particles were spherical with an unimodal normal distribution as we can see at Table 1 and Fig. 2 (Morejón *et al.*, 2005).

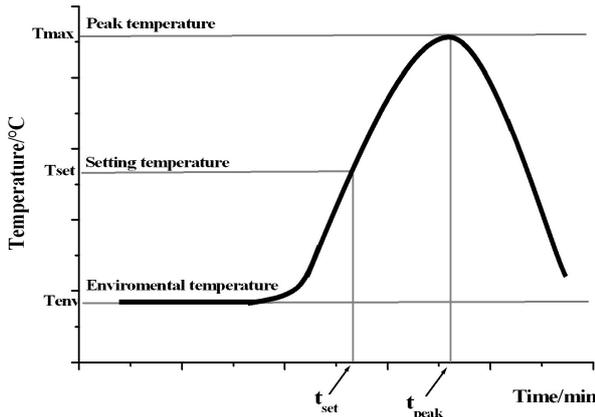


Figure 1. - T vs t diagrams for thermo analytical studies

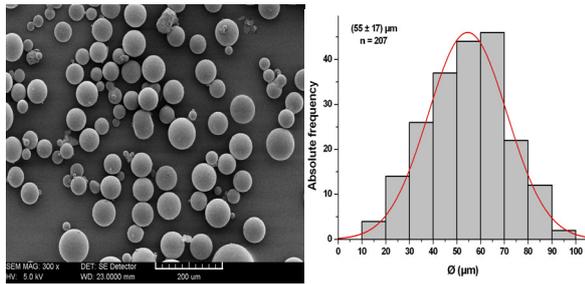


Figure 2. PMMA micrograph and particle size distribution

In the case of loads, HAP-200, HA 3 and calcium carbonate, the average range was limited by a size distribution of an experimental design as seen at Table 1.

But, as we can see at Fig. 3, the (-) level of the experimental planning, it means, the (56-80) µm range present a classic normal particle size distribution with coincidence of major frequencies and maximum value of Gaussian (similar to PMMA). In both cases, it's a product of the technological procedure to obtain the lowest range of a particle great size by crushing, milling and distribution. The same behavior showed both ranges in case of calcium carbonate, especially remarkable for the major range (+ level).

In the HAP-200, the (100-200) µm range showed a displacement to right of the frequencies and the unimodal normal distribution, but most remarkable to the frequencies. They were well-defined the differences between the Gaussian and the correspondent frequencies; perhaps due to the HAP-200 raw material is of the natural coral structure. In contrast, the HA 3 was obtained by a typical neutralization reaction in aqueous phase, which improve the possibility of interaction between particles and reduction of the sizes.

**B. Physical and chemical characterization**

*FTIR results*

In general, all the bone cements present the same aspect without changes in the position of the main functional groups, and small changes at intensities due to the composition of the bone cements formulations.

Figure 4 shows a FTIR spectrum of C5 bone cement formulation. From left to right it can be observed at 3550 cm<sup>-1</sup> the main vibration of structural hydroxyl corresponding to hydroxyapatite overlapped for a wide

band at 3440 cm<sup>-1</sup> assigned to OH from absorption of water due to a calcium carbonate and hydroxyapatite preparation process. At 2964 cm<sup>-1</sup> appear the main vibration correspondent to Csp<sup>3</sup> due to the polymeric contribution.

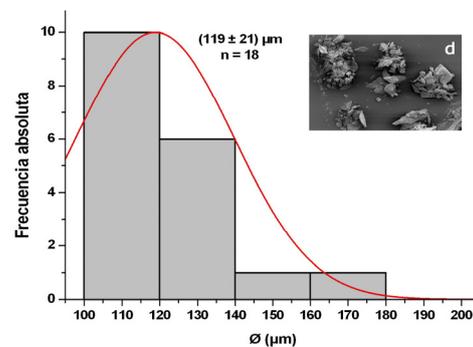
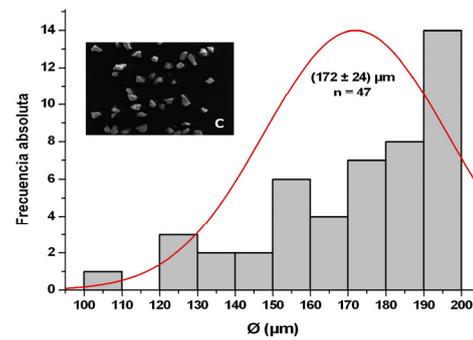
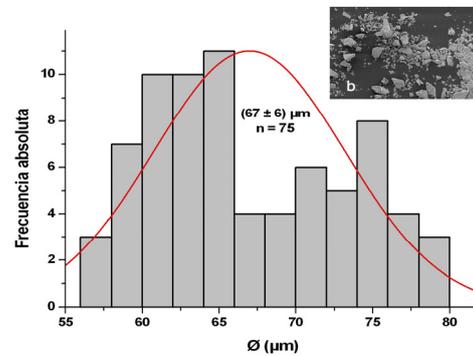
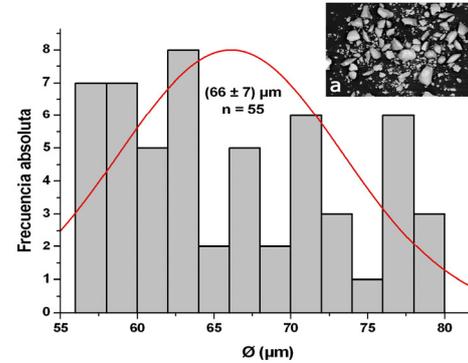


Figure 3. Hydroxyapatite micrographs and particle size distribution: a → HAP-200 (56-80), b → HA 3 (56-80), c → HAP-200 (100-200) and d → HA 3 (100-200).

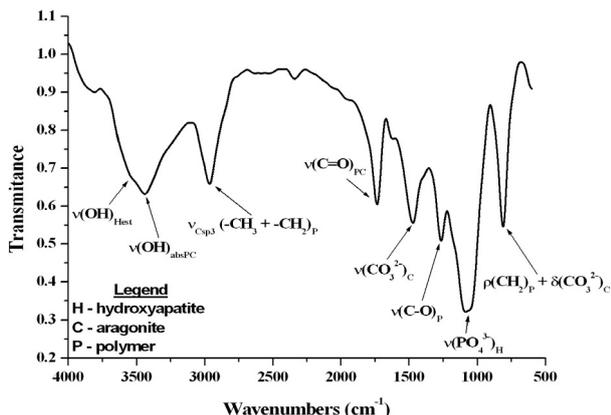


Figure 4. FTIR spectrum of C5 bone cement.

The zone between 1000-2000  $\text{cm}^{-1}$ , so called “mark zone”, have been interesting because it shows the main vibrations corresponding to the loads (hydroxyapatite and calcium carbonate) and to the main functional groups of the polymers which can be overlapping each other.

The carbonylic band, originally at 1760  $\text{cm}^{-1}$  in the polymer, appears at 1730  $\text{cm}^{-1}$ , due to a double contribution of polymer and calcium carbonate. The main vibration of carbonate, usually a symmetric double band at 1420-1450  $\text{cm}^{-1}$ , is showed as a widening and overlapping band (1470  $\text{cm}^{-1}$ ) due to small content of aragonite, into a wider band centered at 1084  $\text{cm}^{-1}$  which includes the vibration corresponding to C-O bond from the polymer at 1263  $\text{cm}^{-1}$ . This great and widen band at 1084  $\text{cm}^{-1}$  corresponds to the asymmetric double band of phosphate groups of hydroxyapatite, so called  $\nu_3^{\text{as}}$  (Fowler *et al.*, 1974).

Figure 5 shows combined FTIR spectra of three of the bone cements formulations. An increment of load (C1<C6<C2) induce changes in the intensities related to the hydroxyls and in the zone around 1000  $\text{cm}^{-1}$  in which appear the main signals of phosphate groups, carbonate and polymer trace. When it refers to C1 (10%) and C6 (30%) is only hydroxyapatite and C2 refers to 30% of hydroxyapatite plus 30 % of calcium carbonate, that is 60%.

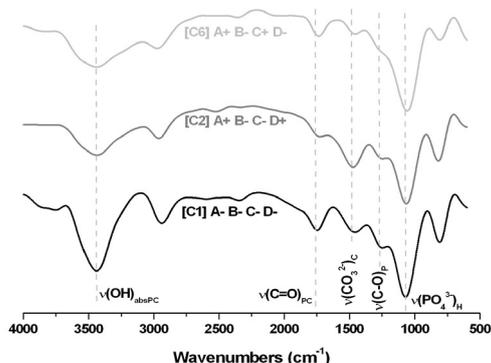


Figure 5. FTIR spectra of C1, C2 and C6 bone cements (H = hydroxyapatite, C = aragonite and P = polymer).

Comparing C1 and C6, it is observed a decrease of signal intensity at 1263  $\text{cm}^{-1}$  due to an increment of the load. It could be appreciate as a decrease of the polymer content and the subsequent polymer contribution to the  $\nu(\text{C-O})$ . In the same way a reduction of the intensity of the band at 1470  $\text{cm}^{-1}$  is observed due to its dependence on the polymer trace contribution and not on the carbonate groups. The same explanation justified the behavior in the hydroxyls zone, around 3500  $\text{cm}^{-1}$ .

But if they are comparing C2 and C6, where the hydroxyapatite type and the incorporation or not of the calcium carbonate vary, it is not observed an appreciable change because the main bands of the bone cements are overlapping at the hydroxyapatites and calcium carbonate fundamental vibration zone. The alternation of the hydroxyapatite type neither generated any change in position nor intensity of the spectra. It causes change at morphological level but not structural (functional groups). It is remarkable a little increment of the band intensities at 1470 and 810  $\text{cm}^{-1}$  in C2 due to the inclusion of carbonate (Pouchert, 1985).

*XRD results*

As FTIR studies, all the bone cements present the same aspect without changes in the peak positions, and small changes at broad of the peaks due to the composition of the bone cement formulation. Figure 6 shows a XRD spectrum of C4 bone cement formulation as example.

The XRD analysis of all bone cement formulations, showed a pattern similar to hydroxyapatite, even in angular positions as intensities. Table 3 shows the comparison between 9-432 ASTM card (ICDD, 1998) corresponding to synthetic hydroxyapatite and C4 bone cement as it was observed above. Notice the very little value of percent deviation.

Figure 7 shows the patterns of C1, C2 and C6 samples. Similar to FTIR results, the components variation do not provoke any representative changes respect pure substances patterns (HAP-200, HA 3 and calcium carbonate) while keeping the accurately intensities ratio.

When analyzing C1 and C6 bone cements where they are modified the hydroxyapatite type (C) and load content (A), it's not observed any appreciable change at the original positions of the hydroxyapatite. In fact, the deviation percent was less than 0.15 % respect to the

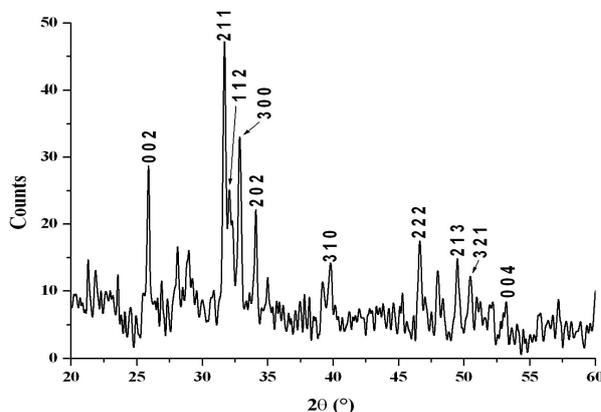


Figure 6. XRD spectrum of C4 bone cement

Table 3. 9-432 ASTM card vs C4 bone cement

h k l	2 $\theta$ (°) ICDD	2 $\theta$ (°) C4	pd (%)
0 0 2	25.879	25.901	0.085
2 1 1	31.773	31.770	0.009
1 1 2	32.196	32.301	0.325
3 0 0	32.902	32.900	0.006
2 0 2	34.048	34.097	0.144
3 1 0	39.818	39.804	0.035
2 2 2	46.711	46.599	0.240
2 1 3	49.468	49.501	0.067
3 2 1	50.493	50.507	0.028
0 0 4	53.143	53.200	0.107

pd = percent deviation

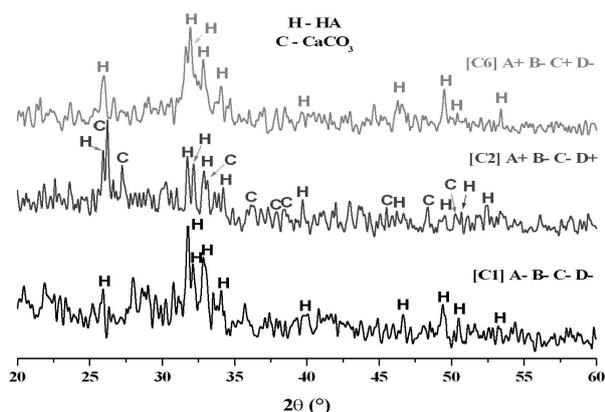


Figure 7. XRD patterns of C1, C2 and C6 bone cements

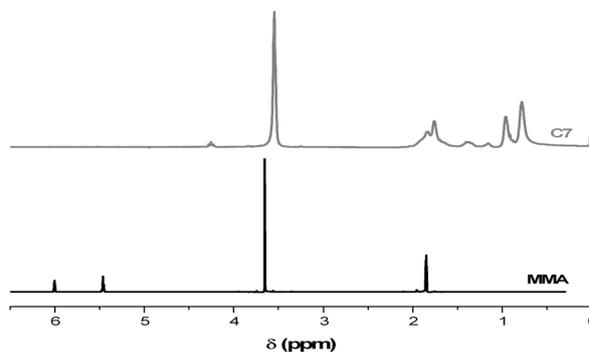
ASTM 9-432 and the increment of the load did not reflect the position but the intensities. The rest of the peaks could be assigned to the combination of the characteristic noise of the equipment and the polymeric contribution because of its amorphous phase.

The analysis of C2 formulation showed a characteristic behavior. The increment of load, 60% = 30% HAP-200 + 30 % CaCO<sub>3</sub>, accurately indicated the contribution of crystalline inorganic materials to the pattern of bone cement. Comparing with C1, for example, C2 showed the peaks corresponding to the calcium carbonate contributions besides hydroxyapatite. C2 patterns peaks wide at the position (50° in 2 $\theta$ ) where appear significant signals of loads, hydroxyapatite and calcium carbonate, but do not cause crystalline loss (Peón *et al.*, 2004 b). C6 showed a peak broadening in all the pattern respect to C1, because the HAP-200 (C1) was obtained by hydrothermal treatment of coral structures (González *et al.*, 1993) and the HA 3 (C6) was obtained by means of neutralization reaction at liquid phase (González and Melo, 1996).

#### <sup>1</sup>H NMR results

The self cured bone cements were characterized by <sup>1</sup>H NMR spectroscopy as it can be observed at Fig. 8. The assignments of signals, having different intensity depend on the bone cements compositions and correspond to the organic functional groups.

In general, the developed cements do not present the signal assigned to the protons coupled to vinyl double bond, which can be observed at the bottom of Fig. 8, in

Figure 8. <sup>1</sup>H NMR spectra of MMA and C7 bone cementTable 4. Assignments of <sup>1</sup>H NMR

Assignment	$\delta$ (ppm)		
	MMA pattern	Autocril MMA liq	C7
H from C=C	6.098	6.10	0.78
H from C=C	5.554	5.50	0.97
-O-CH <sub>3</sub>	3.752	3.65	3.55
-CH <sub>2</sub>	1.946	1.85	1.81

a MMA pattern from Autocril (liquid phase of the cements).

The signals corresponding to this protons appears at 0.78 and 0.97 ppm, (top Fig. 8, C7 formulation, Table 4) and not after 5 ppm which it should be if cement does not setting (bottom, Fig. 8).

The level of the residual monomer was determined by this technique, being lower than the detection threshold of it, *i.e.* < 1 mol % respect to the whole formulation (Espigares *et al.*, 2002).

#### C. Thermo analytical characterization

Curing of the acrylic cement is a complex process because the contact between the liquid and the solid part marks the onset of several physical and chemical events that take place simultaneously. The solvation of the polymeric beads by the monomer dissolution of the free radical initiator, diffusion from the liquid to the solid phase and monomer evaporation from the mixture are some of the physical events occurs (Lautenschlager *et al.*, 1987). The most important chemical process is the free radical polymerization of the MMA. If exist inhibitors, after their consumption, polymerization reactions starts, the monomer is rapidly consumed by the propagation rate and the viscosity increases, producing an increment in reaction rate and temperature because of the so called "gel effect" (O'dian, 1991).

#### Setting time

The hardening (setting) of the mixed mass, with the corresponding heating of the curing composite is due to the polymerization process. The setting time gives a clear idea of the working time, the dough time or the time during which the polymerizing mixture can be manipulated and applied without rheological problems (Pascual *et al.*, 1996).

The data collected at Fig. 9 show that there is an expected influence of the monomeric composition and interesting influence by adding or not calcium carbonate and hydroxyapatite type.

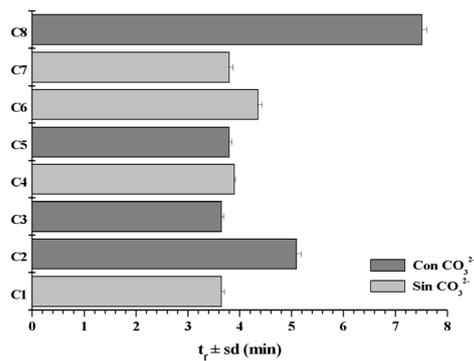


Figure 9. Setting time of the bone cements.

In fact, the setting time was very homogeneous despite the monomeric composition and the other variables, although the statistical differences were relevant ( $\alpha=0.05$ ). This can be explained for the small range of the independent variables which do not induce a great range in the response variable as we can see at Eq. 2 ( $R^2 = 85.40\%$ ).

$$ts = 4.5 + 0.7 A + 0.4 C + 0.5 D + 0.5 B \cdot C \quad (2)$$

The specific cases of the C2 and C8 bone cements can be attributed to 60 % of load. The great content of hydroxyapatite and calcium carbonate provoke a more difficult way to polymerize the mixture and in consequence, an increase of the setting time (Pascual *et al.*, 1996). The response surface (Fig. 10) illustrated the combined influence from two of the most important variables, load and hydroxyapatite type on setting time.

#### Peak temperature

It is recognized that if temperature of the mass rises to values near to the boiling point of the MMA monomer (100.3°C at standard pressure), the vaporization of MMA molecules could give rise to the appearance of voids inside the cured system. In this case a large number of very small spherical pores are distributed randomly in the cured specimen (Lautenschlager *et al.*, 1987).

From Fig. 11, some aspects should stand out. There is not significant variation in the peak temperature involving formulations from C1 to C7, although it results evident that C2 bone cement formulation is of the higher value of the peak temperature after C8.

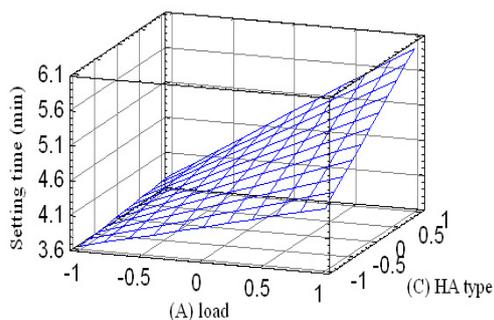


Figure 10. Response surface of setting time

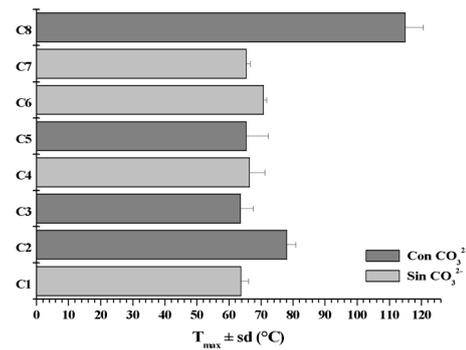


Figure 11. Peak temperature of bone cements.

The average value of the peak temperature in this conditions was (68±5) °C, but if considering C8 the values ranging (74±17) °C. This could be explained by the presence of solid material that is homogeneously distributed in the cement dough and it is able to absorb some of the heat involved in the exothermic reaction of polymerization, causing a decrease of the environment temperature respect to MMA monomer. This phenomenon is also called mesophase theory (Fuentes *et al.*, 2005).

However, the load content could not be further increased because it could cause hardness and difficulty in mixing and processing of the cement dough, as well as imperfections as a result of aggregation of load particles (Şerbetçi *et al.*, 2000). The statistical treatment confirm the results above explained as we have seen at Eq. 3 with  $R^2 = 81.74\%$ .

$$T_{max} = 74 + 9 A \quad (3)$$

In other reports, the increment of load, specially hydroxyapatite, do not induce any tendency at peak temperature, for example, peak temperatures ranging between 75°C and 85°C (Cauich *et al.*, 2001), from 96°C to 103°C (Şerbetçi *et al.*, 2000) and from 85°C to 90°C (Espigares *et al.*, 2002). As we can see, it could be possible that addition of calcium carbonate and hydroxyapatite may reduce the peak temperature of the bone cements, which is a desirable condition to improve the application of these materials in the future.

#### Polymerization enthalpy

It has been estimated that the total heat of polymerization of MMA is 54.4 kJ/mol. As a consequence of the exothermic character of the propagation step a characteristic increment of the temperature is observed, expressed as heat of the polymerized mass to the hand contact (Pascual *et al.*, 1996).

A great part of acrylates has a value of  $\Delta H_p$  that oscillates between 40 and 60 kJ/mol (Coover and McIntire, 1989). In thermo analytical evaluation of the experimental bone cements it is observed an oscillation of the values between 1 and 8 kJ/mol as it is observed in Table 5.

Table 5. Exothermic polymerization enthalpies

Samples	A	B	C	D	$\Delta H_p \pm \sigma_{\Delta H}$ (kJ/mol)
C1	-	-	-	-	$6.69 \pm 0.09$
C2	+	-	-	+	$1.26 \pm 0.06$
C3	-	+	-	+	$5.87 \pm 0.02$
C4	+	+	-	-	$5.53 \pm 0.04$
C5	-	-	+	+	$6.52 \pm 0.08$
C6	+	-	+	-	$2.53 \pm 0.05$
C7	-	+	+	-	$7.77 \pm 0.09$
C8	+	+	+	+	$5.50 \pm 0.07$

Perhaps, the hydroxyapatite in a radical copolymerization, function as a capable agent to adsorb a part of heat generated by the copolymerization process, would make the interpretation of this phenomena more complex as presented in the reality. However, it has been reported that the surface treatment induce a better interconnection between load particles and polymeric matrix which produce an additional ability of the polymeric matrix to accept more load without sacrifice the homogeneity of the cement dough and its mechanical properties (Fuentes *et al.*, 2005 and Veranes *et al.*, 2006).

The statistical treatment of the polymerization enthalpy confirms the results above discussed ( $\alpha = 0.05$ ) because it is obtained an equation in dependence on the monomeric composition and the inclusion of the aragonite or not ( $R^2 = 85.84\%$ ). This last effect can be interpreted as an increase of the load.

$$\Delta H_p = (-48) + 20 A + 9 D \quad (4)$$

The negative sign is related with the exothermic effect in DSC technique which is an international convention established for physico chemical interpretation of the heat phenomena.

#### IV. CONCLUSIONS

The experimental bone cements present adequate values for most of the studied properties. The polymerization reactions do not change the crystalline structure of loads which is very important in order to improve the bioactivity. The residual monomer content was very low, under the detection threshold of technique ( $< 1 \text{ mol } \%$ ).

The setting time obtained ranged between 3.6 and 8.0 minutes and the peak temperature varied between 62 and 110 °C.

In case of polymerization enthalpy, obtained values were ten times lower than reported for the base monomer (MMA) and the most of acrylates reported at hand-book.

#### ACKNOWLEDGEMENTS

The authors wish to thank MSc. Coralia Guerra (from the Technical Development and Research Center) for her help in FTIR analysis, PhD. Jorge Balmaseda (from Structural Analysis Laboratory, Materials Science and Technology Institute, University of Havana) for his assistance in XRD studies and PhD. Mayrelis Ortiz (from Bioinorganic Laboratory, Faculty of Chemistry, University of Havana) for her relevant help in  $^1\text{H}$  NMR analysis.

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Received: October 19, 2006.

Accepted: November 4, 2007.

Recommended by Subject Editor José Pinto.