PMMA/Ca^{2+} 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^{2+} bone cements, besides of their physico chemical characterization. Amounts of mineral component were supplied like a mixture of hydroxyapatite (Coralina® 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 ^1H 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® 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^{2+} cements. An experimental design and a discussion of the possibility of uses of the PMMA/Ca^{2+} bone cements as acrylic resin cement for the orthopedic restoration is carried out.