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Relationship between the morphology of PMMA particles and properties of acrylic bone cements

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Bone cements are mainly based on acrylic polymers, poly(methyl methacrylate) (PMMA) being the most representative. The curing process (cold curing) is the result of the free radical polymerization of a mixture of beads of PMMA and methyl methacrylate (MMA), initiated by benzoyl peroxide (BPO) and activated by the presence of a tertiary amine, the most classical being N,N-dimethyl-4-toluidine (DMT). In this work the results on the effect of the size and size distribution of PMMA beads and the concentration of DMT and BPO on the setting parameters, the residual monomer content and the mechanical properties (tension and compression) of the cured systems are presented. The use of relatively larger diameter PMMA beads improves the characteristic parameters of the curing process (decreasing the peak temperature and increasing the setting time), without detrimental effects on the mechanical properties of the cured cement.

1. Introduction

An important event in orthopaedic surgery occurred when, in the early 1960s, Sir John Charnley presented the preliminary results of a new method for the fixation of joint prostheses to bone [1–3]. The idea was to distribute the contact stresses between the implant and the bone over a large area by means of a filler material, called bone cement, consisting of self-curing polymethylmethacrylate (PMMA).

The main advantages of cemented prostheses lay in their excellent primary fixation, in good load distribution between implant and bone, and in the fact that the technique allows fast recovery of the patient. However, acrylic bone cements also present some disadvantages such as the lack of secondary fixation, the mechanical failure of the cement, and the formation of a fibrous tissue between the cement and the bone. These are partly due to necrosis of bone induced by the heat liberated during the setting stage, and the osteolysis caused by foreign body reaction activated by wear particles and debris, part of which could come from the same bone cement, and the toxicity of the liquid monomer of the cement [4–6].

In spite of such disadvantages, the balance is favourable and acrylic bone cements still have a long way to go and a promising future ahead.

Acrylic bone cements are based in PMMA, which is accepted as a biocompatible polymer when cured. The curing process, "cold curing" [7, 8] is the result of free radical polymerization of a mixture of beads of PMMA and methyl methacrylate (MMA), initiated by benzoyl peroxide (BPO) and activated by the presence of a tertiary amine, the most classical one being N,N-dimethyl-4-toluidine (DMT).

During the polymerization process the dough mixture becomes stiff in a short time (10–15 min), allowing application *in situ* and primary fixation of a joint prostheses.

The PMMA particles or beads constitute approximately 70% by weight of the polymerized cement. Their microstructure, and the physical and chemical

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characteristics play a relevant role in the final properties of the cement.

The objective of the present work is to study how the mechanical properties of the material are influenced by different parameters such as the size and size distribution of the PMMA powder component, and the concentrations of DMT and free radical initiator BPO. The effect of such parameters on the peak temperature, the setting time and the residual monomer content have been carefully studied elsewhere [9], although they are briefly reviewed in the present work.

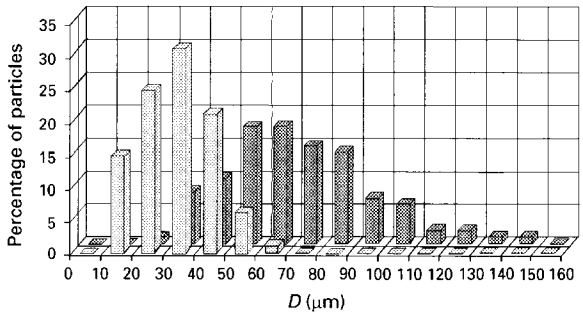

Figure 1 Particle size distribution for the PMMA powders A (▒) and B (▓).

2. Materials and methods

The polymethyl methacrylate used in this work were IQL and BONAR, kindly supplied by Indústrias Quirúrgicas de Levante and Unidesa, respectively. In this work they will be coded as cement A and cement B, respectively. The particles forming the powder had a spherical shape, and were prepared by suspension polymerization.

The morphological characteristics of each powder, particle size (mean diameter, $\bar{D}$), average molecular weight ($\bar{M}_n$), tacticity and residual monomer content are collected in Table I. These parameters were determined by size exclusion chromatography ($\bar{M}_n$ and $\bar{M}_n/\bar{M}_w$) and ^{1}H-NMR (nuclear magnetic resonance) spectroscopy (tacticity). The monomer content was also determined by ^{1}H-NMR spectroscopy and gas liquid chromatography (GLC). NMR spectra were recorded with a VARIAN VXR-300 spectrometer operating at 300 MHz at room temperature. The size ($\bar{D}$, in μm), and size distribution of the PMMA beads in the two different powders were determined using image analysis coupled to an optical microscope, by making the average for 7000 particles randomly distributed in different images. The results for the particle size distribution can be seen in Fig. 1.

The monomer used was methyl methacrylate (MMA) by Fluka A.G., stabilized with 100 ppm of monomethylether of hydroquinone. Benzoyl peroxide (BPO, Fluka A.G.) and N,N-dimethyl-4-toluidine (DMT, Merck) were used without further purification.

The activator DMT was mixed with the MMA and the BPO was blended with the PMMA beads. A liquid/powder ratio of 2:1 was employed in all the experiments.

In order to know the influence of the most important parameters controlling the peak temperature and the setting time, we analysed the kinetic parameters obtained with formulations prepared with different concentrations of the activator, DMT (0.5, 1, 2 and 2.7% v/v) and free radical initiator, BPO (0.75, 1 and 2% wt/wt) in combination with the two PMMA powders considered in this work.

TABLE I Morphological characteristics (mean diameter $\bar{D}$), molecular weight, tacticity and residual monomer content for the two PMMA powders studied

Powder	$\bar{D}$ (μm)	$\bar{M}_n \times 10^3$	M_n/M_w	Tacticity	Residual MMA (%)
A	33.1	97	1.78	0.262	0.71
B	69.4	> 350	5	0.239	3.80

The temperature evolution with time in the reacting mass was registered automatically with a thermocouple, using a cylindrical teflon mould specifically designed to obtain reproducible data at a working temperature of 37 °C.

The time elapsed from the moment at which the powder and liquid components were mixed until the cement is set is known as the setting time [10, 11], and was determined according to the ASTM standard (F451) as the time when the temperature of the polymerizing mass has the following value:

$$T_{amb} + (T_{max} - T_{amb})/2$$

where T_{amb} is the ambient temperature, taken as 23 ± 1 °C, and T_{max} is the maximum temperature reached by the polymerizing cement (in °C).

The amount of residual monomer in the cured cement was measured by means of ^{1}H-NMR spectroscopy.

In order to evaluate the effect of different amounts of activator (DMT) and initiator (BPO) on the mechanical properties of the cement, formulations were prepared containing 0.5, 1, 2 and 2.7% (v/v) DMT and 0.75, 1.25 and 2% (wt/wt) BPO. The samples for compressive and tensile mechanical testing were prepared by hand-mixing the powder and the liquid and injecting the paste in the dough state into teflon moulds that had previously been sprayed with a demoulding agent based on silicone and water. The dimensions of the samples followed the standards UNE 53023 for tension and ASTM F451-86 for compression.

The tensile and compressive properties of the cured cements at room temperature were determined by means of an Adamel Lhomargy and an Instron electromechanical testing machine, at a constant crosshead speed of 1 mm min^{-1} for the tensile test and 22 mm min^{-1} for compression. The aspect of the fracture surfaces obtained in tension was studied with a scanning electron microscope (SEM).

3. Results and discussion

When the powder and liquid components of bone cement are mixed, both physical and chemical phenomena take place simultaneously which affects the

TABLE II Setting times t_{set} and maximum temperatures T_m (°C) for the A and B cements, with different concentrations of DMT (%v/v) and BPO (%wt/wt)

		DMT (%)							
	BPO (%)	0,5 T_m	t_{set}	1.00 T_m	t_{set}	2.00 T_m	t_{set}	2.70 T_m	t_{set}
A	0.75	83.3	7'10"	85.4	7'00"	87.7	5'15"	92.4	6'05"
	1.25	83.0	6'50"	89.3	6'40"	94.2	5'25"	94.8	4'50"
	2.00	84.0	5'50"	91.0	4'45"	95.3	4'24"	95.2	4'10"
B	0.75	60.0	13'00"	61.6	11'45"	62.8	10'10"	62.9	9'30"
	1.25	60.4	12'00"	63.9	10'30"	64.4	9'15"	66.3	8'30"
	2.00	61.1	11'15"	68.9	9'25"	68.6	8'40"	68.1	8'00"

setting process, microstructure and mechanical properties of the set material [9].

The results obtained for the setting time and the maximum temperature for the two different powders and for different concentrations of DMT and BPO are shown in Table II. As was expected, the peak temperature increases for increasing concentration of both DMT and BPO, the effects being rather similar for both components. The difference in peak temperature for the formulations prepared with the highest concentrations of DMT and BPO and those prepared with the lowest are about 10 °C. It has to be noticed that these data have been obtained at 37 °C, and therefore it is not strange that in some cases they are slightly higher than the maximum value specified in the F451 standard, where the measures are supposed to be done at 23–25 °C.

It is clear that the effect of the size of PMMA beads is more important than the effect of DMT and BPO concentrations, with differences up to 30 °C in the peak temperature of the curing cements. As has been reported by Lautenschlager *et al.* [12], the problems of temperature and setting time are greatly complicated by the fact that while the amount of heat released is given by the quantity of reacting monomer, the temperature reached is dependent upon the rate at which the heat is dissipated. It is assumed that the smallest beads of the PMMA phase ($< 20\,\mu m$) undergo complete dissolution in the presence of MMA, and only large beads survive the mixing, maintaining a spherical shape in the cured systems. This fact could explain the variation in the peak temperature with the average size and size distribution of PMMA beads. Moreover, the smallest particles would contribute in the opposite direction because of their dissolution in the polymerizing MMA medium, with the corresponding increase of viscosity of the curing mass.

As expected, the setting times are also influenced by the size of PMMA beads, with differences as large as 5–6 min for the two powders. Fig. 2 shows the time–temperature diagram obtained for the two systems studied in this work, for a 0.75% BPO (wt/wt) and 1% DMT (v/v). Note the shift of temperature evolution function towards longer times and the decrease of the maximum temperature reached during the curing process.

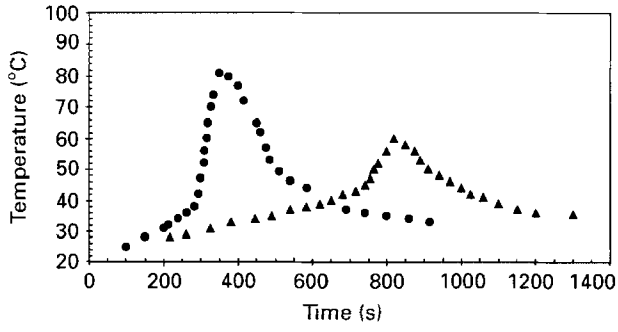

Figure 2 Time-temperature diagram obtained for the cements A (small beads) (●) and B (bigger beads) (▲), for a 0.75% BPO (wt/wt) and 1% DMT (v/v).

TABLE III Residual monomer content in the cured cements A and B

Cement	BPO (%)	DMT (%) 0.5	1.00	2.00
A	0.75	5.93	4.80	3.25
	2.00	5.03	4.29	3.2
B	0.75	8.48	5.84	5.29
	2.00	7.11	4.35	3.84

The results obtained for the residual monomer content in the cured specimens are presented in Table III. This parameter depends on the monomer content in the PMMA beads, and on the polymerization process. The values are higher for the B cement. This could be due in part to the higher monomer content in the initial powder, and to the lower peak temperature reached during the polymerization process, which could hinder diffusion of the monomer between the formed chains of polymer. As expected, the use of higher concentrations of BPO and DMT produce a decrease in the final amount of residual monomer in the cement. It is necessary to keep in mind that both DMT and MMA have side-effects when released in the human body [13]. However, it is interesting to consider the fact that the amount of residual monomer present in the dough state of the cement paste, that is, at the moment when the cement is supposed to be introduced into the patient's body, is approximately the same in all cases, around 20%.

TABLE IV Mechanical properties of cements A and B with different concentrations of DMT and BPO. σ_c and E_c are, respectively, the compressive strength and elastic modulus in compression, while σ_t and E_t are the ultimate stress and the elastic modulus in tension, respectively. The standard deviation is given in parenthesis

Cement	DMT (%)	BPO (%)	σ_c (MPA)	E_c (GPA)	σ_t (MPA)	E_t (GPA)
A	0.5	0.75	122.5 (3.6)	2.2 (0.2)	41.7 (3.4)	1.36 (0.13)
		2.00	123.3 (3.7)	2.3 (0.1)	42.8 (2.3)	1.37 (0.03)
	1.0	0.75	117.4 (4.7)	2.5 (0.2)	44.8 (1.3)	1.52 (0.04)
		2.00	133.5 (2.6)	2.5 (0.2)	46.5 (1.6)	1.52 (0.05)
	2.0	0.75	107.5 (4.3)	2.3 (0.2)	41.9 (1.8)	1.47 (0.03)
		2.00	134.6 (6.1)	2.7 (0.2)	41.7 (3.1)	1.50 (0.08)
B	0.5	0.75	115.5 (5.0)	2.0 (0.2)	40.9 (2.0)	1.42 (0.02)
		2.00	128.9 (1.3)	2.3 (0.6)	43.1 (1.8)	1.44 (0.01)
	1.0	0.75	125.1 (2.9)	2.3 (0.1)	42.4 (2.5)	1.35 (0.03)
		2.00	134.1 (6.7)	2.6 (0.1)	38.4 (3.4)	1.39 (0.02)
	2.0	0.75	104.5 (5.3)	2.1 (0.1)	34.1 (3.1)	1.35 (0.03)
		2.00	136.8 (5.3)	2.4 (0.7)	36.2 (6.2)	1.49 (0.05)

The effect of the morphology of PMMA beads and the concentration of DMT and BPO on the mechanical behaviour of the cement was studied by means of tensile and compressive tests. Table IV shows the results obtained. σ_t and E_t are, respectively, the ultimate stress and the elastic modulus in tension, while σ_c and E_c are the compressive strength and elastic modulus in compression, respectively. For each material the mean value and its standard deviation are given. It can be concluded that the compressive strength is poorly affected by either particle size or DMT, but an increase in BPO content produces an increase both in compressive strength and modulus. However, in all cases, the compressive strength is higher than the minimum value required by the F451-86 ASTM standard (70 MPa). Also the average values for the tensile strength are similar for the different formulations, but somewhat lower for the B cement. The elastic modulus shows a slight decrease in the cement with larger particles (B), and this could be due to the higher monomer content, which acts as a plasticizer.

The total and plastic strain are shown in Fig. 3. There is no significant difference between the A and B cements, probably due to the fact that although the modulus is lower for the second one, the tensile strength is also lower. However, the influence that the increase in concentration of DMT and BPO has in decreasing the ductility of the cement is noticeable in both cases. This embrittlement is probably an immediate consequence of the reduced amount of residual monomer.

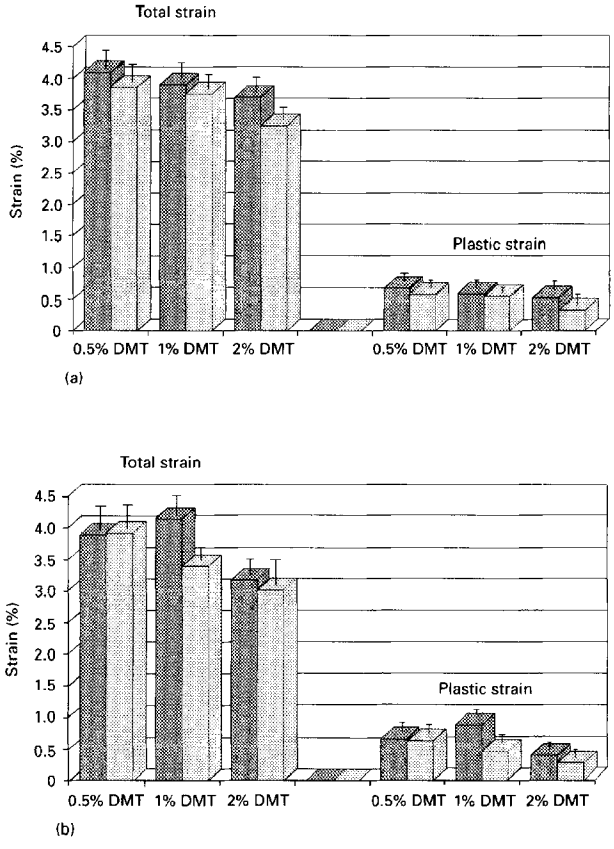

Figure 3 Total and plastic strain (%) for: (a) the cement prepared with powder A; and (b) the cement prepared with powder B, with different concentrations of DMT (% v/v) and BPO (%wt/wt). ▒ 0.75% BPO; ▒ 2% BPO.

Fractographic analysis of the tensile specimens did not show any relevant difference in the fracture behaviour of cement A and B. The fracture surfaces were flat in both cases, with the PMMA particles fractured with brittle aspect and looking "cleaved". Fig. 4 shows a representative fracture surface, corresponding to a specimen of cement A containing 2% DMT and 0.75% BPO. As can be seen, the cohesion between the particles and matrix is good, since the crack always cuts straight through the spheres, and does not follow the boundary between particles and matrix. The typical morphology produced by crazing (patch patterns) is clearly visible, specially in the matrix, but not inside the PMMA beads. This could be due to the fact that, as can be seen in Table I, the residual monomer content in the PMMA powder for the A cement is quite low (0.71%). In contrast, the residual monomer content in the cured cement is 3.25%. This means that the monomer content in the matrix is much higher than in the PMMA beads. Therefore, taking into account the plasticizing effect of the residual monomer, it is reasonable to expect

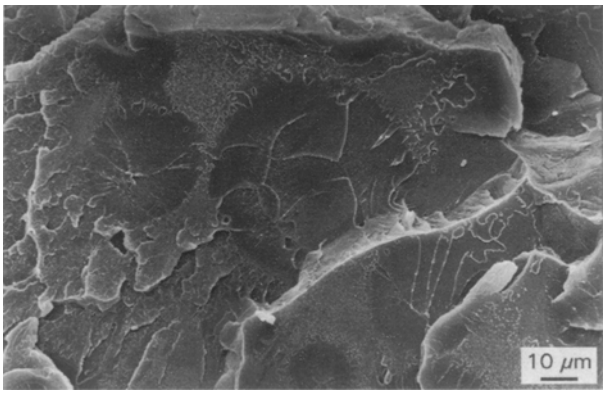

Figure 4 SEM micrograph of a fracture surface corresponding to a tensile specimen of cement A, containing 2% DMT (v/v) and 0.75% BPO (wt/wt).

a more brittle behaviour, without deformation by crazing inside the PMMA spheres.

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