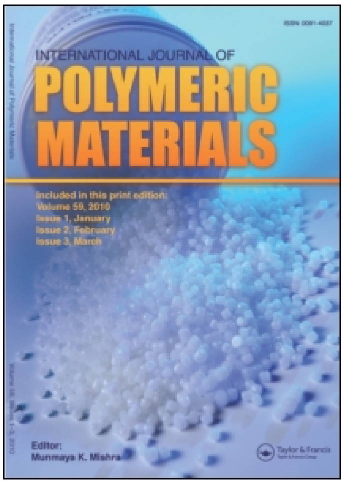

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Barium titanate-filled bone cements. I. Chemical, physical, and mechanical characterization

Raúl García Carrodeguas[a]; Blanca zquez[b]; Julio San Roman del Barrio[b]; Antonio Madronero de la Cal[c]
[a] Centro de Biomateriales, Universidad de La Habana, Habana, Cuba [b] Instituto de Ciencia y Tecnología de Polímeros, CSIC, Madrid, Spain [c] Centro Nacional de Investigaciones Metalúrgicas, CSIC, Madrid, Spain

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BARIUM TITANATE-FILLED BONE CEMENTS. I. CHEMICAL, PHYSICAL, AND MECHANICAL CHARACTERIZATION

Raúl García Carrodeguas
Centro de Biomateriales, Universidad de La Habana,
Habana, Cuba

Blanca Vázquez and Julio San Román del Barrio
Instituto de Ciencia y Tecnología de Polímeros, CSIC,
Madrid, Spain

Antonio Madroñero de la Cal
Centro Nacional de Investigaciones Metalúrgicas,
CSIC, Madrid, Spain

Bone cements filled with $BaTiO_3$ particles were prepared and characterized. The powders of the cements consisted of poly(methylmethacrylate) (PMMA) beads, benzoyl peroxide (BP), and $BaTiO_3$ (BT) powder ($< 145\,\mu m$). The liquid composition was methyl methacrylate (MMA), N-vinyl-2-pyrrolidone (VP), and N,N-dimethyl-2-aminobencyl alcohol (DMOH). The observed dough and setting times were strongly influenced by the BT and VP contents. However, neither the filler nor the VP contents significantly affected the maximum temperature during setting. VP provided the cements with certain hydrophilic character and solubility. At the early stage, the process of water uptake obeyed the Fick Second Law but at the end a deviation was observed as consequence of the partial dissolution of the absorbing matrix. BT particles effectively increased the compressive strength of the cements.

Keywords: bone cements, composites, barium titanate

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Address correspondence to Raúl García Carrodeguas, Centro de Biomateriales, Universidad de La Habana, Ave. Universidad s/n e/ G y Ronda, C. Habana 10400, Cuba. E-mail: rgc@biomat.uh.cu

INTRODUCTION

Patients carrying open and composed fractures of long bones are very frequent in orthopedic services. Lose of bone tissue is often associated to these traumas and intersegmental gaps exceeding 2.8 mm are not rare. An important role in fracture repairing has been attributed to the appearing of a cathodic potential peak in the zone of the fracture [1]. When the intersegmental gap is higher than 2.8 mm the cathodic biopotential peak normally present for lower gaps disappears [2], and the result is the delay of fracture consolidation or the occurrence of the pathology so called pseudoarthrosis or false union, at less than special long lasting and uncomfortable treatments are applied [1, 3]. The implantation of biomaterials able to be polarized "*in situ*" by mean of an external electric field or by the action of biomechanical stresses could contribute to restore the cathodic potential in the zone of the fracture.

Such biomaterials could be designed as a partially biodegradable polymer matrix composite filled with a ferro and piezoelectric ceramic. Partial biodegradability would permit the osteointegration of the implant and the ceramic filler would generate the desired "*in situ*" electrical stimulation.

On the other hand, the ferro- and piezoelectric properties of barium titanate ceramics are widely known and are the basis for a large number of electrical and electronic applications. The results of preliminary tests suggest that barium titanate is well tolerated by the living tissues [4, 5]. Also in order to provide bioactivity and osteoconductivity a biological hydroxyapatite layer can be growth on barium titanate particles [6].

Additionally, self-curing acrylic bone cements have been extensively used in orthopedic and maxillo-facial surgery for prosthesis fixation and filling or remodeling of bone defects since their appearance in the late fifties [7].

Poly (N-vinyl-2-pyrrolidone) is a biocompatible hydrophilic monomer very soluble in water and physiological fluids [8]. Its solubility can be controlled by co-polymerization with hydrophobic monomers [9]. Copolymers of N-vinyl-2-pyrrolidone with several acrylic polymers have been extensively studied as biomaterials, particularly as matrixes for drug delivery systems [10 – 12].

Thus in this paper hydroxyapatite-coated barium titanate granules were employed as a filler for poly (methyl methacrylate), PMMA, and poly(methyl methacrylate-co-vinyl-2-pyrrolidone), PMMA/PVP, – based bone cements and several chemical, physical and mechanic properties of the resulting materials were studied.

MATERIALS AND METHODS

The powder component of conventional acrylic bone cements was prepared by mixing commercial poly(methyl methacrylate), PMMA, beads

(Industrias Quirúrgicas de Levante, Spain), with 1.5 wt.-% of benzoyl peroxide, BP (Fluka, Cat. No. 33581, previously recrystallized from methanol). The liquid component consisted of methyl methacrylate, MMA (Acros Organics, Cat. No. 12714) or a mixture of MMA and N-vinyl-2-pyrrolidone, VP (Aldrich, Cat. No. V340-9, vacuum distilled) in weight ratio of 1 : 1, added with 1.0 wt.-% of N,N-dimethylaminobenzyl alcohol, DMOH, synthesized as elsewhere [13]. A powder to liquid weight ratio of 2 : 1 was used.

Composite bone cements were prepared by adding 2.0, 5.0, 10.0, 30.0, 35.0, and 40.0 vol.-% (9.0, 20.3, 35.0, 67.5, 72.3, and 76.3 wt.-%) of hydroxyapatite-coated barium titanate granules, BT, respect to total volume of the cements. Particles of BT with size $< 150\,\mu m$ were used. They were obtained as described elsewhere [6]. The needed amounts of BT were added to the powder of the composite bone cements. The compositions of the experimental cements are displayed in Table 1. Compositions are named with a letter followed by digits, the letter meaning the composition of the polymer matrix, A for PMMA, and B for P(MMA-co-VP). The digits correspond to the filler content expressed in vol.-%.

Setting Parameters

Setting parameters, *i.e.*, dough time, DT, setting time, ST, and maximum temperature, MT, were measured for each cement in Table 1 employing the

TABLE 1 Compositions of the experimental cements, in wt.-%

	Powder			*Liquid*		
Cement	*PMMA*	*BP*	*BT*	*MMA*	*VP*	*DMOH*
A	65.67	1.00	–	33.00	–	0.33
A2	59.77	0.91	8.99	30.03	–	0.30
A5	52.34	0.80	20.30	26.30	–	0.26
A10	42.70	0.65	34.97	21.46	–	0.22
A30	12.43	0.59	67.47	19.32	–	0.19
A35	10.59	0.50	72.27	16.47	–	0.17
A40	9.04	0.43	76.34	13.45	–	0.14
B	65.67	1.00	–	16.50	16.50	0.33
B2	59.77	0.91	8.99	15.01	15.02	0.30
B5	52.34	0.80	20.30	13.15	13.15	0.26
B10	42.70	0.65	34.97	10.73	10.73	0.22
B30	12.43	0.59	67.47	14.08	5.24	0.19
B35	10.59	0.50	72.27	12.01	4.46	0.17
B40	9.04	0.43	76.34	10.24	3.21	0.14

ASTM standard methods [14]. For the determination of maximum temperature an specially designed device described elsewhere was used [15].

Samples weighting 3.0 g were employed. The powder components were thoroughly mixed and DMOH was completely dissolved in the monomer liquid. Both solid and liquid were conditioned not less than 2 hr at (23 ± 1)°C prior the determinations. Two measures of each parameter were taken.

Compressive Strength

Compressive strength tests were carried out in a universal testing machine (Microtest, Instron) provided with a load cell of 5 kN. It was employed a crosshead speed of 20 mm/min. Cylindrical specimens of diameter 6 mm and height 12 mm were prepared by forcing the cement dough into the holes of a Teflon mold. Both sides of the mold were covered with Teflon plates and the assemble was secured with clamps. The specimens were maintained 1 hr in the mold at (37 ± 1)°C, then dismolded, finished to a perfect cylindrical shape, and tested at least 1 week after the preparation. Six specimens were tested from each cement formulation.

Water Sorption and Diffusion Measurements

Water sorption and diffusion studies were made on cured cement plates of width 10 mm, length 35, and thickness 1.0 – 1.5 mm. The plates were immersed in Simulated Body Fluid [16] and maintained at (37 ± 1)°C. The weight variation was followed by periodical weighting of previously surface-wiped specimens. Two replicas were employed for each cement sample.

Thermogravimetric Analysis

Dynamic thermogravimetric analysis of set cements was carried out in a TGA7 thermogravimetric analyzer (Perkin Elmer) coupled to a thermal analysis control unit TAC7/DX. Analysis was performed with 15 – 30 mg of sample in a platinum pan under nitrogen flow. Heating rate and final temperature were $10°\mathrm{C} \cdot \mathrm{min}^{-1}$, and 600°C, respectively.

Differential Scanning Calorimetry

Calorimetric analysis of set cements was performed in DSC7 calorimeter (Perkin Elmer) coupled to a TAC7/DX control unit. All runs were carried out under nitrogen flow at a heating rate of $20°\mathrm{C} \cdot \mathrm{min}^{-1}$.

The final temperature was over 10°C before the decomposition temperature determined by thermogravimetric analysis for each sample.

Statistical Treatment

One-way ANOVA and Tukey's test were carried out on the results by using the Statistica for Windows 4.0 software (Statsoft Inc., 1993). The p level selected was always 0.05.

RESULTS AND DISCUSSION

Other authors have previously reported the typical composition A of Table 1 for experimental acrylic bone cements [15]. The rest of compositions in Table 1 were previously established by trial and error. Those compositions with filler content lower than 30.0 vol.-% were prepared with a ratio (PMMA + BP) : LIQUID of 2 : 1, the same as in the typical composition A. However for filler contents of 30.0 vol.-% or higher, the ratio (PMMA + BP) : LIQUID had to be lowered to 2 : 3 to assure the complete embedding of the mixture of PMMA and BT.

The introduction of a hydrophilic monomer, VP, in the LIQUID of the cements must increase both the hydration degree and the solubility of the set cements [9, 17]. On the other hand, the replacement of part of the MMA in the LIQUID by VP conduces to the increasing of the setting time due to the decrease in polymerization rate. That is the reason why in cements with filler contents inferior to 30.0 vol.-% only 50 wt.-% of MMA could be replaced by VP, the replacement of a higher amount causing too large setting times. In those cements with filler contents of 30 vol.-% or higher the polymerization rate is additionally decreased by the mesophase effect [18], so only 27.1 wt.-% of MMA could be replaced by VP in B30 and B35, and 23.8 wt.-% in B40.

Setting Parameters

Table 2 displays the results obtained for the setting parameters of the experimental cements of Table 1. The dough state is the result of the process of partial dissolution of the PMMA in the LIQUID component of the cement. For charged cements the "immobilization" of part of the liquid on the surface of the filler particles also contributes to the increasing of viscosity of the system, *i.e.*, to reach the dough state.

The observed dough time for series A and B decreases for charged cements (up to 10 vol.-% of filler content) with regard to the unfilled ones. For filler contents of 30 vol.-% or higher, the dough time exceeds that of the corresponding unfilled cements as a result of the decrease of (PMMA + BP) : LIQUID ratio. In these cases a greater extension of PMMA dissolution in the liquid must be reached prior to get the dough state.

By comparison of series A and B higher dough times were observed for the last one. This effect is a consequence of the lower solubility of the hydrophobic PMMA beads in a more hydrophilic liquid containing VP.

TABLE 2 Setting parameters, mechanical properties, water uptake and solubility of experimental cements

Cement	*DT* (*min*)	*ST* (*min*)	*MT* (°*C*)	m_{max} *T-t* (°*C*/*min*)	σ_c (*MPa*)	m_{30-70} *L-D* (*N*/*mm*)	*HD* (%)	*S** (%)
A	2.12(0.18)	9.75(0.24)	68.0(1.4)	80(8)	133(4)	175(9)	1.71	0.02
A2	0.75(0)	9.25(0.35)	67.0(2.8)	78(8)	134(7)	177(5)	1.59	0
A5	1.21(0.30)	9.67(0.35)	63.0(1.4)	60(13)	120(3)	160(8)	1.32	0
A10	0.75(0)	10.71(0.30)	57.0(2.8)	44(2)	126(6)	174(5)	1.15	0.04
A30	6.00(0.35)	18.12(1.00)	52.0(2.8)	21(4)	138(23)	251(10)	1.02	0.03
A35	5.34(0.47)	20.50(1.40)	52.0(0)	23(1)	133(5)	294(34)	1.01	0.01
A40	4.50(0.71)	18.04(0.53)	46.5(0.7)	20(1)	148(7)	286(12)	0.99	0.01
B	3.12(0.18)	8.42(0.12)	43.0(0)	6(1)	86(9)	135(6)	15.85	2.35
B2	1.12(0.18)	8.42(0.12)	42.0(1.4)	4(1)	76(3)	138(10)	11.88	1.83
B5	1.00(0)	9.45(0.99)	39.5(0.7)	3(0)	89(4)	147(10)	8.65	1.87
B10	1.00(0)	8.42(0.59)	38.0(1.4)	2(1)	82(6)	151(5)	5.95	1.22
B30	8.92(0.12)	21.42(0.59)	45.5(0.7)	9(1)	145(7)	274(22)	2.02	0.35
B35	11.00(0)	22.17(0.71)	40.5(0.7)	6(1)	116(14)	270(8)	1.72	0.31
B40	3.25(0.35)	16.84(0.47)	40.5(0.7)	9(1)	130(4)	285(18)	1.47	0.26

Standard deviations in parentheses. n = 2.
* $S = ((m_0 - m_{end})/m_0) \cdot 100$.

The monomer composition and the (PMMA + BP) : LIQUID ratio affected strongly the setting time. Cements of series A with filler contents between 0 and 10.0 vol.-% displayed setting times higher than those of series B. For filler levels of 30 vol.-% or more, corresponding to a ratio (PMMA + BP) : LIQUID of 2 : 3, the inverse situation was observed.

However the increase in filler content for both series A and B had no effect on setting time up to the level of 10.0 vol.-%. Beyond this level significantly higher setting times were found. The change in trend corresponds again, as for dough time, with the change in (PMMA + BP) : LIQUID ratio.

Maximum temperature was strongly influenced by the nature of the monomers and in a lesser extension by the filler content. A drastic decrease was caused by VP addition reaching almost the level of the physiological temperature. Taking into account the similarity of both heats of polymerization ($\Delta H_P(MMA) = 55{,}1$ kJ/mol; $\Delta H_P(VP) = 57{,}7$ kJ/mol) [19] this effect can be attributed to the lower polymerization rate in those systems containing VP, as evidenced by the maximum slope of the ascending part of the T *vs.* t curve (m_{max} T − t) listed for all formulations in Table 2. The lowering effect of filler content on maximum temperature is more evident for series A. In series B it is observed the same trend up to 10.0 vol.-% of charge. The effect of the nature of the monomers and the filler content on the shape of the curves T *vs.* t is displayed in Figure 1.

ASTM Standard F451-86 establish for acrylic bone cements a maximum dough time of 5.0 min, a maximum temperature of 90°C, and a setting time between 5 and 15 min [14]. According to this all formulations fulfil the requirements of ASTM except those with filler content of 30.0 vol.-% or higher. Particularly, the setting time of B40 cement is quite close from the upper limit of the specified value.

Compressive Strength

The addition of VP to the liquid reduced significantly the ultimate compressive strength, σ_c of the cements up to a filler content of 10.0 vol.-% (see Tabs. 2 and 3). The same effect was observed for the slope of the curve load *vs.* deformation calculated in the interval of 30 to 70% of maximum load (m_{30-70} L-D), which should be directly proportional to the elastic modulus, E. So the cements formulated with liquids containing VP present higher strain to failure. For charge contents of 30.0 vol.-% or higher this behavior disappears and series A and B practically do not differentiate with regard to compressive strength and slope of the L-D curve.

None significant reinforcing effect of charging the cements with BT particles was observed for charge contents up to 10.0 vol.-%. However, the cements containing 30.0 vol.-% or more of BT exhibited higher ultimate

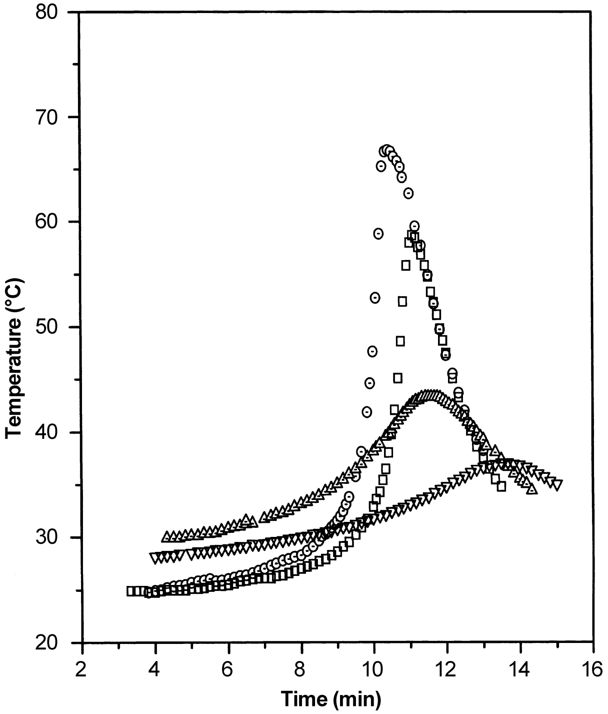

FIGURE 1 Temperature *vs.* time experimental curves for the setting cements. (○) A, (□) A10, (△) B, (▽) B10.

TABLE 3 Results of Tukey's test performed on compressive strength data. (Arrows link groups of means no significantly different for p-level = 0.05)

<table>
<tr><th>A40</th><th>B30</th><th>A30</th><th>A2</th><th>A</th><th>A35</th><th>B40</th><th>A10</th><th>A5</th><th>B35</th><th>B5</th><th>B</th><th>B10</th><th>B2</th></tr>
<tr><td>148</td><td>145</td><td>138</td><td>134</td><td>133</td><td>133</td><td>130</td><td>126</td><td>120</td><td>116</td><td>89</td><td>86</td><td>82</td><td>76</td></tr>
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compressive strength than the rest, reaching the maximum values of both series for A40, 148 MPa, and for B30, 145 MPa. The corresponding values for uncharged cements are 133 MPa for A and 86 MPa for B, so in A40 and B30 the strength increases 11.3% and 68.6%, respectively, as the result of the reinforcing action of the filler. For levels of charge of 30.0 vol.-% or more the deleterious effect of VP on the ultimate compressive strength practically vanishes.

All cements exceeded the minimum limit of 60 MPa established by the ASTM standard. The cements of series A and those of series B containing 30.0 vol.-% or more of filler exhibited ultimate compressive strength higher than the interval of 73 to 117 MPa reported for commercial acrylic bone cements [20].

Water Sorption and Diffusion Measurements

The weight of thin cement plates immersed in SBF at 37°C was followed up for 600 hours. The results for cements of series A and B are shown in Figure 2 as plots of the hydration degree *vs.* time. The hydration degree, H, is expressed as $((m_t - m_0)/m_0) * 100$, where m_t, is the weight of the cement plate

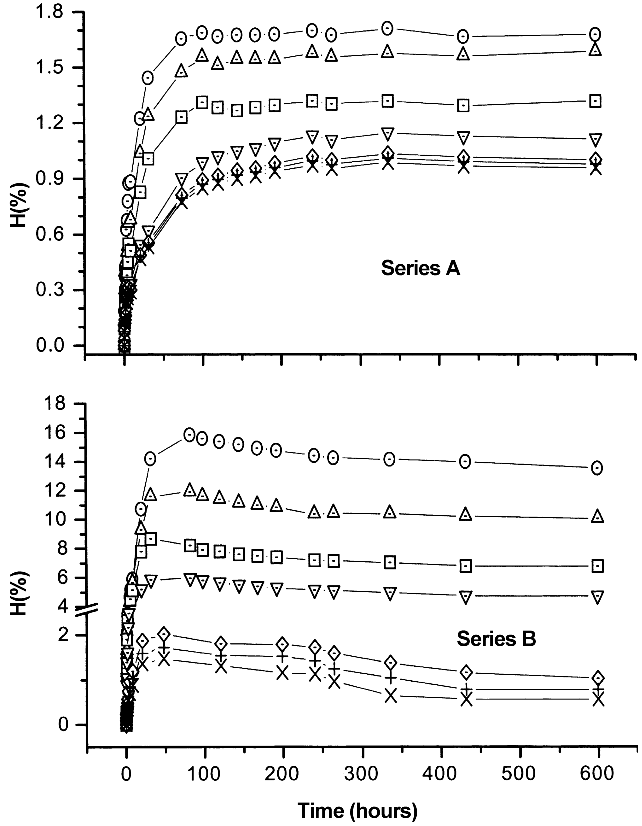

FIGURE 2 Water sorption behavior of the experimental cements. (○) unfilled, (△) 2 vol.-% of BT, (□) 5 vol.-% of BT, (▽) 10 vol.-% of BT, (◇) 30 vol.-% of BT, (+) 35 vol.-% of BT, (×) 40 vol.-% of BT.

at time t, and m_0 is the initial weight of the plate. During the water sorption experiments it was noticed that probes made from cements of series A kept their size and stiffness whereas those of series B swelled and became flexible. Besides, after a few days in SBF at 37°C the VP-rich soluble part of series B cements suffers some kind of hydrolysis reaction conducing to the formation of an aldehyde as suggested by the characteristic smell detected.

Cements of series A reached its maximum hydration degree after soaking for 100 hr and no significant weight decrease by dissolution can be observed in the hydration degree *vs.* time curve during the follow up period. The maximum hydration degree for the series was 1.71%, corresponding to the unfilled cement. As a consequence of the inertia to diffusion of BT the hydration decreases as the filler content increases (see Tab. 2).

In series B the maximum hydration degree increases drastically as the result of the presence of hydrophilic VP units in the polymer matrix. The highest hydration corresponds again to the unfilled cement B, 15.85%, and it is reached sooner than in series A (70 hr).

As a consequence of partial dissolution, the hydration degree starts to decrease after 70 hr of soaking. The highest solubility, S, of cements of series B, corresponding to the unfilled cement, is 2.35%. The partial dissolution of cements from series B should affect the results of hydration degree obtained so they only can be considered from a qualitative point of view.

The solution of the Fick's Second Law for unidirectional planar diffusion into a thin plate is:

$$\mathrm{M_t} = M_\infty \left\{ 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{(2n+1)^2 \pi^2 D}{4\ell^2} t \right] \right\} \tag{1}$$

where $\mathrm{M_t}$ is the mass uptake per unit area at time t, $\mathrm{M_\infty}$ is the mass uptake at equilibrium, 2ℓ is the thickness of the plate, and D is the diffusion coefficient or diffusivity of the permeant. For the early stage of the diffusion Eq. (1) can be approximated to [21]:

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{\pi\ell^2}\right)^{1/2} \tag{2}$$

Figure 3 shows the experimental and calculated curves of $\mathrm{M_t}$ *vs.* time for cements A and B. For calculated curves the Eq. (1) ($n = 0$, 1 and 2) was employed.

In cements of series A, where dissolution effect can be neglected, the experimental data fit quite well those predicted by Eq. (1) along the complete range of time.

On the other hand, for cements of series B, where appreciable dissolution occurs, fitting to Eq. (1) was observed only for the very early stages of

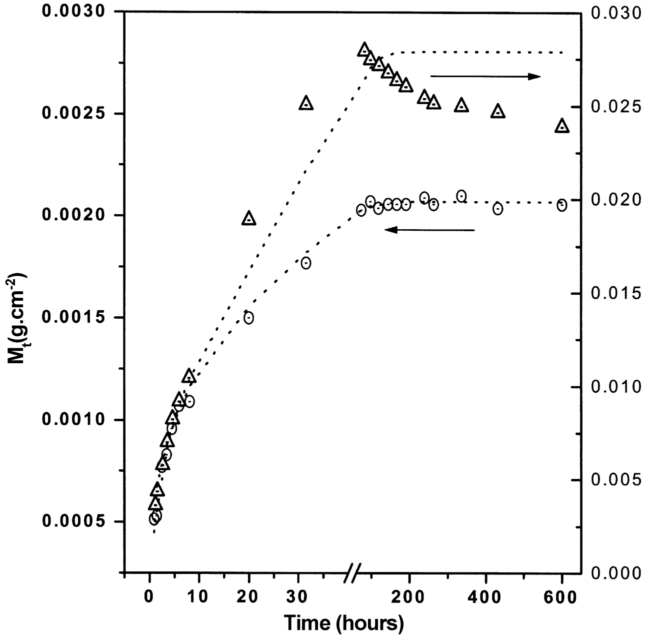

FIGURE 3 Experimental and calculated plots of mass uptake *vs.* time for cements A and B. (○) A, (▽) B, (……) calculated.

diffusion. However, as the diffusion time increases and the dissolved mass too, the poorer becomes the fitting of data to Eq. (1).

Figure 4 displays the linear plots according to Eq. (2) for the early stage of mass uptake corresponding to cements A and B. Acceptable fittings to straight lines are observed for both cements. These results evidence that Fick's Second Law rules the mass uptake process for both series of cements, but in series B the partial dissolution masks the Fickean behavior especially at large times.

Thermoanalytical Results

Figure 5 shows the TG/DTG curves for cements A, A35, B, and B35 registered in the temperature range of 50–600°C at a heating rate of 10°C/min under nitrogen. In Table 4 are indicated the temperature intervals, peak temperatures, weight losses, and residues for other representative cements of series A and B.

The thermal degradation of unfilled cement A proceeds in one step. The decompositions starts at 250°C, reaches its maximum rate at 386°C and finishes at 425°C, without any residue, as expected for PMMA [22, 23]. The

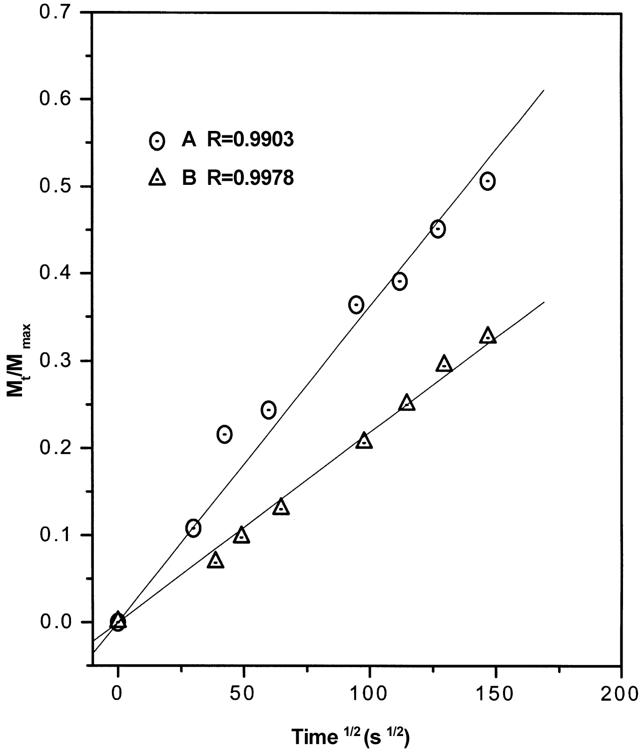

FIGURE 4 Dependance of the ratio M_t/M_{max} with time for the early stage of diffusion. (○) A, (▽) B.

presence of 16.5 wt.-% VP units in the cement B does not affect the shape of the TG/DTG curves nor onset and peak temperatures. However, decomposition only reaches 98.9% weight loss, remaining a 1.1 wt.-% residue. These results coincide with reports on the thermal decomposition of pure PVP under nitrogen where the process occurs in one step and the residue at 600°C is about 3.4 wt.-% [24].

The addition of up to 10 vol.-% of filler to the matrixes A and B has no detectable effect on the decomposition temperature range and peak. However, cements of both series with 35 vol.-% of filler presented peak temperatures exceeding in 8–9°C those of the less charged cements.

The filler recovery was calculated from the residue values of Table 4 and the added filler contents of Table 1. For cements of series B the residue corresponding to the polymeric matrix was considered in the calculations. The calculated filler recovery always surpasses the value of 100%. This deviation can be attributed to the partial volatilization of monomers during the preparation of the cements.

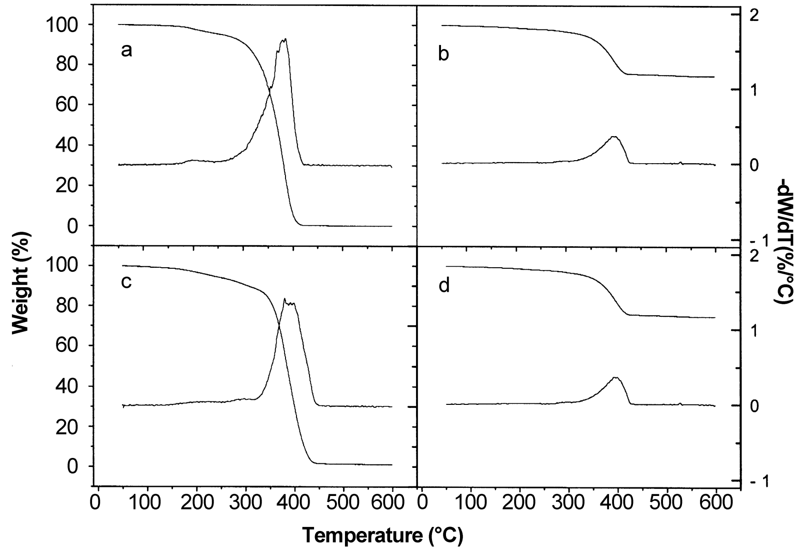

FIGURE 5 TG and DTG scans of representative experimental cements. (a) A, (b) A35, (c) B, (d) B35. (Conditions: 10°C · min^{-1} HR, 50–600°C TR, under N_2).

TABLE 4 Thermal analysis data for some representative cements of series A and B

Cement	*Temperature interval (°C)*	*Peak temperature (°C)*	*Weight loss (wt.-%)*	*Residue at 600°C (wt.-%)*	*Filler recovery (%)*	*T_g (°C)*
A	250–425	386	100	0	–	102
A2	240–435	390	90.3	9.5	105.7	101
A5	256–424	387	76.2	23.7	116.8	100
A10	258–436	386	61.2	38.90	111.2	101
A30	–	–	–	–	–	101
A35	258–436	395	25.1	74.9	103.6	99
A40	–	–	–	–	–	102
B	255–452	390	98.9	1.1	–	97
B2	270–461	392	88.3	11.6	118.2	98
B5	304–467	389	75.6	24.5	116.6	99
B10	313–456	387	64.4	35.7	100.1	98
B30	–	–	–	–	–	101
B35	334–427	399	25.0	75.0	103.4	100
B40	–	–	–	–	–	97

Table 4 shows the glass transition temperatures, T_g, determined from the DSC curves of the set cements. The observed T_g values are very similar for all cements, however it is seem to be that series B has slightly lower T_g's. The found T_g values agree acceptably with the reported value of 99°C for heterotactic PMMA [25].

CONCLUSIONS

Bone cements filled with $BaTiO_3$ particles, which can potentially act as implant materials for *in situ* electrical stimulation of the bone healing in cases of false or delayed union, were prepared and their setting parameters, compressive strength, water sorption capacity, and thermal behavior were studied. The observed dough and setting times varied in the ranges 1 – 9 min and 8 – 22 min, and both are strongly influenced by the BT and VP contents. However, neither the filler nor the VP contents significantly influenced on the maximum temperature. It was always lower than 46°C for the VP-containing cements, minimizing the risk of tissue damage. VP provided the cements with certain hydrophilic character and solubility. Hydration degree of 15.85% and solubility of 2.35% were found for unfilled cement. At the early stage the process of water uptake obeys the Fick Second Law but at the end a deviation is observed as consequence of the partial dissolution of the absorbing matrix. Compressive strengths of 115 – 145 MPa, close to the cortical bone and twice the minimum required by the ASTM standard, are reached for filler contents of ≥ 30 vol.-%.

The thermal decomposition of the cements was not affected by the presence of up to 10 vol.-% of filler, however, for greater filler contents, the peak temperature of decomposition slightly shifted (8 – 9°C) to higher values. No significant change in T_g was found for filled-cements respect to uncharged ones.

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