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New radiopaque acrylic bone cement. II. Acrylic bone cement with bromine-containing monomer

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Abstract Bromine-containing methacrylate, 2-(2-bromopropionyloxy) ethyl methacrylate (BPEM), had been used in the formulation of acrylic radiopaque cements. The effect of this monomer incorporated into the liquid phase of acrylic bone cement, on the curing parameters, thermal properties, water absorption, density, compression tests and radiopacity was studied. A decrease of maximum temperature and an increase of the setting time were observed with the addition of the bromine-containing monomer in the radiolucent cement composition. Adding BPEM in radiolucent acrylic bone cements composition results in the decrease of glass transition temperature and increase of its thermal stability. Acrylic bone cements modified with bromine-containing comonomer are characterized by polymerization shrinkage lower than the radiolucent cement. Addition of bromine-containing comonomer in radiolucent acrylic bone cement composition determines the increase of compressive strength. Acrylic bone cements modified with bromine-containing comonomer proved to be radiopaque.

1 Introduction

Poly(methyl methacrylate) (PMMA)—based acrylic bone cements are extensively used in orthopedic surgery (e.g., as anchoring agents in hip or knee joint replacement), neurosurgery (e.g., to repair skull defects) and spinal surgery (e.g., for injection into vertebroplasty and kyphoplasty) [1–8]. Chemically, the conventional acrylic bone cement, also known as a cold curing, is the result of the free radical polymerization of methyl methacrylate (MMA, as a liquid phase) in presence of the solid phase, as the PMMA polymer [1–3]. Also, in all current commercially available formulations of these cements, benzoyl peroxide (POB) (in powder form) and aromatic tertiary amine, N,N-dimethyl-4-toluidine (DMPT) (in liquid monomer form), serves as both initiator and activator, respectively, in the polymerization reaction [1–8].

As the surgeon should monitor the healing process after joint replacement, the acrylic bone cement must maintain a sufficient radiopacity so that it may be differentiated from the bone, and yet to appear in the radiographs [9, 10]. The acrylic bone cement itself is not radiopaque, once it is mainly composed of elements such as carbon, oxygen and hydrogen, all with low electronic density. Therefore, this property is achieved by incorporating inorganic radiopaque compounds, such as barium sulfate or zirconium oxide [2, 9–14]. Since they are incompatible with polymer matrix, their introduction in the acrylic bone cement composition has a negative influence upon mechanical, tribiological and biological properties of cements [9, 10, 15–27].

Considering all these, some alternatives to the traditional inorganic radiopacifying agents have been put forward [28–30]. A first approach consists in introducing radiopaque monomeric units during the polymer synthesis. Monomers having covalent bounded halogen atoms such as iodine or bromine, known as possessing radiopaque properties, can be copolymerized, in small amounts, with other monomers, forming the bulk of the implant. In this line, some iodine methacrylates are successfully developed for different clinical applications [28–30]. More specifically, in the field of acrylic bone cement, the possibility to confer radiopacity by introducing an X-ray opaque methacrylate

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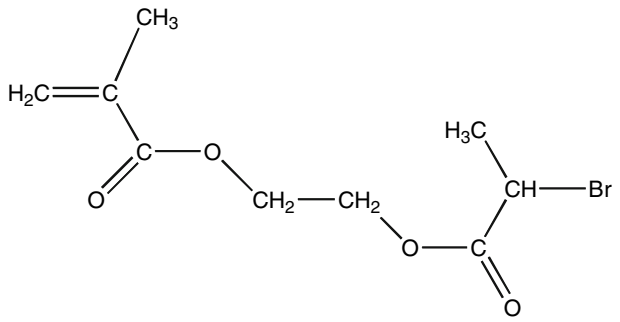

Scheme 1 Chemical structure of BPEM

containing iodine in the liquid phase of the acrylic bone cement has been studied [9, 10, 31–35].

Recently, Davy et al. [36–38] reported the preparation of some bromine-containing polymers, although a higher radiopacity is attainable with appropriate iodine monomers.

This paper deals with the modification of acrylic bone cement formulations by introduction, in the liquid phase, of a bromine containing monomer. In this case, 2-(2-bromopropionyloxy) ethyl methacrylate (BPEM) was synthesized in the laboratory (Scheme 1) [39].

2 Experimental

2.1 Materials

Methyl methacrylate monomer (MMA) (Aldrich) stabilized with 100 ppm of monomethylether of hydroquinone was used as received, without further purification. 2-(2-bromopropionyloxy) ethyl methacrylate (BPEM) was synthesized as described in [39]. Dimethyl-p-toluidine (DMPT) (Aldrich) and benzoyl peroxide (BPO) (Aldrich) were used as received. Poly (methyl methacrylate) (PMMA) beads (medical grade) were supplied by Astar S.A., (Cluj-Napoca, Romania).

2.2 Preparation of bone cements

The experimental acrylic bone cements were formulated by adding the liquid component to the solid component, at room temperature, in a typical solid:liquid ratio of 2:1. In all cases 1.5% (wt/wt) DMPT in the liquid component and 2% (wt/wt) BPO in the solid component were added. The powder, the liquid and all the other devices used in the experiment were allowed to equilibrate at room temperature (23°C) for 2 h prior to mixing.

Acrylic bone cements were prepared from MMA as the base monomer, and BPEM as comonomer. The conventional acrylic bone cement was modified by introducing 5, 10, 15 or 20% (wt/wt) BPEM in the liquid phase. Cements containing only MMA and DMPT in the liquid phase (radiolucent cement) were prepared for the sake of comparison, as reference samples (Table 1). In order to study the influence of composition of the liquid phase without influence of the other components, the addition of the radiopaque agent in the reference samples was avoided. It is also interesting to assess that the absence of the radiopaque addition in this cement samples are transparent or at least translucent, making it easier to examine visually the porosity of the cured cement.

Preparation of the acrylic bone cement was carried out following the traditional method used for classical acrylic bone cements, as described in the ASTM Standard [40]. The components of the acrylic bone cements were hand-mixed in a ceramic bowl with a ceramic spatula, at about 1 Hz. When the dough state was reached, the cement mass was placed in the corresponding mould and allowed to cure for 1 h.

2.3 Characterization

The acrylic bone cement formulations were characterized by measuring the curing parameters, thermal properties, water absorption, density, compression tests and radiopacity.

The *curing parameters* were registered according to the ASTM Standard [40]. Time and temperature were measured from the onset of the mixing powder with the liquid. Two determinations were performed for each acrylic bone cement formulation.

The *thermal properties* of the new formulations of acrylic bone cements were analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC was performed on a Pyris Diamond DSC (Perkin Elmer, USA). The samples prepared in powder form obtained by cryogenic grinding of the cured cement (8–12 mg) were introduced in aluminum pans and heated from 10 to 160°C at a constant rate of 20°C/min. Glass transition temperatures (T_g) were determined on the second

Table 1 Liquid phase composition for the acrylic bone cements modified with BPEM

Formulations	Monomers content (% wt)	
	MMA	BPEM
BPEM-0	100	–
BPEM-5	95	5
BPEM-10	90	10
BPEM-15	85	15
BPEM-20	80	20

scan, considering the onset of transition. Thermogravimetric analysis was performed under nitrogen flow (25 cm^3 min^{-1}) at a heating rate of 15°C/min, from 25 to 700°C with a Mettler Toledo model TGA/SDTA 851 (Mettler-Toledo AG, Analytical, Switzerland). The initial mass of the samples was between 4.5 and 7.5 mg.

The *water absorption* of the prepared formulations was studied by immersing 3.5 mm thick disks, 10 mm in diameter, in distilled water, at 23°C. The samples were weighed at different times until the equilibrium hydration degree was attained. After the water absorption tests, the samples were kept one week into a drying chamber, under vacuum, at 60°C.

The *apparent densities* of new bone cement formulations were determined by picnometer's method [41]. To this end, a 20 ml picnometer and ethylic alcohol were used as immersion liquid. The maximum densities were calculated with the methods presented in literature [42]. The polymerization shrinkage and porosity are directly related to density.

Compressive tests were carried out on cylindrical specimens (6 mm in diameter and 12 mm high), at room temperature, on a mechanical testing machine (TyraTest, Germany) using a load of 100 kN and a cross-head speed of 5 mm/min, at room temperature (23°C). Tests were carried out up to failure or until 70 or 80% reduction in specimen height. Five specimens were tested for each formulation and their compressive strength (CS) was calculated using the following formula:

$$\mathrm{CS} = F/A \quad (1)$$

where F is the applied load and A is the area of the test specimen.

The *radiographic* study was carried out on a standard General Electric X-ray instrument (set at 55 kV and 2.5 MAS). The relative X-ray opacity was determined visually, for the sake of comparison.

3 Results and discussion

3.1 Curing parameters

The temperature reached during setting is directly related to the amount of heat produced from the polymerization reaction of the liquid phase (544 J/g for MMA) [43–45]. The maximum temperature depends on monomer's nature and on their ratio in acrylic bone cement compositions [15, 46, 47]. Thus, the main curing parameters: maximum temperature, setting temperature, setting time and time to reach maximum temperature ($t_{T_{max}}$) should be determined. All these characteristics were established from the polymerization exotherms for each formulated cement (Fig. 1).

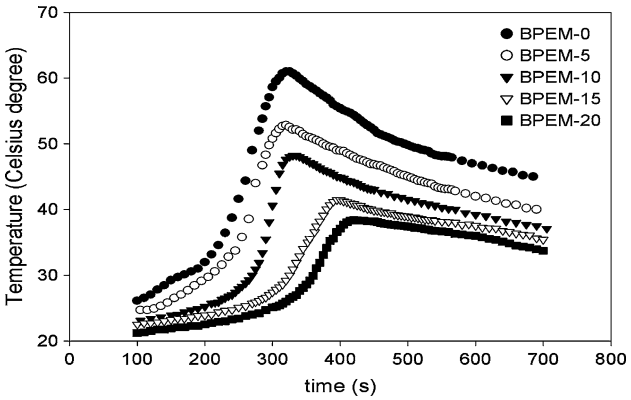

Fig. 1 Polymerization exotherms for acrylic bone cements modified with BPEM

The maximum temperature (T_{max}) was considered as the maximum value reached during the curing reaction. The setting temperature (T_{ts}) and setting time (t_s) were considered as the temperature and time at which temperature rises at a halfway point between the maximum temperature attained and room temperature (T_{amb}), calculated according to the ASTM Standard, as follows: $T_{ts} = (T_{max}–T_{amb})/2$ [40].

Figure 1 plots show the temperature profiles of the formulations with the composition indicated in Table 1. The curing parameters (T_{max}, $t_{T_{max}}$, t_s, T_{ts}) obtained from these diagrams are listed in Table 2.

Analysis of the curing parameters for the acrylic bone cements modified with different amounts of BPEM, shows a decrease in maximum temperature. Formulations with higher amounts of bromine-containing monomer present a more significant decrease of T_{max}. It can be clearly noted that all formulated acrylic bone cements exhibited a T_{max} much lower than the value established by ASTM Standard (90°C) [40]. The T_{max} values obtained for the acrylic cement modified with bromine containing monomer are similar with the values presented in literature for acrylic cements modified with iodine containing monomers (45–75°C) [28, 29, 32–34].

These T_{max} variations can be attributed to total heat polymerization, polymerization kinetics and heat transport phenomena [43].

Table 2 Curing parameters for acrylic bone cements modified with BPEM

Formulation	T_{max} (°C)	$t_{T_{max}}$ (s)	t_s (s)	T_{ts} (°C)
BPEM-0	61	320	250	41
BPEM-5	52.9	320	260	37
BPEM-10	48.2	330	287	34.6
BPEM-15	41.5	395	332	31.3
BPEM-20	38.4	420	358	29.7

The remarkable decrease of T_{max} can be attributed to the molecular weight difference between MMA and the comonomer ($M_{BPEM}/M_{MMA} = 2.66$). In this sense, the exothermic character of the polymerization reaction depends on the number of acrylic groups susceptible to react during the polymerization process, and the addition of monomer with high molecular weight gives a lower amount of energy by mass unit. The lower and slow release of the polymerization heat during the setting reaction allows a gradual heat dissipation through the mass, leading to a lower T_{max}, which is of great importance, since the slower rise in temperature has the advantage that the generated heat can be dissipated easily from the cement during setting, causing less adverse effects on the surrounding tissues [34, 48–50].

The setting temperature is strongly related to the maximum temperature, and its value decreases as the quantity of bromine-containing monomer increases in the formulations.

The setting time and the time of reaching maximum temperature increase with the addition of a higher percentage of BPEM. It is an advantage that the t_s for BPEM formulations was higher than the t_s for radiolucent cement, as the modified bone cements allow a longer working time [34, 50]. It was observed that the values obtained for acrylic bone cements modified with bromine containing monomer are lower than the values reported in literature for acrylic bone cement modified with iodine containing monomers [28, 29, 32–34].

From the analysis of curing parameters, it is observed that the modification of acrylic bone cements with bromine containing monomer presents advantages from biologically point of view (ensures the reduction of the tissues necrosis) and concerning the manipulation time. Preliminary tests showed that the new formulations of acrylic bone cements present a good biocompatibility. A study about the toxicity of bromine containing monomer is in progress.

3.2 Thermal properties

The influence of modified cements formulation on glass-transition temperature (DSC), and the heating behavior (TGA) of the new acrylic bone cements were determined, from the perspective of the thermal properties.

Table 3 Thermal characteristics for acrylic bone cements modified with BPEM

Formulations	T_g (°C)	T_{onset}	T_{peak}
BPEM-0	110.6	182.2	396
BPEM-10	88.3	248.3	401.4
BPEM-20	85.7	231.4	409.4

Glass-transition temperature (T_g) was used to characterize the acrylic bone cements, because it is related to the flexibility and toughness of the cured biomaterials [51]. It was postulated that materials with a too high T_g are brittle in nature, which is indirectly related to the failure of the cement and, subsequently, to components loosening [52].

Table 3 summarizes the results on the influence of bromine-containing monomer on the glass-transition temperature of modified acrylic bone cements.

It was observed that the addition of 10, and respectively, 20% bromine-containing monomer in the liquid phase of the radiolucent cement determines a T_g decrease, which may be attributed to a higher mobility of the chain segments for the copolymer systems (BPEM-co-MMA), a mobility induced by the larger lateral substituent of BPEM. As can be seen, T_g of cement formulated with BPEM tends to decrease with increasing the comonomers concentration. Accordingly, the acrylic bone cements modified with BPEM possess a better flexibility than translucid formulation.

Also, the variation of samples weight with regard to heating temperature (TGA) and samples decomposition speed (DTG) was determined (Fig. 2 and Table 3).

All these results show that the partial replacement of MMA with BPEM, does not modify significantly the heating behavior of the newly modified acrylic bone cements. This observation is based on the form of the TG and DTG diagrams registered for acrylic bone cements, the liquid phase of which was modified with 20% bromine-containing monomer, as well as for the radiolucent cement (Fig. 2). Nevertheless, the temperature at which the

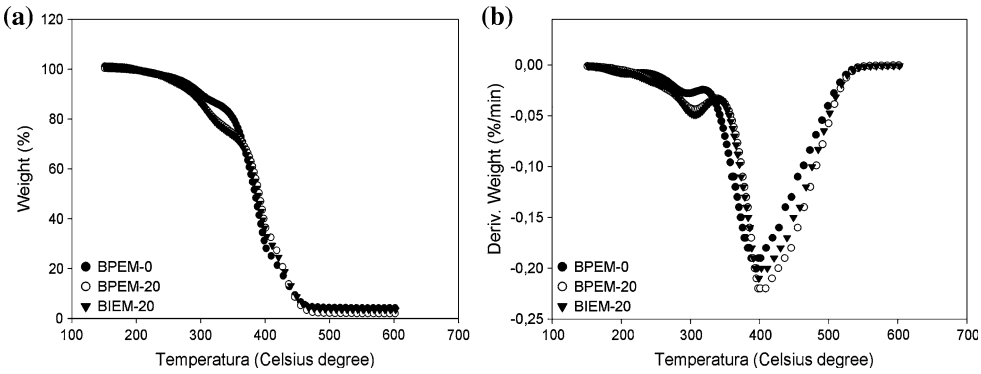

Fig. 2 TGA (**a**) and DTG (**b**) thermograms for acrylic bone cements modified with BPEM

thermal decomposition (T_{onset}) of the modified acrylic cements begins was found to be 50–60% higher than that of the thermal decomposition of radiolucent cement, which proves that the modified cements have a better thermal stability than the one of radiolucent cement.

3.3 Water absorption

The water absorption of any polymeric material is very important for orthopedic applications, as the absorbed water influences the mechanical and biological properties of the bone cement [19, 32, 35, 49, 53–57]. Moreover, water absorption may cause the hydrolysis of some compounds entering the composition of the acrylic bone cement, which negatively influences the mechanical and biological properties [57]. To a certain extent, water absorption may not be always entirely disadvantageous, appearing even beneficial in dental filling materials, for which the accompanying swelling compensates for polymerization shrinkage [53, 58, 59]. Hence, a precise evaluation of the water absorption characteristics of the polymeric biomaterials is important.

When a glassy polymer is introduced into water, it steadily absorbs water until, eventually, the process equilibrates. This kind of polymer follows a Fickian transport mechanism of water, characterized by a water uptake (M_t/M_{eq}) proportional to $t^{1/2}$. According to Fick's law, in the differential form from this sheet, the neglected diffusion through the edges is [60, 61]:

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

where M_t is the mass uptake at time t, M_{eq} is the equilibrium uptake, $2l$—thickness, D is the diffusion coefficient and n is the diffusion exponent, which is indicative of the transport mechanism. The value of n obtained from the linear regression is about 0.5, indicating that the diffusion may be Fickian [60, 61].

The early stages of diffusion-controlled uptake (a zone in which M_t/M_{eq} is linear, which, usually is $M_t/M_{eq} < 0.5$) is describable by a reduced form of an applicable solution of Fick's Second Law of Diffusion (Stefan's approximation), which is [62, 63]:

$$\frac{M_t}{M_{eq}} = 2\left(\frac{Dt}{\pi l^2}\right)^{1/2} \quad (3)$$

where M_t, M_{eq}, D and l represent the same previously presented characteristics.

The diffusion coefficient D, can be determined from Eq. 2 by substitution of the uptake measurement [62, 63]. If uptake M_t, is measured at convenient intervals of time until equilibrium is reached, M_{eq}, the plot of M_t/M_{eq} against $t^{1/2}$, should provide a straight line where slope, s, is given by [53]:

$$s = 2 \cdot \left(\frac{D}{\pi l^2}\right)^{1/2} \quad (4)$$

$$D = \frac{s^2 \pi l^2}{4} \quad (5)$$

To quantify the swelling behavior of the acrylic bone cement formulations, the water absorption data were analyzed by applying the Frisch equation [64]:

$$\frac{M_t}{M_{eq}} = k \cdot t^n \quad (6)$$

where n indicates the type of process associated to water absorption.

The hydration degree (H%) can be determined with the following equation [53, 64]:

$$H\% = \frac{(W_t - W_0)}{W_0} \cdot 100 \quad (7)$$

where W_0 is the initial weight of the specimen and W_t is the weight of the specimen at time t.

Water absorption (A%) and percentage of elution (E%) can be calculated using the following expression [53, 64, 65]:

$$A\% = \frac{W_{eq} - W_f}{W_{eq}} \cdot 100 \quad (8)$$

$$E\% = \frac{W_0 - W_f}{W_0} \cdot 100 \quad (9)$$

where W_f is the weight of the sample after testing.

To obtain water absorption characteristics, the mass gain (W_0) (weighed to 0.0001 g) of a cement disc specimen (diameter = 10 mm, thickness, $2l$ = 3.5 mm, obtained by pouring the acrylic dough into a Teflon mold) was immersed in 100 ml distilled water at room temperature (23°C), and continuously monitored. The samples were weighed at different times until the water uptake was constant within 0.0005 g. For each weighing (W_t), the samples were removed from water, dried on a filter paper and then rapidly weighed. The equilibrated samples were dried to constant weight (W_f) in a dry oven (60°C).

Figure 3a presents the diagrams showing the variation of water absorption as a function of the immersion time.

Analysis of these diagrams shows that the modification of the liquid phase by replacing a part of MMA with BPEM, determines no change in the water absorption mechanism in the modified cements. Nevertheless, it was found that, by addition and then by increasing the amount of bromine-containing monomer, water absorption decreases (Table 4). To explain this behavior, the fact that the bromine-containing monomer, characterized by a

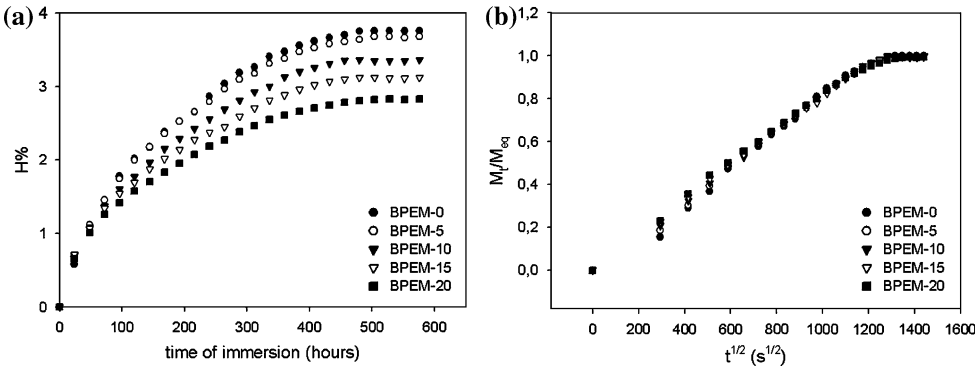

Fig. 3 Water absorption for acrylic bone cements modified with BPEM

higher capacity of chain transfer, can determine a slight cross-linking during curing of the new cements should be considered. The idea is also supported by the fact that all cements modified with bromine-containing monomer are insoluble in ordinary solvents.

Figure 3b shows the typical diagrams of water absorption *versus* $t^{1/2}$ for bone cement with different concentration of bromine-containing comonomer, in liquid phase.

In all cements new formulation, a Fickian diffusion behavior can be assumed, if considering the linear dependence at low values ($M_t/M_{eq} < 0.8$) and the reasonable good agreement with the existing theoretical data. Consequently, the slope enables the calculation of the diffusion coefficients, with values ranging between 1.51 and $1.8 \cdot 10^{-8}$ cm^2 s^{-1} (Table 4). Decrease of the diffusion coefficient, along with the increase of bromine-containing comonomers ratio in the newly formed acrylic bone cements can be explain by a cross-linking process favored by the chain transfer capacity of the comonomer used for modifying the liquid phase.

Addition and subsequent increase of the ratio of bromine-containing comonomers in the liquid phase composition does not modify the diffusion coefficient (n), whose values are maintained between 0.40 and 0.49 (Table 4). This is a proof for that, in all acrylic bone cements analyzed in this paper, the diffusion process obeys Fick's law [60, 61].

The acrylic bone cements modified with BPEM, are characterized by a weight loss (elution) higher than that of the radiolucent acrylic cement (Table 4). This evolution of elution may be due the high content of residual monomer resulted from modification of acrylic bone cements with bromine containing monomer.

Study of the sorption kinetics of all formulations analyzed in this work shows a similar behavior, which fits well with Fick's equation. Thus, a Fickian diffusion can be assumed for these new acrylic bone cement matrices.

Table 4 Water absorption characteristics for acrylic bone cements modified with BPEM

Formulation	A%	E%	D × 10^{-8} (cm^2/s)	*n*
BPEM-0	4.82	1.24	1.8	0.46
BPEM-5	3.77	2.21	1.66	0.44
BPEM-10	3.53	2.80	1.63	0.43
BPEM-15	3.36	3.32	1.54	0.42
BPEM-20	3.02	2.74	1.51	0.40

3.4 Density

Density measurements have contributed to the determination of polymerization shrinkage and porosity of the acrylic bone cements formed by modification of the liquid phase, when replacing MMA with BPEM.

Cement shrinkage is associated with the setting reaction, in which transformation of a viscous material into hardened mass results in an increase in density, with a concomitant decrease in volume [54]. Polymerization shrinkage (Sh), associated with the setting reaction, was determined using the following equations [56]:

$$\%\mathrm{Sh} = \frac{\mathrm{densityofpolymer} - \mathrm{densityofmonomer}}{\mathrm{density\ of\ polymer}} \cdot 100 \tag{10}$$

The experimental shrinkage (Sh_{exp}) was calculated by taking into account the experimentally determined density (apparent density) and also the theoretical shrinkage (Sh_{theor}), calculated from the polymerization shrinkage value determined by formula [42, 56, 66, 67]:

$$\frac{\Delta V}{V}(\%) = 22.5 \cdot \mathrm{DC_{mix}} \cdot \frac{\sum_i (f_i \cdot x_i)}{\sum_i (M_{mi} \cdot x_i)} \cdot \rho_{\mathrm{mix}} \cdot 100 \tag{11}$$

where 22.5 represents the volume change per mole of methacrylate groups (C=C) in MMA (cm^3/mol) when MMA is polymerized [68, 69], DC is the fractional degree of conversion, f_i is the functionality of monomer (i), x_i is the mole fraction of monomer (i), M_{mi} is the molecular mass of monomer (i) and ρ_{mix} is the density of the monomer mixture.

$$\%Sh_{exp} = \frac{\text{apparentdensity} - \rho_{mix}}{\text{apparent density}} \cdot 100 \quad (12)$$

$$\%Sh_{theor} = \frac{\text{maximumdensity} - \rho_{mix}}{\text{maximum density}} \cdot 100 \quad (13)$$

Maximum density (ρ_{th}) is defined as the density of the acrylic bone cement completely free of pores and voids [41, 67]. The results are summarized in Table 5.

Analysis of these results shows that both theoretical (ρ_{th}) and apparent density (ρ_{exp}) increase with the addition and subsequent increase of the ratio of bromine-containing comonomer in acrylic bone cement compositions. This increasing is explained by the higher density of the bromine containing comonomer (ρ_{BPEM} = 1.3421 g/cm^3) *versus* MMA (ρ_{MMA} = 0.936 g/cm^3).

Addition of bromine-containing comonomer in the composition of radiolucent acrylic bone cement reduces polymerization shrinkage (Table 5). This diminution is about 11% for the modified acrylic cement with 20% bromine containing monomer (from 14.41% at 12.84%) and it is explained by the higher molecular mass of the bromine-containing comonomer (M_{BPEM} = 266 g/mol) instead of MMA (M_{MMA} = 100 g/mol).

Experimentally, the volume change per mole of methacrylate groups (C=C) in MMA is $\Delta V_{C=C}$ = 22.5 cm^3/mol [68], when the MMA is polymerized. For a given gravimetric content of bromine-containing comonomer in acrylic bone cements composition, as their molecular mass is higher, the number moles is smaller than that of MMA, which means that the polymerization shrinkage is more reduced, too.

Experimental shrinkage is lower than the theoretically determined one, as due to the presence of the pores in the structure of the cured cements.

Another factor directly related to density and polymer shrinkage is the porosity of the sample, since cements with reduced porosity contract more during setting [15]. Porosity is always present in the cement structure as a consequence of the manual mixing of the powder and liquid components in air and the evaporation of the monomers [15, 70, 71].

Table 5 Density, polymerization shrinkage and porosity for acrylic bone cements modified with BPEM

Formulation	ρ_{th}	ρ_{exp}	$\%Sh_{th}$	$\%Sh_{exp}$	%P
BPEM-0	1.129	1.094	17.11	14.41	3.15
BPEM-5	1.133	1.093	16.77	13.70	3.56
BPEM-10	1.138	1.099	16.43	13.46	3.43
BPEM-15	1.143	1.105	16.09	13.17	3.36
BPEM-20	1.149	1.111	15.74	12.84	3.32

Determination of polymer density gives values of the average percentage of porosity (%P) from the following expression [15, 70, 71]:

$$\%P = \left(1 - \left(\frac{\text{apparentdensity}}{\text{maximum density}}\right)\right) \cdot 100 \quad (14)$$

Results presented in Table 5 show that addition of bromine-containing comonomer in radiolucent acrylic cements composition determine only an insignificant increase of porosity. Increasing of the content of bromine-containing comonomer determines a negligible increase of porosity, which may be explained by the reduction of the quantity of evaporated MMA during mixing, as a result of the reduced ratio of this monomer in liquid phase composition. All these results lead to the conclusion that the porosity of acrylic cements analyzed in this paper is primarily due to the mixing method and, to a lower extent, to the composition of the liquid phase.

3.5 Compressive tests

In clinical service, the prosthesis is subjected to static or quasi-static direct compressive forces during certain activities, such as the one-legged stance [49]. Also, the cement mantle has been postulated as a compressive wedge between the femoral stem and the bone, by acting as shock absorber between the implant and bone [49]. Thus, the static compressive properties of the acrylic bone cement are very important. The result on compressive strength is shown in Table 6.

Analysis of these results shows that addition and then increase of the proportion of bromine-containing comonomer in the composition of liquid phase assures higher compression strength. It can be seen that all formulated cements profiled the minimum compressive strength (70 MPa) required in ASTM Standard [40]. However, the compressive strength of the formulated cements was comparable to that of the commercial bone cements [42, 43]

3.6 Radiopacity

The acrylic bone cements, for which a part of MMA in liquid phase was replaced with BPEM, proved to be radiopaque, as

Table 6 Compressive strength of acrylic bone cements modified with BPEM

Formulation	CS, MPa
BPEM-0	76.46
BPEM-5	87.14
BPEM-10	93.10
BPEM-15	96.78
BPEM-20	100.68

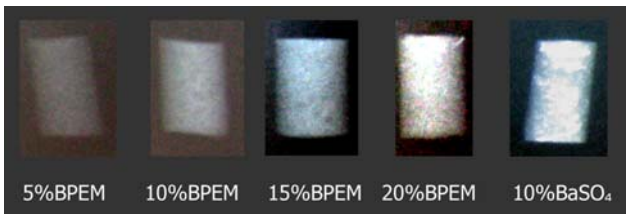

Fig. 4 Radiographs for acrylic bone cements modified with BPEM *versus* acrylic bone cement with $BaSO_4$

shown by the radiographic images presented in Fig. 4, in which the results obtained for new acrylic cements are comparatively analyzed with a composition of acrylic bone cements containing $BaSO_4$. The images from Fig. 4 show that the radiopacity increases with increasing the proportion of bromine-containing comonomer in the liquid phase composition of the newly formed acrylic bone cements.

4 Conclusion

It was established that radiopaque acrylic bone cements can be obtained by adding BPEM in liquid phase. Addition of bromine-containing comonomer in acrylic bone cements composition assures improvement of the curing parameters, flexibility, thermal stability, polymerization shrinkage and compression strength, without changing the swelling behavior in distilled water and porosity of these acrylic bone cements.

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