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Radiopaque acrylic bone cement with bromine-containing acrylic monomer. II

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Abstract: Bromine-containing methacrylate, 2-(2-bromoisobutyryloxy) ethyl methacrylate (BIEM), had been used in the formulation of acrylic radiopaque cements. The effect of this monomer incorporated into the liquid phase of acrylic bone cement (ABC), 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 BIEM in radiolucent ABCs composition results in the decrease of glass transition temperature and increase in its thermal stability. The ABCs modified with bromine-containing comonomer are characterized by polymerization shrinkage lower than the radiolucent cement. Addition of bromine-containing comonomer in radiolucent ABC composition determines the increase of compressive strength. The ABCs modified with bromine-containing comonomer proved to be radiopaque.

Introduction

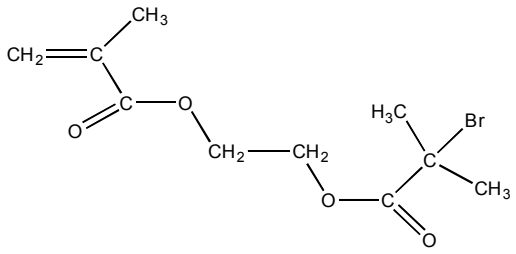
Poly(methyl methacrylate) (PMMA)–based acrylic bone cements (ABCs) have been widely used in orthopedics for the fixation of joint prosthesis [1-5]. The main function of the cement is to serve as interfacial phase between the high modulus metallic implant and bone, thereby assists the transfer and load distribution [1, 3, 6-9]. From a chemical point of view, the curing process of this cement, also known as cold curing [10, 11], is the result of the free radical polymerization of a mixture of PMMA and methyl methacrylate (MMA), initiated by the decomposition of benzoyl peroxide (BPO) and activated by presence of a tertiary amine, the most classical being N,N-dimethyl-p-toluidine [10-15]. During the polymerization process the dough mixture becomes stiff in a short time (10-15 min), which allows the application in situ and the primary fixation of the joint prosthesis [16, 17].

Orthopaedic ABC have to fulfill several medical requirements, such as: moderate sitting time (so that cement does not cure too fast or too slow), low values of maximum cure temperature (to avoid thermal necrosis of the bone tissue, during the setting of the cement), high values of compressive strength (allowing the cured cement mantle to withstand the compressive loads involved in normal daily activities). It is also essential for the cements to be radiopaque, in order to allow radiological detection [7, 18, 19]. However, the radiopacity of ABC itself is very limited, because

of the low density of the polymeric materials (macromolecular structure containing light elements such as hydrogen, oxygen and carbon). Radiopacity has been frequently achieved by X-ray contrast material, such as barium sulfate or zirconium dioxide, which are also known to alter the biological and mechanical properties of the ABC [3, 7, 18-21].

Considering all these aspects, some alternatives to the traditional inorganic radiopacifying agents have been put forward [19, 22-28]. One approach consists in introducing radiopaque-monomeric units during the polymer synthesis [23-25]. Monomers having covalent-bounded halogen atoms such as iodine and bromine, possessing radiopaque properties, can be polymerized with classical monomers (such as MMA), to form the final ABC. In this line, some iodine-containing methacrylates have been proposed for different clinical applications [23, 27-30]. More specifically, in the field of ABC, the possibility to confer radiopacity by introducing iodine and bromine-containing methacrylates in the liquid monomer phase has been studied [18, 19, 26, 27, 30].

This paper deals with the modification of ABC formulations by introducing a bromine containing methacrylate in the liquid monomer phase, the 2-(2-bromoisobutyryloxy) ethyl methacrylate (BIEM) which was synthesized in the laboratory (Scheme 1) [24, 30].



BIEM

Scheme 1. Chemical structure of BIEM.

Results and discussion

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) [31-33]. The maximum temperature depends on monomer's nature and on their ratio in ABC compositions [15, 34, 35]. The main curing parameters like the maximum temperature, setting temperature, setting time and time to reach maximum temperature (t_{Tmax}) should be determined from the polymerization exotherms for each formulated cement (Figure 1, Table 1).

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 the temperature, respectively the time when the temperature reaches half value between maximum temperature and room temperature (T_{amb}), calculated according to the ASTM Standard, as follows: $T_{ts} = T_{amb} + (T_{max} - T_{amb})/2$ [8].

Analysis of the curing parameters for the ABCs modified with different amounts of BIEM 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 ABCs exhibited a T_{max} much lower than the value established by ASTM Standard (90 °C) [8]. The T_{max} values obtained for the ABC modified with bromine-containing monomer are similar with the values presented in literature for acrylic cements modified with iodine containing monomer (45-75 °C) [19,23,26-28,31].

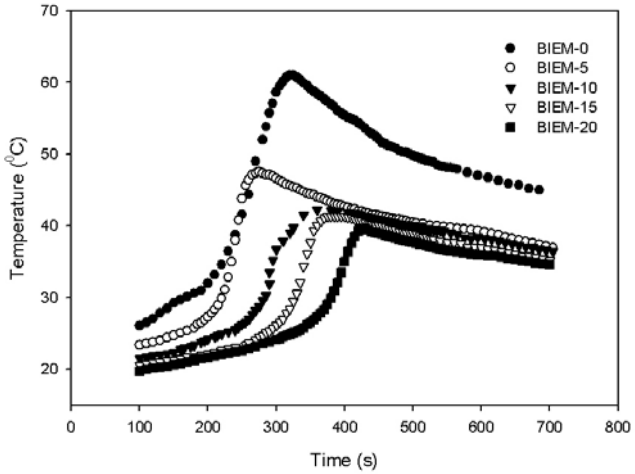


Fig. 1. Polymerization exotherms for the BIEM – ABC formulations.

Tab. 1. Curing parameters for the BIEM – ABC formulations.

Formulation	T_{max} (°C)	t_{Tmax} (s)	t_s (s)	T_{ts} (°C)
BIEM-0	61.0	320	250	41.0
BIEM-5	47.5	275	234	34.3
BIEM-10	42.2	360	288	31.6
BIEM-15	41.3	380	331	31.2
BIEM-20	39.6	430	380	30.3

The remarkable decrease of T_{max} can be attributed to the molecular weight difference between MMA and the comonomer (M_{BIEM}/M_{MMA} = 2.83). 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 [19, 32, 33, 36].

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

The setting time and the time of reaching maximum temperature increase with the addition of a higher percentage of BIEM. It is an advantage that the t_s for BIEM formulations was higher than the t_s for radiolucent cement, as the modified ABC

allows a longer working time [19, 36]. It was observed that the values obtained for ABCs modified with bromine-containing monomer are lower than the values reported in literature for ABC modified with iodine containing monomer [19, 23, 26-28].

From the analysis of curing parameters, it is observed that the modification of ABCs 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 ABCs present a good biocompatibility. A study about the toxicity of bromine containing monomer is in progress.

Thermal properties

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

Glass-transition temperature (T_g) was used to characterize the ABCs, because it is related to the flexibility and toughness of the cured biomaterials [37]. 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 [38].

Table 2 summarizes the results on the influence of bromine-containing monomer on the thermal properties of modified ABCs.

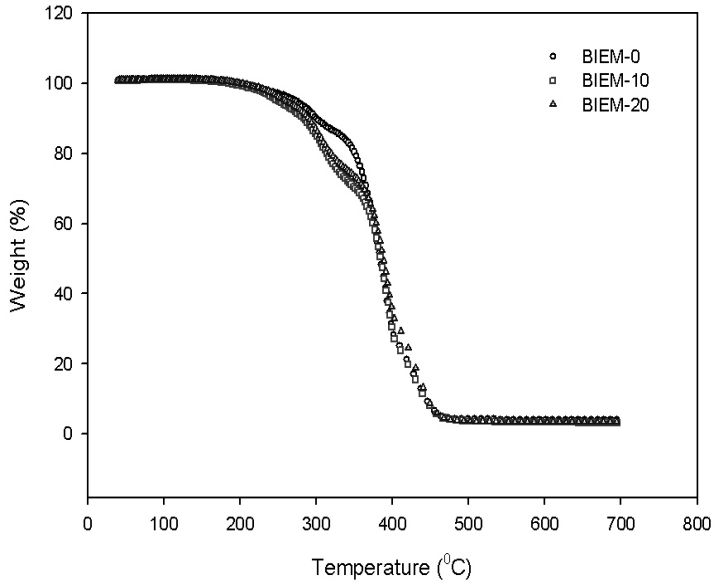
Tab. 2. The T_g, TGA and DTG – values for BIEM – ABC formulations.

Formulation	T_g (°C)	T_{onset} (°C)	T_{peak} (°C)
BIEM-0	110.6	182.2	396.0
BIEM-10	89.5	224.3	402.7
BIEM-20	87.9	232.4	398.9

It was observed that the addition of 10, and respectively, 20% (w/w) 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 (MMA-co-BIEM), a mobility induced by the larger lateral substituent of BIEM. As it can be seen, T_g of cement formulated with BIEM tends to decrease with increasing the comonomer concentration. Accordingly, the ABCs modified with BIEM 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 (Figure 2 and Table 2).

All these results show that the partial replacement of MMA with BIEM does not modify significantly the heating behavior of the newly modified ABCs. This observation is based on the form of the TG and DTG diagrams registered for ABCs, the liquid phase of which was modified with 20% (w/w) bromine-containing monomer, as well as for the radiolucent cement (Figure 2). Nevertheless, the temperature at which the thermal decomposition (T_{onset}) of the modified ABCs begins was found to be 23-27% 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.



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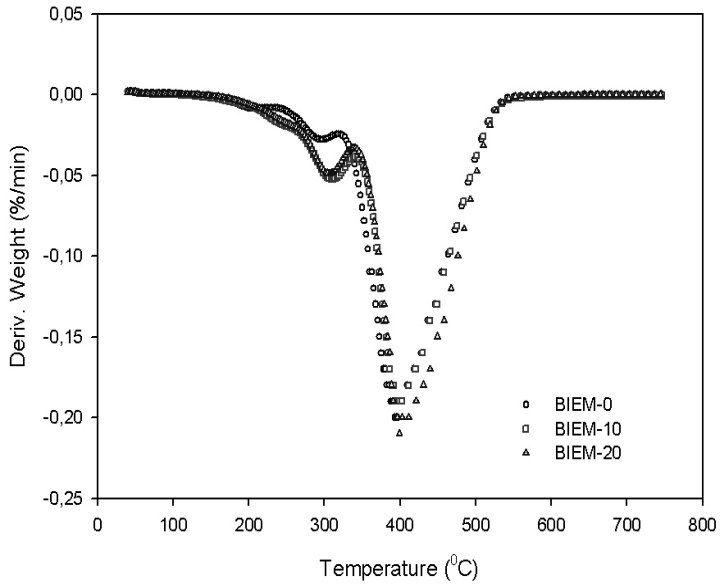
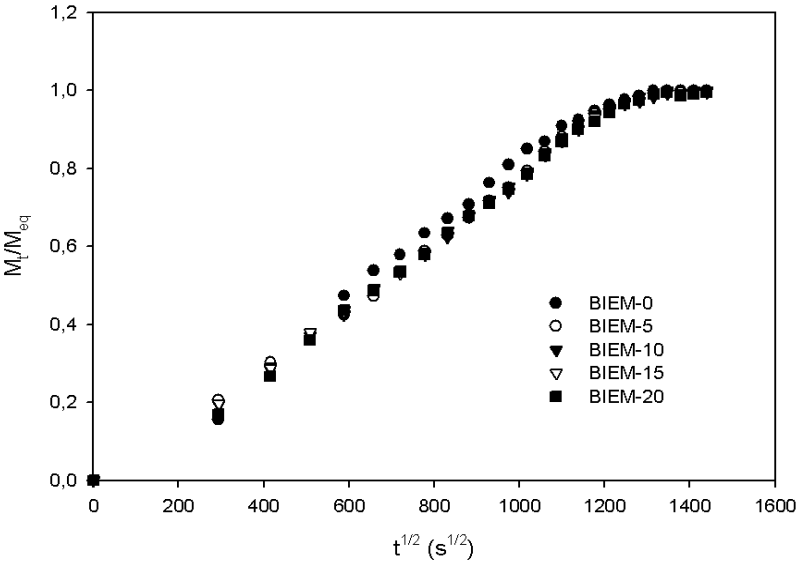


(b)

Fig. 2. The TGA (a) and DTG (b) thermograms for the BIEM–ABC formulations.

Water absorption

Investigating the water absorption of the ABCs is very important for orthopedic applications, as the absorbed water influences the mechanical and biological properties of the bone cement [22, 26, 39-42]. Additionally, water absorption may induce hydrolysis of some ingredients from the acrylic bone cement, which negatively influences the mechanical and biological properties. To a certain extent, water uptake may become beneficial for some medical applications, as for the dental filling materials, since the water swelling may compensate for polymerization shrinkage [39-42].



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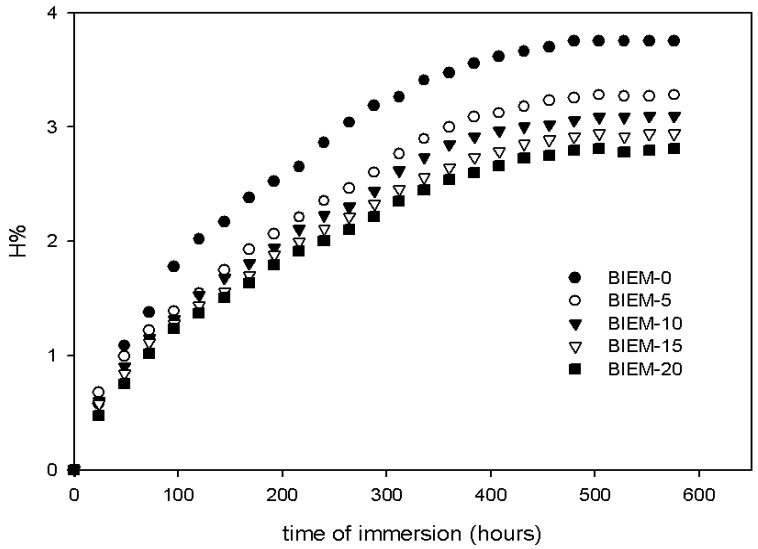

(b)

Fig. 3. Water absorption for the BIEM-ABC formulations: (a) water absorption vs. $t^{1/2}$; (b) hydration degree (H) vs. immersion time.

The water absorption characteristics were determined by immersing cement disks (diameter 10 mm, thickness 3.5 mm) in distilled water, at room temperature (23 ^{o}C), and continuously monitoring the evolution of the samples' weight. More specifically, the samples were weighed at different times until the water uptake was constant within 0.0005 g. Before each weighing (M_t), the samples were removed from water, dried on a filter paper and then rapidly weighed. The equilibrated samples were dried to constant weight (M_f) in a drying oven (60 °C, under vacuum, 72 hours).

The early stages of water uptake by ABC are supposed to be diffusion-controlled and so, reasonably described by a reduced solution of Fick's Second Law of Diffusion (Stefan's approximation) [43]:

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

where M_t is the mass uptake at time t, M_{eq} is the equilibrium uptake, $2l$ - thickness, D is the diffusion coefficient. This approximation is usually valid within the region where M_t/M_{eq} is linearly dependent on $t^{1/2}$, typically for $M_t/M_{eq} < 0.5$. In these conditions, the diffusion coefficient D may be determined from the slope of the plot M_t/M_{eq} versus $t^{1/2}$. The experimental results for different BIEM-acrylic bone cements are presented in Figure 3 and Table 3.

Tab. 3. Water absorption characteristics for BIEM-ABC formulations.

Formulation	D x 10^{-8} (cm^2/s)	n	A%	E%
BIEM-0	1.80	0.46	4.82	1.24
BIEM-5	1.60	0.49	3.46	0.29
BIEM-10	1.59	0.48	3.26	0.25
BIEM-15	1.58	0.48	3.11	0.26
BIEM-20	1.57	0.47	3.09	0.35

Another quantifying way of swelling kinetics of the acrylic bone cement formulations is based on the Frisch equation [44,45]:

$$\frac{M_t}{M_{eq}} = k \cdot t^n \quad (2)$$

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

The results from Figure 3a confirm that the new formulation of Fickian diffusion can be assumed for all ABCs, regardless the BIEM content, if considering the linear dependence obtained up to $M_t/M_{eq} = 0.8$. The corresponding diffusion coefficients vary in the range 1.57-1.8·10^{-8} cm^2/s (Table 3). The decrease of the diffusion coefficient when increasing the BIEM content in the ABCs, may be explained by the slight cross-linking process due to the chain transfer capacity of the bromine-containing comonomer.

If expressing now the M_t/M_{eq} as a function of time, a power law time-dependence is obtained (as described in Eq. (2)), and allows double-checking type of the mechanism assumed for the water uptake, via the n values of the ABCs. The calculated n values range between 0.46 and 0.49 (Table 3), which points out that the water absorption does correspond to Fickian diffusion, for all the ABCs presented in this study [34,35].

It is also worthwhile to determine the hydration degree (H%), water absorption (A%) and the percentage of elution (E%) for each of the experimental ABC formulation, as following [39, 45, 46]:

$$H\% = \frac{M_t - M_0}{M_0} \cdot 100 \quad (3)$$

$$A\% = \frac{M_{eq} - M_f}{M_0} \cdot 100 \quad (4)$$

$$E\% = \frac{M_0 - M_f}{M_0} \cdot 100 \quad (5)$$

where M_0 is the initial weight of the specimen and M_f is the weight of the sample after testing.

One can see that the presence of the new synthesized BIEM comonomer in the ABC formulations have a positive effect on the magnitude of the water absorption: the maximum degree of hydration decreases with increasing the BIEM content (Figure 3b). Furthermore, all the BIEM-modified ABCs exhibit a lower elution (weight loss) than the radiolucent ABC (see Table 3). One possible explanation is that the BIEM comonomer may induce a slight cross-linking during curing of the new cement formulations. This idea is also supported by the fact that all BIEM-modified cements are insoluble in ordinary solvents.

Density, polymerization shrinkage, porosity

Density measurements have contributed to the determination of polymerization shrinkage and porosity of the ABCs formed by modification of the liquid phase, when replacing MMA with BIEM.

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 [47]. Polymerization shrinkage (Sh), associated with the setting reaction, was determined using the following equations [41]:

$$\%\mathrm{Sh} = \frac{\text{density of polymer} - \text{density of monomer}}{\text{density of polymer}} \cdot 100 \quad (6)$$

The experimental shrinkage (Sh_{exp}) was calculated by taking into account the experimentally determined density (apparent density, ρ_{exp}) (Eq. (7)) and also the theoretical shrinkage (Sh_{theor}), calculated from the polymerization shrinkage value determined by Equation (8) [41,48-50]:

$$\%Sh_{exp} = \frac{\rho_{exp} - \rho_{mix}}{\rho_{exp}} \cdot 100 \quad (7)$$

$$\frac{\Delta V}{V}(\%) = 22.5 \cdot DC_{mix} \cdot \frac{\sum_i (f_i \cdot x_i)}{\sum_i (M_{mi} \cdot x_i)} \cdot \rho_{mix} \cdot 100 \quad (8)$$

where 22.5 represents the volume change per mole of methacrylate groups (C=C) in MMA (cm^3/mol) when MMA is polymerized [51, 52], DC_{mix} (0.985, determined by NMR spectroscopy) 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.

To determine theoretical shrinkage, it can be used also Equation (9).

$$\%Sh_{theor} = \frac{\rho_{th} - \rho_{mix}}{\rho_{th}} \cdot 100 \quad (9)$$

where ρ_{th} is maximum density, defined as the density of the ABC completely free of pores and voids [50,51]. The results are summarized in Table 4.

Tab. 4. Density, polymerization shrinkage and porosity for the BIEM – ABC formulations.

Formulation	ρ_{th}	ρ_{exp}	% Sh_{th}	% Sh_{exp}	% P
BIEM-0	1.129	1.094	5.70	4.80	3.15
BIEM-5	1.133	1.093	5.59	4.57	3.54
BIEM-10	1.138	1.100	5.47	4.49	3.41
BIEM-15	1.144	1.106	5.35	4.39	3.32
BIEM-20	1.150	1.112	5.23	4.28	3.28

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 ABC compositions. This increase is explained by the higher density of the bromine-containing comonomer (ρ_{BIEM}=1.3073 g/cm^3) *versus* MMA (ρ_{MMA}=0.936 g/cm^3).

Addition of bromine-containing comonomer in the composition of radiolucent ABC reduces polymerization shrinkage (Table 4). This diminution is about 11% for the modified acrylic cement with 20% (w/w) bromine containing monomer (from 4.80% at 4.28%) and it is explained by the higher molecular mass of the bromine-containing comonomer (M_{BIEM}=283 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 [51], when the MMA is polymerized. For a given gravimetric content of bromine-containing comonomer in ABCs composition, as their molecular mass is higher, the number of 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 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 [53]. 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 monomer [53-55].

Determination of polymer density gives values of the average percentage of porosity (%P) from the following expression [53-55]:

$$\%P = \left(1 - \left(\frac{\text{apparent density}}{\text{maximum density}}\right)\right) \cdot 100 \qquad (10)$$

Results presented in Table 4 show that addition of bromine-containing comonomer in radiolucent ABCs composition determines only an insignificant increase of porosity. Increasing 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 ABCs analyzed in this paper is primarily due to the mixing method and, to a lower extent, to the composition of the liquid phase.

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 [33]. 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 [33]. Thus, the static compressive properties of the acrylic bone cement are very important. The result on compressive strength is shown in Table 5.

Tab. 5. Compressive strength for the BIEM – ABC formulations.

Formulation	σ_c (MPa)
BIEM-0	76,46
BIEM-5	88,70
BIEM-10	102,20
BIEM-15	108,85
BIEM-20	121,82

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 [8]. However, the compressive strength of the formulated cements was comparable to that of the commercial ABCs [48].

Radiopacity

The ABCs, for which a part of MMA in liquid phase was replaced with BIEM, proved to be radiopaque, as shown by the radiographic images presented in Figure 4, in which the results obtained for new ABCs are comparatively analyzed with a composition of ABCs containing $BaSO_4$. The images from Figure 4 show that the radiopacity increases with increasing the proportion of bromine-containing comonomer in the liquid phase composition of the newly formulated ABCs.

Fig. 4. Radiographs for the BIEM – ABC formulations and comparison with an ABC containing 10% wt of $BaSO_4$.

Conclusions

It was established that radiopaque ABCs can be obtained by adding BIEM in liquid phase. Addition of bromine-containing comonomer in ABCs compositions 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 ABCs.

Experimental part

Materials

Methyl methacrylate (MMA) (Aldrich), 2-hydroxyethyl methacrylate (Aldrich), 2-bromoisobutyryl acid (Acros Organics), thionyl chloride (Acros Organics), tetrahydrofuran (Acros Organics), pyridine (Aldrich), N,N-dimethyl-p-toluidine (DMPT) (Aldrich) and benzoyl peroxide (BPO) (Aldrich) were used as received. The 2-(2-bromoisobutyryloxy) ethyl methacrylate was synthesized in the laboratory. Poly (methyl methacrylate) (PMMA) beads (medical grade, with particle size distribution of 10-160 μm, an average diameter of $\overline{D}$ = 120 μm and molecular weight of M_w = 720,000) were supplied by Astar S.A. (Cluj- Napoca , Romania).

Synthesis of 2-(2-bromoisobutyryloxy) ethyl methacrylate

The synthesis comprises of two steps [29]. In the first step, 2-bromoisobutyryl chloride was synthesized by the reaction between 2-bromoisobutyryl acid and thionyl chloride. Secondly, the 2-(2-bromoisobutyryloxy) ethyl methacrylate (BIEM) was synthesized by the reaction between 2-hydroxyethyl methacrylate and 2-bromoisobutyryl chloride using tetrahydrofuran as solvent and pyridine as HCl acceptor. After purification, the product structure was identified via ^{1}H NMR and ^{13}C NMR (Figure 5 and 6):

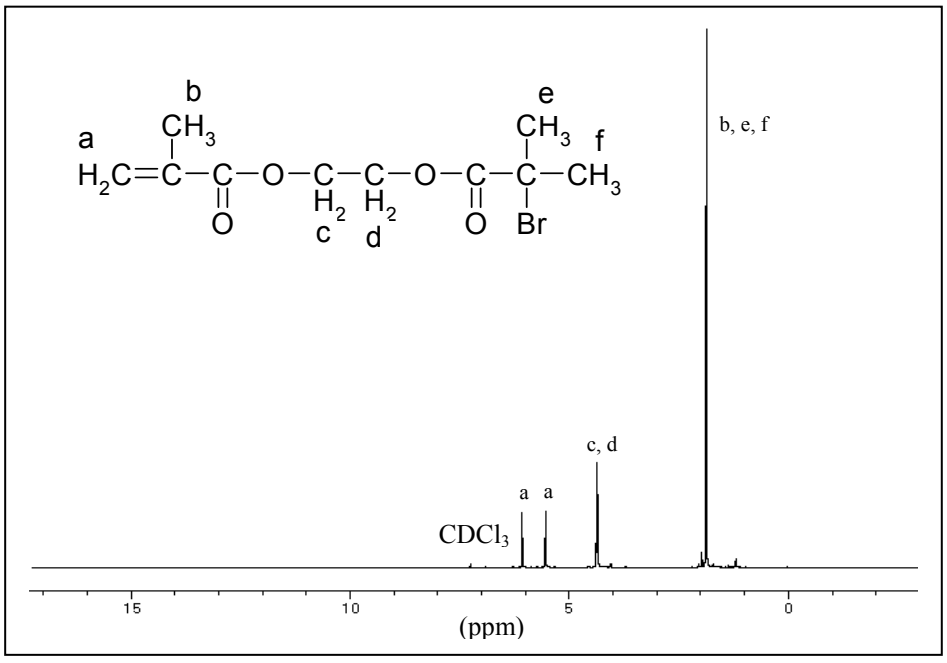

Fig. 5. ^{1}H NMR spectrum of BIEM.

^{1}H NMR (400 MHz) $CDCl_3$, δ(ppm): 6,063 (a, 1H, H-C=C), 5,526 (a, 1H, H-C=C), 4,366 (c,d, 4H, -O-CH_2-CH_2-O-), 1,882 (b,e,f, 9H, CH_3-C=C şi CH_3-CBr-CH_3).

^{13}C NMR (100.6 MHz) $CDCl_3$: 171,514 (g, 1C, O=C-C-Br), 167,384 (d, 1C, O-C-O=CH_2), 136,404 (b, 1C, -C=CH_2), 126,410 (a, 1C, CH_2=C-), 63,762 (e, 1C, -O-CH_2-), 61,678 (f, 1C, -CH_2-O-), 55,162 (h, 1C, -C-Br), 30,653 (i,j, 2C, CH_3-CBr-CH_3), 18,673 (c, 1C, CH_3-C=CH_2).

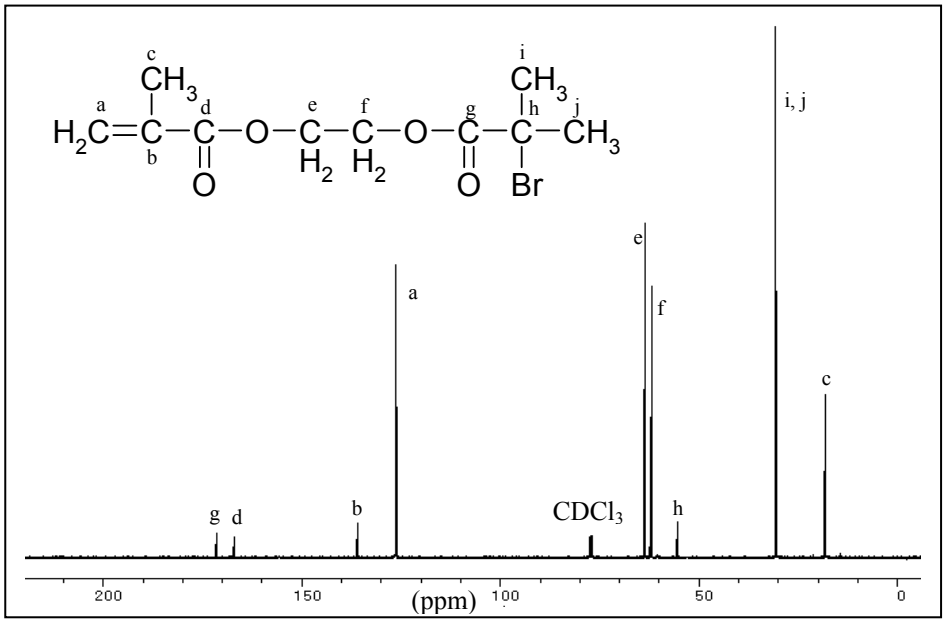

Fig. 6. ^{13}C NMR spectrum of BIEM.

Methods

-Preparation of bone cements

The experimental ABCs were formulated by adding the liquid component to the solid component, at room temperature (23 °C), in a typical solid:liquid ratio of 2:1. In all cases 1.5% (w/w) DMPT in the liquid component and 2% (w/w) 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 for two hours prior to mixing.

Tab. 6. Composition of the liquid and final phases for the BIEM - ABC formulations.

Formulations	Monomer ratio		BIEM content in the feed composition (%w)
	MMA	BIEM	
BIEM – 0	100	-	-
BIEM – 5	95	5	1,66
BIEM – 10	90	10	3,33
BIEM – 15	85	15	5,00
BIEM – 20	80	20	6,66

Acrylic bone cements were prepared from MMA as the base monomer, and BIEM as comonomer. The conventional ABC was modified by introducing 5, 10, 15 or 20 % (w/w) BIEM in the liquid phase. Cements containing only MMA and DMPT in the liquid phase (radiolucent cement) were prepared, as reference sample (Table 6). 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 sample was avoided. It is also interesting to observe that the absence of the radiopaque agent in

this cement sample make it transparent or at least translucent, which is easier to visually examine the porosity of the cured cement.
Preparation of the ABC was carried out following the traditional method used for classical ABCs, as described in the ASTM Standard [8]. 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 hour.

Characterization

The ABC formulations were characterized by measuring the curing parameters, thermal properties, water absorption, density, compressive tests and radiopacity.

The *curing parameters* were registered according to the ASTM Standard [8]. Time and temperature were measured from the onset of the mixing powder with the liquid. Two determinations were performed for each ABC formulation.

The *thermal properties* of the new formulations of ABCs 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 scan, considering the onset of transition. Thermogravimetric analysis was performed under nitrogen flow (25 $cm^3 \cdot min^{-1}$) 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 4.5-7.5 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 ABC formulations were determined by picnometer method [51]. 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 [48]. 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. 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 (σ_c) was calculated using the following formula:

$$\sigma_c = F/A \quad (11)$$

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.

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