JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 12, No. 2, February 2010, p. 339 - 346

Properties of acrylic bone cements modified with poly(butyl methacrylate)

M. C. RUSU[a], D. L. RUSU[b], M. RUSU[a*], I.C. ICHIM[a]
[a]*Technical University « Gh. Asachi » Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Natural and Synthetic Polymers, 700050, Iasi, Romania*
[b]*Polymers and Composite Tehcnology and Mechanical Engineering Department, Eolde des Mines d Douai, 941 Rue Charles Bourseul,59508, Douai , France*

Poly(methyl methacrylate) (PMMA) bone cements are extensively used in certain types of total hip or total knee replacements and are of potential utility wherever mechanical attachments of metal to living bone is necessary. The main function of the cement is to serve as interfacial phase between the high modulus metallic implant and the bone, thereby assisting to transfer and distribute loads. The advantages of cemented prosthesis with acrylic bone cements (ABC) lay in their excellent primary fixation, in good load distribution between implant and bone and in the fact that technique allows fast recovery of the patient. In this work are presented the studies about new formulations of ABC, based on PMMA and poly(butyl methacrylate) (PBMA). The effect of PBMA incorporated into the solid phase of ABC, on the curing parameters, density, water absorption, dynamic mechanical thermal tests and mechanical properties were studied. An increase of maximum temperature and a decrease of the setting time were observed with the addition of the PBMA in the cement composition. The density and the shrinkage polymerization show a decrease and the porosity of ABCs increases by introducing and increasing the PBMA content in these compositions. The addition of PBMA in conventionally ABCs composition doesn't modify appreciably their water absorption kinetic. Also, by adding PBMA in the formulation of ABCs the mechanical properties decrease.

(Received December 3, 2009; accepted February 18, 2010)

Keywords: Acrylic bone cements, Water absorption, Polymerization shrinkage, DMTA

1. Introduction

Poly(methyl methacrylate) (PMMA) bone cements are extensively used in certain types of total hip or total knee replacements and are of potential utility wherever mechanical attachments of metal to living bone is necessary [1,2]. The main function of the cement is to serve as interfacial phase between the high modulus metallic implant and the bone, thereby assisting to transfer and distribute loads [3-5].

From a chemical point of view, the curing process of the PMMA-based acrylic bone cement (ABC), also known as cold curing, 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 tertiary amines [1,2,6-9]. 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 [10,11].

Orthopedic ABC have to fulfill several medical requirements, such as: low values of maximum cure temperature (to avoid thermal necrosis of the bone tissue, during the setting of the cement), moderate sitting time (so that cement does not cure too fast or too slow), high values of compressive strength (allowing the cured cement mantle to withstand the compressive loads involved by normal daily activities).

The advantages of cemented prosthesis with acrylic bone cements (ABC) lay in their excellent primary fixation, in good load distribution between implant and bone and in the fact that technique allows fast recovery of the patient.

However, despite the relatively good rate of implant fixation with ABC, a number of persistent problems are encountered. PMMA-based ABCs are associated with high exoterm polymerization, brittleness, chemical necrosis due to linkages of unreacted monomer, hypotensive effect of the monomer, shrinkage and the stiffness mismatch between the cement and the bone [12-20]. Although, there fave been numerous attempts to improve the thermal, mechanical and biological properties of ABCs [6, 7, 20-25].

Studies showed that ABC's properties can be improved by replacing one part of PMMA with other polymers or copolymers [26-31]. Among the polymers that can be used in this purpose, poly(butyl methacrylate) (PBMA) is of great interest [32-36].

There are two important differences in the properties of PBMA and PMMA. Because the glass-transition temperature of PBMS is 27 ^{o}C (compared to 114 ^{o}C for PMMA) the beads are rubbery at body temperature (37 ^{o}C) and give the cement reduced elastic modulus and increased ductility [32]. PBMA has an elastic modulus of 0.27 GPa at 37 ^{o}C (compared to 2.17 GPa for PMMA) and an ultimate tensile elongation over 40% (compared to 3%

for PMMA) and much greater work for fracture than PMMA [33].

The results reported in literature concerning the possibility of using PBMA in the ABCs, mainly treat the mechanical properties.

In this paper, are presented the results obtained concerning the influence of partial replacing (5-20% wt) of PMMA with PBMA from the solid phase of a conventionally ABC on their characteristics (curing parameter, density, polymerization shrinkage, porosity, water absorption, dynamic mechanical thermal analysis, and mechanical properties).

2. Experimental

2.1. Materials

The following materials were used to obtain the acrylic bone cements formulated in this work:

- Poly (methyl methacrylate) (PMMA) in the form of beads prepared by suspension polymerization (medical grade), M_w=736.000 (GPC), d=1.2970 kg/m^3, the average diameter of particles is 120μm, supplied by Astar S.A. (Cluj-Napoca, Romania);
- Poly (butyl methacrylate) (PBMA) in the form of beads (Aldrich Chemical Co. Inc.), M_w=337.000 (GPC), T_g=15°C, inherent viscosity=0.5;
- Methyl methacrylate (MMA) (Aldrich Chemical Co. Inc.), stabilized with 100 ppm of monomethylether of hydroquinone, as monomer;
- N,N-bis-(2hydroxyethyl)-p-toluidine (DHEPT) (Aldrich Chemical Co. Inc.), as activator;
- Benzoyl peroxide (BPO) (Aldrich Chemical Co. Inc.), as initiator;
- Distilled water, physiological serum (0.9% NaCl solution, Zentiva, Romania) and dextrane solution (Dextrane 40, 6% in glucose solution 50g/l, Sicomed, Romania), used like immersion liquids.

All the materials were used as received, without any additional purification.

2.2. Methods

2.2.1. Preparation of bone cements

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

Acrylic bone cements were prepared from MMA as the base monomer. The conventional ABC was modified by introducing 5, 10, 15 or 20 wt% PBMA in the solid phase. Cements containing only PMMA and BPO in the solid phase (radiolucent cement) were prepared for the sake of comparison, as reference samples (Table 1).

Table 1. Composition of the new prepared formulations ABCs.

Formulations	Solid phase composition, wt%	
	PMMA	PBMA
PBMA-0	100	0
PBMA-5	95	5
PBMA-10	90	10
PBMA-15	85	15
PBMA-20	80	20

Preparation of the ABC was carried out following the traditional method used for classical ABCs, as described in the ASTM Standard [37]. The components of the ABCs 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.

2.2.2. Characterization

The ABC formulations were characterized by measuring the curing parameters, density, water absorption, dynamic mechanical thermal analysis, and mechanical properties.

The *curing parameters* were registered according to the ASTM Standard [37]. Time and temperature were measured from the onset of the mixing powder with the liquid. Two determinations were performed for each ABC formulation.

The *apparent densities* of new ABC formulations were determined by picnometer's method [38]. 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 [39]. The polymerization shrinkage and porosity are directly related to density.

The *water absorption* of the prepared formulations was studied by immersing 3.5 mm thick disks, 10 mm in diameter, at 23 °C in three different aqueous medium: distilled water, physiological serum (0.9% NaCl solution) and dextrane solution. 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.

Dynamic mechanical thermal analyses were determined by a DMTA analyzer (Perkin-Elmer Diamond DMA). The tests were carried out using a temperature program mode from 20°C to 250 °C with a heating rate of 4°C / minute and a frequency of 1 Hz. Three samples (20 mm x 12 mm x 4 mm) of each ABC formulations were tested.

Mechanical properties were analyzed as a function of tensile, compressive and flexural tests. All mechanical testing was carried out at room temperature (23°C), for samples stored under dry conditions approximately one month before testing, using a traction machine Zwick 010 (Germany).

The specimens for the *tensile tests* were obtained by placing the cement dough in a high density polyethylene (HDPE) mould and subsequently under pressure of 1.4 MPa for approximately one hour. The average cross-section of the specimens was 3.4mm. Tensile tests were conducted as cross-head displacement speed of 1 mm/min, with load of 100 kN. Five specimens were tested for each formulation and their tensile strength (σ_t) was calculated using the following formula [40]:

$$\sigma_t = F_t / A \quad (1)$$

where: F_t is the load at break and A is cross-section of the specimen.

Compressive tests were carried out in cylindrical specimens (6 mm diameter and 12 mm high) obtaining according to ASTM standard [37], using a load of 5kN and a cross-head speed of 5 mm/min. Tests were conducted up to failure or until 70 or 80% reduction in specimen high. Five specimens were tested for each formulation and their compressive strength (σ_c) was calculated using the following formula [41]:

$$\sigma_c = F_c / A \quad (2)$$

where: F_c is the implicated load and A is cross-section of the specimen.

Specimens for *flexural tests* were obtaining by placing the cement dough in the HDPE mould (100x10x3.5mm) and subsequently under pressure of 1.4 MPa for approximately one hour. Flexural tests were carried out using the same machine and cross-head displacement rate used at the compressive tests. The length between supports was equal to 60 mm. The bars were loaded to failure in three-points bending and the flexural strength (σ_f) was calculated from following standard equation [42]:

$$\sigma_f = 2F_fL / 4bd^2 \quad (3)$$

where: F_f is the load at break, b and d are width and thickness of the specimen, L is the length between the supports.

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) [13, 43]. The maximum temperature depends on monomer's nature and on their ratio in ABC compositions [15,44]. The main curing parameters: maximum temperature (T_{max}), setting temperature (T_{ts}), setting time (t_s) and time to reach maximum temperature (t_{Tmax}) should be determined from the polymerization exotherms for each ABC formulations (Figure 1).

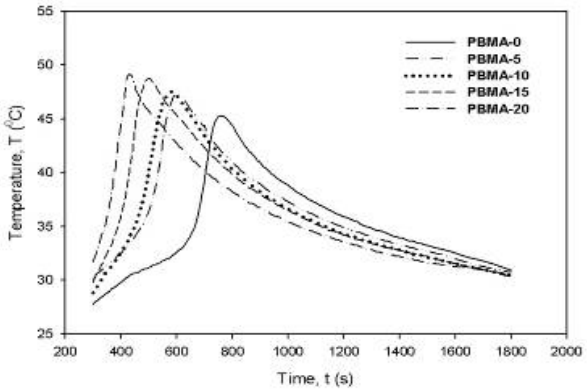


Fig. 1. Exotherms of the ABC formulations

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 [37], as follows: $T_{ts} = (T_{max} - T_{amb})/2$ (Table 2).

Table 2. Curing parameters of the ABC formulations.

Formulations	T_{max} ,°C	t_{Tmax}, s	T_{ts},°C	t_s, s
PBMA-0	45.3	760	34.15	652
PBMA-5	47.3	600	35.15	477
PBMA-10	47.5	580	35.25	452
PBMA-15	48.7	500	35.85	398
PBMA-20	49.2	430	36.10	353

Analysis of the curing parameters for the ABCs modified with different amounts of PBMA shows that introducing and increasing the PBMA content has as result an increasing of the maximum temperature values. However, it can be clearly noted that all formulated ABCs exhibited a T_{max} much lower than the value established by ASTM Standard (90°C) [37].

The setting temperature is strongly related to the maximum temperature, and its value increases as the quantity of PBMA increases in the ABC formulations.

The setting time and the time of reaching maximum temperature decrease with the addition of a higher percentage of PBMA.

From the analysis of curing parameters, it is observed that the modification of ABCs with PBMA presents disadvantages from biologically point of view (the rise of maximum temperature increases necrosis of the surrounding tissue) and concerning the manipulation time (decrease of the setting time results in reducing of the working time).

3.2. Density, polymerization shrinkage, porosity

Density measurements have contributed to the determination of polymerization shrinkage and porosity of the ABCs formed by modification of the solid phase, when introducing PBMA.

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 [45]. Polymerization shrinkage (Sh), associated with the setting reaction, was determined using the following equations [46]:

$$\%\mathrm{Sh} = \frac{\text{density of polymer} - \text{density of monomer}}{\text{density of polymer}} \cdot 100 \quad (4)$$

The experimental shrinkage (Sh_{exp}) was calculated by taking into account the experimentally determined density (ρ_{exp}) [46,47]. To determine the theoretical shrinkage (Sh_{theor}), calculated from the polymerization shrinkage value determined by formula [39,46,47]:

$$\frac{\Delta V}{V}(\%) = 22.5 \cdot DC_{mix} \cdot \frac{\sum(f_i \cdot x_i)}{\sum(M_{mi} \cdot x_i)} \cdot \rho_{mix} \cdot 100 \quad (5)$$

where 22.5 represents the volume change per mole of methacrylate groups (C=C) in MMA (cm^3/mol) when MMA is polymerized [38,48], 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.

$$\%Sh_{exp} = \frac{\rho_{exp} - \rho_{mix}}{\rho_{exp}} \cdot 100 \quad (6)$$

$$\%\mathrm{Sh}_{theor} = \frac{\rho_{th} - \rho_{mix}}{\rho_{th}} \cdot 100 \quad (7)$$

Maximum density (ρ_{th}) is defined as the density of the ABC completely free of pores and voids [38,44]. The results are summarized in Table 3.

Analyze of these results shows that both theoretical (ρ_{th}) and experimental density (ρ_{exp}) decrease with the addition and subsequent increase of the ratio of PBMA in ABCs compositions.

Table 3. Obtained values for the density, polymerization shrinkage and porosity of the ABC formulations.

Formulations	ρ_{th}, g/dl	ρ_{exp}, g/dl	Sh_{th}, %	Sh_{exp}, %	P, %
PBMA-0	1.0936	1.0845	7.21	6.85	0.83
PBMA-5	1.0902	1.0792	7.07	6.63	1.00
PBMA-10	1.0868	1.0658	6.94	6.09	1.93
PBMA-15	1.0835	1.0592	6.81	5.82	2.24
PBMA-20	1.0801	1.0429	6.67	5.13	3.45

Addition of PBMA in the composition of conventionally ABC reduces polymerization shrinkage (Table 3). 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. 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 [49].

Determination of polymer density gives values of the average percentage of porosity (%P) from the following expression [49]:

$$\%P = \left(1 - \left(\frac{\rho_{exp}}{\rho_{th}}\right)\right) \cdot 100 \quad (8)$$

Results presented in Table 3 show that addition of PBMA in conventionally ABCs composition determines only an insignificant increase of porosity. Increasing of the content of PBMA determines an increase of porosity, which may be explained by the reduction of the quantity of evaporated MMA during mixing, as a result of the lower solubility of PBMA in MMA. 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.

3.3. 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 [19,46,50]. Additionally, water absorption may induce hydrolysis of some ingredients from the ABC, 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 compensates for polymerization shrinkage [46,50].

The water absorption characteristics were determined by immersing cement disks (diameter 10 mm, thickness 3.5 mm) in 100 ml of three aqueous medium (distilled water, physiological serum and dextrane solution) at 37°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 aqueous solution, 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, one week).

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) [51]:

$$\frac{M_t}{M_{eq}} = 2\left(\frac{Dt}{\pi l^2}\right)^{1/2} \quad (9)$$

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 depending 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 $t^{1/2}$.

Another way for quantifying the swelling kinetics of the acrylic bone cement formulations is based on the Frisch equation [52,53]:

$$\frac{M_t}{M_{eq}} = k \cdot t^n \quad (10)$$

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

The hydration degree ($H\%$) can be determined with the following equation [52,53]:

$$H\% = \frac{M_t - M_0}{M_0} \cdot 100 \quad (11)$$

where M_0 is the initial weight of specimen and M_t is the weight of specimen at time t.

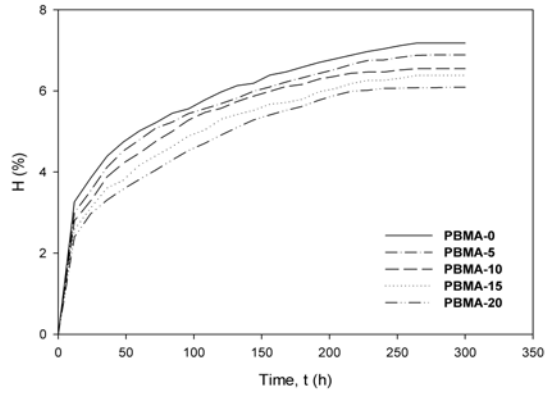
Water absorption ($A\%$) and percentage of elution ($E\%$) can be calculated using the following equation [43,50,51]:

$$A\% = \frac{M_{eq} - M_f}{M_{eq}} \cdot 100 \quad (12)$$

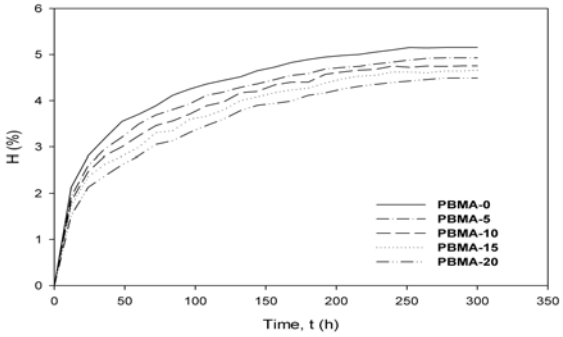
$$E\% = \frac{M_0 - M_f}{M_0} \cdot 100 \quad (13)$$

where M_f is the weight of sample after testing.

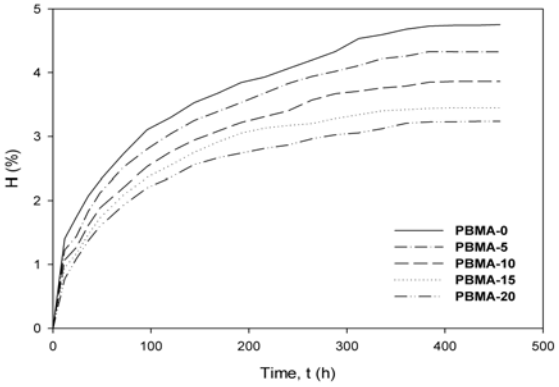
Fig. 2 presents the variation of water absorption as a function of immersion time. Analysis of these diagrams shows that the modification of the solid phase by replacing a part of PMMA with PBMA, for all 3 immersion mediums, determines no change in the water absorption mechanism in the modified cements. Nevertheless, it was found that, by addition and than increasing the amount of PBMA, water absorption decreases (Table 4).



(a)



(b)



(c)

Fig. 2. Water absorption for ABCs modified with PBMA: a-immersion in distillated water, b-immersion in physiological serum and c - immers ion in dextrane solution

Table 4. Properties concerning the water absorption of the prepared ABC formulations.

Formulations	Aqueous medium	D x 10^{-8} (cm^2/s)	n	A%	E%
PBMA-0	Distilled water	2.11	0.24	8.06	0.82
PBMA-5		1.99	0.25	7.53	0.59
PBMA-10		1.95	0.26	7.12	0.53
PBMA-15		1.79	0.28	6.92	0.49
PBMA-20		1.69	0.30	6.57	0.37
PBMA-0	Physiological serum	2.16	0.24	5.56	0.69
PBMA-5		2.04	0.25	5.09	0.42
PBMA-10		1.99	0.27	4.85	0.33
PBMA-15		1.85	0.29	4.73	0.29
PBMA-20		1.61	0.31	4.49	0.21
PBMA-0	Dextran solution	10.51	0.33	5.14	0.63
PBMA-5		9.84	0.34	4.54	0.41
PBMA-10		9.67	0.34	4.07	0.37
PBMA-15		9.50	0.32	3.64	0.31
PBMA-20		9.34	0.33	3.38	0.25

For the same content of PBMA in ABCs, the water absorption decreases in the following order: distillated water > physiological serum > dextrane solution (Table 4).

Figure 3 shows the typical diagrams of water absorption versus $t^{1/2}$ for the cements with different concentration of PBMA, in solid phase.

In all cements new formulation, a Fickian diffusion behavior can be assumed, if considering the linear dependence at low values ($M_t/M_{eq}<0.5$) and the reasonable good agreement with existing theoretical data. Consequently, the slope enables the calculation of the diffusion coefficient, with values ranging between 1.61 10^{-8} cm^2/s and 2.11 10^{-8} cm^2/s (Table 4).

The results presented in table 4 show also that addition and subsequent increase of the ratio of PBMA in the solid phase composition does not modify the type of process associated of water absorption (n), whose values are maintained between 0.24 and 0.34. This is a proof for that, in all ABCs analyzed in this paper, for all the immersion liquids used, the diffusion process obeys Fick's law [54,55].

For all the immersion mediums used it's noticed that the hydratation degree decreases linearly with increasing the PBMA content. Furthermore, all PBMA-modified ABCs exibit a lower elution (weight loss) than the radiolucent ABC.

The study of the sorption kinetic of all formulations analyzed in this work shows a similar behavior, which fit with Fick's equation. Thus a Fickian diffusion can be assumed for these new ABC matrices.

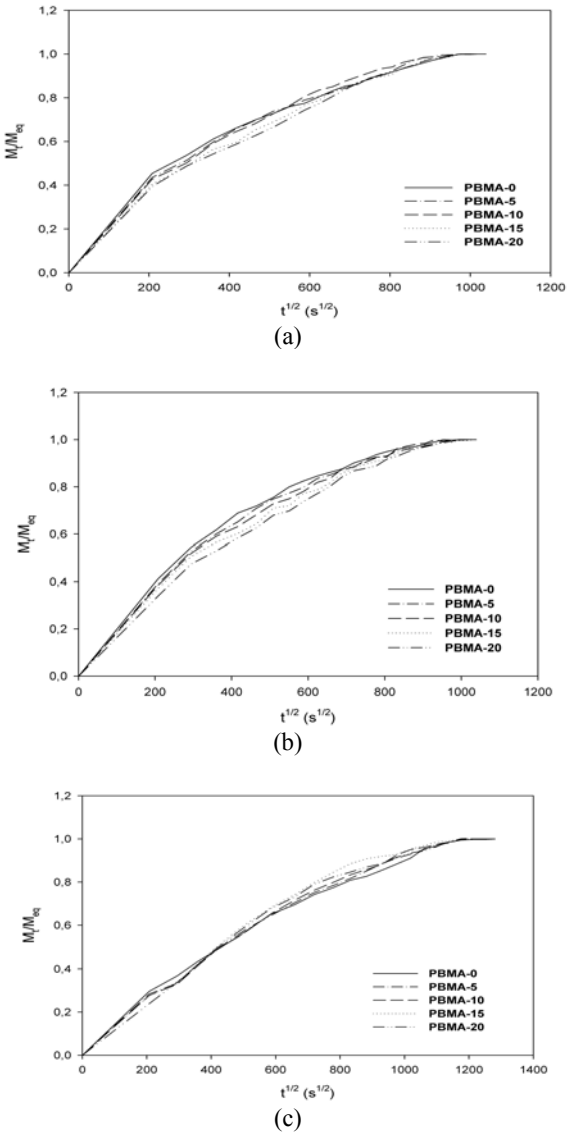


Fig. 3. M_t/M_{eq} versus $t^{1/2}$ for ABCs modified with PBMA: a-immersion in distillated water, b-immersion in physiological serum and c - immersion in dextrane solution.

3.4. Properties of DMTA

Dynamic mechanical thermal analysis (DMTA) was carried out in bending mode from 20 to 250°C by means of a DMTA Pyris instrument. Loss modulus and storage modulus depend on the chain's structural characteristics and morphology of multiphase systems. Glass transition temperature of the cements was read off as the temperature at which the loss modulus or loss factor passed through a maximum.

The results for storage modulus (E'), loss modulus (E'') and tan δ obtained from DMTA tests onsamples with different percentages of PBMA are plotted in Fig. 4.

The slight differences found between the various formulations require some explanation, because very small changes appear in E' and E'' (Fig. 4.a and 4.b) as the PBMA content changes. It seems that this peak is related to the relaxation process associated with PMMA beads. Differences observed in Figure 4.c are also very slight, showing T_g values that practically do not change as the ABC composition changes. The loss tangent curves are totally symmetrical, showing a peak at 118°C. This peak remains approximately constant in all the formulations.

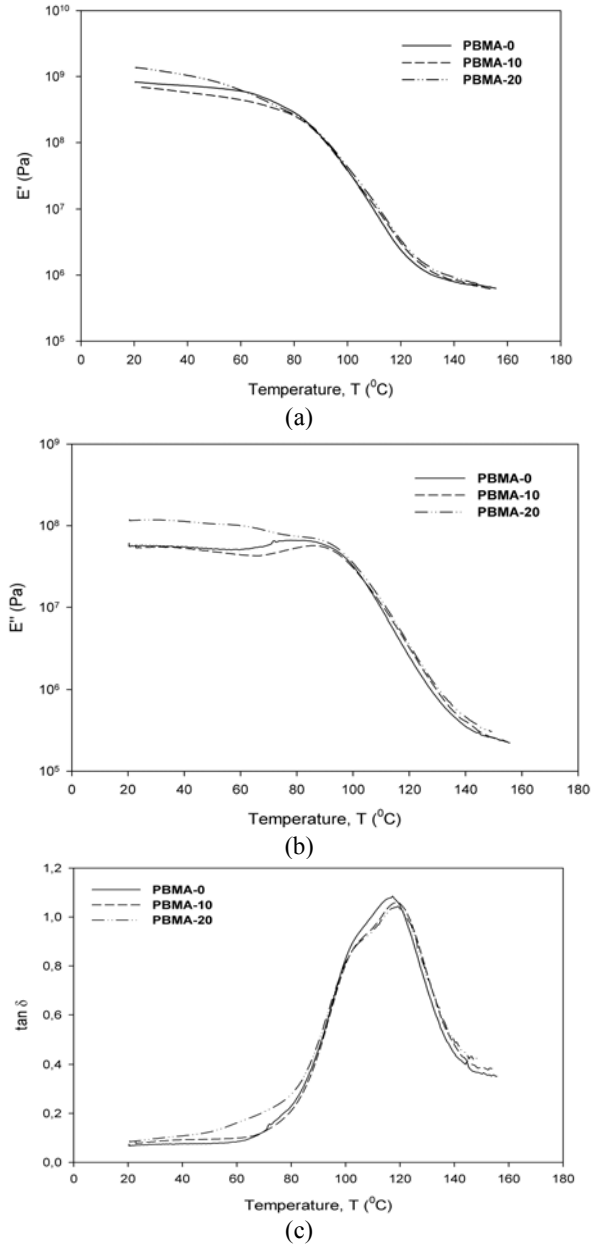


Fig. 4. Dynamic storage modulus (a), loss modulus (b) and tan δ (c) diagrams for ABCs formulations modified with PBMA

3.5. Mechanical Properties

For the ABCs modified with PBMA were analyzed compression strength (σ_c), tensile strength (σ_t) and flexural strength (σ_f). The results are presented in Table 5 and they are showing that the addition and then the increase of the PBMA amount in the solid phase of modified ABCs determine a significant decrease of all analyzed mechanical properties. In the case of the ABCs with 20%w PBMA, the decrease was 25.27% for compression tests, 58.86% for tensile strength and 72.66% for flexural strength.

Table 5. Mechanical properties of the prepared ABCs formulations.

Formulations	Compressive strength, σ_c (MPa)	Tensile strength, σ_t (MPa)	Flexural strength, σ_f (MPa)
PBMA-0	76.46	39.04	68.36
PBMA-5	65.96	27.79	51.08
PBMA-10	63.50	26.70	46.87
PBMA-15	61.74	24.28	31.12
PBMA-20	57.14	16.06	25.00

4. Conclusions

We have analyzed the influence of partial replacing (5-20% wt) of PMMA with PBMA from the solid phase of a conventionally ABC on their other characteristics (curing parameter, density, shrinkage polymerization, porosity, water absorption, thermal characteristics, and mechanical properties).

Introducing the PBMA in PMMA-based ABCs compositions determines an insignificant increase of the maximum temperature values and a decrease of the sitting time. The density and the shrinkage polymerization shows a decrease and the porosity of ABCs increases by introducing and increasing the PBMA content in these compositions.

The addition of PBMA in conventionally ABCs composition doesn't modify appreciably their water absorption kinetics.

References

[1] J. Charnley, Acrylic Cement in Orthopaedic Surgery, Williams and Wilkins, Baltimore, USA, (1970).
[2] S. J. Breush, K. D. Kuhn, Ortyhopaedics, **32**, 41(2003).
[3] F. R. DiMaio, Orthopaedics, **25**, 1399 (2002).
[4] W. R. Krause, In: J.G. Webster (ed), Encyclopedia of Medical Devices and Instrumentations, Vol. I, Willey, New York, USA, 491 (1988).
[5] J. Charnley, J Bone Joint Surg, **42B**, 28 (1960).
[6] F. R. Jr. Meyer, E.P. Lantenschlager, B. K. Moore, J Bone Joint Surg, **55A**, 149 (1973).

[7] E. P. Lantenschlager, B. K. Moore, C. M. Schoenfeld, J. Biomed. Mater. Res., Symp. No.**5**, 185 (1974).
[8] R. P. Kusy, J. Biomed. Mater. Res, **12**, 271 (1978).
[9] J. M. Yang, Biomaterials, **18**, 1293 (1997).
[10] A. Nizihou, L. Attias, P. Sharrock, A. Ricard, Powder Technol, **99**, 60 (1998).
[11] M. K. D. Nicholas, M. G. J. Waters, K. M. Halford, J . Mater. Sci: Mater Med, **18**, 1407 (2007).
[12] K. D. Kuhn, Springer Verlag, Berlin, Germany, 245 (2000).
[13] C. D. Jefferis, A. J. K. Lee, R. S. M. Ling, J. Bone Joint Surg, **57B**, 511 (1975).
[14] G. M. Brauer, D. R. Steinberger, J. W. Stanburg, J. Biomed. Mater. Res., **20**, 839 (1986).
[15] E. Yoshii, J. Biomed. Mater. Res. **37**, 524 (1997).
[16] R. Milner, J. Biomed. Mater. Res. Part B: Appl. Biomat. **68B**, 180 (2004).
[17] G. A. Gresham, F. Kuczynscky, Br. Med. **2**, 619 (1971).
[18] G. Lewis, J. Biomed. Mater. Res. Part B: Appl Biomater **38**, 155 (1997).
[19] G. Lewis, C. S. van Hooy-Corstjens, A. Bhattaram, L. H. Koole, J. Biomed. Mater. Res. Part B: Appl Biomater, **73**, 77 (2005).
[20] M. P. Ginebra, J. San Roman, B. Vazquez, J. A. Planell, Biomaterials, **23**, 1873 (2002).
[21] D. W. Ching, I. M. Goned, J. A. Rennie, P. H. Gibson, J. Antimicrob. Chemother. **23**, 676 (1989).
[22] A. F. Wadmer, A. Gaechter, P. E. Ocnsner, Chin. Infect. Dis. **14**, 1251 (1992).
[23] W. Petty, S. Spainer, J.J. Shuster, J. Bone Joint Surg. Am., **78**, 512 (1996).
[24] A. B. Welch, J. Biomed. Mater. Res. **12**, 843 (1978).
[25] H. Van de Belt, D. Neut, W. Schenk, J. R. Van Horn, H. C. Van der Mey, H. J. Busscher, Acta Orthop. Scand. **72**, 553 (2001).
[26] J. P. Davies, D. O. O'Connor, J. A. Greer, W. H. Harris, J. Biomed. Mater. Res., **21**, 719 (1987).
[27] S. C. Weber, W. L. Bargar, Biomat. Med. Div. Art. Org. **11**, 3 (1983).
[28] W. R. Krause, S. R. Mathis, J. Biomed. Mater. Res., Part B: Appl. Biomater. **22**, 37 (1988).
[29] A. Murakami, J. C. Behiri, W. Bonfield, J. Mater. Sci. **29**, 2024 (1988).
[30] M. M. Vila, M. P. Ginebra, F.J. Gil, J.A. Planell, J. Biomed. Mater. Res. Part B: Appl. Biomat. **48B**, 121 (1999).
[31] M. M. Vila, M. P. Ginebra, F. J. Gil, J. A. Planell, J. Biomed. Mater. Res. Part B: Appl. Biomat. **483**, 128 (1994).
[32] R. M. Rose, A. S. Litsky, Biochemical consideration in the loosening of hip replacement prothesis. In: D.F. Williams, editor, Current perspectives on implantable devices, vol I, London, JAI Press, 1-45 (1989).
[33] A. S. Litsky, R. M. Rose, C. T. Rubin, E. L. Thrasher, J. Orthop. Res., **8**, 623 (1990).
[34] B. Pascual, I. Goni, M. Gurruchaga, J Biomed Mater Res, **48**, 447 (1999).
[35] C. R. Jacob, B. R. Davies, S. Naidu, R. H. Danchardt, D. V. Pellegrini, Trans 44th Ann. Mtg. Orthop. Res. Soc., New Orleans, 848 (1998).
[36] J. M. Funk, A. S. Litsky, Biomaterials **19**, 1561 (1998).
[37] *** American Society for Testing and Materials (ASTM). Standard F451-99a, 2000 Annual Book of ASTM Standard, Vol. **13.01**, 55 (2000).
[38] M. M. Coleman, J. F. Graf, P. C. Painter, Technomic Publishing Company, USA, (1991).
[39] N. Silikas, A. Al-Kheraif, D. C. Watts, Biomaterals, **26,** 197 (2005).
[40] ***ISO 527–1, Plastics – Determination of tensile properties—Part 1: General principles, International Standard Organization, 1993.
[41] *** ISO150-5833/1. Implants for Surgery, Acrylic Resins Cements, Part 1: Orthopaedic Applications, TC 150, N215, International Standard Organization, 1987.
[42] *** ASTM D7980-95a, Standard test method for flexural properties of unreinforced an reinforced plastics isolation materials, 1996 Annual Book of ASTM Standard, Vol. 08.01: Plastics (I) Philadelphia, P1, American Society for Testing and Materials, 1996, 155-165.
[43] J. M. Cevantes-Uc, H. Vazquez-Torres, J. V. Canich-Rodriguez, B. Vazquez-Lasa, J. San Roman, Biomaterials, **26,** 4063 (2005).
[44] A. Artola, M. Gurruchaga, B. Vazquez, J. San Roman, I. Goni, Biomaterials, **24**, 4071 (2003).
[45] M. Pascual, M. Gurruchaga, M. P. Ginebra, F. J. Gil, J. A. Planell, I. Goni, Biomaterials, **20**, 465 (1999).
[46] S. Deb, L. DiSilvio, B. Vazquez, J. San Roman, J. Biomed. Mater. Res. Part B: Appl. Biomater. **48**, 719 (1999).
[47] R. Labella, M. Braden, K. W. M. Davy, Biomaterials, **13**, 937 (1992).
[48] E. Rose, J. Lal, R. Green, J. Am. Dent. Assoc., **56**, 375 (1958).
[49] S. S. Hass, G. M. Braner, G. A. Dickson, J. Bone Joint Surg., **57A**, 380 (1975).
[50] R. L. Bowen, J. E. Rapson, G. Dickson, J. Dent. Res., **61**, 654 (1982).
[51] J. Crank, The Mathematics of Diffusion, Oxford University Press, London, UK (1956).
[52] P. E. M. Allen, D. R. G. Williams, Eur. Polym. J., **28**, 347 (1992).
[53] C. Larraz, C. Elvira, J. San Roman, Biomacromolecules, **6**, 2058 (2005).
[54] P. L. Ritger, N. A. Peppas, J. Controlled Release **6**, 23 (1987).
[55] A. Berriej, In: J. Crank, Park G.S. (eds), Water in polymers, First Edition, Academic Press, New York, USA (1968).

*Corresponding author: mrusu@ch.tuiasi.ro