WEAR AND MECHANICAL BEHAVIOUR OF VARIOUS POLYMETHYLMETHACRYLATE BONE CEMENTS

J. Balko, B. Ballóková, D. Jakubéczyová, P. Hvizdoš, S. Hloch, J. Kľoc, P. Monka

Abstract
Various bone cements with different compositions were prepared in several model configurations which differed in volume (i.e. setting temperature profile) and mode of mixing (manual and vacuum bowl). The wear behaviour of all states was studied using pin-on-disc technique and related to microstructure and local mechanical properties (nano-hardness, elasticity modulus) measured by nanoindentation. The results were compared to a natural biological material. The role of the preparation route as well as influence of composition, particularly of the presence of antibiotics, on the measured properties was investigated. The results are discussed with respect to the possibilities of using the advanced technique of cutting by water jet in orthopaedic surgery.
Keywords: bone cements, mixing, pin-on-plate, porosity, nano-hardness, elasticity modulus

INTRODUCTION

Polymethylmethacrylate (PMMA) based bone cements, particularly those impregnated with antibiotics, are widely used to join prosthesis to the surrounding bone, and are required to provide sufficient mechanical strength. Although the mechanical properties and exothermic behaviour as well as other factors affecting their overall performance have been examined extensively [1-7], the mechanical properties of bone/bone cement interface under load bearing are not fully understood. Besides these properties, relevant for static loading, characteristics describing response under relative motions are also of interest. Differences in mechanical properties lead to certain micro-movements at the bone-implant interface during normal functions in vivo even after the host bone grows in close contact to the implant material [8]. Fatigue behaviour of acrylic bone cements has been widely studied, as can be found in well known reviews such as [9] or in recent papers [10]. These studies, however, do not address all the aspects of the problems, since in joint replacement the wear behaviour of all materials in the contact zone is also of vital importance. Gispert and co-workers [11] studied various commonly used prosthetic materials for substitution of hip joints by pin-on-disc tribological testing in four types of lubricants. They found that the coefficient of friction increased significantly with time. For alumina and Co–28Cr–6Mo alloy its value reached a maximum of about 0.25. However, data for joining materials such as bone cements are not available.

Ján Balko, Beáta Ballóková, Dagmar Jakubéczyová, Pavol Hvizdoš, Institute of Materials Research, Slovak Academy of Sciences, Košice, Slovak Republic
Sergej Hloch, Peter Monka, Faculty of Manufacturing Technologies, Technical University Košice with a seat in Prešov, Prešov, Slovak Republic
Sergej Hloch, Institute of Geonics, Academy of Sciences of Czech Republic, v. v. i., Ostrava-Poruba, Czech Republic
Ján Kľoc, Faculty of Health Care of Prešov University, Prešov, Slovak Republic

The aim of the present study is to examine a range of practically used bone cements (high and low viscosity, the presence and absence of antibiotics) with emphasis on their microstructure development (temperature of polymerization, porosity), the consequences on hardness and modulus of elasticity and also on the resulting wear and friction properties.

EXPERIMENTAL MATERIALS

Several types of bone cements were reviewed, both with and without antibiotics. There is a range of cements by Zimmer: - radio-opaque cements Palacos R and Palacos R+G (with antibiotic admixed) with a short waiting time to "dough-up" followed by a long working time for the surgeon; Osteobond® Copolymer Bone Cement wets out quickly and stays in a low viscosity state longer than dough-type cements; Hi-Fatigue G Bone Cement (with antibiotics) is a high viscosity bone cement which has low viscosity properties when mixed, followed by a quick dough time; COPAL® G+C for revision surgeries is a high-viscosity radio-opaque (containing ZrO_2) cement with two types of antibiotics (gentamicin and clindamycin). In addition, the study was complemented by Antibiotic Simplex with Tobramycin®, (by Stryker / Howmedica Osteonics, Ireland). All materials are listed in Table 1 together with comments about sample preparation.

Tab.1. Experimental materials, way of mixing, size of specimens prepared, presence of antibiotics and other additives.

Material	Producer	mixing		additives		
		manual	DePuy†	radioopaque agent	colorant	(antibiotics)
Palacos R	Zimmer	S,M,L	S,M,L	ZrO_2	chlorophyll	–
Palacos R+G		S,M,L	S,M,L	ZrO_2	chlorophyll	gentamicin
Osteobond		–	S,M,L	$BaSO_4$	–	–
Hi-Fatigue +G		S,M,L	S,M,L	–	–	gentamicin
Copal G+C		–	S,M,L	ZrO_2	chlorophyll	Gentamicin +clindamycin
ATB simplex	Howmedica	S,M,L	S,M,L	$BaSO_4$	–	Tobramycin

†mixed in the vacuum mixing bowl.

All specimens were prepared directly in an operation theatre by an experienced surgeon so as to maintain the conditions as close to practice as possible. All steps were done in strict compliance with manufacturers' instructions and in exactly the same way as during normal operations. Two types of mixing were used - manual mixing and using a vacuum mixing bowl, in this case SmartMix® CTS by DePuy, Fig.1.

The samples were embedded in specially prepared resin holders. Into these holders three types of holes were drilled with depth about 10 mm. Diameters of the holes were 2 mm, 5 mm and 12.5 mm, henceforth denoted as small (S), medium (M) and large (L), respectively. Three types/sizes of prepared specimens are illustrated in Fig.2. Freshly mixed cements, while soft, were inserted into the prepared receptacles and then, during the exothermic polymerization, the temperature of each specimen was measured at 1 min intervals for 40 minutes. The temperature was measured by infrared Thermometer UNI-T

UT305C with single point laser and with output < 1mV, wavelength 630 – 670 nm, accuracy 1.8°C, repeatability 0.5°C and resolution 0.1.

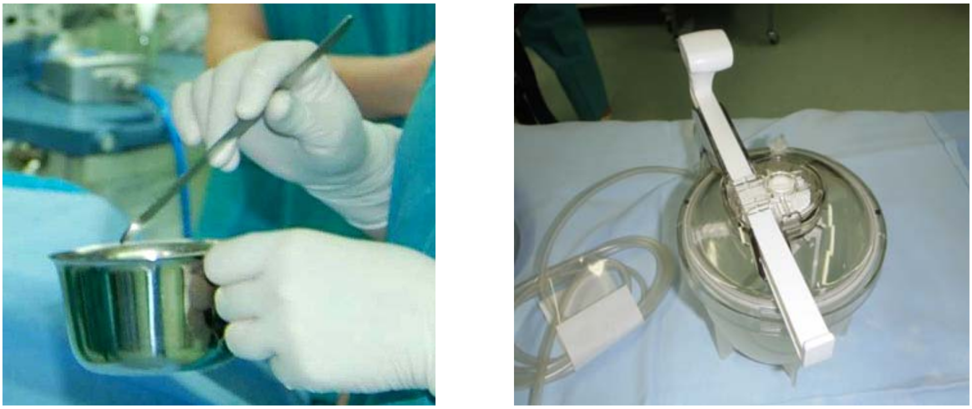

Fig.1. Preparation of specimens in an operating theatre: (a) manual mixing in air, (b) vacuum mixing bowl SmartMix® CTS by DePuy.

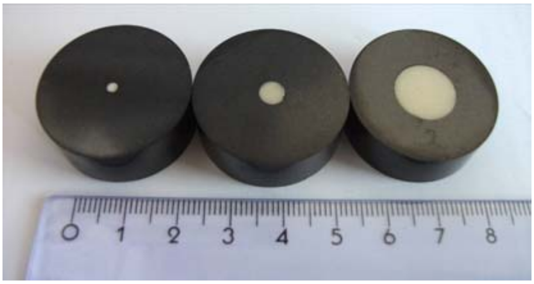

Fig.2. Example of three specimen sizes.

EXPERIMENTAL METHODS

Investigation of microstructure focused on assessment of the resulting porosity. The samples were prepared by standard metallographic method with emphasis on preserving fine soft microstructure. It was polished by a series of sandpapers and finished by diamond spray with grit size of 0.25 μm. The samples were finally ultrasonicated in methanol. The prepared samples were observed and photographed using a confocal microscope Plu Neox 3D Profiler by Sensofar, Spain. The obtained photographs were treated by image analysis. The software package ImageJ 1.46r was used to evaluate the porosity of the material. In each case pores of at least 1 mm^2 area were taken into account.

The samples` sections for nanoindentation were metallographically polished down to roughness lower than 0.1 μm. All nanoindentation measurements were performed by nano-indentation tester TTX-NHT (by CSM Instruments, Switzerland). A Berkovich pyramid diamond tip was used in simple monotonic mode with maximum loading of 10 mN. Loading and unloading rate was 20 mN/min., the hold time at maximum was 10 s. The resulting load-penetration depth curves were evaluated according to the analysis of Oliver and Pharr [12]. From the applied load and corresponding contact area, hardness values can be calculated very precisely. Apart from that, the completely elastic character of the unloading part of a *P-h* curve enables one to calculate the modulus of elasticity for each indent also according to the formula of Fischer-Cripps [13].

$$E^* = \beta / \sqrt{A(h_c)}\ dP/dh\ |_{h=hmax}, \quad (1)$$

where:

β - the indenter shape factor; $A(h_c)$ - the contact area corresponding to the contact depth of penetration h_c; P - the applied load, E*- the composite sample/indenter elasticity modulus, from which E for the sample is then determined. Up to 20 indentations were performed, values of hardness (H) and modulus of elasticity (E) were calculated and the data obtained were statistically evaluated.

Wear behaviour of the experimental materials was studied in dry sliding in air on the largest samples, L. The surfaces were carefully prepared by polishing down to a surface roughness below 0.5 μm where possible. This is valid for the dense part of the specimens; otherwise the quality of the surface was determined mainly by presence of relatively. The wear testing was carried out on the tribometer HTT by CSM Instruments in dry conditions at room temperature (24°C, air humidity 30-35%) using the pin-on-disk technique, where the tribological partner was a highly polished (roughness Ra < 0.25 μm) alumina ball with 6 mm diameter. The applied load was 5 N, sliding speed 5 cm/s, and the sliding distance was 50m.

The tangential forces during the test were measured and friction coefficients calculated. The material losses (volume of the wear tracks) due to wear were measured by a high precision confocal microscope PLu neox 3D Optical Profiler, by SENSOFAR, and then specific wear rates (W) were calculated in terms of the volume loss (V) per distance (L) and applied load (F_p) according to the standard ISO 20808 [14]:

$$W = V / (L.F_p)\ [mm^3/m.N] \quad (2)$$

RESULTS

The influence of bone cements` mass on temperature is documented in Table 2. The values for S and M samples remain very close to the ambient temperature and would in no way jeopardize surrounding tissue. In large samples a notable increase of temperature was observed but only in one instance (Palacos R+G, sample L) it exceeded critical temperatures 47°C [15] or 55°C when osteonecrosis appear [16]. An example of development of temperature over time for two materials with highest temperature increase is given in Fig.3.

Tab.2. Maximum temperature reached during the sample setting [°C].

Material	Mixing					
	manual			DePuy		
	S	M	L	S	M	L
Palacos R	23.5	23.5	36.2	23.2	23.8	35.4
Palacos R+G	23.5	23.5	63.3	23.4	23.5	38.8
Osteobond	-	-	-	23.4	23.5	38.8
Hi-Fatigue +G	23.5	23.5	34.3	23.5	24.5	39.9
Copal G+C	-	-	-	24.2	23.9	36.2
ATB simplex	23.6	35.7	42.5	24.3	24.3	39.0

Volume fraction of pores and pore sizes in terms of Feret diameter are given in Figs.4 and 5. There is a slight tendency for lower porosity in materials mixed in the vacuum bowl and for materials without antibiotic additives which is in agreement with findings reported in literature [17]. In the present stage, however, only one specimen of each state was prepared so the statistical significance is low. The pore size is relatively large and it seems to also be connected to the presence of antibiotics.

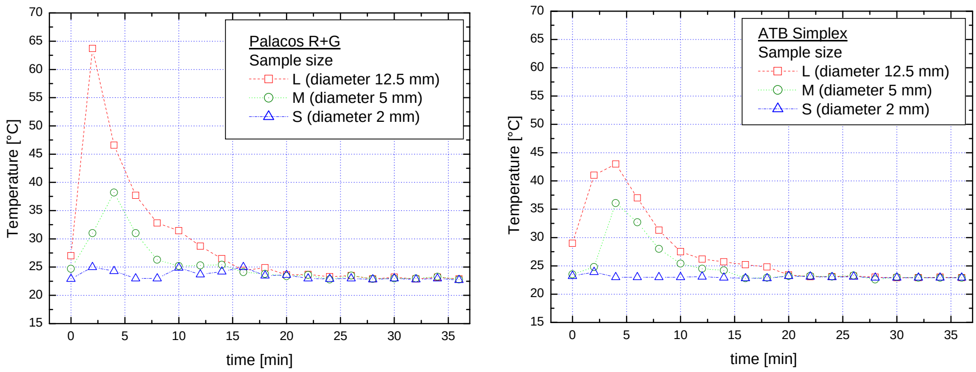

Fig.3. Influence of sample size on temperature during curing time for Palacos R+G and Antibiotic Simplex with Tobramycin.

Results of nano-hardness and elasticity modulus measurements are summarized in Figs.6 and 7 where mean values and their scatter are presented. Since the testing was done in dense parts of materials and at low loads these values reflect true hardness and elasticity of the material without the influence of porosity. No clear difference due to sample size, i.e. setting temperature, is visible. Also no significant reduction due to the presence of antibiotics in the freshly mixed materials is apparent. However, studies such as [18,19] indicate that in practice the elution of antibiotics in blood and body fluids rapidly, within several hours or few days, creates channels and pores within the matrix and compromises the mechanical properties of bone cement. This is particularly serious at higher doses of antibiotics [18].

The average elastic modulus of trabecular bone measured by Zysset et al. [20] using nanoindentation was 11.4 ± 5.6 GPa. The review paper by Guo and Goldstein [21] reported values in the 1.3 to 14.8 GPa range. The nanoindentation results [20] correspond to the upper part of this range, because they do not account for local strain heterogeneities due to lacunae or cement lines. Our results show (Fig.6) that all bone cements have elasticity within this range (4.5 – 5.2 GPa). This suggests that under loading the deformation of bone cements would be similar to that of the surrounding bones so that their use in a patient's body should not lead to large local mechanical stresses. Additionally, the hardness of bone cements (280 MPa – 370 MPa) is similar to that of natural bone lamellae which were reported to be between 250 MPa and 780 MPa [20].

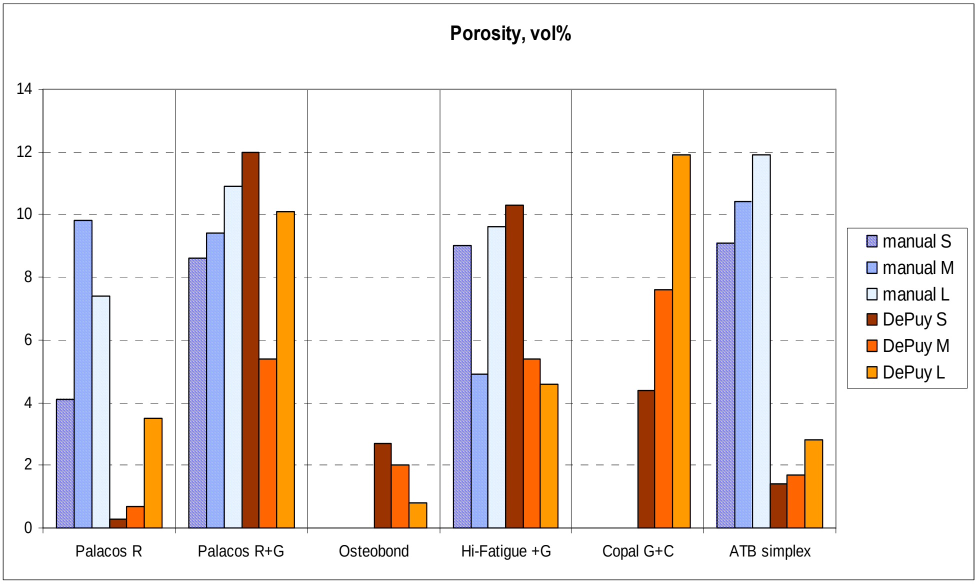

Fig.4. Porosity, measured by image analysis on polished surfaces.

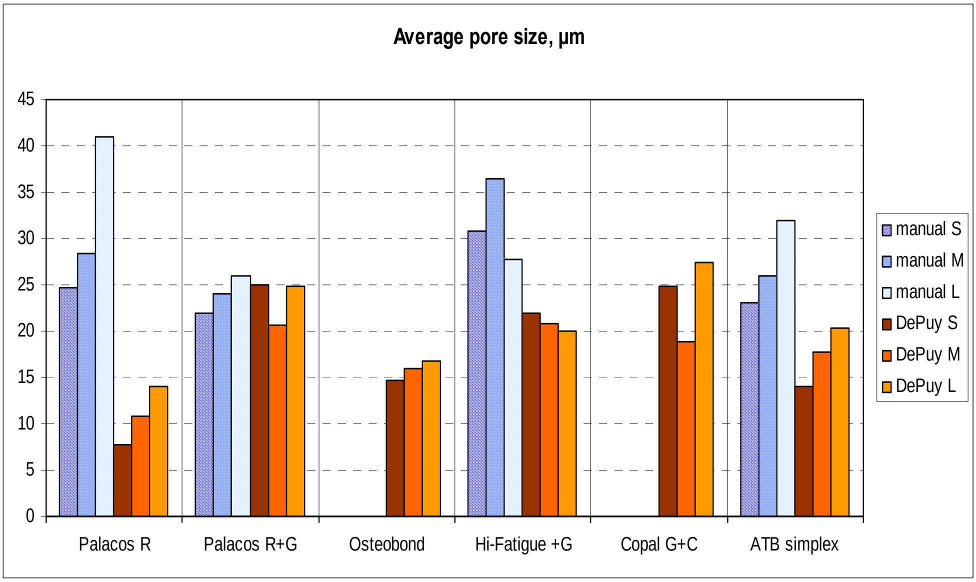

Fig.5. Average pore size in terms of Feret diameter.

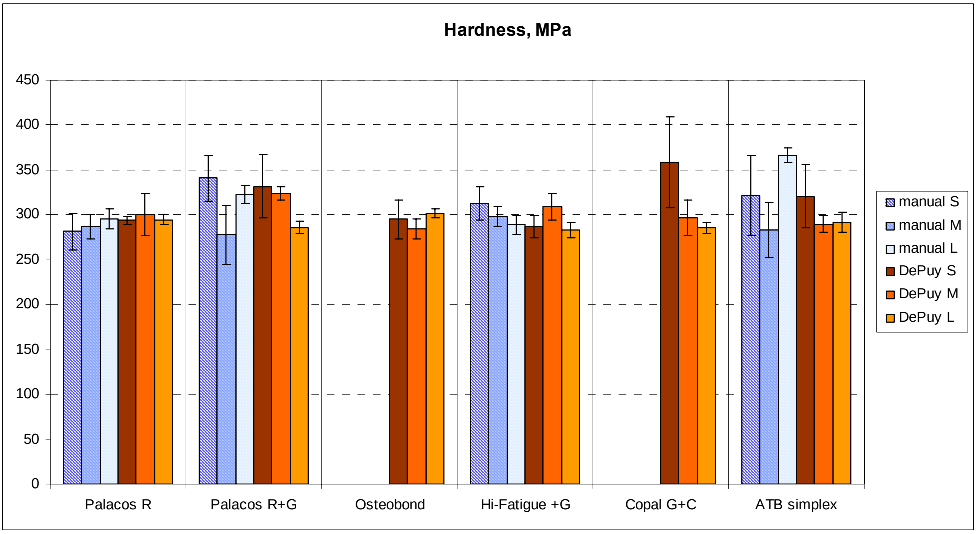

Fig.6. Nano-hardness of the experimental samples.

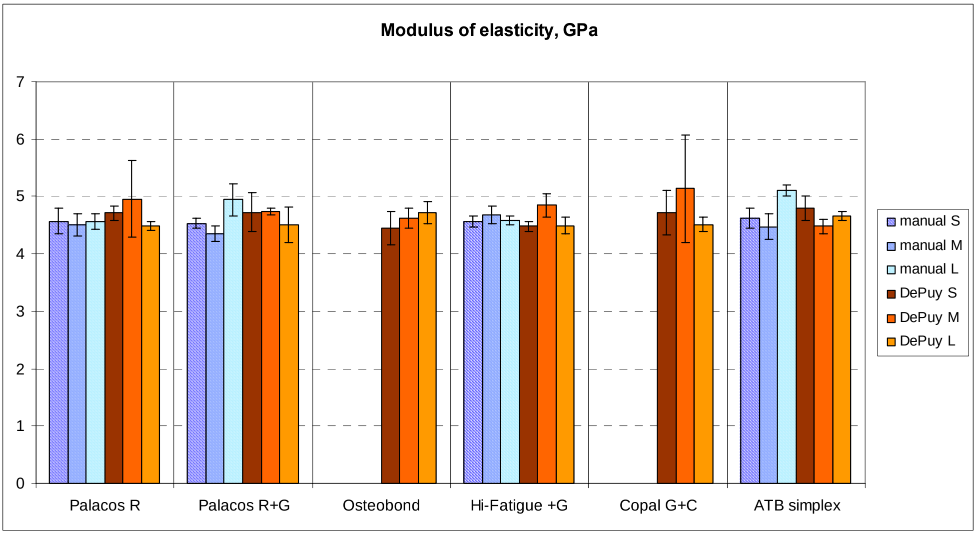

Fig.7. Indentation elasticity modulus of the experimental samples.

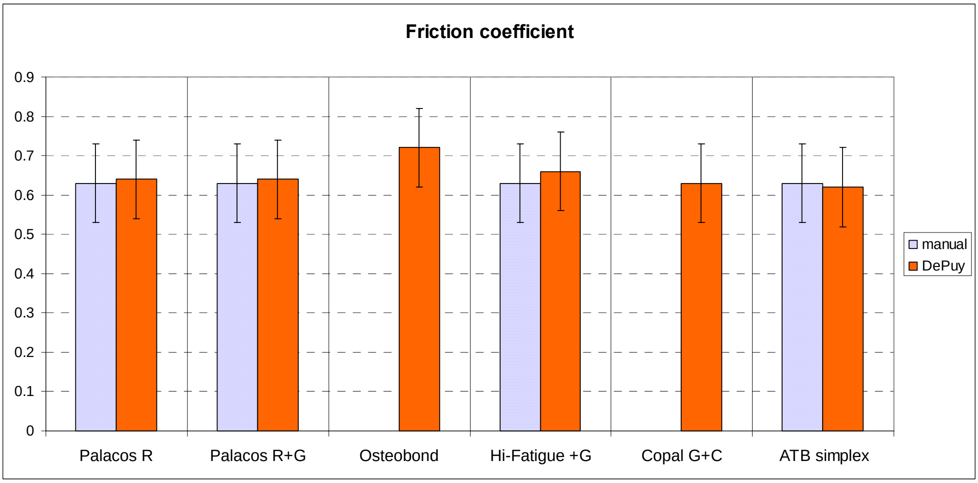

Fig.8. Coefficient of friction, pin-on-disc, with alumina sphere as counter body.

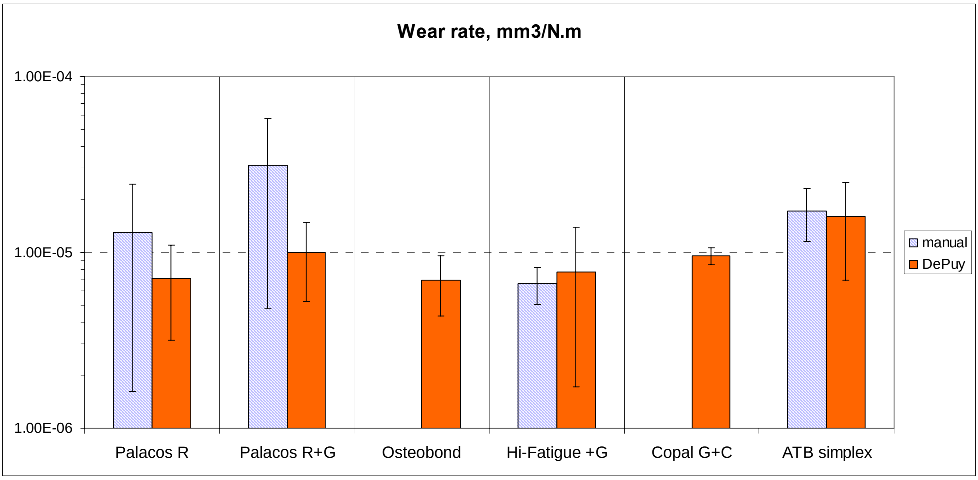

Fig.9. Wear rate measured by pin-on-disc method.

Figures 8 and 9 show results of pin-on-disk testing – coefficient of friction (COF) and wear rates, respectively. Data for friction and wear behaviour of natural materials is difficult to compare to our situation. In the body, friction takes always place in a lubricating environment while in the present stage our data have been collected for dry sliding.

Regarding the frictional behaviour of natural bones, COF depends strongly on the state of the bone surface. Gao et al. [22] performed scratch testing on a human mandible cortical bone by a Brinnel diamond indenter using loads from 0.1 to 80 mN in dry contact. They found that COF had low values (around 0.2) for low loads under 20 mN, where only slight elastic-plastic deformation and no cracking took place. In the second stage, up to about 50 mN the COF increased sharply (from 0.4 up to 0.7) and the damage was accompanied by cracking. At the last stage, above 50 mN, the COF had almost constant high values around 0.8 and large cracks formed. Yu et al [23] studied the fretting behaviour of cortical bone against titanium alloys. They found that in the beginning the friction coefficient was comparably low (0.23) thanks to the protective effects of the surface membrane on bone (tissue chips absorbing layer, physiological lubricants). When the displacement was larger and the surface membrane was destroyed, micro-cracking became more severe, the friction coefficient increased up to 0.34. A further increase of displacement lead to higher shear stresses and the COF reached the maximum of 0.6. These findings are, in some sense, comparable to our results for the PMMA bone cements which in all studied materials have a friction coefficient between 0.6 and 0.72. These results suggest their compatibility with natural bones.

The results of wear rates can be relevant for prosthesis lifetime prediction as well as with regard to the possibility of machining of bone cement. Recently, there has been an effort to use water jet cutting in medicine [24-26]. In such a case the resistance of the material against abrasive and erosive wear would be also an important parameter. The results also suggest that mixing in a vacuum bowl generally improves the wear resistance.

CONCLUSIONS

A range of bone cements was prepared in various sizes and mixing modes in such a way so as to mimic real use. The results show that all materials were well mixed, their polymerization was complete regardless of the sample size, and a good quality of microstructure was achieved. Vacuum mixing lowered porosity and present doses of antibiotics did not compromise the measured mechanical properties of the freshly made samples. The friction coefficient of all materials was very similar, 0.61 – 0.65, the highest value had Osteobond, 0.71. Under present conditions, a severe wear regime by abrasion was dominant. The wear resistance was similar in all materials, the differences were within the scatter of measurements and the effect of additives (radio-opaque agents, colorant, antibiotics) seems to be unimportant. The vacuum mixed specimens performed slightly better than the manually mixed ones, which is consistent with their respective levels of porosity.

Acknowledgement

The study was supported by project VEGA 2/0075/13.

REFERENCES

[1] Lee, C.: Properties of bone cement: The mechanical properties of PMMA bone cement, in The Well-cemented Total Hip Arthroplasty: Theory and Practice. Ed. S.J. Breusch, H. Malchau. Heidelberg : Springer Medizin Verlag, 2005, p. 60
[2] Hengsberger, S., Kulik, A., Zysset. P.: Eur Cells and Mater, vol. 1, 2001, p. 12
[3] Armstrong, MS., Spencer. RF., Cunningham, JL., Gheduzzi, S., Miles, AW., Learmonth, ID.: Acta Orthop. Scand., vol. 73, 2002, no. 6, p. 688
[4] He, Y., Trotignon, JP., Loty, B., Tcharkhtchi, A., Verdu, J.: J. Biomed. Mater. Res., vol. 63, 2002, no. 6, p. 800
[5] Anagnostakos, K., Furst. O., Kelm, J.: Acta Orthop., vol. 77, 2006, no. 4, p. 628
[6] Lewis, G.: J. Biomed. Mater. Res. B: Appl. Biomat., vol. 89, 2009, no. 2, p. 558
[7] Diez-Perez, A., Guerri, R., Nogues, X., Caceres, E., Pena, MJ., Mellibovsky, L., Randall, C., Bridges, D., Weaver, JC., Proctor, A.: J. Bone Miner. Res., vol. 25, 2010, no. 8, p. 1877
[8] Marco, V., Roberto, M., Marek, B., Massimiliano, B., Luca, C.: J. Biomech., vol. 33, 2000, p. 1611
[9] Lewis G.: Journal of Biomedical Materials Research Part B: Applied Biomaterials, vol. 66, 2003, no. 1, p. 457

[10] Sheafin EM., Tanner KE.: Journal of the mechanical behaviour of biomedical materials, vol. 29, 2014, p. 91
[11] Gispert, MP., Serro, AP., Colaço, R., Saramago, B.: Wear, vol. 260, 2006, p. 149
[12] Oliver, WC., Pharr, GM.: J. Mater. Res., vol. 7, 1992, p. 1564
[13] Fischer-Cripps, AC.: Nanoindentation. New York : Spinger, 2002
[14] ISO 20808:2004(E). Fine ceramics – Determination of friction and wear characteristics of monolithic ceramics by ball-on-disc method, 2004
[15] Allan, W., Williams, ED., Kerawala, CJ.: Br. J. Oral Maxillofac. Surg., vol. 43, 2005, p. 314
[16] Boner, V., Kuhn, P., Mendel, T., Gisep, A.: J. Biomed. Mat. Res. – B: Applied Biomat., vol. 90, 2009, p. 842
[17] Zivic, F., Babic, M., Grujovic, N., Mitrovic, S., Favaro, G., Caunii, M.: J. Mech. Behav. Biomed. Mater., vol. 5, 2012, p. 129
[18] Musib, M., Jones, J., Chakote, K., Hayes, W., Saha, S.: Progress in Biomaterials, vol. 1, 2012, p. 3, doi:10.1186/2194-0517-1-3
[19] Simpson, PM., Dall, GF., Breusch, SJ., Heisel, C.: Der Orthopäde, vol. 34, 2005, p. 1255
[20] Zysset, PK., Guo, XE., Hoffler, CE., Moore, KE., Goldstein, SA.: Journal of Biomechanics, vol. 32, 1999, p. 1005
[21] Guo, XE., Goldstein, SA.: FORMA, vol. 12, 1997, p. 185
[22] Gao, S., Qian, L., Yu, H.: Tribol. Lett., vol. 33, 2009, p. 73
[23] Yu, HY., Cai, ZB., Zhou, ZR. Zhu, MH.: Wear, vol. 259, 2005, p. 910
[24] Hreha, P., Hloch, S., Magurová, D., Valíček, J., Kozak, D., Harničárová, M., Rakin, M.: Tehnicki Vjesnik, vol. 17, 2010, no. 2, p. 237
[25] Hloch, S., Kl'oc, J., Hreha, P., Magurová, D. , Kozak, D., Knapčíková, L.: Tehnicki Vjesnik, vol. 20, 2013, no. 2, p. 351
[26] Hloch, S., Foldyna, J., Sitek, L., Zeleňák, M., Hlaváček, P., Hvizdoš, P., Kl'oc, J., Monka, P., Monková, K., Kozak, D., Magurová, D.: Tehnicki Vjesnik, vol. 20, 2013, no. 4, p. 593