PA 2200 vs. PMMA: Comparison Between the Mechanical Proprieties Obtained for the 2 Biocompatible Materials

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The use of Additive Manufacturing methods in the manufacture of custom implants and the development of new biocompatible materials that can be processed by Selective Laser Sintering Technology, represent a trend in biomechanics. In this study two types of biomaterials were analysed and tested – PA 2200, the most used material for cranioplasty, obtained at different laser powers and polymethyl-methacrylate (PMMA). In order to analyse the mechanical behavior of the evaluated materials, the mechanical tests were made for tension, flexure and compression. It was found that the values for PA 2200 material are within the limits of the mechanical characteristics required for cranioplasty implants.

Keywords: polyamide, polymethyl-methacrylate, selective laser sintering, cranioplasty

Worldwide development of new plastics is not expected mainly for economic reasons. Therefore, future development will be focused on improving the existing plastics' properties and processing technologies [1].

The significantly growing use of Additive Manufacturing (AM) enables the fabrication of innovative parts, characterized by lightness and good mechanical properties. The biomedical field takes great advantage of these capabilities: in particular, the ability of producing porous or lattice structure-based parts allows to obtain prostheses with human bone like stiffness, with a positive influence in patient's lifestyle [2].

The Selective Laser Proces (SLS) is based on a simple mechanism. The SLS machine produces the parts builded layer by layer. For each layer three stages are repeated: the platform descends by the thickness of one layer; the powder is spread across the build platform by a leveling roller and preheated to a temperature close to the material's melting point by a radiant heater. Then, a CO_2 laser beam covers the powder by tracing the actual cross section line after line, using a scanner system. This procedure are repeated until the parts are completed [3,4].

Customized properties of parts manufactured using the selective laser sintering process are achievable by variation of build parameters. The energy density, controlled by laser power, distance between scan lines and speed of the laser beam across the powder bed, all have a very strong influence on the density and the mechanical behavior of the parts [5].

The composites made by SLS exhibited higher tensile modulus, comparable or better flexural properties and lower impact strength than those made by Injection Molding Technique [6].

Engineering Thermoplastics like Acrylics, Polycarbonates, Polyurethanes, Polyacetals, Polyesters, and Polyamides have a combination of excellent thermal, mechanical, electrical, and chemical properties. These plastics can be formed into parts that can bear loads and high stresses, perform at elevated temperatures (typically above 100°C), and be modified to approach the properties of ceramics, metal, glass, and wood [7].

In literature, there are many studies regarding the use of Polyamide and other materials that have on their base Polyamide, in medical applications like implants.

The results of a study made by Huanan Wang et all [8] show that n-HA/PA composite scaffolds manufactured by Selective Laser Sintering technology using EOS 380P Sinterstation Machine, exhibit good biocompatibility and extensive osteoconductivity with host bone. Moreover, the introduction of MSCs to the scaffolds dramatically enhanced the efficiency of new bone formation, especially at the initial stage after implantation.

J.C. Zhang and al. [9] evaluated the healing of critical-size surgical defects after implantation of porous nano-hydroxyapatite/polyamide composite (nHA/PA) blocks based on a bilateral mandible model using adult New Zealand white rabbits. The porous nHA/PA composite promotes bone formation over the extension of the defect, particularly in the early stage. The observation period was between 4 and 24 weeks post-implant, during which time, there was no local inflammation or rejection of the implanted piece. Four weeks, macroscopic observations showed that the implant was stable jaw defect and extent of callus formation was so great that almost 70% of the implant surface was covered. After 24 weeks, the implant was osteointegrated. Porous nHA/PA offers interesting potential for maxillofacial reconstructive procedures in load-free areas.

Actually, the most used material for a cranioplasty implant is Polymethyl-methacrylate (PMMA). Polymethyl-methacrylate has a good degree of compatibility with human tissue, and can be also used, in the manufacture of rigid intraocular lens in cataract surgery [10].

In the literature, there are several definitions for Bone Cement. Michel Vert, [11], considers that Bone Cement is a synthetic material, organic or inorganic, with self-solidification properties, used to fill a cavity, or to create a mechanical fixing.

Cranioplasty for the surgical correction of cranial defects is often performed using polymethyl-methacrylate (PMMA), or bone cement. Immediately prior to PMMA application, a liquid monomer form (methylacrylate) and a benzoyl

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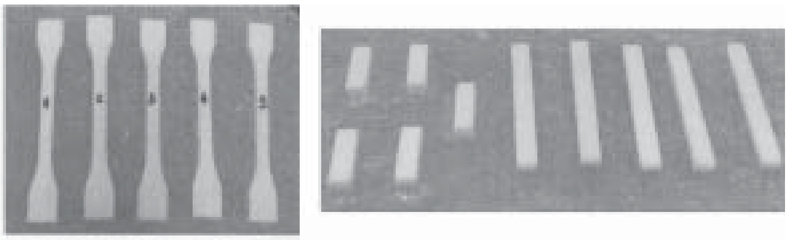

Fig. 1 The Simplex Bone Cement (PMMA) Samples

peroxide accelerator are mixed resulting in polymerization, an exothermic reaction during which monomer linking and subsequent formation of solid polymer occur [12]. There are studies [12] which shows that even small volumes of PMMA used for cranioplasty may cause severe side effects related to thermal damage or to exposure of neural tissue to methylacrylate monomer.

Although PMMA is characterised by excellent biocompatibility with low intrinsic toxicity and inflammatory activation, a minor portion of patients develop irritant and allergic reactions [13 - 15]. A patch test, made specific for bone cement components confirmed the diagnosis of a PMMA delayed-type hypersensitivity reaction [16].

Often the PMMA implants for cranioplasty are manufacured using a silicone rubber mould in which is casted the material. So, first must be produced a master model and on its base will be achived the silicone rubber mould.

Taking into account the economical aspect, the potential allergic reactions that can occur after the surgery when PMMA material is used and the advantages that PA 2200 sinterised material have, a solution for cranioplasty is the use of implants obtained by selective laser sintering method of PA 2200 powder.

Because PMMA is the most used material for implants type cranioplasty, the comparison of the mechanical proprieties between these two materials was necesarry. Thus, PMMA and PA 2200 samples were manufactured.

Experimental part

Materials and methods

A testing sample can help to determine standard basic mechanical proprieties such as: tensile strength, yield strength, elastic modulus and Poisson's ratio [17].

In this study a number of 75 specimens from PA 2200 (with melting point between 172 and 180°C) were produced by Selective Laser Sintering Technology (SLS) on DTM Sinterstation 2000 Machine, at 5 different laser powers (3.5 W; 4 W; 4.5 W; 6 W and 7.5 W). For each laser power were manufactured 5 samples. In order to obtain the ultimate stress values, the specimens were subjected to tensile, flexural and compressive tests.

The working parameters used to manufacture the PA 2200 specimens were: temperature - 170°C, thickness of the deposited layer - 100 μm, type of laser - CO_2 and scan speed - 1257.3 mm/s.

The shapes and the dimensions of the specimens respect the standards for mechanical testing of plastics (tensile test: EN ISO 527-4, flexural test: EN ISO 178:2011, compressive tests: EN ISO 604:2004).

For the manufacturing of test specimens from Simplex Bone Cement (PMMA) manufacture of silicone rubber molds was necessary. Achieving the mold tool could be obtained also by machining, but given the applicability of the study to the realization of customized implants for cranioplasty, it was considered appropriate to follow technological itinerary required by these cases.

The specimens necessary for the physico-mechanical tests have been obtained by casting the Simplex Bone Cement (based on PMMA) into manufactured molds. The obtained Bone Cement Simplex (PMMA) specimens are shown in figure 1.

All the mechanical tests were conducted in the Strength of Materials Laboratory from Technical University of Cluj-Napoca. Mechanical tests were performed using INSTRON 3366 testing machine (10 kN). To determine the tensile mechanical properties an INSTRON 3560 biaxial mechanical extensometer was used. Test speeds were 2 mm / min for tensile test and 5mm / min for flexure and compression tests.

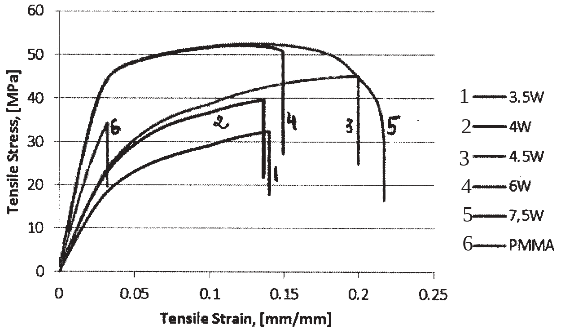

Fig. 2 The average values of specific stresses and strains for tensile tests

Results and discussions

Tensile tests

The data from table 1 and figure 2 shows the mean values of the specific stresses and strains in the tensile test for the six types of materials used in manufacture test specimens.

At the tensile tests of the specimens it can be observed constant increase up to 6 W of the mechanical properties of the material PA 2200 once the laser power is increased. Thus, the maximum tensile stress is obtained for the PA 2200 material made at 7.5 W (52.41 MPa) and minimum tensile stress is for the PA 2200 material made at 3.5 W (31.57 MPa), resulting a 66% increase, even if the maximum load (2606.16 N) was obtained at 6 W laser power.

In contrast, the specimens made from PMMA, have the mean value of the maximum tensile stress 32.70 MPa, very close to the minimum value (31.57 MPa) of the specimens made of PA 2200 at 3.5 W laser power.

It can be noted a stronger growth in maximum tensile stress for specimens made of PA 2200, with increasing laser power from 4 W to 6 W and between 6 and 7.5 W laser power a much slower gradient was recorded (from 52.00 MPa to 52.41 MPa).

For specimens made of PA 2200, in terms of total elongation at tensile testing is found a similar increase with increasing laser power, more stronger was registered between 4 W and 4.5 W (from 7.39 to 10.60 mm/mm).

Test specimens made of PMMA had the lowest average values of strain (Tensile strain at Maximum Load) in tensile test (1.48 mm / mm) is approximately 8 times lower than the recorded value for the specimens made of PA 2200 to a laser power of 7.5 W.

For specimens made of PMMA, were recorded the highest average values of Young's modulus to tensile test (2392.19 MPa) compared to much lower values of Young's

Material type	Maximum Load, [N]	Tensile stress at Maximum Load, [MPa]	Tensile strain at Maximum Load, [%]	Modulus (E-modulus), [MPa]	Poisson's Ratio
PMMA	**1846.77**	**32.70**	**1.48**	**2392.19**	**0.36**
Standard Deviation	232.12	3.60	0.19	82.69	0.03
PA2200 3.5 W	1704.79	31.57	5.88	1060.46	0.35
Standard Deviation	95.85	1.77	0.88	63.74	0.02
PA2200 4 W	2163.00	40.06	7.39	1375.60	0.32
Standard Deviation	92.50	1.71	1.14	99.41	0.05
PA2200 4.5 W	2404.46	44.53	10.60	1400.35	0.35
Standard Deviation	45.33	0.84	0.97	54.64	0.03
PA2200 6 W	2606.16	52.00	11.07	1626.37	0.34
Standard Deviation	496.97	1.09	1.97	57.32	0.03
PA2200 7.5 W	2124.47	52.41	12.33	1646.50	0.37
Standard Deviation	625.09	0.38	1.03	18.26	0.04

Table 1
THE AVERAGE VALUES OF PROPERTIES OBTAINED FROM TENSILE TEST SPECIMENS

modulus recorded for specimens made of PA 2200 (between 1060.46 MPa at 3.5 W laser power and 1646.50 MPa at 7.5 W laser power).

The average values of the Poisson ratio at tensile test for specimens made from PA 2200 at 3.5 and 4.5 W laser powers were lower than those recorded for specimens made of PMMA (0.36) and those of PA 2200 at 7.5 W (0.37). The lowest value occurred in PA 2200 specimens at 4 W laser power (0.32).

Bending tests (flexural tests)

Table 2 and figure 3 show the average values of specific stresses and strains at bending tests for the six batches of samples from materials taken into the study.

The maximum bending force for PMMA specimens had the highest values – 153.82 N compared to all types of specimens made of PA 2200 at different laser powers. The lowest maximum flexural strength was recorded for specimens of PA 2200 made at 3.5 W (72.37 N), while the highest value of maximum force was for 7.5 W manufactured specimens (137.02 N). It was found the increase of the maximum bending force for PA 2200 specimens once with the increase of laser power used in the sintering process.

The same trend was observed for maximum bending stresses, where once with the increase of the laser power, increased also their values. The PMMA specimens having the maximum tensions value at bending (57.86 MPa) were below the values recorded for PA 2200 specimens between 4 and 7.5 W, but higher than samples manufactured at 3.5 W the laser power.

Between 3.5 and 4.5 W laser power, specimens made of PA 2200 had identical behaviour, mean of the specific strains for bending test was 0.07 mm / mm. Together with the augmentation of the laser power from 4.5 W to 6 W, respectively 7.5 W, the specific bending deformation of the specimen increased from 0.07 to 0.08 mm / mm. Lower values for specific strains have been found for PMMA, where was determined 0.02 mm / mm.

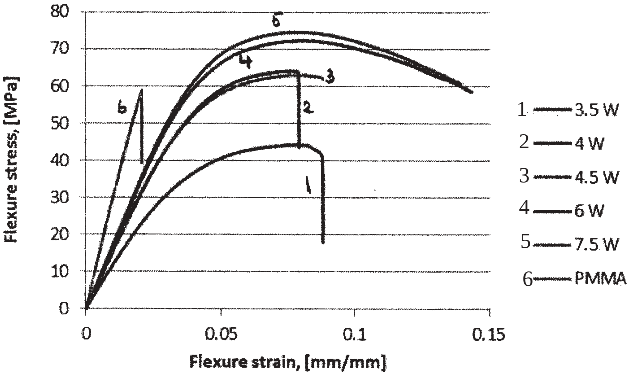

Fig. 3 Average values of specific stresses and strains for flexural test

Material type	Flexure load at Tensile Strength, [N]	Flexure stress at Tensile Strength, [MPa]	Flexure strain at Tensile Strength, [mm/mm]	Modulus (E-modulus) [MPa]
PMMA	**153.82**	**57.86**	**0.02**	**2664.87**
Standard Deviation	7.10	3.50	0.00	191.15
PA 2200 3.5W	72.37	45.71	0.07	1284.04
Standard Deviation	10.59	6.69	0.003	115.23
PA 2200 4W	101.53	64.13	0.07	1613.81
Standard Deviation	4.91	3.10	0.004	77.46
PA 2200 4.5W	100.97	63.77	0.07	1637.14
Standard Deviation	6.84	4.32	0.01	82.68
PA 2200 6W	127.00	73.52	0.08	1665.62
Standard Deviation	2.34	2.07	0.001	74.42
PA 2200 7.5W	137.02	74.48	0.08	1687.05
Standard Deviation	1.96	1.31	0.00	29.33

Table 2
THE MEAN VALUES OBTAINED IN FLEXURAL TESTS OF SPECIMENS

Material type	Compressive load at Tensile Strength, [N]	Compressive stress at Tensile Strength, [MPa]	Compressive strain at Tensile Strength, [mm/mm]	Modulus (E-modulus), [MPa]
PMMA	**7404.00**	**77.77**	**0.08**	**1766.95**
Standard Deviation	260.84	2.98	0.01	76.49
PA2200: 3.5W	4129.59	45.88	0.16	928.43
Standard Deviation	103.88	1.15	0.01	24.01
PA2200: 4W	5320.70	59.12	0.18	1234.99
Standard Deviation	223.91	2.49	0.04	67.20
PA2200: 4.5W	5521.60	61.35	0.15	1297.39
Standard Deviation	310.44	3.45	0.05	20.57
PA2200: 6W	6250.88	63.29	0.12	1403.15
Standard Deviation	311.58	3.33	0.01	18.72
PA2200: 7.5W	6326.96	62.39	0.10	1378.57
Standard Deviation	253.31	2.45	0.01	16.82

Table 3
THE MEAN VALUES OBTAINED FROM COMPRESSION TEST SPECIMENS

For specimens made of PMMA, were recorded the highest average values of the Young's modulus for bending test - 2664.87 MPa, compared to much lower values of Young's modulus recorded for PA 2200 specimens (between 1284.04 MPa at 3.5 W and 1687.05 MPa at 7.5 W laser power). It can be noted the same trend of higher growth in average values of Young's modulus with the increase of the laser power between 3.5 and 6 W.

Compression tests

Table 3 and figure 4 present the average values of specific stresses and strains for compression test for the six batches of samples from studied materials.

The average values of maximum forces at compressive test of PA 2200 specimens performed at the laser powers between 3.5 (4129.59 N) and 7.5 W (6326.96 N) are lower than the results for specimens of PMMA (7404.00 N) and also increased with the increasing of laser power.

The same increasing trend was recorded for mean values of the compression stresses for PA 2200 specimens from 45.88 MPa - at 3.5 W laser power up to 63.29 MPa for specimens sintered at 6 W. The mean values of compressive stress for PMMA specimens were superior than PA 2200 and had a value of 77.77 MPa.

The lowest values of specific strains to compression test were found for PMMA specimens (0.08 mm / mm), the highest values recorded for PA 2200 specimens manufactured at 4 W laser power (0.18 mm / mm), followed by those of specimens manufactured at 3.5 W laser power (0.16 mm / mm). On increasing the laser power from 4.5 W to 7.5 W, a decrease of average specific strain values from 0.15 mm / mm to 0.10 mm / mm, was found for PA 2200 specimens.

It should be noted that the results obtained are consistent with the structure of the materials analyzed. Thus, at a low laser power, the material is more porous, the layers have a lower adhesion, which generates lower forces and also higher deformations.

The average values of Young's modulus, at compressive test for PMMA specimens were highest (1766.95 MPa) compared to the values of Young's modulus for PA 2200 specimens.

It can be observed a progressive increases in Young's modulus for specimens made at the increasing laser power.

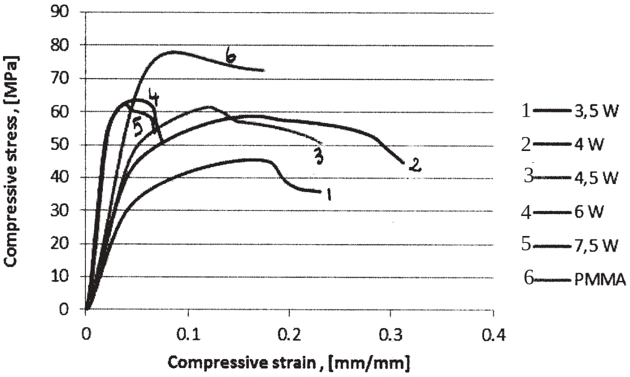

Fig. 4 The average values of specific stresses and strains for compression test

Analyzing test pieces resulting from compression of PA 2200, has been shown that at low laser power, layer delamination occurs in the specimens (fig. 5a). At higher laser power, the phenomenon has been less visible, specimens made at 7.5 W being more compact. A possible interpretation for this phenomenon could be production technology, "layer by layer" of PA 2200 specimens (selective laser sintered at a temperature below the melting point of the powder).

In contrast to PA 2200 specimens, the PMMA being a molded material, with a homogeneous structure, had only cracks (fig. 6).

In the scientific literature, for the tests on the parietal bone compression testing, different values were found [18]. Thus, Evans [19] tested 56 parietal bone specimens from embalmed adult human cadavers and estimated the compressive failure strength of the diploe (trabecular bone lying between the cortical tables of the skull) to be 25.1 ± 13.3 MPa. Robbins [20] tested 70 through the thickness specimens and reported an average elastic modulus of 1.4 GPa and a mean failure stress of 36.54 MPa. McElhaney [21] tested 237 through the thickness skull cores under quasi static compression and estimated the elastic modulus to be 2.4 ± 1.5 GPa and failure stress of 73.8 ± 35.2 MPa.

It should be noted that the values for the Young's modulus in compression, at test pieces from PA 2200, regardless of the laser power used in the manufacturing process, are

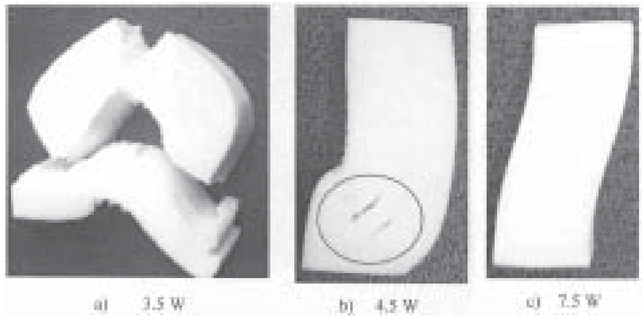

Fig. 5 PA 2200 specimens after compression test

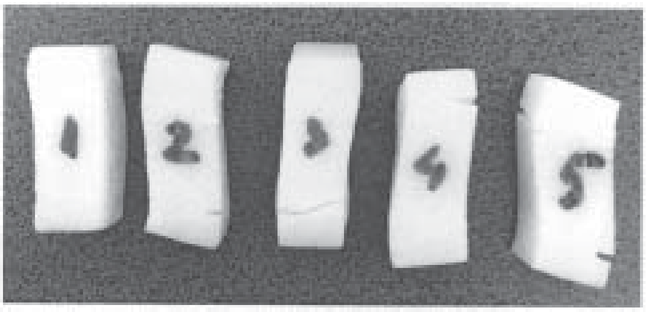

Fig. 6 PMMA specimens after compression test

close to the existing values in the scientific literature, for the tests on the parietal bone.

Conclusions

In this study were manufactured and tested samples of two types of biocompatible materials: PA 2200 and Simplex Bone Cement (based on PMMA). PA 2200 specimens were manufactured using five laser powers (3.5 W; 4 W; 4.5 W; 6W; 7.5 W) on the Sinterstation 2000 machine. The results obtained for PA 2200 selective laser sintered specimens, and those obtained from specimens produced by casting Bone Cement Simplex (PMMA) were compared.

This study shows that the recommended laser power to be used for the material PA 2200, considering the variation obtained reported with maximum strain, and stress is 7.5 W. For this laser power were obtained mechanical properties similar to those of PMMA material and even higher in the case of elongation.

Considering the destination of the future implant and the mechanical properties values of the parietal bone reported in the literature, it can be concluded that the values for PA 2200 material are contained within the limits the mechanical characteristics required for implants for cranioplasty.

References

1. BUTORA, P. NAPLAVA, A. RIDZON, M., BILIK, J.M, TITTEL,V., Particle filled polyethylene composites used in the technology of rotational moulding, In Vedecké práce MtF STU v Bratislave so sídlom v Trnave. Research papers Faculty of Materials Science and Technology Slovak University of Technology in Trnava. Vol. **19**, No. 31 (2011), ISSN 1336-1589, p. 9-18.

2. CERARDIA, A., CANERIA, M., MENEGHELLOA, R., CONCHERIA, G., RICOTTAB, M., Mechanical characterization of polyamide cellular structures fabricated using selective laser sintering technologies, Materials & Design, Volume **46**, April 2013, p. 910–915.

3. WEGNER, A.,WITT, G., Correlation of process parameters and part properties in laser
sintering using response surface modeling, Physics Procedia,Volume **39**, 2012, p. 480–490.

4. GEBHARDT, A.: Generative Fertigungsverfahren - Rapid Prototyping - Rapid Tooling - Rapid Manufacturing. 3rd ed. Munich: Carl Hanser Publishing; 2007.

5. CAULFIELD, B.,. MCHUGH, P.E., LOHFELD, S., Dependence of mechanical properties of polyamide components on build parameters in the SLS process, Journal of Materials Processing Technology, Volume **182**, Issues 1–3, 2 February 2007, p. 477–488.

6. KAREVANA, M., ESHRAGHIA, S., GERHARDTB, R., DASA, S., KALAITZIDOU, K., Effect of processing method on the properties of multifunctional exfoliated graphite nanoplatelets/polyamide 12 composites, Carbon, Volume **64**, November 2013, p. 122–131.

7. SASTRI, V.R., – Engineering Thermoplastics: Acrylics, Polycarbonates, Polyurethanes, Polyacetals, Polyesters, and Polyamides, Plastics in Medical Devices (**2**nd Edition) Properties, Requirements and Applications, 2014, p. 121–172.

8. WANGA, H., LIA, Y. ZUOA, Y., LIB, J., MAB, S., CHENGA, L., Biocompatibility and osteogenesis of biomimetic nano-hydroxyapatite/polyamide composite scaffolds for bone tissue engineering, Biomaterials, Volume **28**, Issue 22, August 2007, p. 3338–3348.

9. ZHANG, J.C., LU, H.Y., LV, G.Y.,. MO, A.C., YAN, Y.G., HUANG, C., The repair of critical-size defects with porous hydroxyapatite/ polyamide nanocomposite: an experimental study in rabbit mandibles, International Journal of Oral and Maxillofacial Surgery, Volume **39**, Issue 5, May 2010, p. 469–477.

10. MEYERS, R. A., Molecular biology and biotechnology: a comprehensive desk reference, Wiley-VCH, 1995, ISBN 1-56081-925-1, p. 722

11. VERT, M., DOI, Y., HELLWICH, K.-H., HESS, M., HODGE, P., KUBISA, P., RINAUDO, M., SCHUE, F., Terminology for biorelated polymers and applications (IUPAC Recommendations 2012), Pure Appl. Chem., Vol. **84**, No. 2, 2012, p. 377–410.

12. PIKISA, S., GOLDSTEINB, J., SPEKTOR, S., Potential neurotoxic effects of polymethylmethacrylate during cranioplasty, Journal of Clinical Neuroscience, Volume **22**, Issue 1, January 2015, p. 139–143.

13. LUNG, C.Y.K., DARVELL, B.W., Dental Materials, 21, nr. **12**, 2005, p.1119-1128

14. MARCAUTEANU, C., STOICA, E.T., BORTUN, C. , NEGRUTIU, M.-L., SINESCU, C., TUDOR, A., Advantages of a Polyethylene Terephthalate Glycol-modified Coated with a Thermoplastic Polyurethane as an Occlusal Appliance Material, Rev. Chim. (Bucharest) **65**, no.6,2014, p. 734..

15. ORBAN, H., CIRSTOIU, C., ZAHARIA, C., CINCU, C., Acrylic Cement Advantages or Disadvantages in Orthopaedic Surgery, Rev. Chim. Bucuresti, **59**, no. 6, 2008, p. 688.

16. GAUTSCHIA, O.P., SCHLETTB,C.L.,. FOURNIERA, J.Y., CADOSCHC,D., Laboratory confirmed polymethyl-methacrylate (Palacos®)-hypersensitivity after cranioplasty, Clinical Neurology and Neurosurgery, Volume **112**, Issue 10, December 2010, p. 915–916.

17. RIDZON, M., ZAVACKA, A., Effect of Drawing Tubes Without Interoperation Recrystallization Annealing on the Orientation of Boudaries Grain – longitudinal Direction, Applied Mechanics and Materials Vol. **421**, 2013, p. 329-333.

18. BORUAH, S., HENDERSON, K., SUBIT, D., SALZAR, R.S., SHENDER, B.S., PASKOFF G., Response of Human Skull Bone to Dynamic Compressive Loading, IRCOBI Conference 2013, avaiable online at http://www.ircobi.org/downloads/irc13/pdf_files/54.pdf

19. EVANS, F.G, LISSNER, H.R, Tensile and compressive strength of human parietal bone, Journal of Applied Physiology, **10**, 1957, p. 493 497.

20. ROBBINS, D.H., WOOD, J.L., Determination of mechanical properties of the bones of the skull, Experimental Mechanics, 9(5), 1969, pag. 236 240.

21. McELHANEY, J.H., et al, Mechanical properties of cranial bone, Journal of
Biomechanics, **3**, 1970, p. 495 511.

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