ELABORAREA UNOR STRUCTURI CERAMICE CU FORME COMPLEXE PE BAZĂ DE HIDROXIAPATITĂ FOLOSIND TEHNICA DE TURNARE ÎN FORME DE IPSOS CU POSIBILE APLICAȚII MEDICALE

DEVELOPMENT OF CERAMIC STRUCTURES WITH COMPLEX SHAPES BASED ON HYDROXYAPATITE USING THE TECHNIQUE OF CASTING IN PLASTER MOLDS WITH POSSIBLE MEDICAL APPLICATIONS

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The main objectives of this work are represented by both the development of hydroxyapatite (HAP) and the technique of casting it into plaster forms order to develop of ceramic structures with complex shapes for applications in neurosurgery. The tested models were made from ceramic powders based on HAP and, shaped by the casting technique in plaster molds. In order for the process of casting ceramic suspensions to be more efficient, specific techniques were performed such as: rheological curves of shear stress variation depending on the speed gradient and the dependence of the viscosity of the HAP suspensions on the speed gradient. Experimental models of cranial prostheses were developed in the form of a skull cap with an average thickness of ~3.5 mm, rods with a diameter of 5 mm, length of 50 mm. The samples were sintered at temperatures of 1275˚C and 1350˚C, for 2 hours. The variation of density and porosity with sintering temperature were determined by Archimedes' method and the mechanical properties were investigated by bending and compression tests. The average values for the bending strength, for the two obtained models, are in the range of 32.64-36.68 MPa and for the compression strength they range from 44.54 to 50.10 MPa. Furthermore, the obtained samples were characterized by scanning electron microscopy (SEM) and the X-ray diffraction data for the HAP powder were confirmed by FT-IR spectra and thermogravimetric measurements. In order to establish the biocompatibile character, a first set of bacteriological and sterility determinations was performed. The novelty of this work consists in the fact that both the rheological characteristics have been optimized (ceramic suspensions with a solid phase content of min. 60%) as well as the technique of casting ceramic suspensions in plaster molds through ultrasonic and degassing processes/deaeration, obtaining shaped products with a raw density of min. 50% of ρ_{th}.

Obiectivele principale ale acestei lucrări sunt reprezentate atât de elaborarea hidroxiapatitei (HAP) cât și de tehnica de turnare în forme de ipsos a acesteia, pentru elaborarea unor structuri ceramice având forme complexe cu posibile aplicații în neurochirurgie. Modelele obținute și testate au fost realizate din pulberi ceramice pe bază de HAP, fasonate prin tehnica de turnare în forme de ipsos. Pentru eficientizarea procesului de turnare a suspensiilor ceramice au fost efectuate curbe reologice de variație a tensiunii de forfecare în funcție de gradientul de viteză și respectiv, dependența vâscozității suspensiilor de HAP funcție de gradientul de viteză. Au fost realizate modele experimentale de proteze craniene sub formă de calotă cu grosimea medie de ~3,5 mm și baghete cu diametrul de 5 mm și lungimea de 50 mm iar în final probele au fost sinterizate la temperatura de 1275˚C și 1350˚C, timp de 2 ore. Variația densității și porozității cu temperatura de sinterizare a fost determinată prin metoda lui Arhimede iar proprietățile mecanice au fost investigate prin teste de încovoiere și compresiune. Valorile medii pentru rezistența la încovoiere, pentru cele două modele obținute, sunt cuprinse în intervalul 32,64-36,68 MPa iar pentru rezistența la compresiune sunt cuprinse în intervalul 44,54-50,10 MPa. De asemenea, probele obținute au fost caracterizate prin microscopie electronică de baleiaj (SEM) iar datele din difracția cu raze X pentru pulberea de HAP au fost confirmate prin spectre FT-IR și măsurători termogravimetrice. În vederea stabilirii caracterului de biocompatibilitate, s-a efectuat un prim set de determinări bacteriologice și de sterilitate. Noutatea acestei lucrări constă în faptul că au fost optimizate atât caracteristicile reologice (s-au realizat suspensii ceramice cu conținut de fază solidă de min. 60%) precum și tehnica de turnare a suspensiilor ceramice în forme de ipsos prin procese de ultrasonare și degazare/dezaerare, obținându-se produse fasonate cu densitatea pe crud de min. 50% din ρ_{th}.

Keywords: *hydroxyapatite, biomaterials, casting in plaster forms, viscosity curves*

1.Introduction

The great challenge regarding the medical industry represented by "surgical interventions in which the implants can be fully adapted to the specific requirements for the needs of each patient". This "vision" will be perfected on the one hand through the development of new biomaterials, and on the other hand through the implementation of new technologies for the rapid design and development of these implants [1-3].

The results presented in the specialized literature showed that the most used synthetic ceramic material for making implants and/or repairs of cranial bones/neurosurgery is hydroxyapatite (HAP), used in the form of powders/granules, ceramic paste (cement) or shaped under form of products [4-7]. Moreover, HAP represents the major

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compound in biological bone and presents, on the one hand, an excellent biocompatibility due to the chemical and crystallographic structure of living bone tissue, as well as a bioactivity due to partial resorption and replacement of natural bone shortly after implantation [8-10]. However, due to the poor mechanical properties of hydroxyapatite, it is not suitable in load-bearing applications [11, 12]. The implants used in medicine for bone osteosynthesis must satisfy the functional requirements defined by the working environment of the human body. Ideally, they should have biomechanical properties comparable to those of human tissues, without generating adverse effects in the body [13]. The main requirements of implantable devices in the human body are: corrosion resistance, biocompatibility, biofunctionality and bioadhesion [14].

Apatite is a general name used to define a larger group of ceramic materials differentt chemical properties, but similar crystalline structure [15]. HAP is the most well-known compound for different types of applications and it is one of the most used bioactive materials in clinical applications. HAP has a crystalline structure with hexagonal symmetry, with 44 atoms contained in the elementary cell, related to the space group P63/m and the cell parameters a=9.418, c=6.881, b=120°. The stoichiometric hydroxyapatite has a Ca/P ratio (stoichiometry) equal to r = 1.67 and a density ρ = 3.156 g/cm^3, the cellular unit being oriented along the c axis justifying the preferential orientation [16].

Casting the suspension in plaster forms/shapes represents the process, to obtain a homogeneous mixture under the action of forces and molds, as semi-finished products with complex shapes and predetermined dimensions. These semi-finished products can be made by shaping suspensions, pastes or ceramic powders. The process of forming the ceramic wall when pouring ceramic suspension in the form of plaster consists in the absorption of water from the suspension through the capillaries of the plaster form. Thus, the initial amount of water of 30-35% drops to 20-25%, and the particles form a coagulation structure, corresponding to the paste of the normal consistency of the ceramic wall. Depending on the complexity of the product and the thickness of its wall, could be performed by two methods: by draining with the removal of the surplus suspension left after the formation of the ceramic wall of the desired thickness, and respectively by filling, i.e. by feeding with suspension until the wall is fully formed in the cavity of the porous form [17]. Shaping by casting the suspension is represented in Figure 1 and consists of: preparing the suspension and the form, casting the suspension in the form, forming the wall, removing the excess suspension, drying and detaching the shaped part and finally, sintered.

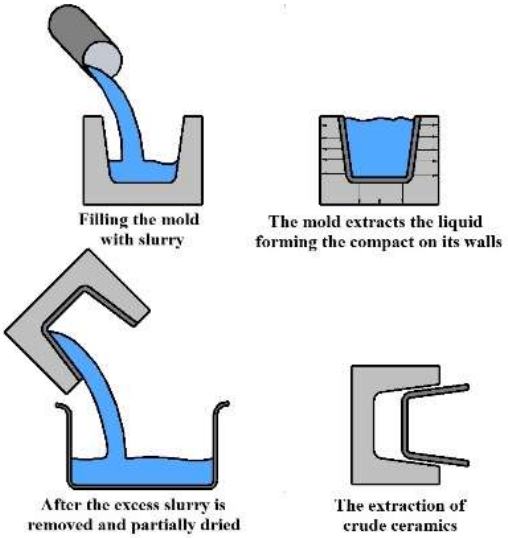

Fig. 1 - Casting ceramic slurry in plaster forms / *Fluxul tehnologic al turnării suspensiilor ceramice în matrițe de ipsos*

The process of forming the ceramic wall, when pouring into the plaster molds, consists in the absorption of water from the suspension layer adjacent to the mold, in their capillaries. Also, casting in plaster forms is a common process for shaping ceramic products with complex shapes, even large sizes and low costs [18, 19].

A particularly important stage in the products development using the casting method in plaster molds is the drying process of the cast products. This is carried out gradually, so after removing most of the water, the shaped product keeps its geometric integrity, without showing superficial or deep cracks. The raw density is an important parameter that indicates the quality of the shaping and whether the sintered product can achieve a higher densification. In the case of the casting process in plaster molds, the fluid (ceramic suspension of HAP) will flow inside the porous interior of the plaster mold due to the phenomenon of transport by capillarity. Thus, a high crude density and suspension with a high concentration of solids are an encouraging premise for obtaining uniform and well-densified products.

The technique of casting ceramic materials based on HAP in plaster forms could represent a suitable alternative, especially for patients who have suffered from an initial failed treatment, but also for the final reconstruction of large and complex cranial bone defects. Ceramics based implantable materials have shown good aesthetic results and at the same time, due to the fact that they are synthetic materials, they can avoid the problems related to morbidity associated with the donor [20].

The excellent biocompatibility of HAP represents an important characteristic for an implantable device and makes this material a promising candidate for the development of medical applications, such as bone substitutes for

neurosurgery [21]. Neurosurgery is the research field dominated by the interest of both medical doctors and engineers, promoting constantly new materials and specific technologies [22]. Some of the advantages of the technique of casting in plaster molds consist in obtaining parts with complex shapes, large and precise dimensions, relatively uniform surfaces, at relatively low cost prices.

The novelty element of this work is represented by the protocol optimization for the rheological characteristics and the technique of pouring ceramic suspensions into plaster molds. The realization of homogeneous suspensions with optimal casting characteristics requires stable, de-agglomerated suspensions, with a as high as possible solid phase content (ceramic powders with a small specific surface area) and sufficient fluids. In order to achieve them, the complex interface reactions between the ceramic powder, the dispersion medium, additions and surfactants must be taken into account. The aim of the work consists in the development of ceramic structures with complex shapes based on hydroxyapatite using the technique of casting in plaster molds for medical applications.

2.The experimental part

2.1. Materials and methods

In order to develop the ceramic suspension, microcrystalline HAP developed by solid phase synthesis was used as a precursor. The hydroxyapatite was made in the laboratory of ceramic materials within INCDIE ICPE-CA laboratories and the raw materials used for the experiments were of purity p.a. (>99%), such as $CaHPO_4$ and respectively $CaCO_3$, (Fluka, Germany). The raw materials were homogenized in an aqueous environment on a planetary mill (type Fritsch-Pulverisette 5, Germany), for 6 hours. The dry material (moisture < 5%) was calcined at a temperature of 1200˚C and the granulometric fraction 45÷63 μm was selected to achievement of the two types of slurry. The compound was formed through a sequence of reactions at temperatures between 210 and 1200˚C.

To obtain the first suspension, coded M1, sodium polyacrylate (PAA - Na) was used as a dispersant in a proportion of 2% and sodium carboxymethyl cellulose (CMC-Na) in a proportion of 2% as a binder. For the second suspension coded M2, a mixture of sodium carboxymethyl cellulose (CMC-Na) in a proportion of 1% and polyvinyl alcohol 5% (APV) added in a proportion of 1% was used as a binder. The two suspensions obtained for a ratio of 65% solid were homogenized using a planetary ball mill for 30 minutes. The rheological behavior of 65% HAP solutions was studied by measuring the viscosity and the shear stress for different values of the velocity gradient. The dispersant added to make the suspensions was in proportions of 1-2% relative to the amount of HAP and the viscosity of the solutions thus prepared was measured under constant temperature conditions, for a pH ~ 10.50. After homogenization, deaeration of the ceramic suspension followed, which was carried out in an installation consisting of a desiccator with a cover equipped with a valve, a magnetic stirrer and a vacuum pump with a membrane and then, the obtained suspensions were poured into plaster molds, according to those shown in Figure 1, and the formation time of the wall varied between 1-3 hours depending on the size of the landmark and the nature of the suspension. After 30 minutes of casting the slurry into the molds, the excess material is drained and the formed ceramic wall was made in 2 hours. After removing the landmarks from the plaster molds, they were air-dried (for 24 hours) followed by a slow drying treatment in a controlled-atmosphere oven up to a temperature of 120 °C. The sintering of the cast samples was carried out with the help of a heat treatment furnace (Nabertherm, Germany), at a temperature of 1275 and 1350°C for 2 hours and, and the cooling was uncontrolled and was carried out in 20 hours. The Figure 2 shows the cranial skull and wand models obtained by casting in plaster molds within the INCDIE ICPE-CA.

Fig. 2 - Experimental model of skull cap and wand obtained by casting in plaster molds in the INCDIE ICPE-CA laboratory / *Calotă craniană și baghetă obținute prin turnare în forme de ipsos la INCDIE ICPE-CA*

2.2.Viscosity measurements

Viscosity measurements were used for the rheological characterization of concentrated suspensions used in the development of ceramic products. These measurements are considered a specific method for establishing the optimal dispersant content necessary to produce a stable suspension. For the analysis, the Brookfeld DV-II+ device (manufacturer-USA), was used at room temperature (~24°C) and the recorded values were for a rotation speed of 60 rpm.

2.3.Measurement of density and porosity

The measurement of the density and respectively the apparent porosity was carried out by the method of Archimedes, using a hydrostatic balance (Mettler Toledo, Germany), by successive weighing in air of the dry sample and then immersed

in distilled water. For each sample, 3 measurements were made, and their average values are presented.

2.4.FT-IR analysis

Infrared spectroscopy (FTIR) allows the analysis of material characteristics, especially the identification of functional groups, being complementary to the RX diffraction. The measurements of the ceramic powders were done on FTIR Spectophotometer Bruker Tensor 27 (Bruker Optik GmbH, Germany), within the domain 4000 ÷ 600 cm^{-1}.

2.4.1.Simultaneous thermal analysis measurements TG/DTG/DSC

The thermal analysis measurements were performed using the STA 409 PC Luxx device (Netzsch, Germany) in the temperature range: 30 – 1000°C, with a heating rate of 10°C min^{-1}, in static air atmosphere.

2.5.Microstructure analysis

Scanning electron microscopy (SEM) was used to visualize the microstructure and qualitative distribution of granular phases and pores in ceramic materials. SEM analysis of the sintered materials was performed using an FESEM-FIB Auriga (Carl Zeiss SMT, Oxford Instruments.ltd, England) scanning electron microscope and a maximum acceleration voltage of 5 kV.

2.6.Mechanical tests

The mechanical properties (flexural and compressive strength) of the sintered HAP samples were measured at room temperature using a universal machine for static mechanical testing of materials model LFM 30kN, Walter&Bai AG Switzerland, equipped with a maximum nominal test force cell of 30 kN. Loads were applied during bending and compression tests at a transverse speed of 1 mm/min until the specimens cracked. The presented results are the mean values of 3 determinations.

2.7.Sanitation/sterility tests

Sanitation and sterility tests were carried out at the Directorate of Public Health of the Municipality of Bucharest (DPHMB), the Diagnostic and Investigation Laboratory in Public Health - Microbiological Examination. For the sanitation test, samples were collected from the tested materials using sterile swabs with peptone water. In order to determine the total number of germs (NTG), the the inoculum, represented by original suspension and serial dilutions, was plated on agar or differential media (for specific pathogenic bacteria such as E. coli, Proteus sp. Staphylococcus sp etc.). The plates were incubated at 37ºC for 48 hours.The tests were performed for following germs: yeasts, molds, enterobacteria, coliform bacteria, Escherichia coli, coagulase-positive staphylococcus, Proteus sp., Bacillus sp. For the sterility test, the product to be tested is introduced directly into the culture medium (medium 1-Thioglycolate for aero-anaerobic microorganisms and medium 2 -liquid Sabouraud for yeasts and molds), or the object is wiped with a swab which is then inoculated. The samples were incubated at 37ºC for 7 days. As a method to determine the microorganisms growth in a culture, the turbidity measurement was employed. The method consists in measuring the absorbance value of a liquid microbial culture in a photometer at 600 nm. Results were interpreted as follow: on one hand, if there is no turbidity (liquid media) or gas (solid media) present, the product is sterile (no bacterial growth), on the other hand if the samples present gas or become turbid, it is recommended to use differential media for microorganisms identification and characterization.

3.Results and discussions

The ceramic suspensions made for casting in plaster molds present a homogeneous appearance and a pseudo-plastic character according to the rheology graphs. Also, the experimental models based on HAP display a homogeneous appearance and a superior quality after casting in plaster molds. Both the technological flow and the process parameters selected for casting in plaster molds have contributed to the development of these ceramic products without defects visible to the naked eye. Considering the above, the experimental models obtained by casting in plaster molds were suitable for further processing and investigation. Experimental models of cranial prostheses are made in the form of a spherical cap, with a thickness of ~3.5 mm (according to the data from the literature - the average thickness of the cranial bone is 3-5 mm) [23] but also rods with the dimensions 5 x 50 mm. The samples were further sintered at temperatures of 1275˚C and 1350˚C for 2 hours. The thickness of the cast samples can be adjusted by changing the characteristics of the ceramic suspensions, but also by changing the process variables - the casting time in the plaster molds.

3.1.Spectrophotometric measurements (FT-IR)

The spectrophotometric measurements show the qualitative identification of the phase and the ionic species (groups characteristic of the HAP compound). The spectrogram of the HAP powder compound displays only the characteristic peaks of the functional groups PO_4^{3-} (at the wavelength of 630 cm^{-1} and 1089-963 cm^{-1}), and respectively OH^- (at wavelength 3573cm^{-1}). On the other hand, there is no evidence of the presence of impurity with CO_3^{2-}. The spectrograms of the elaborated compounds are presented in Figure 3.

3.2.Simultaneous TG/DTG/DSC analysis measurements

The thermogravimetric analysis (TG), derivative thermogravimetric analysis (DTG) and differential thermal analysis (DSC) curves in Figure 4 show the

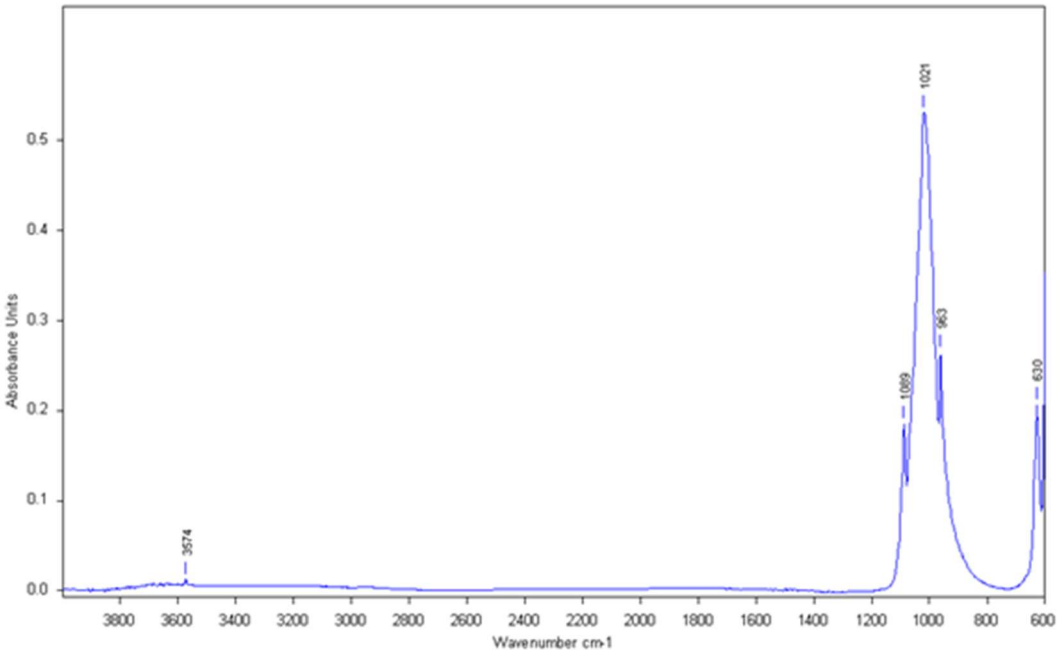

Fig. 3 - FT-IR spectrum of the microcrystalline HAP compound, calcined at 1200˚C-2h / *Spectru FT-IR al compusului microcristalin HAP, calcinat la 1200˚C-2h*

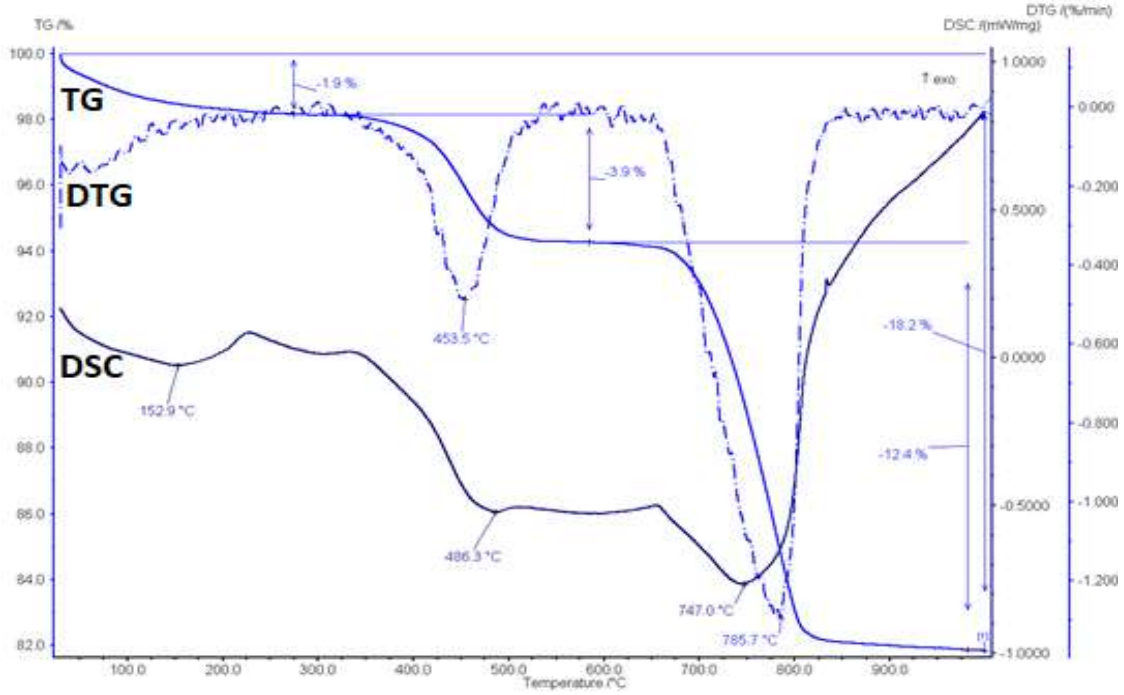

Fig. 4 - TG, DTG and DSC curves for the HAP powder / *Curbele TG, DTG şi DSC pentru pulberea de HAP*

Table 1

Characteristic parameters of the non-isothermal degradation for the HAP powder / *Parametrii caracteristici degradării neizoterme pentru pulberea **HAP***

Proces	ΔT (°C)	%Δm	T_{min}(DTG) (°C)	Pic DSC (°C)	ΔH	$\%\Delta m_{tot}$
1.	25-300	1,9	-	152,9	endo	18,2
2.	300 - 575	3,9	453,5	486,3	endo	
3.	575 - 900	12,4	785,7	747	endo	

stages of compound formation and the characteristic phenomena (effects) are summarized in Table 1. According to the formation mechanism of the hydroxyapatite compound, the total water loss of ~ 18% is attributed to the dehydration of the raw materials (up to at ~300˚C), the formation reaction

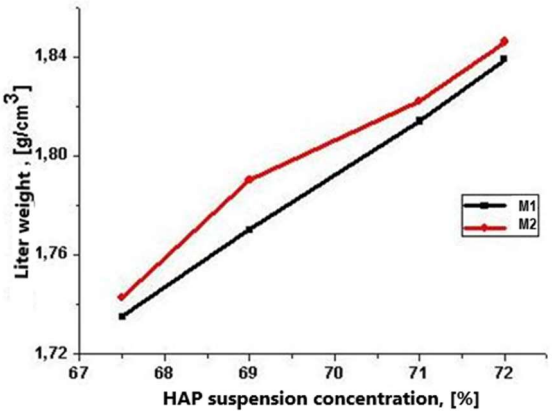

Fig. 5 - Dependence of the liter weight depending on the concentration of ceramic suspensions HAP / *Dependenţa greutății litrice în funcţie de concentraţia suspensiilor ceramice HAP*

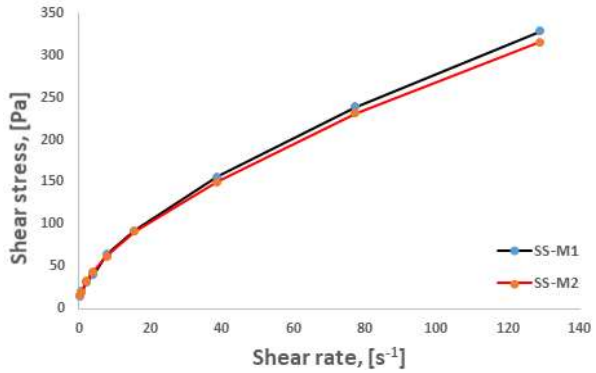

Fig.6 - The variation of the shear stress with the speed gradient for suspension M1 and M2 / *Variația tensiunii de forfecare cu gradientul de viteză pentru suspensiile M1 și M2*

of the intermediate compound β-$Ca_2P_2O_7$ (300 - 575˚C), and respectively the formation of hydroxyapatite for temperatures higher than 786˚C (Figure 4).

The method allows the elaboration of the hydroxyapatite compound (powder) with high yields, good stoichiometry, and an increased degree of crystallinity. Taking into consideration the results, this specific version of the raw material (precursor) was chosen for the elaboration of ceramic suspensions and finally the realization of an experimental model using the technique of casting in plaster forms.

3.3. Viscosity measurements

The rheology of suspensions represents the key element for the casting process in plaster molds and for this technique, fluid systems are needed to be able to penetrate and fill in all areas of the mold. Regarding the establishment of the pseudoplastic nature of ceramic suspensions for casting into plaster molds, rheological curves of shear stress variation depending on the speed gradient and dispersant concentration were plotted and, furthermore, the dependence of the viscosity of HAP suspensions considers the gradient speed and dispersant concentrations.

Ceramic suspensions based on HAP were used for the preparation of ceramic samples and experimental models, with the optimal liter weight of 1.73...1.86g/L, directly dependent on the concentration of the suspension, Figure 5.

The nature and the optimal amount of dispersant were determined by viscosity studies which were carried out on solutions with a concentration of ~65% by weight, homogenized in a planetary mill at 100 rpm for 30 minutes. The viscosity of the solutions was measured under constant temperature conditions, for a pH ~ 10.50. The rheological behavior of the solutions was determined by measuring the viscosity (Cp) and the shear stress (Ss) for different values of the velocity gradient (Sr). The lowest shear stress values were obtained for ceramic suspensions with the addition of max. 0.5% surfactant. The rheology of the

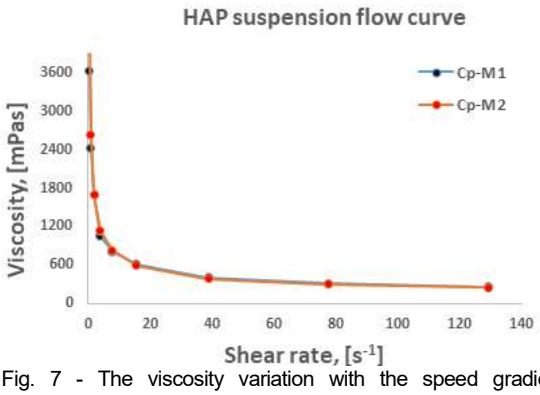

Fig. 7 - The viscosity variation with the speed gradient for suspensions M1 and M2 / *Variația vâscozității cu gradientul de viteză pentru suspensiile M1 și M2*

suspensions shown in Figure 6 is typical of pseudoplastic fluids that show the variation of shear stress with the velocity gradient [24].

According to the profile and viscosity values, it can be stated that the two elaborated suspensions present a pseudoplastic or "shear thinning" behavior (Figure 7) [25]. This behavior is characterized by the decrease in viscosity with the increase of the velocity gradient, and it is common to suspensions with a relatively high HAP content [26].

3.4.Measurement of density and porosity

A low content of solid material in suspension will cause the products to crack after the drying stage as a result of the high contraction. In contrast, a high content of the solid component will determine the obtaining of suspensions with high viscosity. Ideally, a suspension should contain as much solid phase as possible and a viscosity as low as possible. The high amount of solid phase will help to reduce product shrinkage during sintering, while a low viscosity will diminish defects such as cracks. Increasing the amount of binder with APV solution, present an additional role in fluidizing the suspension, and it will determine better casting conditions, implicitly obtaining products with higher

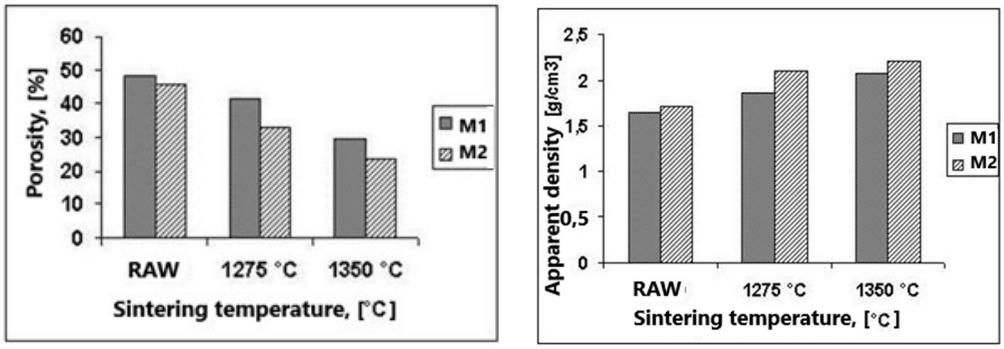

Fig. 8. Variation of porosity and apparent density with sintering temperature for M1 and M2
Variația porozității și a densității aparente cu temperatura de sinterizare pentru M1 și M2

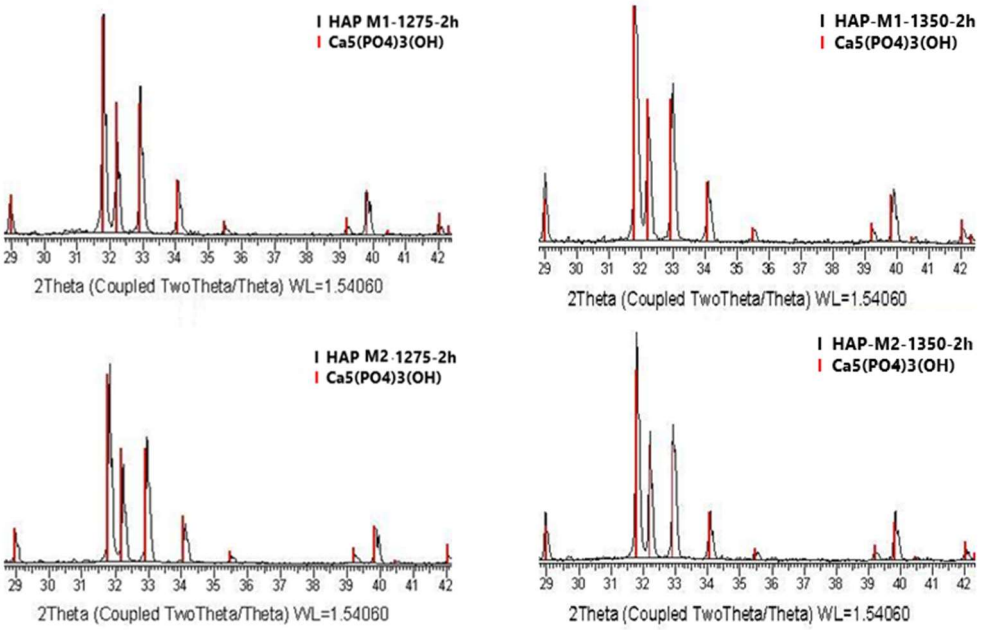

Fig. 9- X-ray diffraction for the two types of sintered products (M1 and M2) at 1275 and 1350°C
Difracție de raze X pentru cele două tipuri de produse sinterizate (M1 și M2) la 1275 și 1350°C

values for density, both raw and after sintering. The main density and porosity values for the unfired product and for the sintered products in correlation with the sintering temperature are shown in Figure 8, for the two suspensions/shaped products.

The values for the raw relative density (unburned material) have comparable values from the specialized literature, between 51 and 54% of the theoretical value. Conversely, the density values for the sintered products have quite low values, including at the sintering temperature of 1350°C. For both raw and fired products, the density values for the M2 version are higher than the M1 version by ~6% for the unfired products, and respectively by ~14% for the products fired at 1350°C. The APV solution has an obvious role in the densification of the products, generating a better cohesion between the particles. In this regard, the development of a precursor calcined at max. 1000°C and the sintering of the shaped products at lower temperatures under the conditions of a higher densification.

3.5. Compositional analysis (XRD)

For both types of products shaped and sintered at 1275 and 1350˚C respectively for 2 hours, compositional measurements were made to check the compositional "stability" at the respective sintering temperatures (Figure 9). In addition, the influence of various additive additions (dispersants and binders) on the compositional stability was verified. It is also known from the literature that small amounts of organic substances can destabilize the crystalline network of hydroxyapatite with the formation of secondary mineralogical phases such as tricalcium phosphate.

From a compositional point of view, the two types of products sintered at 1275 and 1350°C, respectively, show the mineralogical phase hydroxyapatite. The temperature of 1350 °C did not disturb the hydroxyapatite structure, and the diffractograms show those specific decomposition products, CaO and β-TCP. Considering the small amount of dispersant and binder used, no traces of contamination of the analyzed samples were reported.

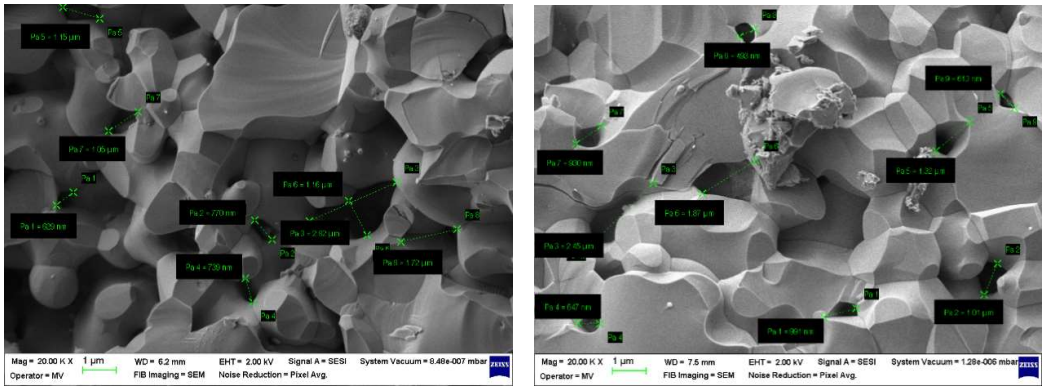

Fig. 10 - Scanning electron microscopy for M1 and M2, sintered at 1350ºC/ *Microscopie electronică de baleiaj pentru M1 și M2, sinterizate la 1350ºC*

Table 2

Average values of the mechanical characteristics for the samples (M1 and M2) sintered at 1275 and 1350°C
Valori medii ale caracteristicilor mecanice pentru probele (M1 și M2) sinterizate la 1275 și 1350°C

Sample code	Sintering temperature (ºC)	Flexural strength (MPa)	Compression strength (MPa)
M1	1275	32,64± 3.48	44,54± 5.22
M1	1350	36,12± 4.11	49,63± 6.10
M2	1275	33,01± 5.01	44,96± 4.98
M2	1350	36,68± 6.14	50,10± 7.01

Tabel 3

Sanitation tests on an experimental model (M1 and M2) / *Teste de salubritate pe model experimental (M1 și M2)*

Bacteriological determinations	Sample No.									
	1	2	3	4	5	6	7	8	9	10
NTG aerobic mesophiles/cm^2	0	0	0	0	0	0	0	0	0	0
Molds	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent
The enterobacteria	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent
Coliform bacteria	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent
Escherichia Coli	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent
Coagulase-positive staphylococcus	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent
Proteus bacillus	absent	absent	absent	absent	absent	absent	absent	absent	absent	absent

Table 4

Sterility tests on experimental model (M1 and M2) / *Teste de sterilitate pe model experimental (M1 și M2)*

No. sample	RESULT	
	ENVIRONMENT I	ENVIRONMENT II
1.	sterile	sterile
2.	sterile	sterile
3.	sterile	sterile
4.	sterile	sterile
5.	sterile	sterile

3.6.Microstructure analysis

Figure 10 shows the photomicrographs for the two types of products (M1 and M2) developed and sintered at a temperature of 1350ºC.

Figure 10 presents quite clearly the form of organization of the hydroxyapatite granules, hexagonal and slightly elongated. It is also observed that the samples have micropores (0.5-2 μm) and isolated cases of large pores ~5 μm. Moreover, the closed, isolated pores with submicrometric dimensions (values between 400-700nm) are highlighted. Microporosity is non-homogeneous, non-communicating, and in the absence of adequate heat treatment it may generate stresses and even cracks in the final product.

3.7.Mechanical tests

The values for flexural and compressive strength show a degree of dispersion. By eliminating the extreme values for the two types of measurements, and processing the results, the average values were obtained and, presented in Table 2.

The average values for the bending strength, shown in Table 3, were in the range of 32.64-36.12 MPa for suspension M1 and, respectively, values of 33.01-36.68 MPa for suspension M2. The

mechanical resistance values increased with the degree of densification, and were comparable with the values reported in the literature for products obtained through similar shaping processes [27-29]. Also, the average values for the compressive strength were included in the range of values 44.54-49.63 MPa for the M1 suspension and, respectively, values of 44.96-50.10 MPa for the M2 suspension.

3.8.Sanitation and sterility tests

The results regarding the bacteriological and sterility determinations for the experimental models based on HAP cast in plaster molds are presented in Table 3 and Table 4.

Following the results obtained, the tested samples show a biocompatible character, and the absence of biological pathogenic agents classified according to the literature. Nevertheless, due to the fact that only preliminary tests were performed on the sanitation and sterility tests, there is a need for further investigations regarding biomedical applications to define the characteristics obtained on the tested samples compared to the data from the specialized literature.

4.Conclusions

In this work, experimental models of HAP-based products were produced, using the technique of casting in plaster molds. The micrometric ceramic powders were calcined at a temperature of 1200 ˚C in order to improve the rheological characteristics for the suspensions developed later. From the compositional point of view, the two types of suspensions cast and sintered at 1275°C, respectively at 1350°C are mainly composed of HAP, with traces of β-TCP, without influencing the mechanical performance of the sintered products. By increasing the temperature to 1350°C, it did not disturb the HAP structure. Ceramic HAP suspensions with optimal casting characteristics (liter weight of 1.73...1.86g/L) were developed and the suspensions presented a homogeneous appearance and a pseudoplastic character according to the rheology graphs performed. The rheological characteristics of the HAP-based casting suspensions were optimized (solid phase content of min. 60%, and optimal content of dispersant and binder additives). Furthermore, the technique of casting ceramic suspensions in plaster molds was optimized (using ultrasonication and degassing/deaeration processes, molded products with a raw density of min. 50% of ρth were obtained). The average values for the two suspensions were in the range of 32.64-36.68 MPa regarding the bending strength, and the average values for the compression strength were in the range of 44.54-50.10 MPa. The mechanical resistance values increase with the degree of densification, and are comparable with values communicated in the specialized literature for products obtained through similar shaping processes. According to the results regarding the bacteriological and sterility determination, the tested samples show a potential biocompatibility character, displaying an absence of growth of biological pathogenic agents. By adapting the characteristics of the casting suspension and by changing the process parameters (remaining time in the casting mold - plaster), we develop models of cranial prostheses in the form of a skullcap with an average thickness of ~3.5mm. The ceramic materials developed in this work show properties that recommend them to be promising candidates for biomedical applications as bone substitutes for neurosurgery. However, considering the results obtained so far, it is considered appropriate to continue the research to complete the results by performing bio-medical tests to evaluate their biological properties.

Acknowledgements

The research was financed by the Ministry of National Education–Executive Unit for Financing Higher Education, Research and Development and Innovation (MEN–UEFISCDI) in the PARTNERSHIP, Nucleus project PN 23140302 "Development of Composite Materials Intelligence for Special Applications" No. 5302/2023, PFE Contract No. 25/2021 and Nucleus project No. 09350301/2014

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