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SPECIFIC ASPECTS IN USING SEASHELL POWDER (RAPANA THOMASIANA) IN ELABORATION OF COMPOSITES FOR MEDICAL PURPOSES

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Abstract: *Rapana Thomasiana (RT) seashell is an important source of natural calcium carbonate that can be used to produce composites dedicated to medical purposes. Cracking processes were detected during the sintering process, and/or low mechanical characteristics were measured for the composites based on calcium carbonate provided by the RT seashell. Remnant organic elements were supposed to cause the cracking and the low characteristics, due to specific resistance to the pressing process before sintering. Preheating of the powder, before the pressing in dye, was proposed to 300/400/500°C. The reason was to completely burn the organic materials remained from the mollusc. Improvement of the ceramic material's behaviour has been recorded: an increasing of the hardness with values up to 15%, and an increasing of the maximum supported force during the compression test with values up to 25%.*

Key words: *seashell, calcium carbonate, composite material, microwave heating, specific costs.*

1. INTRODUCTION

Rapana Thomasiana (RT) shells are a rich and available source of calcium carbonate ($CaCO_3$). From calcium carbonate, hydroxyapatite (HA) can be synthesized by chemical coprecipitation [1], [2], by sol-gel [3] or hydrothermal processes [3], [4], and even by microwave field synthesis [5]. At the same time, however, the calcium carbonate from shells can be used as a ceramic material for making the matrix of a composite or for reinforcing a composite [5].

Both, $CaCO_3$ and HA proved to have significant importance material in industrial applications, due to its properties, such as bio-compatibility and non-toxicity [6], [7], [8]. Sintering would be the main process to elaborate materials using the $CaCO_3$ and HA extracted from seashells [8], [9], as well as other types of composite materials with different destinations [10], [11].

Tihan and its collaborators [9] used specific tools as Fourier transformation infrared spectroscopy (FT-IR) analysis and the scanning electron microscopy (SEM) to characterize the bio-substances extracted from seashells. Those bio-materials, being mainly $CaCO_3$, were used to produce HA.

Mocioiu and his collaborators reported [12] concluded their research in a new route to produce from hydroxyapatite 3D scaffolds dedicated to the bone tissue reconstruction.

Generally, the synthesis of HA from seashells is an important subject for research, and many authors reported new methods to extract HA [12], [13], [14], [15].

In previous research [6], [7] the authors observed that by pressing the powder directly after grinding of the seashells, the powder shows a certain resistance to pressing. Behaviour is specific to an elastic material and less to a ceramic material. Such a resistance causes a compact with a lower density than in the case of a normal ceramic powder. Thus, the paper aims to study this phenomenon, attributed to the organic remains of the mollusc that inhabited the shell.

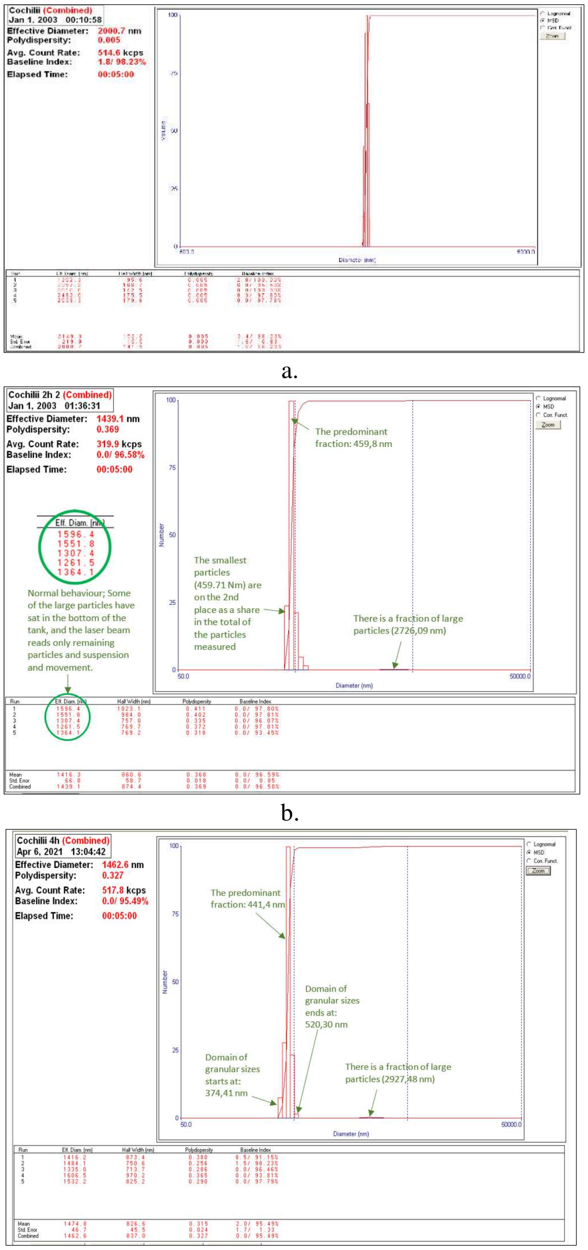
2. MATERIAL AND PRELIMINARY RESEARCH

The powder used to produce the ceramic material by sintering was obtained from RT seashells. The shells were subjected to two milling sessions of 10 hours, in a planetary ball mill, the ratio powder/balls being 1/10 (20 g of powder and 200 g of balls). The speed used for milling was 400 rpm. After every 6/8/10 hours of grinding, the milling process was interrupted and samples of powder were extracted for granulometry analysis. The milling was restarted for another 2 hours, after each extraction of powder. For granulometry analysis, Brookhaven 90 Particle Sizer Analyzer (Brookhaven Instruments Corporation, USA, 2008) equipment was used. To define the analysis parameters' ranges, the material has been assimilated to $CaCO_3$, substance that exists over 95% in the structure of the shell. Thus, to carry out the suspension necessary for granulometry analysis were used:

- dispersant: water
- additive: P40, sodium, hexametaphosphate solution

The suspension created consisted of: 6 ml distilled water + 0.03 g powder RT + 0.01 g NaCl. The suspension was agitated (t = 10 min) in an ultrasonic bath for homogenization and for removing any sediments. The granulometric analysis was performed for 1 min, with 5 repetitions, at an ambient temperature of 25°C.

The effective diameters for samples milled 6, 8, and 20 hours, were recorded and they are presented in Figure 1. The small fractions of 2700-2900 nm, presented in the 3 distributions, show that softer material is present into the powder and that soft material is difficult to mill. The existence of such extremely soft component of the powder could only be highlighted as the size of the granulation, without being able to identify its nature. The influence of this soft material on the characteristics of the material could be verified. By a simple pressing process, which was meant to obtain the raw material intended for sintering, an attempt was made to evaluate the influence of the respective material on the capability of the material of whole powder mixture to be pressed.



Cochilii (Combined)
Jan 1. 2003 00:10:58
Effective Diameter: 2000.7 nm
Polydispersity: 0.005
Avg. Count Rate: 514.6 kcps
Baseline Index: 1.8/ 98.23%
Elapsed Time: 00:05:00

a.

Cochilii 2h 2 (Combined)
Jan 1, 2003 01:36:31
Effective Diameter: 1439.1 nm
Polydispersity: 0.369
Avg. Count Rate: 319.9 kcps
Baseline Index: 0.0/ 96.58%
Elapsed Time: 00:05:00

Eff. Diam. (nm)
1596.4
1551.8
1307.4
1261.5
1364.1

Normal behaviour; Some of the large particles have sat in the bottom of the tank, and the laser beam reads only remaining particles and suspension and movement.

The predominant fraction: 459,8 nm

The smallest particles (459.71 Nm) are on the 2nd place as a share in the total of the particles measured

There is a fraction of large particles (2726,09 nm)

Run	Eff. Diam. (nm)	Half Width (nm)	Polydispersity	Baseline Index
1	1596.4	1023.1	0.411	0.0/ 97.80%
2	1551.8	984.0	0.402	0.0/ 97.81%
3	1307.4	757.0	0.335	0.0/ 96.07%
4	1261.5	769.7	0.372	0.0/ 97.81%
5	1364.1	769.2	0.318	0.0/ 93.45%
Mean	1416.3	860.6	0.368	0.0/ 96.59%
Std. Error	66.8	58.7	0.018	0.0/ 0.85
Combined	1439.1	874.4	0.369	0.0/ 96.58%

b.

Cochilii 4h (Combined)
Apr 6, 2021 13:04:42
Effective Diameter: 1462.6 nm
Polydispersity: 0.327
Avg. Count Rate: 517.8 kcps
Baseline Index: 0.0/ 95.49%
Elapsed Time: 00:05:00

The predominant fraction: 441,4 nm

Domain of granular sizes ends at: 520,30 nm

Domain of granular sizes starts at: 374,41 nm

There is a fraction of large particles (2927,48 nm)

Run	Eff. Diam. (nm)	Half Width (nm)	Polydispersity	Baseline Index
1	1416.2	873.4	0.380	8.5/ 91.15%
2	1484.1	750.6	0.256	1.5/ 98.23%
3	1335.0	713.7	0.286	0.0/ 96.46%
4	1606.5	970.2	0.365	0.0/ 93.81%
5	1532.2	825.2	0.290	0.0/ 97.79%
Mean	1474.8	826.6	0.315	2.0/ 95.49%
Std. Error	46.7	45.5	0.024	1.7/ 1.33
Combined	1462.6	837.0	0.327	0.0/ 95.49%

c.

Fig. 1 Grain size distribution for milling time of
a. 6 h, b. 8 h, c. 10 h

Two types of dyes were used for this test (Figure 2 a, b):

- dye for elaboration of specimens dedicated to compression testing
- dye for bending test pieces

and the two types of equipment used to operate the dyes were (figure 2 c, d):

- a universal testing machine, max 100 kN
- a hydraulic press, max 1000 kN.

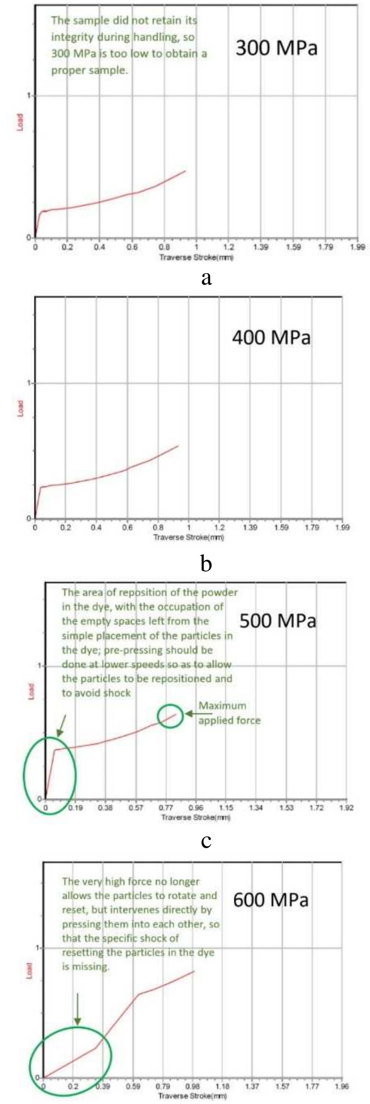
Fig. 2 Dyes (a and b) and equipment (c and d) used to press the powder

The raw specimens for the compression test were developed with the universal test machine, the dimensions of the specimens (diameter 15 mm) allowing the use of forces less than or equal to 100 kN. The raw specimens for the bending test were developed with the hydraulic press, the dimensions of the specimens (section 55 x 10 mm x mm) requiring the use of forces greater than 100 kN. For the specimens intended for the compression test, the value of 300 MPa was started at the level of the punch surface, the value being established based on experience. The raw sample could not be manipulated, immediately after being removed from the dye it lost its integrity. The force was raised successively, so as to obtain pressures of 400, 500, respectively 600 MPa. For each of these the raw sample was appropriate, so the values of the 70, 85 and 100 kN forces used were declared appropriate. The records of the pressing equipment, as well as the 3 raw samples that have preserved their integrity, are shown in Figure 3. Obviously, experience in making compacts for sintering also allowed the use of lower forces, but in this situation, it would have been necessary to use binders, such as zinc stearate. It was decided not to use zinc stearate due to the fact that during sintering it would have vaporized producing an accentuated porosity of the sintered sample, which is not desirable.

It should also be noted that powder granulation is one of the factors influencing the pressing process, as it is known that a grain size of less than 50 nm makes pressing almost impossible. 1400 nm granulation powder was used for the raw samples.

3. RESULTS AND DISCUSSIONS

During the tensile tests, the curves of load against the stroke were recorded

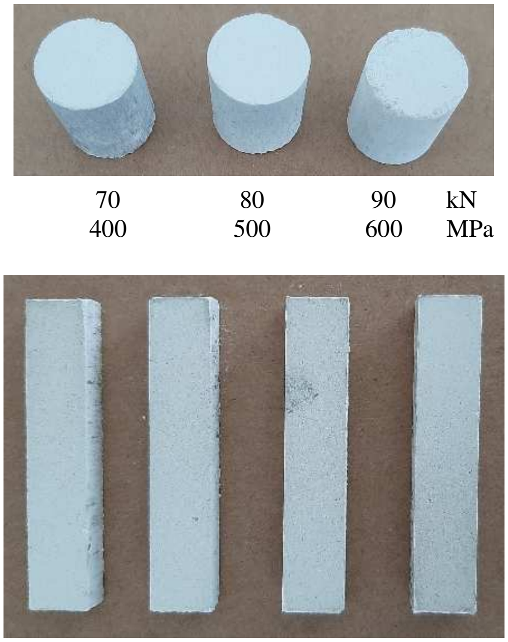

The sample did not retain its integrity during handling, so 300 MPa is too low to obtain a proper sample.

The area of reposition of the powder in the dye, with the occupation of the empty spaces left from the simple placement of the particles in the dye; pre-pressing should be done at lower speeds so as to allow the particles to be repositioned and to avoid shock

Maximum applied force

The very high force no longer allows the particles to rotate and reset, but intervenes directly by pressing them into each other, so that the specific shock of resetting the particles in the dye is missing.

Fig. 3 Curves load against transverse stroke to analyse the behaviour of the seashell powder during pressing process



70 80 90 kN
400 500 600 MPa

220 kN
400 MPa

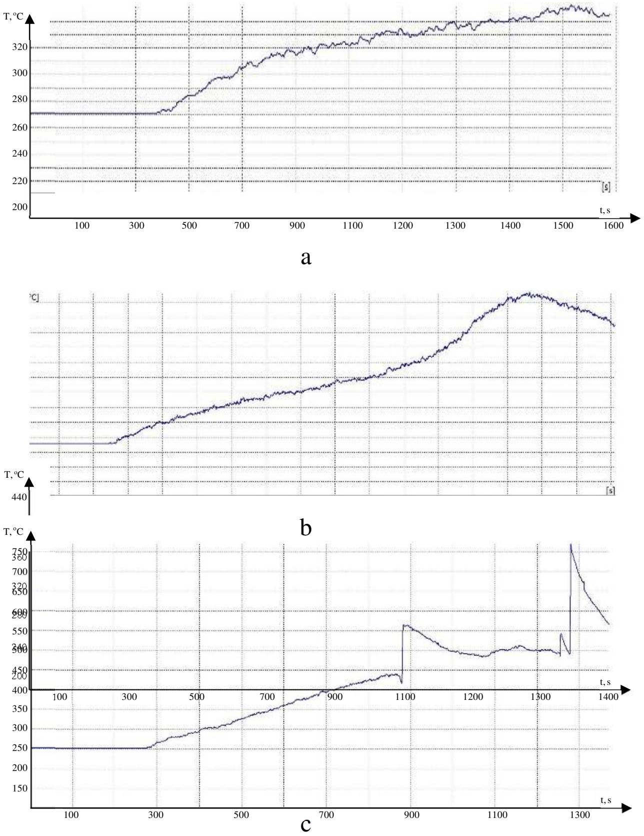
Fig. 4 Compacts done by pressing in dye

The compacts showed microcracks, so the pressing behaviour was not appropriate. This behaviour when applying pressure has led to the hypothesis that the soft material is a factor influencing the presability of seashell powder. The only hypothesis regarding the nature of the soft material in the seashell powder was that it was reminiscent of certain amounts of organic material from the mollusc that lived in that shell.

As the exact identification of these traces of molluscs, in order to be removed in time from the calcium carbonate powder, was not possible, we resorted to the technological solution of burning the organic elements in a preheating of the scattered powder, before introduction into the dye. We opted for fast burning in the microwave field. For this purpose, a one-way unidirectional microwave flux heating machine was used (Figure 5). The seashell powder was heated to 300ºC, 400ºC and 500ºC to identify the optimum combustion temperature. Ungureanu and collaborators [2] used 80ºC for preheating and 800ºC for initiating chemical reactions to synthesize hydroxyapatite. Therefore, the choice of the three temperatures places them in the interval between an adaptation preheating and a process initiation preheating.

Fig. 5 Powder into the microwave furnace before preheating process

The heating cycles are presented in figure 6 a, b, and c.



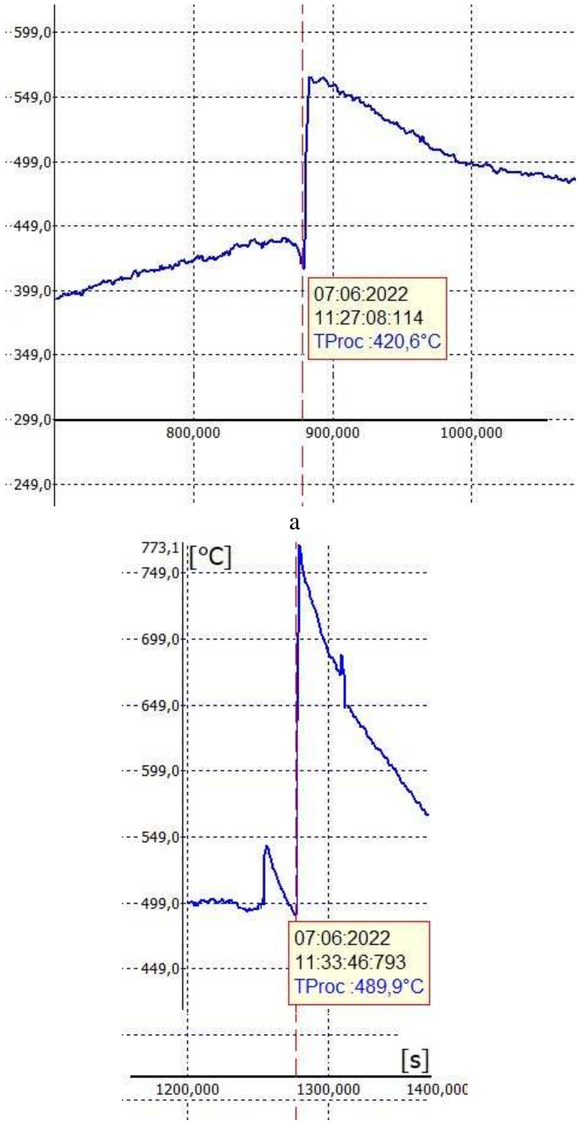
a

b

c

Fig. 6 Preheating cycles
(Temperatures: a. 300ºC, b. 400ºC and c. 500ºC)

From the different shapes of the two curves, it can be seen that the three sets of RT powders underwent different heating processes. Applying a preheating at 300°C, the evolution of the temperature in the material was smooth, no variations were observed from the specifics of traditional heating. The increase in temperature to 400°C and then to 500°C was accompanied by some increasing thermal shocks. As no additional heat input was brought, there is a potential explanation for the burning of some existing organic materials in the RT powder.



a

b

Fig. 7 Sharp increasing of the temperature for a preheating at 500°C

The hardest temperature variation was recorded for the temperature of 500°C, it can be concluded that at this temperature the burning of organic residues was manifested with high intensity. The sudden change in temperature is twofold. The process begins in the immediate vicinity of the temperature of 500°C and continues its evolution with a new increase, up to about 750°C (figures 7 a, and b).

In order to verify the theory of the existence of organic material that manifests itself as a fuel during heating to over 400°C, after preheating to 500°C a new heating was performed at the same temperature, observing the heating curve. Sudden variations in temperature rise were not recorded. This can be explained by burning and removing traces of organic material from the first preheating phase.

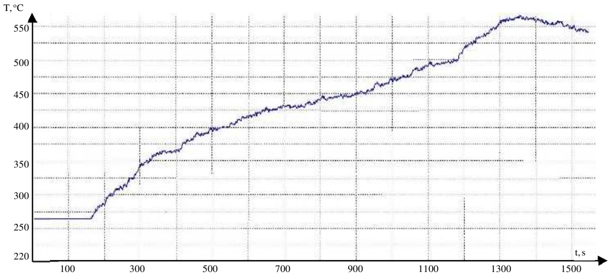
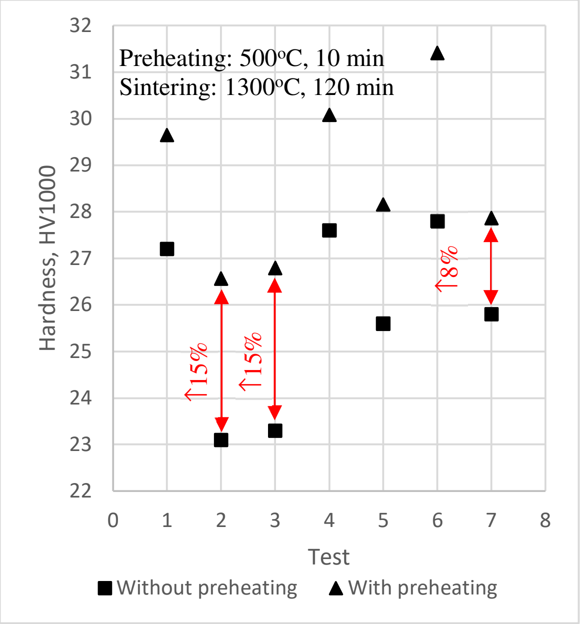
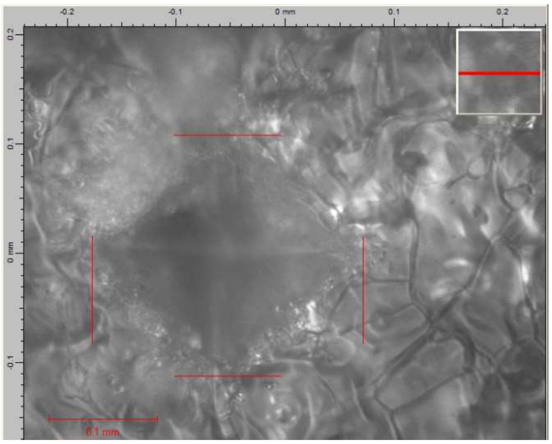


Fig. 8 Lack of sharp increasing of the temperature for a preheating at 500°C

Preheating to 500°C produced some changes in the behaviour of the subsequently sintered ceramic material, using traditional heating and technology. There was an increase in hardness values by 8-15% and also an increase in compressive strength by about 22-25%.

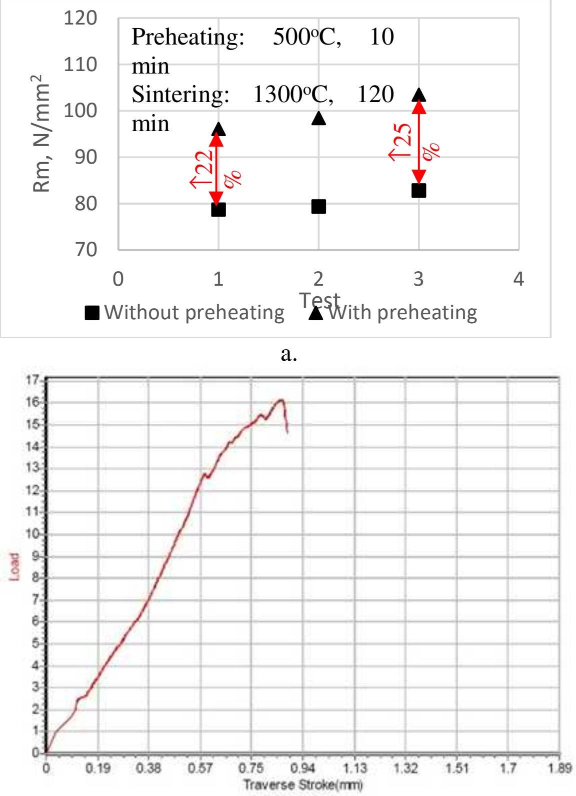


a.



b.

Fig. 9 Hardness test results – increasing of values after the preheating (a.) and example of clear print on the sintered material (b.)



a.

b.

Fig. 9 Compression test results – increasing of values after the preheating (a.) and example of stress-strain curve for the sintered material (b.)

4. CONCLUSION

RT seashells is a sustainable source of bio-obtained calcium carbonate. Such a raw material is a material that can be used to develop biocompatible ceramic materials dedicated to medical applications. As future work, we take into consideration the study and development of orthopaedic implants used for human bones osteosynthesis or reconstruction, based on other previously published research based on other new, biocompatible materials with properties remarkable, like shape memory alloys, which have been studied and used successfully by our team in the field of orthopedic implants [16-20]. Sintering is the main used process to elaborate ceramic and composites materials containing RT powder. Simply milling the seashells, followed by pressing the powder, and subsequently sintering of the compact, returns a material with specific, in terms of integrity (cracks) and characteristics (compression maximum force, low hardness). Existence of organic material inside the seashells, which cannot be removed by cleaning even with alcohol, is considered to be the reason of those low characteristics. The heating of the powder at 500ºC produced a burning of the organic material. In that way, the organic material, which is an elastic one comparing to the ceramic powder, acts no more in opposition to the pressing process. That increases the density of the compact, and the elastic force of opposition, reducing the cracks occurrence.

It has been recorded, when used preheating at 500ºC, an increasing of the hardness of the sintered ceramic material within the range of 8-15%. In the same time, due to the increasing of the compaction and, subsequently, the important decreasing of the number of cracks and micro-cracks, the maximum force supported during the compression tests increased with 22-25%.

Preheating of the seashells powder seems to be mandatory, in order to be burned all the remnant organic materials from the mollusc. The removal of the organic material improves the behaviour of the powder during the compaction process and during the sintering process. The recommended temperature for the preheating process would be 500ºC.

5. ACKNOWLEDGEMENT

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Aspecte specifice în utilizarea pulberii de cochilie de RAPANA THOMASIANA în elaborarea compozitelor dedicate aplicațiilor de natură medicală

Cochilia de Rapana Thomasiana (RT) este o sursă importantă de carbonat de calciu natural care poate fi folosită pentru a produce compozite dedicate unor aplicații medicale specifice, cum ar fi implanturile osoase. Problema pusă este legată de identificarea unor procese de opunere la presare și de fisurare detectate în timpul procesului de sinterizare. De asemenea, au fost măsurate valori scăzute pentru caracteristicile mecanice ale compozitelor pe bază de carbonat de calciu extras din cochilia de RT. Aceste fenomene au fost puse pe baza existenței unor rămășițe de elemente organice provenind din molusca RT. Soluția propusă pentru verificarea acestei ipoteze a fost preîncălzirea pulberii, înainte de presare, temperaturile de preîncălzire fiind 300/400/500°C. Motivul a fost arderea completă a materialelor organice rămase din moluște. S-a înregistrat o îmbunătățire a comportamentului materialului ceramic: o creștere a durității cu valori de până la 15% și o creștere a forței maxime suportate în timpul testului de compresiune cu valori de până la 25%.

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