

Consolidated microcapsules with double alginate shell containing paraffin for latent heat storage

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Abstract

Double-shell alginate microcapsules containing paraffin phase change material (PCM) were prepared for latent heat storage by a method of repeated interfacial coacervation/crosslinking. The proposed process consisted of three main steps: (1) preparation of paraffin containing core particles by dripping an O/W emulsion of melted paraffin and aqueous sodium alginate into a calcium chloride ionic cross-linking solution, (2) encapsulation of the core particles into double alginate shell by ionic gelation/crosslinking by repeated interactions between the sodium alginate and calcium chloride solutions, and (3) consolidation of the capsule shells by contact heat treatment. The effects of process parameters such as the sodium alginate concentration, the calcium chloride concentration in certain stages of the process, and the contact time between the formed core particles and the surrounding alginate solution on the paraffin content and the mean diameter of capsules were studied by experimental design and statistical evaluations. The prepared PCM capsules had uniform sizes, core/shell structure, double-walled non-porous alginate coating, tunable void space inside the core, and suitably high paraffin content at properly selected process conditions, corresponding to 95.0 J/g melting and 91.7 J/g freezing latent heat capacity. Thermogravimetric analysis and repeated thermal cycling evidenced good thermal stability, and proper mechanical strength for leakage free microcapsules.

Keywords: alginate-paraffin microcapsules, phase change material, latent heat storage

1. Introduction

Thermal energy storage has received more and more attention due to the endeavour of energy saving. Latent heat storage is one of the most efficient ways of thermal energy storing [1]. Phase change materials (PCMs) are used for latent heat storage. Most promising fields of application of PCMs are waste heat recovery systems, solar heating systems, building energy conservation systems and air-conditioning systems [2,3]. Using PCMs in solar heating systems heat energy can be stored with much higher energy storage density with a smaller temperature swing when compared with the sensible heat storage. The volume of heat storage tank can be reduced, thus

the cost of the solar heating system becomes lower. The operation of air-conditioning systems can be shifted to nighttime hours when the cooling load is low [4].

Most of the organic PCMs are non-corrosive and chemically inert, stable, recyclable and compatible with numerous building materials. They have desirable cohesion, high latent heat capacity per unit weight, low vapour pressure, no supercooling, and offer congruent melting and self-nucleation. They have disadvantages such as low thermal conductivities, flammability and relatively higher changes in volume during phase change.

Paraffins are versatile PCMs, since they are chemically inert and reliable, non-corrosive, non-toxic and commercially accessible at rational cost. They have large latent heat capacity, negligible supercooling, low vapour pressure, good thermal and chemical stability, self-nucleating behaviour, high latent heat of fusion and wide range of solid–liquid phase change temperatures for many latent heat energy storage applications [5,6]. However, they have some drawbacks such as low thermal conductivity, flammability and high volume change during phase change [7,8]. To overcome these drawbacks, microencapsulation can be an efficient tool. By this way the heat transfer surface area can be increased, the volume change problem can be eliminated, leakage of PCM during its phase changing from solid to liquid can be prevented, moreover, the reactivity of PCM with its close environment might be lessened [7]. The microencapsulated PCMs, suspended in a heat transfer fluid phase, form heat storing solid–liquid slurry [8]. Due to the embedment of PCM particle in a plastic shell, the core material is always separated from the heat transfer or carrier fluid, which makes the slurry behave like a liquid, while the latent heat effect substantially increases the heat capacity of the carrier fluid [9]. In addition, the heat transfer coefficient and surface may be greatly increased because of the latent heat effect and the particle to particle interactions.

Calcium cross-linked alginate hydrogels with its natural origin and environmental friendly character have been used in many biomedical applications, such as cell transplantation and drug delivery [10]<http://www.sciencedirect.com/science/article/pii/S0142961200000338> - BIB7.

Alginate typically has the physical form of a hydrogel with small or large pores which is advantageous in some utilization. However, porosity and capability of absorbing large quantities of water are obstacles of its use in PCM microencapsulation. Nevertheless, in a few work alginate was used as shell material in PCM incorporation. E.g. Wang et al [11] prepared alginate macrocapsules containing n-octadecane phase change material shape-stabilized with high-density

polyethylene by using a traditional coating pan. Lan et al [12] stabilized an inorganic phase change material, disodium hydrogen phosphate dodecahydrate by a novel gelling method by polymerizing sodium alginate grafted sodium acrylate in its molten salt. In another approach shape stabilized PCMs ranging from 1 to 5 mm with calcium alginate matrix were formed, and then were coated with calcium complex compound as shell in order to obtain microPCMs [13]. Macrocapsules containing acrylic-based copolymer microPCMs were also prepared through the piercing-solidifying incubator method. PCM microcapsules were prepared by using a co-extrusion minifluidic device with melted paraffin wax Rubitherm RT27 as the inner fluid and sodium alginate solution as the outer fluid, and the capsules were collected in a container with CaCl_2 solution [14]. Although none of these processes considered all of the disadvantages of alginate materials mentioned above.

Our aim was to prepare microcapsules containing paraffin as PCM incorporated into double alginate shell which was then treated by heat. The contact heat treatment resulted in the loss of water, and the formation of a non-porous, glassy coating on the surface of the capsules. Due to the heat treatment the alginate shell shrank, reducing its wall thickness, hence void space formed inside the capsules, which was advantageous allowing the volume change during phase change without harmful stress in the capsule wall. As for the process of preparation, the effects of most important variables were analyzed by a 3-level 3 factors Box-Behnken experimental design.

2. Material and methods

2.1. Materials

Sodium alginate (NaAlg) and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ were purchased from Sigma-Aldrich, paraffin of melting temperature in interval 55-57 °C was kindly provided by the MOL Plc, Hungary. Petroleum ether (boiling temperature 60-62 °C) was purchased from Lach-Ner s.r.o., Nercetovice, Czech Republic. All chemicals were of analytical grade and were used as purchased. For all aqueous solutions distilled water was used.

2.2. Methods

The objective of the work was to produce uniform capsules containing paraffin for latent heat storage in non-porous alginate shell of suitable mechanical and thermal stability. The process, schematically shown in Fig.1, consisted of three main steps: (1) preparation of core particles, (2)

encapsulation of core particles into double alginate shell by repeated ionic gelation/crosslinking, and (3) consolidation of capsule shells by heat treatment.

2.2.1. Preparation of capsules

Step1. Preparation of core particles

Step 1.1. First 50.0 g O/W emulsion was prepared by emulsifying melted paraffin (O) in aqueous sodium alginate solution (W).

For the continuous phase, 4.0 g sodium alginate powder was dissolved in 41.0 g distilled water by heating and stirring at 600 rpm by magnetic stirrer. When the temperature reached 65 °C, 5.0 g paraffin was added in solid form. After melting, it was emulsified in the aqueous phase to get the O/W emulsion by sonication for 3×30 s with Vibra cell VCX130 (Sonics and Materials Inc., Newtown, USA) sonicator with 40 % of its 130 Watts maximal power. The mass ratios of the continuous aqueous (W) and dispersed oil (O) phases were 90.0 and 10.0 % (wt/wt), respectively, identical in each experiment. The final mass fractions of paraffin (5.0 g) and sodium alginate (4.0 g) in the emulsion were 10.0 % (wt/wt) and 8.0 % (wt/wt), respectively.

Step 1.2. This emulsion was slowly dropped by a pipette into gently stirred aqueous gelling solution (500 g), containing 8.0 % (wt/wt) CaCl₂, prepared preliminary by dissolving 53.0 g CaCl₂·2H₂O in 447.0 g distilled water. The size and mass of drops were practically uniform (24.05 mg per droplets) containing 2.405 mg paraffin as an average.

Step 1.3. After 30 min time of gelation, the particles were transferred into another CaCl₂ solution of various concentrations to provide excess Ca²⁺ ions near the surface region of core particles. The concentration in this solution was varied according to the experimental program shown in Table 1, identically as in Step 2.2, setting to 4.0, 8.0 or 12.0 % (wt/wt), respectively. The core particles were then stored in this gelling solution until use.

Step2. Encapsulation of core particles into the alginate shell

Step 2.1. The core particles were withdrawn from the gelling solution and were put into a gently stirred sodium alginate solution prepared similarly as in Step 1.1, but with various concentrations of 4.0, 8.0, 12.0 % (wt/wt), shown in Table 1. In this step the excess Ca²⁺ ions near the surface and inside the core particles reacted with the sodium alginate, forming gel-like calcium alginate layer on them as a first capsule shell. Reaction time for this was varied according to Table 1, from 1.0 to 13.0 min with 7.0 min central value. At the end of this step, non-reacted sodium-

alginate was also present around and inside the first shell, shown in Fig.1, due to the excess sodium-alginate in the surrounding solution.

Step 2.2. The particles were then removed from the sodium alginate and were put into a gently stirred third CaCl_2 solution for 30.0 min, whose concentration was varied between 4.0, 8.0 and 12.0 % (wt/wt) respectively (Table 1). At this stage the excess sodium alginate inside and around the first shell reacted with Ca^{2+} ions, forming a second cross-linked alginate layer outside (Fig.1) Finally, the raw capsules were taken out and rinsed three times with distilled water.

Step 3. Heat treatment of the capsule shell

To consolidate the coating layers special heat treatment was applied (not shown in Fig.1). For this, the row capsules were placed onto a hot stainless steel plate held at 125 °C, keeping them in continuous rolling movement. In about 15 min the water content of alginate shell evaporated and removed from the capsules and somewhat above the glass transition a dense, non-porous, glassy capsule wall formed.

2.2.2. Determination of particle mean size

In each run, the size of 50 sampled particles was measured by optical microscope (Carl Zeiss, Jena) and the average value and standard deviation of their diameters were calculated.

2.2.3. Determination of paraffin content

About 0.1 g weighed particles was ground with Narva Vibrator (Brand Erbisdorf) micro-ball mill for 5 min. Then 20 ml of petroleum ether was added and the suspension was stirred for 60 min at 30 °C, then vacuum filtered. The petroleum ether was evaporated in vacuum by Heidolph Laborota 4001 equipment and the remained paraffin was weighed to calculate its relative amount in the capsules.

2.2.4. Tests of thermal behavior and capsule stability

Thermogravimetric measurements were carried out by a Q-1500 D MOM (Hungary) type TGA instrument, between 30 and 500 °C, with 10 °C/min heating rate in air atmosphere.

The thermal properties of the microcapsules were determined using a Setaram $\mu\text{DSC3evo}$ differential scanning microcalorimeter (microDSC). Each sample was weighed into 100 μL aluminium crucibles, then the system was hermetically closed by crimping a cap. The samples were three times cycled from 20 to 70 °C, with a scanning rate of 1 °C/min. The results were processed by using the thermoanalyzer's Calisto Processing (v1.12) software. The corresponding

melting/freezing enthalpies, and the onset temperatures were calculated using the baseline integration method (Tangential sigmoid baseline type).

Cyclic thermal tests were carried out similarly to the method of Sari and Karaipekli [15] in a simple testing tool consisted of a metal sample holder with trays for the PCM microcapsules, a thermoelectric heating and cooling (Peltier) unit and a PC based control system. The latter allows setting of the lower and upper temperature limits, the heating/cooling rate and number of thermal cycles. In a test, a weighed sample amount of particles (about 0.15-0.20 g) was placed into the holder, and 1000 heating/cooling cycles between 35 and 85 °C were carried out corresponding to about 44 hours duration. After thermal cycling, the potential leaking was analyzed by microDSC as well as by measuring the remained paraffin content.

3. Calculation

An experimental program was generated by the STATISTICA^(R) (Statsoft Inc. USA) software package using 3-level 3 factors Box-Behnken experimental design. Based on preliminary studies, the following 3 process variables were supposed to have influence on the size and paraffin content of the obtained capsules:

- (1) Sodium alginate concentration in Step 2.1,
- (2) CaCl₂ concentration in Step 2.2 (also Step 1.3), and
- (3) Contact time between the core particles with the sodium alginate solution in Step 2.1.

Sodium alginate concentration in Step 1.1 and calcium chloride concentration in Step 1.2 were kept constant. The experimental program shown in Table 1 consisted of 15 runs, including 3 repetitions in the centrum (indicated with capital C in the Table). Other conditions and variables were unchanged taking the following requirements into consideration:

- (1) To form oil-in-water (O/W) emulsion in Step 1.1, the volume of oil phase had to be less than that of the aqueous phase. Selected mass ratios were: 10 % oil (5.0 g) and 90 % (45.0 g) aqueous phase.
- (2) Sodium alginate concentration in the aqueous phase was restricted to get not too high viscosity for proper emulsification and dripping. Therefore 4.0 g sodium alginate was used in 41,0 g distilled water (8.89 % wt/wt NaAlg concentration).

- (3) The ratio of sodium alginate in Step 1.1 had to be high enough to get suitable shape stability and to form continuous alginate shell in the subsequent steps. For this purpose 4.0 g sodium alginate and 5.0 g paraffin (i.e. 44.44:55.56 fixed mass ratio) was used.
- (4) The paraffin content in the capsules should be high enough to achieve suitable heat storage capacity. With the applied range of variables the maximum achievable paraffin content was estimated about 50 % (wt/wt).

4. Results and Discussion

4.1 Variation of capsule size

The resulted mean capsule diameters and their standard deviations in various runs after heat treatment are listed in Table 1. Mean capsule sizes varied between 2.16 and 3.04 mm as a function of different combinations of experimental variables. Standard deviations were reasonably low between 0.11 and 0.19 mm, (5.5 % in average).

Proving by statistical evaluation, linear effects of three process variables on capsule size were significant, shown in the Pareto chart in Fig.2a. Among them, contact time and sodium alginate concentration had the highest effects, but the influence of CaCl₂ concentration was also significant. The *p* values, indicating the significance levels of contact time, sodium alginate and CaCl₂ concentrations within ±95 % confidence intervals, were 0.0086, 0.0100, and 0.0327, respectively, i.e. well below the generally accepted value of 0.05. The reliability of experiments was adequate: the pure error in the centrum point was ±0.0036 mm (i.e. 0.14 %).

Diagrams in Figs.2b and 2c show that the capsule size clearly increases by enhancing the contact time, or sodium alginate and calcium chloride concentrations. This is reasonable because all the three factors promote the chemical reaction resulting in progressively growing cross-linked calcium alginate mass on the capsules.

The dependence of capsule size on the studied process variables was determined by multivariate regression analysis, taken only the significant influences (see Pareto chart) into account. For this, the following linear equation was obtained:

$$D = 0.05287 \cdot X_{NaAlg} + 0.02875 \cdot X_{CaCl_2} + 0.03817 \cdot t + 1.63597 \quad (1)$$

where D (mm) is the mean diameter of capsules, X_{NaAlg} (% , wt/wt) is the concentration of sodium alginate in Step 2.1, X_{CaCl_2} (% , wt/wt) is the concentration of calcium chloride in Steps 1.3 and 2.2, and t (min) is the contact time between the capsules and the recipient $CaCl_2$ solution in Step 2.1.

The measured and predicted capsule sizes are compared in Fig.2d, indicating reasonable agreement. For all the 15 experiments, the relative deviations between the observed and predicted values were between 1.0 and 7.6 % with an average of $\pm 3.7\%$, which is considered reasonable prediction.

4.2 Variation of paraffin content

Evaluation revealed that paraffin content in the capsules depended on the same process variables as for capsule sizes. But, in addition to the linear effects of contact time, sodium alginate and $CaCl_2$ concentrations, quadratic relations with sodium alginate concentration and contact time were also found. Among them, contact time had the highest effect, seen on the Pareto chart in Fig.3a.

Response surfaces fitted to the experimental data by regression analysis showed clear dependency on the studied variables. Fig.3b shows at medium contact time ($t=8$ min) that relative paraffin content decreases with increasing calcium chloride concentration, and with increasing sodium alginate concentration between about 4.0 and 8.0 % (wt/wt). Above 8.0 % this effect practically disappears, which is also seen in Fig.3c. The dependence on $CaCl_2$ concentration is linear and somewhat weaker.

The effect of contact time shown in Fig.3c is also non-linear, and the paraffin content of capsules considerably decreases between 2.0 and 8.0 min, then this influence becomes negligible. It should be noticed that the contact time in Fig.3b and $CaCl_2$ concentration in Fig.3c were constant at their central values.

The dependence of paraffin content on the studied variables was determined by multivariate quadratic regression, resulting in the following equation:

$$Y_p = -5.96 \cdot X_{NaAlg} + 0.30 \cdot X_{NaAlg}^2 - 1.27 \cdot X_{CaCl_2} - 4.305 \cdot t + 0.189 \cdot t^2 + 80.45 \quad (2)$$

where Y_P (% , wt/wt) is the paraffin content of capsules, X_{NaAlg} (% , wt/wt) is the sodium alginate concentration, X_{CaCl_2} (% , wt/wt) is the calcium chloride concentration, and t (min) is the contact time between the capsules and sodium alginate solution.

The pure error of paraffin content determined by repeated experiments in the centrum point was 2.38 absolute % (wt/wt) at the centrum point, corresponding to 11.3 % standard deviation around the average. Fig.3d compares the paraffin content calculated by Eqn.2 to the measured data, showing reasonable agreement.

The change of paraffin content is simply explained by the growing mass of the alginate shell. Since the net mass of paraffin in the core was not varied (2.41 mg per capsule), its mass ratio decreased with increasing size, as is seen in Fig.4.

4.3 Capsule morphology

The capsules produced by the proposed method were almost spherical, having smooth surface with few shallow pits. Micrographs in Figs.5a and 5b show the outer view and fractured cross section of a capsule, respectively, obtained in the experiment #1 as an example. The relative paraffin content obtained in this run was one of the lowest values among all experiments, therefore relative large void space (air bubble) can be seen inside. As was mentioned above, other process variables resulted in much higher paraffin ratio due to the reduction of the mass (and thickness) of capsule wall.

Fig.5c shows a fractured capsule in higher magnification. The alginate shell of this capsule obtained in Run#1 is about 300 μm thick, and gives evidence that repeated ionic crosslinking and final heat treatment resulted in a compact and pore-free capsule wall with smooth and glassy fracture. It can also be recognized that capsule wall is composed of two alginate layers fused together. An explanation of this structure will be given later. Because no alginate matrix is seen in the core it is supposed that this material which was originally present in the core particles migrated to the capsule wall during the heat treatment. However, some residues of this matrix structure can be seen on the inner surface of the wall.

Experimental data give information on the diameter and average wall thickness of a heat treated capsule, as well as on the amount of paraffin and its mass ratio in a capsule. From these data other properties can also be calculated, such as capsule mass, mean density of a capsule, the mass of the wall, volume and mass ratios of capsule wall, void (air) volume fraction inside the capsule.

Two examples are shown in Table 2 for one of the lowest and for the highest paraffin contents (Runs #1 and #5, respectively).

From the data it was concluded that the increase of relative paraffin content relates to the reduced mass of capsule wall, corresponding to smaller capsule diameter. Therefore the mass and volume ratio of capsule wall were also drastically reduced by increasing the paraffin ratio. However, the volume ratio of void space (air) inside the capsules remained in the same order of magnitude, between about 33 and 39 % (v/v), because the reduction of the void volume was accompanied by the simultaneous reduction of the whole capsule volume.

In three experiments (Runs # 1, 9 and 11) the mean capsule sizes were determined also before the heat treatment, which were 5.33, 4.32 and 5.41 mm, respectively. Comparing them to the final capsule sizes (3.04, 2.27 and 2.60 mm, respectively), it suggests that water lost and structural change (glass transition) of the wall material during heat treatment resulted in 43-53 % reduction of the outer diameter of capsules, corresponding to 81-89 % volume reduction.

4.4 Suggested mechanism of capsule formation

Supposedly, encapsulation of paraffin in the studied process takes place by interfacial coacervation/crosslinking mechanism, which consists of at least three distinct steps. First, after dripping the O/W emulsion into the crosslinking CaCl₂ solution (Step 1.2), the sodium alginate in the droplets reacts with Ca²⁺ ions, resulting in at least partially cross-linked calcium alginate, which forms a coacervate phase inside the droplets and around them. Because sodium alginate is found mainly inside the droplets and transport of calcium ions goes on by diffusion from outside to the inner regions of droplets, radial concentration gradient can evolve within the formed core particles with decreasing cross-linking density from outside to inside. It means that excess calcium ion concentration is the highest near the surface of core particles, close to the interface of the continuous liquid and particulate phases. The process continues in Step 1.3, where various CaCl₂ concentrations were used according to the experimental design. Due to this process, a gel-like cross-linked alginate layer (first coating layer) forms on the particles, which will be the base of the first shell.

In Step 2.1 the core particles are soaked in sodium alginate solution, which reacts with the free calcium ions found in the first coating layer and on its surface. Thus a second coacervate layer will form on the first one, whose thickness may increase with the concentration of calcium ions in

the first layer, and also with the sodium alginate concentration in the surrounding liquid, as well as with the reaction time available for crosslinking.

Because the amount of free calcium ions in the first layer is limited and are consumed by the sodium alginate excess in the surrounding liquid, at the end of this step partially or non-cross-linked alginate molecules will also be present in the second layer. In Step 2.2 these alginate molecules react with the third CaCl_2 solution, resulting in higher crosslinking density in the second coating layer. The process leads to the formation of the second outer layer of the shell.

During the heat treatment (in Step 3) of the alginate coating significant dehydration and structural transition from gel-like to glassy state takes place. In Figs.5c and 5d it can be seen that the formed two shells are tightly attached, but have visible interface between the inner (I) and outer (II) layers, and they show appearance of the fractured surface, probably because the outer shell lost all of its water content owing to high contact heat, while due to the outer glassy state formation, the inner shell could retain some water. Due to considerable contraction the diameters of capsules decrease to about half of its initial value, which corresponds to 81-89 % volume reduction. Because the encapsulated paraffin itself does not shrink, volume reduction takes place in the capsule wall only, leading to considerable decrease of the wall thickness. Because some water evaporates also through the inner surface of the coating, and some water pressure can evolve inside the capsules, void space is formed there as is seen in Fig. 5b. This is beneficial during the use of PCM capsules because less stress occurs when phase transition is accompanied with volume change.

4.5 Thermal behavior and stability

The thermal behavior and stability of the capsules was monitored by thermogravimetric analysis and repeated thermal cycling. TGA measurements were carried out between 30 and 500 °C to inspect the hazard of thermal degradation of capsules of low, medium and high paraffin content. No perceptible difference was found between the behavior of different paraffin contents. Fig. 6 gives an example for the capsules obtained in Run #4, with relatively low paraffin content, i.e. high alginate mass ratio. The TG curve shows 12 % weight loss between 30 and 184 °C, indicating remained water content in the glassy alginate wall after heat treatment. Intense weight loss took place between 185 – 208 °C, what can be assigned to the thermal degradation of alginate [16] and to the evaporation of the paraffin wax [17].

The heat storing capacity of the microencapsulated paraffin and the alginate-paraffin capsules was analysed by microDSC (Fig.7). The latent heats of melting and freezing were found to be 185.0 J/g and 195.2 J/g for the pure paraffin (Fig.7a). The primary (higher) peak corresponds to the solid–liquid phase change, whilst the secondary peak at a lower temperature denotes the solid–solid phase change [18]. The heat storage capability of microcapsules manufactured as described in Run #5 with the highest paraffin content (48 %, Fig.7b) was as high (95.0 J/g and 91.7 J/g melting and freezing enthalpy change, respectively) in accordance with their paraffin content. The PCMs designed for application should withstand repetitive cycles of heating and cooling without any degradation in their life period. Hence, thermal cycling of weighed samples was carried out by heating them up to 85 °C and cooling down to 35 °C periodically. After 1000 cycles no paraffin leakage from the capsules was observed. The paraffin content in the capsules after thermal cycling was also measured as was described in section 2.2.3 indicating no significant paraffin loss. Using e.g. 0.167 g capsules with the highest paraffin content obtained in Run #5, the paraffin content decreased only by 0.1 % (wt/wt) after 1000 heating-cooling cycles, which is negligible. DSC analysis of the capsules including the highest paraffin ratio was also achieved after 1000 heating-cooling cycles (Fig.7c), and it showed negligible decrease of the heat capacity of the capsules (94.2 J/g and 91.0 J/g melting and freezing enthalpy change, respectively).

5. Conclusions

New preparation method was proposed to produce double-shell alginate microcapsules for latent heat storage, containing paraffin phase change material. The process consisted of three main steps: (1) preparation of core particles by dripping an emulsion of melted paraffin in aqueous sodium alginate solution into an ionic cross-linking solution of calcium chloride, (2) encapsulation of the core particles into double alginate shell by repeated ionic gelation/crosslinking steps utilizing the interactions between the sodium alginate and calcium chloride solutions, and (3) consolidation of the capsule shells by contact heat treatment.

It was found that three process variables, namely the sodium alginate and the calcium chloride concentrations in certain stages of the process, as well as the contact time between the core

particles and the surrounding alginate solution had significant effects on the paraffin content and the mean diameter of capsules. These influences were studied by an adequate experimental program, determined by experimental design, and evaluating the experimental data by a statistical analysis and multivariate regression.

It was evidenced that the mean size of capsules increased by rising the sodium alginate and calcium chloride concentrations and contact time, which is reasonable because all the three factors contribute to the increase of the cross-linked alginate mass surrounding the core particles. For the paraffin content of capsules a quadratic correlation was obtained with the three studied process variables. The relative mass ratio of the paraffin inside the capsules strongly diminished with increasing sodium alginate concentration within certain ranges (4.0-8.0 %) and with increasing contact time between 2.0 and 8.0 min. The dependence on calcium chloride concentration was linear and weaker. A correlation was found between the relative paraffin content and the mean capsule size, explained by the enhancement of alginate mass, and thus with the increasing capsule diameter and wall thickness.

The study on the morphology of capsules showed almost spherical particles with core/shell structure and smooth outer surface with very few and shallow pits. The core was composed of the encapsulated paraffin and a void space, which formed during the heat treatment of the capsules due to the shrinkage of the capsule wall, water lost and structural transformation to a glassy state. Micrographs evidenced a double wall structure, too, explained by the probable change of wall composition in radial direction, which could evolve due to the different concentration distribution in the subsequent gelation steps. First the cross-linking calcium ions diffused from outside toward the alginate cores. Then, in the second step, alginate solution surrounded the semi-finished capsules, interacting with the excess calcium ion remained in the surface region of capsules. Finally, in the last gelation step calcium ions diffuse radially from outside again, cross-linking the alginate molecules on the surface remained from the previous step.

Due to the final heat treatment a thermally and mechanically stable capsule wall was formed, as was evidenced by thermogravimetric analysis and repeated thermal cycling. Differential scanning calorimetry indicated that the heat storage capacity of the capsules with highest paraffin content was sufficiently high. Thermal reliability of the capsules was proved after 1000 heating-cooling cycles.

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Run #	3 factors Box-Behnken design, 1 block, 15 runs - 3 repetitions in centrum point					
	Sodium alginate concentration in Step 2.1, % (wt/wt)	CaCl ₂ concentration in Steps 1.3 and 2.2, % (wt/wt)	Contact time in solution in Step 2.1, min	Mean capsule size after heat treatment, mm	SD of capsule sizes around their mean, mm	Paraffin weight ratio in capsules, % (wt/wt)
1	12.0	8.0	13.0	3.04	±0.18	23.44
2	12.0	8.0	1.0	2.50	±0.19	34.39
3	8.0	4.0	1.0	2.26	±0.13	42.07
4	12.0	4.0	7.0	2.52	±0.15	26.85
5	4.0	8.0	1.0	2.16	±0.17	47.99
6	4.0	4.0	7.0	2.29	±0.11	36.61
7 C	8.0	8.0	7.0	2.72	±0.11	20.81
8	8.0	4.0	13.0	2.56	±0.14	21.6
9	8.0	12.0	1.0	2.27	±0.12	35.98
10 C	8.0	8.0	7.0	2.65	±0.13	22.59
11 C	8.0	8.0	7.0	2.60	±0.11	19.52
12	4.0	8.0	13.0	2.49	±0.11	24.42
13	8.0	12.0	13.0	2.93	±0.15	11.13
14	4.0	12.0	7.0	2.39	±0.13	26.00
15	12.0	12.0	7.0	2.96	±0.15	13.37

Table 1. Experimental conditions with the resulted capsule size and paraffin content.

<i>Property</i>	<i>Low paraffin content (Run #1)</i>	<i>High paraffin content (Run #5)</i>
Outer mean diameter, mm	3.04	2.16
Estimated mean wall thickness, mm	0.3	0.04
Paraffin mass per capsule, mg	2.4	2.4
Paraffin mass ratio, % (wt/wt)	23.4	48.0
Wall mass ratio, % (wt/wt)	76.6	52.0
Estimated mean capsule mass, mg	10.3	5.0
Estimated wall mass, mg	7.9	2.6
Capsule mean density, g/mL	0.70	0.95
Estimated wall ratio, % (v/v)	48.3	10.7
Estimated paraffin ratio, % (v/v)	18.2	50.6
Estimated air ratio, % (v/v)	33.5	38.7
Latent heat capacity, J/g	46.6	95.5

Table 2. Properties of typical PCM capsules with low and high paraffin content

Graphical abstract

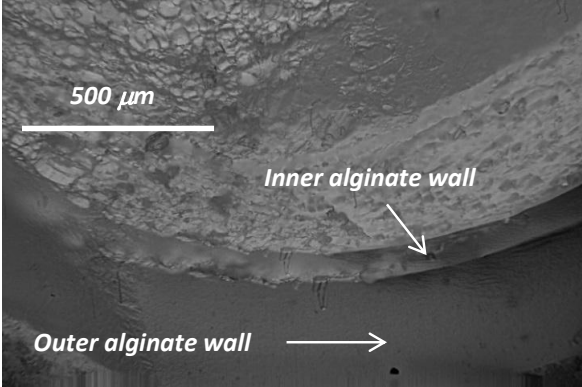
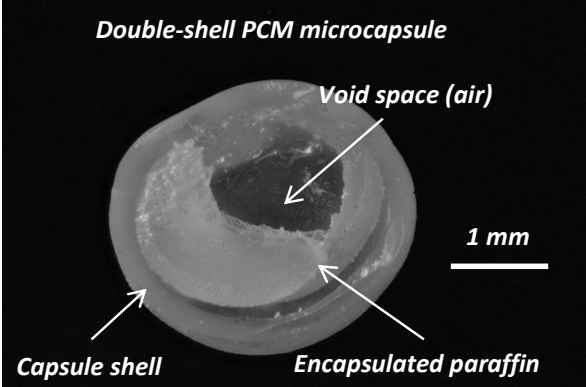


Fig.1. Schematic illustration of the capsule preparation method.

Fig.2. Effects of selected process variables on capsule size after heat treatment - Pareto chart (a), effects of CaCl_2 and sodium alginate concentrations (b), effects of contact time and sodium alginate concentration (c), comparison of the observed and predicted mean capsule sizes (d).

Fig.3. Effects of selected process variables on paraffin content after heat treatment –Pareto chart (a), effects of the CaCl_2 and sodium alginate concentrations (b), effects of the contact time and sodium alginate concentration (c), comparison of the observed and predicted paraffin contents(d).

Fig.4. Correlation between the measured mean capsule size and paraffin content.

Fig.5. Micrographs of a typical PCM capsule: outer view of the capsule (Run #1) (a), cross-section of a fractured capsule (Run #1) (b), layered capsule wall in higher magnification (Run #1, 1-inner layer, 2-outer layer) (c).

Fig.6. Thermogravimetric curves of the resulted PCM capsules with high paraffin content
TG: solid line, DTG dotted line.

Fig.1.

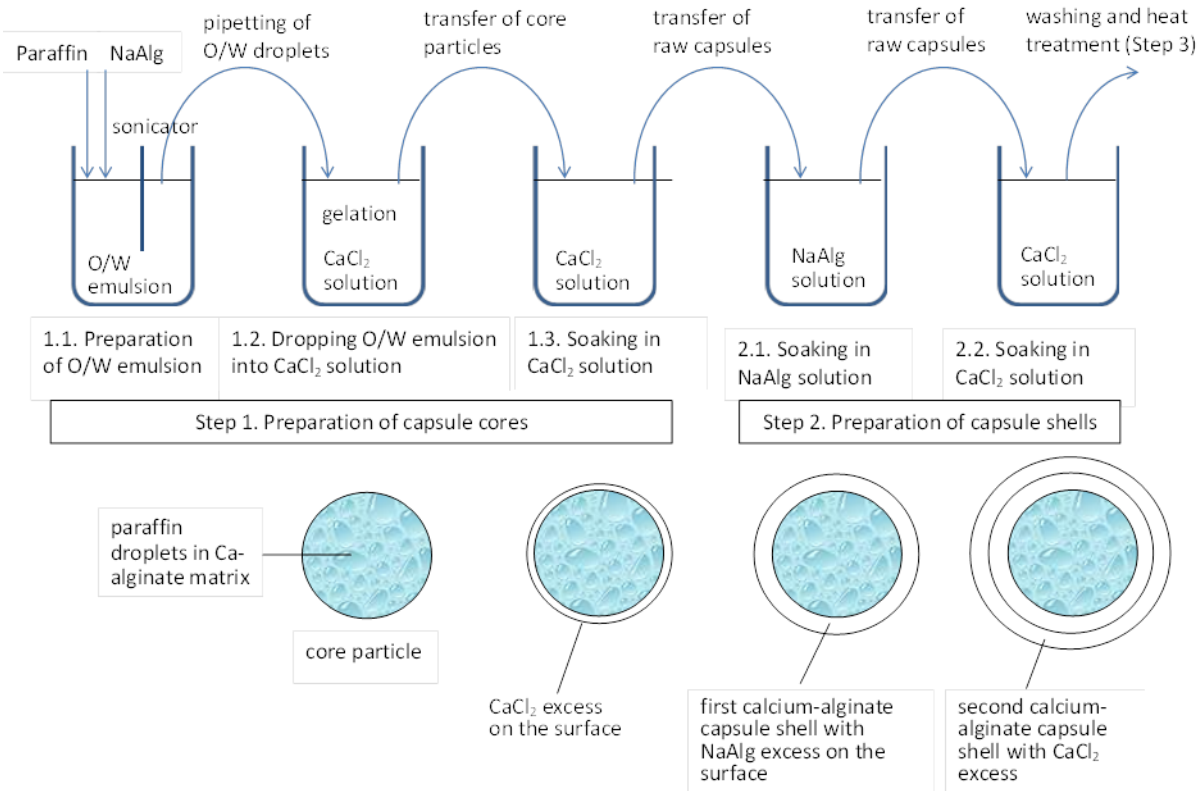


Fig.2a

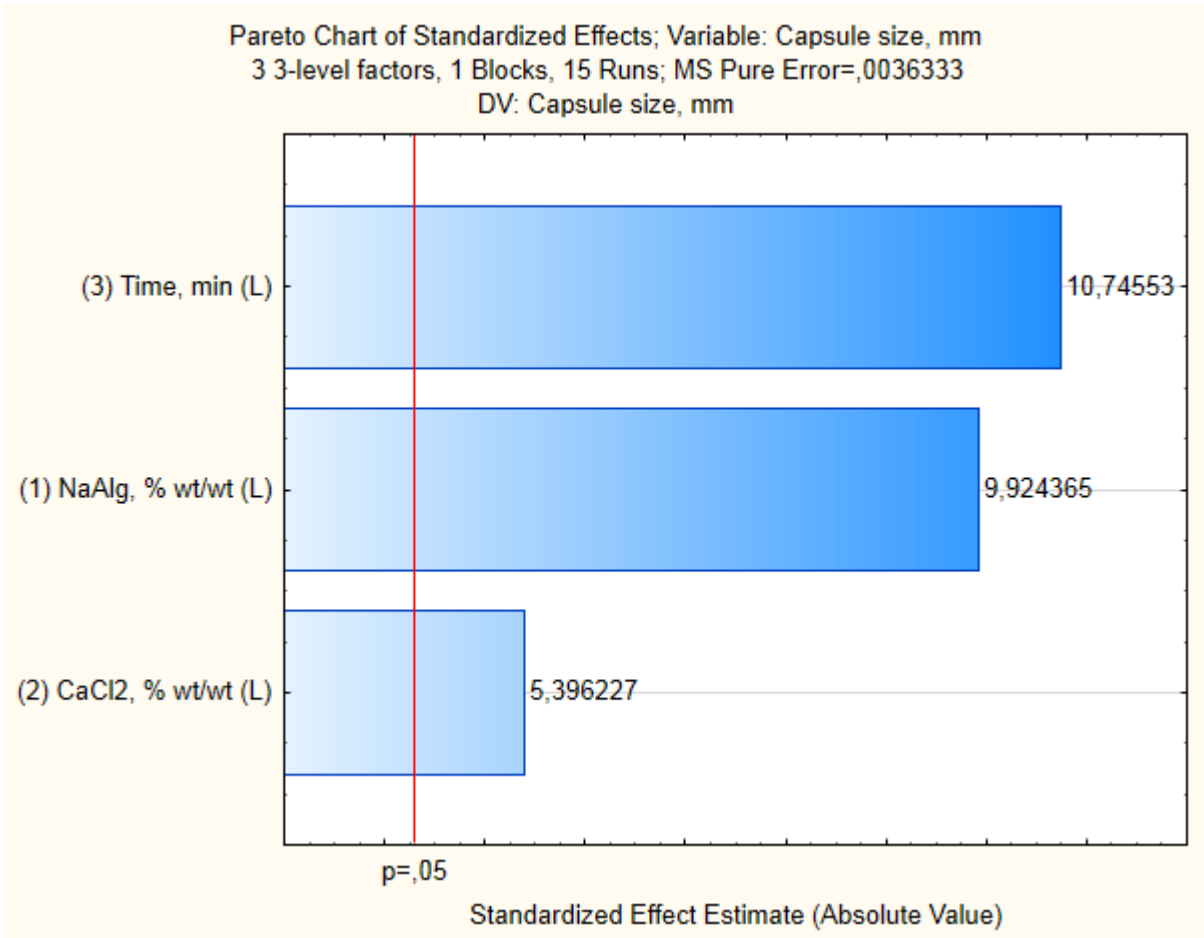


Fig.2b

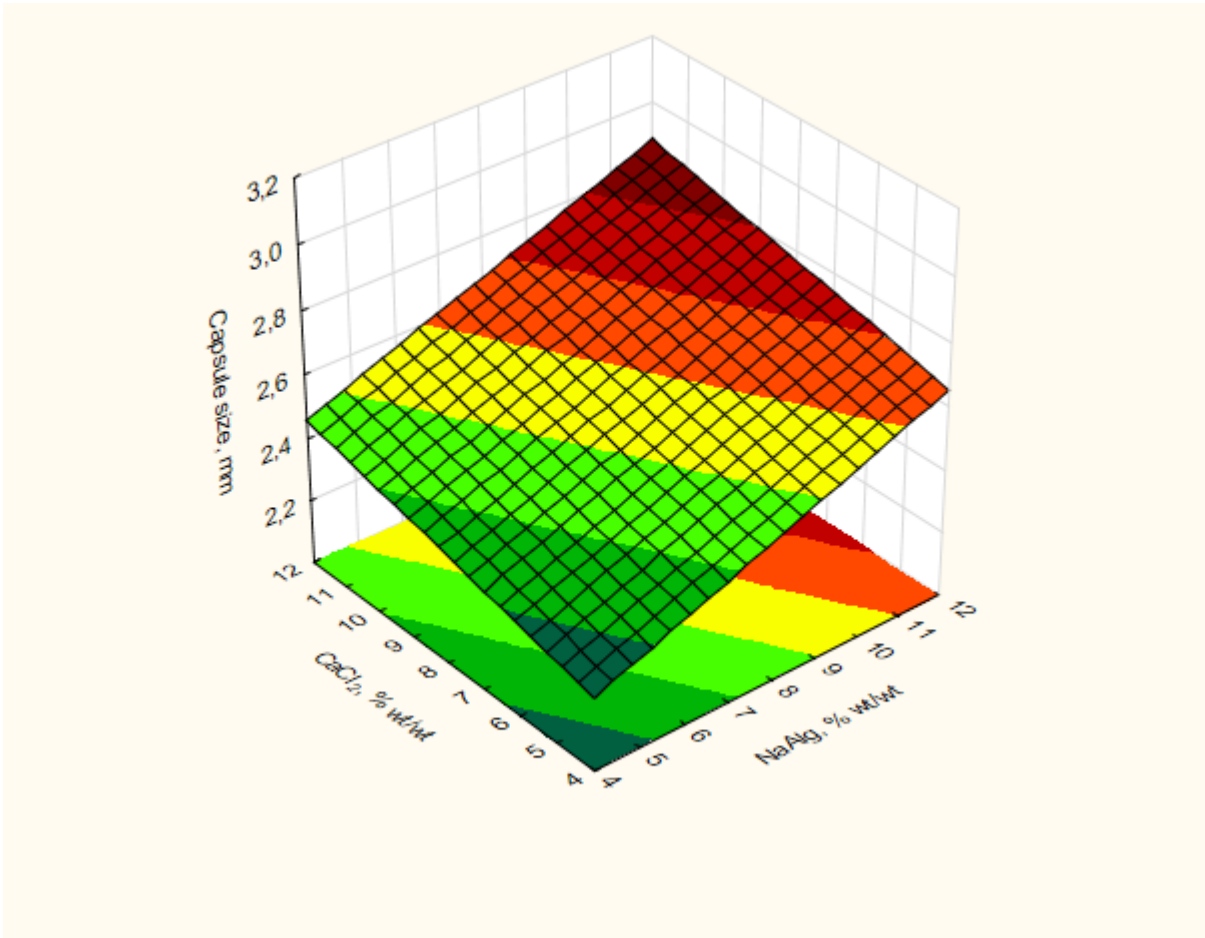


Fig.2c

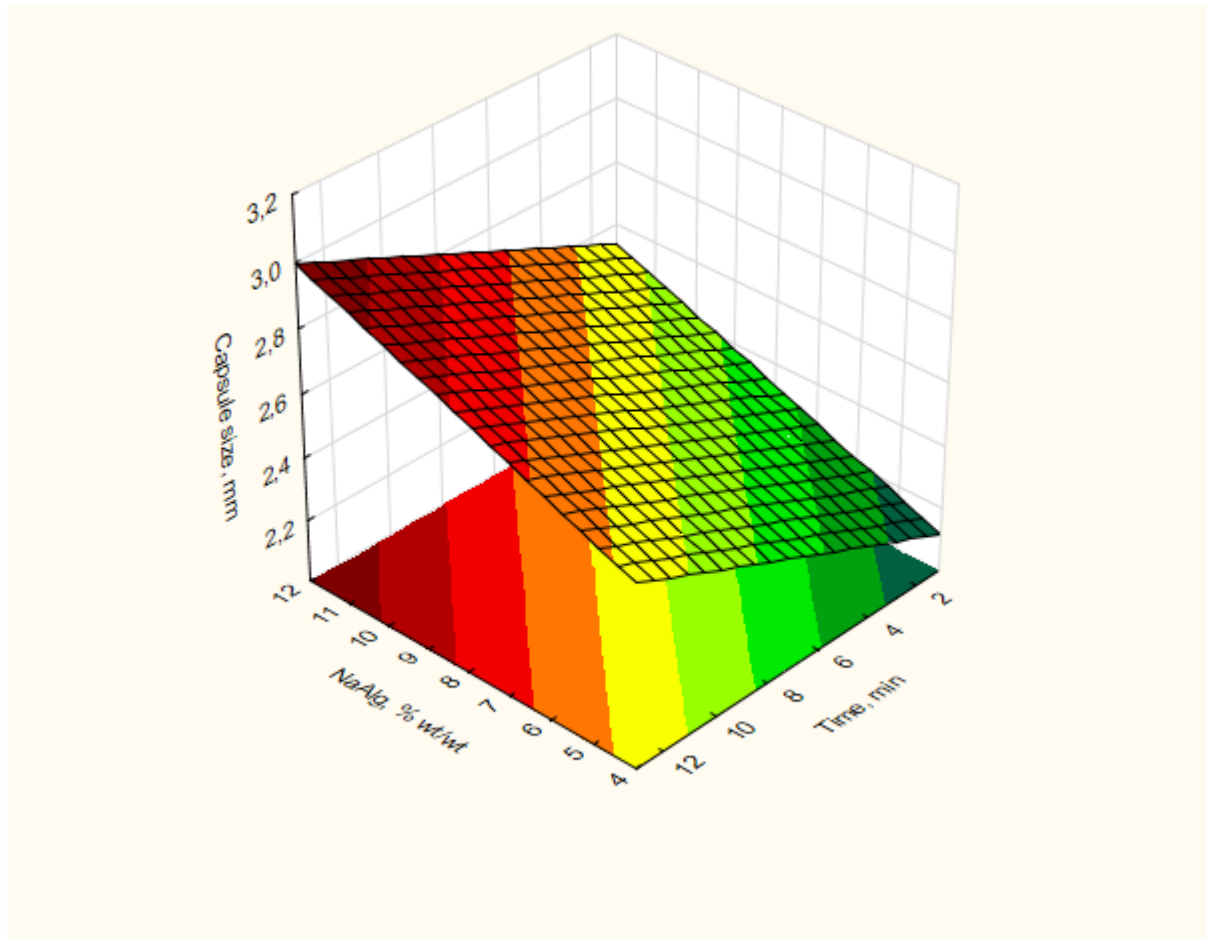


Fig.2d

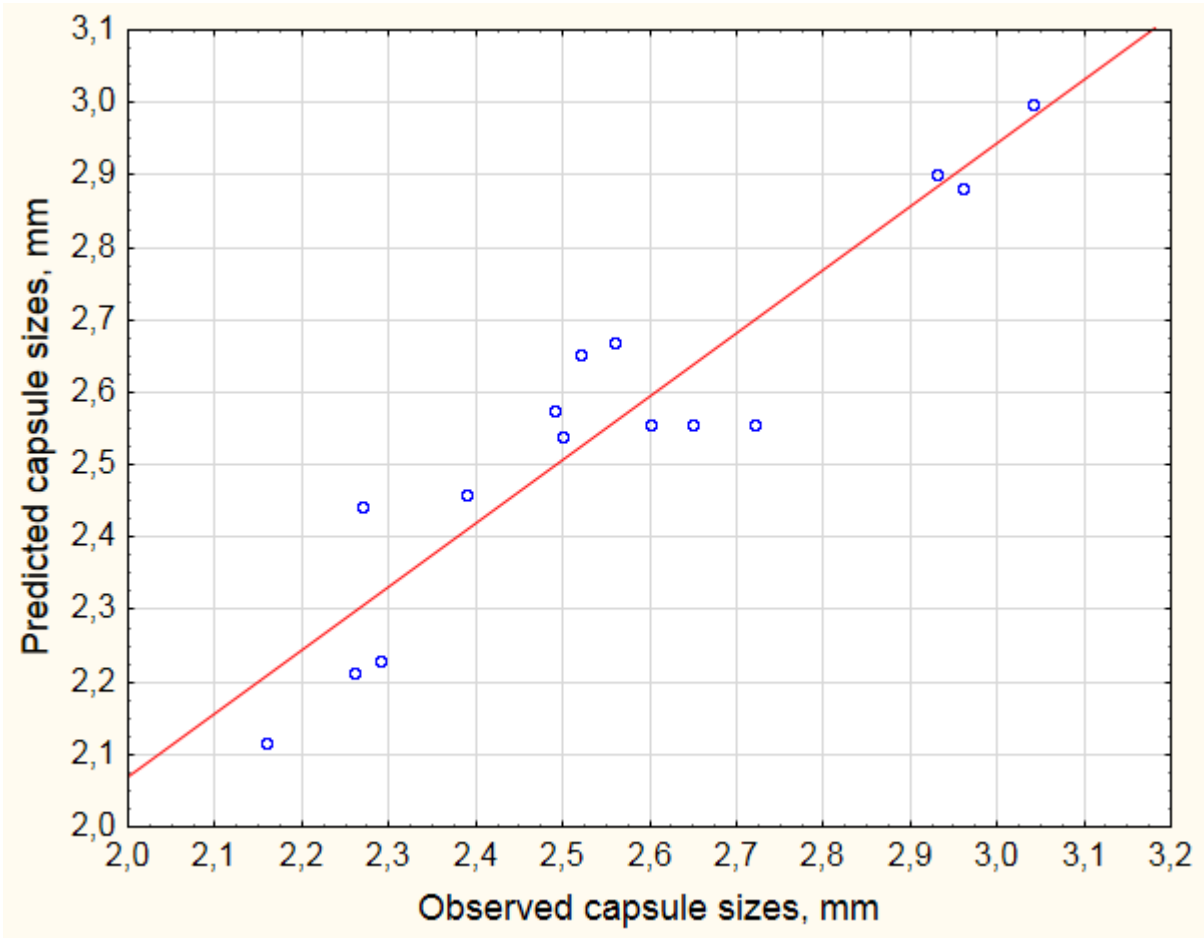


Fig.3a

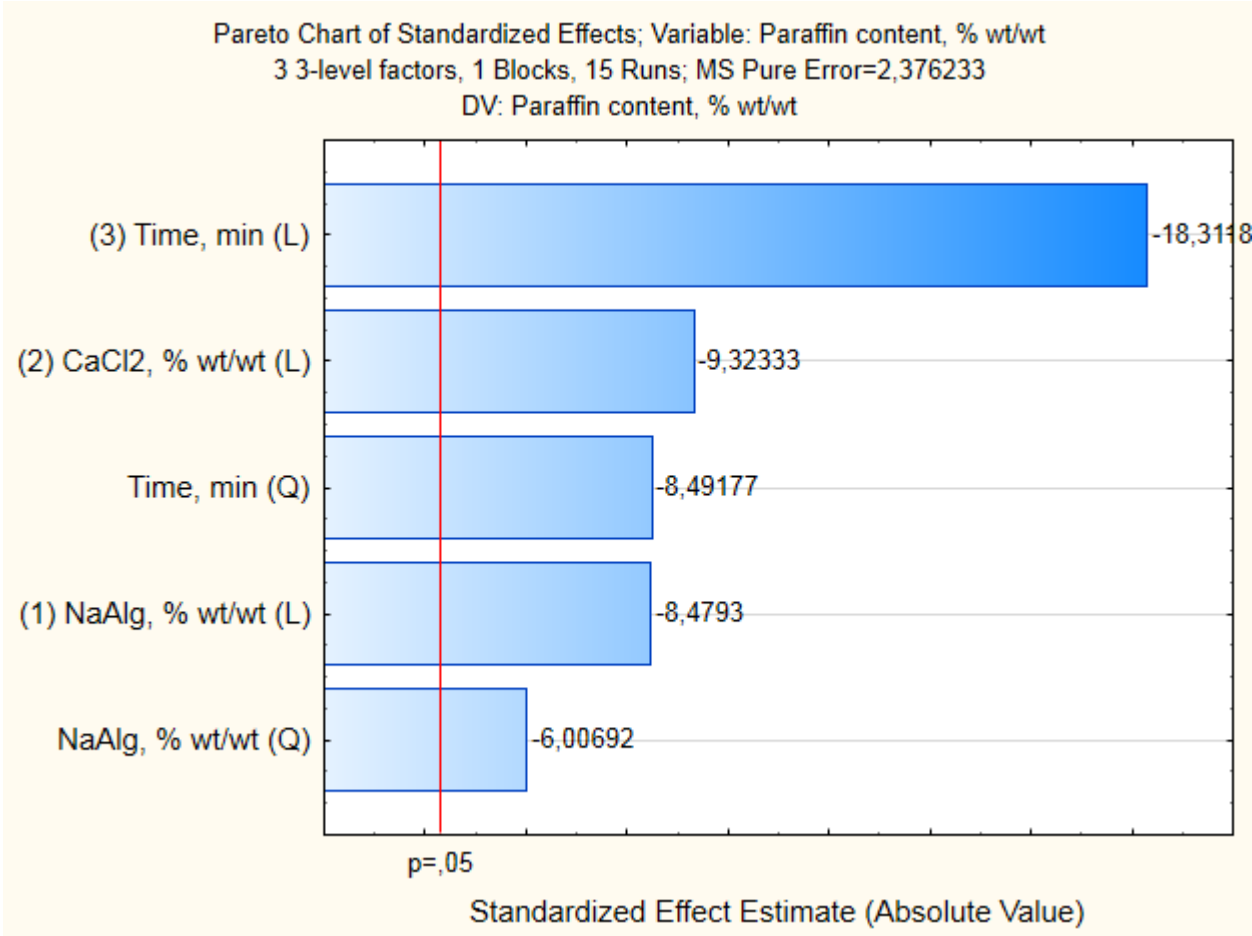


Fig.3b

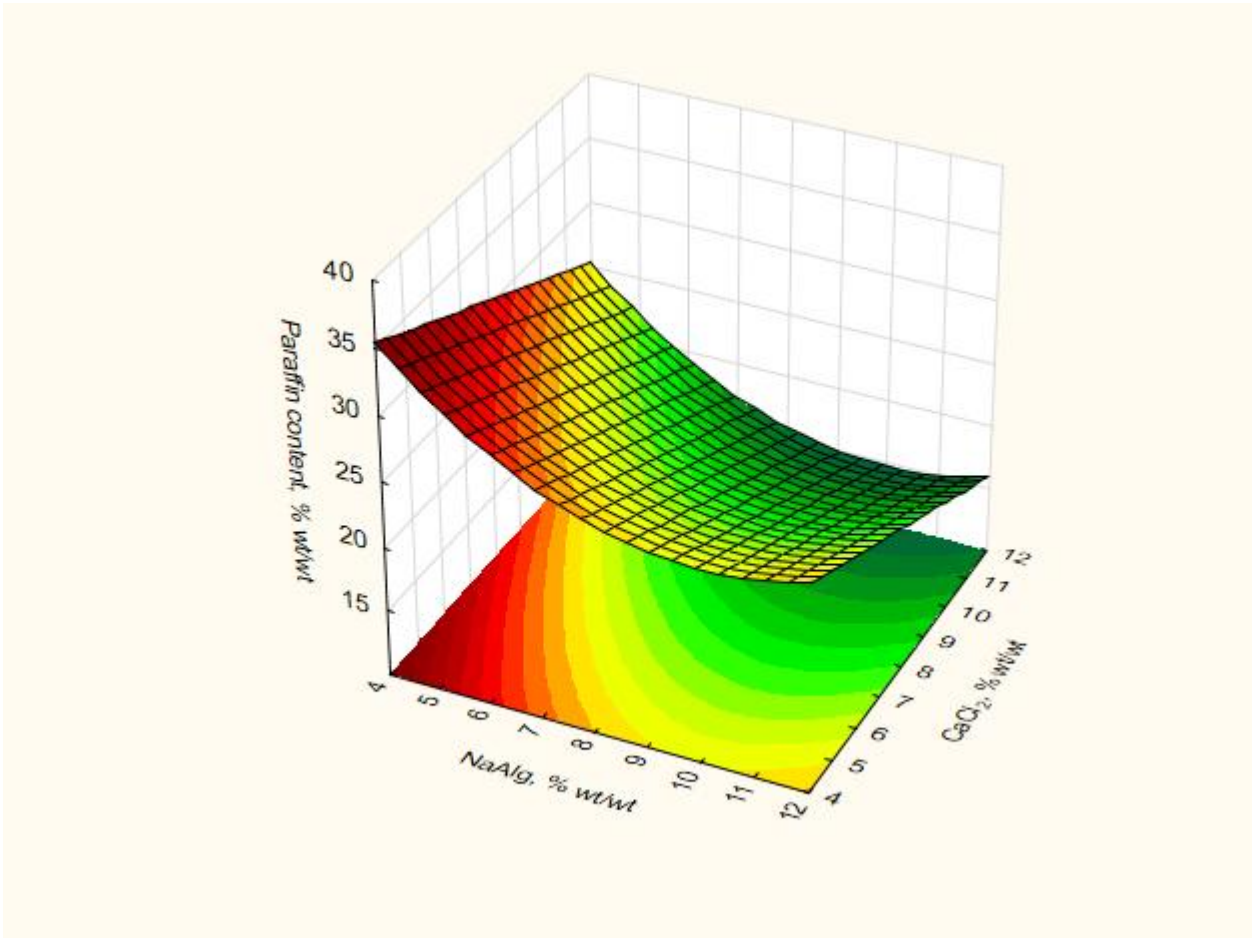


Fig.3c

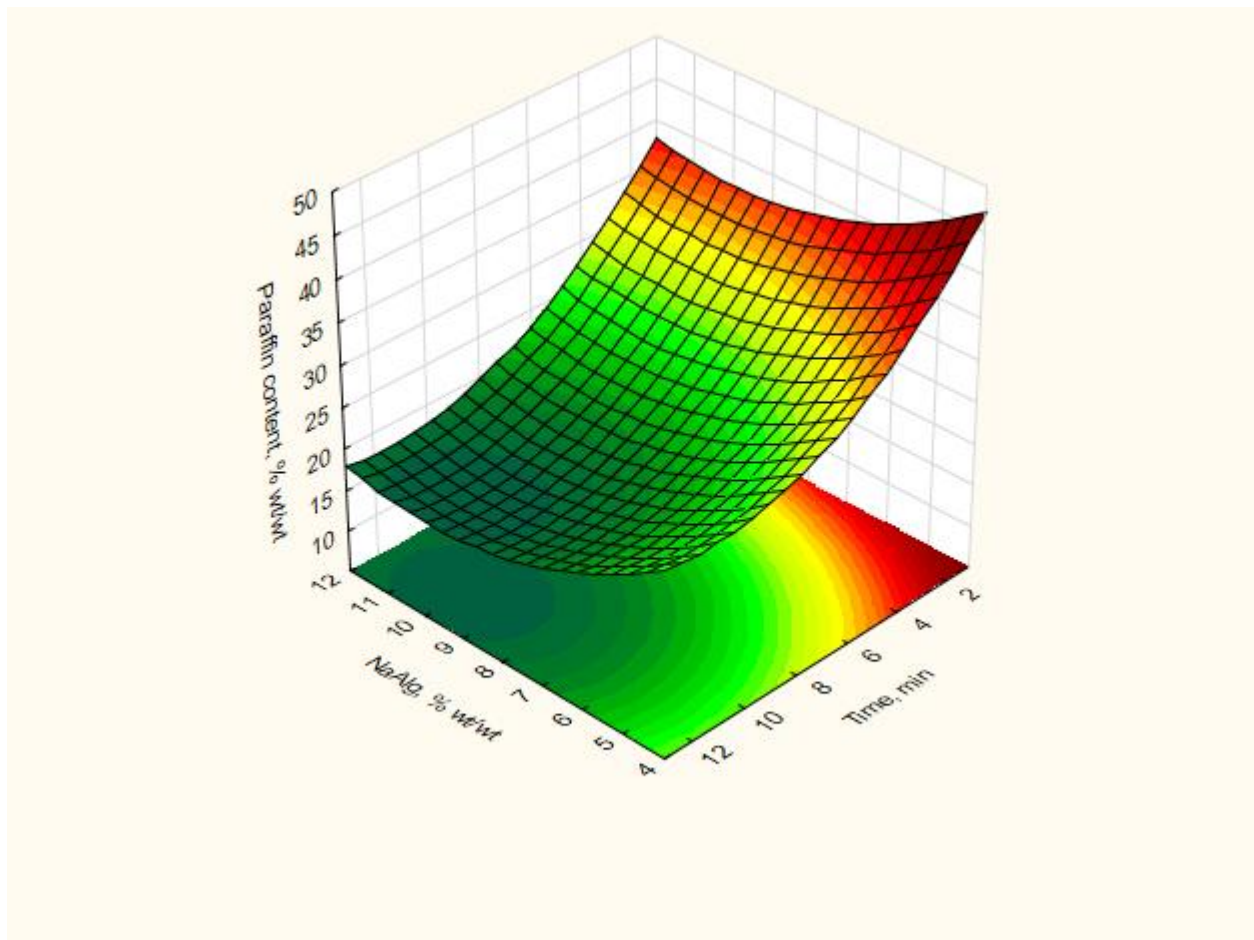


Fig.3d

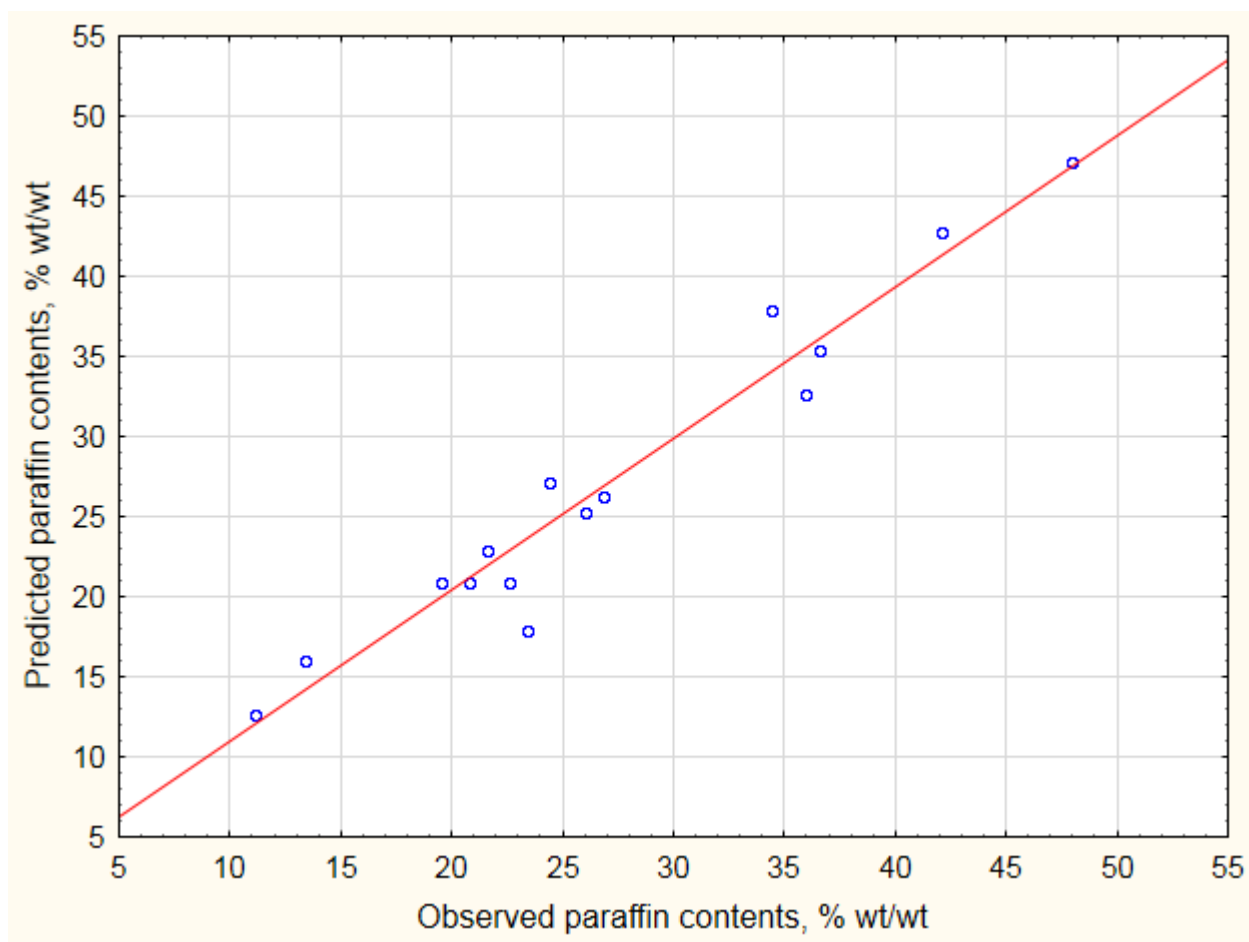


Fig.4

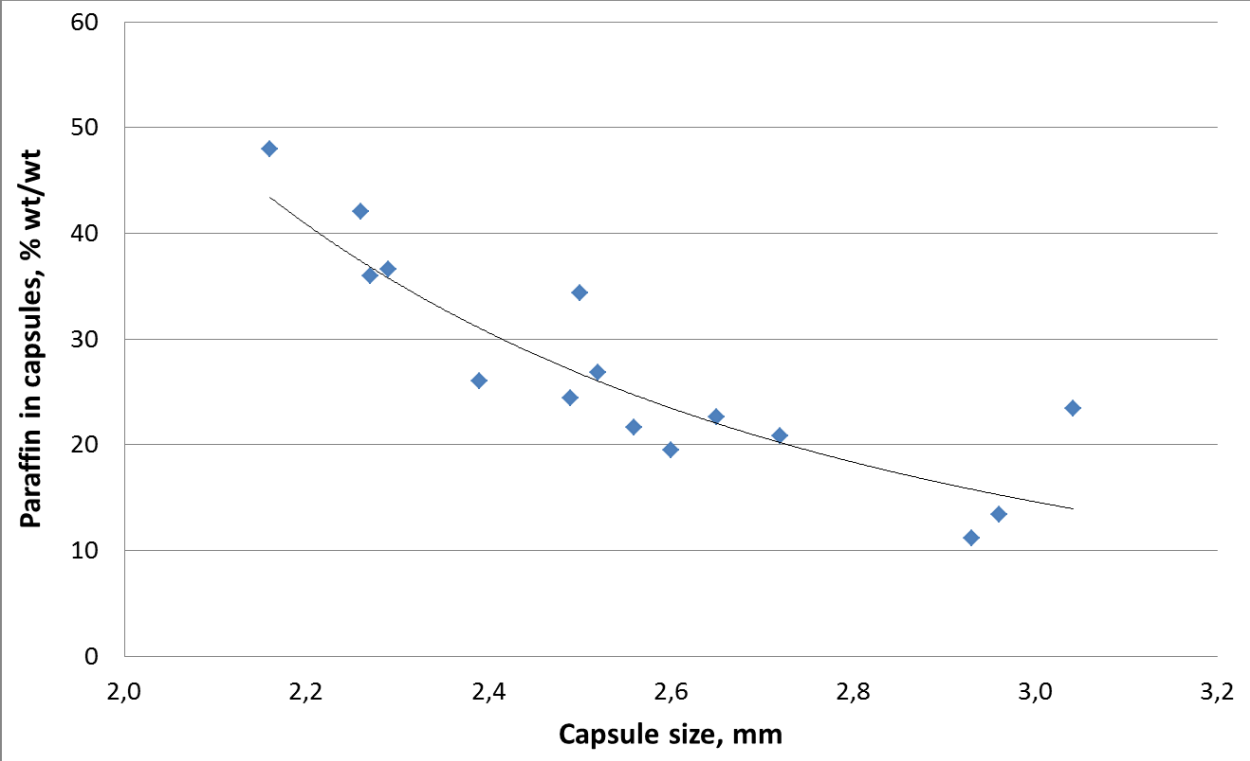


Fig.5a

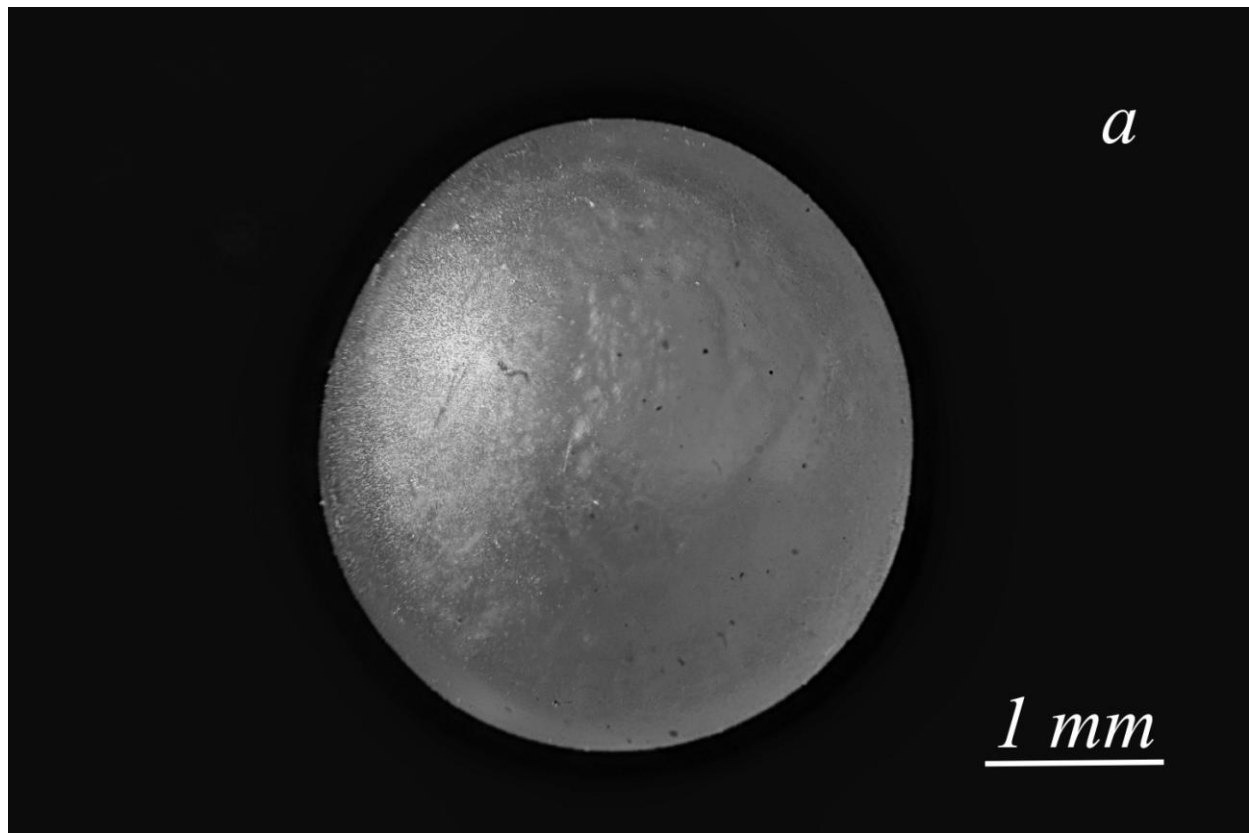


Fig.5b

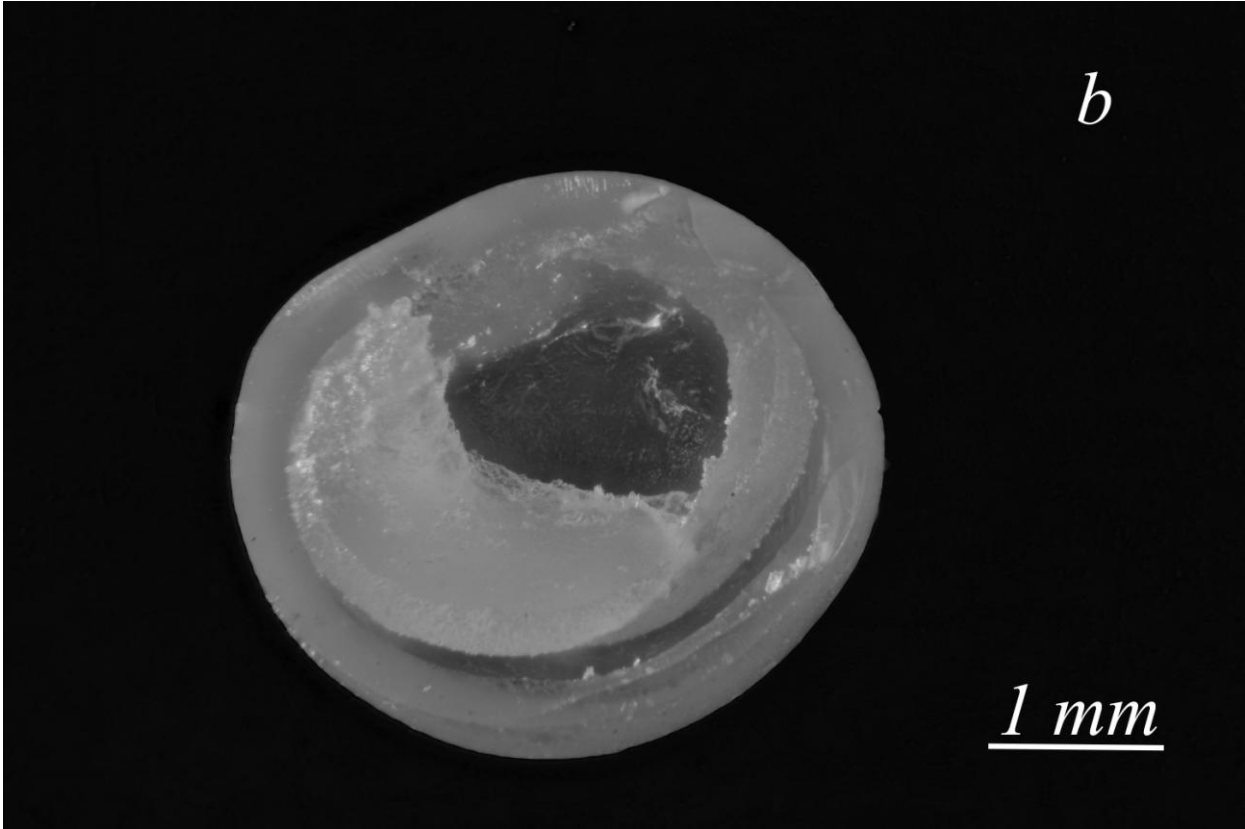


Fig.5c

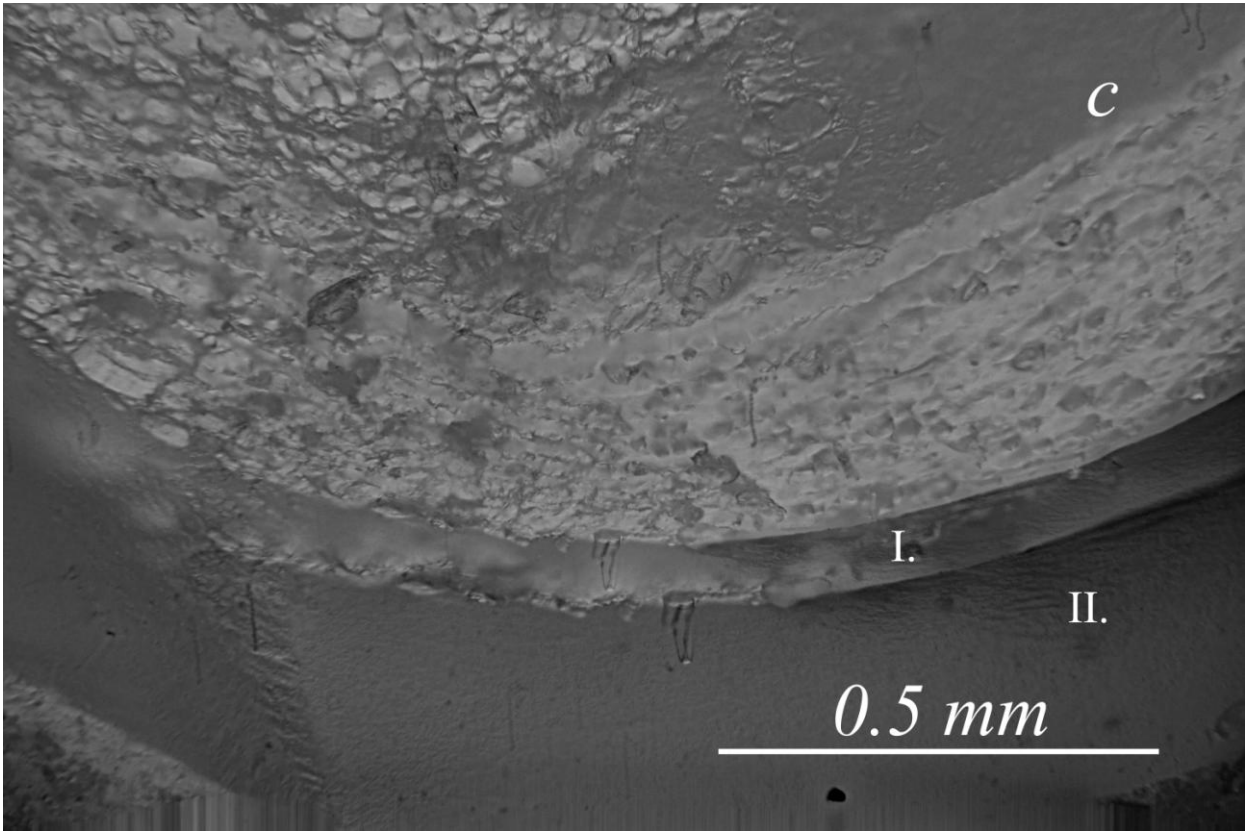


Fig.5d

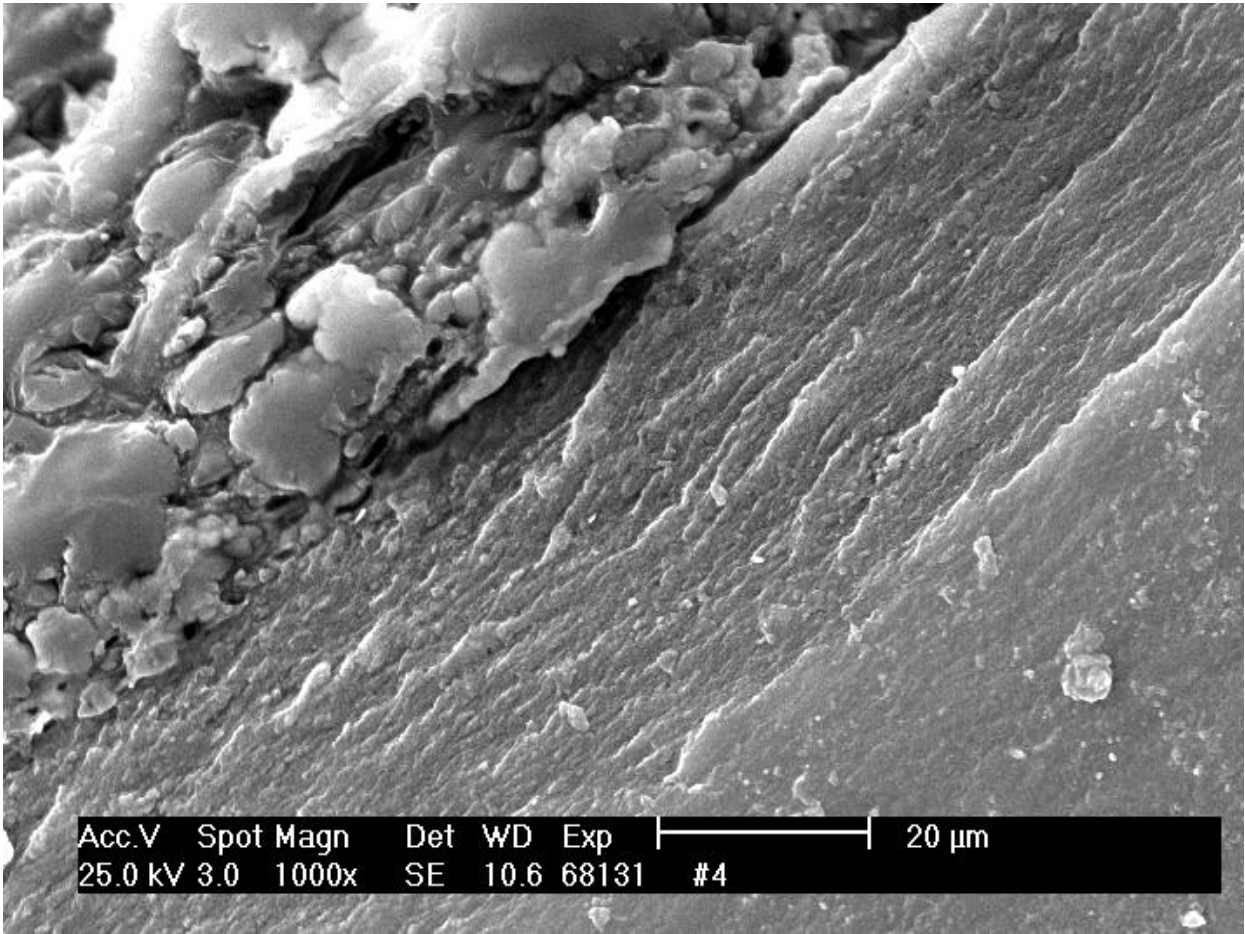


Fig.6

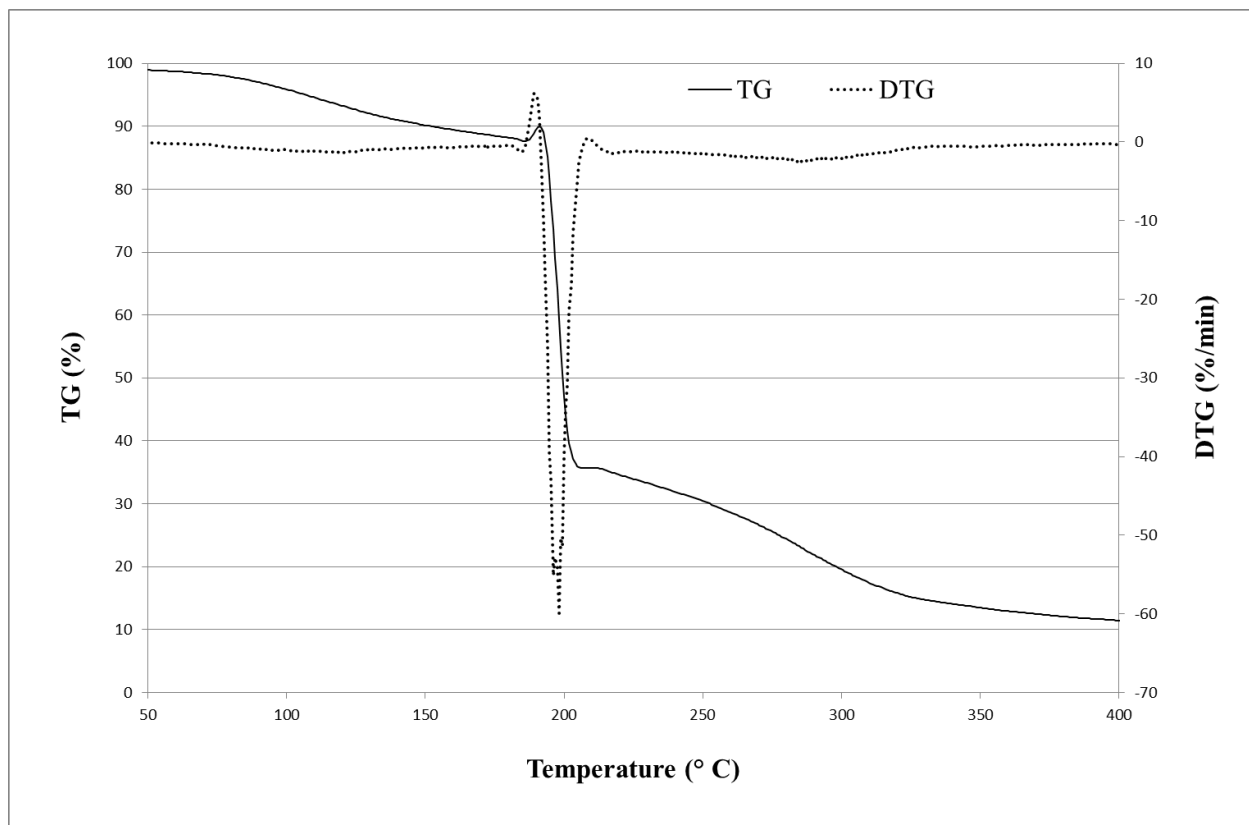


Fig.7a

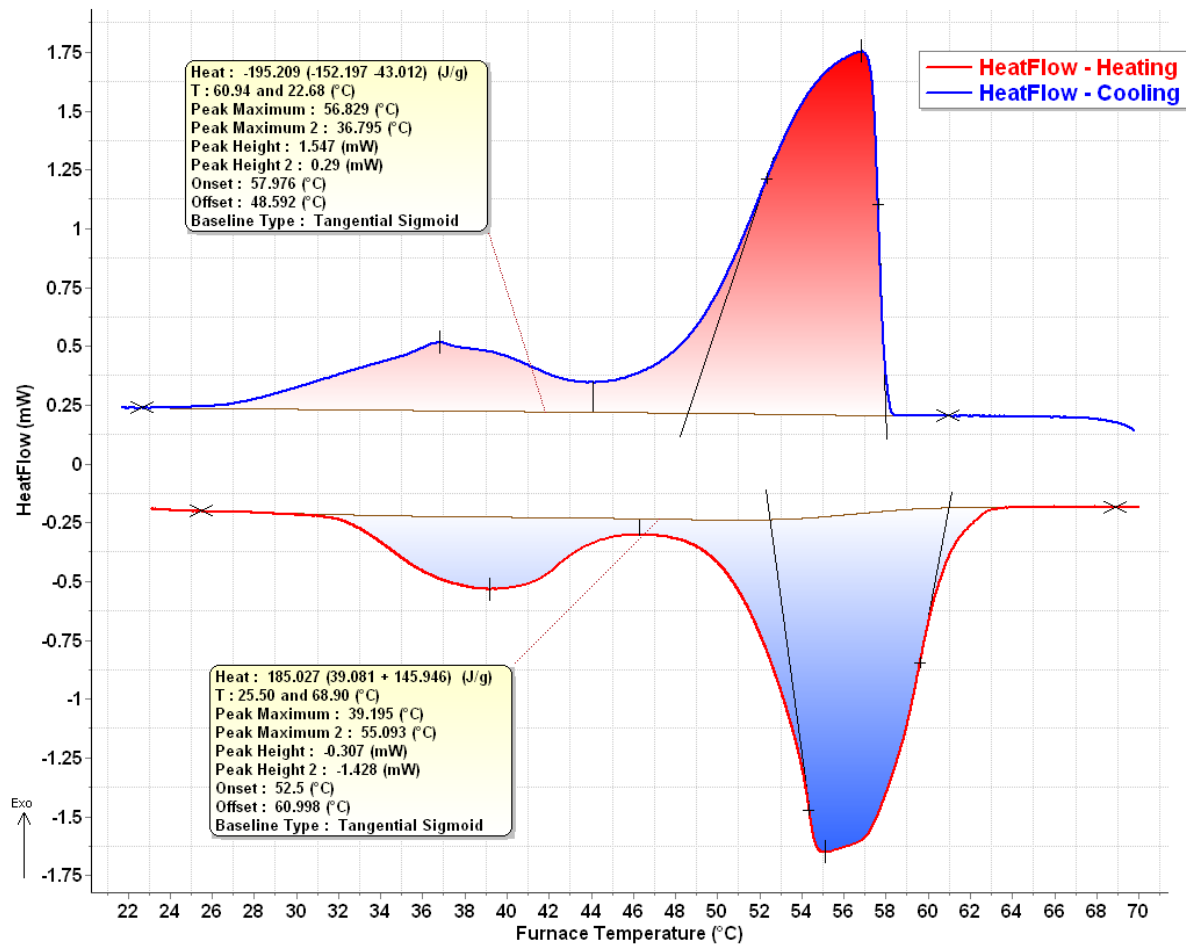


Fig.7b

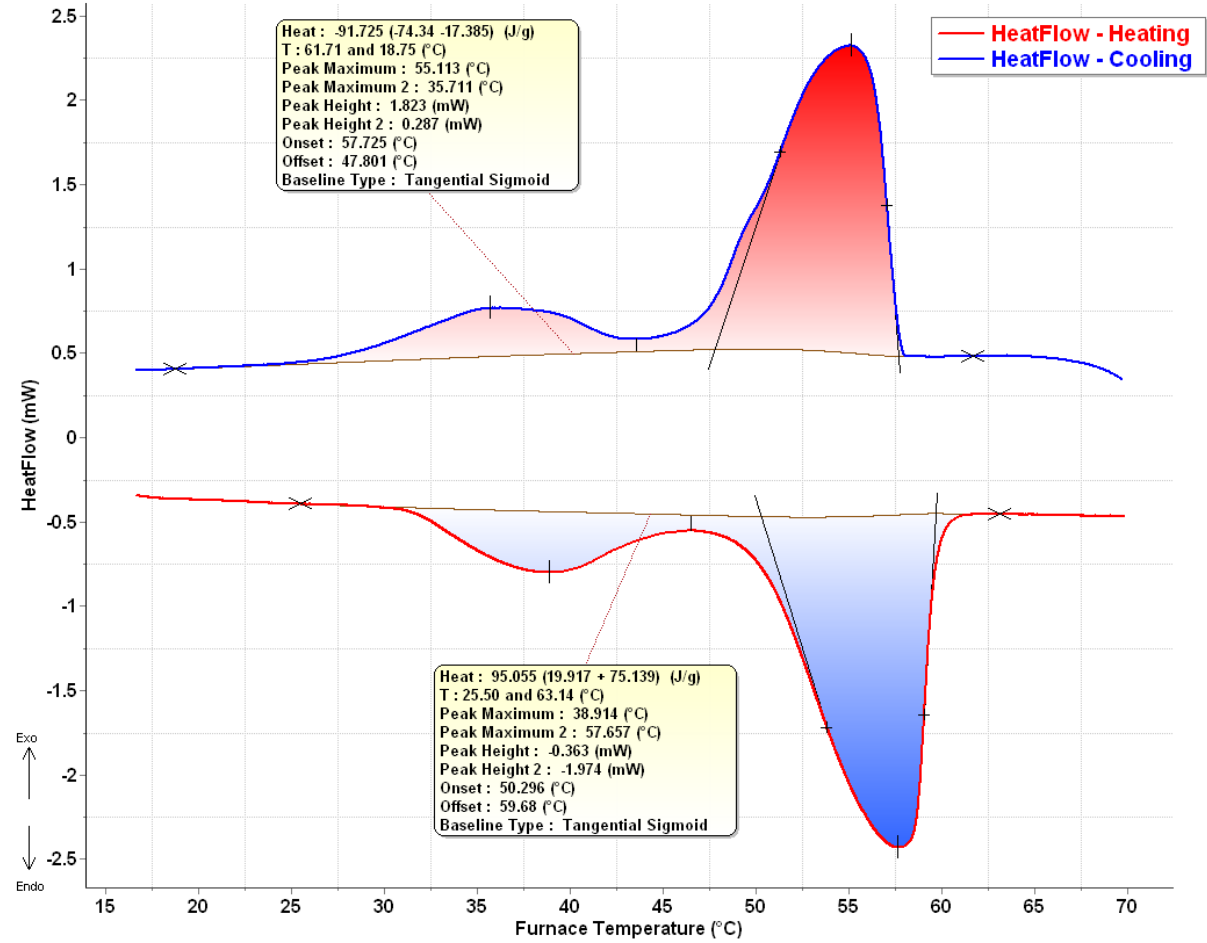


Fig.7c

