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Annual Report 1998

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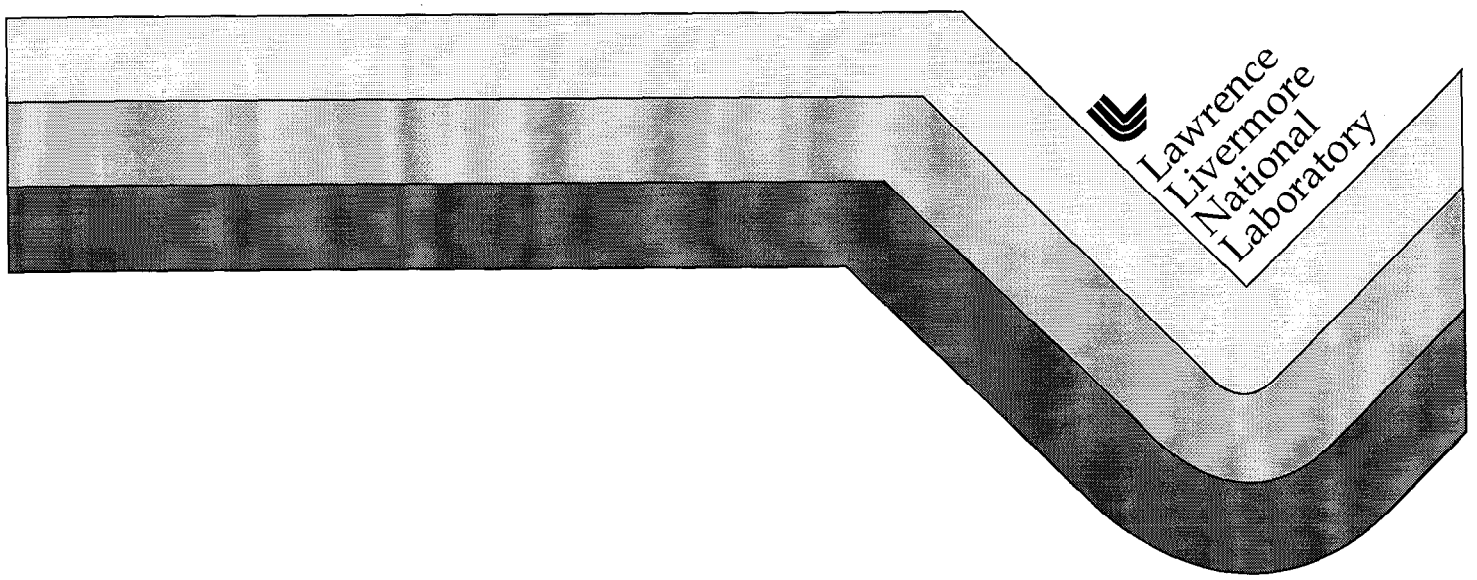

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According to the fourth-year program of the large polystyrene shells fabrication technology investigating and Ballistic Furnace designing under Material Support Agreement Number B338329, signed December 12, 1997, Laboratory of Thermonuclear Target (TTL) of Department of Neutron Physics (DNP) of Lebedev Physical Institute a number of different investigation had been made. We will describe our activity quarter by quarter.

Q1.1. Introduction.

At first quarter works of four variety were fulfilled:

1 - research of polystyrene shell formation conditions in Ballistic Furnace with 1.5m hot zone and new cooling zone;

2 - auxiliary research of solid polystyrene granule saturation by easy-boiling agents (methyl acetate, ethyl acetate and water at high pressure);

3 - comparative research of polystyrene shell formation conditions in drop tower furnace for granule with different quantity of blowing agents;

4 - simulation of shell formation processes in granules with different quantity of blowing agents and various blowing agents. Besides that polystyrene shells with diameter up to 2 mm transmitted to LLNL in parcel.

Shell formation experiments with the Ballistic Furnace have been carried out at LPI in collaboration with LLNL for the last 2 years and good quality polystyrene shells up to 1.6 mm in diameter have been produced. Based on this investigation we determined that modifications in existing installation were necessary in order to produce larger shells with better quality. In this report, we describe the general design of the upgraded Ballistic Furnace and its new features arisen after upgrading. The results of our first shell formation experiments with the new facility are discussed.

Influences of blowing agent concentration on polystyrene shell formation from solid granules in drop tower furnace are discussed. The concentration of blowing agents (solvent) has typically been 2 to 5 mass percentage /1, 2/, and under these conditions high temperature and low pressure in the furnace is necessary for polymer shells formation. We have found both computationally and experimentally that increasing of blowing agent concentration allows us to produce a high yield of large shells at lower furnace temperatures. An important benefit of the lower furnace temperature is a reduction in thermally induced polymer degradation /3, 4/ which results in fragile shells. In our report we will discuss both the experimental results and the agreement of these results with our computational modeling studies /4, 5/.

At first quarter, we paid serious attention to careful experiments with larger initial granules. We used in those experiments 0.7 - 0.8 - mm granules with narrow size distribution. Each granule fractions was carefully examined and characterized

just before experiment. Many shells' formation experiments were carried out and results of these experiments were compared with theoretical calculations. However, this experiments were carried out with initial granules contained 3.5% (weight) of blowing agents (ethyl acetate, water, monomer etc.). New experiments on drop tower furnace had goal to research dependence of shell diameter from quantity of blowing agents. Besides that on drop tower furnace dependence of large (about 2mm) shell surface quality from temperature profiles were researched.

Experiments showed that large solid polymer granules, which contain easy-boiling solvent transform into foam fragments, when heated quickly. In other words, there are many initial supercritical nuclei of new (gas) phase. If heating is continued then the foam is destroyed, and foam fragments turn into monoshells. In one part of this work we offer a mathematical model of viscous fluid dynamics for this process, but using of model are not possible without knowledge of calculation of nucleus homogeneous and heterogeneous formation velocity. The method of calculation of nucleus homogeneous and heterogeneous formation is discussed at the abolition (foaming) of polymer with a small amount of the low-temperature boiling admixture. We take into account the influence of the non-ideal molecular mixture and the non-equilibrium chemical state of gas bubbles. Calculation results agree satisfactory with experimental data, obtained in our experiments.

At first quarter computer program were improved, it helped user to introduce physical constants and technological conditions. Besides that in model and computer's codes, new physical processes were included. We begin to take into account energy of boiling and energy of connection between boiling agent and polymer on surface of polymer shells.

Q1.2. Preparation of polystyrene granules.

Microballoon Group created installation for the fabrication of polystyrene granules producing up to 150-200g for one synthesis. Classical scheme of the installation for the suspension polymerization was used, but its construction was scaled to the reaction volume of 3 liters. Impeller mixer with three pair of paddles and with impingement plate was used. Mixer drive permits to change the speed of mixing from 50 to 2500 revolutions per minute. Heating of reactor and temperature support is provided by ultrathermostate of U-10 type, made in Germany.

The basic conditions for the production of granules with necessary parameters were found earlier using the setup with reactor volume of 200cm3. Therefore, the main problem which required investigation on the new installation was to determine conditions for the fabrication of granules with maximum of size distribution in the necessary size range of 600-800mkm. For this purpose we fixed all synthesis parameters in series of experiments and varied dispersion velocity only. Synthesis parameters are presented in the table Q1.1.

Fabricating the polystyrene granules by method of dispersive polymerization one produce granules, which are widely size-scattered. Inasmuch as granules with

narrow range of size dispersion must be used in experiments (in perfect case they must be monodispersed ones), especially in ballistic furnace, then the small part of granules is used from the granule batch for each synthesis. This causes the restrictions on providing overall investigations of foaming processes in the wide range of technological conditions.

More widely, granule distribution in sizes depends on the following factors: speed of mixer rotation, concentration of surface-ctive substance (SAS) and of its type. Dispersion velocity restricts the sizes of obtained granules, and in the case of lower velocities we obtain granules which sizes varies in the wide range, from large ones to very small ones. At higher mixer velocities sizes become less and size spectrum contracts. SAS concentration also influences the width of size spectrum. However, it weakly affects the distribution shape. As it is known, the sharpness of spectrum distribution in sizes depends on the type of SAS, but in our experiments we used the copolymer of methyl methacrylate with methacrylate acid as SAS, as it was almost in all preceding experiments.

Table Q1.1 Technical conditions of polystyrene synthesis.

Bath [tank,vat] modulus	4:1
SAS concentration	0.05 mole/l
Synthesis temperature	80°C
Time of polymerization	12 hours
Speed of mixer rotation	20-660 rpm

*Initiator of polymerization is benzoyl peroxide. SAS is 0.5% water solution of MKM in water, neutralization level is .6.

For the obtained polystyrene granules, we measured molecular-mass characteristics and molecular-mass distribution of polymer. MMD parameters were calculated by method of gel-penetrating chromatography at the chromatograph of the firm "Waters". Results of the measured MMD are presented in the following Table Q1.2.

Table Q1.2 Molecular-mass characteristics of polystyrene granules.

Synthesis	A38	F1-3	F1-4
Mean numbers MM	$0.60 \cdot 10^5$	$0.61 \cdot 10^5$	$0.60 \cdot 10^5$
Mean masses MM	$1.69 \cdot 10^5$	$1.51 \cdot 10^5$	$1.56 \cdot 10^5$
Polydisp Index	2.8	2.5	2.6

It comes from the table Q1.2. that under above conditions and for the polymerization time about 12 hours polystyrene attains molecular mass about 60 thousand.

In this case, MM is independent of the reacting mass value and of dispersion velocity. Our preceding experience proves that reological properties of polystyrene with such molecular mass are quite satisfactory and that this polymer is useful for the hollow microsphere fabrication. Increase of the polystyrene molecular mass requires the increase of synthesis time.

High coefficient of polydispersivity (2.5-3.0) is characteristic of the reaction of polymerization by radical mechanism. It is possible to decrease polydispersivity to limit level 1.5, but it requires some strict conditions on the polymerization process. It is necessary to provide complementary investigation in order to find these conditions.

Q1.3 Introduction of a foamer into polystyrene granules.

Foamer was introduced into polystyrene granules by diffusion, when polymer dwelled in the appropriate solvent. The following substances were taken for analysis as a foamer: methyl acetate, ethyl acetate, toluene, and heptane. These substances are "good" solvents for polystyrene, that is seen from close values of solubility parameters. Therefore, in order to transfer the process of dissolving into the regime of dwelling it is necessary to make a "bad" solvent from "good" one. For this purpose the solvent is mixed with the substance which is not the polymer solvent, but they must be able to dissolve in each other unreservedly. The ratio of mixed components varies from 1:4 to 1:8, where the larger number belongs to the polymer nonsolvent. The process of dwelling is provided for the time not less than 2 hours at the periodical mixing of the mixture. The long time of dwelling is necessary for the uniform distribution of the solvent in polymer. Microspheres, which are, obtained from granules 600-800 mcm in diameter with the time of saturation less than 40 hours were found to possess imperfect surfaces. All the attempts to improve their characteristics by any possible changes in the process of microsphere fabrication were not a success.

Q1.4. Experiments on drop tower furnace.

Q1.4.1. Introduction.

Research of the formation processes for large (from 1.8 mm up to 3.0 mm) microspheres by a method of foaming has shown, that temperature of a hot zone and gradients of temperature on the entrance and exit of a hot zone strongly influences on the yield and surface quality of shells.

Q1.4.2. Experiments.

All experiments were conducted with spherical polystyrene particles saturated with ethyl acetate (mass concentration of 6 %). The pressure in the furnace was 0.1 atm., atmosphere composition - 50% Ar and 50% He.

These experiments were conducted with the heated first section of a hot zone (0.5 m). Thus, we had an opportunity to observe the initial stage of a boiling process. With various temperature modes, the particles of three types were obtained: a) Particles remaining without changes,

b) Non spherical foam particles,

c) Spherical foam particles. (see table Q1.3).

Table Q1.3

Temperature °C		600	650	700	750	800	850	900
1	Particles remaining without changes	0.65	0.5	0.4	0.15	0.05	0.05	-
2	Non spherical foam particles	-	0.05	0.15	0.2	0.35	0.5	0.8
3	Spherical foam particles	0.35	0.45	0.45	0.65	0.6	0.45	0.2

The content of each type of particles depends on temperature of a hot zone. Initial granules size 2Rs=0.7 + 0.015 mm.

We regard T=800° C to be an optimum temperature of foaming process.

The influence of initial temperature gradient on the boiling process is presented in tableQ1.4. Content of each type of particles depends on a gradient of temperature on the entrance of a hot zone. Temperature of the hot zone is 800°C.

Table Q1.4

dT/dx °C/M		400	800	1200	1600	2000	2400
1	Particles remaining without changes	0.05	0.05	0.05	0.1	0.1	0.15
2	Non spherical foam particles	0.55	0.45	0.4	0.4	0.55	0.6
3	Spherical foam particles	0.4	0.5	0.55	0.5	0.35	0.25

Table Q1.5 shows dependence of temperature on the content of each type of

a) spherical monoshells;
b) Spherical foam particles;
c) Nonspherical foam particles;
d) Particles remaining without changes.

Table Q1.5

Temperature °C		600	650	700	750	800	850	900
1	Particles remaining without changes	0.2	0.15	0.05	0.05	0-	-	-
2	Nonspherical foam particles	0.3	0.35	0.4	0.4	0.4	0.4	0.35
	Spherical foam particles	0.4	0.35	0.3	0.2	0.15	0.05	-
3	Spherical monoshells	0.1	0.15	0.25	0.35	0.45	0.55	0.65

The size of initial particles 0.7_+0.015 mm, length of the hot zone is 1 m. T=850 C - temperature, at which "condition of explosion" occurred.

Q1.4.3. Conclusions.

The studies carried out have shown, that the temperature gradients on the entrance and the exit of a hot zone influence essentially the processes of formation of large (from 1.8 up to 3 mm) good quality surface polystyrene shells.

Q1.5 Modeling of shell formation. Improvements in numerical simulations.

In the first quarter some improvements have been fulfilled in the complex of simulating programs.

The program for preparation of initial data (STARINI) was essentially improved. Two new ASCII files were introduced:

1.for destructive gas data,

2.for data controlling heat sources due to polymer decomposition and evaporation of gas-foamer and destructive gas from outer surface.

Besides, the interface to introduce necessary data was remade. Now this operation became easier.

In addition, we modernized the main program (STARMOV). There was introduced possibility of shell cooling due to gas-foamer evaporation from outer surface. Heat flow from outer surface is proportional to mass flow of gas-foamer:

$$\frac{dQ}{dt} = -k_{vol}^{(1)} \cdot \left.\frac{dM}{dt}\right|_{r=r_o}$$

where $k_{vol}^{(1)} = E_1\left(1-\frac{T}{T_1}\right) + E_2\left(1-\frac{T}{T_2}\right)$, T is temperature. Coefficients E_1, E_2 and crytical temperatures T_1, T_2 depend on matter of gas-foamer. We take into

consideration in our calculations two substances as gas-foamer: water and ethylacetat. The table Q1.6 shows the constants for these substances.

Table Q1.6

Substance	E_1, J/kg	E_2, J/kg	T_1, K	T_2, K
Water	$4.0 \cdot 10^6$	$0.7 \cdot 10^6$	523	657
Ethylacetat	$0.8 \cdot 10^6$	$0.2 \cdot 10^6$	1000	1000

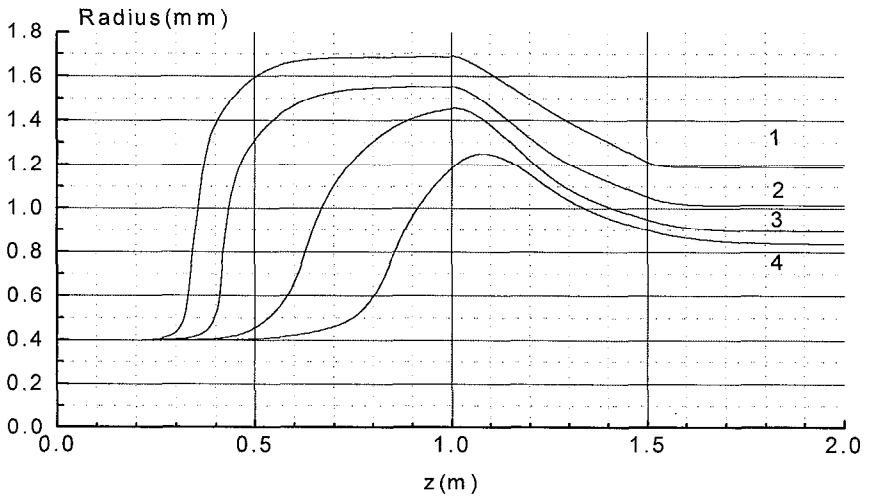


Fig. Q1.1.Shell radius as a function of coordinate in furnace. Hot zone temperature is 1073 K (800° C), furnace pressure is $0.2 \cdot 10^5$ *Pa. Numbers 1,2,3,4 correspond to oversaturation values S = 240, 120, 60, 30. Water is a foamer.*

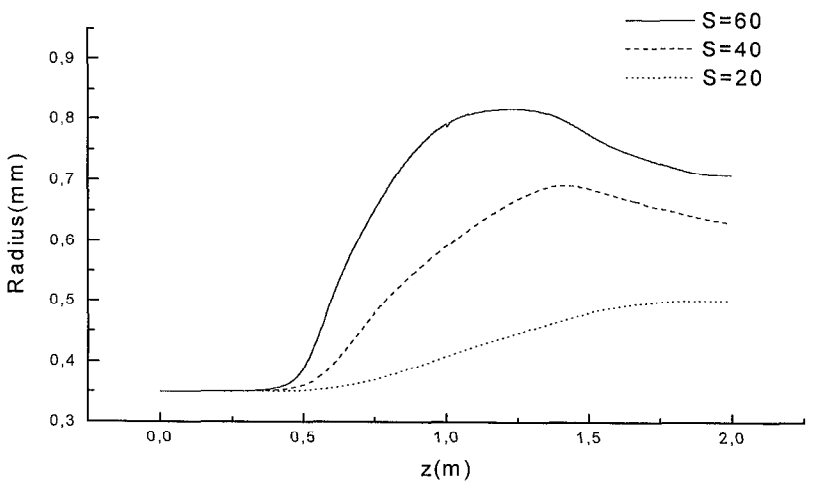


Fig.Q1.2 Shell radius as a function of coordinate in furnace. furnace pressure is $0.2 \cdot 10^5$ *Pa. Oversaturation values S = 60, 40, 20. Ethylacetat is a foamer.*

Besides, these constants can be considered as free parameters and selected from comparison with experimental data. The results of simulating are shown in figs.Q1.1 – Q1.2. These figures show dependencies of radius on coordinate in furnace z for gases-foamers from table Q1.5.

The optimum regime of polystyrene shell formation is defined. The temperature, gas pressure, and atmosphere composition are found for the Ballistic Furnace with hot zone of 1-meter height.

Q1.6. Ballistic furnace first quarters activity.

Q1.6.1 Introduction.

At first quarter, upgraded Ballistic Furnace had been finally assembled and first shell formation experiments had been started. The length of hot zone is 1.56m and the length of cooling zone is 1.2m now. We used in the first experiments 0.7 - 0.8-mm granules with narrow size distribution.

Q1.6.2 Facility description.

General view of the upgraded Ballistic Furnace in comparison with initial version is presented on fig. Q1.3.

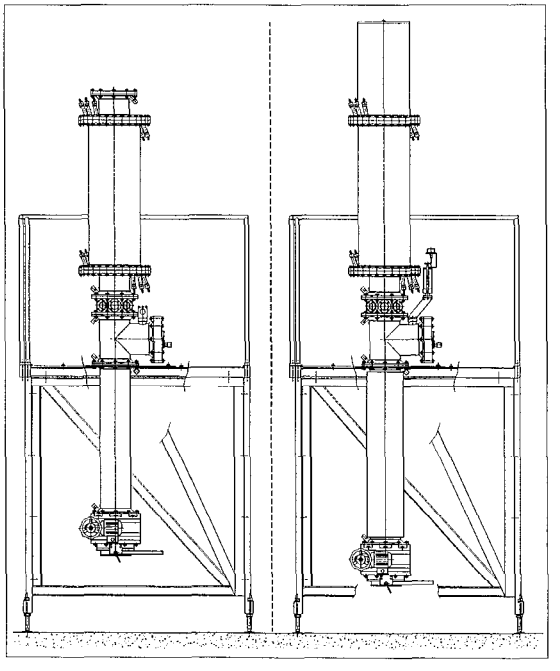


Fig. Q1.3 Drawing of the Ballistic Furnace general view. Initial version – left, upgraded version - right

Photo of the installation can be seen on Q1.4.

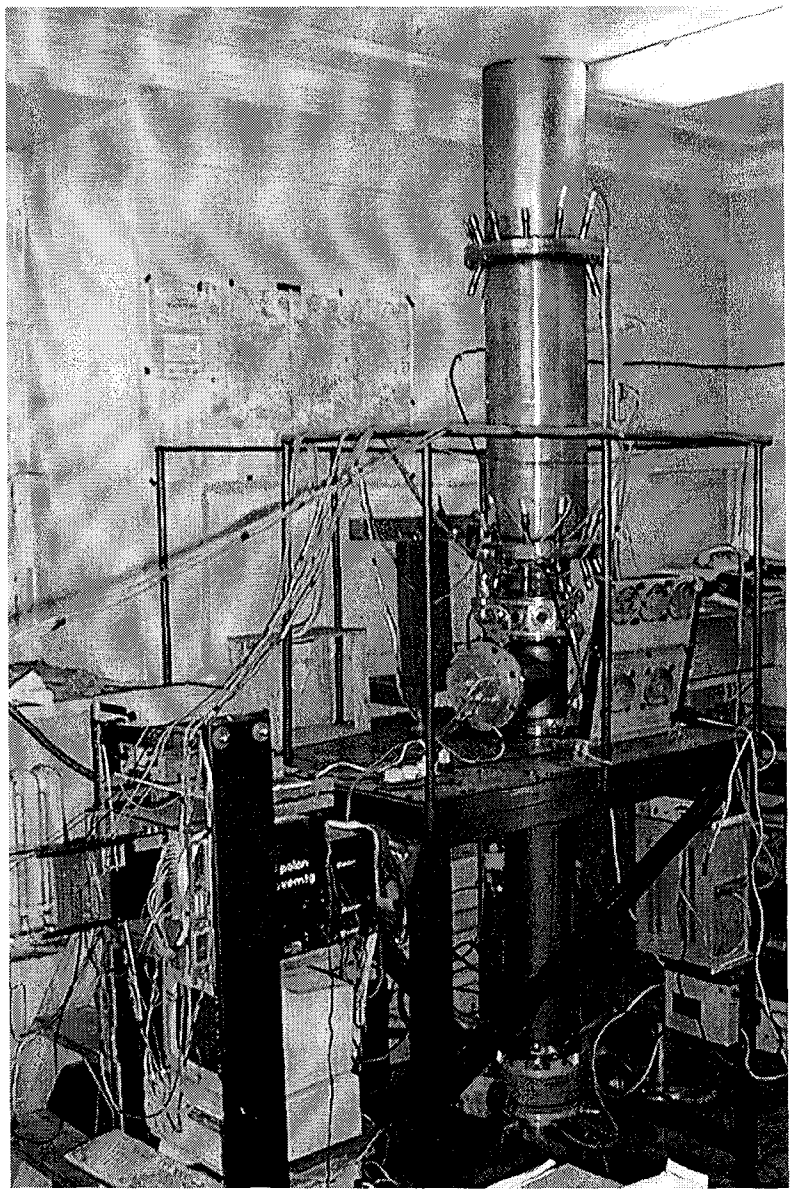


Fig. Q1.4 General view of the installation.

The design of an additional hot zone is presented on fig. Q1.5 This design is very similar to previous one used in 1 m hot zone (see our previous reports). We do not use in this hot zone inner quartz tube and electrical heater (2) is hold in place by thermoinsalation tiles (1). New hot zone was tested up to 850 °C and its good operation was observed.

The length of new cooling zone is 0.2-m longer (1.2m) than old one and has a water jacket. Gas temperature inside cooling zone is 10-15 °C that corresponds to the temperature of water from water pipeline.

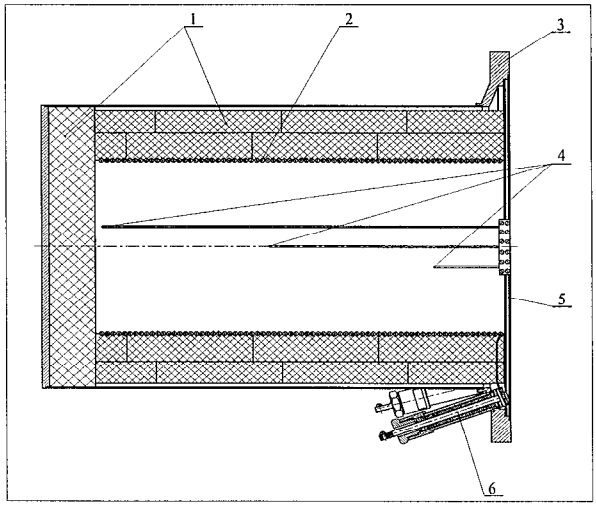


Fig.Q1.5 Additional hot zone.
1-thermoinsulation tiles; 2-electrical heater (high resistance wire in porcelain beads); 3-body; 4-thermocouples; 5-stainless steel membrane; 6-power lead in.

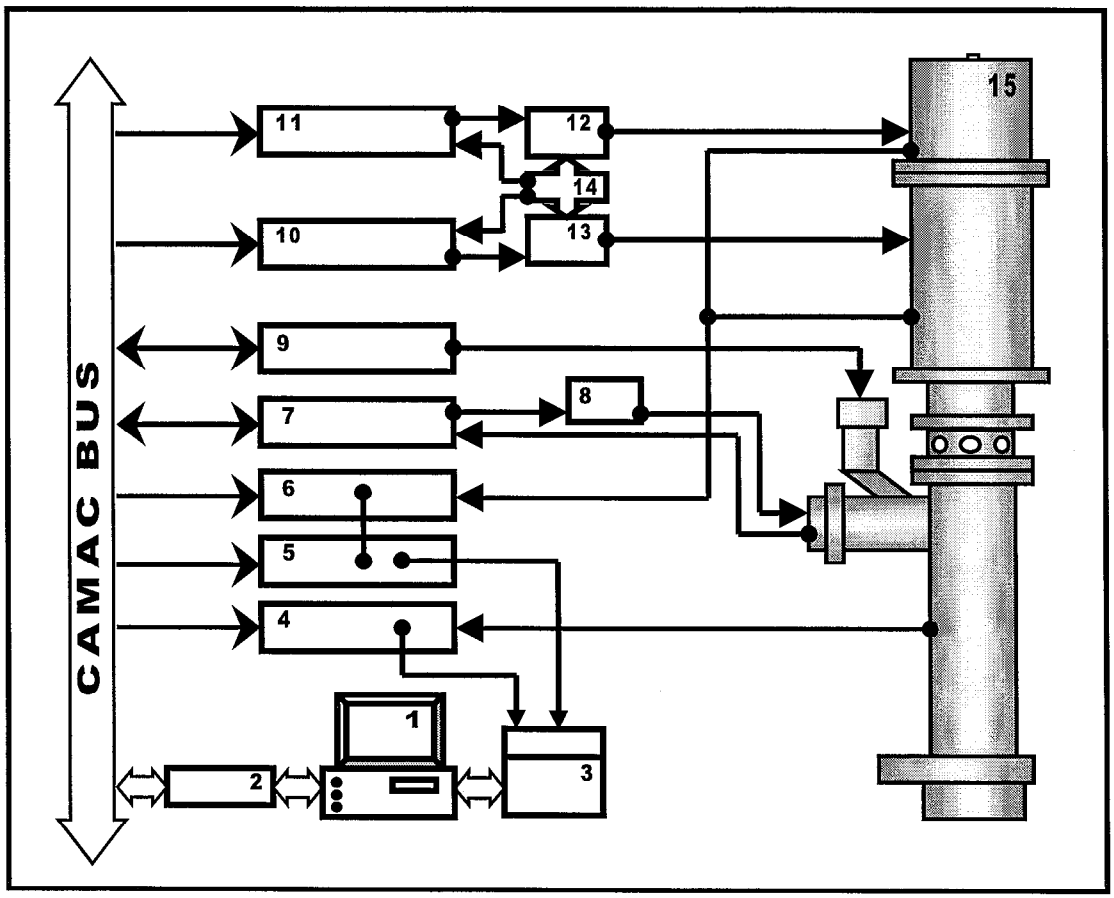


Fig. Q1.6 Schematic diagram of upgraded Ballistic Furnace control system.
1-computer; 2-crate-controller; 3-data acquisition board; 4-low temperature control unit; 5-thermocouple amplifier; 6-relay multiplexer; 7-injector control unit; 8-power switch; 9-loading device control unit; 10,11-heaters control unit; 12,13-powerful thyristor unit; 14-power supply; 15-Ballistic Furnace.

Control system for upgraded Ballistic Furnace had been changed too. Additional logic control unit (11 on fig.Q1.6) and powerful thyristor unit (13) for upper hot zone had been made and number of inner thermocouple channels had been increased up to 13. A new low temperature monitoring system (4) based on transistor sensors had been designed, built and put into operation. Using this system, we can measure temperature in seven points inside and outside cooling and injector zone. Besides that we use data acquisition board (3) in ISA standard instead of ADC in CAMAC standard. New software had been written for this control system configuration. Schematic diagram of new control system is presented on fig.Q1.6.

Q1.6.3 First shell formation experiments.

Our first experiments with upgraded Ballistic Furnace was intended to study shell formation process under conditions close to that one we have used early with 1m hot zone. The first results surprised us in unpleasant manner. Yield of good shells sharply decreased and often no good shells were obtained under conditions suitable for previous furnace configuration. It is interesting that practically in each experimental run we observed appearance of distorted shells having unusual shape. Those shells look like miniature Dewar vessel. Quantity of such specific shells was remarkable, sometimes up to ~50% of all objects produced in the experimental run. This shell's shape was observed early in our experiments with 1m hot zone very seldom. Other objects were mostly pieces of foam, broken and strongly deformed shells 1.5-2.5 mm in diameter and good small shells (0.2-1mm).

We have spent a lot of time testing different operational conditions and looking for good shells yield increasing. We varied operational temperature from 650°C to 850°C, pressure from 0.03 atm to 0.3 atm, injected granule velocity from 5.8 to 8.5 m/sec. Also in some experiments we worked with different furnace atmosphere gas composition. Initial granule used in this experiments had diameter from 0.7 to 0.8 mm. No noticeable increasing of good shells yield had been observed under any operational condition specialized above.

What conclusion could we do from extended set of experiments described here? First of all the conditions of shell formation in the upgraded furnace are essentially changed in comparison with old furnace version. The second idea – there is one (may be more than one) physical factor strongly influencing on shell formation process, that was out of our careful consideration before. Here we can point out at least two physical parameters: temperature profile inside Ballistic Furnace (especially along the hot zone) and convectional gas movement in the furnace atmosphere. As for gas movement we can not directly measure and control it. On the other hand we can easily vary the hot zone's temperature profile in a wide range.

Two last shell formation experiments were carried out with temperature profile sharply different from previous one. Both temperature profiles are shown on fig. Q1.7.

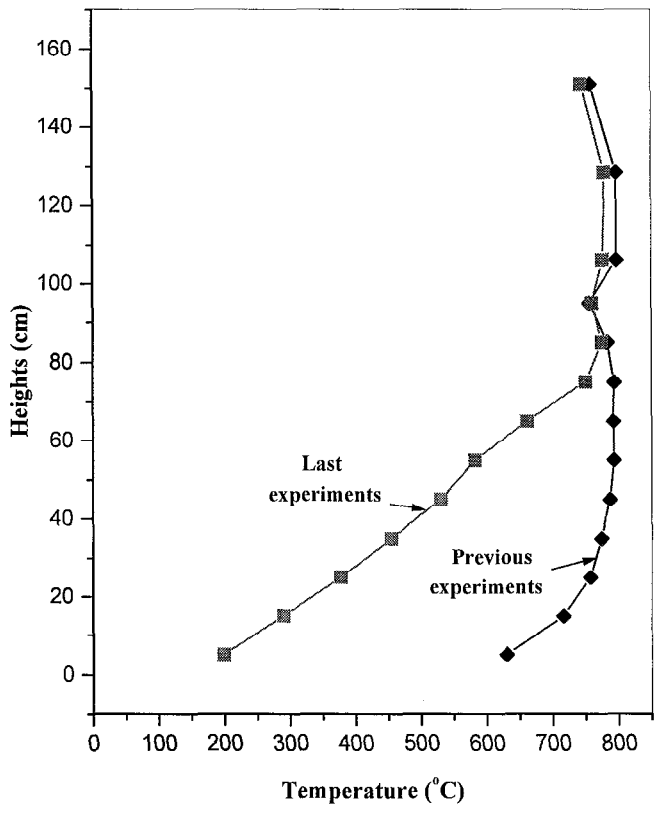


Fig. Q1.7. Temperature profile in the hot zone.

The last experiments were in opposite to previous ones notably successful. Good shells yield is increased noticeably. Good shells up to 1.9mm were produced. Pattern of produced material in an experimental run is changed. A little amount strongly deformed shells were observed. There were mostly broken and slightly distorted shells (shells with dints and undulated wall) up to 2.6 mm in diameter.

Summarizing obtained results we can make following preliminary deductions:

-change of the Ballistic Furnace configuration have led to significant changing in operational conditions suitable for shells production;

-temperature profile in the hot zone influence on shell formation process more strong than most of other operational parameters;

-apparently it is possible to produce good 2mm shells with upgraded Ballistic Furnace optimizing temperature profile and some other operational parameters;

-necessary next step for adequate understanding physics of shell formation in the Ballistic Furnace is experimental and modeling studying of temperature profile influence on shell quality, size and yield.

Q2.1 Ballistic furnace second quarter activity.

Q2.1.1 Introduction.

At 2nd quarter a lot of shell formation experiments had been carried out. In those experiments we were trying to find optimal operational conditions giving us high yield of good shells and to understand influence of operational parameters on shell's quality and size. The first problem had been solved for some grades of initial granules and second is in progress now. One small change in the ballistic furnace design had been made at this quarter. We had added computer controlled absolute manometer to measure precisely gas pressure inside the furnace.

Q2.1.2. Shell formation experiments.

The last set of experiments was intended to determine operational parameter range for production of good shells with high yield and to investigate an influence of operational parameters on shell's size, quality and yield. There are eight such parameters:

- temperature in the hot zone;
- temperature profile;
- gas pressure;
- gas composition;
- initial velocity of an injected granule;
- angle of a trajectory slope;
- initial granule diameter;
- initial granule properties (foamer content, molecular weight and so on).

Most of our experiments were carried out with smooth temperature profile. Typical temperature profiles are presented on fig.Q2.1.

Relatively small variations of the temperature profile shape did not bring on any noticeable changes in shell's yield, quality and size.

We could say the same things about maximum temperature in the hot zone. Shells with high yield can be produced at temperatures in upper part of the hot zone (see fig.Q2.1) between 750°C and 870°C and its size independent on temperature.

We were varying gas pressure in our experiments from 0.05 to 0.35 atm. The size of produced shells is slightly decreased at pressures >0.2 atm, and yield had fallen sharply at pressures below ~ 0.07 atm.

This time we have used initial granules from 0.64 to 0.75 mm in diameter with narrow size distribution of each size grade. It was surprising that size of produced shells does not depend on granule's size, furthermore sometimes average shell's size decreased for larger initial granules.

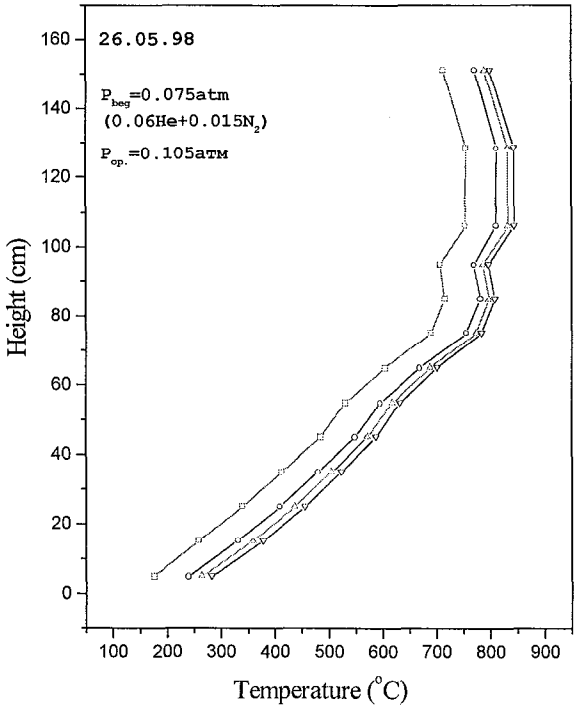


Fig. Q2.1. Typical temperature profiles inside ballistic furnace during an experimental run.

As it turned out only two operational parameters significantly influence on good shell's yield – an initial granule velocity and a trajectory angle. We could obtain high shell's yield only in narrow range of these parameters. Every time as we change initial granules diameter, we need to spend a lot of time to search new values of trajectory angle and initial velocity - to reach the highest yield.

The typical initial velocity distributions are presented on fig. Q2.2.

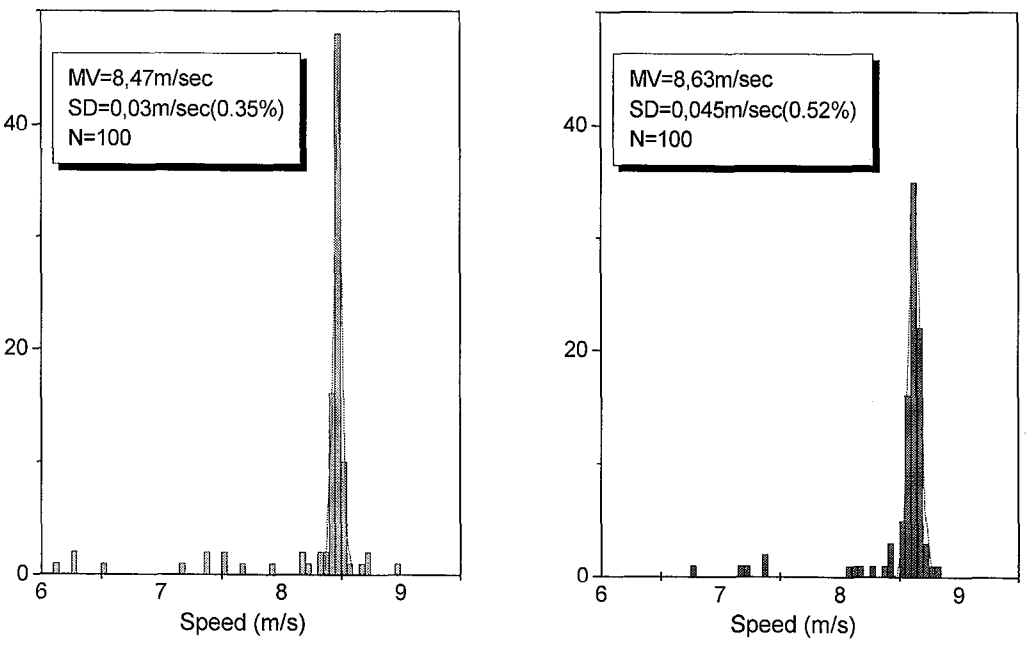


Fig. Q2.2. Typical initial velocity distributions.

0.3-0.5 percentage velocity spread corresponds to 3-5 cm trajectory heights spread. This fact indicates that shell formation at given initial velocity occur in small area of the hot zone.

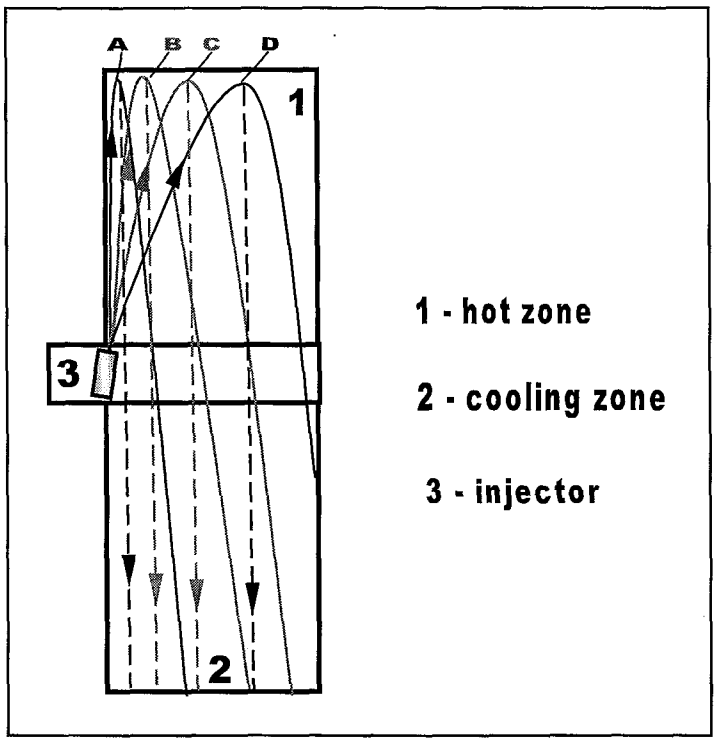


Fig. Q2.3 Possible trajectories of injected initial granules and falling shells inside the ballistic furnace.

We had observed high shell's yield only for certain trajectories (see fig. Q2.3).

We have drawn on this picture in diagram form several trajectories tested in our experiments. Solid lines define initial granules trajectories as they may be in vacuum without shell formation, dashed lines are prospective trajectories of a formed shell falling through immovable gas.

We had produced good shells with quite small yield using trajectory A. No good shells at all had been produced using trajectory B and D. Trajectory C gave us best yield but results were very sensitive to angle of a trajectory slope. At the same time deformed and broken shells 1.8 – 2.3 mm in diameter were produced with 70-90% yield (relatively number of injected granules) in all experiments with trajectory B. Almost no objets were found in the receiving cup with trajectory D.

We had obtained in these experiments good shell's yield 5-25% of injected granules or 15-80% of all objects found in the receiving cup. About two thirds of injected granules are disappeared inside furnace, we think shells formed from those granules are gone on hot zone wall. Saying "good shell", we mean shell ≥1.5 mm in diameter, which has no defects bringing out by usual optical microscope.

We would like to bring here two additional experimental observations:

- every time when we obtained high yield of good shells we observed many small shells < 1.5 mm (up to 0.1 mm);

- most of produced good shells were placed near the receiving cup edge opposite to injector.

We present here shell's size distribution for some experiments in which high yield was obtained.

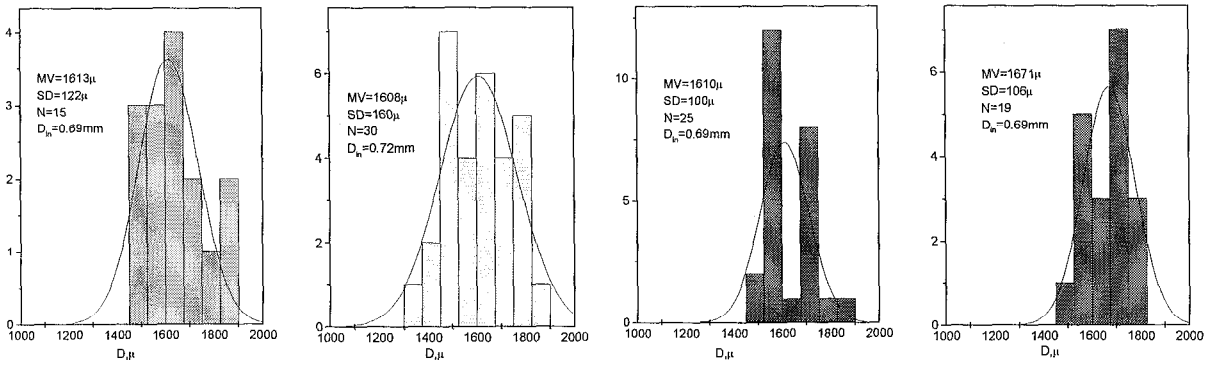


Fig. Q2.4. Shell's size distributions.

Summary distribution is presented on fig. Q2.5.

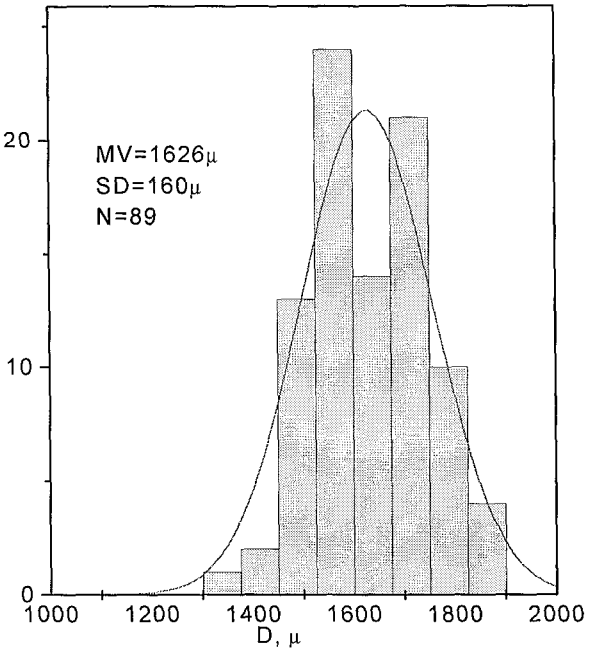


Fig. Q2.5. Summary distribution of shell's size for shells produced in several experiments.

The distributions are quite broad and mean diameters of produced shells are very close in limit of statistic deviations in spite of different operational conditions in these shell formation experiments (see fig. Q2.4 - fig. Q2.5).

Q2.1.3 Discussion.

It seems to us that some unconsidered earlier factor (or several factors) influences on shell formation process. It follows from our result presented above. Modeling calculation of shell formation process can predict final shell's size. It is interesting that this theoretically predicted size is in good agreement with our experimental results but only for bad quality deformed shells with many various defects. We can easy produce such shells with diameter 1.8-2.3mm, its mean diameter increase with initial granule diameter according to theoretical predictions. On the other hand, modern model can not explain size of good shells produced in the last experiments.

To overcome this contradiction let us consider two possible physical phenomena that may play important role in shell formation process.

In many experiments especially in experiments with high yield of good shells, we had observed a formation of small shells. Such shells can be formed from small debris of initial granule if it is bursts in hot zone being in liquid state. Quite large shell can form in this case, if initial granule is divided into two or several unequal parts. It's mass will be less than initial granule mass minus possible mass loss caused by polymer thermal decomposition in the hot zone. Broad size distributions of good shells can be explained by this process.

Existing of this effect can be proved (or disproved) experimentally by measuring mass of obtained shells (practically it means wall thickness measurement). We are going to make this measurement in our future work.

Second possible important effect – convection motion of gas in the hot zone. According to modeling calculation liquid polymer shell formed from initial granule has diameter 2.5-3.5mm in the hot zone. Our calculation have shown that maximum speed of such free falling shell in the hot gas is quite small (1-2m/sec), and it mass is small too. In this case convection flows in the hot gas can strongly influence on shell motion and remarkably increase time of shell being in hot zone. Our estimation of Grassgoff and Rayleigh numbers made for real experimental condition shown that convection gas movement can exist inside ballistic furnace. This idea has another indirect confirmation. Strong convection gas movement in the furnace for glass shell production was experimentally observed early. Position of produced shells in the receiving cup is another confirmation of the idea. According to Bernulli equation, if convection exist, it leads to two effects:

- free falling shell will move in direction perpendicular to its trajectory;
- shell will rotate around its center;

The second effect can lead to shell quality improvement.

Detailed consideration of these effects and their role in the shell formation process is in progress now.

Q2.1.4 Conclusion

In conclusion, we want to summarize the results of our activity at second quarter.

- a large set of experiments with 0.64-0.75 mm narrow size distribution initial granules was carried out and stable shells fabrication regimes for these granules fractions were found;
- a good quality shells up to 1.9 mm in diameter were produced;
- a strong influence of an initial granule velocity and a trajectory angle on good quality shells yield was observed;
- some different physical phenomena (convection and initial granule defragmentation) to explain good shell formation were considered.

Q2.2 Experiments on saturation of initial polystyrene granules.

Q2.2.1 Introduction.

The purpose of these experiments is to study the process of foamer introduction into polymer granules up to 12-16 weight percents. That could be allowed us to increase evaporation factors during microshells production. Water as a foamer agent for polystyrene initial granules had been considered too. Saturated processes for various kinds of evaporators (water, methyl acetate, ethyl acetate) in polystyrene under various external conditions had been studied. Dynamic of saturation and evaporation in polystyrene granules had been studied using the drop tower furnace.

The order of operation in our experiments was consisted of:

- preparation of initial granules;
- saturation of granules by evaporator under various conditions;
- light component control (measurement of dissolved evaporator quantity);
- obtained results analysis;
- studying of shell formation from saturated granules using the drop tower furnace.;
- experimental results analysis.

Initial polystyrene granules by the size of 0.4-0.63mm were used for experiments. We used polystyrene that was produced by our usual method. The technique of the researched evaporator is described below. Saturated material was washed by an ethyl alcohol, after that it was processed by antystatics and dried at room temperature in a flow of atmospheric air.

The small amount of a researched material was placed in glass of known mass. The glass with polystyrene was placed in the furnace under following conditions:

- the pressure is p ~ 0.01 atm,
- atmosphere composition is 50%He end 50%Ar,
- temperature T=150C. Polystyrene was maintained at this temperature during 2 hours.

We shall name these conditions **standard conditions** in our experiments.

After heating we measured mass of glass with polystyrene. Knowing initial and final significance of polystyrene mass and glass mass, we obtained loss of mass, stipulated by evaporation of boiling agent.

At the first stage the quantity of light component contained in an initial material was checked. Measurements have shown that loss of mass at heating under standard testy conditions is about 2%. At heating such material up to 300°C and under the same conditions the defect of mass has been about 3.7 %. As the main reason of inquiring defect of mass in this case, as appear, it should consider evaporation of light polystyrene fractions with more high temperature of boiling and polymer thermodestruction processes. When hot polystyrene at temperature 300°C was placed in atmospheric conditions for cooling the defect of mass has became about 20 %.

In all experiments a heating time was two hours.

Knowing the initial contents of light components we have carried out experiments on study of saturated processes of evaporator in polystyrene granules. In this experiments we used conventional chemical evaporator such as – methyl acetate and ethyl acetate and, as well as, water as an evaporator was investigated.

Q2.2.2 Water saturation of granules.

The saturation of granules by water was carried out at various pressures - from atmospheric pressure up to external one about 120atm. The saturation was carried in isolated volume. The external pressure was created by compressed Ar. Working environment was separated from a gas with a rubber membrane. The first experiments were made under the atmospheric conditions. Initial polystyrene granules were placed in isolated volume with clear water. This system was kept at room temperature T= 20°C during three dais. At atmospheric pressure the contents of water in granules was about 0.5%.

Other experiments carried out at higher pressure. Dependence of water concentration in polystyrene granules from external pressure is presented on fig.Q2.6. The saturation lasts for three days at room conditions.

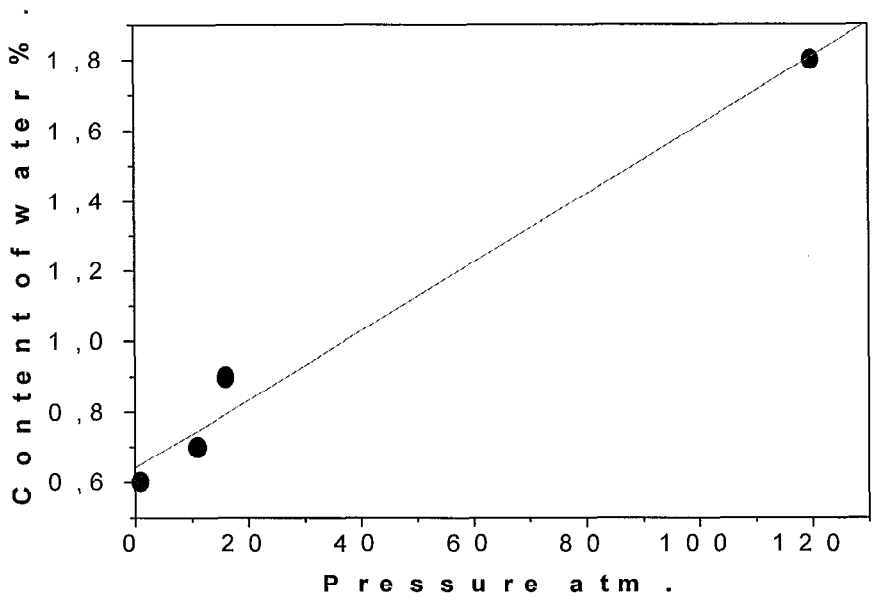


Fig.Q2.6 Dependence of water concentration in polystyrene granules from external pressure.

Control of water saturated granules evaporation has shown that coefficient of polystyrene evaporation is about 1.1, i.e. the increase of volume does not exceed 10%.

We compare results of above experiments with results of not saturated granules evaporation. This comparison has shown that shells produced from water saturated granules don't differ from nonsaturated granules.

Q2.2.3 Saturation of polystyrene granules by methyl acetate and ethyl acetate.

Usually, for initial granule saturation we use solutions of ethyl or methyl acetate in ethyl alcohol.

We investigated dependence of concentration evaporator in polystyrene granules from:

- external pressure at saturation;
- concentration of evaporator in ethyl alcohol at normal conditions;

The dependence of evaporator concentration in granules from pressure at room temperature(t=20°C) is presented on fig.Q2.7 The given content of evaporator takes into account initial amount of light components.

Analysis of experimental data confirms the assumption that solubility methyl and ethyl acetate has chemical character. Mass concentration dependence of dissolved substance from pressure is $\sim p^{1/2}$, where p – external pressure

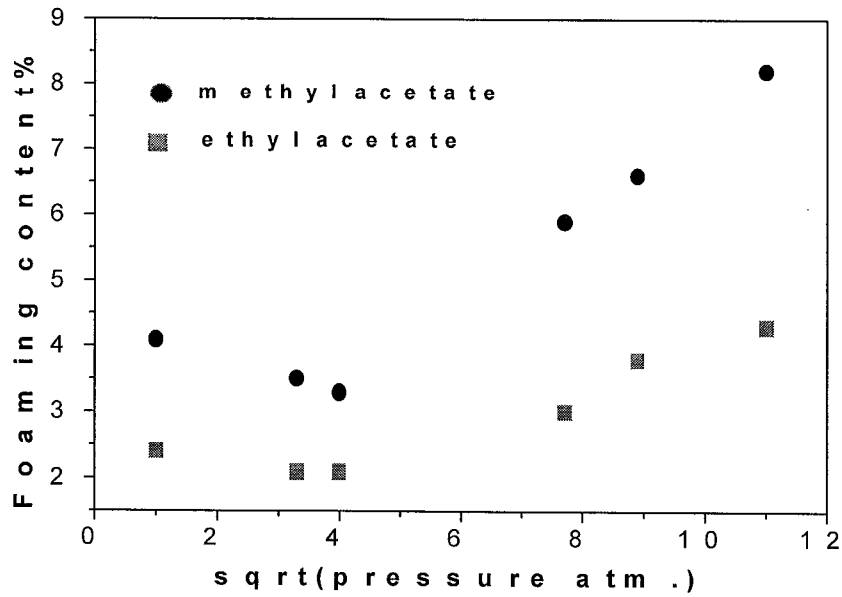


Fig.Q2.8 Results of experiments on study of dependence of evaporator concentration in granules from pressure at room temperature (t=20°C).

Saturation of polystyrene at various concentration of methyl acetate in alcohol solution and various pressures is presented on fig.Q2.9.

The quantities of evaporator saturated in polystyrene for different times are presented in tab.Q2.1

Tab.Q2.1.

Pressure atm.	1atm	80atm
24 hours	4.1%	6.3%
48 hours	4.2%	6.3%

From this results one can see that saturation during three days is enough for equilibrium concentrations evaporator in granules.

We considered only water content in the analysis of water solved process. Crossing of water concentration dependence from pressure with Y-axis (see fig.2.9) will give us an amount of light component in initial granules, that will be in good agreement with experimental meaning of 2 %.

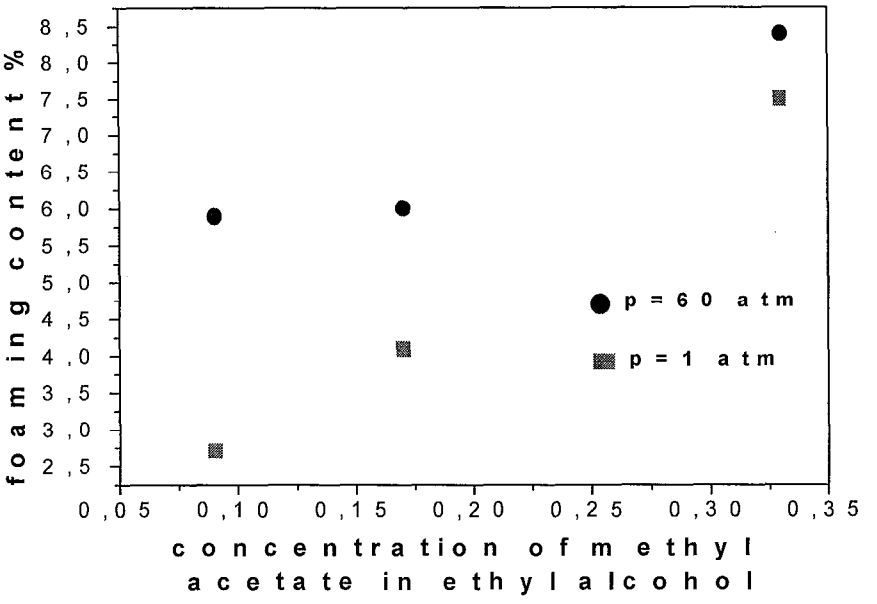


Fig.Q2.9 The equilibrium concentration in systems methyl acetate – ethyl alcohol – polystyrene is shown.

In the analysis of chemical solubility we took into account total amount of evaporator in saturated granules. The experimental data give the square-law dependence of total concentration evaporator from pressure. This fact show that initial light component is dissolved in polystyrene chemically.

We have also checked influences of argon on the saturated process of evaporator in polystyrene. Ar saturated some amount of granules at pressure 120atm. during 3 days. The same amount of initial material was used. Heating process show equivalence of mass loss in each probe. Changes of polystyrene volumes were equal too (about 10 %).

Results of experiments have shown weak influence of the external pressure creating gas on the process of saturation.

Q2.2.4 The influence of evaporation agent concentration on the foaming temperature.

A set of experiments was carried out to study the influence of concentration evaporated agent on polystyrene foaming temperature. For this purpose we drop methyl acetate saturated and nonsaturated granules (fraction 0.5 - 0.63 mm) in a furnace at standard operation conditions (the length of hot zone is 1m; pressure 0.1atm of 50 % He and 50 % Ar).

The experiments were carried out at temperatures 500°C, 550°C, 600°C and 650°C.

Experiments have shown, that the foaming process of saturated material begins at the temperature about 550°C, while non-saturated - at 650°C. Quantity of foaming granule against temperature is shown on fig.Q2.10

The content of foaming granules includes all kinds of particles:

- spherical monoshells;
- spherical foam particles;
- nonspherical foam particles.

The measurements have shown that the temperature of polystyrene foaming turns on the quantity of evaporator agent. From fig II.4. it can be seen that the temperature of foaming is lowered with increasing of evaporator concentration.

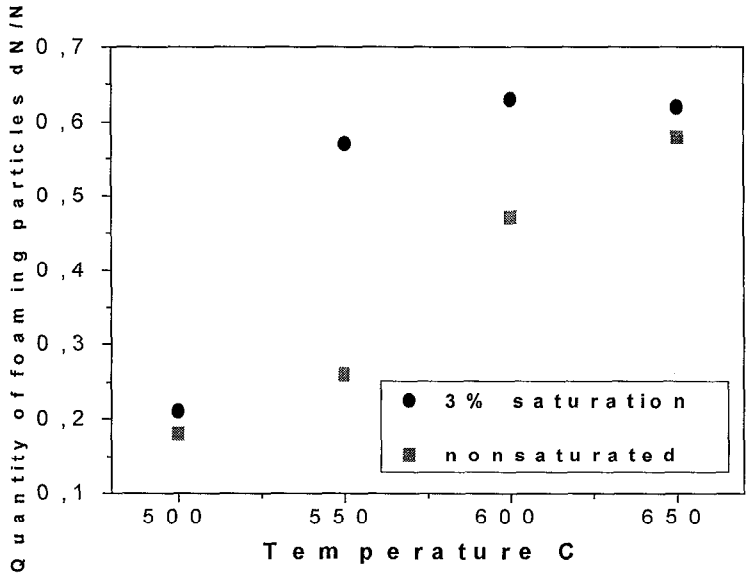


Fig.Q2.10. Dependence of a boiling granule content from temperature is shown.

Q3.1 Ballistic furnace third quarter activity.

Q3.1.1 Introduction.

At third quarter a few of shell formation experiments had been carried out. Operational conditions were maintained in these experiments close to optimal ones and many good shells were produced in several last experiments. However maximum diameter of produced shells was ~1.9mm. Main attention had been paid to analysis of results obtained in these experiments and early ones. We were trying to understand physical processes in the ballistic furnace during shell formation.

Q3.1.2 Shell formation experiments.

The last set of experiments was intended to compare results for several initial granule grades. We have used the next series of initial granule diameters: 0.62, 0.67, 0.69 and 0.73mm. Methyl acetate had been used as a foamer. Its weight content was about 3%. Initial granules size distributions for three grades are presented on fig. Q3.1.

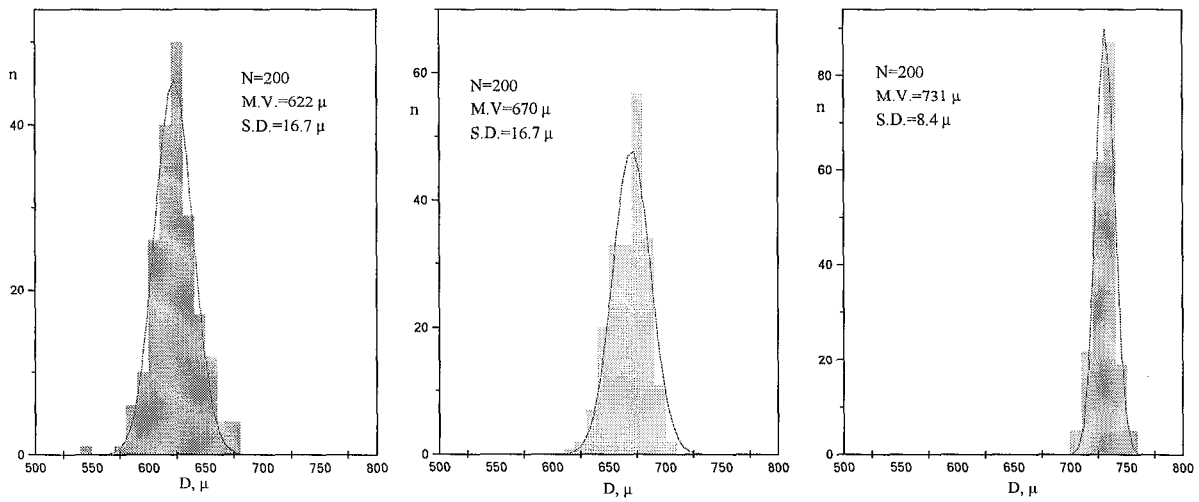


Fig.Q3.1 Initial granules size distributions for three granule grades.

These experiments were carried out with smooth temperature profile. (Typical temperature profile curves one can see on fig I.1 in our previous report.) Temperature in upper part of the hot zone was between 780°C and 860°C in all experiments.

Pressure was maintained about 0.1atm. Furnace atmosphere was composed of 75% He and 25% N_2. We slightly varied this proportion (±20%) in some experiments but we didn't notice any influence on the result.

Initial velocity of injected granules was 8.5-8.9 m/sec. Its optimal value was different (in this range) for different granule size. Pointed above figures are correspond to 3.7-4 m (almost two times more than the hot zone size) of trajectory height, supposing the granule moves through vacuum. However, there is no experimental evidence that they reach the hot zone top moving in the furnace atmosphere. On the other hand, granules or very likely partially formed liquid shells at higher initial velocities are reached hot zone top, touched thermoinsulation and most of them gone on. In this case, good shells yield is decreased sharply and a small amount of deformed shells with tiny pieces of thermoinsulation melted into the wall material are observed. (Thermoinsulation of the hot zone top is a porous brick made from a very thin quartz fiber pressed

together by special technology. This material is quite soft and small pieces of a quartz fiber can be easily picked off from its surface.)

Trajectory angle was set near its optimal value.

Q3.1.3 Experimental results.

Many good shells were produced in every experiment (except experiments with 0.73mm granule fraction). Total yield was 80-150 good shells in a day in our last experiments. We mean that "good shell" has no defects visible under usual microscope and its diameter ≥1.5mm.

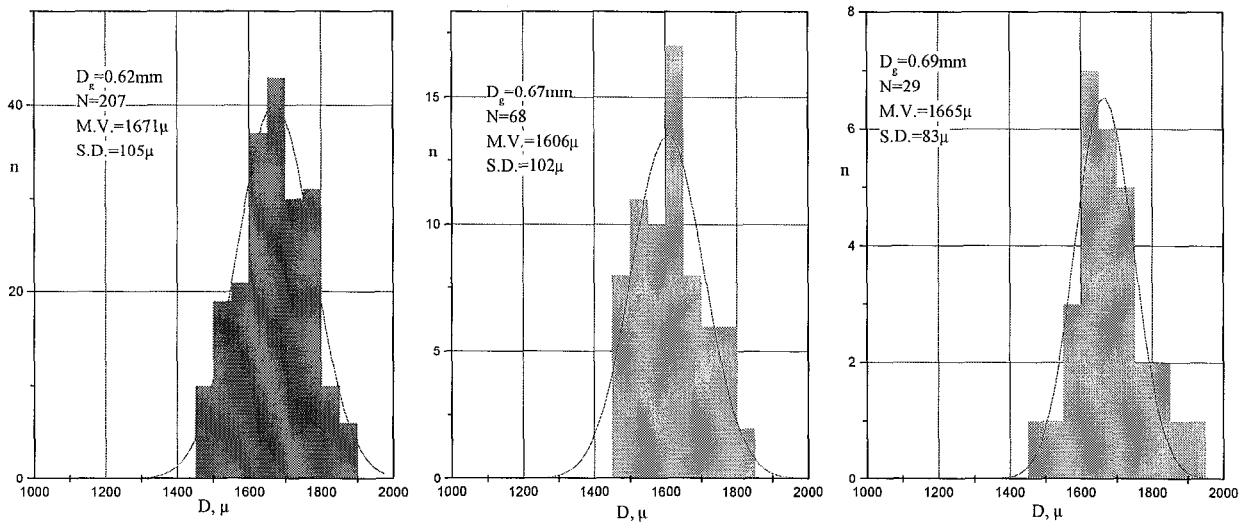


Fig. Q3.2. Shell size distribution for shells produced from different initial granule grades.

Shell diameter distributions are presented on fig. Q3.2. As one can see from figure, there is no difference in limits of statistic between diameters of shells produced from different initial granule. We don't present here shell size distribution for shells produced from 0.73mm granules because of low statistic, but its mean diameter is in the same range. It is surprising fact because difference in mass between 0.62mm and 0.73mm granule is about 60%.

Good shells yield is remarkably depended on initial granules size, though we were trying to keep up an operational conditions close to optimal ones in any case. Figures are presented in table Q3.1.

Table Q3.1. Shells yield in experiments with different granule grades

Granule diameter	0.62mm	0.67mm	0.69mm	0.73mm
Good shell yield	30-35%	20-25%	10-15%	≤5%

We didn't measure wall thickness of produced shells, but there is indirect confirmation that average wall thickness may be change with initial granule size. We have observed in the collection cup after the experiment much small debris together with shells. Such debris may be appeared because of some shells destruction under outer atmospheric pressure. The higher initial granule size, the less amount of debris in the collection cap. It could be explained by increasing of shell wall thickness with the initial granule diameter.

We have tried in several experiments to change pressure in the collecting cup from operational to atmospheric very slowly (during 0.5-1 hour). We hoped to increase average shell size by this method. Large thin shells could be destroyed by inner-outer pressure difference, if pressure in the collecting cup is increased fast. In the case of slow pressure increasing gas have enough time to permit into the shell through its wall by diffusion and outer - inner pressure difference is kept low during collection cup filling. Unfortunately, one hour is not enough time to decrease remarkably pressure difference at room temperature. We didn't notice any reliable average shell size increasing in these experiments.

We have roughly measured increment of pressure grows into the shell caused by air diffusion at room temperature. We have crushed shells in liquid and measured diameters of gas bubble. The first test was made just after collection cup opening and was repeated two times later. In every test, we have crushed several shells made in the same experiment. The results are presented on fig. Q3.3. Of course, precision of such measurements is quite poor, but it gave us reasonable estimation of time increment.

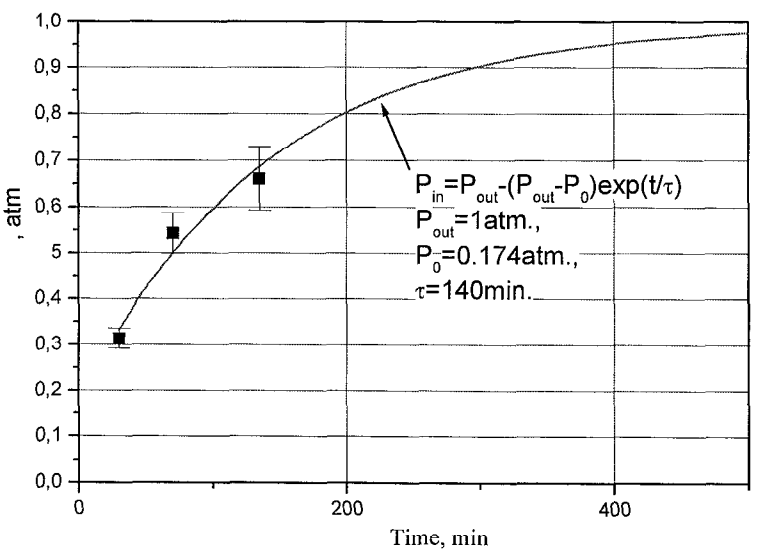


Fig. Q3.3. Growth of shell inner pressure on air with time. (Squares – results of measurement, solid line – fit according to expression presented on figure.)

Measured characteristic time is ~140min – too much for real experiment. We cannot spend more than two hours for one experiment. There is apparent possibility to lower this time. We must heat shells in the collecting cup during filling up to 60-70°C to increase gas permeability of shell's wall. We plan this experiment in near future.

We want to point out here another interesting experimental observation. Most of good shells with high probability were located in small area near the edge of the collection cap opposite injector. We have observed this tendency earlier, but good shells yield in last experiments was higher and the tendency come out clear. This observation is in collision with model of shell formation in an unmovable gas.

Q3.1.4Discussion.

It seems to us that there are two essential questions in the problem of shell formation.

1. Results of our experiments (last and previous) lead us with high probability to the conclusion that convectional gas movement in the hot zone plays important or even determinative role in formation of good shell.

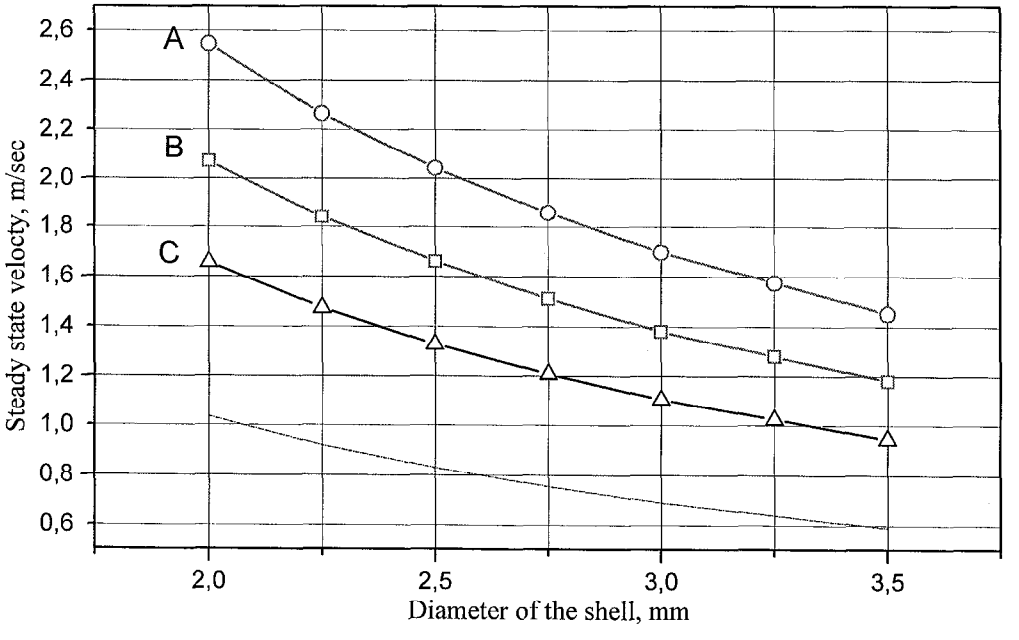


Fig.Q3.4 Velocity of free falling shell in a hot gas

2. Very high mass loss has been observed in shell formation experiments. In all

probability the main reason of this is granule defragmentation during blowing (may be before blowing).

Let's consider the questions in detail. First, let us estimate how strong can the influence of gas currents in the furnace on a shell movement be? We have calculated the velocity of free falling shell in a gas for several cases (see Fig.Q3.4).

Steady state velocity V of free falling shell in unmovable gas is described by following expression:

$$V = \frac{\rho d^3 g}{36 \eta R} \qquad (1)$$

ρ = 1g/cm^3 – polymer density, d – diameter of granule from which shell was formed, g – gravity constant, η - dynamic viscosity of a gas ($\eta \approx 450 \cdot 10^{-6}$ g/cm·sec for mixture of He and N_2 at 800°C), R – shell radius.

Curve A on fig.Q3.4 corresponds to shells formed from 0.75 mm initial granule, B – 0.7 mm, C – 0.65 mm. We didn't take into account any mass loses for these three cases. Dashed curve corresponds to 50% mass lose for 0.7 mm initial granule.

It is seen from the figure, that shell velocity can be quite small. The next question - is there any condition for gas currents appearance in the hot zone? Let us consider this questions from physical and engineering point of view.

Physical considerations:

- if the temperature along a gas filled vertical tube with closed top (this is a simplest model of the ballistic furnace) is constant or increase monotonously from bottom to top, any gas motion is absent;
- temperature field can be easily calculated in this case using two-dimensional equation of thermoconductivity;
- if there are zones, where temperature decrease with heights in some parts of a tube, appearance of any convectional flows becomes possible;
- convectional flows is started when Rayleigh number achieve a given value (different for different gas composition);
- different type of a gas motion (modes) is possible. Character of gas flows (mode number) depends on Rayleigh and Grassgoff numbers;
- in the simplest case gas movement has axial symmetry - gas flow up along the hot walls and flow down in the center.

Engineering consideration:

- thermoinsulation in the hot zone is quite good, but nonideal of course (temperature on the outer wall is about 150°C, when temperature inside is 850°C);
- heaters is distributed evenly on lateral wall, but there is a small gap (~3cm) between the old part of the hot zone and additional one;
- there is unavoidable way to additional heat lose through supporting metal membranes in the same place;

- another important place for a heat drain – top of the hot zone, where is no heaters;
- during experiment we feed hot zone by 5-10 kWa of an electrical power. This is high figure in comparison with entalphy of gas at low pressures (~0.1atm);
- direct measurement of a temperature profile in the hot zone shows two places with inverse vertical temperature gradient (hot zone top and old-new zone connection).

Based on the reasons presented above the next conclusion could be done.

There is enough energy inside the hot zone and several places with inverse thermal gradient to force a remarkable gas movement. Existing of gas flows with velocity ~1m/sec or higher can essentially change shell formation condition in the ballistic furnace.

Full system of hydrodynamic equations describing convectional gas movement in the furnace is highly complicate, and can be solved only in numerical form in our case. Moreover, we guess it makes a little sense to do it, because not all-necessary parameters can be experimentally measured now.

We will try to show below existing of convection in the furnace and to estimate roughly possible range of gas current velocity using simple reasoning and approximate expressions. Firstly, let us estimate some non-dimensional criteria concerned with convection - Grassgoff (Gr), Rayleigh (Ra) and Prandtl (Pr) numbers.

$$Gr = \frac{\beta g z^3 \Delta T}{\nu^2} \qquad (2)$$

$$\Pr = \frac{\nu}{a} \qquad (3)$$

$$Ra = Gr \cdot \Pr \qquad (4)$$

where β is coefficient of volume dilation (in our case its value is close to one for ideal gas $\beta=1/T$); g – gravity constant; ν - kinematic viscosity; z – distance in vertical direction; ΔT - temperature difference (for typical experiment $\Delta T \approx 20°C$ at z = 20 cm); a - temperature conductivity.

In our case $Gr \approx 100$, $Pr \approx 0.8$, $Ra \approx 80$. The solution of system of convectional equations for simple cylindrical case is presented in [6]. The critical Rayleigh (Ra) number according to this solution is 68. It shows actual existing of convectional instability in the ballistic furnace. Let us highly approximately estimate possible gas velocity. There is known solution for vertical plate in non restricted media [7].

$$V = \left[\frac{\beta g \Delta T}{4\nu^2}\right]^{1/4} \cdot 4\nu z^{-1/4} \varphi \qquad (5)$$

where φ is non-dimensional numerically calculated parameter [7] ($\varphi_{max} \approx 0.27$ in our case). This expression gives us $V_{max} \approx 4.5$ m/sec (maximum velocity is reached at 1/3 of width of boundary layer $\delta \approx z \cdot Gr^{1/4} \approx 60$cm). Apparently, this

value may be only the upper estimation, because the estimated width of boundary layer is broader than the hot zone.

We clearly understand that our estimation is very rough, however if even there is a ten-fold error in the worse case, the convectional gas velocity is high enough (comparing with data from fig.Q3.4) to change significantly condition of shell formation.

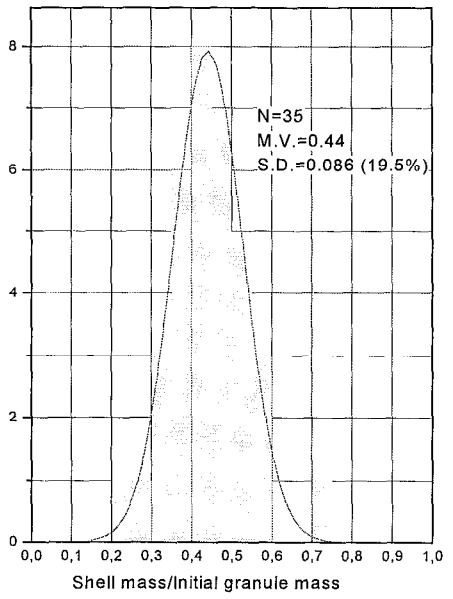


Fig.Q3.5 Mass distribution of produced shells.

The second question is mass losses during shell formation. The mass distribution of shells from last delivery according LLNL's data is presented on fig.Q3.5. It looks like quite narrow Gaussian distribution. In principal this curve could be explained by both models – blowing granule fragmentation and polymer thermal decomposition. To our opinion, it is impossible to explain existing of solid, transparent and quite strong polymer after losing more than a half of its mass.

Model of granule defragmentation looks more adequate. Additional confirmation of the model is appearance of small shells together with larger ones in almost every successful shell formation experiment. However, the moment of defragmentation is unknown for the present. It could be occur directly in the moment of blowing or before it. For example, granule could be destroyed being in solid stage by thermal stress. It is very important to understand - how can we depress the granule fragmentation? May be the experiments with granules produced by differing from routine LPI's method or with granules, containing less amount of foamer could answer this question.

There is another important point in the problem of large shells production concerned with abnormal high mass loss. The wall thickness of produced shell can

be quite small considering high mass loss. The last LLNL measurements gave wall thickness range 5-12μ. Thin large shells could be destroyed under outer pressure by stability loss. Critical pressure of destruction for ideal spherical symmetric thin-walled shell can be determine by the next expression:

$$P_{critical} = \frac{2E(\Delta R)^2}{R^2\sqrt{3(1-\xi^2)}} \qquad (6)$$

where E – modulus of elasticity; ΔR – wall thickness; R – shell radius; ξ - Pousson coefficient. This expression gives upper value of destruction pressure.

If ΔR=5μ and R = 1mm, E = $0.255 \cdot 10^{10}$ N/m^2 (data from [8]) and ξ = 0.3 $P_{critical} \approx 0.75$ atm. There is nothing ideal in the world, so critical pressure for real shells must be lower. Just after formation pressure inside shell is about 0.15-0.3 atm (depend on operational conditions), so inner-outer pressure difference is 0.7-0.85atm after receiving cup opening and the shell can be destroyed in this case. It means that large shells could be formed in the experiments, but they are destroyed by outer pressure during receiving cup air filling and opening. Noticeable amount of small debris observing in every experiment confirms this suggestion.

To avoid the problem we are planning to carry out slow receiving cup air filling experiments with it's simultaneous warming.

Q3.1.5 Conclusion

In conclusion, we want to summarize the results of our activity at third quarter.

- a set of experiments with 0.62-0.73 mm narrow size distribution initial granules was carried out
- a good quality shells up to 1.9 mm in diameter were produced with high yield in every experiment;
- the velocity of possible convectional gas currents in the hot zone is estimated;
- deduction about initial granules fragmentation based on shell mass date is made;
- strength of formed shells is estimated and proposals how to conserve larger shells are presented.

4.1 Ballistic furnace fourth quarter activity.

Q4.1.1. Introduction.

At 4th quarter a set of shell formation experiments had been carried out. Operational conditions were maintained in these experiments close to optimal ones and many good shells were produced. Slow gas filling of the collection cup had been employed in several experiments to avoid large shell destruction under inner-outer pressure difference. However mean diameter of produced shells wasn't increased remarkably, though a few shells about 2mm had been produced in these experiments. We continue to analyze possible reasons of the shell's mass loss. Calculations of elastic stress in the initial granule caused by thermal shock are presented in this report.

Q4.1.2. Shell formation experiments.

The last set of experiments was intended to produce shells with maximum diameter. We have used several grades of 0.67-0.72 mm initial granules. This granule's size was chose based on previous results. Among shells produced previously from smaller initial granules fewer large shells had been observed (we mean here shells with diameter >1.8 mm), though shell's yield was high. Shell's yield decreased dramatically for >0.75 mm initial granules, but shell's size didn't grow remarkably. It seems to us pointed above granule's size is optimal. Methyl acetate had been used as a foamer. Its weight content was about 3%. We don't present here initial granules size distributions because they were very similar to another ones presented in previous reports.

These experiments were carried out with smooth temperature profile. Temperature in upper part of the hot zone was between 810°C and 860°C in all experiments.

Pressure was varied from 0.06 to 0.13 atm. Best results were obtained at 0.07 – 0.08 atm. Furnace atmosphere was composed of 75% He and 25% N_2.

Initial velocity of injected granules was 8.5-8.8 m/sec. These figures are corresponding to 3.7-4 m (almost two times more than the real hot zone size) of trajectory height, supposing the granule moves through vacuum.

Trajectory angle was set near its optimal value.

Many good shells were produced in every experiment. Total yield was 50-100 good shells in a day. We mean that "good shell" has no defects visible under usual microscope and its diameter ≥1.5mm. Unfortunately only a few shells have diameter more than 1.9 mm. Mostly such shells were formed at furnace pressure ~ 0.07 – 0.08 atm. Results were worse at lower and higher pressure. Photos of four large shells are presented on fig. Q4.1.

We raise pressure in the collecting cup in several experiments very slowly (~24 hours from operating pressure to atmospheric). This method allows us to

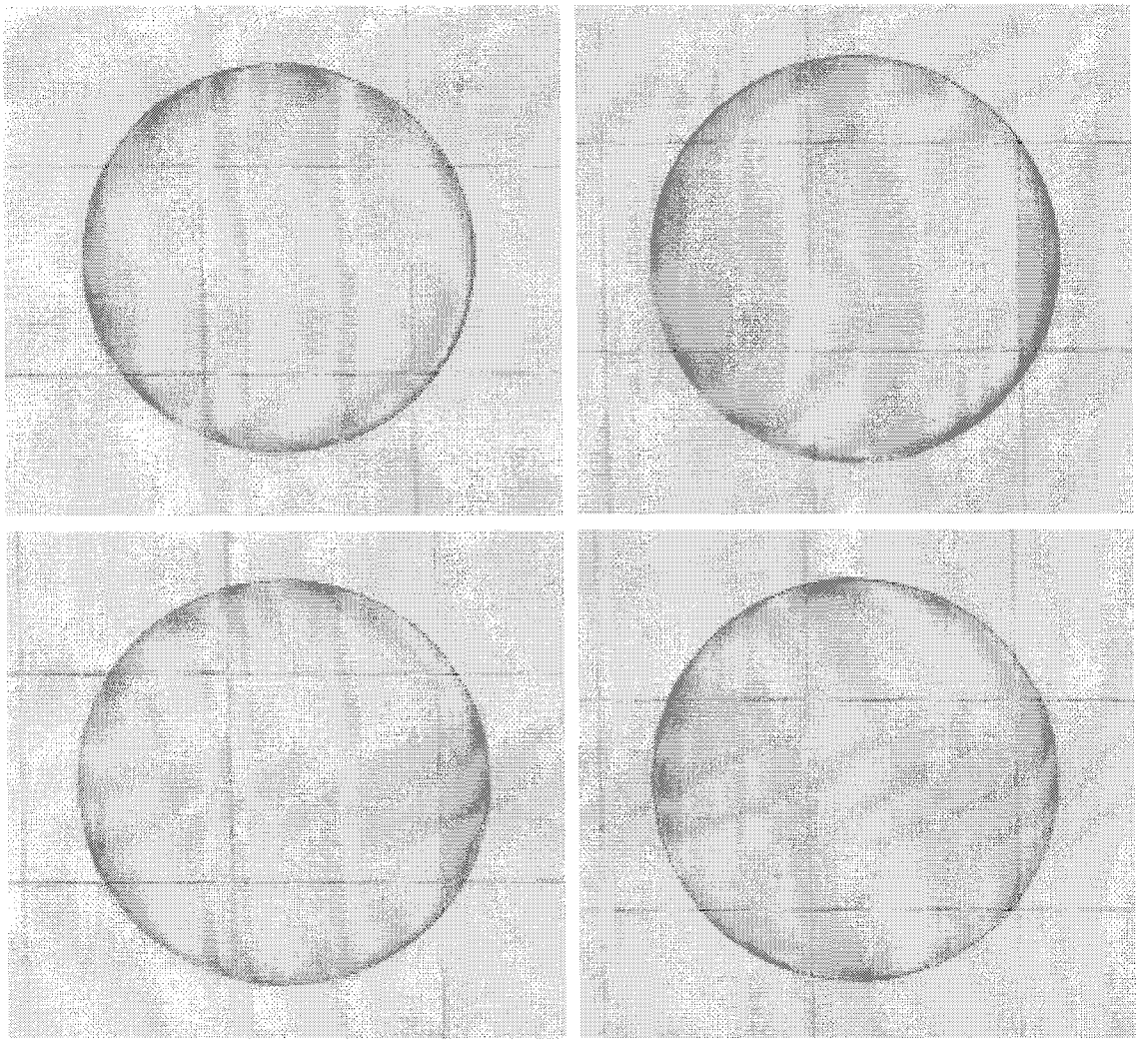


Fig.Q4.1. Large shells produced in the last ballistic furnace experiment. Diameters of these shells are 1883, 1972, 1971, and 1916 μ. One division of scale is equal to 1 mm.

protect thin shells from destruction by inner - outer pressure difference. We have measured roughly critical outer pressure (P_{cr}) for 1 – 1.5 mm shells. Results are presented on fig. Q4.2. High spread of P_{cr} is observed and P_{cr} mean value is low enough. P_{cr} for larger and thinner shells can be less than 1 atm because it depends on aspect ratio (A) as A^{-2} (for ideal sphere). It must be lower for shell with any defects.

Just after formation pressure inside shell is 0.1 – 0.3 atm (exact figure depends on operating pressure, temperature, temperature profile and so on), and measured increment of pressure grows into the shell is ~140 min (see our previous report). So time of filling in these experiment was long enough to save all formed shells.

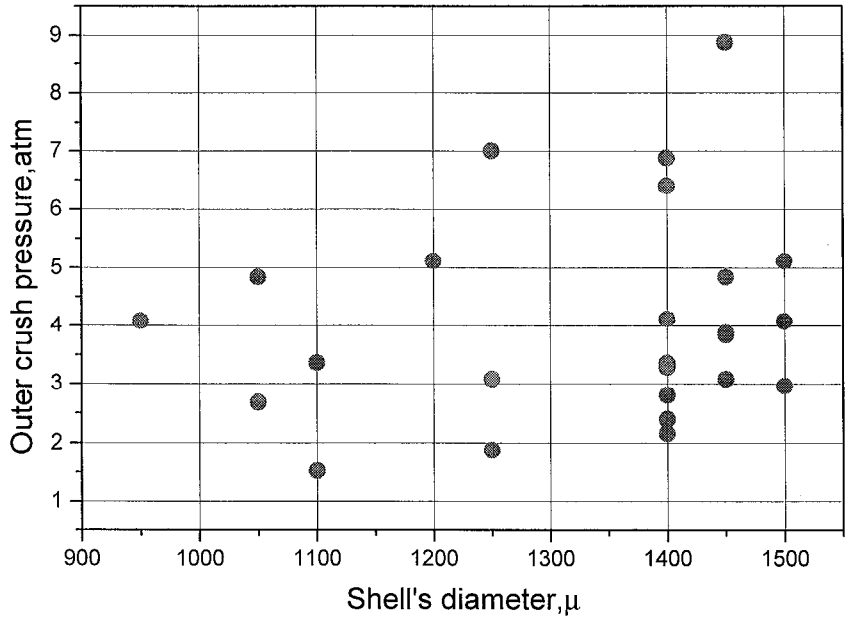
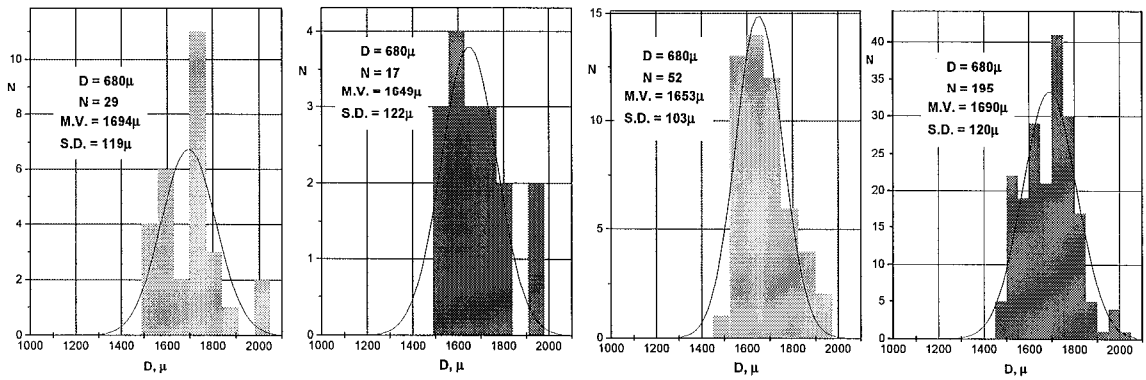


Fig.Q4.2. Critical outer pressure for ballistic furnace shells.

Results of experiments with slow gas filling were interesting, though unfortunately amount of largest shells increases insignificantly. The largest produced shell without defects had diameter about 2 mm.

Size distributions of shells produced in several experiments are presented on fig.Q4.3.



1 2 3 4

Fig.Q4.3. Shell size distribution observed in different experiments.
1 - usual experiment; 2,3 – experiment with slow gas filling; 4 – summary distribution for shells produced in all experiments.

As one can see from the figure, there is no difference in limits of statistic between mean diameters of shells produced in different experiments. Looking on these graphs more carefully it seems qualitatively that right part of the distribution

(larger shells) on graphs 2 and 3 more "fat", than on graph 1. Anyway, difference is too small to make any solid conclusion.

On the other hand, slow gas filling experiments seems to us interesting because a remarkable amount almost perfect 2 – 2.5 mm shells had been produced. These shells have spherical shape, smooth surface and no visible defect excepting one or several smooth dents on one side (see fig.Q4.4). Such dents could be brought about by inner - outer pressure difference while shell is in a state of high viscosity before solidification.

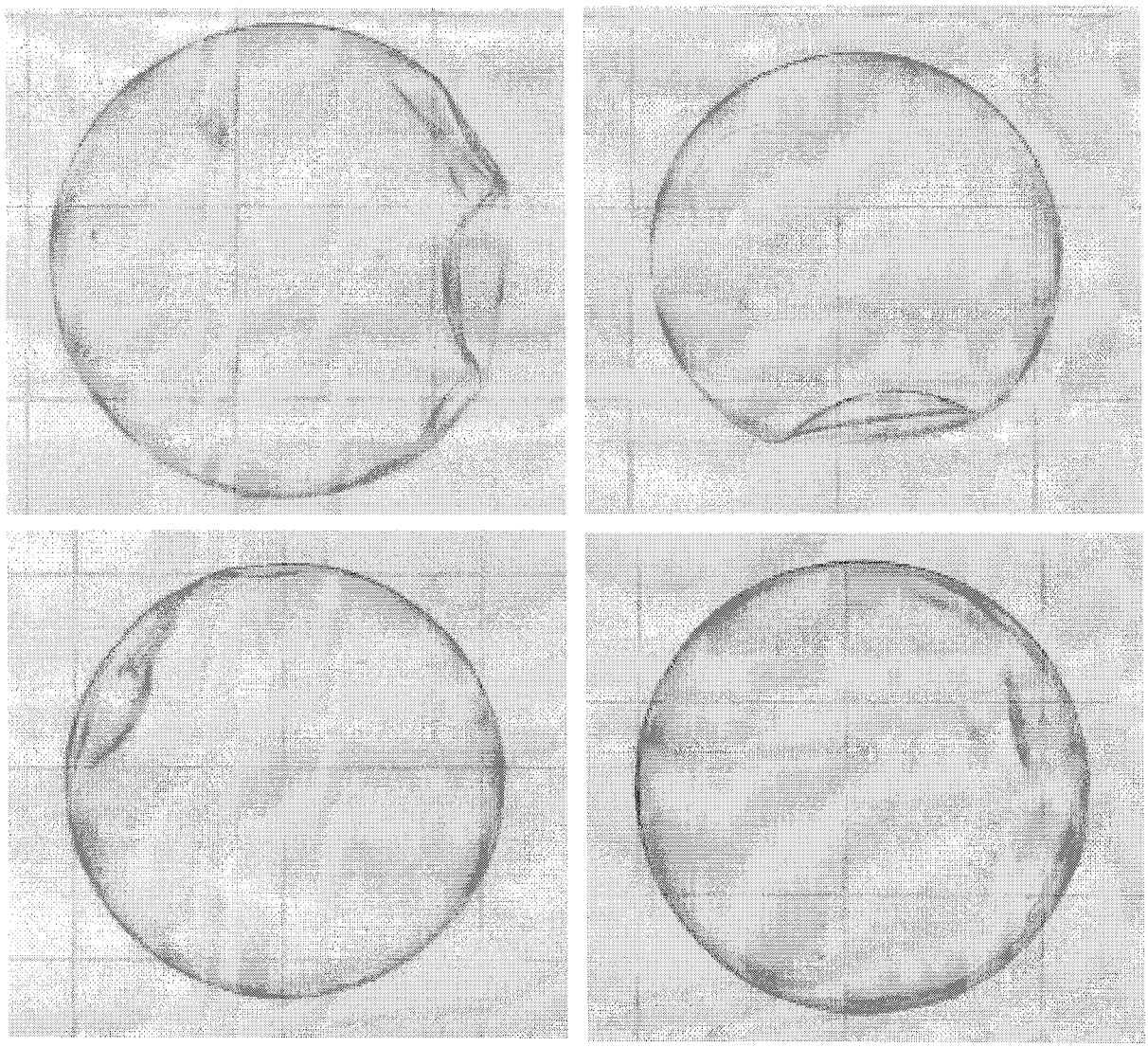


Fig.Q4.4. Large deformed shells produced in slow gas filling experiments. One division of scale is equal to 1 mm.

We observed similar shells in previous experiments quite seldom and considered its as accidental fact. Actually all they were destroying by outer

pressure during collection cup filling. Based on the last experiments we can conclude that appearance of such shells shows general rule.

Apparently such kind of shell deformation could be caused by small inner – outer pressure difference at temperatures near polymer solidification temperature (glass transformed point at T≈85°C). At higher temperatures gas diffusion through shell's wall is fast enough to match inner pressure according outer. At lower temperatures polymer becomes strong to prevent deformation.

There are several possible ways to avoid this problem:

- to increase a helium content in the furnace gas mixture to force diffusion processes;
- carefully adjust temperature profile in a lower part of the furnace;
- to lengthen cooling zone;
- to create a weak upward gas flow in a lower part of the furnace to decrease vertical velocity of a falling shell.

Another methods could be applied too. In any case, we need to pay more attention to processes taking place during formed shell cooling.

Q4.3. Initial granule defragmentation by thermal shock.

We have performed calculations of elastic stress arisen into an initial granule during its fast heating. This problem is relatively simple and can be solved exactly.

Solution is based on equilibrium equation (see for example [9]):

$$(\lambda+\mu)\text{grad div } \mathbf{u} + \mu\Delta\mathbf{u} - K\alpha\text{grad } T = 0 \qquad (1)$$

where T – temperature; **u** – vector of displacement; K – module of volume compression; α - coefficient of thermal expansion; λ and μ - coefficients in generalized relation between deformation tensor and stress tensor.

Our problem is one-dimensional (all variables depend on r only) and spherically symmetric, so we can rewrite (1) in spherical coordinates using ordinary derivatives:

$$\frac{d}{dr}\left[\frac{1}{r^2}\frac{d}{dr}(r^2 u)\right] = \frac{d}{dr}\left(\frac{K\alpha}{\lambda+2\mu}T(r)\right) \qquad (2)$$

Connection between vector of displacement and radial component of stress tensor is giving by the next relation:

$$\sigma_{rr} = \lambda\text{div } \mathbf{u} + 2\mu\varepsilon_{rr} \qquad (3)$$

where ε_{rr} – radial component of deformation tensor.

K, λ and μ can be express through elasticity module E and Poisson's coefficient:

$$K = \frac{E}{3(1-2\nu)} \qquad \mu = \frac{E}{2(1+\nu)} \qquad \lambda = \frac{\nu}{(1-2\nu)(1+\nu)} \tag{4}$$

We can get elastic stress radial dependence σ(r) now from (2) – (4). Skipping evident details of calculation, we shoe the final common solution:

$$\sigma(r) = \frac{\alpha}{3}\frac{1+\nu}{1-\nu}E\left\{\frac{1-\nu}{(1-2\nu)(1+\nu)}[T(r)-T(R)] + \frac{1}{2(1+\nu)}\left[\frac{1}{R^3}\int_0^R r^2 T(r)dr - \frac{1}{r^3}\int_0^r r'^2 T(r')dr'\right]\right\} \tag{5}$$

In the case of linear temperature grows from granule center to its edge (grad T = const) (5) can be reduce to:

$$\sigma(r) = \frac{E\alpha(r-R)}{6(1-\nu)(1-2\nu)} gradT \tag{6}$$

It is evident from (6) that stress is negative (it means expanding stress) and stress has maximum in the sphere center. Let us estimate its value. $\nu = 0.23$; $\alpha = 7 \cdot 10^{-5}$ deg^{-1}; $E = 2.55 \cdot 10^9$ N/m^2 for polystyrene. Assuming temperature difference between sphere center and its surface 65°C (it is possible if sphere center is at room temperature and its surface is near glass transformed point) maximum stress is $\sigma_{max} = 46.5 \cdot 10^5$ N/m^2.

This figure is not so far from polystyrene strength taking from tables - (340 – 390)$\cdot 10^5$ N/m^2. If initial granule has any defects (cracks, gas bubbles inside or something else), its strength could be reduced significantly. In this case initial granule defragmentation becomes possible. Furthermore, **grad T** isn't constant in the real experiment. That is why we have performed more careful calculation using exact solution (5). Actual temperature profiles (see fig. Q4.5) were calculated using part of Startsev's modeling code.

Radial dependencies of thermal stress inside a granule are presented on fig.Q4. 6. As one can see from the figure, thermal stress in a granule can exceed 1/3 – 1/4 of bulk material strength. It means that an initial granule could be fragmented by thermal shock into two or several pieces under some condition, if it has any defects. Apparently, it is a probability but not a necessity. Results will be depending on an initial granule quality.

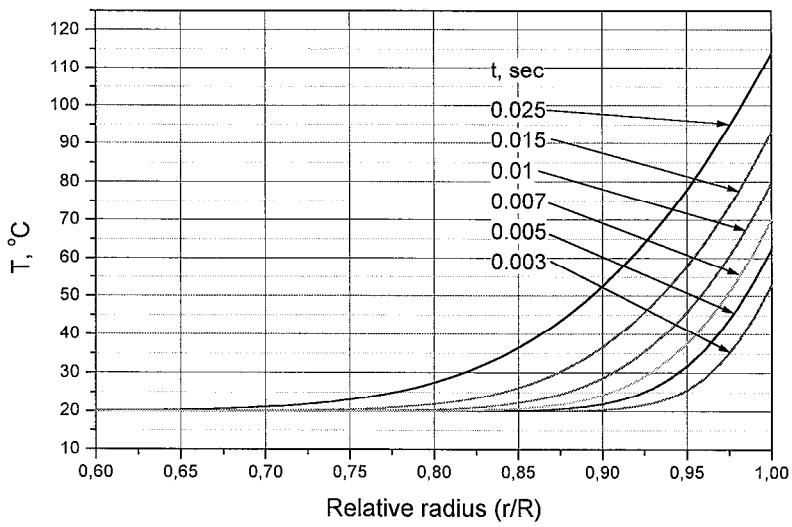


Fig.Q4.5. Radial dependence of temperature for granule heated in the ballistic furnace. Granule radius – 0.35 mm; furnace gas temperature - 800°C; initial temperature - 20°C. Different curves correspond to different time of heating.

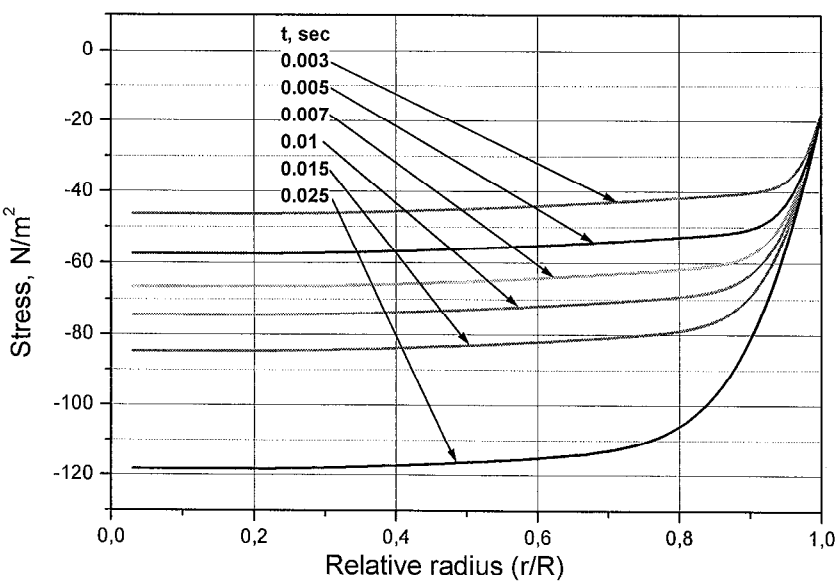


Fig. Q4.6. Thermal stress inside a granule heated in the ballistic furnace. Granule radius – 0.35 mm; furnace gas temperature - 800°C; initial temperature - 20°C. Different curves correspond to different time of heating.

Q4.4. Conclusion

In conclusion, we want to summarize the results of our activity at fourth quarter.

- a set of experiments with 0.67-0.72 mm initial granules was carried out and a good quality shells were produced with high yield in every experiment;
- large shells up to 2.0 mm were produced in experiments with slow gas filling;
- thermal stress in an initial granule caused by its fast heating in the ballistic furnace is calculated.

Summary.

During the fourth contract year, we continued to develop Ballistic technology of shell formation. A new upgraded version of Ballistic Furnace with longer hot zone (1.56m.) and cooling one (1.2m) had been finally assembled, and a lot of shell formation experiments had been carried out. The change of the Ballistic Furnace configuration has led to significant changing in operational conditions suitable for shells production. We had found optimal operational conditions for some grades of initial granules giving us high yield of good shells. A serious attention was paid on initial granules preparation. In the experiments some unexpected results were obtained – first of all it was a strong influence of temperature profile, an initial granule velocity and a trajectory angle on good quality shells yield. Those observations made us to consider some additional physical phenomena (initial granule defragmentation and gas convection inside hot zone) to explain good shell formation. Appropriated estimations of the velocity of possible convectional gas currents in the hot zone, strength of formed shells, thermal stress in an initial granule caused by its fast heating in the ballistic furnace etc. were made. Good quality shells up to 2mm in diameters with high yield were produced. Although a production of good quality shells in diameter range >1.8 mm stays uneasy job, our experience lets us to declare that Ballistic technology doesn't reach its boundaries, and future development will allow to obtain perfect results.

Chapters Q1.1 – Q1.5 were written by Merkuliev Yu.A. and Startsev S.A.
Chapter Q2.2 was written by Akunets A.A.,Dorogotovtsev V.M.,Turivnoy A.P.
Chapters Q1.6 – Q2.1, Q3.1 – Q3.5, Q4.1-Q4.4 were written by Nikitenko A. I. and Tolokonnikov S. M

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