

UDC 661.11; 66.074.38

REMOVAL OF RESIDUAL MONOMER FROM THE GENERAL PURPOSE POLYSTYRENE

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Abstract. The problem of removal of residual monomer from the general purpose polystyrene (GPPS) is discussed in the article. The features of the degassing stage of GPPS, which obtained by block polymerization, are studied. Optimal conditions of degassing process are suggested. Basic methods of residual monomer removing are described.

Keywords: General purpose polystyrene (GPPS), degassing, polymerization, residual monomer, styrene

Current bulk polymerization processes convert styrene to about 80 % [2]. So certain amount of residual volatile compounds is always contained in obtained polymer: unreacted monomer, one or more solvents, which added to monomer, by-products, which formed during the reaction (for example, benzene – the decomposition of benzoyl peroxide, etc.), as well as oligomeric products. These residual volatile compounds decrease quality of polymer: make physical-mechanical properties and toxicological properties worse. It is especially necessary when polymer is used for the production of food packaging [1].

The polymer syrup exits the polymerization reactor at about 170 °C. The most common devolatilization technology involves increasing the temperature of the syrup to > 230 °C by passage through a heat exchanger connected to a vacuum tank. The syrup foams, forming strands which fall into a vacuum tank at 5 - 10 mm Hg as they exit the heat exchanger. Equilibrium concentrations of styrene in the polymer and in the vapor phase dependent upon the temperature and the pressure in the tank. Figure 1 shows the vapor–polymer equilibrium (calculated data [3]) for styrene in polystyrene at various levels of vacuum (one stage devolatilizer) [2]. Typically, devolatilizers operate at 230 - 240 °C and 5 - 10 mm Hg. Therefore, the level of residual styrene monomer left in the polymer is typically in the range of 300 - 500 ppm. If the polymer temperature is increased to greater than 240 °C, polymer degradation begins to take place resulting in the formation of styrene monomer.

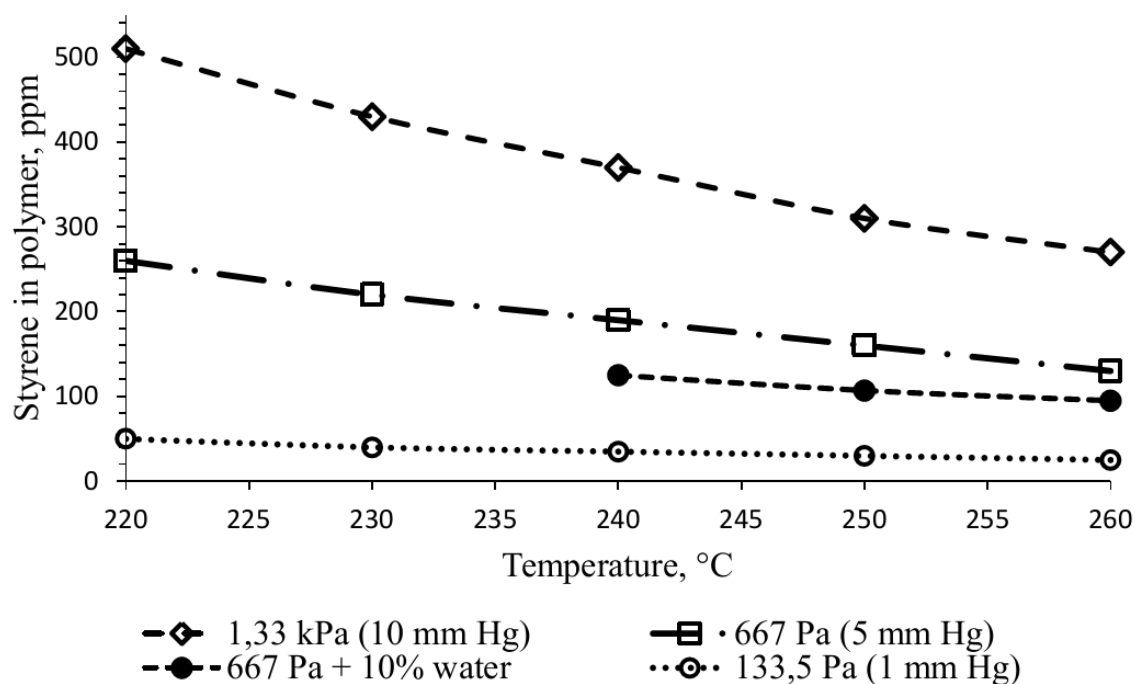


Fig. 1. Vapor-polymer equilibrium partitioning data for styrene in polystyrene vs temperature and pressure

Content of indicated compounds is cannot be allowed above the acceptable level in some foods packaged in polystyrene (PS). These sensitive applications require PS having residual styrene monomer levels below 200 ppm. It is not feasible to consistently lower the styrene level to < 200 ppm without special techniques [3].

Experimental technics

At the moment degassing stage in GPPS production unit at JSC «Gazprom neftekhim Salavat» is carried out at following conditions:

$T = 220 - 230 \text{ }^\circ\text{C}$;

$P = 23 \text{ mm Hg (3,07 kPa)}$

Thus, the goal of this research is modeling of degassing section in vitro, optimization of process, as well as selection of effective system in order to decrease content of residual monomer.

To simulate stages of the polymer degassing was used a method based on gravimetric mass change of polymer melt sample during drying under vacuum. In our experiment we applied vacuum dry box IICB-65/5,0, which aimed for drying and heating of different materials in air and under vacuum at the maximum temperature 500 °C. Vacuum dry box assures residual pressure 10 mm Hg.

Porcelain cup was brought to a constant weight by burning in the muffle furnace during two hours. Then powdered sample of polystyrene was put into cup and placed in

Vacuum dry box that was heated to the desired temperature. Then we kept up to melt of polymer and turned on the vacuum pump. There after time reading of drying was done.

Samples of GPPS melt (samples from shop after reactor of polymerization before vacuum tank) were analyzed. These samples against grade of synthesized polystyrene had differences in the range of allowable values of melt index and physical-mechanical properties. We identified factors of chain-length distribution for more accurate description of polymer melt sample.

Chain-length distribution (CLD) of samples was tested on liquid gel-chromatograph Agilent Technologies 1200 Series, that furnished with degasser Degasser G1379B, isocratic pump Iso Pump G1310A, manual injector G1328B, chromatographic oven TCC G1316A, refractometric detector RID G1326A and data handling system Agilent ChemStation Rev.B.03.02. Polystyrene standards in the range of molecular weights from 162 to 5000000 were used for construction of calibration curves.

Conditions of chromatography:

- column: PLgel MIXED-C, size 300×7,5 mm, 5 μm;
- composition of mobile phase: 100 % of tetrahydrofuran (THF);
- recovery rate: 1 ml/min;
- temperature of chromatographic oven: 25 °C;
- volume of injection: 50 μl;
- concentration: 0,01 g/5 ml THF.

Parameters:

- molecular weights (M_w – weight-average and M_n – number-average, M_z – z-average);
- polydispersity ($n_d = M_w/M_n$);
- maximum of CLD curve (M_p);
- low-molecular part of CLD curve (10 % of polymer).

Results of chain-length distribution testing are shown in Table 1.

Check of investigations was done by loss of polymer mass and the residual styrene content.

The residual styrene content was identified by chromatography on «Crystallux-4000» that furnished with ionization-type detector; detection limit of testing substance is 0,001 % with peak height is no less 10 mm; device for injection; with temperature control of heating до 200 °C; column with length 3 m, diameter 3 - 4 mm.

Conditions of chromatography:

- carrier gas: helium;
- flow rate of carrier gas: 40 cm³/min;
- flow rate of hydrogen: 60 cm³/min;
- flow rate of air: 550 cm³/min;
- temperature of column: 116 °C;
- temperature of evaporator: 180 °C;

Results and discussion

The main properties of researched GPPS melt samples are presented in Table 1.

From the data in Table 1, it follows that significant variations of molecular characteristics are watched in process of GPPS production. Molecular weight of low-molecular part of the polymer can vary from 21×10^3 to 32×10^3 g/mol. It will influence on conditions of monomer and other volatile impurities degassing.

Table 1. Factors of CLD of researched samples and characteristics of marketable products

Factor	Sample 1	Sample 2	Sample 3
$M_n \times 10^3$, g/mol	46,5	67,0	59,2
$M_w \times 10^3$, g/mol	178	219	210,8
$M_z \times 10^3$, g/mol	392	432	443,4
Polydispersity n_D	3,83	3,27	3,60
$M_p \times 10^3$, g/mol	135	179,9	164,6
$10\% \times 10^3$, g/mol	20,7	32,1	26,9
Melt index of the marketable product, g/10 min	5,6	6,5	5,7
Residual monomer of the marketable product, % mass	0,08-0,066	0,068-0,071	0,074-0,069

Dependences, which obtained in experiments, are shown on Fig. 2, 3, 4. Results showed that residual monomer content in GPPS, which required in State Standard 20282-86 (no more 0,10 - 0,15 wt%) and specification 2214-078-05766575-99 (no more 0,08 wt %), is not reached at temperature of degassing $T = 220$ °C and at time of drying 60 minutes.

Then we changed conditions of drying: temperature $T = 230$ °C, pressure $P = 10$ mm Hg (Fig. 3). Apparently according to the obtained curves that required styrene content in polymer at rates (0.08 wt %) is reached after 30 min of drying. Quantity of residual monomer decreases up to 0.03 % wt with increasing of residence time. It assures high degree of polymer degassing and expanding opportunities to use it to manufacture products that come into contact with food and goods for children (toys, etc.)

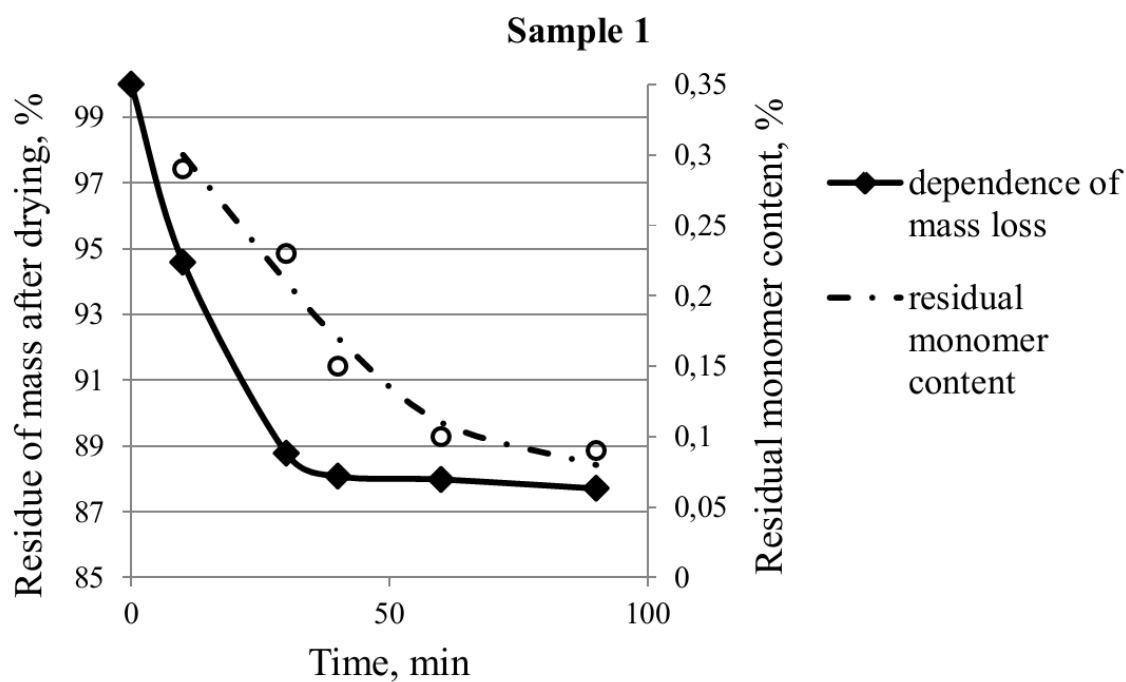


Fig. 2. Dependence of mass loss of Sample 1 and respective residual monomer content on vacuum drying conditions ($T = 220\text{ }^{\circ}\text{C}$, $P = 10\text{ mm Hg}$)

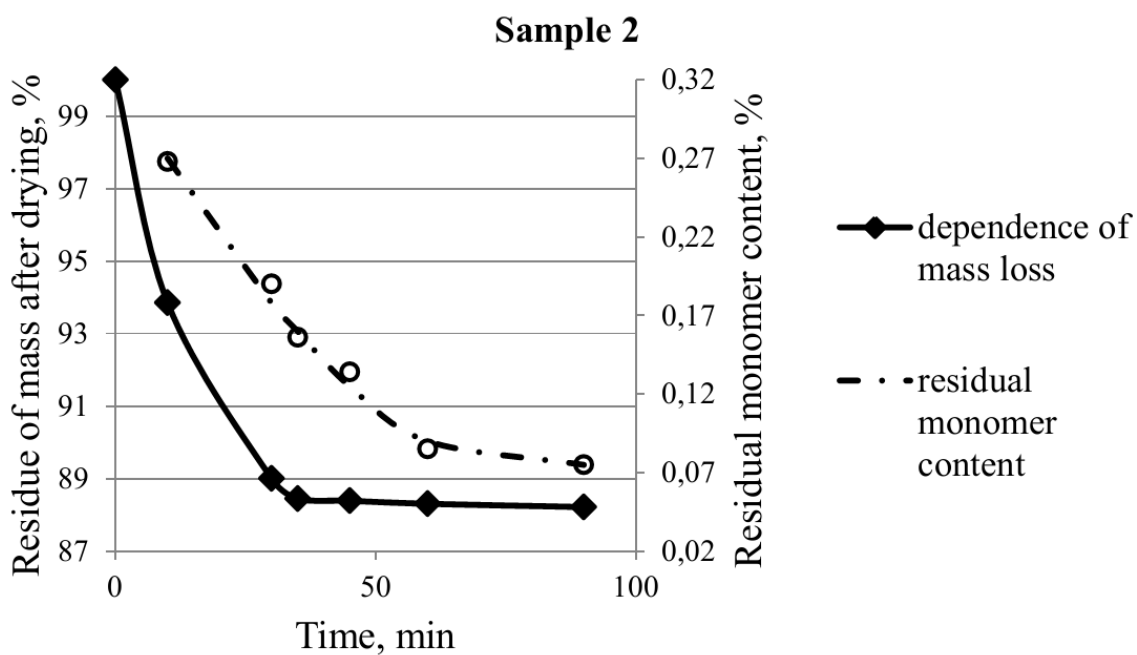


Fig. 3. Dependence of mass loss of Sample 2 and respective residual monomer content on vacuum drying conditions ($T = 220\text{ }^{\circ}\text{C}$, $P = 10\text{ mm Hg}$)

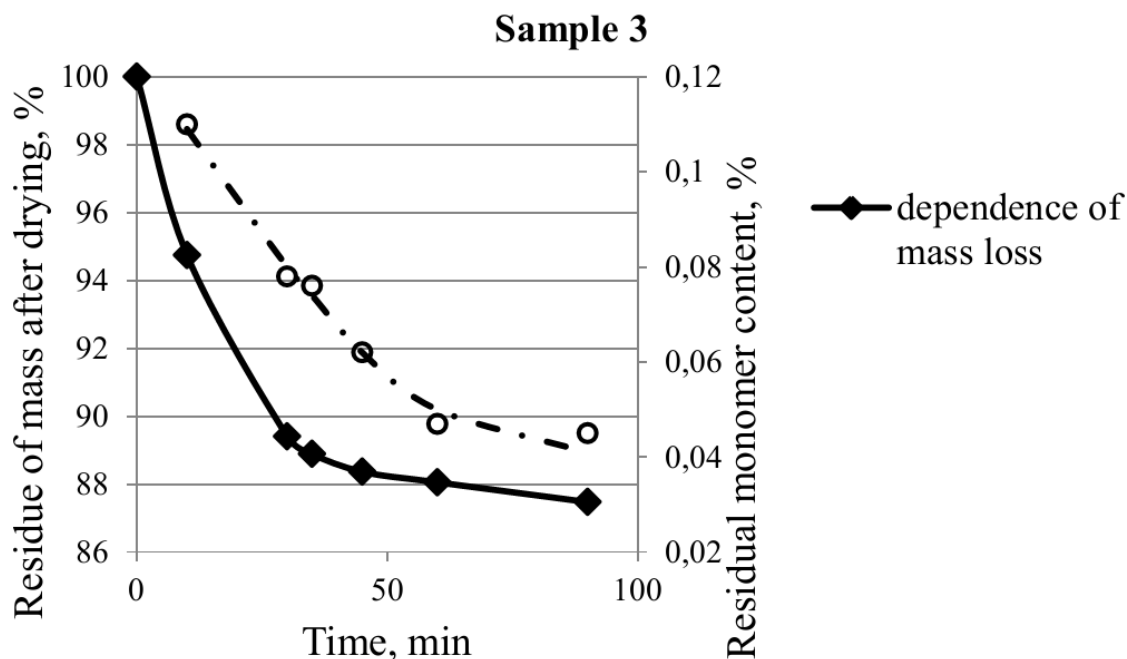


Fig. 4. Dependence of mass loss of Sample 3 and respective residual monomer content on vacuum drying conditions ($T = 230\text{ }^{\circ}\text{C}$, $P = 10\text{ mm Hg}$)

Based on these data we can conclude that it is necessary to ensure residual pressure $P = 10\text{ mm Hg}$ for guaranteed achievement of required residual monomer content at drying in the shop.

But existing equipment cannot provide such pressure, especially in maximum capacity.

Industrial methods of polystyrene melt degassing

In works [4 - 10] polymer is suggested extrude in flash box in melt form. Melt of polymer is divided into fibers for effective recovery of residual volatiles. This method that applied in the unit of GPPS production doesn't ensure enough removal of residual styrene.

There are several ways of degassing carried out by adding inert and a volatile substance to polymer. This matter is called «foaming agent», «cellulating agent» or «stripping agent», as well as «promoted removal of volatile compounds liquid » or «degassed agent». Large quantity of bubbles is formed in the polymer melt at the evaporation of foaming agent in flash box. It is accompanied by significant increasing of surface area of foaming mass and removal volatile compounds from polymer in the issue of diffusion. The most common currently foaming agents are substances that are described in patents [11 - 17].

Using of supercritical fluid instead of conventional foaming agents is proposed in the patents [18] and [19]. This liquid at the injection goes into a gaseous state and

remains in the polymer solution due to the high pressure that is created during the injection. These supercritical fluids used as foaming agents include, for example, liquefied nitrogen, liquefied carbon dioxide and alkanes, in particular, the C₄-C₆ alkanes.

Another technique to expedite the transport of the volatile components from the molten polymer is to increase the number and rate of bubbles formed [20].

Techniques that have been used to increase the number of bubbles and their rate of formation (nucleation) are the addition of chemical nucleating agents [21] and ultrasound [22]. Nucleation of bubbles in the molten polymer can help expedite achievement of equilibrium in conventional falling strand devos. However, this facilitation mechanism cannot get below equilibrium and thus has marginal value.

Conclusions

The following conclusions can be made based on these results and the analysis of the unit:

1. In order to ensure the level of residual styrene content less than 0.08 wt% requires that at 230 °C and a residual pressure of 10 mm Hg residence time is at least 30 minutes.

2. A vacuum equipment of operating production of general purpose polystyrene is strongly depreciated; the period of its operation is more than 40 years. The equipment does not provide the required level of degassing at the maximum capacity.

3. The installation of two serial vacuum chambers for the purpose of deep purification of polymer from the residual styrene or consider adding foaming agent could be recommended based on the research and analysis of foreign units for the reconstruction of the vacuum degassing section at the unit of polystyrene production.

Reduction of the residual monomer will significantly improve the quality of the marketable polymer, and the related possible of capacity unit increasing will allow to receive additional profit.

Also, low content of residual monomer expands the application of GPPS in food packaging and consumer goods.

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