

CHANGES IN MOLECULAR MASS DISTRIBUTION OF POLYSTYRENE DURING ITS PROCESSING

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There is written about molecular mass characteristics of polystyrenes, which are used in EPS production. There is analyzed change in molecular mass distribution and melt index after thermal action on polystyrene.

Keywords: molecular mass distribution, melt flow index, polystyrene, thermal decomposition

Traditionally expandable polystyrene (EPS) is produced by suspension polymerization of styrene in presence of foaming agent. During last decade an intensive search of new ways of production of EPS by impregnation of foaming agent in to the melt of general purpose polystyrene (GPPS) is taking place. In 2004 JSC "Salavatnefteorgsintez" put into operation a block of EPS production by impregnation of foaming agent (C₅) in to the melt of general purpose polystyrene. Distinctive feature of this process is that the polymer melt, received by block polymerization, is send into mixing block (fig. 1). Such configuration increases flexibility of manufacture. Depending on the market requirements there is an opportunity to get pellets of EPS or pellets of general purpose polystyrene by traditional scheme.

Process of imregnation is carried out in static mixers and consist of the following basic stages:

- doping of general purpose polystyrene melt with foaming agent and additives;
- homogenization of foaming agent and additives in melt of general purpose polystyrene;
- underwater granulation in conditions excluding foaming of polymer;
- drying and storing of EPS granules.

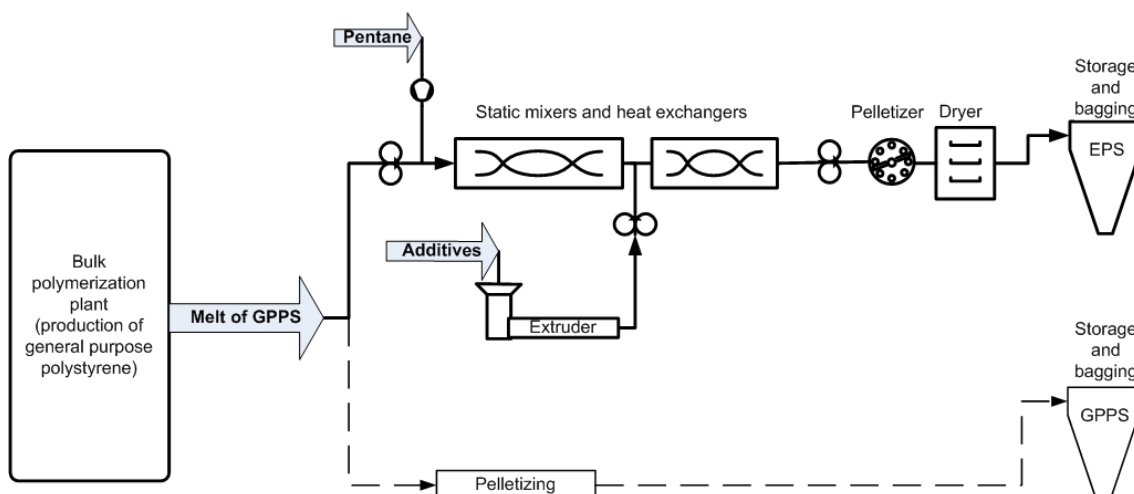


Figure 1. Principle scheme of JSC "Salavatnefteorgsintez" block producing EPS by means of impregnation of foaming agent in to the melt of general purpose polystyrene

General purpose polystyrene made by JSC "Salavatnefteorgsintez's" by Specification 2214-078-05766575-99 is used in this block as raw material. Irganox 1010 is used as thermo stabilizer in quantity of 0,2 % by mass.

The mixing block works at temperature up to 250 °C and pressure up to 25 MPa. Average residence time of polystyrene melt in the block, after devolatilization, can exceed 60 minutes. Such long residence time at high temperatures cause decomposition of polystyrene. Decomposition of polymer results in change of molecular mass characteristics, melt viscosity, melt flow index. These parameters are interconnected and all of them characterize expandability of polymer and have influence on processing parameters of polymer and on properties of final products. The fire retardant additive is hexabromocyclododecane (HBCD). In real industrial conditions of process partial decomposition of HBCD is possible. That decomposition is accompanied with discharge of bromic hydrogen which also have an influence on molecular mass distribution.

Therefore it is important to estimate the influence of residence time and polystyrene melt temperature in EPS production line. The analysis of dependence of weight average molecular weight (Mw), molecular mass distribution, and melt index of initial polystyrene on residence time and temperature in line will allow to choose optimal operating conditions of EPS production line with the set properties.

In accordance with literature thermal-oxidative decomposition of polystyrene with noticeable speed occurs at temperature above 200 °C [1], and thermal degradation above 260 °C [1; 2].

The preferred weight average molecular weight should be more than 170000 [3, 4] since its reduction cause abrasive wear of polymer during its granulation. In other sources preferred interval of molecular weights is indicated, for example 150 000... 300 000 [5], 130 000...180 000 [6]; 180 000...300 000 [7]; 60 000...128 000 [8], this variety of mass distribution testifies, that the using of various grades of polystyrene give a product with necessary consumer properties. The form of distribution curve is also important, in which "the high molecular weight flank drops steeply" [6, 9]. Value of polydispersity lays within limits of 1,7 ... 1,98 [9]; 1,0 ... 2,5 [7]; 1,5 ... 3,0 [4].

We investigated changes in molecular mass characteristics of general purpose polystyrene depending on temperature and the time of thermal action.

In parallel with molecular mass analysis of polystyrene subjected to thermal action we analyzed its melt index.

EXPERIMENTAL PART

1. Thermal action

The chamber of IIRT-5 tool (intended to analyze melt flow index of polymers) was used to simulate the process conditions. Extrusion chamber of the device is isolated from air and is under pressure (a 5 kg load on the piston provides 0,7 MPa pressure) that makes conditions of thermal action in the device similar to operating conditions in a EPS line and practically excludes oxidizing decomposition of polymer. The temperature set in the chamber was constant throughout the volume (the maximal deviation from the set temperature did not exceed 0,5 °C).

After thermal action a central part of strand was selected by weight of not less than 4 grams for analysis of molecular mass characteristics and melt flow index.

Thermal action was carried out at temperatures 200, 210 and 240 °C. At each temperature the residence time was 30, 60 and 90 minutes.

2. Molecular mass distribution and melt flow index analysis

The research of molecular mass characteristics was carried out with the help of a highly effective liquid chromatography with Agilent 1200 tool. The device is supplied with manual input of samples. The analysis was carried out in isocratic mode, with the use of refractometric detector. Temperature of a column was 25 °C. Tetrahydrofuran (THF) served as solvent. Calculation of received elution curve was made automatically with mathematical complex ChemStation for LC systems (version B.03.02). The tool was calibrated on samples of narrow polystyrene. Samples of polystyrene with weight of 0,01 gram each, were dissolved in 5 ml THF. Dissolution was carried out at room temperature within not less than 24 hours.

Characteristic molecular mass distribution curves of thermostated samples of polystyrene are presented in figure 2.

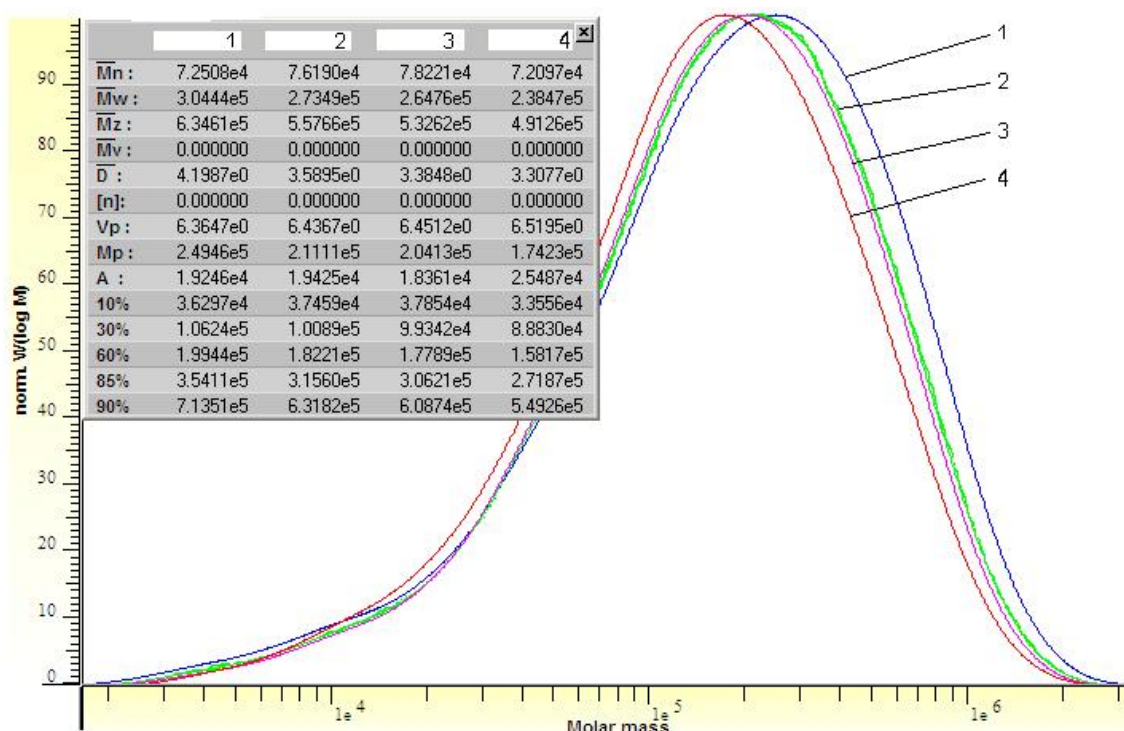


Figure 2. Change of molecular mass distribution of general purpose polystyrene after thermostating at 240 °C

(1 - initial polystyrene; 2 - 30 minutes residence time;
3 - 60 minutes residence time; 4 - 90 minutes residence time)

The same samples were analyzed on melt flow index. The tests were carried out with IIRT - 5M tool, in accordance with State standard 11645 - 73. Standard time - 600 sec. Load weight - 5 kg. Temperature of the tests - 200 °C. Time between two serial cuts - 30 sec.

Change of melt flow index of polystyrene after soaking at 240 °C during 30, 60 and 90 minutes is presented in figure 3.

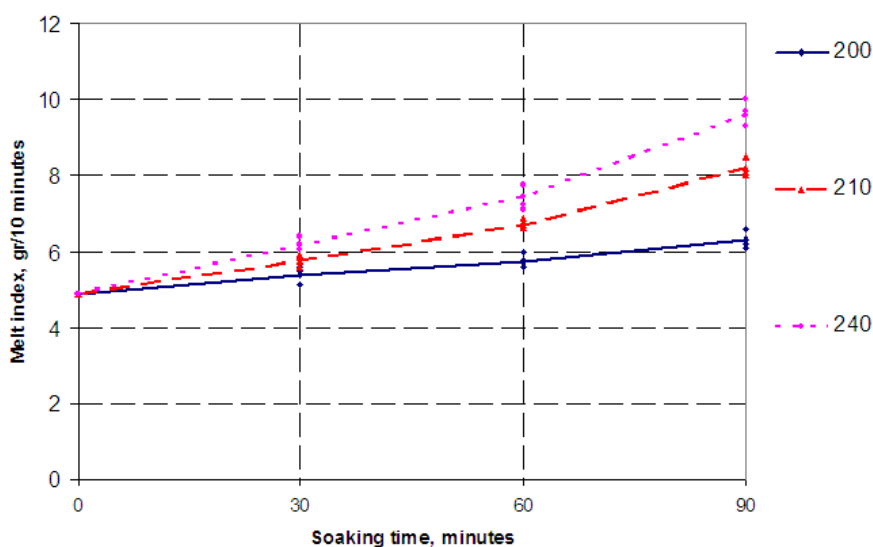


Figure 3. Change of melt flow index of polystyrene of GPPS after being soaked at 240 °C during 30, 60 and 90 minutes

Table 1

Weight average molecular weight and polydispersity of general purpose polystyrene after thermal action

Time	30 min		60 min		90 min	
	M _w	D	M _w	D	M _w	D
200 °C	306000	4,08	288000	4,03	298000	4,02
210 °C	285000	4,03	283000	3,79	291000	3,75
240 °C	273000	3,59	261000	3,48	238000	3,31

CONCLUSIONS

1. Analyzes of molecular mass characteristics of polystyrene after being soaked at 240 °C has shown significant influence of temperature action. All parameters of the molecular mass distribution of polystyrene are decreasing. The decrease of weight average molecular weight after presence within 30, 60 and 90 minutes is accordingly 9,0, 11,5 and 20,3 %. Meanwhile the decrease of polydispersity is accordingly 8,3, 12,4, 14,8 %. This implies, that mainly molecules with high molecular weight are exposed to decomposition.

2. After being soaked at 200 and 210 °C no decrease of parameter M_w is observed. It can be explained by the presence of effective thermo stabilizer. Change of melt index is more considerable (table 2). After 200 °C soaking within 30, 60 and 90 minutes the increase of the melt index is accordingly 9,6, 16,3 and 28,9 %.

3. To prevent strong decompositions of polystyrene, it is possible to accept temperature in EPS production line as 210 °C.

The received data will allow to choose optimal parameters for the process of EPS production.

Table 2

Melt flow index of general purpose polystyrene after thermal action

Temperature, °C	Soaking time		
	30 minutes	60 minutes	90 minutes
200	5,37	5,7	6,32
210	5,75	6,71	8,23
240	6,18	7,45	9,61

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