The Indirect Methods of Conversion Monitoring Throughout Polymerization Processes in Bulk

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Abstract— Two methods of monitoring the conversion throughout polymerization process in bulk (polymerization of isoprene as an example) are considered. Both techniques are built so to define the conversion in the terms of indirect running parameters of polymerization process in mold − i.e. the reactor with a thin fixed bed of the reaction mixture. Due to the first of named these parameters are the temperature of the bed top, and also the wall reactor temperature. Due to the second technique to check-out the conversion in real time it's enough to control and analyze the bed top temperature bound up to conversion with rigorous dependence.

Keywords— conversion monitoring; polymerization in bulk; indirect methods

I. INTRODUCTION

Bulk polymerization in carried out itself in monomer medium in the presence of catalyst or starters. The absence of diluents provides the maximum purity of final product and excludes the necessity of apparatuses for their recycling. Due to maximum concentration of the monomer in bulk polymerization there's achieved the maximum rate and, often, maximum conversion − i.e. degree of polymerization. However, polymerization in bulk being widely used when producing homopolymers and copolymers, has no application in the production of diene rubbers. This point of matter is explained by the higher viscosity of the reaction mixture, a situation that excludes the use of any mixing devices, and also hindered heat removal in conditions of very high rate of polymerization process.

According to [1–3] bulk polymerization in apparatuses with a thin reaction − mixture bed has the preferences while producing cis -1,4-polyisoprene. In apparatuses of this type the problem of heat removal may be solved in simple, by comparison, way. An additional gain they give to efficient thermal mode that may be easily attained. Structurally the most simple instrumentation for bulk polymerization process is a reactor (polymerization mold) as a cylinder of a large diameter and a small height − i.e. the disc. However, the certain difficulty to introduce in practice the innovate technology of rubber production, and, in particularly, to implement the automatic control of polymerization process, is the absence of continuous conversion monitoring technique. Actually, monitoring the conversion with the help of dielectric principle [4] (through variation of dielectric constant and dielectric loss tangent of monomer and polymer) in question is not applicable therefore dielectric properties of isoprene (the nonpolar liquid) and polyisoprene (the dielectric of high - quality) are extremely close: $\varepsilon_1 \approx \varepsilon_2 = 2,1$; $\mathrm{tg}\delta_1 \approx \mathrm{tg}\delta_2 = 0,005 \div 0,006$ [5]. The ultrasonic technique based on monitoring the conversion via polymer viscosity is efficient only as batch (-operated) technique [6].

The present study is dedicated to work out the indirect methods of monitoring conversion via the current parameters of polymerization process (isoprene polymerization in bulk as an example).

II. METHODOLOGY

Let us suppose that the heat conductivity of the reactor wall or, otherwise, the wall of polymerization mold is infinitely large. The heat exchange is considered to proceed in the reaction bulk via the mechanism of heat conductivity. In addition let's suppose that the reaction constant depends on temperature according to the Arrhenius equation and that the pre-exponential factor z does not depend on temperature. A mathematical model based on the named assumptions is as follows:

$$c_{\mathrm{p}}\rho\frac{\partial T}{\partial \tau} = \lambda\frac{\partial^2 T}{\partial x^2} + Qz\exp\left(-\frac{E}{RT}\right)(1-U)[\mathrm{M}]_{\mathrm{o}} \tag{1}$$

$$\frac{\partial U}{\partial \tau} = z\exp\left(-\frac{E}{RT}\right)(1-U) \tag{2}$$

with the boundary conditions:

$$-\lambda\frac{\partial T}{\partial x}\bigg|_{x=x_{\mathrm{o}}} = \alpha\left(T\big|_{x=x_{\mathrm{o}}} - T_{\mathrm{R}}\right), \qquad \frac{\partial T}{\partial x}\bigg|_{x=0} = 0,$$

$$T\big|_{\tau=0} = T_{\mathrm{o}}, \quad U\big|_{\tau=0} = 0. \tag{3}$$

where E is the activation energy of polymerization factor; R is the universal gas constant; T is the local temperature of the reaction mixture; T_{o} is the initial temperature of the reaction mixture; T_{R} is the temperature of the coolant (water) in reactor jacket; x is the current in height coordinate; x_{o} is the height of the reaction-mixture bed; c_{p}, ρ and λ are the specific heat capacity, density, and heat − conductivity coefficient of the reaction mixture; Q is

the specific heat of polymerization; α is the heat emission (from water to reactor wall) coefficient; τ is the time; U is the conversion (the degree of conversion of the monomer into the polymer): $U = ([M]_o - [M])/[M]_o$, and $[M]_o$ and $[M]$ are the initial and current concentration of isoprene in the reaction mixture.

Set of equation (1) – (3) was solved numerically at the following factors of the reaction mixture (isoprene – a catalytic system based on neodymium bis-(2-ethylhexyl) phosphate [Nd]) and kinetic parameters: $c_p = 2.25$ kJ/(kg·K),

$\rho = 680$ kg/m^3, $\lambda = 0,13$ W/(m·K), $Q = 74.8$ kJ/mol, $R = 8.314$ J/(mol·K), $z = 1.209$ 1/s, $E = 20.67$ kJ/mol, $[C_5H_8] = [M]_o = 10$ kmol/m^3, $[Nd] = 2 \cdot 10^{-4}$ kmol/m^3. The heat emission coefficient is calculated proceeding from the condition that heat be freely able to conduct away from the reactor volume (the reactor diameter is $D = 0,3$ m and $x_o = 3$ mm): $\alpha = 1500$ W/(m^2·K); the rate of water flow in the reactor jacket: $G_R = 0.26 \cdot 10^{-3}$ m^3/s.

Fig. 1 shows the dependences of (1) the bed-top temperature, $T_т$, (2) the temperature of the reactor wall, $T_w(\tau) = T(\tau, x_o)$, and average conversion of the monomer, U_{av}, on time.
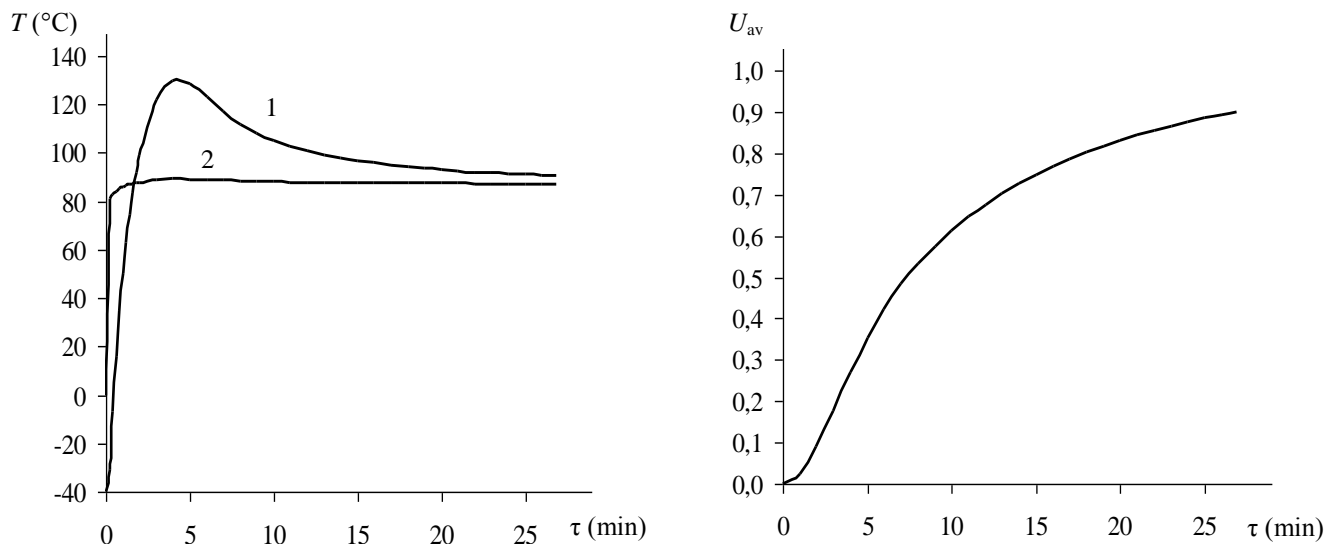

Fig. 1. Dependences of (1) the bed – top temperature, $T_т$, (2) the temperature of the reactor wall, T_w, and average conversion of the monomer, U_{av} , on time during the bulk polymerization of isoprene in a disc reactor ($x_o = 3$ mm) of $T_o = -40°$C, $T_{max} = 130°$C, $T_R = 87°$C, $\alpha = 1500$ W/(m^2·K).

III. RESULTS AND DISCUSSION

The maximum achieved value of $T_т$ is determined by the fraction of the monomer that has reached by this time. When the maximum is passed, the reaction-mixture temperature $T_т$ falls sharply and then tends toward a constant value: the reactor-wall temperature T_w. The tendency of $T_т$ variation is specified because the process of fast exhaustion («burning») of the monomer is predominant under the process of progressing release of heat caused by the exothermic polymerization reaction. The reactor-wall temperature T_w (see curve 2 in Fig 1) even after a short time from the beginning is of constant value close to the coolant temperature T_R.

While considering curves in Fig. 1 it follows a method of continuous monitoring the conversion (technique 1) based on estimation the indirect process characteristics – the temperature $T_т$ and the temperature T_w. With the help of their current difference there's determined a dependence: $U_{av} = f(T_т - T_w)$.

Fig. 2 illustrates an example of technique 1 run-up. Temperature measurements and recording were fulfilled with the help of IR-thermometer *Testo* 845 and automatic controller – tester TRM-202.
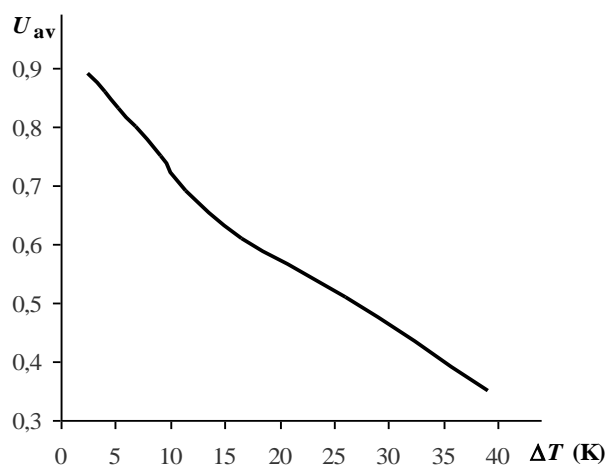

Fig. 2. Monitoring the conversion in a disc reactor ($x_o = 3$ mm) during isoprene polymerization process in bulk according to technique 1 – a calibration curve.

Technique 1 demonstrates an adequate accuracy in particularly at the final time interval of polymerization process: the error of conversion definition is not more than 5%. But it needs in dial layout of the dependence $U_{av} = f(T_т - T_w)$, an

individual one for each reactor design, depended on the height of the reaction – mixture bed as are the heat exchange conditions between the reactor wall and the coolant. With connection to indicated let us regard a second method of conversion monitoring.

In assumption that the reactor wall temperature is constant: this condition may be realized under the conditions of correct option of the temperature and the flow mode of coolant in the reactor jacket, the mathematical model of polymerization process corresponds to equation (1), (2) but with new boundaries:

$$\left.\frac{\partial T}{\partial x}\right|_{x=0} = 0, \ T|_{x=x_o} = T_W ,$$
$$T|_{\tau=o} = T_o, \ U|_{\tau=o} = 0. \tag{4}$$

Set of equation (1), (2) with conditions (4) were calculated numerically at the factors of the reaction mixture and kinetic parameters as before.

Fig. 3 shows the bed height distribution of temperature and conversion at various times. It is noticeable that distribution of conversion is close to uniform during full time. The temperature profiles proportional at the beginning straighten at the second half of polymerization process. Weak current in height coordinate dependence of local temperature gives a possibility to consider reactor mode with a thin fixed bed close to isothermal one. Then $T(x) = T$, and equation (4) is analytically tractable:

$$U(\tau,T) = 1 - \exp\left[-z\tau\exp\left(-\frac{E}{RT}\right)\right]. \tag{5}$$

According to expounded, conversion monitoring technique, i.e. – technique 2, incorporates calculation of conversion in real time by equation (5) rest on the data of current temperature measuring at arbitrary position of the reaction – mixture bed. An example of technique 2 run-up in comparison with primary standard (introduction of ethanol as a stopper, periodical taking the samples outside the reactor, monitoring the conversion with the help of gravimetric analysis) is given on Fig. 4. Temperature measurements, i.e. $T_\tau(\tau)$, and calculation of conversion in real time were fulfilled using IR-thermometer *Testo* 845 and computer.
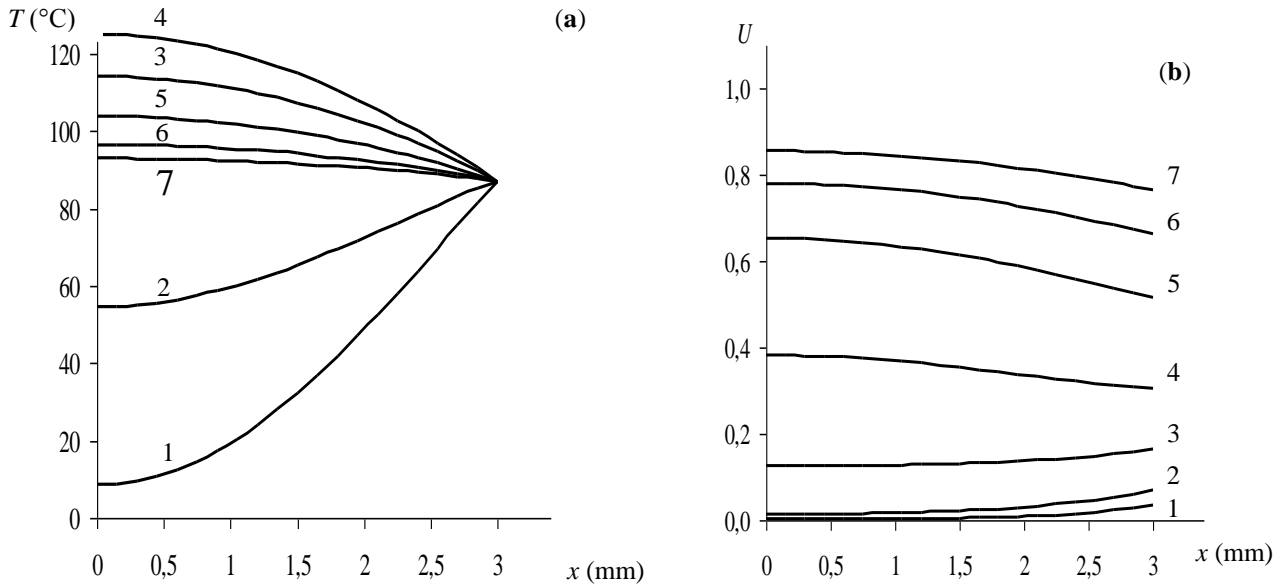

Fig. 3. Profiles of (a) temperature and (b) monomer conversion during the bulk polymerization of isoprene in a disc reactor ($x_o = 3$ mm, $T_o = -40°C$, $T_w = 87°C$) at $\tau =$ (1) 0.5, (2) 1, (3) 2.5, (4) 5, (5) 10, (6) 15, and (7) 20 min

The technique 2 demonstrates a (high-) precision accuracy of conversion monitoring at major times corresponding to deep degree of polymerization that is of prime importance when you need to control the process in polymerization molds.

IV. CONCLUSIONS

The considered techniques are referred to indirect methods of process characteristic check-up. General for both techniques is the definition of conversion by the means of the composite experimental and also calculated manner, based on continuous monitoring of the polymerization process in apparatus with a thin fixed bed reaction-mixture. The best advantage both techniques demonstrate at the final time stage of polymerization.

Moreover, in contrast to technique 1, the technique 2 is not required in dial layout of conversion dependence on measured in reactor and therefore deflected its thermal features characteristics of polymerization process. According to technique 2, the calculation of conversion is carried out in real time with the help of the strict analytical dependence conversion against temperature

of the reaction mixture, the latter being measured at arbitrary bed position.

As a whole the proposed techniques may be suitable for continuous conversion monitoring in different catalytic bulk polymerization processes.
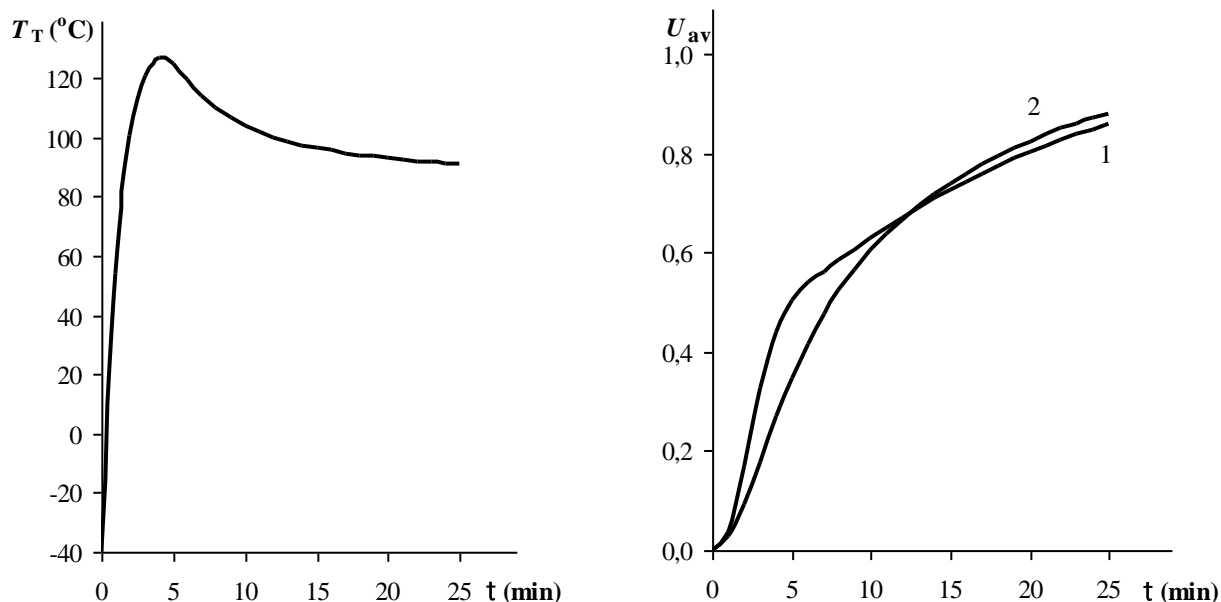

Fig. 4. Monitoring the conversion in a disc reactor during the bulk polymerization of isoprene according to technique 2 ($T_o = -40°C$, $T_w = 87°C$, $x_o = 3$ mm): 1 – technique 2; 2 – primary standard technique

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