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# MODELLING THE COMBINED POLYMERISATION AND DRYING OF POLYACRYLAMIDE PREPOLYMER

# MODELOWANIE ŁĄCZONEGO PROCESU POLIMERYZACJI I SUSZENIA DLA PREPOLIMERU POLIAKRYLOAMIDOWEGO

## Abstract

In the paper, the mathematical model of combined polymerisation and drying of polyacrylamide prepolymer is presented. It allows to predict the change of monomer conversion degree, polymer moisture content, the temperatures of gas and polymer in the dryer as well as dryer sizes. Using a developed model, values of technological parameters were established, providing faster polymerisation than in the case of drying.

*Keywords: acrylamide, polyacrylamide, polymerization, aqua solution, drying, combined process, mathematical model, belt dryer*

## Streszczenie

W ramach pracy stworzono model matematyczny dla łączonego procesu polimeryzacji i suszenia prepolimeru poliakryloamidowego. Proponowany model umożliwia wyznaczenie zmiany stopnia konwersji monomeru, zawartość wilgoci polimeru, temperatury gazu i polimeru w suszarce oraz wymiary suszarki. Z użyciem modelu wyznaczono wartości parametrów technologicznych procesu, umożliwiając szybszy proces polimeryzacji w porównaniu z suszeniem w aparacie.

Słowa kluczowe: *akryloamid, poliakryloamid, polimeryzacja, roztwór wodny, suszenie, proces łączony, model matematyczny, suszarka taśmowa*

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## 1. Introduction

Polyacrylamide is a water soluble polymer. Owing to the unique combination of properties, it is widely used as thickener, film former, stabiliser of suspensions, sizing agent in the textile industry, coagulant and flocculant, agent reducing of hydraulic resistance, soil builder as well as protective reagent in the drilling technique [1]. This necessitates a significant increase in the production efficiency of polyacrylamide.

One way of improving polyacrylamide production technology is to combine prepolymer polymerisation to high conversion degree with drying [2]. In the laboratory scale, this process was implemented in the belt drier with radiation-convective heat supply. For industrial production of polyacrylamide with the use of this method, it is necessary to design the apparatus of industrial-scale. A suitable tool for the calculation and prediction of technological and constructional parameters of industrial-scale apparatus is the mathematical modelling method. Therefore, developing a mathematical model of the combined polymerisation and drying is an important goal.

## 2. Mathematical model

The combined process of polymerisation and drying of polyacrylamide prepolymer is carried out in a belt drier with radiation-convective heat supply. Infrared drying is used because it allows to provide high values of the specific heat flow. It is necessary due to a high moisture content of prepolymer (about 60%). As a source of infrared radiation, it is advisable to use gas-fired panels. Flue gases move inside these panels, heating them. Air serves to remove water vapour and it moves in the dryer by natural convection. The prepolymer is fed into the dryer as a gel. It moves by belt countercurrent to air. The diagram of dryer is shown in Fig. 1.

The mathematical model of the combined process includes a system of equations (1 - 5), complemented by equations of chemical kinetics (6 - 10) with closing relations (11 - 19).

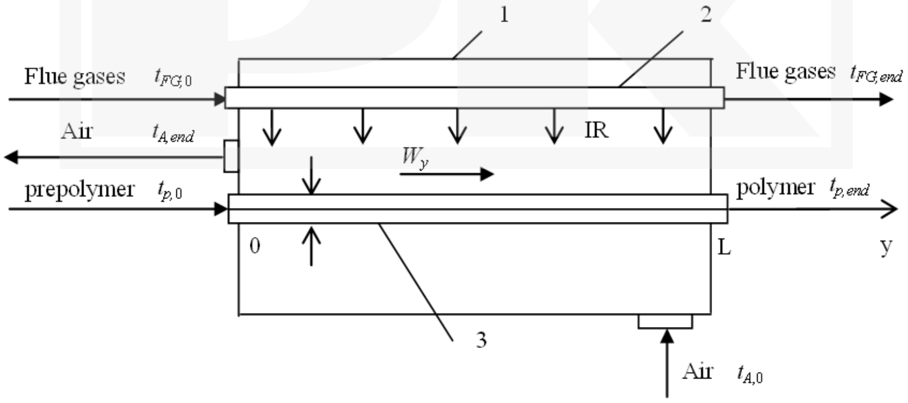

Fig.1. The diagram of dryer: 1 – the shell; 2 – heat-radiating panel; 3 – material

Changes of heat-radiating panel temperature $T_{IR}$, flue gases temperature $T_{FG}$, moisture content $U$ and drying polymer temperature $T_p$ upon the dryer length are calculated by solving the system of equations (1 - 5).

$$\alpha_{FG}\left(T_{FG}-T_{IR}\right)=c_{12}\left[\left(\frac{T_{IR}}{100}\right)^{4}-\left(\frac{T_{p}}{100}\right)^{4}\right] \tag{1}$$

$$\frac{\mathrm{d}t_{FG}}{\mathrm{d}y}=-\frac{\alpha_{FG}\cdot B\cdot\left(t_{FG}-t_{IR}\right)}{G_{FG}\cdot c_{FG}} \tag{2}$$

$$\frac{\mathrm{d}t_{p}}{\mathrm{d}y}=\frac{c_{12}\cdot\left[\left(\frac{T_{IR}}{100}\right)^{4}-\left(\frac{T_{p}}{100}\right)^{4}\right]\cdot B+r^{*}\frac{\mathrm{d}U}{\mathrm{d}y}\cdot G_{p}+\alpha_{A}\cdot\left(t_{A}-t_{p}\right)\cdot B+\Delta H\cdot\left(\frac{\mathrm{d}C_{M}}{\mathrm{d}y}\right)\cdot W_{y}\cdot B\cdot h}{G_{p}\cdot\left(c_{p}+c_{w}\cdot U\right)} \tag{3}$$

$$\frac{\mathrm{d}U}{\mathrm{d}y}=\frac{\beta\cdot B\cdot\left(p_{p}-p_{A}\right)}{G_{p}} \tag{4}$$

$$p_{p}=p_{s}\left(t_{p}\right)\cdot\psi\left(U\right) \tag{5}$$

where: $\psi(U)$ – empirical coefficient considering reduction of water vapour partial pressure by reducing the moisture content of the prepolymer.

Initial conditions for equations (2)-(4) are as follows: $t_{FG}(0) = t_{FG,0}$, $t_p(0) = t_{p,0}$, $U(0)=U_0$.

The polymerisation kinetics was described in [3]. Free radical-forming reaction, growth and chain termination reactions were considered having simulated of the acrylamide radical polymerisation kinetics, initiated by a redox system.

The system of kinetic equations for concentrations of redox system compounds (oxidant and reductant), monomer concentration, and initial moments of the molecular weight distribution of both active and inactive chains, is as follows:

$$\frac{\mathrm{d}I}{\mathrm{d}y}=-\frac{a\cdot k_{i}\cdot I^{a}\cdot J^{b}}{W_{y}} \tag{6}$$

$$\frac{\mathrm{d}J}{\mathrm{d}y}=\frac{-b\cdot k_{i}\cdot I^{a}\cdot J^{b}}{W_{y}} \tag{7}$$

$$\frac{\mathrm{d}C_{M}}{\mathrm{d}y}=\frac{-k_{p}\cdot C_{M}\cdot\mu_{0}}{W_{y}} \tag{8}$$

$$\frac{\mathrm{d}\mu_0}{\mathrm{d}y} = \frac{f_i \cdot k_i \cdot I^a \cdot J^b - k_{td} \cdot \mu_0{}^2}{W_y} \tag{9}$$

$$\frac{\mathrm{d}\lambda_0}{\mathrm{d}y} = \frac{k_{td} \cdot \mu_0{}^2}{W_y} \tag{10}$$

Initial conditions for the system of differential equations (6 - 10) are as follows: $\mu_0(0) = \lambda_0(0) = 0$, $C_M(0) = C_{M,0}$, $I(0) = I_0$, $J(0) = J_0$.
The average value of the polymer molecular weight was predicted by:

$$\overline{M}\ n = \frac{M_M \cdot \left(C_{M,0} - C_M\right)}{\mu_0 + \lambda_0} \tag{11}$$

Constants of elementary reactions rates were calculated by following equations:

$$k_i = 1.039 \cdot 10^8 \cdot \exp\left(-\frac{42000}{R \cdot T}\right) \tag{12}$$

$$k_p = 0.8 \cdot 10^7 \cdot \exp\left(-\frac{11700}{R \cdot T}\right) \tag{13}$$

$$k_{td}^0 = 6.8 \cdot 10^{11} \cdot \exp\left(-\frac{11700}{R \cdot T}\right) \tag{14}$$

Laws of change of growth and chain termination rate constants with conversion increasing are approximated by the following dependencies:

$$\frac{k_{td}}{k_{td}^0} = \frac{1}{1 + 122.2 \cdot X^2} \tag{15}$$

$$\frac{f_i}{f_i^0} = \frac{1}{1 + s \cdot X^m} \tag{16}$$

$$m = 4 + 0.2 \cdot t \tag{17}$$

$$s = 121767 + 0.395 \cdot t^3 - 23202 \cdot t^{0.5} + 7.418 \cdot 10^{14} \cdot \mathrm{e}^{-t} \tag{18}$$

$$X = 1 - \frac{C_M}{C_{M,0}} \tag{19}$$

The system of equations (1 - 19) was solved numerically by means of the Mathcad software. Runge-Kutta 4th order numerical method was used. Mesh with step $\Delta y = 0.001$ m was used along the dryer length.

Proposed model has been practically validated. In the laboratory scale experiments two technological parameters were measured: the temperature and moisture content of the polymer. The relative error for temperature was 5.5%, for moisture content it was 7%. The relative error in both cases did not exceed 10%, so we can make a conclusion about the adequacy of the proposed mathematical model.

## 3. Results and discussion

Computation of the dryer was performed using the developed mathematical model. Initial conditions of the processes occurring in the prepolymer for the drying step are characteristic of the reaction mass obtained under isothermal conditions at temperature of 30°C. The initial moisture content is 1 kg/kg, degree of conversion is 50%. Calculations were performed for a 2 mm thickness of the prepolymer layer.

Figure 2 presents the change of prepolymer temperature $t$, air temperature $t_A$, heat-radiating panel temperature $t_{IR}$ and flue-gases temperature $t_{FG}$ along the dryer length. The model considers the inconstancy of flue gases temperature $t_{FG}$ inside of heat-radiating panels. Flue gases move inside these panels heating them; therefore, the temperature of radiation surface $t_{IR}$ changes also. The prepolymer is heated by a stream of infrared radiation. Its temperature changes from 25°C to 95°C. The air moves counter current to prepolymer and heats from 20°C till 93°C (Fig. 2).

Figure 3 shows the change of prepolymer moisture content $U$ and the degree of monomer conversion $X$ during time of combined polymerisation and drying processes. The initial stage of the process is characterised by rapid growth of the prepolymer temperature (see curve 1 in Fig. 2), which leads to a reduction of diffusion limitations on the initiation reaction and chain growth reaction, and hence to an increase of the polymerisation rate. Water is a required component of the reaction mass. The prepolymer moisture content decreases rapidly, but it is sufficient to complete the polymerisation. Thus, at a conversion of 99%, the polymer moisture content is about 0.2 kg/kg. Figure 3 shows that the monomer conversion increases rapidly and achieves 99.5% conversion degree on the 2/3 of dryer length. It corresponds to 4 meters. The prepolymer moisture content reaches the required value only at 6 meters. So, we can conclude that for the chosen range of parameters, the polymerisation proceeds faster than drying. This is achieved due to drying being carried out by natural air convection. Heating the material is provided by IR radiation sources.

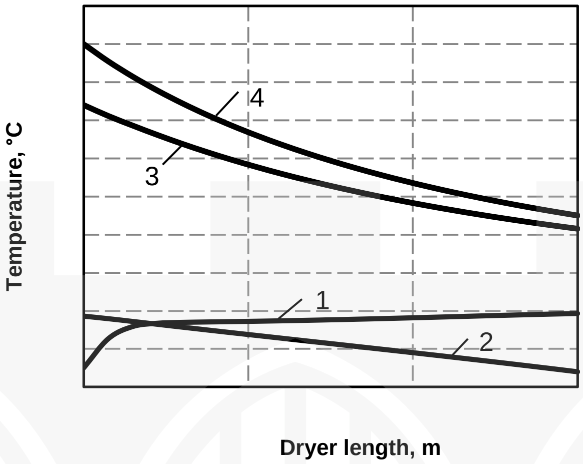

Fig. 2. The temperature upon the dryer length
1 – polymer temperature; 2 – air temperature; 3 – heat-radiating panel temperature; 4 – flue gases temperature

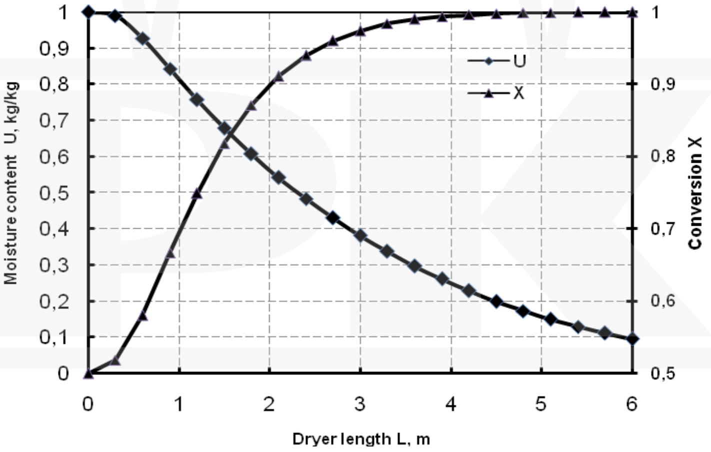

Fig. 3. The polymer moisture content *U* and monomer conversion *X* upon the dryer length *L*

Thus, the developed mathematical model describes the kinetic laws of combined polymerisation and drying as well as the influence of polymerisation kinetics on the heat and mass transfer. It allows to predict the change of monomer conversion degree, moisture content of polymer, temperatures of gas and polymer in the dryer as well as dryer sizes.

In a practical industrial scale application the combined polymerisation and drying of polyacrylamide prepolymer can be carried out in existing commercial IR dryers. But these dryers should be upgraded for new product.

## Nomenclature

$a$, $b$ – stoichiometric factors, – ;
$B$ – belt length, m;
$c_{12}$ – mutual emissivity coefficient, W m$^{-2}$ K$^{-4}$;
$C_M$ – monomer concentration, [mole l$^{-1}$;
$c$ – heat capacity, J kg$^{-1}$ K$^{-1}$;
$f_i$ – initiation efficiency, – ;
$G$ – mass flow, kg s$^{-1}$;
$h$ – gel layer thickness, m;
$I$ – oxidant concentration, mole l$^{-1}$;
$J$ – reductant concentration, mole l$^{-1}$;
$k_p$ – chain growth rate constant, l mole$^{-1}$ s$^{-1}$;
$k_{td}$ – chain termination rate constant, l mole$^{-1}$ s$^{-1}$;
$k_i$ – initiation rate constant, l$^{a+b-1}$ mole$^{1-a-b}$ s$^{-1}$;
$m$ – empirical coefficient, – ;
$p$ – pressure, [Pa;
$R$ – universal gas constant, J mole$^{-1}$ K$^{-1}$;
$r^*$ – vaporisation heat, J kg$^{-1}$;
$s$ – empirical coefficient – ;
$t$ – temperature, °C;
$T$ – temperature, °K;
$U$ – moisture content, kg kg$^{-1}$;
$W_y$ – velocity of the prepolymer, m s$^{-1}$;
$X$ – degree of monomer conversion, – ;
$y$ – coordinate along the dryer length, m;
$\alpha_{FG}$ – heat-transfer coefficient from flue gases to heat radiating panel, W m$^{-2}$ K$^{-1}$;
$\alpha_A$ – heat-transfer coefficient from polymer to air, W m$^{-2}$ K$^{-1}$;
$\beta$ – mass transfer coefficient, kg m$^{-2}$ s$^{-1}$ Pa$^{-1}$;
$\Delta H$ – heat of reaction, J mole$^{-1}$;
$\mu_0$ – initial moment of the molecular weight distribution of active chains, mole l$^{-1}$;
$\lambda_0$ – initial moment of the molecular weight distribution of inactive chains, mole l$^{-1}$;

Subscripts

$A$ – air
$FG$ – flue gases

*IR* – infrared radiation
*w* – water
0 – initial value
*end* – end value

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