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MODELLING AND COMPUTER SIMULATION OF POLIMERISATION AND DEGRADATION PROCESSES

PhD Theses Summary

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1. Introduction and objectives

Polymers are widely used materials in various areas of everyday life like packaging materials, protective layers, dyes, construction or structure materials *etc*.

The specific conditions of use require special characteristics of the applied materials, which can be only fulfilled by "tailored" properties, and the use of novel industrial processes. To avoid costly and time consuming experimentation, modelling is a more and more often used R&D tool.

The aim of the present thesis work is the modelling and computer simulation of two important polymeric processes: the formation of polymers with a specific molecular weight distribution, and the degradation of flame retarded and untreated polymers.

The characteristics of different polymers are mainly determined by the relative ratio of the building blocks at various chain-lengths. Modelling of living anionic homopolymerisation has been used to design a continuous production process of polymers with a target molecular weight distribution considering various equipment and process parameters. There are a number of well known methods for the prediction of the molecular weight distribution of a polymeric product. Most of these methods solve the differential equation set of the component balances.[1,2] However, due to the complexity of the equation set, in these methods the inverse calculation direction is usually difficult or impossible. Therefore, the determination of the reactor parameters and the monomer and initiator concentration profiles from the molecular weight distribution of the product has not been readily available.

For living polymerisation, the relatively simple reaction mechanism gives rise to a simplified and reversible calculation to predict the ratio of the starting materials based on the characteristics of the product polymer.

Living anionic polymerisation consists of a chain initiation step (1) and a chain propagation step (2). Termination or chain-transfer steps can be neglected usually. The initially formed active centres grow continuously (i.e. "live") during the reaction, until all the

[1] Ray, W. H.: On the matematical modelling of polymerization reactors. J. Macromol. Sci.-Rev. Macromol. Chem., C8, 1-56 (1972).

[2] Wulkow, M. (1993). PREDICI simulation package, Computing in Technology GmbH, 200 Oldenburger Str., Rastede, Germany

monomers are consumed, or until they are deactivated by a proton donor (most often an alcohol) addition to the mixture.

$$I + M \xrightarrow{\quad k_i \quad} P_1 \qquad\qquad (1)$$

$$P_n + M \xrightarrow{\quad k_{pn} \quad} P_{n+1} \qquad\qquad n=1,2,3,\ldots \quad (2)$$

In Equations (1-2) k_{pn} is the reaction rate constant of the chain elongation with one monomer unit, k_i is the rate constant of the initiation step, I is the initiator (in the balance equations: the initiator concentration), M is the monomer (monomer concentration) and P_n is the n unit long polymer (polymer concentration).

The chemical industry uses anionic polymerisation to produce elastomers and thermoplasts in large amounts. Widely used plastics like polyamides or polystyrene are produced in anionic polymerisation processes. If initiation is not very slow, the reaction gives a well-defined, narrow molecular weight distribution, which makes the product suitable for research studies, like the investigation of star polymers.

The molecular weight distribution (MWD) from a living polymerisation process carried out in various reactor configurations with constant or unsteady feed profiles can be very well approximated with a simplified, very fast, direct algorithm, the method of monodisperse growth.[3] The burden of the precise MWD calculations is eased off by simplifying the multi-step chain growth to a single-step (monodisperse) process. As it is possible to reverse this method, it is suitable for design purposes and leads to an obvious advantage compared to the other known molecular weight distribution calculation methodologies. The previously established algorithms are only able to handle design objectives with iterative loops. The aim in this work has been to create a design methodology which helps exploring the production possibilities and barriers of single and multi-reactor systems. An inverse calculation process has been developed that delivers the necessary production parameters to produce the best fit to a target MWD taking into account the restrictions of the process.

The modelling of polymer degradation phenomena focuses more on the heat and mass transport processes. The material properties at various heat effects, the fuel gas emissivity of

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[3] Meszena, Z. G.; Viczian, Z.; Gosden, R. G.; Mohsin, M. A.; Johnson, A. F.: Towards tailored molecular weight distributions through controlled living polymerisation reactors: a simple predictive algorithm. Polym React Eng, 7(1), 71-95 (1999)

different modified polymers have been investigated in order to identify the fire hazard of these materials. The fire degradation characteristics of materials were investigated earlier by others – many measurement standard were developed during the years, which made the properties comparable. However, these measurements are not able to answer the various questions of hazard analysis, e.g. the rate of change of heat emissivity of material layer with the amount of material and surface size, or the change of the polymer degradation rate with changing flame properties, etc.

The aim of this work was to model the heat and mass transport phenomena of burning polymer layer. The model can forecast the behaviour of material and helps to understand the degradation mechanisms. Through the years many complex models were published, but the presently available computational power is still not sufficient enough, and some simplifications are needed to solve the model equations of such constantly moving systems.

The upper surface of polymer layer is exposed to constant level of heat irradiance, which initiates the degradation. Most related publications handle this as an instantaneous reaction on the surface of char and virgin polymer.[4]. The rate of degradation is defined by the heat transfer equilibrium of char - virgin polymer interface. Another important effect on the degradation rate is the flux and burning of produced gas. The char layer over the reaction zone hinders the gas transport and builds up a pressure profile in the porous char layer. Which is of interest is the mechanical strength of the layer, i.e. the maximal pressure that the system can bear without fracture. In general, most of previously published models do not take into account the effect of burning of produced gas as a secondary heat source on the sample surface. In simple cases it is treated as a constant value.[5].

Based on this knowledge, the aim here was to develop a model, which is able to describe the mass loss cone calorimeter measurements of the Department of Organic Chemistry and Technology, handles both of mass and heat transport phenomena and contains the additional dynamic heat source of burning fuel gases.

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[4] Staggs JEJ. Heat and mass transport in developing chars, Polymer Degradation and Stability 2003;82:297–307.
[5] Hopkins Jr D and Quintiere JG. Material Fire Properties and Predictions for Thermoplastics. Fire Safety Journal 1996;26:241-268.

2. Methods and materials

The fire resistance of the polymer is characterized by ignition time, mass loss of sample and the heat release rate. The experiments have been carried out with mass loss calorimeter, according to ISO 13927, Fire Testing Technology, at heat flux of 50 kW/m². The polymer matrix was epoxy resin (ER) type Eporezit AH-16 applied with Eporezit T-58 curing agent. A synthesized phosphorus-containing reactive amine, TEDAP was used as flame retardant.[6]

The differencial equation set of the cone calorimeter model has been solved in Matlab using a special combination of various numerical methods.

The molecular weight distribution calculations have been carried out in Microsoft Excel.

3. New scientific achievements

A model has been developed for living anionic polymerization to design the molecular weight distribution of polymers. The algorithm is based on the method of monodisperse chain growth, where the dispersion effect of chain growth is neglected and the residence time distribution of reactor defines the shape of produced molecular weight distribution. Additionally, it has been assumed that the monomer concentration can be keep at constant level in the reactor during the polymerization. With these assumptions the product molecular weight distribution can be determined quickly and with low calculation effort compared to other known methods.

Another advantage of the method is its reversibility and so it is possible to calculate from the product molecular weight distribution the necessary polymerization circumstances. In this work the possibility of producing arbitrary molecular weight distributions with different reactor types has been explored. A new design process has been developed for polymerization in a cascade of continuous stirred tank reactors at steady state conditions. Steady state continuous reactor systems are the closest to industry standards, since difficult

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[6] Toldy A, Tóth N, Anna P, Keglevich Gy, Kiss K, Marosi Gy. Flame retardancy of epoxy resin with phosphoruscontaining reactive amine and clay minerals. Polym. Adv. Technol. 2006;17:1–4.

feed strategies are impossible to realize in big reactor volumes. In lab scale with semi-continuous production the range of feasible molecular weight distributions becomes wider and it is possible to create unique distributions using complex monomer and initiator feed strategies.

The results of the design method established have been compared with other independent calculation methods and it has been proven that the neglected effects would not change significantly the shape of the resulting molecular weight distribution.

The second part of this work, carried out in cooperation with the Center of Pharmaceutical, Environmental and Safety Materials, focuses on the modelling of polymer layers heat degradation phenomena. The decomposition is initiated by an external heat source. After reaching a critical temperature the polymer degrades to a fixed fraction of char and gas instantaneously, and the gas leaving the matrix ignites above the sample surface. The established one-dimensional model calculates the degradation rate, the temperature and quality change in the whole depth of the polymer layer. The thickness of the degradation zone is assumed to be infinitely small: there is a sharp interface between the char and virgin polymer, therefore, the gas and the molten polymer cannot coexist in the same volume in the model.

Mass transport in the char has been modelled with Darcy expression combined with the expression of conservation of mass and corrected with the gas conservation of char layer (3)

$$\frac{dm''}{dt} = -(1-r)\rho_p \frac{ds}{dt} - \int_{s(t)}^{l} \phi \frac{d\rho_g}{dt} dy \tag{3}$$

where m'' mass of leaving gas on the upper surface per unit area, y local coordinate, t time coordinate, ρ the density of gas (g) and char (c), ϕ porosity of char, r char mass fraction, $s(t)$ the location of reaction zone.

In the heat transport model three transport mechanisms have been built in: bulk conduction, convection by gas releasing and radiation across the pores.

$$k_{eff} \frac{\partial \hat{T}}{\partial y} = \frac{\varepsilon \dot{q}_0''}{T_a} + h_1(\hat{T}_{fl} - \hat{T}) + \varepsilon \sigma T_a^3 (\hat{T}^4{}_{fl} - \hat{T}^4) + \frac{\varphi \varepsilon H_c}{T_a} \frac{dm''}{dt} \tag{4}$$

where $\hat{T}$ relative temperature, T_a ambient temperature, T_{fl} flame temperature, $\dot{q}_0''$ external heat flux of cone heater, k_{eff} heat transport coefficient in char–gas system, H_c combustion heat, ε emissivity of exposed surface, σ Stephan-Boltzmann constant, h_1 convection heat transfer coefficient at the exposed surface.

The amount of absorbed pyrolysis heat is an important factor in the degradation model. Two different models have been developed in order to take into account the reflected heat. In the first case the energy is a linear function (φ) of gas emission, in the second model a more complex, non-linear function is applied, which describes the dynamic nature of flame. It has been found that there is no significant difference between the results. However, further investigations are needed to develop the functional form of the reflected heat.

The heat transport in the char takes place by conduction of char and gas in the mixture and by convection of the flowing gas in the char. The heat conservation of char and gas was taken into account, too (5):

$$\left(\phi\rho_g c_g + (1-\phi)\rho_c c_c\right)\frac{\partial \hat{T}}{\partial t} + \rho_g c_g q \frac{\partial \hat{T}}{\partial y} = \frac{\partial}{\partial y}\left(k_{eff}\frac{\partial \hat{T}}{\partial y}\right) \tag{5}$$

where q gas flux per unit area and c heat capacity of gas (g) and char (c).

The moving grid problem has been solved with the Landau transformation. An in-hous program in Matlab programming environment has been developed using a combination of different numerical methods. Various time and space coordinate discretization schemes have been investigated. The amount of produced gas has been determined and has been compared with Eporezit AH-16 epoxy resin measurements. Using the developed model the heat conductivity and heat capacity of material were fitted to the measurements in the temperature range used, and the temperature and pressure profiles were predicted for the whole dept of sample.

4. Theses

1) An algorithm and a computer program have been developed to model the burning of polymer layers. The program can be used in scale-up calculations. It is able to calculate the degradation rate and the temperature and pressure profiles in depth of the polymer sample. (F2, F3, K10, K11, K14)

2) The model has been applied to simulate the phase change of samples burned in a cone calorimeter. Heat conductivity and heat capacity values predicted were compared to literature data and fitted to the cone calorimeter measurements in the observed temperature range. It has been found that the ignition time is defined by the heat conductivity of sample if absorbed heat is constant (F2, F3, K14)

3) Applying the method of monodisperse chain growth a novel algorithm has been developed and simulations have been carried out to calculate the molecular weight distribution (MWD) of isotherm living polymerization in a cascade of continuous stirred tank reactors. It has been found, that at constant monomer level the MWD is determined by the initiator feed stategy and the residence time distribution of the reactor. (F1, F4, F5, K2, K3, K4, K5, K7)

4) A design algorithm has been developed by inverting the method of monodisperse growth. The algorithm is able to determine the necessary production parameters of living polymerization carried out in a cascade of continuous stirred tank reactors. (F4, K6, K7, K8, K9, K12, K13)

5) It has been found that using a single continuous stirred tank reactor the final molecular weight distribution of the polymer is always the Schulz-Flory distribution, independent of the shape of the initiator feed profile, if it is periodically changed. (F1, F5, K2, K3, K4)

6) Applying the molecular weight distribution design process the necessary process strategy and production parameters have been calculated for a bimodal molecular weight distribution produced in a cascade system of four continuous stirred tank reactors. (F4, K1, K13)

5. Application related activities

The steady-state reactor cascade model developed uses simple, constant rate raw material feeds, and therefore it is well suited for industrial-scale living anionic polymerisation. In addition to the reactor cascade design process described in this work, the method is suitable for the quick calculation of any reactor configurations.

The method for the design and dynamic calculation of the molecular weight distribution is suitable for the design of special polymers, and also gives an opportunity to study the characteristics of these materials. It is also suitable for molecular weight distribution optimization.

The fast speed and reversibility of the method developed open new opportunities in the field of reaction and process control. Combined with process control algorithms, the present calculation enables an adaptive and predictive control method for obtaining the desired target polymer characteristics. This opportunity is not discussed here in details, further work is needed, and are going to be published elsewhere.

Based on the results of the cone calorimetric measurements, the degradation model established can give a first estimation for the heat conductivity and heat capacity characteristics of new flame retarded materials under heating and burning conditions. Information offered by the model predictions is difficult or impossible to get from experiments. By estimating the characteristics and degradation mechanism of materials, the model can help with the design of flammable constructions (buildings, transport vehicles etc.) if the exact physicochemical properties are known.

Related publications

English publications

F1 **E. Farkas**; Z. G. Meszena; A. F. Johnson: Molecular Weight Distribution Design with Living Polymerization Reactions.
Ind. Eng. Chem. Res. 2004**,** *43,* 7356-7360 (Imp.Fact. 1,424)

F2 **E. Farkas**, Z.G. Meszena, A. Toldy, S. Matkó, B.B. Marosfői and G.Y. Marosi Modelling of transport processes in a developing char, chars, *Polymer Degradation and Stability* 2008, *93,*1205–1213 (Imp.Fact. 2,073)

F3 **E. Farkas**, A. Toldy, S Matkó, B. B. Marosfői, G. Marosi, Z. G. Meszena Degradation of Neat and Flame Reatarded Polymer – Comparison of Simulation and Experimental Results, *Chemie Ingenieur Technik* 2008, *80*, No.9 1430 (Imp.Fac. 0,401)

F4 **E. Farkas**, Z. G. Meszena, MWD design in a series of CSTRs with living polymerisation reactions *Periodica Polytechnika* 2009, *(submitted)*

Hungarian publication

F5 **E. Farkas**; Z. G. Meszena Molekulatömeg-eloszlás tervezése élő polimerizációs reakciónál *Acta Agraria. Kaposváriensis* 7(3), 119-133., 2003

Conference publication

K1 **Farkas, E.**, Meszéna, Z., G. Tailored molecular weight distribution for anionic homopolymerization – possibilities and barriers of a reactor cascade system (Proc. of 28th ChEM Conference, p.22-25, ISBN 978-963-420-960-7 Meissen, Germany, (2008)

Presentations and posters

K2 **Farkas E.**, Meszéna Z.: Molekulatömeg-eloszlás tervezése kevert tartály-reaktor illetve csõreaktor esetén, Műszaki Kémiai Napok, Veszprém (2003)

K3 **Farkas E.**, Meszéna Z.: Molekulatömeg-eloszlás tervezése élő polimerizációs reakciónál (poster), Alkalmazott Informatikai Konferencia , Kaposvár (2003)

K4 **E. Farkas**, Z. G. Meszena: Molecular weight distribution design with living polymerisation reactions (poster), Polymer Reaction Engineering: Modelling, Optimisation and Control Conference, Lyon France (2003)

K5 **Farkas E.**, Meszéna Z.: Méretre szabott molekulatömeg-eloszlás folyamatos kevert tartályreaktorban és csőreaktorban IX. Nemzetközi Vegyészkonferencia, Kolozsvár, Románia (2003)

K6 **Farkas E.**, Meszéna Z.: Polimerizációs reakció modellezése kaszkád rendszerben, Műszaki Kémiai Napok, Veszprém (2004)

K7 **E. Farkas**, Z. G. Meszena: MWD design with tubular and cascade reactors (poster), 8th International Workshop on Polymer Reaction Engineering, Hamburg Germany (2004)

K8 **Farkas E.**, Meszéna Z.: Polimerizációs reakció modellezése kaszkád rendszerben, II. Alkalmazott Informatikai Konferencia, Kaposvár (2004)

K9 **Farkas E.**, Meszéna Z.: Molekulatömeg-eloszlás számítása csőreaktorban és kaszkád rendszerben (poster) Műszaki Kémiai Napok, Veszprém (2005)

K10 **E. Farkas**, Z. G. Meszena: Temperature profile calculation in a polymer degradation process, 10th International Workshop on Chemical Engineering Mathematics, Budapest Hungary (2005)

K11 **E. Farkas**, Z. G. Meszena: Modelling of transport processes in developing char, 26th International Workshop on Chemical Engineering Mathematics Bad Honnef Germany (2006)

K12 Meszena Z.G., Johnson A.F., **Farkas E.,** Control of Polymerisation Processes: A dial-a-polymer concept and the practical challenges presented (poster) 19th Int. Symposium on Chem React Eng, Berlin, Germany (2006)

K13 **Farkas, E.,** Meszéna, Z., G. Tailored molecular weight distribution for anionic homopolymerization – possibilities and barriers of a reactor cascade system , 28th International Workshop on Chemical Engineering Mathematics, Meissen, Germany, (2008)

K14 **E. Farkas**, A. Toldy, S Matkó, B. B. Marosfői, G. Marosi, Z. G. Meszena Degradation of neat and flame retarded polymer – comparison of simulation and experimental results (poster), ProcessNet Jahrestagung, Karlsruhe, Germany (2008)