

Transport and Reaction in Reconstructed Polyolefin Particles

A. Zubov, L. Pechackova, L. Seda, J. Kosek*

*Department of Chemical Engineering, ICT Prague
Technicka 5, 166 28 Prague 6, Czech Republic*

1. Introduction

The contribution addresses several problems associated with morphology of porous polyethylene and polypropylene particles produced in catalytic gas- and liquid-dispersion reactors. The knowledge of transport characteristics of monomers and diluents in these polyolefin particles is important for the quantitative prediction of particle growth. Transport of monomers and diluents affects the rate of polymerization, the rate of particle growth, the copolymer composition distribution within the particle, and the morphology of the growing particle. Moreover, transport characteristics have a strong impact on the degassing of polyolefin powder in the post-polymerization processing.

2. Reconstruction of porous polyolefin particles

Polyolefin particles used in our simulations are digitally reconstructed from X-ray microtomography images. The progress of reconstruction is visualized in **Fig. 1**. At first, the original tomography image is binarized and then processed by binary operations (opening, closing, erosion, etc.) to remove noisy data from pictures. Sets of binary images are then discretized to ones (porous phase) and zeros (solid phase), cf. Eq. (1), and stored in the three dimensional matrix $f_g(\mathbf{r})$ representing spatial domain, cf. **Fig. 1c**.

$$f_g(\mathbf{r}) = \begin{cases} 1 & \text{if } \mathbf{r} \in \text{pore} \\ 0 & \text{otherwise} \end{cases} \quad (1)$$

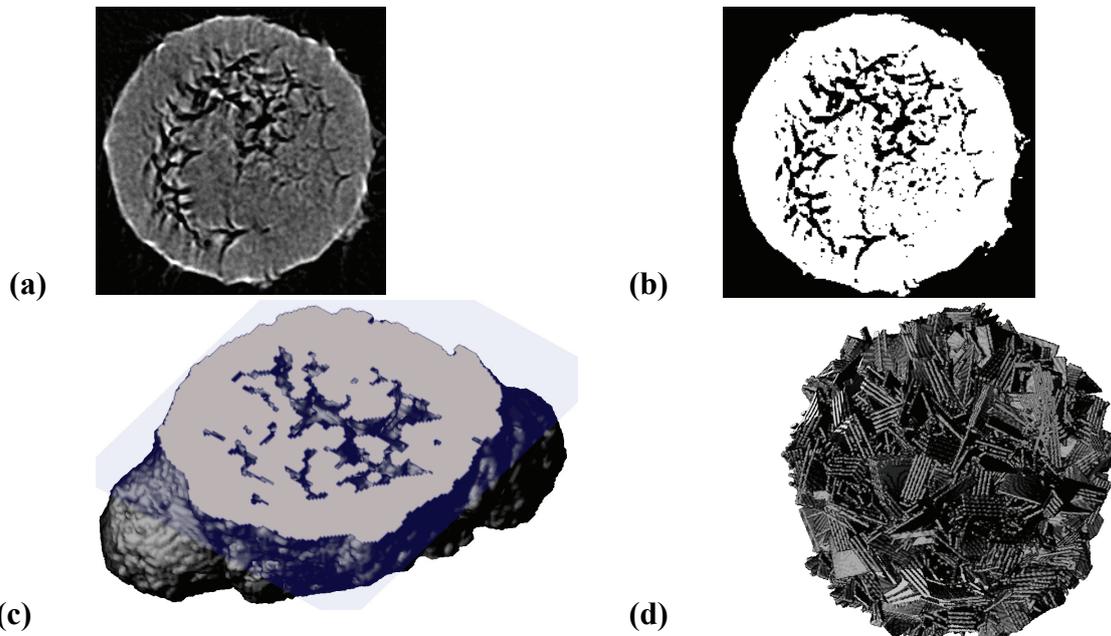


Fig. 1. Digital reconstruction of polyolefin particle; (a) original X-ray tomography image; (b) binarized image; (c) reconstructed particle; (d) reconstructed lamellar structure of spherulite.

* Corresponding author, E-mail: Juraj.Kosek@vscht.cz

Symbol $\mathbf{r} = (x, y, z)$ represents the spatial position of the voxel. The spatial resolution of the tomograph with laboratory source of photons is of the order of micrometers so that the finer structures are not distinguished. However, the techniques like AFM and WAXS provide information about the morphology of sub-micron spherical structures in polyolefin particles. These structures are called spherulites and they are composed of amorphous and crystalline polymer. The thickness of crystalline lamellae is approximately 10 nm. We are also able to reconstruct the spherulite particles, cf. **Fig. 1d**, compute their transport properties and use the obtained results for computations further on larger, i.e., micron scale.

3. Dynamics of degassing of reconstructed polymer particles

The second addressed problem is the dynamics of diffusion of penetrants away from the polymer particle because this process is crucial for the post-polymerization processing of the polymer. We showed in [1] that in case of porous particles with broad distribution of solid polymer zones the degassing curve cannot be approximated with simple Fick's diffusion from compact spherical particle, cf. **Fig 2**.

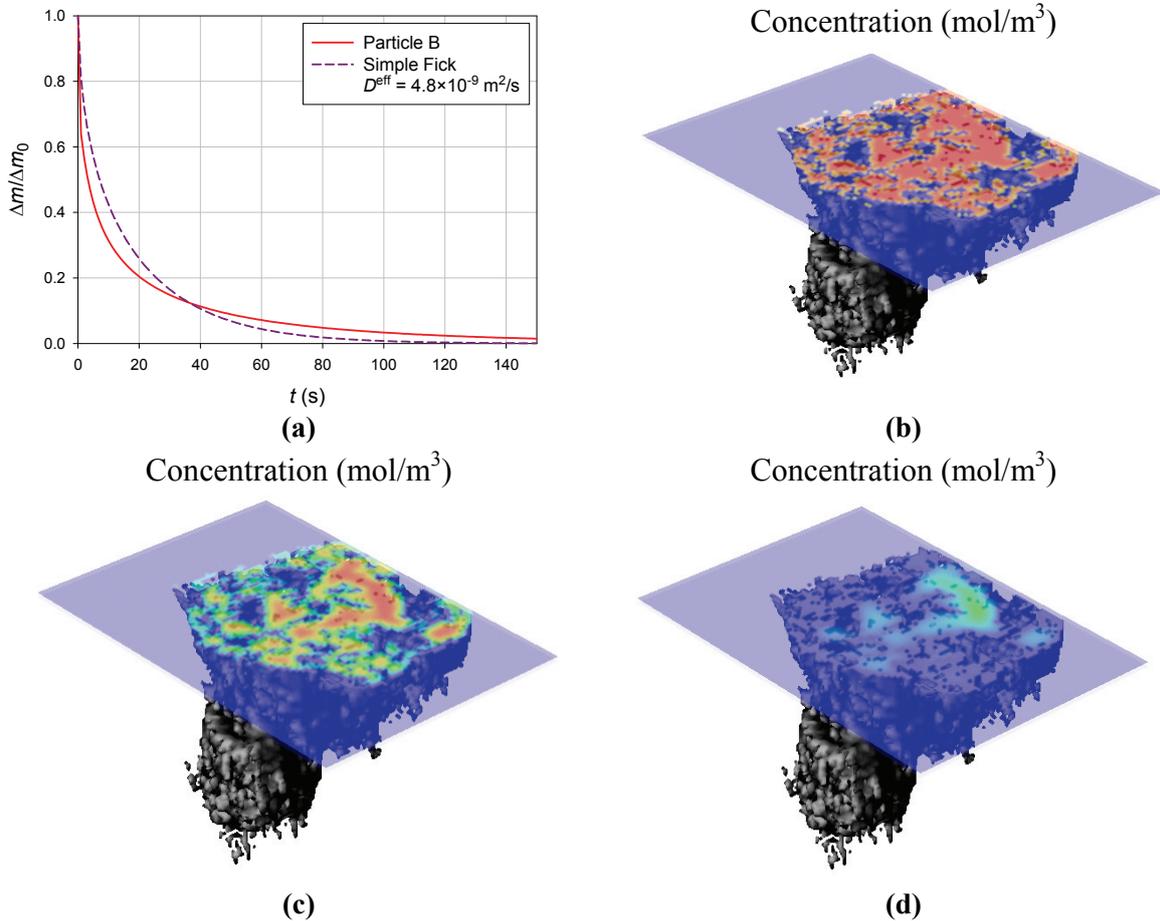


Fig. 2. Evolution of mass of sorbed monomer in polymer particle. **(a)** full line corresponds to degassing of particle B and the dashed line corresponds to degassing of spherical particle with the same volume of solid phase; **(b)** concentration profile in particle B in simulation time $t = 1$ s; **(c)** concentration profile in particle B in simulation time $t = 10$ s; **(d)** concentration profile in particle B in simulation time $t = 100$ s.

4. Polymerization reaction in polyolefin particles

The third addressed problem is the interaction of reaction and transport processes in spatially 3D polyolefine particles. We demonstrate that monomer mass transport limitations are important not only in the early stage of particle growth, but also in fully-developed polyolefin particles, cf. **Fig. 3**.

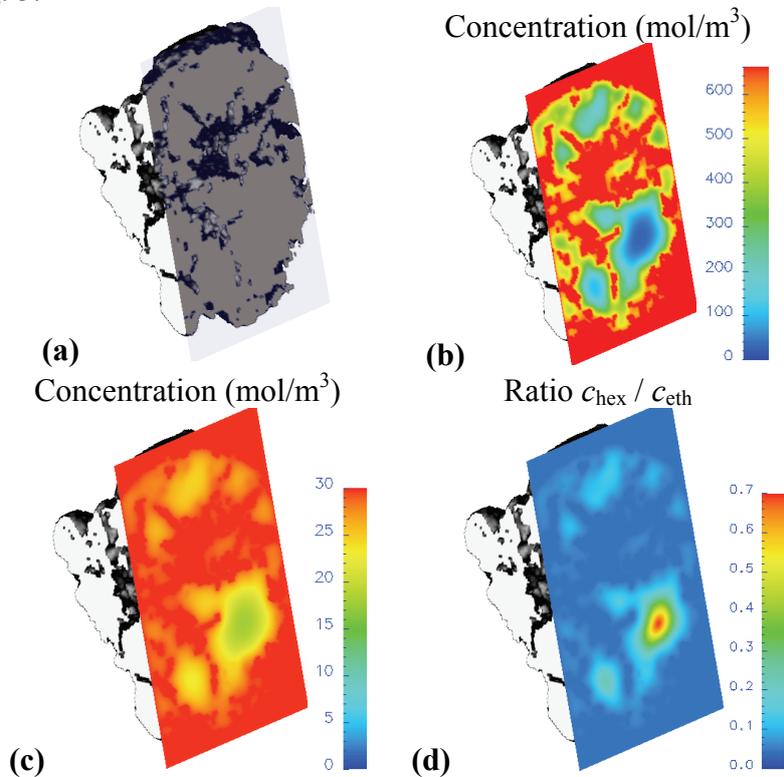


Fig. 3. Concentration profiles of (b) ethylene and (c) 1-hexene in porous polymer particle (a); (d) ratio of concentration of 1-hexene to ethylene.

3. Conclusions

We demonstrate the utilization of digital reconstruction of polyolefin particles from Roentgen tomography for computing the transport properties of real porous media and the effect of diffusion limitations for dynamics of degassing and for reaction-diffusion problems.

4. References

- [1] Seda L., Zubov A., Bobak M., Kosek J., Kantzas A.: Transport and reaction characteristics of reconstructed polyolefin particles, *Macromolecular Reaction Engineering* Vol. 2, 2008, 495-512.
- [2] Kosek J., Stepanek F., Marek M.: Modeling of transport and transformation processes in porous and multiphase bodies, in *Advances in Chemical Engineering*, Vol. 30 „Multiscale Analysis“, edited by Marin G.B., Elsevier (2005).
- [3] Bobak M., Gregor T., Bachman B., Kosek J., *Macromolecular Reaction Engineering* 2008, 2, 176.
- [4] A. Novak, M. Bobak, J. Kosek, B. J. Banaszak, D. Lo, T. Widya, W. H. Ray, J. J. de Pablo, *J. Appl. Polym. Sci.* 2006, 100, 1124.
- [5] Grof Z., Kosek J., Marek M., Adler P.M.: Modelling of morphogenesis of polyolefin particles: Catalyst fragmentation, *AIChE J.* 49(4), 1002-1013 (2003).
- [6] Grof Z., Kosek J., Marek M.: Morphogenesis model of growing polyolefin particles, *AIChE J.* 51(7), pp. 2048-2067, (2005).