Simulation of the Decontamination Efficiency of PET Recycling Processes based on Solid-state Polycondensation

Alexandra Mauer, Frank Welle

Fraunhofer Institute for Process Engineering and Packaging (IVV), Giggenhauser Straße 35, 85354 Freising, Germany, email: welle@ivv.fraunhofer.de, phone: ++49 8161 491 724

Introduction

The use of poly(ethylene terephthalate) (PET) bottles for softdrinks and mineral water is increasing all over the world. Together with the extended use also the recollection rates for post-consumer PET bottles are increasing year by year. For example, in Europe 1.450.000 t of post-consumer PET bottles were recollected in 2010. This is a growth of 6.5% in comparison to 2009. The overall recollection rate, which is the ratio between the PET bottles on the market and the collected post-consumer bottles, was 48.3% in Europe. The recollected post-consumer PET bottles were recycled either to fibres or to new packaging applications after decontamination (super-cleaning). The main task of the super-clean recycling processes is to remove traces of contaminants from the recyclates. In most cases, the super-clean processes are based on solid-state polycondensation (SSP) processes. Within these processes the PET pellets are heated up to temperatures of about 200 °C. In addition, vacuum or an inert gas atmosphere (e.g. nitrogen) is applied to remove the contaminants from the PET pellets. An overview of the different recycling technologies and process steps is given in the literature[1].

Aim of the study was the simulation of the decontamination of a SSP super-clean recycling process by use of migration models[2].
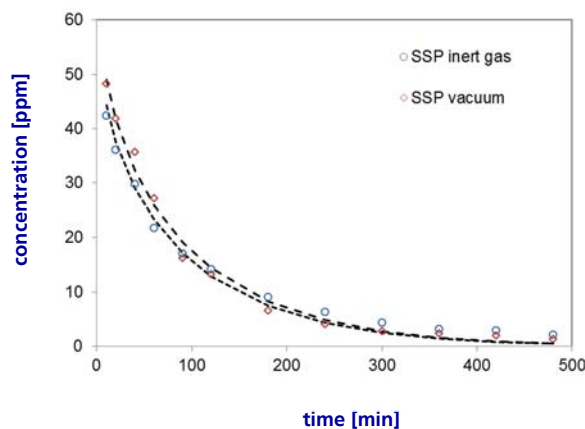
Results and Discussion

Within this study experimentally analysed concentration of model substances were determined from a challenge test with model contaminants. The residual concentrations of the surrogates in the PET pellets at different residence times in the decontamination reactor were used for the fitting of the curves. The results of the decontamination kinetics in the PET pellets for phenyl cyclohexane is shown in Figure 1. It is interesting to note, that in the beginning of the solid-stating reaction, the concentrations of both surrogates are higher for the vacuum process in comparison to the inert gas process even if the re-extruded pellets are coming from the same batch. The reason is most probably the lower thermal transfer in the case of the vacuum system. Therefore, the heating time of the PET pellets to reach the final decontamination temperature is longer for vacuum processes as for inert gas processes. During heating, the model substances were also removed from the pellets. This leads to a higher starting concentration for the vacuum process in comparison to the inert gas process. On the other hand, the decontamination rates are similar under vacuum or inert gas treatment, which is in agreement with the (expected) result that the diffusion of the surrogates in the PET polymer follows exactly Fickian laws. The diffusion of the model contaminants in PET is not influenced significantly by the vacuum or inert gas system at the outside of the pellets. Therefore, both decontamination processes can be simulated by using the same diffusion coefficients for the applied model contaminants.

The best fit of the mathematical simulation for phenyl cyclohexane is given as dotted lines in Figure 1. The diffusion coefficients of all applied surrogates determined from the best fit of the experimental data of the decontamination kinetics at 205 °C are summarized in Table 1. For comparison, also the diffusion coefficients derived from literature data of the activation energies determined by high temperature migration from PET bottle wall stripes into the gas phase of diffusion are given[3]. Using these activation energies, the diffusion coefficients at 205 °C can also be calculated using the Arrhenius approach. The diffusion coefficients determined in this study are in good agreement with the diffusion coefficients derived from the activation energies. However, the diffusion coefficients derived from the decontamination reaction are slightly lower than found from the high temperature migration kinetics. The reason is most probably that the pellets are crystalline whereas the PET bottles used for the determination of the high temperature migration kinetics are only partly crystallised (approx. 40%). The lower crystallinity in the PET bottles compared the crystallised PET pellets lead to lower diffusion rates of the contaminants.

Figure 1: Correlation between the concentration of the surrogate phenyl cyclohexane and the square root of time for the SSP samples (dashed lines: simulation from activation energy)

Conclusions

The results of this study show that the decontamination of PET pellets in solid-state polycondensation processes is following Fickian laws. Therefore the diffusion equations used in commercial available software packages for migration calculation can be used for the simulation of the decontamination efficiency. This might be a useful tool for the process development and optimization of PET recycling processes. Another important result of this study is that the diffusion coefficients of the artificial contaminants are not influenced by the vacuum or inert gas system. Therefore, the diffusion rate of a certain contaminant in the PET material is (nearly) the same independent if a vacuum or an inert gas stream is used for the evaporation of the contaminants from the PET pellet surface. This result is obvious because the contaminant trapped in the polymer does not know which conditions are applied at the outside of the PET pellet. So only the temperature (or more precisely the diffusion coefficient) is influencing the cleaning efficiency of a recycling process. However, when the contaminant reaches the outside of the PET pellet it must be removed from the surface. The vacuum or inert gas conditions applied in this study seems to be enough efficient to remove the contaminants satisfactory from the surface of the PET pellets. Another point is also important: the simulation was done only on one single pellet. Therefore, it can be concluded, that the up-scaling of the recycling plant does not influence the cleaning efficiency of the recycling plant. Only the heating time of the material might be influenced by the plant scale. But typically the heating time was not considered in the cleaning efficiency evaluation. As consequence, the cleaning efficiency of small scale processes (e.g. several kg per hour) are the same as for industrial scale plants with 1000 to 2000 t per hour.

References

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[2] C. Simoneau (editor), Applicability of generally recognised diffusion models for the estimation of specific migration in support of EU Directive 2002/72/EC. 2010. EU report 24514 EN. ISBN 978-92-79-16586-3.

[3] J. Ewender, F. Welle, Determination of the Activation Energies of Diffusion of Organic Molecules in Poly(ethylene Terephthalate), *Journal of Applied Polymer Science*, in press, DOI: 10.1002/APP.38623.

Table 1: Experimental determined diffusion coefficients in crystalline PET pellets at 205 °C

Surrogate	Diffusion coefficients [cm² s⁻¹]	
	this study	calculated from activation energy
Toluene	$9.0 \cdot 10^{-7}$	$1.9 \cdot 10^{-7}$
Chloroform	$9.0 \cdot 10^{-7}$	/
Chlorobenzene	$7.0 \cdot 10^{-7}$	$4.0 \cdot 10^{-7}$
Methyl salicylate	$2.6 \cdot 10^{-6}$	/
Phenyl cyclohexane	$5.0 \cdot 10^{-7}$	$7.0 \cdot 10^{-8}$
Benzophenone	$6.0 \cdot 10^{-7}$	$1.9 \cdot 10^{-7}$
Methyl stearate	$7.5 \cdot 10^{-7}$	$1.3 \cdot 10^{-7}$