Determination and prediction of the lag times of hydrocarbons through a PET film

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Introduction

Polymeric materials can be used as functional barriers to prevent contamination of food from the environment or from other packaging components e.g. mineral oil hydrocarbons from printing inks. Polyethylene terephthalate (PET) is such a promising barrier material. From permeation studies found in the scientific literature lag times, diffusion coefficients or permeation rates towards organic chemicals could not derived in most cases due to the slow diffusion process of the permeants in PET. Knowledge about lag times or diffusion coefficients for different permeants, however, is essential for the evaluation of the barrier properties of PET films towards organic contaminants e.g. mineral oil hydrocarbons.
Aim of the study was to develop automated permeation testing method in order to determine the lag times of high barrier films. From the lag times the diffusion coefficients as well as the partition coefficients of the alkanes were calculated. In addition, the permeated amounts were simulated by use of diffusion models. Therefore the lag times can be predicted under different experimental conditions as used in the current study.

Method

The investigated 12 µm PET film was placed in a permeation cell with a lower and an upper space separated by the investigated PET film. The permeation cell was made of aluminium and had an area of 191 cm^2. On both sides a sealant ring is embedded into the aluminium cell. The PET film is clamped between both sealant rings. The lower space of the permeation cell with a volume of 7437 cm^3 was spiked with the *n*-alkanes. The upper side of the cells was rinsed with pure nitrogen. The constant nitrogen flow moved the permeated substances out of the cell. The nitrogen stream was analysed for the applied *n*-alkanes by a connected enrichment unit and gas chromatograph with flame ionisation detection (GC/FID). Permeation was measured at constant temperatures in a climate chamber between 70 °C and 120 °C. From these experimental data the permeation rates of the applied *n*-alkanes are available. Calibration was performed with injections of known amounts of the applied *n*-alkanes.

Results and Discussion

Within the study, the lag times of *n*-alkanes were determined through a 12 µm PET film between 70 °C and 120 °C. Examples of the permeated amounts of *n*-octane, *n*-nonane and *n*-decane at 100 °C through the investigated PET film are shown in Figure 1. The permeated amounts of the investigated *n*-alkanes were calculated from the permeation rates, which are the original measures. The permeation rates for *n*-octane, *n*-nonane and *n*-decane at 100 °C are also given in Figure 1. In the steady state the permeation rate is (nearly) constant. Therefore the permeation rates are used within this study to find the asymptote which determines the lag time. As expected, *n*-nonane and *n*-decane are reaching the steady state after significantly longer storage times. Further results are given in Lit.[1]. Diffusion modelling was used within this study to predict the lag times at ambient temperatures[2]. The predicted lag times for temperatures between 20 °C and 100 °C up to molecular weight of 350 g mol^{-1} are given in Figure 2 together with the experimentally determined lag times.

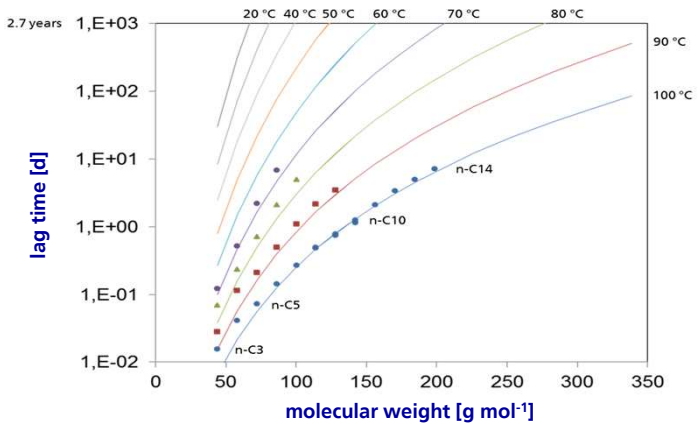

Figure 2: Correlation between the lag time and the molecular weight of the permeants. Dots: experimental data from this study, lines predicted according to Lit.[2].

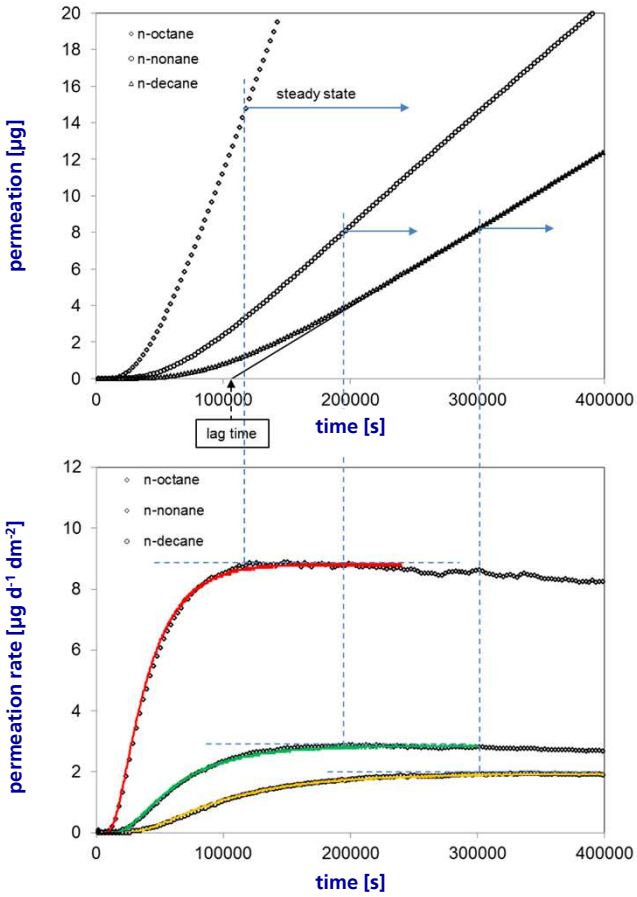

Figure 1: Above: Experimental data for the permeated amount of *n*-octane, *n*-nonane and *n*-decane as a function of time through PET (12 µm) at 100 °C; Below: Permeation rates as a function of time at the same temperature (black dots: experimental data, red, green and yellow lines: simulation)

As a result, the experimental data (dots) are in good agreement with the predicted values (lines). Therefore the lag times *n*-alkanes at various temperatures can be calculated from predicted diffusion coefficients[2].

Conclusions

Within the study an automated method for the determination of lag times for high barrier films was developed. The method applied was able to determine the lag times of alkanes from *n*-propane to *n*-tetradecane at temperatures between 70 °C and 120 °C. But also other barrier films or permeants can be measured with the applied method.
The results of this study show that the investigated 12 µm PET film is an effective barrier towards mineral oil hydrocarbons. For example, the predicted lag time for *n*-octane or *n*-dodecane at 40 °C is 8.8 years and 210 years, respectively.

References

[1] J. Ewender, F. Welle, Determination and prediction of the lag times of hydrocarbons through a PET film, *Packaging Technology and Science*, in press.
[2] F. Welle, A new method for the prediction of diffusion coefficients in poly (ethylene terephthalate), *Journal of Applied Polymer Science*, **2013**, *129(4)*, 1845-1851.

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