Oligomers in poly(ethylene terephthalate) - Diffusion coefficients and migration

Maria Hoppe[a], Roberta Fornari[b], Pim de Voogt[c], Roland Franz[a]

[a] Fraunhofer Institute for Process Engineering and Packaging IVV, Giggenhauser Straße 35, 85354 Freising, Germany
[b] Department of Food, Environmental and Nutritional Sciences, Food packaging Lab, University of Milan, via G. Celoria 2, 20133 Milan, Italy
[c] Institute for Biodiversity and Ecosystem Dynamics, University of Amsterdam, Science Park 904, 1098 XH, Amsterdam, The Netherlands

Introduction

Polyethylene terephthalate (PET) is one of the most important food contact polymers. It is used for many food and beverage packaging applications due to its excellent properties like light-weight, flexibility, resistance to high temperature and low carbon dioxide permeability. Low molecular weight (LMW) oligomers can be formed during the synthesis process of PET as side products of incomplete polymerization[1]. Other ways of oligomer formation can be external induced degradation processes through sunlight and food and beverage contact. Since these LMW oligomers are potential migrants into food and beverages[2] it is of interest to know their diffusion characteristics in the polymer and hence their actual occurring migration levels.

Method

Experiments were carried out such that PET beverage bottle material was subjected to conditions simulating accelerated migration: 50% ethanol in water (v:v) for 15 h at 80°C using an Büchi speed extractor (100 bar). The migration solutions were analysed every hour with LC-MS. The total oligomer content in the PET material was determined by extraction with dichloromethane.
Analyses were conducted using an Acquity UPLC system coupled to a Synapt G2Si (Waters).
Column: Acquity CSH™ Fluoro-Phenyl 1,7 µm 2,1x75 mm (Waters)

LC conditions: 0.5 ml/min, solvent A: methanol, solvent B: water, from 65% A to 100% A in 2.5 minutes, keep at 100% for 1 min and then to 65% in 0.1 min and keep at 65% for 1 min

Ionization: ESI positive

Mass range: 50 – 1200 m/z

External standard: cyclic PET trimer (LOQ = 0.1 ng/mL)

Results and discussion

Twelve different PET oligomers were identified and quantified in the migration solutions. Nine of them were cyclic, three of them were linear and assigned to the reaction products of cyclic oligomers with ethanol. Cyclic oligomers of a first series consisted of terephthalic acid (TPA) and ethylene glycol (EG), cyclic oligomers of a second series consisted of TPA, EG and one diethylene glycol (DEG) unit replacing an EG, in cylic oligomers of a third series two EG units were replaced by two DEG units. Cyclic oligomers represent the biggest oligomer group (85%) besides the linear ones. The cyclic trimer of the first series and cyclic dimer of the second series were the most abundant oligomers. Five oligomers showed a Fickian migration behavior which is depicted in Figure 2 for the first series trimer and the second series dimer. Under the applied test conditions the measured values would correspond to a migration up to 0.07 mg/kg food for the first series trimer and 0.03 mg/kg food for the second series dimer.

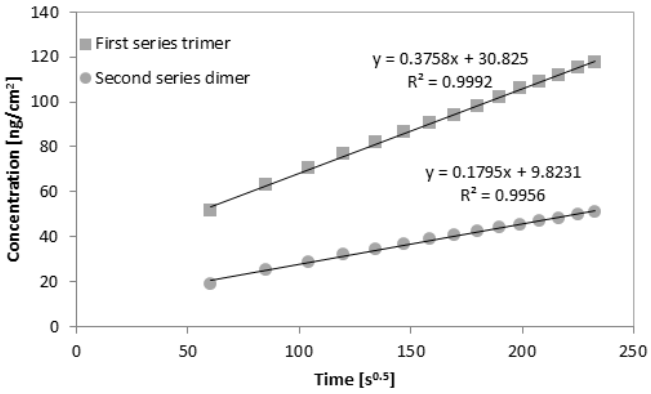

Figure 1: Migration kinetic of the first series PET trimer and second series PET dimer from a PET bottle into 50% ethanol at 80°C. Food simulant was replaced and analysed every hour for 15 cycles.

	Bottle wall concentration [µg/g]	Experimental D [cm²/s]	Calculated D[3] [cm²/s]
First series cyclic oligomers			
Dimer	33.50	$5.85*10^{-14}$	$3.71*10^{-15}$
Trimer	2921.78	$5.62*10^{-15}$	$1.57*10^{-16}$
Second series cyclic oligomers			
Dimer	280.80	$1.39*10^{-13}$	$8.47*10^{-16}$
Trimer	156.52	$1.80*10^{-15}$	$9.49*10^{-17}$
Third series cyclic oligomers			
Dimer	65.00	$1.35*10^{-13}$	$4.37*10^{-16}$

Table 1: PET oligomer diffusion coefficients (D) determined experimentally (into 50% ethanol, at 80°C and 100 bar), calculated using the model of Welle[3].

For the five oligomers showing Fickian behavior the experimental diffusion coefficients could be determined using the slope of the linear correlation between the concentration in the food simulant plotted against the square root of time and the total concentration of the oligomers in the polymer. The other oligomers identified in the material stopped showing migration after the first or second cycle. Additionally the diffusion coefficients of the oligomers were predicted using the equation published by Welle[3] which was developed especially for diffusion in PET. The values are shown in Table 1.
Diffusion coefficient values calculated with the equation by Welle were by 99.3 to 94.7% lower than the experimental D values which can be attributed to the swelling ability of ethanol for PET which causes a higher migration rate. However, calculating the diffusion coefficients using the Piringer equation which is a conservative approach gives by 99.0 % higher diffusion coefficient values than the experimentally determined ones. Even taking into account the swelling effect of ethanol, the experimental diffusion coefficients fit better with the model of Welle. Therefore the Welle equation might be a simple and fast way to calculate the migration of PET oligomers conveniently at very low migration levels which otherwise would not be easily directly accessible by analytical means.

References

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Contact person:
Maria Hoppe
Phone: +49 (0) 81 61 / 491-466
maria.hoppe@ivv.fraunhofer.de

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UNIVERSITÀ DEGLI STUDI DI MILANO
UNIVERSITEIT VAN AMSTERDAM
Fraunhofer IVV