Migration of poly(ethylene terephthalate) oligomers into lipophilic food simulant at different temperature and pressure conditions

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Introduction

Polyethylene terephthalate (PET) consists of terephthalic acid and ethylene glycol and is one of the most important industrial polymers. Due to its excellent properties like light-weight, flexibility, resistance to high temperature and low carbon dioxide permeability it is used for diverse food and beverage packaging applications. During the synthesis process of PET cyclic low molecular weight oligomers can be formed as side products of incomplete polymerization[1]. Other ways of oligomer formation are external induced degradation processes through sunlight, food and beverage contact or mechanical strength. These oligomers are potential migrants into food and beverages[2].

Experimental Procedure

Five stripes (5x1x0.019 cm) obtained from a PET bottle were subjected to 20 mL 50% ethanol at two conditions :

•80°C and 100 bar for 15 hours, solvent was changed every hour and analyzed (experiment was carried out using a Büchi speed extractor).
•80°C and 1 bar for 15 hours, solvent was changed every hour and analyzed.
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

The migration behavior of PET oligomers from a PET bottle material was studied using 50% ethanol:water as food simulant at 80°C and different pressure conditions. Twelve different oligomers have been identified through their accurate mass and fragmentation pattern (some examples are shown in figure 2), mainly cyclic oligomers consisting of terephthalic acid and ethylene glycol or diethylene glycol (D) (figure 1). Diethylene glycol is a side product in the ethylene glycol production. Linear ethanolysis products of the most abundant cyclic oligomers were detected as well.
The amount of oligomers migrating is higher for the extraction at 1 bar than at 100 bar. The increase in concentration varies between 60% for the trimer and 10 – 40 % for the other oligomers. At both conditions the concentration of oligomers in the migration solutions decreases after the first hour between 60 and 80% (figure 3). After the 9th cycle the majority of oligomers could not be quantified any more in the migration solutions except the c_trimer, c_D_dimer and the l_EtOH_trimer.
The total amount of migrating oligomers after 15 h was 0.0209 mg/dm^2 for 80°C and 100 bar and 0.0333 mg/dm^2 for 80°C and 1 bar. The total migration values of the five most abundant oligomers have been as follows (80°C and 100bar/ 80°C and 1 bar): c_dimer-0.20/0.33 mg/kg, c_trimer-6.02/9.47 mg/kg, c_tetramer-0.17/0.61 mg/kg,c_D_dimer-2.02/2.61 mg/kg, l_EtOH_trimer-0.91/1.75 mg/kg.

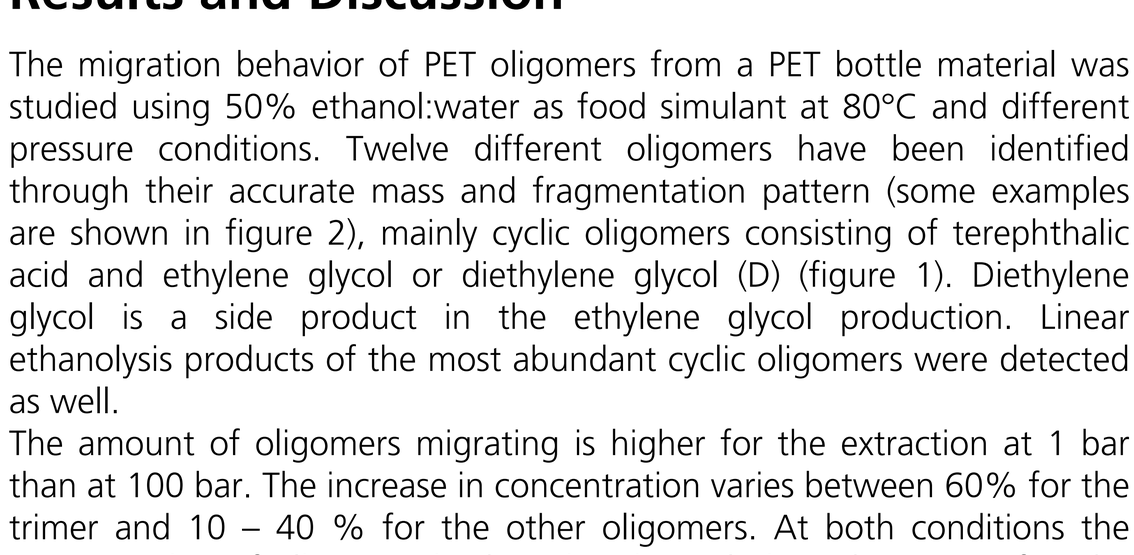

Figure 1: a) PET cyclic trimer, b) PET cyclic trimer with one D unit.

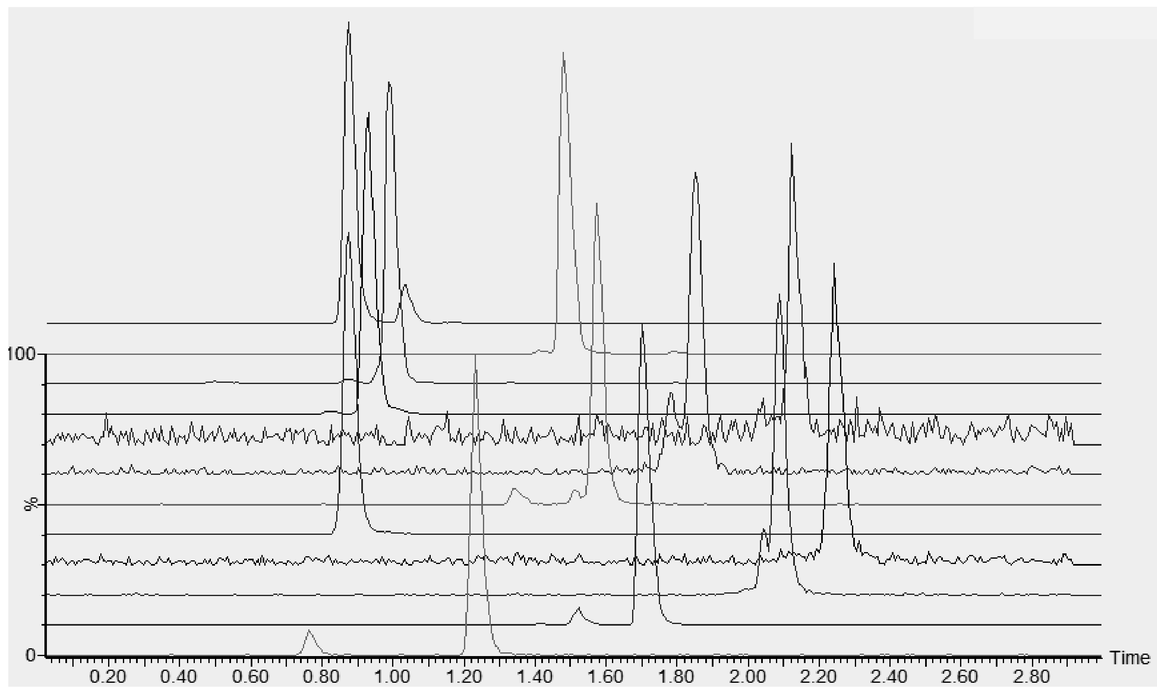

Figure 2: EIC of PET oligomers (from the bottom to the top): c_dimer, c_trimer, c_tetramer, c_pentamer, c_D_dimer, c_D_trimer, c_D_tetramer, c_D_pentamer, c_2D_dimer, l_EtOH_dimer, l_EtOH_timer, l_EtOH_D_dimer (c-cyclic, D-diethylene glycol, l-linear, EtOH_oligomers-oligomers reacted with ethanol).

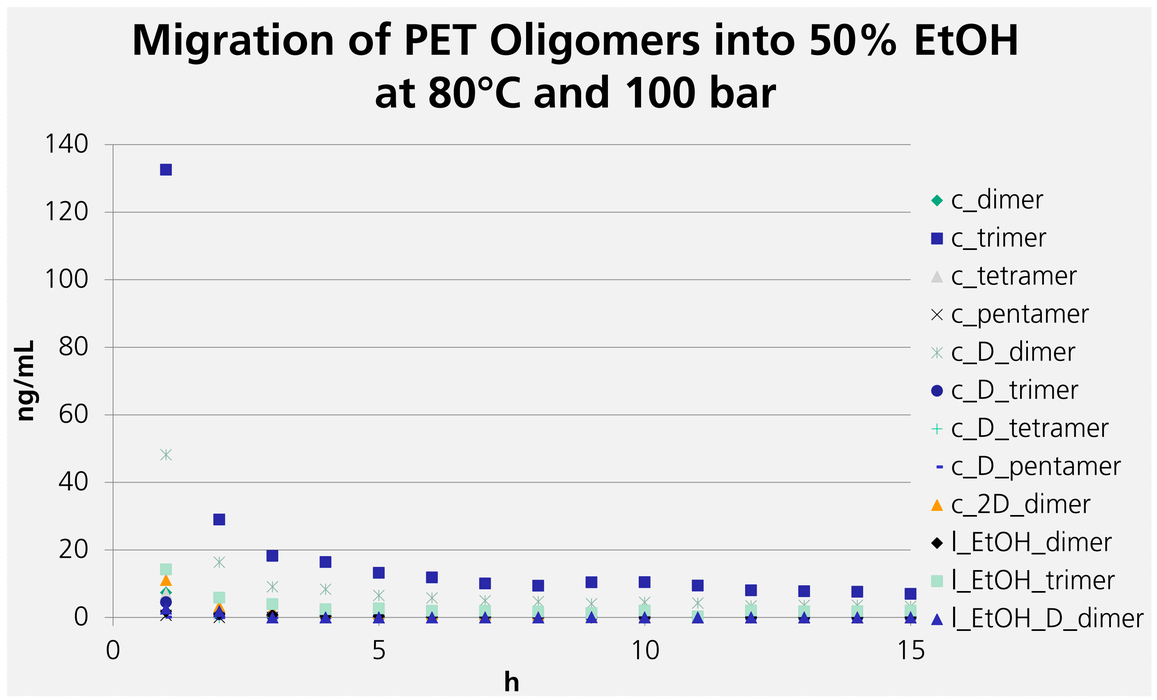

Figure 3: Migration of oligomers out of PET bottle at 80°C and 100 bar. (c-cyclic, D-diethylene glycol, l-linear, EtOH_oligomers-oligomers reacted with ethanol).

Conclusions

Cyclic and linear oligomers (from ethanolysis) are migrating from PET material into the fatty food simulant 50% ethanol at 80°C and 100 bar and 80°C and 1 bar. The migration rates are higher for the experiment at 1 bar. The total amount of migrating oligomers after 15 h was in both cases lower than the overall migration limit of the EU (10 mg/dm^2)[3]. However, the migration of the c_dimer, c_trimer, c_tetramer, c_D_dimer, c_D_trimer, c_2D_dimer, l_EtOH_dimer and l_EtOH_trimer exceeds the migration limit of 0.01 mg/kg for non-listed substances.

References

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[3] EU (2011). Commission regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food.

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