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Oligomers in polyethylene naphthalate and polybutylene terephthalate – Identification and exploring migration

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ABSTRACT

Polyethylene naphthalate and polybutylene terephthalate were investigated regarding their oligomer content. Based on their accurate mass and fragmentation spectra ten oligomers have been identified in extracts of PBT material and seven oligomers in extracts of PEN material. These oligomers were found to be cyclic and linear for both polymers. They consist of the respective diacid and monoglycol monomers as well as diglycol monomers. The total oligomer content in the polyesters was determined with LC-UV using the cyclic PET trimer as external standard and was found to be 0.81% for PEN and 0.34% for PBT. Migration of PBT oligomers was studied into 20% ethanol (v/v) at 40 °C and 60 °C and the diffusion coefficients thus derived were compared to theoretically determined ones. To estimate the PEN and PBT oligomer migration at 23 °C under long time storage conditions the diffusion coefficients were calculated using the approaches by Welle and Piringer. For cyclic PBT oligomers the Welle model underestimates the migration, for one linear PBT oligomer the Piringer model might be suitable to determine the migration. In the chosen scenario the resulting total oligomer migration was below 30 μg kg^{-1} for both materials.

1. Introduction

Polyethylene naphthalate (PEN) and polybutylene terephthalate (PBT) are polyester-type polymers similar to polyethylene terephthalate (PET). PET is one of the most used polyesters for food packaging applications especially for beverage bottles. PEN and PBT are used for food packaging applications as well for example for microwaveable dishware, kitchen utensils and coffee capsules The two polymers are synthesized from different monomers than PET and thus have a different polymer backbone resulting in different material properties. The building blocks of PEN are ethylene glycol (EG) which is also used for PET but instead of terephthalic acid another aromatic diacid monomer – naphthalic acid – is used. PBT in contrast has the same diacid unit like PET – terephthalic acid – but a different dialcohol unit: butane–1,4–diol (BD) instead of ethylene glycol. The structures of the three polymers are shown in Fig. 1. The monomers of PBT and PEN are authorized in the EU Regulation No 10/2011 (EU, 2011) to be used in the production of food contact materials.

Migration, the transport process of substances present in food packaging material into food, has to be studied to exclude health risks for the consumer. In EU Regulation 10/2011 and its amendments the use of substances authorized to be used in the food packaging polymer production are regulated including specific migration limits (EU, 2011). This comprises starting substances, additives and dyes. Oligomers which consist of a few monomeric units and are formed during the polymerisation process or due to degradation are coming more and more under risk assessment consideration. However, only for a few recent cases a specific migration limit (SML) for the total oligomer migration was set by the EFSA (EFSA, 2014a, 2014b) and in amendments of EU Regulation 10/2011. An overview about different kinds of oligomers and their migration levels was lately presented in a review article (Hoppe, de Voogt, & Franz, 2016). Especially oligomers from PET and their migration into food or food simulants are the topic of several scientific publications (Begley, Dennison, & Hollifield, 1990; Castle, Mayo, Crews, & Gilbert, 1989; Hoppe, Fornari, de Voogt, & Franz, 2017). Cyclic oligomers of PBT and PEN are known (Bryant & Semlyen, 1997; Hubbard, Brittain, Simonsick, & Ross, 1996) and their migration into boiling water was recently investigated by Brenz et al. (Brenz, Linke, & Simat, 2018). Mainly linear oligomers with 0.29 mg per kitchen utensil where found to migrate into water at 100 °C after 2 h after three repetitions of the boiling procedure.

The oligomers in PBT are reported to be either cyclic or linear and

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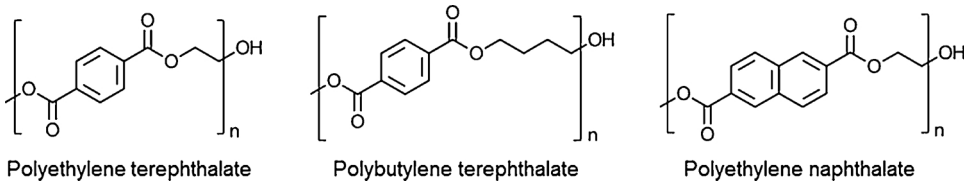

Fig. 1. Chemical structures of the three polyesters PET, PBT and PEN.

comprise up to 1.6% of the polymer weight (Samperi, Puglisi, Alicata, & Montaudo, 2004). The kinds of oligomers and the total oligomer content are comparable with the chemical structure of oligomers present in PET. The total oligomer content in PET is reported to range between 0.5% and 1.3% (Holland & Hay, 2002; Hoppe et al., 2017; Lim et al., 2003). A mixture of cyclic PBT oligomers – mainly the dimer, trimer, tetramer and pentamer – was evaluated by the EFSA for the use in different polymers as additive to lower their viscosity and facilitate the dispersion of colorants. It was concluded that no genotoxicity is expected for those substances and that they can be safely used in the polymers up to 1% w/w in contact with aqueous, acidic and alcoholic foods for long time storage at room temperature (EFSA, 2009). The specific migration of the PBT oligomer mixture was expected to be below 50 μg kg^{-1}. This value was not defined as a migration limit, however it can be used as an indirect migration limit since this level is considered to not raise any concern from a toxicological viewpoint.

When studying the migration of oligomers a suitable analytical method with an appropriate standard has to be developed. In most cases the individual oligomers are not available commercially in a pure form and since their synthesis can be time consuming alternative standards and approaches have to be taken. The generally low diffusivity of polyesters leads to low migration limits which can only be analysed with a sensitive detection method or, if possible, with a reconcentration step for the substances of interest in the respective sample. Another approach to determine the migration of substances from food contact materials, which is also accepted for risk assessment by the EU Regulation, is migration modelling. For the calculation of diffusion coefficients in packaging polymers the Piringer approach is a generally recognised model (Piringer, Franz, Huber, Begley, & McNeal, 1998). However, this model tends to overestimate the diffusion of high molecular weight substances in for example polyethylene terephthalate since it uses a fixed value for the activation energy of diffusion (Welle, 2013). As a consequence the diffusion coefficients of substances in PET are overestimated which could result in some cases to a modelled migration value which is not in compliance with the legislation. To avoid this kind of overestimation another diffusion modelling approach specifically for PET was developed by Welle (Welle, 2013). This model is based on a correlation between activation energy of diffusion in PET and molecular volume of the analyte of interest. For PET this gives more accurate values for diffusion coefficients compared to the Piringer model. Migration modelling saves time and laboratory resources compared to elaborated experimental tests. In recent years migration of oligomers from food contact polymers into the packaged food has been increasingly considered in risk assessment of food by European authorities (EFSA, 2014a; EFSA, 2014b). Therefore it is demanded from the scientific community to study the oligomers and their migration behavior. We recently showed that the Welle model is applicable to determine the diffusion coefficients of PET oligomers (Hoppe et al., 2017).

For oligomers in most cases sufficient toxicity data are lacking. Usually the oligomers, once consumed, are considered to be hydrolysed in the body back to their monomers and the toxicity evaluation is mostly based on these monomers. However, the hydrolysis of oligomers is seldomly studied. An alternative approach to estimate if a substance with a known chemical structure and exposure level would cause possible human health risks is the threshold of toxicological concern (TTC). This approach is recommended by the EFSA and can also be used in the risk assessment of oligomers (EFSA Scientific Committee, 2012). The TTC is based on extensive toxicity data sets and the tiered classification scheme of the chemical structures is described by Cramer et al. (Cramer, Ford, & Hall, 1976).

The aim of this study is to identify and quantify the oligomers in PEN and PBT and to assess their migration potential experimentally. As stated above a suitable migration model which would be applicable for PEN and PBT oligomers and which does not overestimate their migration is desirable. Such a model would save substantial time when risk assessment for a PEN or PBT material regarding the oligomers has to be done. Therefore theoretical considerations regarding diffusivity and data from migration modelling and experimental migration values are compared to establish which theoretical approach is best for the studied oligomers. Using the acquired concentration values of the oligomers, exemplarily a storage scenario for a beverage in contact with PBT or PEN is modelled to show if the theoretical migration would pose possible risks for human health when the TTC approach would be applied.

2. Material and methods

2.1. Samples, chemicals and reagents

Dichloromethane per analysis grade, acetonitrile LC–MS grade, methanol LC–MS grade, ethanol absolute grade, and formic acid per analysis grade were purchased from Th. Geyer (Renningen, Germany). Dichloromethane was distilled before use. Highly purified water was obtained by TKA GenPure water purification system from Wasseraufbereitungssysteme GmbH (Niederelbert, Germany) and used in all procedures. The PET first-series cyclic trimer (3,6,13,16,23,26-hexaoxatetracyclo[26.2.2.$2^{8,11}$.$2^{18,21}$]hexatriaconta-1(30),8,10,18,20,28,31,33,35-nonaene-2,7,12,17,22,27-hexone; CAS No. 7441-32-9) was obtained from Santa Cruz Biotechnology (Heidelberg, Germany) and used as external standard for all oligomers. A bottle made from polyethylene naphthalate, a bottle made from polyethylene terephthalate and plates made from polybutylene terephthalate were available from local suppliers. Glass transition temperatures of these polymers were determined by a DSC 3+ STARe System from Mettler Toledo (Gießen, Germany).

2.2. Determination of oligomer concentration

10-g samples of the PBT and PEN polymer samples were ground at 18,000 rpm using an ultra-centrifugal mill (cooled with liquid nitrogen) fitted with a 750-μm holed sieve. We extracted 1 g of the respective resulting powder with both a) 10 ml dichloromethane for 1 d at room temperature or b) 10 ml acetonitrile for 1 d at 40 °C, followed by ultrasonic treatment for 1 h. The extracts were passed through 0.45 μm PTFE syringe filters and the solvent was gently evaporated under a nitrogen steam. The respective residues were weighted and redissolved in DCM to obtain 1 mg mL^{-1} solutions of the residues which was diluted with acetonitrile and an acetonitrile:water mixture (2:8, v:v) to 10 μg mL^{-1} and 5 μg mL^{-1} for the analysis. A post-extraction step on the same powder samples was conducted following the same procedure to confirm completeness of the first extraction.

2.3. Chromatographic conditions

For LC–MS measurements an Acquity UPLC binary solvent manager

I class and a flow-through-needle sample manager from Waters (Manchester, UK) were used. An Acquity HSS T3 (C18) column (particle size 1.8 µm, 2.1 x 100 mm) with a Security Guard Ultra system from Waters was used as the stationary phase. The mobile phase consisted of methanol with 0.1% formic acid (A) and water with 0.1% formic acid (B). The gradient started at 40% A hold for 1 min and was raised to 100% A in 8 min, held at 100% A for 3 min and equilibrated at 40% A for 2 min. The total runtime of the gradient program was 14 min. The flow rate was 0.35 mL min^{-1}, the column temperature was 40 °C.

LC-UV measurements were carried out using a Surveyor MS pump and Surveyor autosampler from Thermo Scientific (Waltham, USA). A Gemini C18 column with a particle size of 5 µm (3.0 x 150 mm) and a security guard cartridge from Phenomenex (Aschaffenburg, Germany) was used as stationary phase. The mobile phase consisted of ethanol (A) and water (B). The gradient started at 30% A and was raised to 100% A in 15 min, held at 100% for 5 min and reequilibrated at 30% A for 5 min. The total runtime of the gradient program was 25 min. The flow rate was 0.5 mL min^{-1}, the column temperature was 45 °C.

For HPLC-UV quantification the cyclic PET trimer was used as external standard at a wavelength of 241 nm. The stock solution was prepared in acetonitrile, dilutions were freshly prepared in a mixture of acetonitrile and water (2:8, v:v). The limit of detection was 50 ng mL^{-1} (S/N 3) and the limit of quantification was 150 ng mL^{-1} (S/N 10).

2.4. Instrumentation

The Acquity UPLC was connected to the electrospray ionisation probe of the high resolution mass spectrometer Synapt G2Si Q-TOF from Waters. Both positive and negative ionisation modes were used. Instrumental parameters were as follows: resolution mode, capillary at 3.5 kV, sampling cone at 40 V, source offset at 80 V, source temperature at 120 °C, desolvation temperature at 450 °C and desolvation gas flow at 1000 L h^{-1}. Two kinds of mass spectra were acquired: one at low collision energy and one using a collision energy ramp. Both were recorded during the same run (MS^E mode). The low energy spectra (CE at 4 V) provide information about the precursor ion and high energy spectra (CE ramp: from 15 to 40 V) provide information about fragment ions. The data were recorded and evaluated using the MassLynx v4.1 software. For all measurements leucine encephalin (supplied by Waters) was used as lock mass (pos mode *m/z* 278.1141 and 556.2771, neg mode *m/z* 236.1035 and 554.2615). Accurate mass and fragmentation spectra were used for identification of the oligomers.

The HPLC was connected to a Finnigan Surveyor PDA Plus detector. Absorption was measured from 200 to 400 nm. The HPLC was also coupled in series to a Finnigan LTQ mass spectrometer all from Thermo Scientific to assign the UV signals to the respective oligomers using the MS spectra. Here APCI in the positive mode was used with following parameters: discharge current 5 µA, tube lens 75 V, vaporizer temperature 450 °C, sheath gas flow 40 arb, aux gas flow 5 arb, sweep gas flow 5 arb.

2.5. Determination of diffusion coefficients and migration modelling

The theoretical diffusion coefficient of each oligomer was calculated using the model approaches developed by Piringer and Welle. With the Piringer equation (Piringer, 2007) the diffusion coefficient is calculated according:

$$D_P = 10^4 * e^{A_P - 0.1351 * M_r^{2/3} + 0.003 * M_r - 10454/T} \quad (1)$$

where D_P is the diffusion coefficient (cm^2 s^{-1}), A_P is a polymer specific parameter, M_r (Da) is the relative molecular weight of the migrant and T (K) is the temperature. The diffusion coefficients according the Piringer model were calculated using the AKTS SML v4.51 software (Advanced Kinetics and Technology Solutions AG Siders, Switzerland).

The Welle approach is based on the molecular volume of the substance and diffusion coefficients were calculated according to Eq. (2)

$$D_P = b * \frac{V^{a-\frac{1}{T}}}{c}^{d} \quad (2)$$

where V is the molecular volume (Å^3) which was calculated using the free internet program molinspiration. The constants a, b, c and d are experimentally determined specific parameters for PET: $a = 1.93 \times 10^{-3}$ K^{-1}, $b = 2.37 \times 10^{-6}$ cm^2 s^{-1}, $c = 11.1$ Å^3 and $d = 1.50 \times 10^{-4}$ K^{-1}.

The four parameters result from the correlation of the activation energy with the molecular volume, the activation energy with the pre-exponential factor D_0 (in Arrhenius approach) and the diffusion coefficient with the molecular volume.

Using the theoretically determined diffusion coefficients the migration of the oligomers was modelled with the AKTS SML software.

2.6. Migration studies

To determine the migration of oligomers from PBT polymer into 20% ethanol (v/v) a PBT plate was cut into strips of 6 cm x 1 cm. Two strips each were immersed in 30 mL of 20% ethanol and stored during 30d at 40 °C or 60 °C. After 1, 3, 7, 10, 20 and 30d three samples for each temperature were analysed for PBT oligomers. An aliquot of 5 mL solvent was evaporated under a nitrogen stream at 60 °C and the residue was redissolved in 750 µL of an acetonitrile-water mixture (1:1, v/v). The samples were analysed with LC-UV. The experimental diffusion coefficients were determined according to Eq. (3).

$$m = 2c_{P,0} * \rho_P * \sqrt{\frac{D_P * t}{\pi}} * A \quad (3)$$

where m is the mass transfer of the oligomer into the food (µg), $c_{P,0}$ is the initial concentration of the oligomer in the polymer (µg g^{-1}), ρ_P is the density of the polymer material (g cm^{-3}), D_P is the diffusion coefficient (cm^2 s^{-1}), t the contact time (s) and A the contact area (cm^2).

3. Results and discussion

3.1. Identification of oligomers in PBT and PEN extracts

To determine the oligomers present in PEN and PBT material, solvent extracts of these polymers were prepared with acetonitrile and dichloromethane and analyzed with LC-HRMS in the positive and negative modes. Only in the positive mode oligomers were detected. The LC–MS (ESI pos) chromatograms obtained from the dichloromethane extracts are shown in Fig. 2.

In the extract of the PBT material ten oligomers where identified according to their accurate mass. These oligomers consist of different compositions of terephthalic acid and butane–1,4–diol – seven of them are suggested to have a cyclic structure, three of them to have a linear structure. In the extract of the PEN material seven different oligomers were identified of which five are cyclic and two linear. As known for oligomers from PET material where oligomeric structures are found which contain the side-monomer-product diethylene glycol (DEG) (Nasser, Lopes, Eberlin, & Monteiro, 2005), analogous PEN oligomers containing diethylene glycol and PBT oligomers containing dibutylene glycol (DBG) were identified as well. It has been already reported that dibutylene glycol can be present in PBT (Rafler, Zimmermann, & Moller, 1988). No qualitative difference for the oligomer structures was found between the dichloromethane and acetonitrile extracts of the polymers. For additional structural confirmation of the oligomers the high collision energy mass spectra were evaluated. As an example, the fragmentation spectra of the cyclic PBT dimer and the cyclic PEN dimer are shown in Fig. 3. The fragments match the suggested structures. The

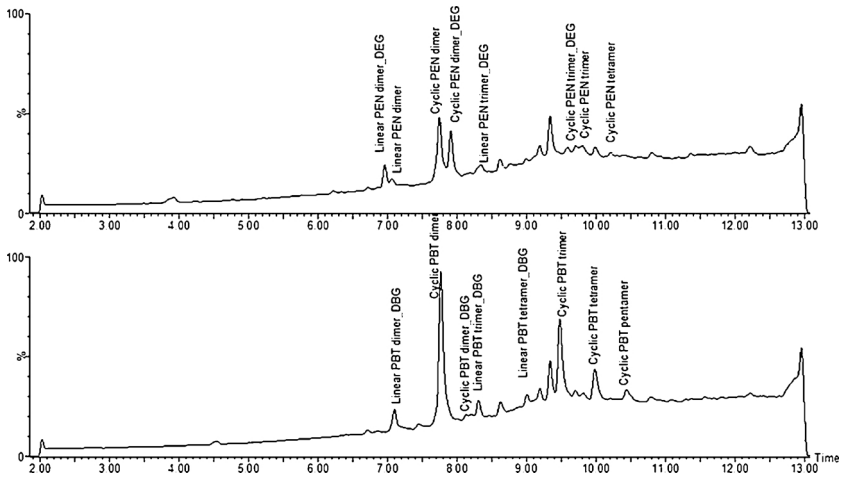

Fig. 2. TIC (LC–MS) of PBT dichloromethane extract (bottom) and PEN dichloromethane extract (top) – positive ESI, acquired with Synapt G2Si. Structures assigned on the basis of the exact mass and fragmentation pattern analysed by HRMS.

high collision energy spectra of the other oligomers show analogue fragments. The molecular masses and sum formulas of the identified oligomers are listed in Table 1.

3.2. Quantification of oligomers in PBT and PEN extracts

Quantification of the oligomers was carried out using UV detection. The oligomers of PEN and PBT showed an absorption maximum between 239–241 nm. The cyclic PET trimer has the same absorption maxima and was commercially available. Therefore this substance was chosen as external standard to semi-quantify the polyester-derived oligomers. Not all oligomers which were detected by MS could be quantified using UV detection due to low abundance in the extracts. In Table 1 the concentrations of the oligomers in the respective polymers

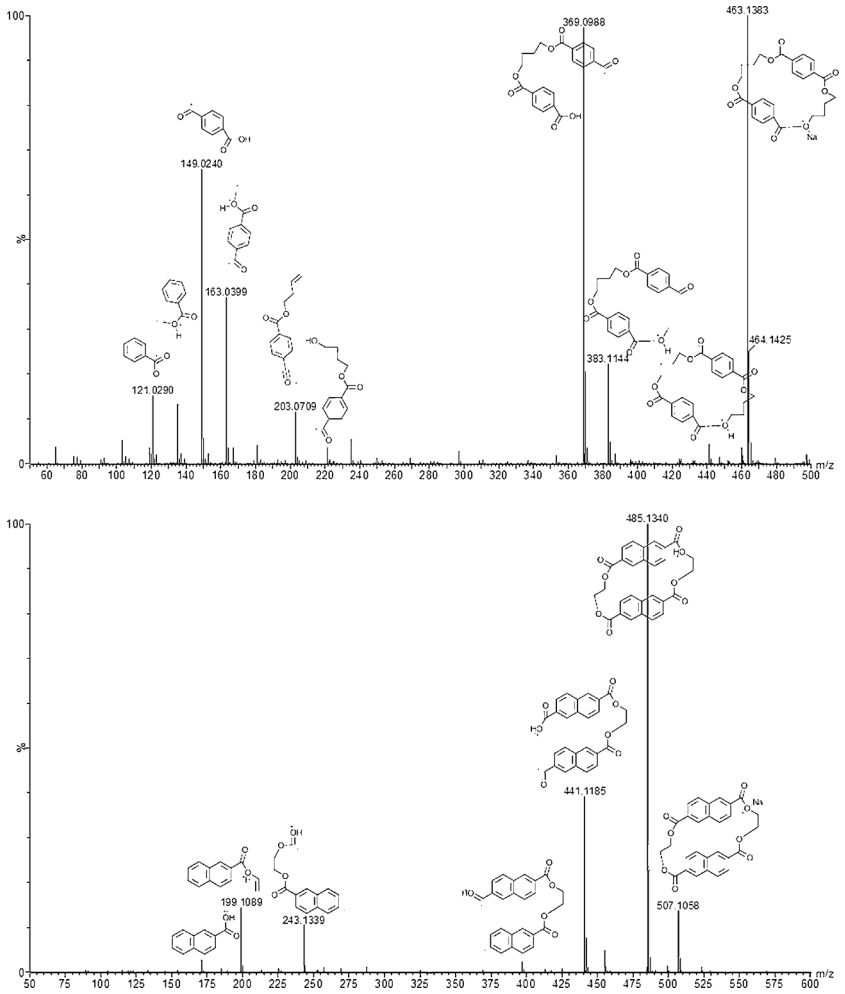

Fig. 3. High collision energy spectrum top: of PBT cyclic dimer (ESI, pos); bottom: of PEN cyclic dimer (ESI, pos).

Table 1
Sum formula, molecular mass (M), molecular volume (V) and concentration in the polymer ($c_{P,0}$) of oligomers identified in the PBT material and PEN material, respectively.

Oligomer	Sum formula	M [g mol^{-1}]	V [Å^3]	$c_{P,0}$ [µg g^{-1}]
Cyclic PBT dimer	$C_{24}H_{24}O_8$	440.15	390.9	2298
Cyclic PBT trimer	$C_{36}H_{36}O_{12}$	660.22	585.5	1049
Cyclic PBT tetramer	$C_{48}H_{48}O_{16}$	880.29	780.0	21
Cyclic PBT pentamer	$C_{60}H_{60}O_{20}$	1100.37	974.6	17
Cyclic PBT dimer_DBG	$C_{28}H_{32}O_9$	512.20	467.1	n.d.
Cyclic PBT trimer_DBG	$C_{40}H_{44}O_{13}$	732.28	661.6	n.d.
Cyclic PBT tetramer_DBG	$C_{52}H_{56}O_{17}$	952.35	856.2	n.d.
Linear PBT dimer_DBG	$C_{28}H_{34}O_{10}$	530.22	485.0	15
Linear PBT trimer_DBG	$C_{40}H_{46}O_{14}$	750.289	679.5	17
Linear PBT tetramer_DBG	$C_{52}H_{58}O_{18}$	970.36	874.1	n.d.
Cyclic PEN dimer	$C_{28}H_{20}O_8$	484.12	411.7	698
Cyclic PEN trimer	$C_{42}H_{30}O_{12}$	726.17	616.6	5487
Cyclic PEN tetramer	$C_{56}H_{40}O_{16}$	986.23	821.6	1135
Cyclic PEN dimer_DEG	$C_{30}H_{24}O_9$	528.14	454.3	245
Cyclic PEN trimer_DEG	$C_{44}H_{34}O_{13}$	770.20	659.2	185
Linear PEN dimer_DEG	$C_{30}H_{26}O_{10}$	546.15	472.2	315
Linear PEN trimer_DEG	$C_{44}H_{36}O_{14}$	788.21	677.1	40

n.d. – not determined, concentration of substance in testing solution below LOQ.

are summarized. It was noticed that for PBT the concentration of oligomers in the dichloromethane and acetonitrile extracts were the same. However, the concentrations of the oligomers in the acetonitrile extract of the PEN material were lower than in the extract prepared with dichloromethane. Due to the naphthalic acid monomer the oligomers of PEN are slightly less polar compared to PBT oligomers and therefore not as well soluble in the more polar acetonitrile. Consequently, dichloromethane was chosen as extraction solvent for both polymers and a second extraction step performed on the same materials showed that less than 5% of the initial oligomer concentration had remained in the polymers. Therefore we regarded one single extraction step with dichloromethane as sufficient to obtain the total oligomer concentration, which was 0.34% in PBT and 0.81% in PEN material, respectively.

With 67% of the total oligomer content, the cyclic PEN trimer represents the most abundant oligomer in PEN material which is fully concurrent with PET oligomers (Hoppe et al., 2017). The levels of the other oligomers range between 0.5% and 14%. In the PBT material the cyclic PBT dimer was found to be the most abundant oligomer with 67%, followed by the cyclic PBT trimer with 30%. This distribution trend was observed by other researches as well (Brenz et al., 2018). The other oligomers were only present in small amounts of around 0.5% of the total oligomer content.

3.3. Considerations about diffusivity and diffusion coefficients

As mentioned above there a two options to determine diffusion coefficients for polyesters – the Piringer Eq. (1) and the PET specific Welle model (Eq. (2)). Since it is very time consuming to set up and validate a separate model for every type of polyester we applied the Welle PET model to PBT and PEN. We justify this by the fact that the three polymers have similar chemical structures and comparable physico-chemical data. The densities of the polymers are 1.31 g cm^{-3} for PBT, 1.37 g cm^{-3} for PET and 1.46 g cm^{-3} for PEN. The glass transition temperatures T_g follow the same trend: 53 °C for PBT, 79 °C for PET and 122 °C for PEN. From these data we expect that the PET model is likely to overestimate diffusion in and migration from PEN and to show similar behavior as PBT. This is supported by a recent publication by Brandsch (2017) in which a linear relationship was shown for the dimensionless polymer specific constant A_P and T_g. A_P constitutes the pre-exponential factor of the Arrhenius equation and gives therefore information about the diffusivity of a polymer. With increasing T_g this factor is decreasing. From this relationship it can be expected that diffusivity in PEN is lower than in PET. Taking this into account the PET-model developed by Welle might be a conservative way to calculate the migration of PEN oligomers without the risk of underestimating the migration. Considering PBT which has a lower glass transition temperature than PET the diffusivity of PBT is expected to be higher compared to PET. Hence the diffusion coefficients of oligomers and other certain substances are expected to be higher in PBT compared to PET. For example Bastioli et al. reported diffusion coefficients of water in PET and PBT which were in the same order of magnitude for all temperatures but slightly higher for PBT (Bastioli, Guanella, & Romano, 1990). Additionally, Tinuvin 234, a product belonging to hydroxyphenyl benzotriazole class that acts as a UV absorber which has a high molecular weight comparable to oligomers, has a predicted diffusion coefficient of 5×10^{-11} cm^2 s^{-1} in PBT at 80 °C (Lazare & Billingham, 2001). From experimentally determined diffusion coefficients at 40°C, 50°C and 60°C of Tinuvin 234 in PET into 95% ethanol reported by Begley et al. (Begley, Biles, Cunningham, & Piringer, 2004) a diffusion coefficient of 9×10^{-12} cm^2 s^{-1} at 80°C was derived. Also this example shows a diffusion coefficient in PBT to be roughly one order of magnitude higher compared to PET. Taking into account the swelling effect of PET caused by 95% ethanol (Franz & Welle, 2008) the diffusion coefficient of Tinuvin 234 in PET might be even overestimated and will therefore be lower under non-swelling conditions. These data support the assumption that PBT is a somewhat higher diffusive polyester compared to PET. Hence, the model developed by Welle is likely to underestimate to some extent the migration of PBT oligomers. On the other hand, the Piringer model – as explained in the introduction – is likely to overestimate the migration of PBT oligomers.

3.4. Migration of oligomers from PBT into 20% ethanol

To investigate the above-mentioned assumptions migration experiments with the PBT material were carried out. As a food simulant 20% ethanol (v/v) was chosen since it is expected that the low ethanol content does not cause significant swelling of the polymer but still allows from solubility considerations to obtaining measurable migration values. Transfer of both the cyclic PBT dimer and the linear PBT dimer DBG into the food simulant 20% ethanol was observed at 40°C and 60°C whereas migration of the cyclic PBT trimer was observed at 60°C only. The other, higher molecular mass oligomers were not detected in the simulant (LOD 50 ng mL^{-1}). These oligomers were less abundant in the polymer and are not expected to migrate to a great extent since the diffusivity decreases with increasing molecular mass. The migration of the single oligomers at the different temperatures against the square root of time is depicted in Fig. 4.

From the slopes of the trend lines the experimental diffusion coefficients were calculated and compared to the theoretical diffusion coefficients of the oligomers calculated according to Piringer and according to Welle. The diffusion coefficients of the PBT oligomers which migrated are shown in Table 2.

For the cyclic PBT dimer and the cyclic PBT trimer the experimental diffusion coefficients are in between of the theoretically calculated values which was expected (see discussion above). The PET specific model by Welle tends to underestimate and the Piringer model overestimates the migration of these oligomers. The linear PBT dimer_DBG is an exception since its experimental diffusion coefficients are for both temperatures higher than the Welle values and also higher than the Piringer values which is unexpected taking into account the discussion above. It appears unlikely that linear oligomers have a higher diffusion rate compared to cyclic ones due to their structure. An explanation could be that the observed concentration of this compound in the migration solution is not only due to migration but also due to decomposition or hydrolysis of other higher molecular mass oligomers in the migration solution. Hydrolysis of PBT oligomers under aqueous conditions was also suggested by Brenz et al. (2018). However, these processes have to be investigated by further studies with a focus on the

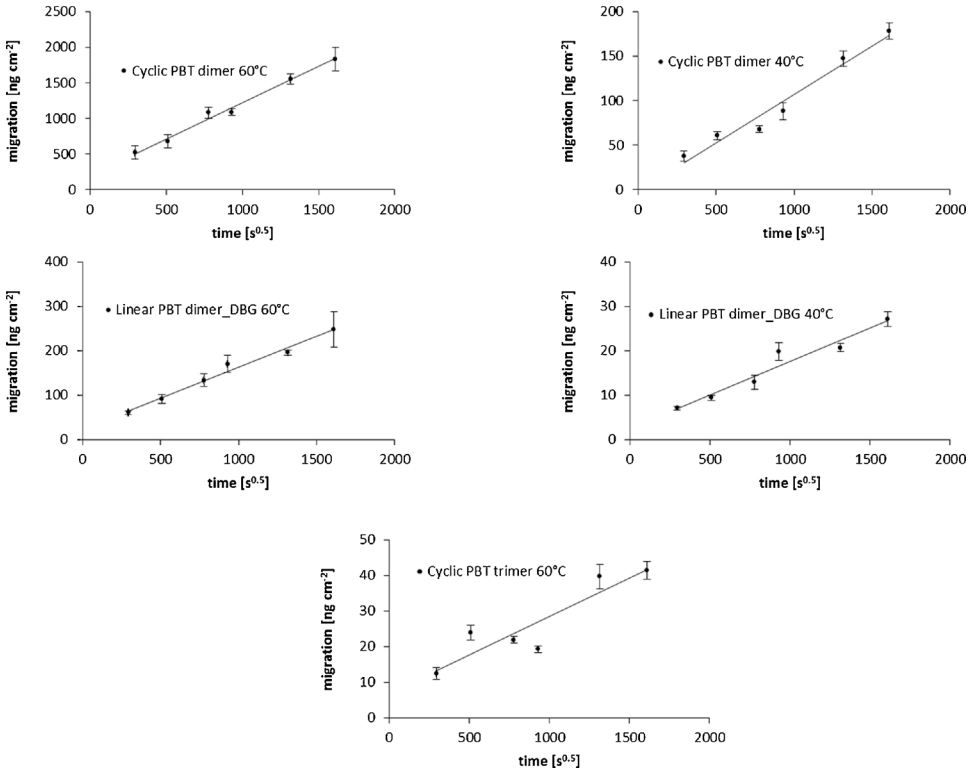

Fig. 4. Migration of PBT oligomers from PBT strips into 20% ethanol at 40°C and 60°C (n = 3).

influence of heat on the stability of higher molecular mass oligomers. It was shown before that the chosen test conditions might influence the behavior of the studied substances like reactions between food simulant and oligomers or polymer matrix or decreasing concentration of high molecular mass oligomers during long time storage due to hydrolysis (Hoppe et al., 2017; Paseiro-Cerrato, Noonan, & Begley, 2016). These and our findings demonstrate that when applying accelerated testing conditions attention must be paid to the interpretation of the migration data. It has to be kept in mind that artefacts can be produced during the test conditions which would not occur under real storage conditions like, for example, storage at room temperature for one year.

It should be noted that even at a storage temperature of 40°C after 3d the migration of the two quantifiable PBT oligomers into the food simulant will exceed 50 µg kg^{-1} ((70 ng cm^{-1} *27 cm^2)/(0.03 kg*1000) = 63 µg kg^{-1}, compare Fig. 4). However, it is still possible that 20% ethanol causes swelling of the PBT polymer at elevated temperatures which will exaggerate the migration of the oligomers. Since the material tested was not an actual ready-to-use food packaging (e.g. a bottle or a bowl), investigations regarding the oligomer migration on ready for use packaging may lead to different results. The intention of this paper is only to explore into methodologies in support of migration evaluation and risk assessment. In this context the use of ethanolic food simulants at elevated temperatures to simulate long-time storage scenarios for polyesters like PBT is debatable. As concluded above the swelling effect caused by the ethanol might be intensified by the temperature and lead to exaggerated migration values. Additionally, transesterification reactions may take place at these temperatures leading to new types of oligomers (for example linear ones) or to an increase in the concentration of oligomers due to degradation reactions like hydrolysis of cyclic oligomers or longer polymer chains. These reactions might not happen under long-term storage conditions at room temperature so the test conditions are not simulating the reality and might overestimate the oligomer migration to some extent. Investigating experimentally the migration of oligomers during longer storage times at room temperature and comparing these values to accelerated migration tests might help to adjust the testing conditions for polyester type polymers.

3.5. Migration modelling

Using the diffusion coefficients derived from the Welle and the Piringer approach, the migration of PEN and PBT oligomers at 23 °C for a long storage period of 900 d was modelled. To this end the hypothetical, but realistic example of a beverage of 0.5 L packed in a bottle with a contact area of 420 cm^2 was taken. The determined oligomer concentration in the studied PEN and PBT material was assumed as $c_{P,0}$. To determine the diffusion coefficients of PEN oligomers Eq. (2) was used and for the oligomer migrants as a safety margin a smaller (by

Table 2
Diffusion coefficients D determined experimentally (at 40°C and 60°C, 20% ethanol), D values of PBT oligomers calculated using the models of Welle and Piringer (at 40°C and 60°C).

	40°C			60°C		
Oligomer	*D* experimental [cm^2 s^{-1}]	*D* (Welle) [cm^2 s^{-1}]	*D* (Piringer) [cm^2 s^{-1}]	*D* experimental [cm^2 s^{-1}]	*D* (Welle) [cm^2 s^{-1}]	*D* (Piringer) [cm^2 s^{-1}]
Cyclic PBT dimer	1.04×10^{-15}	1.47×10^{-18}	2.07×10^{-13}	9.02×10^{-14}	1.05×10^{-16}	2.08×10^{-12}
Cyclic PBT trimer	n. d.	4.89×10^{-20}	3.55×10^{-14}	1.93×10^{-16}	5.84×10^{-18}	3.56×10^{-13}
Linear PBT dimer_DBG	4.71×10^{-13}	2.39×10^{-19}	1.21×10^{-13}	3.97×10^{-11}	2.93×10^{-17}	1.12×10^{-12}

n.d. – not determined, concentration of substance in testing solution below LOQ.

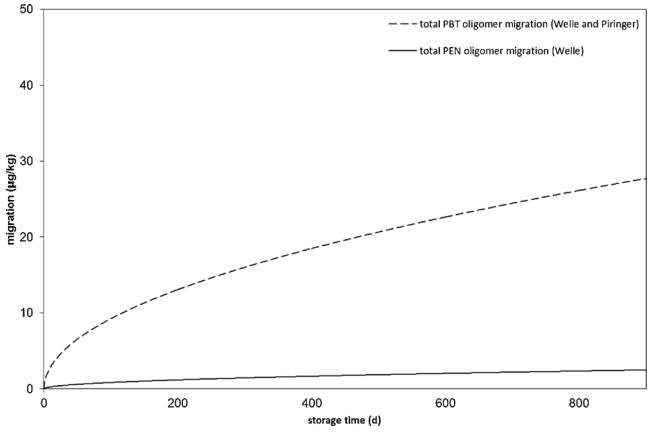

Fig. 5. Calculated total oligomer migration from PBT and PEN bottle with an internal bottle wall surface 420 cm^2 (500 ml bottle) into beverages at 23 °C as a function of storage time (as bottle wall concentration the experimentally values were taken, diffusion coefficients were determined with Welle or Piringer equation, respectively (see text for explanation), the partitioning coefficient K was set to 1 meaning that the substances will solve equally well in the polymer and the beverage).

20%) molecular volume was taken for a worst-case scenario. The diffusion coefficients at 23 °C for PEN oligomers ranged between 10^{-21} cm^2 s^{-1} and 10^{-24} cm^2 s^{-1}. For the calculation of the diffusion coefficients of the cyclic PBT oligomers the Welle approach again with the conservative assumption of -20% for the molecular volume was used. For the linear PBT oligomers the Piringer equation was used to calculate the diffusion coefficient at 23 °C. The *D* values for the cyclic oligomers ranged between 10^{-20} cm^2 s^{-1} and 10^{-24} cm^2 s^{-1} and for the two linear ones the order of magnitude was 10^{-15} cm^2 s^{-1}. The result of the modelled migration of the chosen storage scenario is depicted in Fig. 5.

For a 0.5-mL-PEN-bottle the total oligomer migration would reach 2.5 µg kg^{-1} food after 900 d storage time at 23 °C. The total oligomer migration at the same conditions for a bottle made from PBT material would be 28 µg kg^{-1} food. These migration values are very low. Taking into account the total oligomer migration limit for some polyester type polymers (EFSA, 2014a, 2014b) which is considered to be safe, the studied PEN and PBT materials could also be considered to be safe at the real application conditions. This is further supported by the fact that the oligomers were assigned to Cramer class III and no structural alerts for genotoxicity were identified according the Cramer decision tree (Cramer et al., 1976). Taking into account that a person with a weight of 60 kg would consume 1 kg of food packed in PBT or PEN material the exposure to all oligomers would not exceed the respective TTC of 1.5 µg per kg bodyweight and day. Considering toddlers with a body weight of 10 kg and an estimated daily consumption of milk, milk products and other non-alcoholic drinks of 80 g kg^{-1} (EFSA, 2016), this group would be exposed to 0.2 µg of PEN oligomers per body weight and day and 2.24 µg of PBT oligomers per bodyweight and day. However, when applying the limit of 1.5 µg per kg bodyweight and day per substance, no single oligomer would exceed this value. The risk assessment approach chosen for oligomers – either consideration of all oligomers together or each single oligomer individually – may depend on the type and nature of the polymer and in particular the resulting oligomers.

4. Conclusions

Two polyesters with chemical similarities to polyethylene terephthalate – polybutylene terephthalate and polyethylene naphthalate – were investigated regarding their low molecular weight oligomer content (< 1000 Da). These oligomers could be extracted from the materials with dichloromethane and have been shown to be either cyclic or linear for both polymers. In the PBT material studied ten different oligomers were identified according their accurate mass and fragmentation spectra using LC–MS. In the PEN polyester studied seven oligomers were identified in this way. A similarity between the structure and abundance of the oligomers in the different polyesters can be seen. The total oligomer contents in the materials considered were below 1% of the total polymer weight.

The migration of PBT oligomers into 20% ethanol (v/v) was investigated experimentally. The diffusion coefficients calculated in this way were compared to theoretically determined diffusion coefficients using the Welle and the Piringer models. It was shown that for cyclic PBT oligomers the Piringer model overestimates the diffusion coefficients by two to three orders of magnitude whereas the Welle model underestimates the diffusion coefficients by two to three orders of magnitude. As a consequence the migration of these oligomers would be over- or underestimated to some extent if the models were used. For the only linear PBT oligomer for which migration could be observed, the experimental diffusion coefficients were in the same range as diffusion coefficients estimated by the Piringer model. This is unexpected and the reason for this is not fully clear. Most likely this is due to accelerated migration due to swelling effects caused by the food simulant and decomposition or hydrolysis of longer chained or cyclic oligomers.

To consider the long time migration of PEN and PBT oligomers (at 23 °C) a combination of the model approaches of Welle and Piringer was applied. The total oligomer migration at 23 °C from a beverage bottle was calculated to be 28 µg kg^{-1} for PBT and 2.5 µg kg^{-1} for PEN after 900 d. These relatively low oligomer migration values would not raise any safety concern. It appears to be necessary to evaluate the theoretically derived diffusion coefficients at this low temperature for PEN and PBT with more experimental data, preferably with ready-to-use packaging. Finally, for a more precise migration estimation from PBT and PEN polymers the diffusion determining parameters according to the Welle equation should be established.

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