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.

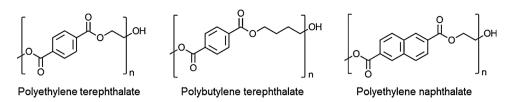The oligomers in PBT are reported to be either cyclic or linear and

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

Polyethylene terephthalate   Polybutylene terephthalate   Polyethylene naphthalate

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