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Chemical characterization of virgin and recycled polyethylene terephthalate films used for food contact applications

Bina Bhattarai¹ · Yukihiro Kusano² · Tommy Licht Cederberg¹ · Lisbeth Krüger Jensen¹ · Kit Granby¹ · Gitte Alsing Pedersen¹

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Abstract

Plastic is commonly used for food packaging, of which plastic polymer polyethylene terephthalate (PET) is widely used in the food and beverage industry. Furthermore, PET is the most suitable and recyclable plastic polymer used in food contact applications due to its functional properties: inertness and low diffusion of gases and migrants. However, using recycled PET (rPET) for food contact applications requires that the rPET is chemically safe. In this study, we use mass spectrometry and spectroscopy-based methods to characterize the chemical composition of virgin PET (vPET) and rPET. The mass spectrometric analysis demonstrated more peaks in rPET and the spectroscopic analysis revealed degradation of the rPET after the recycling process. The tentatively identified peaks in both vPET and rPET were mainly PET oligomers. The present work suggests the importance of testing PET obtained from one or more recycling processes to evaluate the effect on the polymer properties, chemical migration, and chemical safety of rPET for food contact.

Keywords LCqTOF · GCqTOF · Untargeted screening · XPS · Food packaging

Introduction

Nearly 40% of all plastic packaging used in Europe is for food packaging, where polypropylene has the largest share, followed by low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polyethylene terephthalate (PET) [1]. PET is a plastic polymer that is primarily used for beverages such as soft drinks and water and packaging of foods such as hard cheese, meat and salads. It is the most recycled plastic polymer [2] and recycled PET (rPET) is mainly used for producing bottles, sheets and textiles. [2]. It is the preferred polymer for recycling into food contact applications because of its high inertness, low diffusivity of potential migrants and a limited number of additives used [3, 4]. Chemically, PET (molecular structure shown in Fig. 1) is produced by condensation polymerization of ethylene glycol and terephthalic acid or dimethyl terephthalate.

The substances for producing plastic food contact materials (FCM) are authorized by the European Food Safety Authority (EFSA) and they are placed on the European Union (EU) positive list of substances, EU regulation 10/2011, for plastic food contact materials, with restrictions given as specific migration limits [5].

The EU demands that 50% of all plastic packaging is recyclable by 2025, and 55% by 2030. To meet the EU recycling demands, we need plastic packaging that is designed for recycling to ensure that the recycled plastic packaging intended for food contact applications is chemically safe for the given purpose. An overview from 2021 lists over 12,000 intentionally added substances (IAS) used to produce FCM of all kinds [6]. FCM also contains non-intentionally added substances (NIAS), e.g., reaction products formed during production, breakdown products of the polymer and additives, as well as impurities in the starting materials or contamination of the final FCM. NIAS in all FCM have been estimated to be present in numbers above 10,000 [7]. In each FCM, NIAS are largely unknown and need to be identified and evaluated on a case-by-case basis. In post-consumer rPET, potential contaminants of different sources (including misuse of the material by the consumer, mixing of different recycling/waste streams, degradation/reaction of the PET

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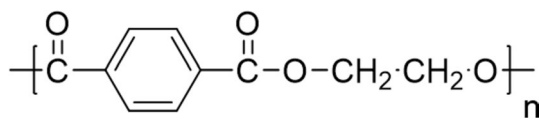


Fig. 1 Structure of polyethylene terephthalate

polymer and contamination of the PET from residual food substances) are considered relevant [8]. Specific substances, including soft drink flavorings (from rPET beverage bottles), PET oligomers, antimony (used as catalyst), acrylates and aldehydes and acetaldehydes have been reported in PET [8–11]. However, more studies are needed to identify more substances, in particular NIAS, in rPET for food contact applications. Moreover, the quantification of many contaminants in PET is lacking, and according to Tsochatzis et al. [12] the analytical test methods need more development and improvement. In a recent study mapping the literature on reported chemicals in PET, 150 substances were detected to migrate from PET bottles into food simulants and food [13].

Identifying and assessing the chemical food safety of NIAS requires appropriate techniques. Mass spectrometry-based techniques have been widely used for identifying chemical food contaminants including NIAS in plastic FCM [14–19]. Furthermore, thermal analysis such as differential scanning calorimetry (DSC) is used to characterize the physical (thermal) properties of polymeric materials [20–22]. These techniques are useful to study the indications of chemical modifications and structural changes (crystallinity) of the polymer.

Characterizations of the molecular and chemical composition of recycled plastic are necessary to assess the properties of the material in scientific research and are of particular interest to the packaging producers who use the recycled material in their production of a packaging material. Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) are widely used for this purpose. FTIR generally exhibits information about the structure and functionality of materials. It is used for the characterization of waste plastics including PET [23], crystallinity of PET [24], radiation damages of PET [25–27], chemical treatment [28], change after recycling [29], and studying copolymer contents in PET [30]. XPS provides information on atomic contents and bonding states of material surfaces, such as surface oxidation effects on PET [31, 32].

The mechanical and thermal properties of PET materials have often been reported [20, 21, 33, 34]. Tensile strength, elongation at break and impact strength are among the mechanical properties reported. The mechanical properties are typically lowered after recycling. The thermal properties are also referred to as rheological properties since differential scanning calorimetry (DSC)

is commonly used to measure the rheology by scanning temperature. Frequently reported thermal properties include glass transition temperature (T_g) and crystallization rates. T_g is affected by the molecular weight, crystallinity, branching of polymer chains, impurities, etc. so indirect information on the structural changes can be studied. The crystallization rates can be measured by first melting the polymers and then recording the heat release during cooling. It is noted that the crystallization rate is different from the degree of crystallinity.

There is a lack of standard for grades of recycled polymers and the quality of rPET produced by different mechanical reprocessing facilities [35]. The exact chemical composition of rPET on the market is not known. Only a case-by-case study can map out the material properties and the presence of potential migrating contaminants in each rPET material [13]. Studies combining mass spectrometry and spectroscopy-based techniques to chemically characterize FCM can provide increased information on the material properties. In the given study, high-resolution mass spectrometry methods and common spectroscopy techniques were combined aiming to perform chemical characterization of mechanically recycled PET. The mass spectrometric analysis includes method development and the creation of an in-house MS library of FCM substances. The performance of the methods in combination was tested by the characterization of two PET films, vPET and rPET. The measured mechanical properties in the present work are similar to those reported in the literature [20]. However, due to confidentiality constraints, they are not reported here.

Materials and methods

Chemicals

1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP, $\geq 99\%$ pure) was purchased from Sigma-Aldrich Co. (St Louis, MO, USA). HPLC-grade methanol was purchased from Rathburn Chemicals (Walkerburn, UK). LC-MS-grade methanol ($\geq 99\%$ pure) and formic acid ($\geq 98\%$ pure) were purchased from Fluka-Analytical. Isooctane was purchased from Merck, Darmstadt, Germany. Water used for sample preparation was obtained from Millipore Milli-QTM (18.2 Mohm, (Merck Millipore, Darmstadt, Germany). The reference substances used for GC-MS and LC-MS analysis are presented in Table 1. The internal standards benzophenone- d_{10} (99 atom% D, CAS 22583-75-1) was purchased from Sigma-Aldrich, and dibutyl phthalate- d_4 (98 atom% D, CAS 93952-11-5) and diethyl hexyl phthalate- d_4 (98 atom% D, CAS 93951-87-2) were purchased from VWR.

Table 1 The list of reference substances used for GC-MS and LC-MS analysis

S. no	Reference substance	CAS No.	Vendor
1	Diethyl phosphite	762-04-9	Sigma-Aldrich Co. (St Louis, MO, USA)
2	Limonene	138-8-6-3	Sigma-Aldrich Co. (St Louis, MO, USA)
3	Cyclohexylbenzene	827-52-1	Sigma-Aldrich Co. (St Louis, MO, USA)
4	Dibutyl maleate	105-76-0	Sigma-Aldrich Co. (St Louis, MO, USA)
5	Benzophenone	119-61-9	Sigma-Aldrich Co. (St Louis, MO, USA)
6	Diisopropyl naphthalene (DiPN)	24,157-81-1	Sigma-Aldrich Co. (St Louis, MO, USA)
7	Diisobutyl phthalate	84-69-5	Sigma-Aldrich Co. (St Louis, MO, USA)
8	1-Octadecene	112-88-9	Sigma-Aldrich Co. (St Louis, MO, USA)
9	Methylstearate	112-61-8	Sigma-Aldrich Co. (St Louis, MO, USA)
10	Diphenyl sulphoxide	945-51-7	Sigma-Aldrich Co. (St Louis, MO, USA)
11	Dibutyl phthalate	84-74-2	Sigma-Aldrich Co. (St Louis, MO, USA)
12	Diethyl hexyl adipate	103-23-1	Sigma-Aldrich Co. (St Louis, MO, USA)
13	Butyl benzyl phthalate	85-68-7	Sigma-Aldrich Co. (St Louis, MO, USA)
14	Dimethyl phthalate	131-11-3	Sigma-Aldrich Co. (St Louis, MO, USA)
15	Diethyl phthalate	84-66-2	Sigma-Aldrich Co. (St Louis, MO, USA)
16	Di-(n-octyl)-phthalate	117-84-0	Sigma-Aldrich Co. (St Louis, MO, USA)
17	Diethyl hexyl phthalate	117-81-7	Sigma-Aldrich Co. (St Louis, MO, USA)
18	Octacosane	630-02-4	Chiron AS, Trondheim, Norway
19	Di-n-octyl-adipate	123-79-5	Chiron AS, Trondheim, Norway
20	Butyl stearate	123-95-5	VWR (Pennsylvania, USA)
21	Diphenyl phthalate	84-62-8	Sigma-Aldrich Co. (St Louis, MO, USA)
22	Dicyclohexyl phthalate	84-61-72	Sigma-Aldrich Co. (St Louis, MO, USA)
23	Triphenyl phosphate	115-86-6	Sigma-Aldrich Co. (St Louis, MO, USA)
24	2-aminobenzamide	88-68-6	Sigma-Aldrich Co. (St Louis, MO, USA)
25	4-methylbenzophenone	134-84-9	Sigma-Aldrich Co. (St Louis, MO, USA)
26	ET cyclic dimer	24,388-68-9	Toronto Research Chemicals (Toronto, ON, Canada)
27	ET cyclic trimer	7441-32-9	Toronto Research Chemicals (Toronto, ON, Canada)
28	ET linear trimer	16,033-73-1	Toronto Research Chemicals (Toronto, ON, Canada)
29	Isophthalic acid	121-91-5	Sigma-Aldrich Co. (St Louis, MO, USA)

The reference substances (11–17) were purchased as EPA 506 Phthalate Mix. ET: ethylene terephthalate. The first 20 reference substances were used for GC-MS analysis and the later eight for LC-MS analysis

PET samples

Films of virgin polyethylene terephthalate (vPET, 23 μm thick, Folia PET corona 23 my/333 mm, EUROCAST Sp. Z o. o.) and casted recycled polyethylene terephthalate (rPET, 150 μm thick, Folia CASTFOL APET-150-NN-00-000 333 mm, EUROCAST Sp. Z o. o.) were used for food contact applications. The rPET samples were produced from post-consumer PET by a mechanical recycling process evaluated by the European Food Safety Authority, EFSA, [36] in accordance with the EFSA scientific opinion [37] on safe rPET intended for food contact applications.

X-ray photoelectron spectroscopy (XPS)

XPS data were collected using a micro-focused, monochromatic Al K α X-ray source (1486.6 eV) with a lateral

resolution of 30 μm (K-alpha, ThermoFischer Scientific, UK). Atomic concentrations of all elements were calculated by determining the relevant integral peak intensities using the Shirley background. The K-alpha was also used for a high-resolution analysis on the carbon 1 s (C1s) spectra acquired over 30 scans. The binding energies were referred to as the hydrocarbon component (C–H, C–C) at 285 eV. The spectra were de-convoluted through curve fitting, taking purely Gaussian components with linear background subtraction. The full width at half maximum (FWHM) for all peaks of C1s was constrained to 1.5 eV.

Fourier transform infrared (FTIR) spectroscopy

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy (NICOLET iS50 FT-IR, Thermo

Scientific, USA) was carried out on the PET films using a diamond prism with 32 scans and a resolution of 4 cm^{-1} .

Optical transmission

Optical transmission of the PET films was measured using UV/Vis/NIR spectroscopy (Lambda 18, PERKIN ELMER, Germany) in a range between 300 and 850 nm with a scan speed of 120 nm min^{-1} and a resolution of 1 nm.

Sample preparation for mass spectrometric analysis

To perform a complete screening of all potential migrants in the samples, total dissolution of vPET and rPET with HFIP was conducted using a slight modification of the method described by Ubeda et al. [11]. When performing total dissolution of the samples, the analytical sensitivity of potential contaminants in the PET samples is improved compared to solvent extraction methods as shown by Ubeda et al. [11].

Briefly, the PET films were cut into pieces and weighed (0.2 g). The PET pieces were placed into a burned glass tube and 2 ml of HFIP and internal standards were added. The tube was closed using aluminum foil and a lid and left at room temperature overnight for a complete dissolution of the film. Room temperature was chosen to provide gentle conditions for extraction to avoid any potential degradation of the polymer that might occur at a higher temperature. Aluminum foil was used together with the plastic lid while covering the glass tube, because we noticed precipitation in the procedural blank samples that were covered only with the plastic lid. This might be explained by HFIP being a volatile liquid that can extract substances present on the inner surface of the plastic lid, which has a PET coating. To precipitate the polymer, 4 ml of methanol was added and mixed, and samples were placed in the refrigerator for 1 h. The mixture was centrifuged at 4000 rpm, for 10 min. The supernatant was collected and filtered using Mini-Uniprep G2 syringeless filters (0.45 μm glass membrane filter, GE Healthcare Life Sciences Whatman) prior to GC–MS and LC–MS analysis. The samples and procedural blanks were prepared and analyzed in quadruplicates.

LC–qTOF analysis

The samples were analyzed using an ESI quadrupole time of flight (qTOF) mass spectrometer (Bruker Daltonics) coupled with a Dionex Ultimate 3000 RS (Thermo Scientific, CA) LC system using an InfinityLab Poroshell 120 SB-C18 chromatographic column (2.1 mm \times 100 mm, 2.7 μm , narrow bore LC column). All LC–MS analyses were performed using electrospray ionization in positive ionization mode and negative ionization mode. The conditions used for analysis were flow rate of 0.3 ml/min, injection volume 2 μl ,

autosampler at 10 °C and column oven temperature 35 °C. The eluents used were 0.1% formic acid in water (eluent A) and 100% methanol (eluent B). The gradient used for the chromatographic separation was as follows: 0 min at 2% B, 0–6 min ramped to 100% B, 6–8 min held at 100% B and 8–8.2 min ramped to 2% B and held until 12 min. The instrument parameters used were as follows: nebulizer pressure 2 bars, drying gas flow 10 l/min, dry gas temperature 200 °C and capillary voltage 4500 V. The mass scan range was 80–1500 m/z . Hexakisperfluoroethoxyphosphazene was used as an internal lock mass calibrant. Sodium formate (prepared in 50% 2-propanol) was used for internal calibration of the data files at a time segment of 0.2–0.4 min. The samples were acquired using data-dependent acquisition (DDA) (called AutoMS/MS mode in the Bruker instrument) that enabled the acquisition of the full scan along with the precursor ion and its product ions in a single run. The DDA method was built to acquire three ions above the set threshold to exclude the acquisition of the same ion for 1 min after three occurrences. The ions were acquired at a spectral rate of 2 Hz and at a collision energy of 20 eV.

GCqTOF analysis

The samples were analyzed using an Agilent GC 6890 (Santa Clara, CA, USA) with a GC model 7890A, and MS 7200 Accurate-Mass qTOF GC/MS. A volume of 3 μl sample was injected using programmed temperature vaporization (PTV) inlet in solvent vent mode with temperature starting at 50 °C, held for 0.8 min, ramped to 290 °C and held for 2 min, ramped to 330 °C and held for 10 min. Two chromatographic columns J&W Select PAH capillary column (Agilent Technology, 15 m \times 150 μm \times 0.1 μm) and an HP5MS ultra inert capillary column (Agilent Technology, 15 m \times 250 μm \times 0.25 μm) were coupled with backflush between the columns for chromatographic separation. The GC oven temperature program was initially set at 70 °C for 2 min, ramped to 310 °C at a rate of 15 °C/min and held for 10 min. After each run, the column was backflushed to prevent column contamination. The carrier gas used was helium (1.2 ml/min). All the analyses were performed in electron ionization positive mode at 70 eV with source temperature 230 °C and quadrupole temperature 150 °C. The MS data were acquired in scan mode that included mass range from 50 to 500 amu at an acquisition rate of 5 spectra/s.

Data analysis of LCqTOF and GCqTOF

The data files from LCqTOF analysis were processed using MetaboScape 2022b (a software from Bruker Daltonics). The generated list of molecular features by the software was normalized. The software allowed visualization of the relative peak intensity between the samples and reference

substances and to flag the peaks detected in the blanks. The MS peaks detected in the samples were searched against an MS library created from a recently published food contact chemical database (FCCdb containing over 12,000 substances) [6] and an in-house database containing 4160 substances relevant to FCM. The MSMS of the peaks were further confirmed using the in silico fragmentation tool MetFrag, PubChem and ChemSpider included in MetaboScape. The confidence level on the identified peaks was based on the classification provided by Schymanski et al. (2014).

The full scan MS data from GCqTOF was processed using Agilent Qualitative Analysis version 7 of the Masshunter software. The deconvoluted spectral data files were searched against Wiley10NIST14 spectral library where the hits with a score of > 80 were considered for further analysis. The MSMS of selected hits were further compared against MS Interpreter (built in the NIST spectral library) and public databases such as PubChem for confirmation.

Results and discussion

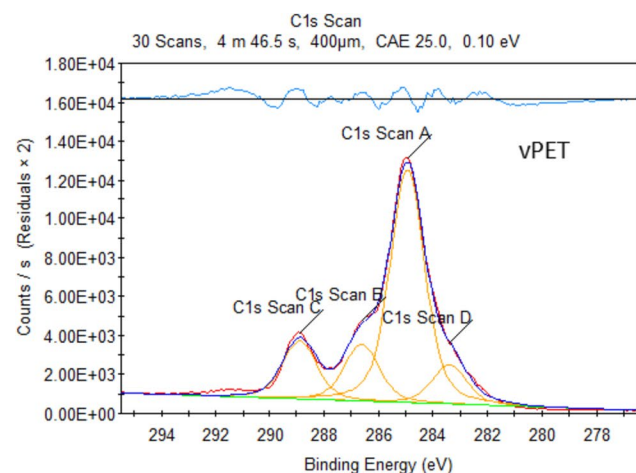
XPS measurements

XPS measurement was carried out to analyze the elemental composition of the PET surfaces. The result is summarized in Table 2.

In vPET, a small amount of silicon was detected, which was not seen in the rPET sample (Table 2). It can be regarded

Table 2 Elemental compositions (%) of virgin polyethylene terephthalate (vPET) and recycled polyethylene terephthalate (rPET) surfaces measured by XPS

	C1s	O1s	Si2p
vPET	73	26	1
rPET	78	22	0



as a contamination [38], as silicon was not always detected on the same specimen. Furthermore, the raw materials of rPET are normally more oxidized than those of vPET. During use, PET can be degraded by ultraviolet radiation and exposure to oxygen-containing molecules such as O₂, ozone and CO₂ that generally cause oxidation. CO₂ is known to be an oxidant [39]. PET has a repeating (C₁₀H₈O₄) unit, and the theoretical contents of carbon and oxygen excluding hydrogen are estimated to be approximately 71.4% and 28.6%, respectively, which are closer to those of the actual vPET than rPET. It is therefore indicated that a certain amount of oxygen was removed during the recycling process of the given rPET samples.

Figure 2 illustrates the regional C1s spectra of vPET and rPET. Peaks A, B, C and D correspond to C–C/C–H, C–O, COO and carbides. Peak C (COO) of rPET is slightly lower than that of vPET in line with the results shown in Table 2. Peak D is detected only in vPET due to the small amount of Si detected in vPET and can be attributed to SiC.

FT-IR spectroscopy

ATR-FTIR spectra of vPET and rPET are shown in Figs. 3 and 4. No difference was seen between the spectra of both sides of vPET and rPET. They represent a general PET structure. However, absorption bands in vPET at 844, 968, 1.340 and 1.470 cm⁻¹, are significantly weaker in rPET, corresponding to trans CH₂ rocking, O–CH₂ or C(=O)–O stretching, CH₂ wagging and CH₂ bending [29]. More specifically, they are associated with a structure derived from ethylene glycol. It is known that the recycling process can induce degradation including chain scission [40]. However, the change in the above absorption bands indicates the elimination or modification of ethylene glycol. It is suggested that the number of the ethylene glycol group as a terminal of the

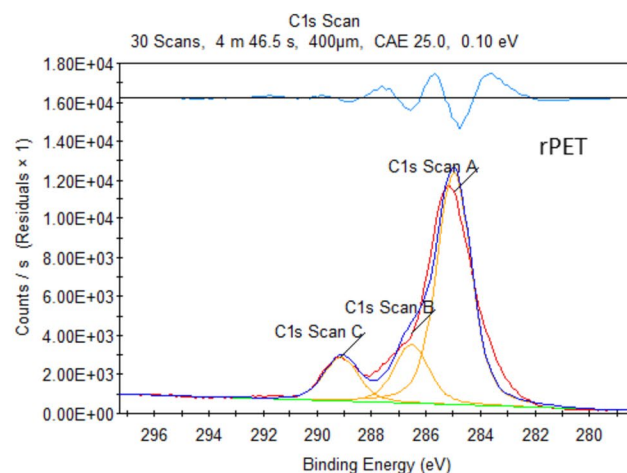


Fig. 2 C1s spectra of virgin polyethylene terephthalate (vPET) and recycled polyethylene terephthalate (rPET)

Fig. 3 ATR FTIR spectra of virgin polyethylene terephthalate (vPET) and recycled polyethylene terephthalate (rPET) films in the region between 500 and 2000 cm^{-1}

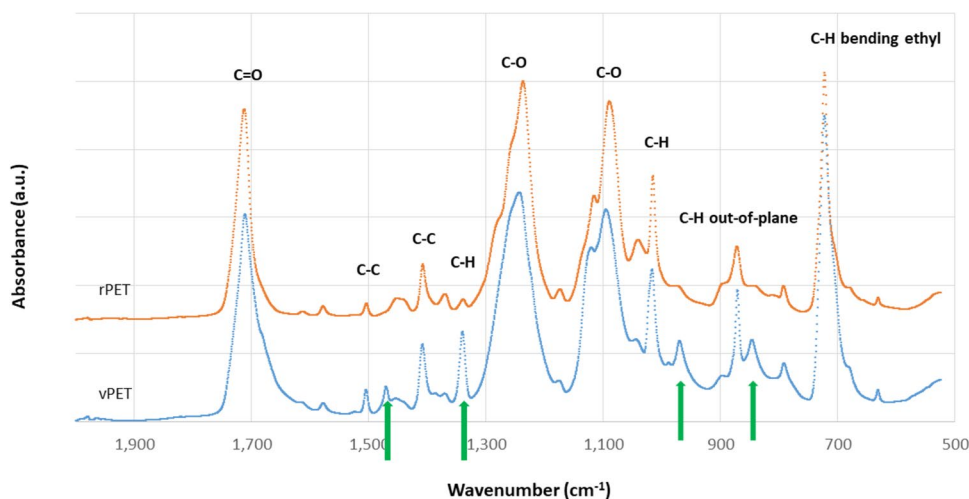
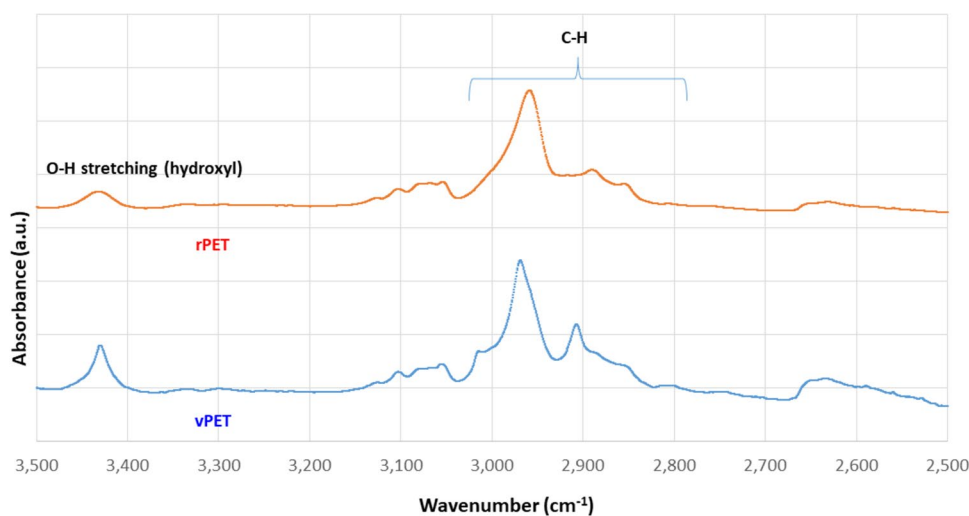


Fig. 4 ATR FTIR spectra of virgin polyethylene terephthalate (vPET) and recycled polyethylene terephthalate (rPET) films in the region between 2500 and 3500 cm^{-1}



polymer chain has changed [41]. López et al. indicated that chain scission during PET recycling often generates polymer radicals with hydroxyl groups. However, the given rPET shows a lower intensity of the absorption band at 3430 cm^{-1} , corresponding to the hydroxyl groups, than vPET (Fig. 4), suggesting that the recycling process does not necessarily generate the hydroxyl group. The result agrees with the elemental analysis by XPS, indicating that the oxygen content is decreased in rPET (Table 2). In addition, the absorption band at 2910 cm^{-1} corresponding to C–H stretching [30] in vPET is not seen in rPET, also indirectly indicating the change in the polymer structure associated with modification of ethylene glycol that contains $-\text{CH}_2-\text{CH}_2-$.

Furthermore, all these changes can be associated with change in crystallinity [25]. In other words, the FTIR result also indicates that the degree of crystallinity of PET may be lowered after the recycling process. When the crystallinity is lowered, ductility and processability of the polymer can be degraded [42]. Figures 3 and 4 show that absorption bands

at 900 cm^{-1} (CH_2 rocking), 1040 cm^{-1} (C–O stretching) and 1370 cm^{-1} (CH_2 wagging) are pronounced for rPET. Lopez et al. attributed these changes to the gauche/amorphous conformation of PET [29]. This may be confirmed by observing the slight increase in the intensity of the absorption band at 1090 cm^{-1} (gauche and trans conformers or the amorphous conformation) and the decrease in that at 1120 cm^{-1} (trans conformers in crystalline PET) [29]. Here, crystalline PET contains only the trans conformers. IR absorption associated with the gauche and trans conformers indicates amorphous conformations. However, the changes are much more obvious in the present work. Further analysis has not been carried out since ATR-FTIR is not suitable for quantitative characterization.

Optical transmission

Figure 5 shows the optical transmittance of vPET and rPET. The rPET samples show a slightly light gray color, indicative

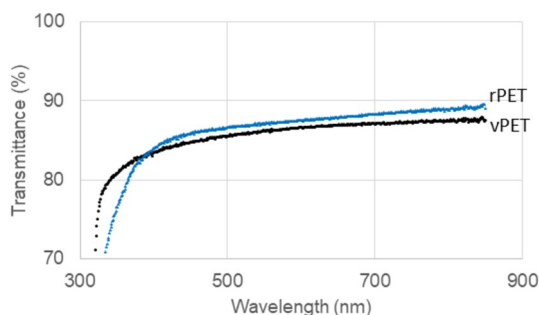


Fig. 5 Optical transmittance of virgin polyethylene terephthalate (vPET) and recycled polyethylene terephthalate (rPET)

of PET waste [43]. However, the optical transmittance of the rPET in the visible ray range is comparable to that of vPET. Kang et al. [44] reported that the optical transmission of rPET is lower compared to vPET [45]. In addition, absorption at ca. 680 nm is observed. Neither of these was seen in the present work. Therefore, the type of rPET by Kang et al. [44] is different.

Mass spectrometric analysis

Method development

For the MS method, all ion fragmentation is commonly employed when using LCqTOF. One challenge with this method, especially when performing untargeted analysis where we do not have reference substances, is to specify the correct product ions to the corresponding precursor ion. To overcome this challenge, we employed a DDA method where one can see precursor ions along with their product ions. This enabled us to generate a list of precursor ions with product ions that were further processed using the data processing tool. To develop the DDA method for untargeted purpose, we selected different types of reference substances that have been found relevant for the PET samples [15, 46, 47] (Table 1). We included plasticizers (diphenyl phthalate, dicyclohexyl phthalate, triphenyl phosphate), a photoinitiator (4-methylbenzophenone), an acetaldehyde scavenger (2-aminobenzamide), a plastic additive (Chimassorb 81) and PET oligomers (ethylene terephthalate cyclic dimer, ethylene terephthalate cyclic trimer, ethylene terephthalate linear trimer) and isophthalic acid. We developed a DDA method and tested the method on the selected reference substances. We were able to detect all the reference substances (Table 1) using the developed DDA method and the method was further used for analyzing the PET samples.

For the GC–MS method development, we selected reference substances that have been found relevant for GC–MS analysis of PET plastic FCM [14, 47] (Table 1). The reference substances were plasticizers (di-*n*-octyl-adipate,

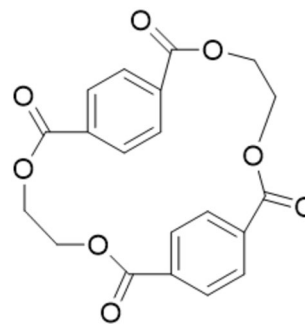


Fig. 6 3,6,13,16-Tetraoxatricyclo[16.2.2.2 ~ 8,11 ~]tetracosal(20),8,10,18,21,23-hexaene-2,7,12,17-tetrone

EPA 506 phthalate mix, details are in “Chemicals”), non-intentionally added substances (diethyl phosphite, dibutyl maleate, diisobutyl phthalate), a UV blocker (benzophenone) and contaminants (methyl stearate, cyclohexylbenzene, DiPN, 1-octadecene limonene, butyl stearate, diphenyl sulfoxide, octacosane). We tested the GC–MS method using the reference substances (Table 1) and internal standards (mentioned in “Chemicals”) and were able to detect all of them.

GC–MS analysis

From the GC–MS analysis of PET samples, eight peaks were found out of which six peaks were also found in the procedural blanks. Two unique peaks were detected in the samples. One peak was detected in both the vPET and rPET at a retention time of 24.8 min. However, the peak could not be identified. Another peak was detected only in rPET at a retention time of 22.05 min and was tentatively identified as 3,6,13,16-tetraoxatricyclo[16.2.2.2(8,11)]tetracosal(20),8,10,18,21,23-hexaene-2,7,12,17-tetrone), which is a cyclic dimer (Fig. 6), for which the exact mass and mass fragments were verified using the MS Interpreter. The number of substances found in both the vPET and the rPET using the GC–MS analysis was lower than that in other studies [18, 19, 48], which can be attributed to differences in the samples used in the studies. Franz and Welle [19] analyzed post-consumer PET bottles from non-food applications where they found several volatile and semi-volatile substances using GC–MS analysis. The samples analyzed in the given study were produced from an EFSA-approved process [36] and directly supplied to the laboratory by the manufacturer without any consumer use. Van Velzen et al. [18] analyzed rPET from beverage companies directly after the recycling process where they detected four volatile substances using headspace analysis, which was not a part of this study. In addition, they detected cyclic dimers and trimers of PET using GC–MS analysis; however, we detected only one dimer as given above.

LC–MS analysis

We detected a total of 72 peaks in vPET and 80 peaks in rPET in negative ionization mode. Only one peak was identified as terephthalic acid (m/z 165.018, 121.029) at a confidence level of 2a (match of MSMS fragmentation to available databases, according to Schymanski et al. 2014). Two peaks (m/z 325.184 annotated as dodecylbenzenesulfonic acid, and m/z 241.216 annotated as pentadecanoic acid) were identified at a confidence level of 5 (match of exact mass, according to Schymanski et al. 2014). Terephthalic acid was semi-quantified based on isophthalic acid (LOD 7 ng/g, calculated as a signal to noise ratio of 3; and LOQ 24 ng/g, calculated as a signal to noise ratio of 10).

In the positive ionization mode, we detected in total 76 peaks in vPET and 90 peaks in rPET (after subtracting peaks detected in the procedural blank samples). In Fig. 7, the total ion chromatograms of rPET and vPET are shown. In vPET, 18 peaks were identified, while in rPET, 4 more peaks were identified giving a total of 22 peaks. The peaks identified were mostly oligomers besides one monomer, one acrylate, an ester and benzofuran (Table 3). The three peaks that were detected only in rPET were one first-series cyclic trimer, one tetramer and one second-series cyclic trimer.

We detected similar cyclic and linear oligomers in vPET and rPET (Table 3). We detected ten cyclic oligomers from the first series to the third series and six linear oligomers from the first to second series. The cyclic oligomers detected were dimers, trimers, tetramers and pentamer. The linear oligomers detected were dimers, trimers and tetramers. The analysis demonstrated seven first-series oligomers that are composed of an equal number of terephthalic acid and ethylene glycol, five second-series oligomers where one ethylene glycol is replaced by

one diethylene glycol, two third-series oligomers where two ethylene glycol units are replaced by two diethylene glycol unit.

All the oligomers showed product ions m/z 193.050 corresponding to cyclic monomer ($C_{10}H_9O_4^+$), and m/z 385.092 corresponding to dimer ($C_{20}H_{17}O_8^+$) as also reported by [11, 16]. Furthermore, we detected m/z 149.023 ($C_8H_5O_3^+$) as also reported by [11, 16] and m/z 237.076 ($C_{12}H_{13}O_5^+$) frequently in different oligomers (Table 3). Out of 22 identified peaks, 3 peaks (first-series cyclic dimer and trimer, second-series linear trimer) were confirmed using the reference substances. Other peaks were identified by comparing the MSMS of the peaks with the public databases and literature [11, 16, 49] which correspond to an identification confidence level of 2a according to [50]. The types of oligomers in vPET and rPET films found in our study were similar to the findings from Ubeda et al. [11]; however, we detected three different types of oligomers (first-series linear tetramer, second-series linear tetramer, third-series cyclic trimer) in both vPET and rPET. Oligomers of linear and cyclic dimers were mainly detected as hydrogen adducts, while oligomers of trimer and onward were mainly observed as ammonium adducts. López et al. [29] had a similar observation that longer molecular chain oligomers were observed dominantly as Na adduct, and not as H adduct.

Several chromatographic peaks that contained molecular ions with similar MSMS fragments were observed at different retention times. To confirm the identity of the peaks, relevant oligomer reference substances were used. In the case of the first-series cyclic dimer, three chromatographically separated peaks were observed at retention times 5.97, 6.33 and 6.48 min. In the case of the second-series linear trimer, two chromatographically separated peaks were observed at retention times 6.09 and 6.2 min. In the case of first-series cyclic trimer, three chromatographic peaks were observed

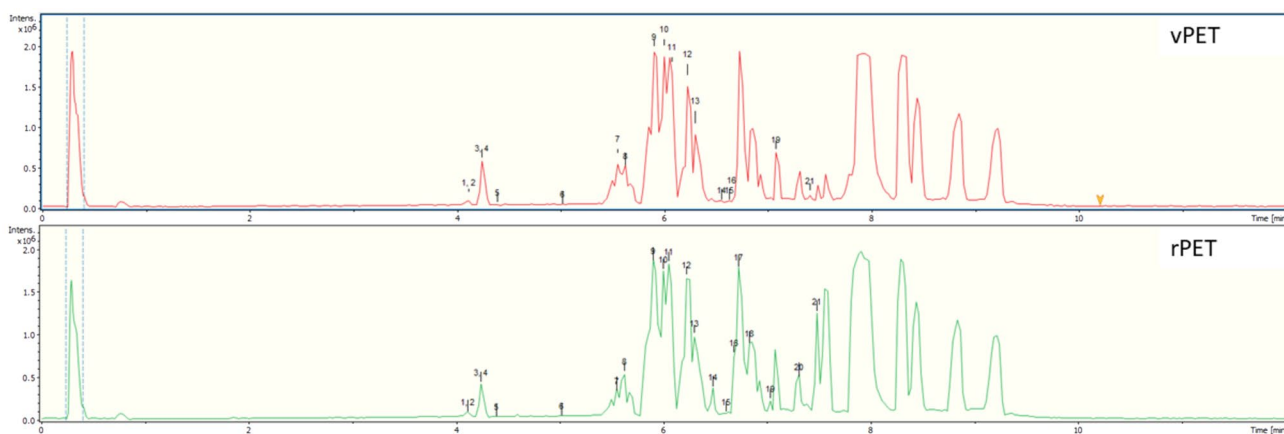


Fig. 7 Total ion chromatograms of virgin polyethylene terephthalate (vPET) and recycled polyethylene terephthalate (rPET) from LCqTOF analysis. The annotated peaks are numbered. The details of the annotations are presented in Table 3

Table 3 List of substances identified from total dissolution of virgin polyethylene terephthalate and recycled polyethylene terephthalate using LCqTOF

S. no.	R _t (min)	Precursor ion	Ions	Molecular formula	Name	Product ions
1	4.0	165.018	[M–H]–	C ₈ H ₆ O ₄	Terephthalic acid	121.029
2	4.12	149.023	[M+H] ⁺	C ₈ H ₄ O ₃	Phthalic anhydride	121.028, 105.033, 93.034
3	4.12	211.060	[M+H] ⁺	C ₁₀ H ₁₀ O ₅	MHET	193.049, 167.034, 149.023
4	4.25	255.087	[M+H] ⁺	C ₁₂ H ₁₄ O ₆	BHET	237.076, 193.050, 149.023
5	4.25	193.050	[M+H] ⁺	C ₁₀ H ₈ O ₄	cyclic monomer	149.024, 101.060, 163.039
6	4.46	299.113	[M+H] ⁺	C ₁₄ H ₁₈ O ₇	Pentaerythritol triacrylate	237.076, 193.050, 129.052
7	5.07	119.049	[M+H] ⁺	C ₈ H ₆ O	2,3-Benzofuran	116.108, 91.054
8	5.56	447.129	[M+H] ⁺	C ₂₂ H ₂₀ O ₁₀	Second series linear dimer	385.093, 237.076, 193.050
9	5.63	403.103	[M+H] ⁺	C ₂₀ H ₁₈ O ₉	First series linear dimer	385.092, 193.050, 149.023
10	5.97	385.092	[M+H] ⁺	C ₂₀ H ₁₆ O ₈	First series cyclic dimer*	359.076, 341.066, 193.049
11	6.03	473.145	[M+H] ⁺	C ₂₄ H ₂₄ O ₁₀	Third series cyclic dimer	429.119, 403.102, 385.091
12	6.07	429.119	[M+H] ⁺	C ₂₂ H ₂₀ O ₉	Second series cyclic dimer	385.093, 359.076, 193.050
13	6.21	656.198	[M+NH ₄] ⁺	C ₃₂ H ₃₀ O ₁₄	Second series linear trimer*	385.092, 237.076, 193.049
14	6.28	612.172	[M+NH ₄] ⁺	C ₃₀ H ₂₆ O ₁₃	First series linear trimer	385.092, 193.050, 429.118
15	6.56	682.213	[M+NH ₄] ⁺	C ₃₄ H ₃₂ O ₁₄	Third series cyclic trimer	237.076, 193.050, 149.023
16	6.60	848.239	[M+NH ₄] ⁺	C ₄₂ H ₃₈ O ₁₈	Second series linear tetramer	385.093, 237.076, 193.050
17	6.66	804.213	[M+NH ₄] ⁺	C ₄₀ H ₃₄ O ₁₇	First series linear tetramer	385.092, 193.049, 149.023
18	6.77	638.187	[M+NH ₄] ⁺	C ₃₂ H ₂₈ O ₁₃	Second series cyclic trimer	621.161, 193.049, 149.023
19	6.85	577.134	[M+H] ⁺	C ₃₀ H ₂₄ O ₁₂	First series cyclic trimer*	279.159, 193.050, 301.141
20	7.04	830.229	[M+NH ₄] ⁺	C ₄₂ H ₃₆ O ₁₇	Second series cyclic tetramer	813.202, 193.049, 385.091, 237.076
21	7.22	786.203	[M+NH ₄] ⁺	C ₄₀ H ₃₂ O ₁₆	First series cyclic tetramer	769.176, 385.091, 193.049
22	7.43	978.246	[M+NH ₄] ⁺	C ₅₀ H ₄₀ O ₂₀	First series cyclic pentamer	961.219, 385.092, 193.050
23	7.59	518.368	[M+NH ₄] ⁺	C ₂₇ H ₄₈ O ₈	Octadecanoic acid,3-bis(acetyloxy)propyl ester	159.065, 381.301, 441.320

*Confirmed with reference substances, others identified at level 2a (according to Schymanski et al. 2014), MHET: Mono(2-hydroxyethyl)terephthalate, BHET: Bis(2-hydroxyethyl)terephthalate, Compound 22 detected only in rPET

at retention times 6.7, 6.85 and 6.89 min. In these three cases, the peaks were confirmed by comparing the retention time and MSMS fragments with that of the reference substances. We also detected two chromatographic peaks corresponding to third-series cyclic trimer (at retention time 6.56 and 6.81 min, where the peak at 6.81 min did not show any MSMS fragments) and first-series cyclic tetramer (at retention times 7.22 and 7.31 min). However, we did not have reference substances of third-series cyclic trimer and first-series cyclic tetramer. These peaks were tentatively identified based on the presence of characteristic MSMS fragments of oligomers (*m/z* 193.050, 385.091).

PET oligomers are often quantified in reference to a single or few reference substances, and often non-oligomer reference substances are used, due to the unavailability of specific oligomer reference substances [11, 16, 51]. We performed semi-quantification of the detected oligomers using three oligomer reference substances. The limit of detection (LOD, concentration where signal to noise ratio was at least 3) and limit of quantification (LOQ, concentration where signal to noise ratio was at least 10) for cyclic dimer and cyclic trimer standard was 6 ng/g and 13 ng/g, respectively.

The LOD and LOQ for linear trimer was 8 ng/g and 25 ng/g, respectively. The concentration present in the samples cannot be compared directly because of different thickness of the two materials. Therefore, the calculated concentrations of the identified oligomers in samples are given in ng g⁻¹ polymer to better compare the level of oligomers in vPET and rPET independently of the different thicknesses of the materials (Fig. 8). The concentration of the second-series cyclic dimer was highest, followed by the first-series linear dimer, first-series cyclic dimer, and second-series linear dimer as given in Fig. 8.

The total oligomer content in the samples was calculated to be 0.14% (w/w) in vPET and 0.16% (w/w) in rPET, which is lower than the value (0.5%) reported by Hoppe et al. [16], and the range (0.6–0.9%) reported by Holland and Hay [30]. The difference may be attributed to the difference in the analytical sample preparation technique or to batch variation in PET manufacturing. A higher concentration of lower molecular weight oligomers (trimer and lower) compared to the level of high molecular weight oligomers was found in both vPET and rPET. This might be attributed to the presence of higher concentration/units of diethylene glycol units

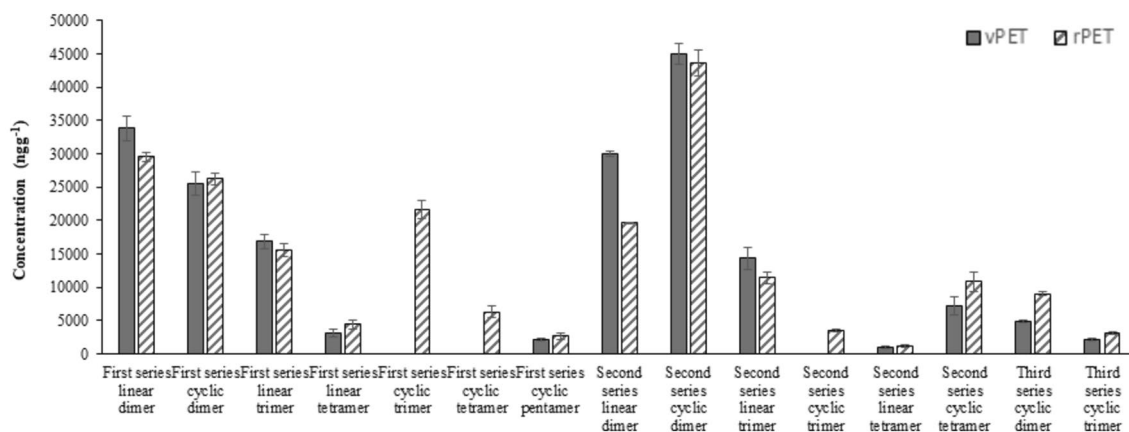


Fig. 8 Concentration (ng g⁻¹ polymer) of first series, second series and third series oligomers in virgin polyethylene terephthalate (vPET) and recycled polyethylene terephthalate (rPET). The relative concentrations of all linear oligomers were calculated using the standard of

second series linear trimer. The relative concentrations of all cyclic dimers were calculated using the standard of first series cyclic dimer. The relative concentrations of cyclic trimer, cyclic tetramer and cyclic pentamer were calculated using the first series cyclic trimer

in the polymer [30]. Among all the cyclic and linear oligomers identified in this study, the second-series cyclic dimer was detected at the highest concentration as in Ubeda et al. [11]. We found higher total concentrations of both linear and cyclic oligomers than Ubeda et al.'s [11] study, in which PET oligomers were quantified relative to cyclic ester oligomers composed of diethylene glycol (DEG), adipic acid (AA) and isophthalic acid (IPA), AA–DEG–IPA–DEG. The total concentration of oligomers (quantified relative to the first-series PET cyclic trimer) reported by Hoppe et al. [16] was higher than ours which might be attributed to the difference in the extraction solvent and extraction time.

In a comprehensive quantification study on the migration of PET oligomers from teabags by Tsochatzis et al. [51], also a second-series cyclic dimer was found to be the dominant migrant. This was followed by first-series cyclic trimer, first-series cyclic dimer and first-series linear trimer in the aqueous food/food simulants (water, simulant C), while in simulant D1 the concentration of first-series cyclic trimer was highest, followed by first-series linear trimer, second-series cyclic dimer and second-series linear trimer.,

A major concern when using rPET for food contact applications is the risk of migration of substances from the food packaging to the food. Migration tests with relevant food simulants are conventionally used to study the migrating substances. As given in this study, we performed worst case testing using total dissolution of the samples to increase the method sensitivity for better identification of unknown substances. However, for preliminary evaluation of the starting concentration of potential migration of oligomers in the vPET and rPET samples, we calculated the given concentrations in ng g⁻¹ polymer into μg kg⁻¹ food using the actual surface area of the samples in the test and the conventional surface/volume factor of 6 (dm²/kg).

The sum of cyclic and linear oligomers was calculated to be 174.18 ± 11 and 198.94 ± 11 μg kg⁻¹ in vPET, respectively. In rPET, the sum of cyclic and linear oligomers was calculated to 1587.34 ± 97 and 1023.28 ± 45 μg kg⁻¹, respectively. In the case of terephthalic acid, the calculated concentration (semi-quantified against isophthalic acid) was 0.01 ± 0.005 μg kg⁻¹ in vPET and 0.09 ± 0.002 μg kg⁻¹ in rPET.

Considering the EFSA migration restriction threshold of 50 μg kg⁻¹ food for the sum of oligomers [51–53], we found that the sum of cyclic oligomers and sum of linear oligomers was higher than the EFSA threshold in both vPET and rPET. Furthermore, when considering the level of the individual oligomers in relation to the threshold of toxicological concern (TTC) of 90 μg/day/person (proposed by EFSA in case of absence of toxicity data), none of the oligomers exceeded the TTC in vPET using the convention of 1 kg food per person per day, while in rPET, nine oligomers (second-series linear dimer, first-series linear dimer, first-series cyclic dimer, third-series cyclic dimer, second-series cyclic dimer, second-series linear trimer, first-series linear trimer, first-series cyclic trimer, and second-series cyclic tetramer) exceeded the TTC using the same convention on food consumption. The difference in the calculated level of oligomers per kg food between vPET and rPET is probably mainly associated with the difference in the thicknesses of the given vPET and rPET. As given in “PET samples” vPET was 23 μm thick, while rPET was 150 μm thick. The calculated concentrations of oligomers in the materials most likely overestimate the potential migration due to low diffusion rate in PET. However, to properly assess the food safety of rPET, migration testing must be performed using relevant worst case migration test conditions.

Conclusion and outlook

The given study performed chemical characterization of two samples of vPET and rPET using a combination of (LC and GC) mass spectrometry and selected spectroscopic techniques (FTIR, XPS). The LC–MS analysis showed more peaks compared to the GC–MS analysis and with 91 versus 76 peaks in, respectively, the rPET and the vPET samples. The tentatively identified substances in both vPET and rPET were mainly PET oligomers. The spectroscopic tests (FTIR, XPS) showed differences between vPET and rPET indicating lower degree of crystallinity of rPET. However, in perspective, we assume that with a dedicated study of multiple samples of repeatedly recycled PET samples using both the spectroscopic and mass spectrometric approaches, it may be possible to notice a correlation.

Data on the influence of repeated recycling on material quality and chemical food safety of PET is sparse. We intend to further use the combination of techniques to investigate the effect of repeated recycling on polymer properties and the chemical composition of PET. Ideally, this testing shall be done by comparing vPET and rPET of the same sample in its whole life cycle including recycling from batch to batch. Additional testing of the materials shall include migration testing with appropriate food simulants and test conditions for the respective FCM products and their uses, to identify and assess the food safety of migrating substances from repeatedly recycled rPET and compare the level of migration with given toxicological thresholds.

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Data availability The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Conflict of interest The authors declare no conflict of interest.

Compliance with ethics requirements This study does not contain any studies with human participants or animals performed by any of the authors.

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References

1. PlasticsEurope (2020) Plastics—the Facts 2020. <https://plasticseurope.org/knowledge-hub/plastics-the-facts-2020/>. Accessed 24 Jun 2022
2. EPBP (2017) How to keep a sustainable PET recycling industry in Europe—EPBP—European PET Bottle Platform
3. ILSI (2017) Packaging Materials: 1. Polyethylene Terephthalate (PET) for Food Packaging Applications. International Life Science Institute, Brussels, Belgium. Commissioned by the Packaging Materials Task Force 1–24
4. Welle F (2014) Food law compliance of poly(ethylene Terephthalate) (PET) food packaging materials. ACS Symp Ser 1162:167–195. <https://doi.org/10.1021/bk-2014-1162.ch016>
5. EU Commission 10-2011 (2011) Commission Regulation (EU) No 10/2011 of 14 January 2011. Official Journal of the European Union Special ed: 1–89
6. Groh KJ, Geueke B, Martin O et al (2021) Overview of intentionally used food contact chemicals and their hazards. Environ Int 150:106225. <https://doi.org/10.1016/j.envint.2020.106225>
7. Geueke B (2018) Dossier—Non-intentionally added substances (NIAS). Food Packaging Forum 7. <https://doi.org/10.5281/zenodo.1265331>
8. Tsochatzis ED, Lopes JA, Corredig M (2022) Chemical testing of mechanically recycled polyethylene terephthalate for food packaging in the European Union. Resour Conserv Recycl 179:106096. <https://doi.org/10.1016/j.resconrec.2021.106096>
9. Triantafyllou VI, Karamani AG, Akrida-Demertzi K, Demertzi PG (2002) Studies on the usability of recycled PET for food packaging applications. Eur Food Res Technol 215:243–248. <https://doi.org/10.1007/s00217-002-0559-1>
10. Otoukesh M, Nerin C, Aznar M et al (2019) Determination of adhesive acrylates in recycled polyethylene terephthalate by fabric phase sorptive extraction coupled to ultra performance liquid chromatography–mass spectrometry. J Chromatogr A 1602:56–63. <https://doi.org/10.1016/j.chroma.2019.05.044>
11. Ubeda S, Aznar M, Nerin C (2018) Determination of oligomers in virgin and recycled polyethylene terephthalate (PET) samples by UPLC–MS–QTOF. Anal Bioanal Chem 410:2377–2384. <https://doi.org/10.1007/s00216-018-0902-4>
12. Tsochatzis ED, Alberto Lopes J, Kappenstein O et al (2020) Quantification of PET cyclic and linear oligomers in teabags by a validated LC–MS method—in silico toxicity assessment and consumer's exposure. Food Chem 317:1–11. <https://doi.org/10.1016/j.foodchem.2020.126427>
13. Gerassimidou S, Lanska P, Hahladakis JN, et al (2022) Unpacking the complexity of the PET drink bottles value chain: a chemicals perspective. J Hazard Mater 430
14. Nerin C, Albiñana J, Philo MR et al (2003) Evaluation of some screening methods for the analysis of contaminants in recycled polyethylene terephthalate flakes. Food Addit Contam 20:668–677. <https://doi.org/10.1080/0265203031000109503>
15. Bentayeb K, Battlle R, Romero J, Nerin C (2007) UPLC–MS as a powerful technique for screening the nonvolatile contaminants in recycled PET. Anal Bioanal Chem 388:1031–1038. <https://doi.org/10.1007/s00216-007-1341-9>
16. Hoppe M, Fornari R, de Voogt P, Franz R (2017) Migration of oligomers from PET: determination of diffusion coefficients and

- comparison of experimental versus modelled migration. *Food Addit Contam Part A Chem Anal Control Expo Risk Assess* 34:1251–1260. <https://doi.org/10.1080/19440049.2017.1322222>
17. Tsochatzis ED, Gika H, Theodoridis G (2020) Development and validation of a fast gas chromatography mass spectrometry method for the quantification of selected non-intentionally added substances and polystyrene/polyurethane oligomers in liquid food simulants. *Anal Chim Acta* 1130:49–59. <https://doi.org/10.1016/j.aca.2020.07.018>
 18. van Velzen TEU, Brouwer MT, Stärker C, Welle F (2020) Effect of recycled content and rPET quality on the properties of PET bottles, part II: Migration. *Packag Technol Sci* 33:359–371. <https://doi.org/10.1002/pts.2528>
 19. Franz R, Welle F (2020) Contamination Levels in Recollected PET Bottles from Non-Food Applications and their Impact on the Safety of Recycled PET for Food Contact. *Molecules*. <https://doi.org/10.3390/molecules25214998>
 20. Celik Y, Shamsuyeva M, Endres HJ (2022) Thermal and mechanical properties of the recycled and virgin PET—part I. *Polymers (Basel)*. <https://doi.org/10.3390/polym14071326>
 21. Torres N, Robin JJ, Boutevin B (2000) Study of thermal and mechanical properties of virgin and recycled poly(ethylene terephthalate) before and after injection molding. *Eur Polym J* 36:2075–2080. [https://doi.org/10.1016/S0014-3057\(99\)00301-8](https://doi.org/10.1016/S0014-3057(99)00301-8)
 22. Pattabiraman P, Sbarski I, Spurling T, Kosior E (2005) Thermal and mechanical properties of recycled PET and its blends. *Annu Tech Conf ANTEC Conf Proc* 8:301–305
 23. Xu X, Leng Z, Lan J et al (2021) Sustainable practice in pavement engineering through value-added collective recycling of waste plastic and Waste Tyre Rubber. *Engineering* 7:857–867. <https://doi.org/10.1016/j.eng.2020.08.020>
 24. Radhakrishnan J, Kaito A (2001) Structure formation during the isothermal crystallization of oriented amorphous poly(ethylene terephthalate) films. *Polymer (Guildf)* 42:3859–3866. [https://doi.org/10.1016/S0032-3861\(00\)00754-0](https://doi.org/10.1016/S0032-3861(00)00754-0)
 25. Prasad SG, De A, De U (2011) Structural and optical investigations of radiation damage in transparent PET polymer films. *Int J Spectrosc* 2011:1–7. <https://doi.org/10.1155/2011/810936>
 26. Laput OA, Vasenina IV, Botvin VV, Kurzina IA (2022) Surface modification of polylactic acid by ion, electron beams and low-temperature plasma: a review. *J Mater Sci* 57:2335–2361. <https://doi.org/10.1007/s10853-021-06687-3>
 27. Awasthi K, Kulshrestha V, Avasthi DK, Vijay YK (2010) Optical, chemical and structural modification of oxygen irradiated PET. *Radiat Meas* 45:850–855. <https://doi.org/10.1016/j.radmeas.2010.03.002>
 28. Drobot M, Gradinaru LM, Ciobanu C, Vasilescu DS (2015) Effect of chemical treatment of poly(ethylene terephthalate) surfaces on mechanical and water-sorption properties. *UPB Sci Bull Ser B Chem Mater Sci* 77:131–140
 29. López MDMC, Ares Pernas AI, Abad López MJ et al (2014) Assessing changes on poly(ethylene terephthalate) properties after recycling: mechanical recycling in laboratory versus postconsumer recycled material. *Mater Chem Phys* 147:884–894. <https://doi.org/10.1016/j.matchemphys.2014.06.034>
 30. Holland BJ, Hay JN (2002) Analysis of comonomer content and cyclic oligomers of poly(ethylene terephthalate). *Polymer (Guildf)* 43:1797–1804. [https://doi.org/10.1016/S0032-3861\(01\)00773-X](https://doi.org/10.1016/S0032-3861(01)00773-X)
 31. Pelagade SM, Singh NL, Qureshi A et al (2012) Investigation of surface properties of Ar-plasma treated polyethylene terephthalate (PET) films. *Nucl Instrum Methods Phys Res B* 289:34–38. <https://doi.org/10.1016/j.nimb.2012.08.010>
 32. Pandiyaraj NK, Selvarajan V, Deshmukh RR, Gao C (2008) Adhesive properties of polypropylene (PP) and polyethylene terephthalate (PET) film surfaces treated by DC glow discharge plasma. *Vacuum* 83:332–339. <https://doi.org/10.1016/j.vacuum.2008.05.032>
 33. Del Mar Castro López M, Ares Pernas AI, Abad López MJ et al (2014) Assessing changes on poly(ethylene terephthalate) properties after recycling: mechanical recycling in laboratory versus postconsumer recycled material. *Mater Chem Phys* 147:884–894. <https://doi.org/10.1016/j.matchemphys.2014.06.034>
 34. Oromiehie A, Mamizadeh A (2004) Recycling PET beverage bottles and improving properties. *Polym Int* 53:728–732. <https://doi.org/10.1002/pi.1389>
 35. Schyns ZOG, Shaver MP (2021) Mechanical recycling of packaging plastics: a review. *Macromol Rapid Commun* 42
 36. Cef PA (2015) Scientific Opinion on the safety evaluation of the following processes based on Starlinger Decon technology used to recycle post-consumer PET into food contact materials: “Baltija Eco PET”, “Eurocast”, “Fernholz”, “Formas y Envases” and “Klößner Pentapla. *EFSA J* 13:1–17. <https://doi.org/10.2903/j.efsa.2015.3963>
 37. EFSA (2011) Scientific Opinion on the criteria to be used for safety evaluation of a mechanical recycling process to produce recycled PET intended to be used for manufacture of materials and articles in contact with food. *EFSA J*. <https://doi.org/10.2903/j.efsa.2011.2184>
 38. Kim HI, Morgan BA, Nokes JP, Zaldivar RJ (2015) Quantitative evaluation of silicone contamination effect on composite bonding. *J Adhes* 91:320–329. <https://doi.org/10.1080/00218464.2014.902761>
 39. Park SH, Kim SH (2014) Poly (ethylene terephthalate) recycling for high value added textiles. *Fashion Textiles* 1:1–17. <https://doi.org/10.1186/s40691-014-0001-x>
 40. Assadi R, Colin X, Verdu J (2004) Irreversible structural changes during PET recycling by extrusion. *Polymer (Guildf)* 45:4403–4412. <https://doi.org/10.1016/j.polymer.2004.04.029>
 41. Sammon C, Yarwood J, Everall N (2000) An FT–IR study of the effect of hydrolytic degradation on the structure of thin PET films. *Polym Degrad Stab* 67:149–158. [https://doi.org/10.1016/S0141-3910\(99\)00104-4](https://doi.org/10.1016/S0141-3910(99)00104-4)
 42. Awaja F, Pavel D (2005) Recycling of PET. *Eur Polym J* 41:1453–1477. <https://doi.org/10.1016/j.eurpolymj.2005.02.005>
 43. Bartolome L, Imran M, Gyoo B et al (2012) Recent developments in the chemical recycling of PET. *Material recycling—trends and perspectives*. InTech, New York
 44. Kang DH, Auras R, Vorst K, Singh J (2011) An exploratory model for predicting post-consumer recycled PET content in PET sheets. *Polym Test* 30:60–68. <https://doi.org/10.1016/j.polymertesting.2010.10.010>
 45. Lim B-H, Kwon S-H, Kang E-C et al (2003) Isolation and identification of cyclic oligomers of the poly(ethylene terephthalate)-poly(ethylene isophthalate) copolymer. *J Polym Sci A Polym Chem* 41:881–889. <https://doi.org/10.1002/pola.10637>
 46. Keresztes S, Tatár E, Czégény Z et al (2013) Study on the leaching of phthalates from polyethylene terephthalate bottles into mineral water. *Sci Total Environ* 458–460:451–458. <https://doi.org/10.1016/j.scitotenv.2013.04.056>
 47. Geueke B, Groh K, Muncke J (2018) Food packaging in the circular economy: overview of chemical safety aspects for commonly used materials. *J Clean Prod* 193:491–505. <https://doi.org/10.1016/j.jclepro.2018.05.005>
 48. Cincotta F, Verzera A, Tripodi G, Condurso C (2018) Non-intentionally added substances in PET bottled mineral water during the shelf-life. *Eur Food Res Technol* 244:433–439. <https://doi.org/10.1007/s00217-017-2971-6>
 49. Kim DJ, Lee KT (2012) Determination of monomers and oligomers in polyethylene terephthalate trays and bottles for food use by using high performance liquid chromatography–electrospray ionization–mass spectrometry. *Polym Test* 31:490–499. <https://doi.org/10.1016/j.polymertesting.2012.02.001>

50. Schymanski EL, Jeon J, Gulde R et al (2014) Identifying small molecules via high resolution mass spectrometry: communicating confidence. *Environ Sci Technol* 48:2097–2098. <https://doi.org/10.1021/es5002105>
51. Tsochatzis ED, Alberto Lopes J, Kappenstein O et al (2020) Quantification of PET cyclic and linear oligomers in teabags by a validated LC–MS method—in silico toxicity assessment and consumer’s exposure. *Food Chem* 317:126427. <https://doi.org/10.1016/j.foodchem.2020.126427>
52. EFSA (2014) Scientific Opinion on the safety assessment of the substance, 2,4,8,10-tetraoxaspiroundecane-3, 9-diethanol, β 3, β 3, β 9, β 9-tetramethyl-, CAS No 1455–42-1, for use in food contact materials. *EFSA J* 12:3863. <https://doi.org/10.2903/j.efsa.2014.3863>
53. EFSA (2014) Scientific Opinion on the safety assessment of the substance, furan-2, 5-dicarboxylic acid, CAS No 3238–40-2, for use in food contact materials. *EFSA J*. <https://doi.org/10.2903/j.efsa.2014.3866>

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