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Analysis of recycled PET bottles products by pyrolysis-gas chromatography

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A B S T R A C T

The impact of the contaminants in post used PET bottles on the decomposition of polymer itself after recycling process was analyzed. For that reason sorption experiments of harmful substances to PET bottles were performed. In order to monitor the presence of contaminants in recycled PET and evolution of thermal decomposition products of samples: virgin PET, contaminated PET flakes (PET K) and recycled PET (PET RM) were studied. The thermal degradation products of PET were achieved by pyrolysis using Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS), temperature-programmed evolved gas analysis-mass spectrometry (EGA-MS) and thermogravimetric analysis (TGA). Reactive pyrolysis with tetramethyl ammonium hydroxide (TMAH) was also performed to gather additional information about degradation products in studied samples. The pyrolysis products analysis of the studied PET samples indicate some changes in decomposition mechanism of PET samples that pass through contamination process due to some diversity in their chemical and structural composition.

1. Introduction

Poly(ethylene-terephthalate) (PET) is a polymer in widespread use in the production of bottles and containers of water and carbonated drinks [1]. In order to minimize polymer waste and ensure environmental protection the methods of polymer recycling are continuously developing. The quantity of collected PET waste is enormously growing but in 2007 just about 40% of all PET bottles in the market were collected for recycling [2]. Unfortunately, the properties of the reclaimed materials of waste polymers, subjected to recycling, are often partly deteriorated in comparison with those of the virgin materials. It is very important to overcome these deficiencies during recycling process and obtain satisfied mechanical properties, durability, aesthetics and especially the health suitability of the recycled material [3,4]. The main concern in recycling of post consumer PET for food contact is secondary use of plastic packaging on the consumer side. It is assumed that in usual distribution and use of PET bottles one of five bottles may be a non-food bottle [5], which is explained by its secondary use for storage of various types of chemicals (cosmetics, solvents, detergents, motor oils etc.). For that reason many published studies [6,7] were focused on PET bottles cleaning efficiency before recycling and to detection of penetrated harmful substances in recycled PET. On the other side, it should be considered the question: does the contaminants in recycling process have the impact on material final properties and its structural stability? For this purpose, to obtain more realistic estimation of the concentration of contaminants in polymer, the simulation of the contamination by secondary use is performed in this work by test mixture of hazardous chemicals. Test mixture contains contaminants [8], which simulate objective conditions that occur during the use of PET bottles. After the contamination procedure and recycling process PET bottles are analyzed but some traces of chemicals are sometimes undetectable due to their very low concentration. Even using advanced spectroscopic methods, such as high-field solution NMR, the characterization of the contaminants traces that can penetrate in recycled polymer has not been an easy task.

That gives us the reason to study contamination of PET bottles to gather more information about PET polymer structure stability by analyzing pyrolysis products that are result of chemical structure of the sample. In this work, recycled PET was studied by Py-GC/MS in terms of establishing the potential remaining contamination and degradation products after material recycling process. Moreover, reactive Py-GC in the presence of organic alkali (thermally assisted hydrolysis and methylation (THM) such as tetramethyl ammonium hydroxide (TMAH) often provides useful information for the condensation type of polymer materials containing ester and/or carbonate linkages [9,10]. Thus, the possible very small amount of contaminants, which penetrated into the structure of the polymer,

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can redirect the pyrolysis decomposition, which can be indentified by following the pyrolysis products.

2. Experimental

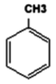
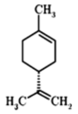
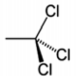
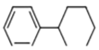
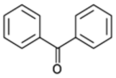
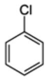
2.1. Materials

The post consumed PET bottles were milled into PET flaks (intrinsic viscosity 0.7495 dl/g) then were contaminated and further were used in recycling process to obtain recycled PET samples. Irganox 1076 (CIBA, phenolic primary antioxidant for processing) and Zn-stearate (Chemson Polymer Additive AG, Austria, lubricant for extrusion) were used during recycling. For the contamination of PET flakes the test solvent mixture [11] was used, containing: toluene (≥99.5%, Carlo Erba), D-limonene (≥99.9%, Fluka) 1,1,1-trichloroethane (≥97%, Sigma Aldrich), phenylcyclohexane (≥97%, Sigma Aldrich), benzophenone (≥99.5%, Dr.Ehrensorfer), and chlorobenzene, (≥99.7%, Sigma Aldrich). Dichloromethane (DCM) (p.a., Kemika, Zagreb) was used as a solvent for the test mixture and reagent of tetramethyl ammonium hydroxide (TMAH) (electronic grade 99.9999%, Alfa Aesar®) in methanol solution, 25 wt% was used to induce reactive pyrolysis.

2.2. Contamination procedure

PET flakes (200 g) were contaminated with the test solvent mixture to simulate the worst possible scenario of contamination of bottles before recycling into new PET bottles for food application. The test solvent mixture was prepared by mixing the chemicals in DCM (152.5 ml) and the concentration of each contaminant in the solution was 1000 ppm, Table 1. The contamination process was carried out in 1 L reactor with reflexive heat sink to prevent mass loss of contaminants because the suspension was heated up to 40 °C for 24 h with continuous mixing. After then suspension was left in the reactor for another 10 days and mixed each day for 2 h. Thus, contaminated PET flakes were filtered from suspension, washed with DCM and dried at air atmosphere for 3 days and for another 6 h under controlled temperature (180 °C) before recycling by melt extrusion. Obtained contaminated PET flakes were denoted as PET K samples and further used in analysis.

Table 1
Chemical properties of six contaminants in the test mixture.

Model compound	CAS number	Molecular mass, g mol^{-1}	Properties	Conc. mg/l
Toluene 	108-88-3	92.1	- aromatic hydrocarbon - volatile, non-polar - used in adhesives and dyes; constituent of motor oils and automotive compounds	1000
D Limonene 	138-86-3	136.2	- hydrocarbon - volatile, non-polar - often found in recycled PET (main Compound of citrus oil based flavors in fruit drinks)	1000
1,1,1-trichloroethane 	25323-89-1	133.4	- halogenated aliphatic hydrocarbon substitute - very volatile, polar	1000
Phenyl cyclohexane 	827-52-1	160.3	- aromatic hydrocarbon - non-volatile, non-polar - substance proposed by ILSI-Europe for application as a model compound in Challenge tests	1000
Benzophenone 	119-61-9	182.2	- aromatic ketone - non-volatile, non-polar - substance proposed by ILSI-Europe for application as a model compound in Challenge tests	1000
Chlorobenzene 	108-90-7	112.6	- halogenated aromatic hydrocarbon - volatile, non-polar - swelling agent	1000

2.3. Recycling process

Contaminated PET flakes were recycled by melt extrusion that was carried out on the Rondol Bench Top 21 twin-screw extruder to obtain recycled PET samples (PET RM). PET flakes were homogenized with thermal stabilizer Irganox 1076 (0.5 mass %) and the lubricant Zn-stearate (1.0 mass %) by dry mixing before extrusion. Temperature profile in the extruder was set to 220/230/230/240/240/245 °C (from hopper to die) and screws rotation speed was set to 100 rpm.

2.4. Py-GC/MS analysis

The pyrolysis of virgin PET, PET K (contaminated flakes) and PET RM (recycled PET) samples were carried out in a multifunctional double-shot pyrolyzer (Frontier Lab., PY-2020iD). The vertical micro-furnace pyrolyzer mounted on a Shimadzu GC–MS-QP2010 Plus was used under a flow of He carrier gas, and data search libraries of Frontier Lab., F-search (MS 08) and NIST/EPA/NIH (NIST 05) were used for the peak identification. The flash pyrolysis temperature was fixed at 600 °C and the resulting pyrolyzates of the PET granule samples of 0.2 mg were placed into the deactivated stainless steel sample cup separated by a metal capillary separation column coated with immobilized 5% diphenyl-95% dimethylpolysiloxane (Frontier Lab, Ultra ALLOY^{+}-5; 30 m long × 0.25 mm i.d, 0.25 μm film thickness) under a programming temperature condition; GC oven was programmed at 40 °C with the heating rate of 20 °C/min up to 300 °C. The pyrolysis interface and GC injector were kept at 320 °C. GC Injection port was in constant linear velocity mode 48.8 cm/s with split ratio 1/60. Mass spectrometer was operated in the EI mode with mass range of 29–600 amu, scanned at 1250 amu/sec.

The reactive pyrolysis with tetramethyl ammonium hydroxide (TMAH) was carried out by the same Py-GC/MS system under the same conditions. About 2 μl of TMAH was added to powdered PET sample (0, 1 mg) into stainless steel sample cup first set at the upper position of the pyrolyzer at around room temperature, and then introduced into the centre of the pyrolyzer heated at 300 °C and for the second measurement at 400 °C.

2.5. EGA-MS analysis

Evolved gas analysis-Mass spectrometry (EGA-MS) measurements have been carried out in a multifunctional double-shot