Off-Flavour Compounds Formed by γ-Irradiation of Polypropylene

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Introduction

Sterilisation of plastic packaging materials for food, pharmaceutical or cosmetic products with ^{60}Co γ-irradiation in the presence of oxygen can result in formation of volatile substances, which may induce off-odours in these materials. In this study, characteristic odour changes of polypropylene (PP) due to irradiation were monitored by sensory analysis. For identification of the odour-inducing substances of PP (irradiated at 10 and 20 kGy) the volatile fraction was analysed by gas chromatography-olfactometry (GC-O), GC-MS and GC-GC-MS. Selected compounds were quantified by stable isotope dilution assays.

Materials and Methods

Description of Samples: Standard commercial PP pellets (white masterbach).
γ Irradiation of PP: γ-irradiation was performed in a ^{60}Co-irradiation plant (Isotron Deutschland GmbH, Allershausen, Germany) with a dose rate of 4,6 kGy/h in normal atmospheric conditions and at room temperature. The irradiation doses were 10 and 20 kGy, respectively.
Sensory Analysis: Panellists were asked to describe the samples (collection of sensory attributes) and to score the intensities on a scale from 0 (no perception) to 3 (strong perception). The samples were presented to the sensory panel in covered glass vessels (capacity 45 mL, i.d. 40 mm) for comparative orthonasal evaluation. Results obtained in three different sessions were averaged and plotted in spider-web diagrams. Values differed by no more than 10 %.
Preparation of Solvent Extracts of PP Samples: PP (15 g) was extracted with dichloromethane (DCM; 3 x 120 mL). After extraction (60 min, RT), the DCM phases were separated and combined, dried over anhydrous sodium sulphate and concentrated to a total volume of 150 mL at 50°C by Vigreux distillation. Then, solvent assisted flavour evaporation (SAFE) [2] was applied for isolation of volatiles from the PP matrix at mild temperature (50°C) and under high vacuum (5 × 10^{-3} Pa). The distillates were separated into neutral-basic and acidic fractions [3], dried over anhydrous sodium sulphate, and concentrated to a total volume of 100 µL [1].
Aroma Extract Dilution Analysis (AEDA): Flavour Dilution (FD) factors of the aroma compounds were determined by AEDA [3] on the original extract (1 µL, FD=1), and stepwise dilutions (1+1, v/v) with DCM using HRGC-O on DB-FFAP and DB-5.
2-dimensional High Resolution Gas Chromatography-Olfactometry/Mass Spectrometry (2D-HRGC-O/MS): Analyses were performed with a system consisting of two gas chromatographs type 3800 (Varian, Darmstadt, Germany), coupled with a mass spectrometer Saturn 2200 (Varian) and sniffing ports ODP (Gerstel) [3]. Mass spectra were generated at 70 eV ionization energy (EI and CI).
Stable Isotope Dilution Assays (SIDA): Defined amounts of the respective isotopically (^{2}H or ^{13}C) labelled odorants were added to each sample, and workup was carried out as described above. From the intensity ratio of labelled or unlabelled compounds in the extract, the odorant amount in PP was calculated.

Results

Sensory Analysis: The descriptive analyses resulted in sensory detection of plastic-like, fatty, sour, wax-like, metallic, burnt, stinging and sweet odour notes in all three samples. Generally, all odour impressions in both irradiated samples were more intense compared to the control non-irradiated sample. Most odour attributes increased in the PP sample of higher irradiation level.
GC-O and AEDA: Characterization of odour-active substances by 2D-HRGC-O/MS in the solvent extract led to olfactometric detection of 29 odour active substances in non-irradiated control sample and 38 odorants in γ-irradiated (10 and 20 kGy) PP. Among the detected compounds in **non-irradiated** control were predominantly fatty and plastic-like or metallic smelling compounds: (Z)- and (E)-non-2-enal, (E,Z)-nona-2,4-dienal, and two unknown compounds (tentatively identified as (Z)-non-4-enal and (Z)-dec-2-enal). Green, citrussy, grassy and fatty odour notes originated from hexanal, octanal and nonanal, while metallic and mushroom-like notes were due to *trans*-4,5-epoxy-(E)-dec-2-enal, oct-1-en-3-one, and non-1-en-3-one.
The most important compounds in **γ-irradiated** (10 and 20 kGy) PP samples were the metallic smelling *trans*-4,5-epoxy-(E)-dec-2-enal, the leather-like smelling 3-propylphenol and vanillin. In comparison to control sample, a series of carboxylic acids were detected with high odour intensities in γ-irradiated (with 10 and 20 kGy) PP samples. These were the cheesy, sweaty smelling butanoic acid, the fruity and sweaty smelling 2- and 3-methylbutanoic acids, the cheesy, sweaty-fruity smelling pentanoic acid, the cheesy-sweaty 2-methylpentanoic acid, the sweaty-fruity 4-methylpentanoic acid, the musty, pungent, coal firelighter-like hexanoic acid, and the sweaty-sweet smelling compounds 2-methylhexanoic acid and 4-methylhexanoic acid.

References

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Tabelle 1. Most odour-active volatiles (Flavour Dilution; FD ≥ 64) in solvent extracts from γ-irradiated (20 kGy) PP.

No.	Odorant [a]	Odour Quality [b]	RI value on	
			DB5	FFAP
1	Hex-1-en-3-one [c]	Glue-like	1102	764
2	Butanoic acid	Cheesy, sweaty	1613	815
3	2-/3-Methylbutanoic acid	Fruity, ripe apple-like, sweaty	1654	867
4	4-Methylpentanoic acid [e]	Cheesy, sweaty	1793	974
5	Unknown	Sweaty	1985	n.d.
6	(*tr*)-4,5-Epoxy-(*E*)-dec-2-enal	Metallic	2000	1385
7	Octanoic acid	n.d.	2051	1252
8	3-Ethylphenol [c]	Leather-like	2160	1171
9	Unknown	Sweet, leather-like	2172	n.d.
10	γ-Undecalactone [c]	Peach-like	2234	1580
11	3-Propylphenol [c]	Leather-like	2243	1288
12	Unknown	Anise-like	2300	n.d.
13	Unknown	Anise-like, medical	2476	1784
14	Vanillin	Vanilla-like, sweet	2578	1410

a) Identification criteria: Comparison with the reference odorant, retention indices on capillaries named in the table, mass spectra (MS-EI and MS-CI), odour quality, and intensity perceived at the sniffing port.
b) Odour quality as perceived at the sniffing port.
c) Identification criteria: Same as in a), but no mass spectral data was obtained due to low concentrations.

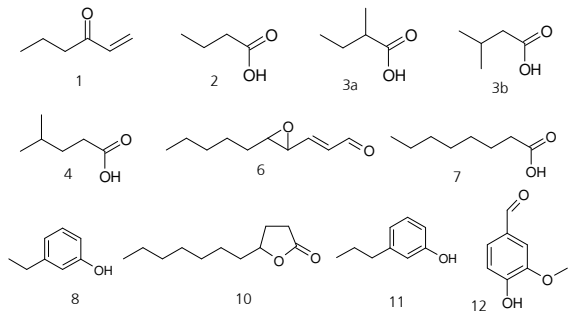

Fig. 1. Most odour-active γ-irradiation induced compounds from PP (20kGy). Numbers correspond to Table 1.

Quantification of selected carboxylic acids by SIDA showed that concentrations continuously increased with γ-irradiation, and that amounts were highest in γ-irradiated PP samples (20 kGy), compared to control sample (Figure 2).

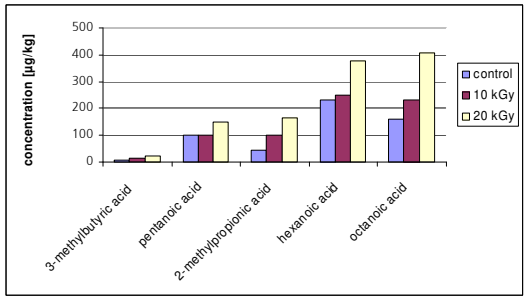

Fig. 2. γ-Irradiation induced increase in concentration of odour-active compounds.

Conclusions

The methodology was successfully applied for identification of potent odor active compounds in non-irradiated control sample and in γ-irradiated (10 and 20 kGy) PP samples. Monitoring of odor changes was accomplished by AEDA and SIDA, and showed that a series of odorants contribute to the smell of native and γ-irradiated PP. Generally, the present study shows that γ-irradiation of PP results in the formation of odour-active compounds, which induce off-odours in these materials.

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