Investigation of non-intentionally added substances (NIAS) in PET bottles and closures

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Introduction

Polyethylene terephthalate (PET) bottles for soft-drinks, mineral water, juices and beer have widely substituted the traditional packaging materials like glass bottles and aluminium cans. In contrast to inert materials like glass and metal, the PET polymer shows a higher diffusivity e.g. for oxygen. Therefore, oxygen scavenger systems have to be applied if oxygen sensitive beverages like beer or fruit juices should be packed in PET. Furthermore, scavengers for acetaldehyde, which is a potential off-taste source in mineral water, are used in order to reduce the acetaldehyde concentration in the PET bottle wall. In addition, additives for a faster reheat of the PET preforms, colorants as light shields for beer bottles as well as additives which reduce the abrasion during preform handling and bottle filling were introduced into or onto the PET bottle wall. Without these additives, PET bottles would not have been able to capture the beverage packaging market to that extent found today. On the other hand, introduction of these technologically needed additives is accompanied by the occurrence of non-intentionally added substances (NIAS) in the PET polymer. These NIAS do have a potential to negatively influence the organoleptic properties of the packed foods rather than to pose a health risk. In addition, NIAS may have an adverse effect on modern closed-loop recycling efforts.
Within this survey study, PET bottles from different applications as well as closures were analyzed in view of their content of migration relevant compounds.

Results

PET bottles were purchased for this study in local supermarkets. The bottles and closures were analysed for migration relevant compounds. The screening was performed using headspace gas chromatography as well as on solvent extracts. Headspace gas chromatography has to be shown as the method of choice for the fast and easy detection of migration relevant NIAS in PET bottles and closures. The method was previously applied for the screening of post-consumer PET recyclates [1]. Using mass spectrometry, identification of the detected compounds was achieved.
Due to the fact, that the investigated bottles were filled with beverages, flavour compounds could also be identified in the PET materials. These compounds are adsorbed into the bottle wall after filling. On the other hand, several substances were founds in PET which cannot be linked to beverages. Examples of gas chromatograms or PET bottles are shown in Figure 1. A compilation of NIAS found in PET bottles and closures is given in Table 1.

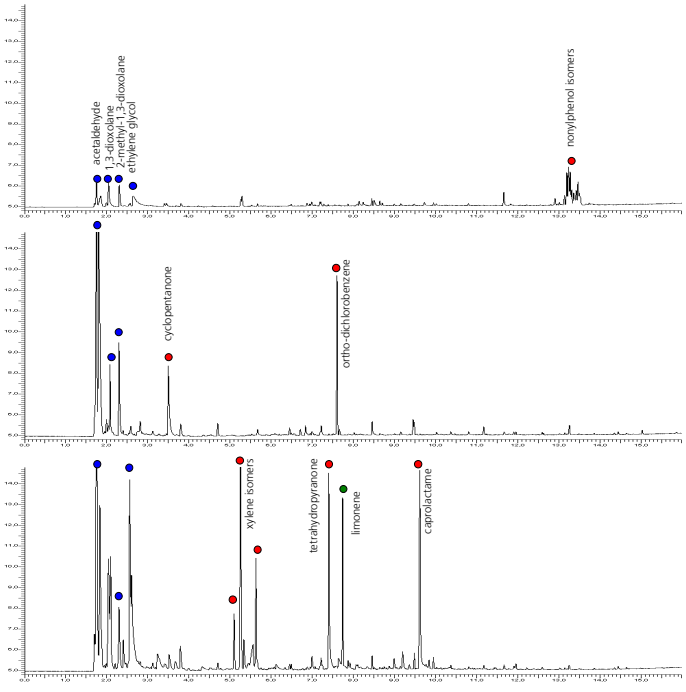

Figure 1: Examples of gas chromatogram obtained from PET bottles drawn from the market with NIAS (chemical structures in blue: PET polymer based, structures in red: additives or masterbatches, green: substances from the beverages

Table 2: Examples for NIAS clearly identified in PET bottles and closures (PP, HDPE)

Compounds	Possible source or introduction pathway
Acetaldehyde, 2-methyl-1,3-dioxolane, ethylene glycol, PET cyclic trimer	Degradation products of the PET polymer
Linear and branched hydrocarbons	Side products from the polymerisation of HDPE and PP
Saturated and unsaturated aldehydes	Degradation products from the HDPE and PP polymer as well as from polymer masterbatches
Propanoic acid, butyric acid	Degradation products from masterbatches found in closures
Isophthaldialdehyde, Caprolactam, cyclopentanone, *ortho*-, *meta*-, *para*-xylene, tetrahydropyranone	Polymerisation side-products and impurities from PA barrier layers in PET bottles
Dichlorobenzene	Impurity of colour masterbatches
Anthranilamide reaction products with aldehydes	Acetaldehyde scavenger in PET bottles
Nonylphenol (several isomers)	Degradation product from additive masterbatches

Conclusions

Within the last few years the amount and concentration of NIAS in PET beverage bottles has been increased steadily. The only substance, which significantly decreases within the last years was the PET degradation product acetaldehyde. NIAS may pose the risk for an unacceptable migration of chemical substances from the bottle wall into the beverages. In several cases off-flavours in beverages could be linked to such a migration. Therefore the reaction pathways and the source of NIAS should be investigated. Screening methods like headspace gas chromatography has shown to be a suitable method for the determination and the control of any unwanted migration relevant substances in PET bottles, preforms of additive masterbatches.
Evaluation of NIAS migration from PET and HDPE closures cannot covered by overall migration nor by the usual specific migration tests. As a consequence, certificates which show the general food law compliance of packaging materials do not prevent the migration of NIAS into the packed foodstuff. Therefore additional screening tests should be applied for the determination of any unwanted substances in food packaging materials.
It could be shown, that NIAS introduced by PET recycling of post-consumer PET by super-clean technologies play a minor role. Most of the NIAS found in PET beverage bottles are linked to additives and colour masterbatches. As a conclusion, masterbatches for PET beverage bottles and closures should therefore be controlled by a suitable method during the PET bottle production process. Finally, key compounds for the typical additives and scavenging systems could be assigned. The results demonstrate the occurrence of NIAS in PET enable to identify whether and if yes which active compound or scavenging system is used for PET beverage packaging.

Reference

[1] R. Franz, A. Mauer, F. Welle, European survey on post-consumer poly (ethylene terephthalate) materials to determine contamination levels and maximum consumer exposure from food packages made from recycled PET, *Food Additives and Contaminants*, **2004**, *21(3)*, 265-286.

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