POLYOLEFIN OLIGOMERS: RESEARCH PROJECT FOR RISK ASSESSMENT

Background and regulation of polyolefin oligomers under EU food contact legislation

Oligomers are an intrinsic part of the molecular weight distribution of polymers and more specifically represent the lowest molecular weight fraction. They are formed during the polymerisation reaction and are thus not intentionally added to the polymer.

Polyolefins such as polyethylene and polypropylene homopolymers and copolymers contain oligomers which are a mix of linear and branched alkanes and alkenes. The specific composition of this oligomeric fraction depends not only on the monomer and comonomer(s) used but also on the type of catalyst and the polymerisation process and conditions.

Please note that this PlasticsEurope Polyolefin oligomers paper is restricted to Polyolefins which are produced with alpha-olefins only and therefore excludes Polyolefins which are produced with other type of alkenes such as aromatic- and cyclic alkenes.

Oligomers are considered NIAS (Non-Intentionally Added Substances) as they are part of the molecular weight distribution of polyolefin plastics and do not require positive listing in Regulation No 10/2011 (see Art 6(4)).
Oligomers with Molecular Weights (Mw) up to1,000 Dalton (Da) are considered potential migrants of concern which after transfer (migration) into food may be absorbed by the gastrointestinal tract after ingestion of the food. Consequently, such substances are subject to Art 19 of Commission Regulation No 10/2011 and the materials and articles that contain them, must be compliant with Art 3 of the Framework Regulation No 1935/2004. This must be documented in the Supporting Documentation to the Declaration of Compliance (DOC).
Polyolefins oligomers are also known as POSH substances (polyolefin oligomeric saturated hydrocarbons), but they are often mistaken for mineral oil-saturated hydrocarbons (MOSH), since they are both long chains (C>20) hydrocarbons compounds. Different to the linear and branched POSH, MOSH however contain a significant fraction of cyclic alkanes.

As plastics producers, supplying raw materials to the converting industry, member companies of PlasticsEurope follow the stringent regulatory requirements laid down in the existing EU Regulations for plastics in contact with foodstuffs. This involves reviewing and conducting scientific research to support the risk assessment of the oligomers.

Characterisation, quantification and modelled migration levels of polyolefin oligomers

From 2013 to 2015 the Plastics Europe Polyolefins Group[1] commissioned the Fraunhofer Institute conducted a research project on the "Determination of the Migration of Oligomers from Polyolefins".

The project objective was to determine the migration potential of oligomers in polyolefins which involved:

- Identification and quantification of oligomers in a set of representative polyolefins samples
- Measurement of oligomers migration into food simulants
- Comparison of measured migration with migration modelling results
- Development of an approach for predicting migration and estimating exposure.

The data obtained could then be used for risk assessment.

Summary of the polyolefin oligomers analytical project

Twelve representative samples of commercial polyolefins, including high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and polypropylene (PP), were collected for analysis. The test specimen for each polymer consisted of pellets, films (100-250µm) and plaques (800-1000µm).

The following approach was taken to perform the analysis:

- Compositional analysis was performed using advanced analytical techniques: Purge and Trap/Gas Chromatography (P&T / GC), Head Space Gas Chromatography (HS GC), solvent (dichloromethane) extraction followed by GC Flame Ionisation Detection (GC/FID) and GC Mass Spectrometry (GC/MS)
- Migration tests were carried out using both 10% and 95% ethanol for 10 days at 40°C and 10 days at 60°C
- Migration modelling was performed using conservative parameters to assess the potential for oligomers to migrate into food and to calculate the resulting potential dietary exposures.

Detected oligomers were characterised as linear or branched alkanes and alkenes. This is consistent with other information on polyolefins available in the public literature and from the companies that are part of PlasticsEurope's Polyolefins Group.

From the analytical data, the majority of linear saturated or unsaturated oligomers could be identified and named as distinct chemical species. For branched oligomers that were predominantly seen in LDPE and PP, an unambiguous identification of substance peaks was not possible due to the complexity of the molecules and the number of possible isomers.

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[1] The PlasticsEurope Polyolefins Group comprises 10 companies : Borealis, Braskem, Dow, ExxonMobil, INEOS, LyondellBasell, Repsol, SABIC,Total, Versalis

Nevertheless, taking all available information into consideration, including reaction chemistry and interpretation of peak patterns, there is sufficient information to adequately characterise the peaks.

In 2019 a follow up study was carried out at the German research institutes Laboratory Lommatzsch & Säger and Institute Kirchhoff on the same representative samples of commercial polyolefins that have been used Fraunhofer Institute study.
The focus of this study was on the **detection** of possible cyclic and oxidised PO oligomers and **not** on their exposure.
The compositional analysis was performed using advanced analytical 2D GC techniques[2]:
An extract[3] of the representative samples of commercial polyolefins was injected in the system. After separation on a polar column (1st dimension) and subsequently on a non-polar column (2nd dimension), the substances were identified via MS.

Results from this study indicated that traces of cyclic oligomers (POSHcy) were observed in two (LDPE) samples out of twelve representative samples of commercial polyolefins samples and in one (LDPE) sample out of twelve representative samples of commercial polyolefins samples analysed, oxidised oligomers (oxPOH) were detected. The other representative samples of commercial polyolefins samples had no presence of cyclic or oxidised oligomers.

POSHcy in the range C10 until >C40 might be produced during the polymerisation process of LDPE, but according to chemistry this is very unlikely. It is more likely that they may be present as artefacts (NIAS) in the used compressor oils in the used production process, which is allowed in Annex I of Commission Regulation (EU) No 10/2011 without a SML restriction.
The presence of oxPOH in only the one sample LDPE cannot be explained, since LDPE is the only polymer that in principle do not need to contain stabilisers to protect it from thermo-oxidative degradation during melt processing or its service life.

Based on the determined concentration levels of extractable oligomers in the plastics, the migration levels into food were estimated through migration modelling for the scenarios 10 days at 25, 40 and 60°C with the partitioning coefficients K=1 (equivalent to 95% ethanol) and K=1,000 (equivalent to 10% ethanol).

The migration modelling results were then compared to the real migration results which showed overall a good agreement, thereby confirming the validity of the modelling approach. Based on the obtained migration levels in the two food simulants, estimated daily intake numbers were calculated using the Matrix exposure assessment computing tool. (https://matrixcalculation.eu)

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[2] GCxGC setup:
Precolumn: 1-2m x 0.53 mm ID untreated fused silica tubing
1st Column: 15 m x 0.25 mm ID DB-17 MS (0.15 µm film)
2nd Column: 3 m x 0.15 mm ID PS-255 (0.04 µm film)
Injection: PTV on-column
Carrier: Helium, 1 ml/min
Program: 50 °C 3.0 min – 5 °C/min – 320 °C 1.0 min
Modulation: 8.0 s
MS: 40 – 800 amu at 50Hz

[3] 500 mg sample (granulate) was extracted with 10ml n-hexane/ethanol (50:50) at 60°C for 24h on a water bath without stirring

Toxicological evaluation

A working group of toxicologists[4] from the Polyolefins Group performed a desk-based review of the available toxicology database[5], providing an update to previous hazard and risk assessments of the oligomers.
To date, studies conducted under REACH support conclusions of existing OECD[6] assessments of relevant aliphatic hydrocarbons and olefins[7]. Overall, there is no evidence of hazardous properties relevant to human health for the oligomers[8].

Based on many studies with alkanes and alkenes, the oligomers have a low potential for acute toxicity. The oligomers are not genotoxic based on a number of in vitro- and in-vivo studies, and there are no structural alerts or other toxicological concerns for carcinogenicity. There is no indication of potential for reproductive and developmental toxicity based on in vivo studies.

In animal studies conducted by the oral route with relevant alkanes and alkenes, no observed adverse effect levels are consistently above 100 mg/kg body weight per day (bw/d) with the exception of:

- male rat alpha-2u-globulin nephropathy, which is not relevant to humans
- adaptive liver effects, which are not relevant to low dose dietary exposures[9]
- indirect effects associated with high dose and gavage studies

For detailed toxicological assessments, it is appropriate to distinguish between the oligomer categories (linear alkanes, branched alkanes, linear alkenes, branched alkenes) and subcategories (C10-14, C15-25, C26-35, >C35). In particular, there are differences in bio-absorption and metabolic pathways across these groups:

- Following oral exposure, bio absorption of the oligomers tends to decrease with increasing molecular weight, with limited bioavailability of C26+ oligomers and negligible bioavailability for C35+ oligomers
- Once absorbed, alkanes undergo oxidation to fatty alcohols with elimination or transformation to fatty acids, whereas alkenes undergo oxidation to glycols or conjugation with glutathione

The above mechanisms for metabolism and elimination are common for such compounds. The body does not differentiate between natural and synthetic sources of these substances or their metabolites.

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[4] From Dow, ExxonMobil, LyondellBasell and SABIC
[5] Only toxicological studies with defined or well characterised chemical substances relevant to the identified oligomers were reviewed. Studies and other information relating substances with aromatic, nitrogen- or phosphorus-containing hydrocarbons, and cyclic structures were excluded.
[6] The Organisation for Economic Cooperation and Development - http://www.oecd.org/
[7] REACH registrations are available for a number of substances relevant to the oligomers. OECD assessments include the following categories: C9-14 Aliphatic Hydrocarbon Solvents; C14+ Aliphatic Hydrocarbon Solvents; Alpha Olefins; Higher Olefins.
[8] Other hydrocarbon components that may potentially also be a result of the polymerisation reactions but not characterized as oligomers were below 1 ppm in the polymer samples. For such linear, branched and even cyclic hydrocarbons, a Cramer class I (low concern) is applicable
[9] Across the toxicological database, there is no evidence liver microgranuloma surrounded by inflammatory cells seen in experiments with certain long chain saturated hydrocarbons.

Substances similar to polyolefin oligomers approved by regulatory authorities

Annex I of Commission Regulation (EU) No 10/2011 on plastic materials and articles intended to come in contact with food, lists a number of authorised polymeric additives that contain a high fraction of polyolefin oligomers. The substances are listed without any restriction.

- Polyethylene wax (FCM substance no 549, CAS no 9002-88-4)
- Polypropylene wax (FCM substance no 550, CAS no 9003-07-0)
- Isobutylene-butene copolymer (FCM substance no 577, CAS no 9044-17-1)
- Hydrogenated homopolymers and/or copolymers made of 1-Hexene and /or 1-Octene and/or 1-Decene and or 1- Dodecene and/or 1- Tetradecene with Mw = 440-12,000 (FCM substance no 789) Specification: average Mw is not less than 440 Da, viscosity at 100°C not less than 3.8 centistokes (cSt).

Overall conclusions

Linear and branched saturated and unsaturated oligomers in polyolefins are an intrinsic part of the polymer, created by polymerisation reaction chemistry. Based on a study of the oligomers in 12 samples of commercial polyolefin plastics from four product families (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and polypropylene (PP), the primary components identified were linear and branched alkanes and alkenes.

The potential migration levels of the oligomers from the plastics to food, and the corresponding potential for dietary exposure, are below any toxicological level of concern. Tolerable Daily Intakes (TDIs) derived for the oligomers are sufficiently high (consistently above 1 mg/kg bw/d) not to be exceeded if the maximum allowed overall migration limit of 60 mg/kg food is respected.
The project work therefore demonstrates that consumer exposures to these oligomers from the polyolefin plastics food packaging under typical conditions of use are not a safety concern to human health.

Based on a risk assessment made, the presence of cyclic oligomers in LDPE as well as the eventual presence of oxidized oligomers in LDPE can be regarded as safe, as long as the limit of 1800 µg/kg food (for POSHcy) and 540 µg/kg food (for oxPOH) is not exceeded.

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