Migration of linear and cyclic polyester oligomers from polyester-phenol-coatings into food and food simulants

Martin **Eckardt***, Lisa **Hetzel**, Thomas **Simat**

Chair for Food Chemistry and Food and Skin Contact Materials, Technische Universität Dresden, Germany

* mail: martin.eckardt@chemie.tu-dresden.de

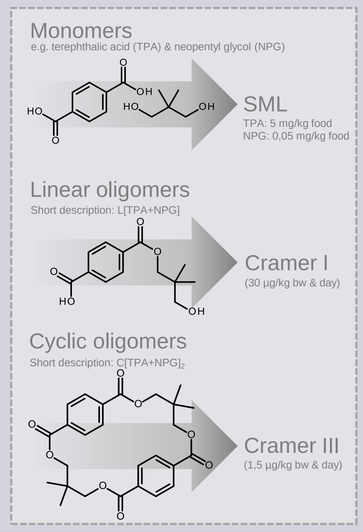
Background

Food contact materials (FCM) made of metal, such as tin cans or closures for baby food, are often lacquered with a coating to protect against corrosion and a possible transfer of undesirable metal ions into food. As an alternative formulation to the etablished but potentially hazardous epoxy-phenol-coating based on bisphenol A (BPA), polyester-phenol-coatings are widely used. However, these coatings can also release substances with unknown toxicological potential into food in direct contact. Especially oligomers formed by polyester monomers are in focus.

In this study, an analytical concept for the identification and determination of polyester oligomers releaseable from a commercial coating, used in closures for baby food, into food and food simulants is presented.

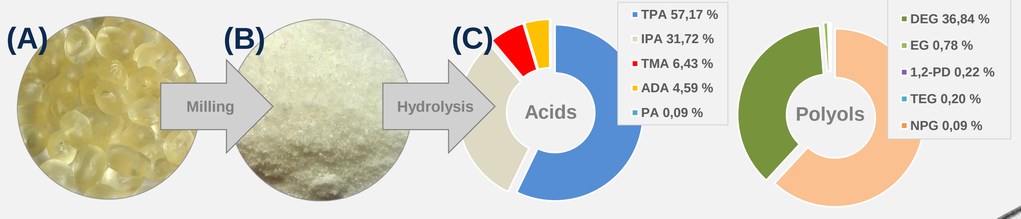
Risk assessment of polyester oligomers

Polyester oligomers are esters of mostly polyvalent carboxylic acids and polyols. Risk assessment of monomers is based on legal specific migration limits (SML), often derived from toxicological studies. No toxicological studies or legal limits exist for polyester oligomers. Therefore, risk assessment is performed by the exposure based TTC concept (threshold of toxicological concern). Linear polyester oligomers are concerned with a threshold of 30 µg/kg bw & day (Cramer class I), cyclic oligomers are evaluated with 1.5 µg/kg bw & day (Cramer class III)[1].



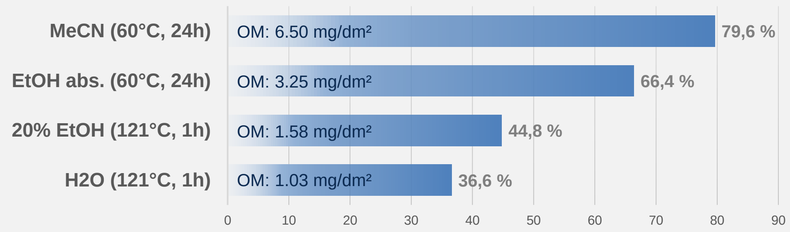
► Polyester monomers: determination of carboxylic acids (LC) & polyols (GC) subsequent to hydrolysis

from polyester resins (raw materials available) → monomer profile
→ prediction of probable linear and cyclic oligomers



(A) Polyester resin granulate; (B) cryogen milled polyester resin granulate; (C) monomer composition of an exemplary polyester resin.
Substances: *caboxylic acids:* terephthalic acid (TPA), isophthalic acid (IPA), trimellitic acid (TMA), adipinic acid (ADA), phthalic acid (PA); *polyols:* 2-methyl-1,3-propanediol (2-MPD), diethylene glycol (DEG), ethylene glycol (EG), 1,2-propanediol (1,2-PD), triethylene glycol (TEG), neopentyl glycol (NPG)

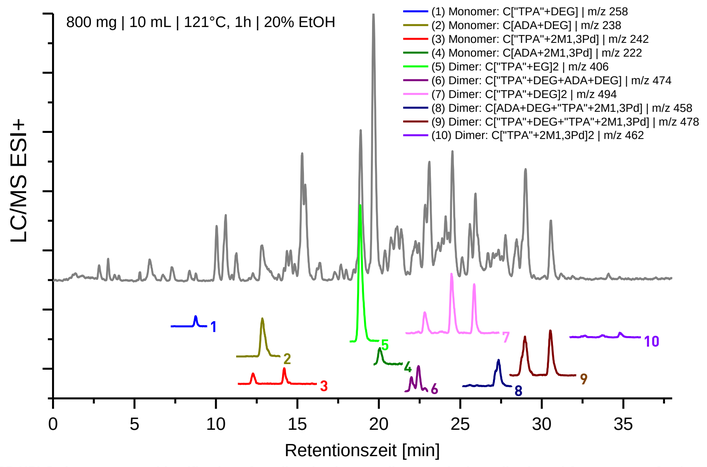
from extracts and migrates of polyester coatings
→ determination of total leachable polyester



Relative hydrolyzable content of polyester-based substances on the gravimentrically determined overall migrate (OM) in % with regard to the extraction conditions of the coating (organic solvent versus aqueous food simulants).

► Identification of oligomers

in extracts from polyester resins
→ verification of predictable oligomers



RP-HPLC chromatogram: identification of predicted polyester oligomers (only cyclic shown) from extract of polyester resin subsequent to sterilization (121°C, 1h, 20% ethanol). Total ion chromatogram (grey) and extracted $[M+H]^+$ ion currents (multicolored) of predicted cyclic polyester oligomers ("predictable NIAS").

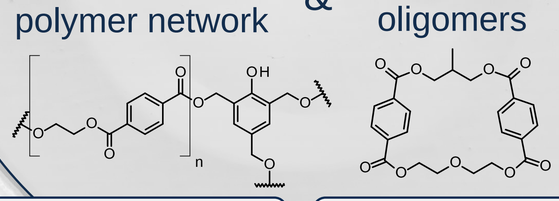
commercial coating formulation

polyester resins + phenolic resins + crosslinker + PVC + waxes + filler …

curing
200°C, 10 min

polyester-phenol-coating

covalent polymer network & releaseable oligomers

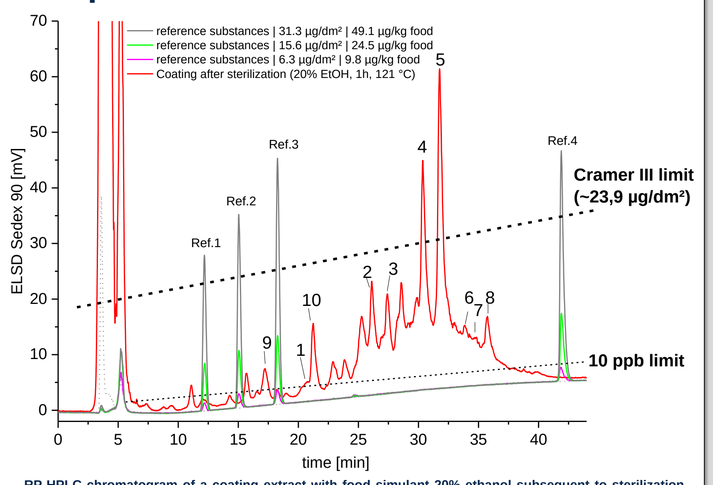


low relevance for migration processes

high relevance for migration

► Application of TTC concept

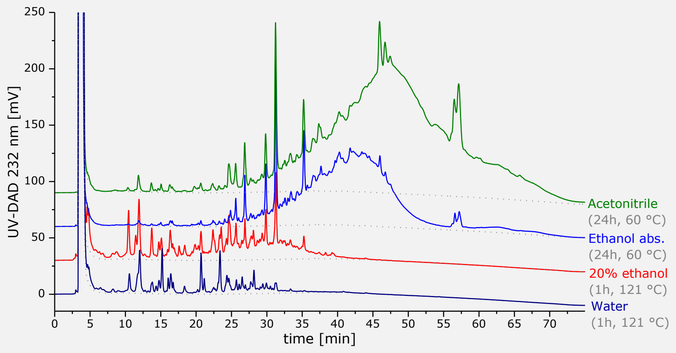
to migrates from polyester-coating
→ exposure based evaluation



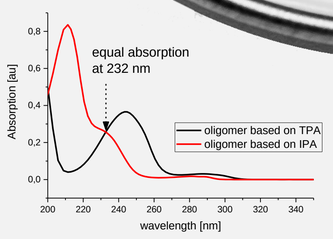
RP-HPLC chromatogram of a coating extract with food simulant 20% ethanol subsequent to sterilization (121°C, 1h). Universal detection for non-volatile substances realized with light scattering detector (ELSD). Estimation of TTC limits via reference substances (Ref.1-4). 1-10: linear and cyclic polyester oligomers.

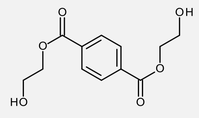
► Quantification of oligomers

HPLC-UV (232 nm) external calibration
with commercial reference substance BHET



RP-HPLC chromatograms of a polyester resin subsequent to solvent extraction (green, blue) and simulated migration (red, dark blue). Effects of hydrolysis lead to increase of short linear polyester oligomers (early elution times) when aqueous simulants were used.





Bis-hydroxyethyl-terephthalate (BHET)

UV spectra of two linear polyester oligomers BHET (Bis-hydroxyethyl-terephthalate; black) and BHEI (Bis-hydroxyethyl-isophthalate; red) at same concentration. Common wavelength for quantification at 232 nm as described by SCHÄFER[2].

Chromophore concentration: $c_c = c_s \cdot \frac{n}{M_w}$

c_c: $Chromophore - cocentration\ [\mu mol \cdot L^{-1}]$
c_s: $Oligomer - concentration\ [\mu g \cdot L^{-1}]$
n: $Number\ of\ aromatic\ rings\ in\ oligomer\ structure$
M_w: $Molecular\ weight\ of\ oligomer\ [g \cdot mol^{-1}]$

► Release of polyester oligomers

"Migrants","Leachables" & "Extractables"

Tab.: Release of cyclic (C), linear (L) and total polyester content from polyester phenol coating (n.d. = not determinable)

		Migrants (Fruit mash, 1h, 121°C)		Leachables (20% ethanol, 1h, 121°C)		Extractables (MeCN, 24h, 60°C)	
Oligomer structure	**Mw [g/mol]**	**µg/dm²**	**µg/kg LM**	**µg/dm²**	**µg/kg LM**	**µg/dm²**	**µg/kg LM**
L[TPA+DEG]	254.2	n.d.	n.d.	9.1	14.3	0.3	0.5
L[IPA+DEG]	254.4	n.d.	n.d.	6.3	9.9	0.1	0.2
L[DEG+TPA+DEG]	342.5	n.d.	n.d.	3.8	6.0	2.1	3.3
L[DEG+IPA+DEG]	342.5	n.d.	n.d.	5.3	8.3	0.9	1.4
L[2MPD+TPA+DEG]	326.5	n.d.	n.d.	9.5	14.9	1.0	1.5
L[2MPD+IPA+DEG]	326.5	n.d.	n.d.	3.2	5.1	0.4	0.6
L[2MPD+TPA+2MPD]	310.3	n.d.	n.d.	9.9	15.6	1.1	1.7
$C[TPA+EG]_2$	384.6	n.d.	n.d.	0.9	1.4	2.6	4.0
$C[TPA+DEG]_2$	472.4	2.2	3.5	8.7	13.7	11.2	17.5
$C[IPA+DEG]_2$	472.4	2.6	4.1	10.1	15.9	24.0	37.7
C[TPA+2MPD]+[TPA+DEG]	456.4	3.3	5.1	15.2	23.8	23.9	37.5
C[TPA+2MPD]+[IPA+DEG]	456.4	5.9	9.3	19.8	31.1	80.8	126.9
$C[TPA+DEG]_3$	708.6	n.d.	n.d.	2.2	3.5	2.5	4.0
$C[TPA+2M\text{-}1,3PD]_2$	440.4	0.9	1.5	4.2	6.7	41.6	65.3
$C[IPA+2M\text{-}1,3PD]_2$	440.4	0.4	0.7	1.9	3.0	2.7	4.2
Total identified linear oligomers		n.d.	n.d.	47.2	74.1	5.9	9.3
Total identified cyclic oligomers		15.4	24.3	63.1	99.1	189.3	297.2
Total released polyester (hydrolyzable)		201.1	314.9	567.4	888.4	6 568.0	10 284.1

Conclusion

- **Linear and cyclic polyester oligomers can migrate from polyester-phenol coatings in relevant amounts into food and food simulants. When aqueous food simulants were used, effects of hydrolysis occur.**
- **Determination of monomer profiles after complete hydrolysis is a valuable tool to predict probable polyester oligomers as well as to estimate the release of total polyester related content into food and food simulants.**
- **Tentative identification of predicted linear and cyclic polyester oligomers can be performed by HPLC-ESI-MS. Quantification of identified oligomers via HPLC-UV is based on external calibration with BHET and requires chromatographic separation.**
- **TTC limits for known substances can be transformed into analytical thresholds by estimation of exposure. Monitoring of threshold values in screening methods can be carried out with the aid of universal detectors.**

References [1] Patlewicz G. et al. (2008) An evaluation of the implementation of the Cramer classification scheme in the Toxtree software. SAR QSAR Environ Res. ;19(5-6):495-524.
[2] Schaefer A., Simat T.J. (2004) Migration from Can Coatings: Part 2: Identification and quantification of migrating cyclic oligoesters below 1000 Da. Food Additives and Contaminants, Vol. 21, No 4. 377-389.

ILSI Europe: 6th International Symposium on Food Packaging – Barcelona/Spain - 11/16/2016 – 11/18/2016

poster online