Task force on varnishes and coatings for food contact materials

Partnering Grant Project
(Grant Agreement Number GP/EFSA/AFSCO/2017/01- GA07)

Task 1: List of essential terms and definitions used in the evaluation of coatings for Food Contact Materials (FCM).

In Progress: 2nd draft prepared and discussed in the Task force.

Living document : It is intended to continue to be discussed, improved and updated by the working group when considers it necessary.

Contents

- Abbreviations
- The aim and the problems.
- Discussion on the term “Coating”.
- Discussion on the term “Polymer”.
- Discussion on other related terms (Oligomer, Prepolymer).
- Naming polymers, oligomers and prepolymers.
- Conclusions/Remarks.

Abbreviations

ISO: International Organization for Standardization.

R 10/2011: Commission Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food, and amendments.

EUG_R 10/2011: Union Guidelines on Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food. Version 1.1, 12.01.2016.

IUPAC: International Union of Pure and Applied Chemistry.

OECD: Organisation for Economic Co-operation and Development.

REACH: Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals, and amendments.

ECHA (2017b): European Chemical Agency. Guidance for identification and naming of substances under REACH and CLP, version 2.1.

Aim

Clarify the meaning of some scientific, technical or legal terms, which frequently are used by operators and agencies involved in risk assessment of chemical substances in the Food Contact Material (FCM) field.

In particular, the goal is to avoid the confusion that the ambiguity in the interpretation of some terms may cause in the field of coatings.

The problems

- Ambiguous terms, the meanings of which should be inferred from the context.
- Disagreements in the definitions used by recognized organizations, institutions, agencies and legal texts, both EU and internationals or nationals.
- Lack of definitions and/or appropriate references for the terms used in the legal texts, generating uncertainties about which substances are authorized and whether or not they should be subject to risk assessment.

Discussion on the term "coating"

Coating: Used to describe both the material (liquid, paste, powder) intended to be applied on a substrate and the resulting "dry" layer.

This ambiguity is strongly rooted in all fields, scientific, academic, technical, legal, etc. It may generate confusion when the term is not rightly inferred.

Proposal: to use ISO definitions

Coating: layer formed from a single or multiple application of a coating material to a substrate.

Coating material: product, in liquid, paste or powder form, that, when applied to a substrate, forms a layer possessing protective, decorative and/or other specific properties

Discussion on the term "Polymer"

Not very clear

clear concepts, but disagree

R 10/2011

Polymer: Means any macromolecular substance obtained by: (a) a polymerisation process such as polyadition or polycondensation, or by any other similar process of monomers and other starting substances; or (b) chemical modification of natural or synthetic macromolecules; or (c) microbial fermentation;

Regulation does not define "macromolecular substance".

EUG_R 10/2011 says ".. macromolecular substances, such as oligomers, pre-polymers and polymers.

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IUPAC

Polymer: A substance composed of macromolecules.

Macromolecule (polymer molecule): A molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass.

A molecule can be regarded as having a high relative molecular mass if the addition or removal of one or a few of the units has a negligible effect on the molecular properties.

REACH / OECD

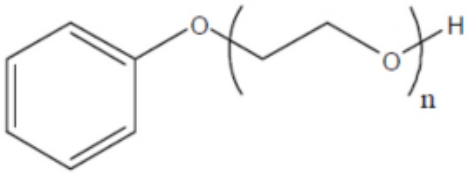
Polymer: Means a substance consisting of molecules characterised by the sequence of one or more types of monomer units. Such molecules must be distributed over a range of molecular weights wherein differences in the molecular weight are primarily attributable to differences in the number of monomer units. A polymer comprises the following:

(a) a simple weight majority of molecules containing at least three monomer units which are covalently bound to at least one other monomer unit or other reactant;

(b) less than a simple weight majority of molecules of the same molecular weight.

Molecular composition of 3 examples of ethoxylated phenol substances

Table from: ECHA (2012). Guidance for monomers and polymers. Version 2.0

	Example 1	Example 2	Example 3	Mw (g/mol)
n=1	0%	40%	5%	138.166
n=2	10%	20%	10%	182.219
n=3	85%	15%	20%	226.272
n=4	5%	12%	30%	270.325
n≥3 n=5	0%	8%	20%	314.378
n=6	0%	5%	10%	358.431
n=7	0%	0%	5%	402.484
Sum	100%	100%	100%	

40 %

85 %

OECD/REACH/EPA	No polymer (Standard substance)	No polymer (Estándar substance)	Polymer
IUPAC	No polymer	No polymer	No polymer
R 10/2011	No polymer ?	No polymer ?	No polymer ?

Discussion on other related terms

Not very clear

R 10/2011

Oligomer & Pre-polymer: Use both terms but does not define them.

EU_R 10/2011

Oligomer means a substance consisting of a finite number of repeating units which has a molecular weight of less than 1000 Da.

Pre-polymer is a polymer of relatively low molecular weight, usually an intermediate between the monomer and the final polymer or resin.

clear concepts

IUPAC

Oligomer: A substance composed of oligomer molecules.

Oligomer molecule: A molecule of intermediate relative molecular mass, the structure of which essentially comprises a small plurality of units derived, actually or conceptually, from molecules of lower relative molecular mass.

A molecule is regarded as having an intermediate relative molecular mass if it has properties which do vary significantly with the removal of one or a few of the units.

Prepolymer: Polymer or oligomer composed of prepolymer molecules.

Prepolymer molecule: Macromolecule or oligomer molecule capable of entering, through reactive groups, into further polymerization, thereby contributing more than one constitutional unit to at least one type of chain of the final macromolecules.

REACH / OECD

Oligomer & Pre-polymer: They are not defined

Discussion on other related terms

Special Interest has the concept of pre-polymer

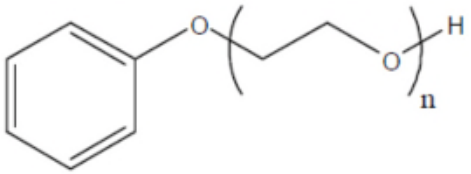
- When used as monomers or other starting substances, Pre-polymers are substances authorized if the monomers or starting substances required to synthesise them are included in the Union list (R 10/2011, article 6).
- They are not included in the Union list and they are excluded from assessment of substances in accordance with internationally recognised scientific principles on risk assessment (R 10/2011, article 19).
- Pre-polymers when migrating are not subjected to specific restrictions, only subject to overall migration limit.
- Usually they are not evaluated as such.

Resin: Complex mixtures of substances that contain mainly polymers and oligomers (including prepolymers). They are usually the main components of coating materials. Sometimes resin is used as synonym of polymer, oligomer or prepolymer, binder, etc.

IUPAC definition: Soft solid or highly viscous substance, usually containing prepolymers with reactive groups.

Molecular composition of 3 examples of ethoxylated phenol substances

Table from: ECHA (2012). Guidance for monomers and polymers. Version 2.0

	Example 1	Example 2	Example 3	Mw (g/mol)
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n=7	0%	0%	5%	402.484
Sum	100%	100%	100%	

40 %

85 %

OECD/REACH/EPA	**No polymer (Standard substance)**	**No polymer (Estándar substance)**	**Polymer**
IUPAC	No polymer (Oligomer/prepolymer)	No polymer (Oligomer/prepolymer)	No polymer (Oligomer/prepolymer)
R 10/2011	**Authorized ?**	**Authorized ?**	**Authorized ?**

Naming polymers, oligomers and prepolymers

IUPAC nomenclature: Recommended, although it is not commonly used.

In the case of reaction products (f.i. complex multi-constituents substances as oligomers, prepolymers and or polymers) usually other formats are used and recommended (**ECHA, 2017b**):

- Main starting material, reaction product(s) of other starting material(s) used in EINECS, or
- Reaction product(s) of starting material(s) used in ELINCS.

Examples

Formaldehyde, oligomeric reaction products with l-chloro-2,3-epoxypropane and phenol (CAS: 9003-35-5, NLP No & EC No.: 500-006-8).

Other names: Epichlorohydrin-phenol-formaldehyde resin; Oxirane, (chloromethyl)-, polymer with formaldehyde and phenol (9CI); Phenol-formaldehyde-epichlorohydrin copolymer; poly(epichlorohydrin-co-formaldehyde-co-phenol), Bisfenol F epoxy resins, novolac glycidyl ethers (NOGE) and more.

4,4'-Isopropylidenediphenol, oligomeric reaction products with l-chloro-2,3-epoxypropane, reaction products with diethylenetriamine (CAS RN 31326-29-1; NLP No & EC No.: 500-072-8).

Other names: Phenol, 4,4'-(1-methylethylidene)bis-, polymer1 with N-(2-aminoethyl)-1,2-ethanediamine and (chloromethyl)oxirane (9CI), Formaldehyde-phenol-m-xylenediamine copolymer 2,2'-[(1-methylethylidene)bis(4,1-phenyleneoxymethylene)]bisoxirane, reaction products with ethylene diamine, 2,2-Bis(p-hydroxyphenyl)propane-diethylenetriamine-epichlorohydrin copolymer, BADGE-DETA-Adduct, and more.

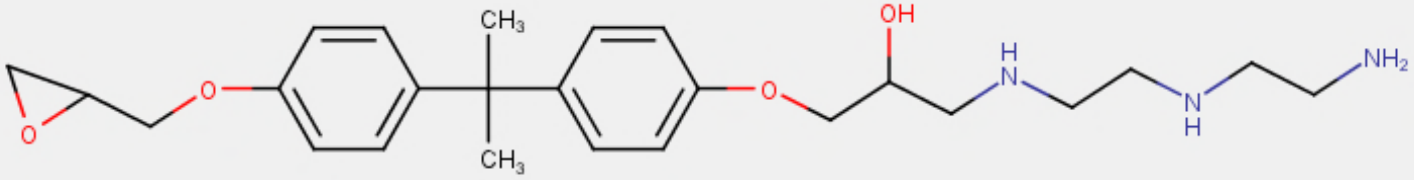
Naming polymers, oligomers and prepolymers

4,4'-Isopropylidenediphenol, oligomeric reaction products with l-chloro-2,3-epoxypropane, reaction products with diethylenetriamine (CAS RN 31326-29-1; NLP No & EC No.: 500-072-8).

Synthesized from authorized monomers in R_10/2011

4,4'-Isopropylidenediphenol (Bisphenol A)	SML = 0.05 mg/kg.
l-chloro-2,3-epoxypropane (Epichlorohydrin)	Restriction = 1 mg/kg in final product.
Diethylenetriamine	SML = 5 mg/kg.

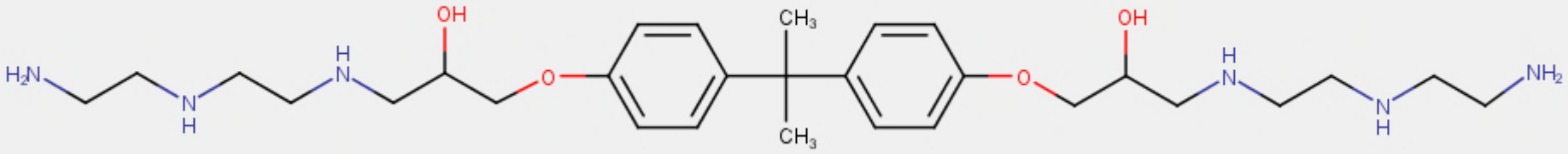
Constituents among other many pre-polymer, the following:



Are they generically authorized ?

Really is not necessary to carry out the risk assessment ?

Cramer test: High (Class III)



Conclusion / Remarks

The terminology used in the field of coatings (coating, polymer, oligomer, pre-polymer, resin, etc.) is ambiguous and it may generate confusion to stakeholders (included those related with risk assessment), when the term is not inferred rightly from the context.

Regardless the meaning of the terms, it should be considered the risk assessment of substances with molecular weight less than 1000 Da (polymers or prepolymer, or oligomers or whatever named), remaining in the coating which can migrate into the food.

It also should be considered if it is appropriate, from a food safety point of view, to translate the generic authorization for pre-polymers of the plastics Regulation (UE) 10/2011 into the coatings field, since pre-polymers are broadly used in their manufacturing.

Thank you for your attention

Questions ?