Open Letter to DG Environment

Which polymers are “natural polymers” in the sense of the single-use plastic ban?

nova-Institute, Hürth, Germany, 18 September 2019; Updated version 08 October 2019

After a relatively short negotiation period, the new rules on single-use plastics to tackle marine litter were adopted and published in June 2019, in brief commonly known as the “single-use plastic ban” (European Parliament and Council 2019). Items that fall under this ban include single-use products made of plastic to which alternatives exist on the market, such as cotton bud sticks, cutlery, plates, straws, stirrers, sticks for balloons, as well as cups, food and beverage containers made of expanded polystyrene and all products made of oxo-degradable plastic.

For the purpose of the Directive and its measures, a **plastic** is defined as a material consisting of a polymer to which additives or other substances may have been added, and which can function as a main structural component of final products, **with the exception of natural polymers that have not been chemically modified** (Annex 3.1 Definition – Plastic).

This means that all previously named items made of plastics defined as such (Annex 3.1 Definition – Plastic) fall under the ban except those made from ‘natural polymers that have not been chemically modified’, in the sense of the REACH definition of a **not chemically modified substance** (Annex 3.3 Definition – Not chemically modified substance).

However, within the Directive, it is not specified which polymers fall into the group of “natural polymers”. Also, the term “natural polymers” as such is not further defined within the proposal of the Directive.

For the definition of a **polymer** as a component of a plastic, the Directive refers to the REACH regulation (European Parliament and Council 2007) (Annex 3.1 Definition – Plastic), here the terms **polymer** (Annex 3.2 Definition – Polymer) and the term **substances which occur in nature** are defined (Annex 3.4 Definition – Substances which occur in nature). By considering, delineating and interpreting these two definitions, the European Chemicals Agency (ECHA) implemented a definition for **natural polymers** in which they are explained **‘as polymers which are a result of a polymerisation process that has taken place in nature, independently of the extraction process with which they have been extracted’** (ECHA 2012) (Annex 3.5 Definition – Natural polymer). Furthermore, it is emphasised that natural polymers are not necessarily **substances which occur in nature** when extracted and assessed according to the **substances which occur in nature** definition (Annex 3.4 Definition – Substances which occur in nature).

Based on this definition of a natural polymer, the following shows an exemplary list of polymers that should be considered as natural and examples of those that should not. It is emphasised that this list makes no claim of being complete.

1 Polymers to be considered as natural polymers

Polymerisation processes that take place in nature are those relying on the metabolism and biosynthesis of organisms and microorganisms such as animals, plants and algae, fungi and bacteria. The majority of these natural polymers are polysaccharides or proteins, but also other forms are possible as it is the case for lignin and polyhydroxyalkanoates (PHAs). In general, these natural polymers fulfil different functions within the organisms and/or microorganism as a texture-forming component (e.g. chitin), cellular interaction component (e.g. glycoproteins) or as energy storage material (e.g. polyhydroxyalkanoates (PHAs)). The biosynthesis either takes place in nature itself or is deliberately induced in artificial cultivation and fermentation processes.

The following examples of chemically unmodified **polymers** and polymer classes are clustered according to their natural origin. They are produced via the explained biosynthesis and should be **considered as natural polymers:**

- **Natural polymers produced via biosynthesis in animals such as:**
    - Polysaccharides and polymers based thereon: chitin, hyaluronic acid
    - Proteins and based thereon: casein, collagen, gelatine, hair, keratin, silk
    - Others: polyphosphates
- **Natural polymers produced via biosynthesis in plants and algae such as:**
    - Polysaccharides and polymers based thereon: agar agar, alginate, cellulose[1], hemicellulose, inulin, levan, pectins, starch (amylopectin, amylose), xanthan
    - Others: cutin, unmodified lignin, polyphosphates, suberin
    - Mixtures of natural polymers and other natural compounds: cotton, gluten, latex
- **Natural polymers produced via biosynthesis in fungi such as:**
    - Polysaccharides and polymers based thereon: α-1,3-glucan, chitin, chitosan
    - Proteins and polymers based thereon: glycoproteins
    - Others: polymalat (PMLA), polyphosphates
- **Natural polymers produced via biosynthesis in bacteria such as:**
    - Polysaccharides and polymers based thereon: alginate, bacterial cellulose, curdlan, dextran, pullulan, xanthan
    - Others: ε-poly-L-lysine, hyaluronic acid, poly-γ-glutamic acid, polyhydroxyalkanoates (PHAs), polyphosphates

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[1] Including rayon fibres, such as viscose and lyocell (Annex 3.6 The chemical structure of viscose and lyocell fibers)

Based on the definition of **polymers** in the REACH regulation (European Parliament and Council 2007) (Annex 3.2 Definition – Polymer), also so-called oligomers (if the number of monomers > 2) fall under this definition and natural varieties of these have to be considered here. In principle, oligomers are intermediates between monomers and polymers, they are lower molecular weight variants of polymers and are systematically named according to the number of monomers involved: dimer (2), trimer (3), tetramer (4) etc.

- **Natural oligomers produced via biosynthesis plants and algae such as:**
  - Secondary metabolites: ellagitannins, gallotannins, oligomeric proanthocyanidins
- **Natural oligomers produced via biosynthesis in fungi such as:**
  - Fatty acid-based oligomers: exophilin A

2 Polymers not to be considered as natural polymers

Besides these natural polymers that can be and are used as such without any further modifications, also natural polymers exist that are **chemically modified** prior to use to obtain specific properties. The following examples of polymers and polymer classes should therefore **not be considered as natural polymers.** Also this list does not make any claim of being complete:

- **Examples of natural polymers that are chemically modified**
  - Cellulose: cellulose acetate, cellulose butyrate and other cellulose derivatives
  - Lignin: ligninsulfonate
  - Starch: starch acetates and other starch derivatives

As defined in Annex 3.2 Definition – Polymer, polymers in general are always consisting of the same or different monomers, also called building blocks. These building blocks can be produced by plants and algae, as well as fungi and bacteria from renewable feedstocks and are therefore from natural, bio-based origin.

Bio-based polymers that are made from these bio-based monomers are always synthesised by a polymerisation reaction outside the plant or microbial cell, which is a chemical modification. The following examples of bio-based polymers should therefore also **not be considered as natural polymers:**

- **Examples of bio-based monomers used for bio-based polymer production such as:**
  - Bio-based monomers from plants and algae: bioethanol for bio-based polyethylene
  - Bio-based monomers from fungi and bacteria: lactic acid for polylactic acid (PLA), sebacic acid for polyamides (PA), succinic acid and 1,4-butanediol for polybutylene succinate (PBS)

Based on these scientific facts and the clear guidance given by REACH (European Parliament and Council 2007) and ECHA (ECHA 2012), we request the European Commission to exempt the above named “natural polymers” from the measures outlined in Directive 2019/904 (European Parliament and Council 2019).

Experts supporting this proposal:

Cologne, September 2019

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3 Annex

3.1 Definition – Plastic

DIRECTIVE (EU) 2019/904 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 5 June 2019 on the reduction of the impact of certain plastic products on the environment

Article 3(1):
‘plastic’ means a material consisting of a polymer within the meaning of Article 3(5) of Regulation (EC) No 1907/2006, to which additives or other substances may have been added, and which can function as a main structural component of final products, with the exception of natural polymers that have not been chemically modified;
(European Parliament and Council 2019)

3.2 Definition – Polymer

Corrigendum to Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC

Article 3(5):
‘polymer’ means a substance consisting of molecules characterized 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.
In the context of this definition a ‘monomer unit’ means the reacted form of a monomer substance in a polymer;
(European Parliament and Council 2007)

3.3 Definition – Not chemically modified substance

Corrigendum to Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC

Article 3(40):
‘not chemically modified substance’ means a substance whose chemical structure remains unchanged, even if it has undergone a chemical process or treatment, or a physical mineralogical transformation, for instance to remove impurities;
(European Parliament and Council 2007)

3.4 Definition – Substances which occur in nature

Corrigendum to Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC

Article 3(39):
‘substances which occur in nature’ means a naturally occurring substance as such, unprocessed or processed only by manual, mechanical or gravitational means, by dissolution in water, by flotation, by extraction with water, by steam distillation or by heating solely to remove water, or which is extracted from air by any means;
(European Parliament and Council 2007)

3.5 Definition – Natural polymer

Guidance for monomers and polymers – Guidance for the implementation of REACH. Version 2.0

3.2.1.3 Case of a natural polymer or a chemically modified natural polymer

Natural polymers are understood as polymers which are the result of a polymerisation process that has taken place in nature, independently of the extraction process with which they have been extracted. This means that natural polymers are not necessarily ‘substances which occur in nature’ when assessed according to the criteria set out in Article 3(39) of the REACH Regulation.

Following Article 2(9) of REACH, any polymer meeting the criteria of Article 3(5), whether natural polymers or not, does not have to be registered. This exemption from registration includes natural polymers which are chemically modified (e.g. post-treatment of natural polymers).
Monomer substance(s) and other substance(s) ending up in the form of monomeric units and chemically bound substance(s) in natural polymers can, for practical reasons, be treated as “non-isolated intermediates” and do not have to be registered.

In the case of chemically modified natural polymers, the building block monomer substance(s) and other substance(s) in the form of monomeric units and chemically bound substance(s) similarly originating from the natural polymers can also, for practical reasons, be treated as “non-isolated intermediates” and do not have to be registered. However, any monomer substance or any other substance (within the meaning of Article 6(3)) used for the modification of the natural polymer and meeting the provisions of Article 6(1) and 6(3) needs to be registered accordingly, unless it has been registered up the supply chain. These registration obligations apply provided the chemically modified natural polymer itself meets the Article 3(5) polymer definition.

Whenever it is not scientifically possible to identify and quantify the building blocks of a substance that is under consideration as to whether it is a natural polymer or not, this substance must instead of a natural polymer be regarded as a UVCB substance (see section 2.2 for further information) that therefore has to be registered.
(ECHA 2012)

3.6 The chemical structure of viscose and lyocell fibers

In order to produce a textile fiber from wood-based cellulose the fiber needs to be dissolved in order to be spun. The biopolymer cellulose in general is insoluble in almost all organic and inorganic solvents. Only very few special solvents are able to generate homogenous cellulose solutions, which can be processed into fibers by spinning. One of those solvents is *N*-methylmorpholine-*N*-oxide monohydrate (NMMO*H_2O), which is being used in the Lyocell process. The process of dissolution is a physical process. In the spinning dope, the cellulose chains are individualized by the solvent, and during spinning, they are aligned and stretched into fibers. The cellulose is “precipitated” (in that case the correct term is: regenerated) from the physical solution by simple addition of large amounts of water. As cellulose is insoluble in water the solvent power of NMMO is rapidly decreased in the spinning bath and the cellulose regenerates as pure cellulose. The only difference to the original cellulose structure in pulp is the alignment of cellulose chains in the crystal lattice. Like many polymers, cellulose is partially crystalline, i.e. the cellulose chains are partially arranged in high order which gives rise to the formation of crystalline domains. Several different such crystalline domains exist for cellulose, the most important are the structures of cellulose I present in all native cellulose forms such as wood or annual plant fibers (cotton, hemp, flax…) and cellulose II, which is formed after treatment with highly concentrated alkali or after regeneration from any solution. The cellulose I allomorph is the thermodynamically less stable form, hence after regeneration all cellulose structures exist in the cellulose II form. The differences in crystal structure are merely physical; chemically, both celluloses are indistinguishable. Both allomorphs solely consist of chemically pure cellulose. If cotton is mercerized (e.g. by treatment with concentrated NaOH) in textile finishing applications the cellulose II allomorph is formed as well.

The situation is similar for rayon (viscose) fibers. Here a different approach is used to render cellulose processible/soluble in order to be spun into fibers. A sufficient number of cellulosic hydroxyl groups are converted into a very labile xanthate ester using carbon disulfide. The xanthate is soluble in sodium hydroxide and spun in this form, but it immediately cleaved under the acidic conditions of the spinning bath. This regenerates cellulose, once more as the allomorph cellulose II. The chemical derivatization was only temporary, and the regenerated cellulose is chemically pure and chemically indistinguishable from the starting cellulose. The final fiber consists of pure cellulose of the cellulose II crystal structure. Both lyocell and viscose fibers are highly pure cellulose, they contain no significant portions of any chemical modification. With respect to chemical properties and molecular structure they are fully comparable to cotton, i.e. strictly stereoregular, glycosidically beta-1,4-linked anhydroglucose units.

Although both processes, the viscose and the lyocell variant, use chemicals as either physical solvents (lyocell) or for temporary derivatization and dissolution (viscose), the regenerated celluloses represent the natural, underivatized cellulose polymers, fully comparable to fibers from cotton. All spectral data confirm the presence of pure cellulose.

Hence, viscose or lyocell are pure cellulose without chemical modification and do not fall into any category of chemically modified or derivatized cellulose fibers, such as cellulose acetate or cellulose nitrate, or even in the categories of semi-synthetic or synthetic polymers and plastics.

(Potthast 2019)

4 References

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