Microplastics restriction

Open session of the Enforcement Forum 29 October 2020

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Microplastics restriction

Polymers within the meaning of Article 3(5) of Regulation (EC) No 1907/2006)

1. Shall not, from [entry into force (EiF)], be placed on the market as a substance on its own or in a mixture as a microplastic in a concentration equal to or greater than 0.01% w/w.

2. For the purposes of this entry:

   a. ‘microplastic’ means particles containing solid polymer, to which additives or other substances may have been added, and where ≥ 1% w/w of particles have (i) all dimensions 0.1µm ≤ x ≤ 5mm, or (ii) a length of 0.3µm ≤ x ≤ 15mm and length to diameter ratio of >3.

   b. ‘microbead’ means a microplastic used in a mixture as an abrasive i.e. to exfoliate, polish or clean.

   c. ‘particle’ is a minute piece of matter with defined physical boundaries; a defined physical boundary is an interface. Single molecules are not particles

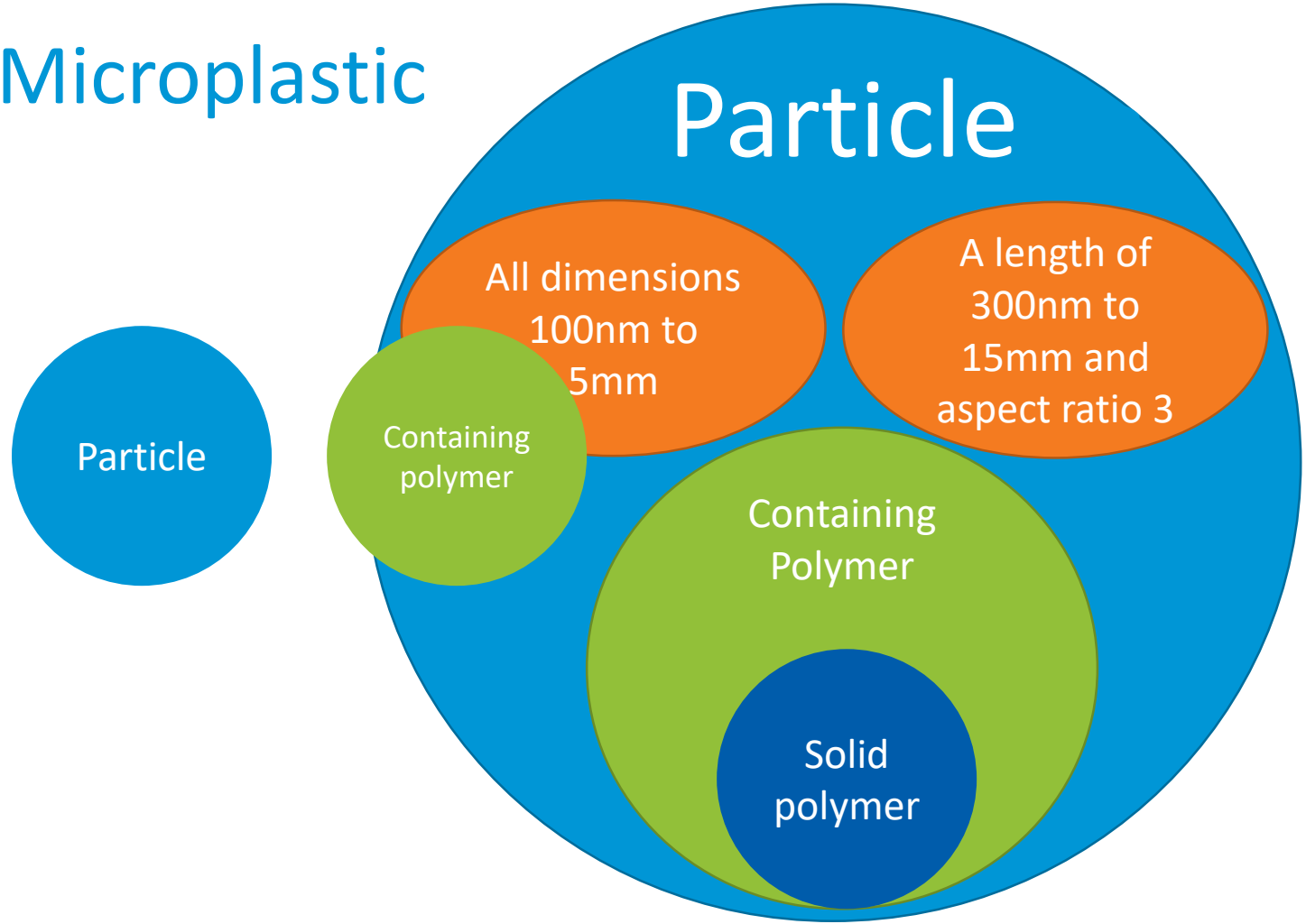
   d. ‘particles containing solid polymer’ means either (i) particles of any composition with a continuous solid polymer surface coating of any thickness or (ii) particles of any composition with a solid polymer content of ≥ 1% w/w.

   e. ‘solid’ means a substance or a mixture which does not meet the definitions of liquid or gas.

   f. ‘gas’ means a substance which (i) at 50 ^{o}C has a vapour pressure greater than 300 kPa (absolute); or (ii) is completely gaseous at 20 ^{o}C at a standard pressure of 101.3 kPa.

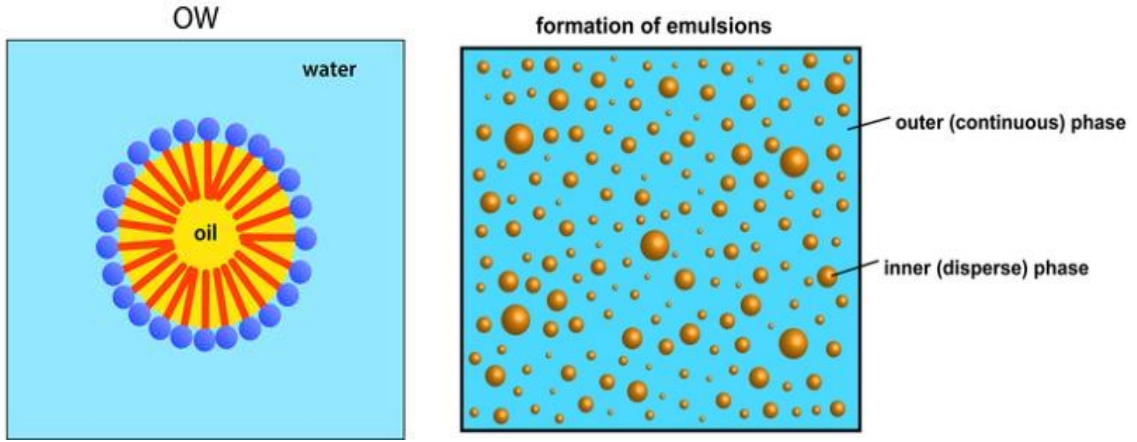
   g. ‘liquid’ means a substance or mixture which (i) at 50 ^{o}C has a vapour pressure of not more than 300 kPa (3 bar); (ii) is not completely gaseous at 20 ^{o}C and at a standard pressure of 101.3 kPa; and (iii) which has a melting point or initial melting point of 20 ^{o}C or less at a standard pressure of 101.3 kPa; or (b) fulfilling the criteria in ASTM D 4359-90; or (c) the fluidity test (penetrometer test) in section 2.3.4 of Annex A of the European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR).

Microplastic



Particle

‘particle’ is a minute piece of matter with defined physical boundaries; a defined physical boundary is an interface. Single molecules are not particles



Particles in complex mixtures

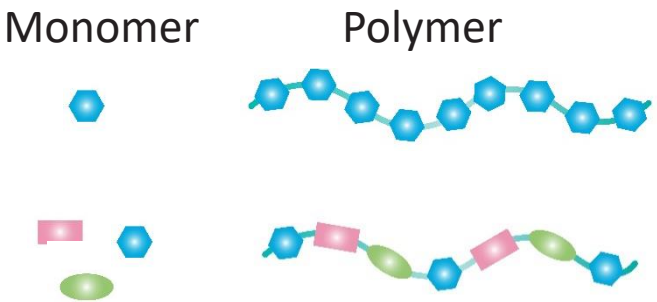
- Micelles fulfil the definition of particles,

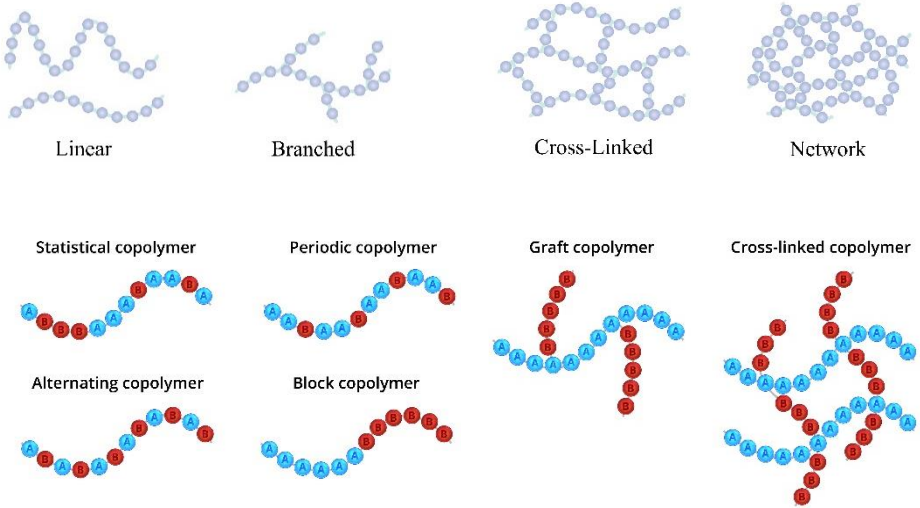
Polymer

‘In accordance with REACH (Article 3(5)), a polymer is defined as a substance meeting the following criteria:

(a) Over 50 percent of the weight for that substance consists of polymer molecules; and,

(b) (b) The amount of polymer molecules presenting the same molecular weight must be less than 50 weight percent of the substance.





Polymer

Polymers according to REACH as a group of substances infinite number of posibilities.

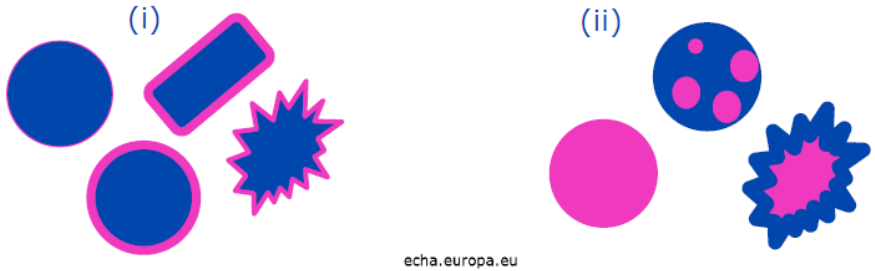
- Wide range of physchem properties and behaviour depending on substance identity, MW, tacticity, crosslink degree
- Not one technique fits all
- In many cases need prior knowledge of identity to detect it

Containing polymer

‘polymer-containing particle’ means either

(i) a particle of any composition with a continuous polymer surface coating of any thickness or

(ii) a particle of any composition with a polymer content of ≥ 1% w/w.



Containing polymer

Particles containing polymer.

- Particles might be present in complex mixtures, need to be isolated
- Need to know presence and concentration of the polymer to avoid extremely extensive analytical requirements
- ≥ 1% w/w requires high sensitivity

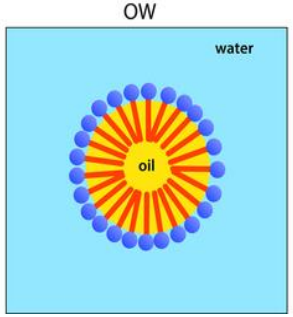
Solid

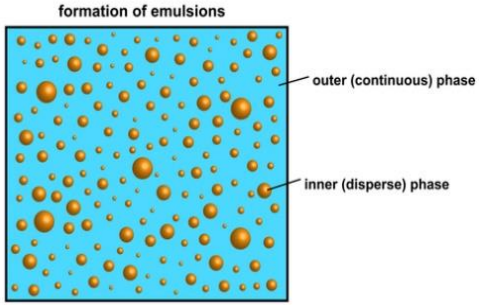
‘solid’ means a substance or a mixture which does not meet the definitions of liquid or gas.

‘gas’ means a substance which (i) at 50 °C has a vapour pressure greater than 300 kPa (absolute); or (ii) is completely gaseous at 20 °C at a standard pressure of 101.3 kPa.

‘liquid’ means a substance or mixture which (i) at 50 °C has a vapour pressure of not more than 300 kPa (3 bar); (ii) is not completely gaseous at 20 °C and at a standard pressure of 101.3 kPa; and (iii) which has a melting point or initial melting point of 20 °C or less at a standard pressure of 101.3 kPa; or (b) fulfilling the criteria in ASTM D 4359-90; or (c) the fluidity test (penetrometer test) in section 2.3.4 of Annex A of the European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR).

Solid

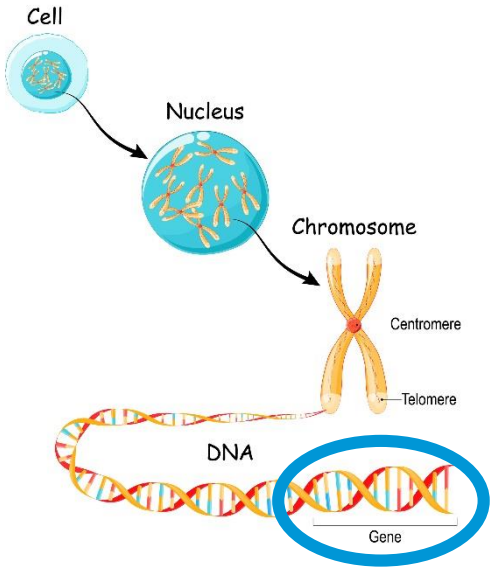




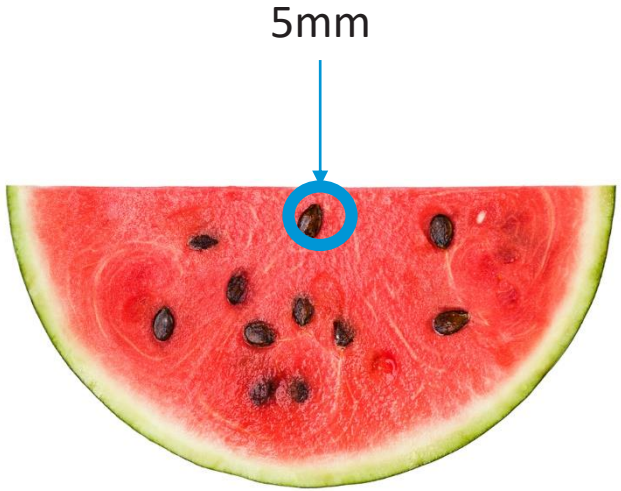
- All polymers have a glass transition temperature (Tg)
- Only semi-crystalline polymers have also melting temperature (Tm)
- Fluidity test on isolated material, but not possible on ‘polymer containing particles’
- Waxes Tg can be very close to 25 ^{o}C

Size

where ≥ 1% w/w of particles have (i) all dimensions 0.1µm ≤ x ≤ 5mm, or (ii) a length of 0.3µm ≤ x ≤ 15mm and length to diameter ratio of >3



100 nm



Size

- Determination of particles in the submicron range is already challenging for isolated particles (JRC report Identification of nanomaterials through measurement)
- In many cases we are dealing with complex mixtures.
- No one technique fits all

250m : 13.000Km

100nm : 5mm

Exemptions

Paragraph 2a and 2b shall not apply to:

2 a. Natural polymers (as defined in REACH Guidance on monomers and polymers) that have not been chemically modified (as defined in REACH Article 3(40)).

b. Polymers that are (bio)degradable, according to the criteria in Appendix X.

c. Polymers with a solubility > 2 g/L, according to the criteria in Appendix Y

Exemptions

Natural: Can we differentiate between natural and synthetic in all cases?

Biodegradable: Even if polymer content in a particle is detected, the polymer can be biodegradable

Soluble: Even if polymer content in a particle is detected, the polymer can be soluble 2g/L

Difficulties to control, specially on imported products and online sales, given the complexity of the material.

Practical case study

- Two unknown but market relevant formulations, FA and FB
- Scoping study to identify appropriate analytical methods
- Focus on identification microplastic in the sense of definition, not quantification

METHODS USED

- Preparative centrifugation with up to 40000 rpm
- Fraunhofer diffraction sizer
- Dynamic light scattering sizer
- Combined dynamic + static light scattering (ALV or Brookhaven like), potentially gel permeation chromatography or field flow fractionation equipped with multi angle scattering detector
- Thermogravimetry
- IR spectroscopy, potentially IR/Raman microscopy or IR-Atomic force microscopy
- Scanning electron microscopy
- Confocal laser scanning microscopy, potentially high resolution optical microscopy
- Potentially pyrolysis-gas chromatography-mass spectrometry

Practical case study conclusions

- Definition of particle as a solid having boundaries (solid matter physics) is not helpful for the objects in sub-micrometer range.
- Concepts from polymer (soft matter) physics might help in differentiation of soluble polymers from particles in the absence of surfactants or microemulsion
- Evaluation of organic matter located on inorganic particles in a liquid phase requires additional guidance and development of new analytical concept
- Identification of polymeric encapsulation was possible, but its quantification and especially chemical description are not straightforward
- Presence of surfactants does not allow any undoubtful conclusion regarding the presence of particles in the size range at least < 50 nm
- Current case study on two formulations took 9 lab-days with involvement of different labs
- Description of traces and especially quantification of potential microplastic will require additional, enormous, effort

Thank you