

EPDLA (European Polymer Dispersion and Latex Association, a Cefic Sector Group) is dedicated to promoting the safe manufacture, transportation, distribution, handling and use of waterborne polymer dispersions, in compliance with regulatory requirements and industry guidelines.

EPDLA members are committed to Responsible Care® principles and have implemented risk management according to the precautionary principles.

Polymer dispersions are used as binders in many waterborne applications, e.g. adhesives, coatings and paints, carpets, non-woven, paper and paperboard coatings, plasters and textile finishing agents.

Polymer dispersions technology has been used safely and successfully for more than 50 years and has contributed to a significant reduction in the release of organic solvents to the environment. The updated BREF STS¹, which will be published soon, will further reduce VOC limits in the next years and by doing so, it will foster the use of waterborne (coating) systems also in the future. Common to all dispersions covered by this paper is a film forming process during application.

Introduction

In the draft restriction proposal on intentionally added Microplastics, the solid state is the first criterion, elaborated in paragraph 2, to decide whether a polymer is in scope (solid) or out of scope (liquid) of the restriction:

Paragraph 2

*a. 'microplastic' means a material consisting of **solid polymer-containing particles**, to which additives or other substances may have been added, and where $\geq 1\%$ w/w of particles have (i) all dimensions $1\text{nm} \leq x \leq 5\text{mm}$, or (ii), for fibres, a length of $3\text{nm} \leq x \leq 15\text{mm}$ 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.

d. '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 $\geq 1\%$ w/w.

¹ The Best Available Technique reference document (BREF) for the surface treatment using organic solvents, STS BREF, is the vehicle through which best available techniques and emerging techniques are determined in a transparent manner, based on sound techno-economic information. The key elements of a BREF are the reference for setting permit conditions to installations covered by the Industrial Emission Directive. The BREFs inform the relevant decision makers about what may be technically and economically available to industry in order to improve their environmental performance and consequently improve the whole environment. (source: <https://www.esig.org/regulatory/stsbref/>)



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 °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.

*g. '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.*

The RAC acknowledged that many polymers do not have a melting point and another criterion is needed to define solid state. Therefore, RAC introduced the penetrometer test and the ASTM D 4359-90 test to determine whether a polymer is liquid. These tests are well known to provide a qualitative measure of the fluidity or softness of a material which is present in bulk form.

The disadvantage of these methods is that they can only be applied to a material present in large quantities. In case of polymer dispersions, the polymer is prepared in an emulsion polymerization in water and evenly dispersed in a nano- to micrometer scale. The strong interaction of formed polymer chains with water and the stabilization of the dispersed polymer with emulsifier lead to a liquid state of the polymer droplet. When water is slowly removed these droplets can flow together and form a coherent film.

By evaporation of the water the polymer droplets move closer together until they touch each other. In case the droplets are liquid, they merge and flow together. This process is a key property of polymer dispersions and known as film formation via coalescence of polymer droplets. (Coalescence is the process where discrete particles lose their identity). Such a film formation is depending on the ability of the droplets to lose shape and flow together and also, amongst others, depending on temperature. Below a certain temperature, the droplets behave rather like solid particle and will not flow together anymore to form a film. This temperature is known as **Minimum Film Formation Temperature (MFFT)**.

MFFT is specific for dispersed polymers and very common to characterize polymers in dispersions.

Therefore, EPDLA would like to suggest MFFT to define whether a dispersed polymer is liquid or solid.

Liquid versus Solid – general reflection

For many non-polymeric substances, the change from solid to liquid state is defined by the melting point. For polymers, only crystalline polymers have melting points. However, many polymers and almost all dispersion polymers are amorphous and thus do not exhibit a melting point.

For these “non-crystalline” (amorphous) polymers the change from solid to liquid is typically characterized by the Glass Transition Temperature (T_g). All polymers have a T_g, which relates to the mobility of polymer chain segments. Amorphous polymers are considered to be liquid above the T_g, with high or low viscosity.



Liquid versus Solid for non-crystalline and dispersion polymers

If the melting point cannot be applied for the solid/liquid differentiation, macroscopic definitions have to be used.

Solid materials have a definitive shape and volume that cannot be altered under standard, conditions (20 °C and 1 atm) and is not a liquid or a gas (GHS, UN definition).

Liquid materials have a defined volume, but no definite shape. Liquids (no matter if molecular or atomic composition) move freely and the smallest amount of force can change its shape through a process called “flowing.” Gravity is also the reason liquids “flow” into whatever shape of the container. There are forms of liquids that flow slowly because of their viscosity. High viscosity liquids such as honey may look almost as if they are solid.

In case of dispersion polymers, the minimum temperature at which a change of shape of the droplets is possible is the Minimum Film Formation Temperature (MFFT). (see DIN ISO 2115)

Why are dispersed polymers different to bulk polymers?

Most polymer dispersions are produced in water phase by polymerization in nano/micro sized micelles through standard radical polymerization processes. Polymers with different chain lengths are created and stabilized in water phase by emulsifiers or colloids in the shape of droplets.

The strong interaction of the polymer chains with water molecules and emulsifier/other adjuvants creates a huge difference to bulk polymers in which such interactions do not exist. This interaction has a large impact on physical properties such as Tg and MFFT - Discrete droplets can't be isolated from such mixtures by simple separation techniques.

With reduced interaction the dispersed polymers would become more and more similar to bulk polymers. Separation of water from the polymer during film formation will change the physical state.

After film formation the dispersion polymer becomes a solid film below Tg. The film remains sticky and is rather a viscous liquid, if the temperature is above Tg.

Minimum Film Formation Temperature (MFFT) as criterion to distinct solid from liquid

The MFFT is the lowest temperature needed to allow polymer droplets to flow together during their separation from water (i.e. the drying process), forming a continuous film. If polymer droplets flow together without external forces, they must be seen as being liquid because they lose their shape (see above).

If the polymer droplets do not flow together at a given temperature, they are most likely solid particles.

The MFFT is an important property of polymer dispersions, which is reported to most products. The method is documented in the easy to apply ISO standard 2115 for determination.



An MFFT above or below room temperature (e.g. 20°C) would be an easy approach to distinct solid and liquid polymers in the dispersed state. Dispersed polymers with MFFT <20°C would be liquids, those with a MFFT above 20°C would be solids.

Summary

Properties of dispersed polymers like fluidity deviate significantly from bulk polymers due to large surface area and the intensive interaction with emulsifying components and water.

The dispersed polymers are hardly accessible to the methods proposed in the draft restriction for intentionally added Microplastics to distinct solid polymers from liquid polymers.

The Minimum Film Formation Temperature would be an easy approach to distinct solid and liquid polymers in the dispersed state.

Disclaimer

- The present position paper has been developed by EPDLA members in good faith, to the best of its knowledge and following the latest scientific evidence.
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About EPDLA

[EPDLA](#) (European Polymer Dispersion and Latex Association), a Cefic Sector Group founded in 1991, is dedicated to promote the safe manufacture, transportation, distribution, handling and use of waterborne polymer dispersions, in compliance with regulatory requirements and industry guidelines. EPDLA members are committed to Responsible Care® principles and have implemented risk management according to the precautionary principles.

