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abstract

Ingredients of cosmetic products end their life to a large extent in wastewater streams or in some cases in surface water. As a result their potential environmental impact and persistency recently raised attention. In particular, the European chemical agency (ECHA) published early 2019 a proposal to restrict the use of intentionally added microplastics in cosmetics and other products. The proposal is still in the consultation phase at the moment this article is written and should enter into force in 2020. Although the restriction only applies to solid particles, the discussions have nowadays extended to all types of synthetic polymers, often wrongly categorized as microplastics or as persistent in the environment. However, liquid film forming polymers do not fulfill the microplastic definition, and some liquid polymers such as polyurethanes can be biodegradable. These examples show the necessity to carefully distinguish between synthetic polymer types while formulating. In this paper an overview of the regulatory and environmental profile of various cosmetic polymers is given, with focus on film forming polymers.

Introduction

Cosmetic products are typically rinsed after use and their ingredients enter the household wastewater stream. In recent years it was demonstrated that solid polymer particles, referred to as microplastics, contribute to plastic marine litter. As a result, several institutions have been evaluating legal means to prevent the use and release of polymer materials showing persistency or damaging environmental effects. A very prominent example is the restriction on intentionally added microplastics from the European Chemical Agency (ECHA), which should result in the interdiction of use of solid persistent polymer particles as of 2020. [1]

Although the ECHA proposal strictly limits its scope to solid polymer particles, many end-consumers quickly came to wrongly assimilate microplastics and synthetic polymers. The lack of data on the biodegradability of synthetic polymers furthermore supported the general assumption that all solid and liquid synthetic polymers are persistent in the environment. The fact is, not all synthetic polymers are microplastics neither are they all persistent. Actually, the ECHA restriction is making an exception for particles made of biodegradable polymers, in line with the REACH regulation and general European policy to promote innovation to more sustainable materials (Fig. 1). [1, 2]

In this context, a proper evaluation of the regulatory status and biodegradability of cosmetic polymers is becoming essential when selecting ingredients for a formulation. In the next paragraphs, some elements allowing a classification of different types of synthetic polymeric ingredients are given, with a focus on film-forming ingredients. Furthermore, the potential of various polymer chemistries for the eco-design of new sustainable and performant polymers is discussed.

The ECHA Definition of Microplastics

The ECHA defines microplastics as polymer-containing solid particles of less than 5 mm in any dimension, wherein the said polymer is synthetic and non-biodegradable. The definition therefore encompasses two conditions, one on the physical form of the object, and one on its chemical nature, that is, a synthetic polymer. As a result, the INCI name, which only gives indication on the polymer composition and not on its physical shape, is insufficient to determine whereas a polymeric ingredient fulfills the microplastics definition. [3] A feeling of mistrust consequently developed within consumers who tend more and more to avoid ingredients of INCI name starting with the prefix "poly".

In fact, only a few polymers used in cosmetics fall in the definition of microplastics, whereas a large variety of synthetic polymers remain out of the scope of the restriction proposal. This is for instance the case of water soluble and liquid film-forming polymers, which do not fulfill the solid state criteria. Film formers such as polyacrylates, polyvinylpyrrolidone or polyurethanes find applications in many cosmetics formulations such as hair care, sun care or makeup products. They

§B.1.2, p24 of Annex of the Annex XV Report

Given that one element of the concern is that „microplastics“ persist in the environment, a derogation for polymers that demonstrate biodegradability [...] appears to be reasonable and would **promote innovation to more sustainable materials in the medium to long-term**, which is one of the objectives of the REACH regulation.

Fig.1 The microplastics restriction proposal is one of the European initiatives to promote innovation towards non persistent ingredients.

§D5, p144 of Annex to the Annex XV - Note on Film forming
 Film forming polymer particles are intended to yield a (non-continuous) polymer film on use, i.e., the particles coalesce and there assumed to be limited release of the free polymer particles to the environment. **Therefore, this use of microplastics is considered to be outside the scope of the proposed restriction.**

Fig. 2 Film forming polymers, independently of their chemistry of biodegradability potential, are outside the scope of the microplastics restriction proposal.

can be available as powder, solution or dispersions. Powders are usually dissolved before use at which stage they lose their particular shape. In dispersions liquid polymers droplets are suspended in water. Dispersion droplets lose their shape either at the formulation or latest at the application stage. Indeed, upon application, the droplets coalesce to form a thin film on the skin or hair surface. [4] The film provides benefits such as mechanical, barrier or sensorial properties. Consequently, film-forming polymers, independently of their chemical nature or ability to biodegrade, have been explicitly reported in the ECHA proposal as not fulfilling the microplastic definition. [1, 2] Their use in cosmetic formulations should therefore not be restricted. (Fig. 2)

End of Life of Microplastics and Liquid Polymers

Most microplastic particles are visible to the naked eye, and their presence in waste and surface water can therefore be easily detected and quantified. One example of microplastics used in cosmetics is microbeads, the particles used in peelings, which are perceivable in the product. For this particular application the negative public opinion motivated the industry to anticipate the legislation. Today already most peelings on the market contain alternative materials. [5] On the other hand, liquid and soluble polymers such as film formers are invisible, and nearly impossible to track. Yet, both microplastics, liquid non-soluble and soluble polymers follow the same disposal path. After being rinsed, they usually enter a waste water treatment plant as part of the influent water.

There, microplastics are to a large extent captured on the solid sludge. Most water-soluble and liquid polymers have a tendency to adsorb at solid interfaces. It is therefore reasonable to assume that a large amount of these polymers are also captured via adsorption on the solid sludge. Efficiency of modern water treatment is high, and only a few percent of the microplastics entering a treatment plant can be detected in the effluents. Nevertheless, the cumulated amounts of microplastics that are globally directly released by waste water treatment facilities are still considerable. [6, 7] In addition, a large proportion of the solid sludge generated globally is still buried or spread in fields. This in particular holds true for sludge of facilities treating domestic waste water, which contains a lot of valuable organic substances that can be recycled and valorized for example as

fertilizer for agriculture. [8] Once part of the soil, the microplastics and liquid polymers contained in the sludge are washed away by rain back to rivers and ocean. In other words, even in areas well equipped with modern water treatment facilities, the release in the environment of microplastics, liquid non-soluble and soluble polymers cannot be completely avoided. Non-biodegradable polymers, solid and liquid, may therefore accumulate in surface water. (Fig. 3)

On the contrary, biodegradable polymers can be degraded by microorganisms, which prevent their accumulation in the environment. Therefore, the ECHA restriction proposal on microplastics further allows the use of solid particles made of biodegradable polymers. The ability of a polymer to biodegrade mainly depends on its chemical nature, and should be tested for each given ingredient. Nonetheless, some categories of polymers are known to be intrinsically more or less able to biodegrade.

Biodegradability of Polymers

By definition, polymers are large molecules composed of several building blocks (monomers) which can be arranged in many different ways. Polymers may be naturally occurring, such as for example cellulose, or be synthesized using monomers based on fossil or on renewable resources. The biodegradability of a polymer is however determined only by its chemical structure, not by its origin. In other words, polymers based on natural resources may not biodegrade, and fully synthetic polymers may be well biodegradable. Unmodified naturally occurring polymers are generally able to biodegrade, which is why particles made out of such materials are also derogated for the ECHA restriction. However, natural polymers are usually chemically modified in order to improve their properties, which tend to decrease their biodegradability. For example, Carboxymethyl Cellulose and Polyquaternium-10, two polymers based on biodegradable cellulose, show poor biodegradability rates. [9, 10]

Interestingly, the ability of a polymer to biodegrade is also independent of its water solubility. For example, polyacrylic acid, a fully water soluble polymer, does not show any level of degradation in waste water nor in soil. [11, 12] Indeed, it has been demonstrated that polymers with carbon-carbon backbones do not biodegrade, because of the lack of functional groups that could be recognized and processed by enzymes. Examples of such polymers include polyacrylic acid as well as

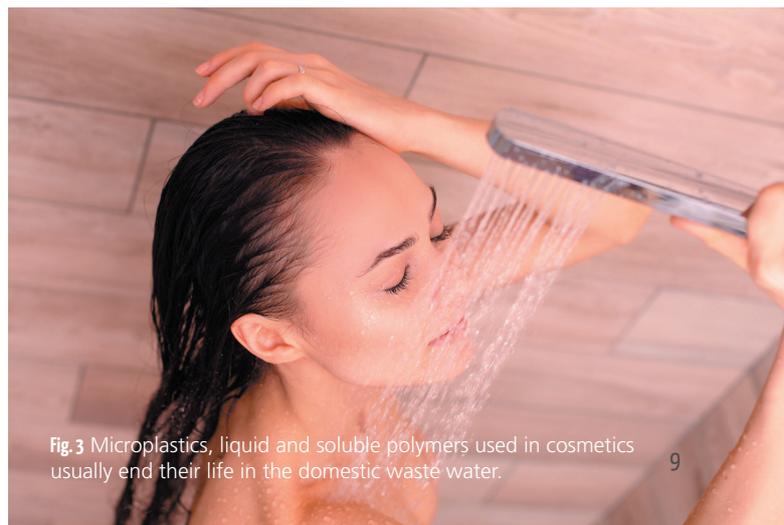


Fig. 3 Microplastics, liquid and soluble polymers used in cosmetics usually end their life in the domestic waste water.

film formers of INCI Polyvinylpyrrolidone, Polyacrylamides, Polyacrylates and their copolymers. On the contrary, the backbones of polyester and polyurethane polymers contain a high density of chemical bonds that can be cleaved by a variety of enzymes and these polymers are usually able to biodegrade both in water and in soil. [13, 14]

There are well established standardized methods to assess biodegradability in the relevant environment. The OECD 301 method for ready biodegradation in water is a reliable method that is often used for cosmetic ingredients. In order to meet the criteria for ready biodegradability, a polymer must reach 60% biodegradation in 28 days. [15] The very stringent interpretation ensures that a fast biodegradation of the substance will actually occur in surface water. After enzymes have cleaved the polymer in segments small enough to penetrate the cell membrane, microorganisms further metabolize the product into CO₂, water and salts.

While the inherent potential of a given polymer to biodegrade is determined by its chemical nature, the rate at which it degrades however depends on its molecular weight. For a given polymer, the higher the molecular weight, the longer it takes until full degradation. Film formation requires polymers of high molecular weight. Consequently, very few film formers meet the ready biodegradability criteria, and are ensured to stay out of the ECHA restriction scope and free of any labelling or reporting obligations. This is for example the case of Polyurethane-34 (Baycusan® C 1001 from Covestro).

In case of solid polymer materials, the biodegradation rate is furthermore limited by the sample surface area: the thicker the sample, the slower it biodegrades. The 28 days threshold of the OECD 301 test, which was developed for small molecules, is therefore too short for polymers, and is likely to be extended for the purpose of the microplastics biodegradability assessment. If so, more biodegradable polymers may fulfill the new criteria.

Innovation Perspectives

Synthetic film-forming polymers bring performance to cosmetic products and are not easy to replace. The choice of film formers combining efficacy and biodegradability is particularly limited. Nonetheless, formulators have no choice but to anticipate regulatory threats and an increasing market pressure to transition towards better biodegradable and more bio-based products. Formulating with only naturally occurring polymers is possible, but requires the development of new formulation concepts. Furthermore, the resulting properties are often not on the level required by end-users. [16] In this context, the demand towards new innovative ingredients is high.

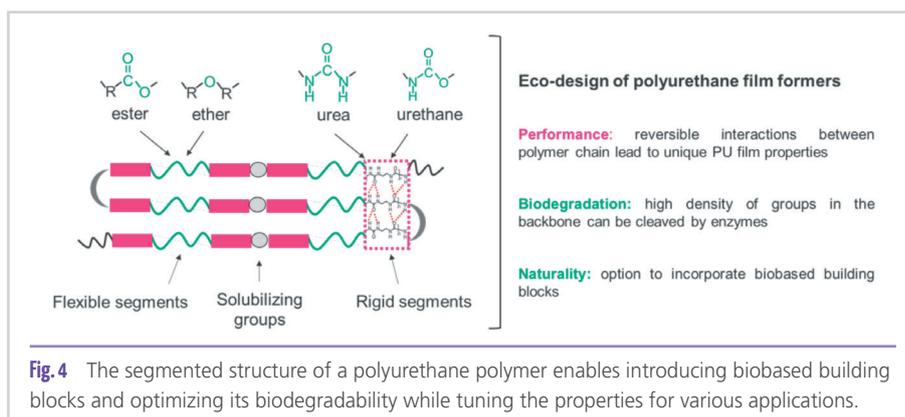
Strategies to create film-forming polymers combining performance, biodegradability and possibly naturality

vary depending on the type of chemistry used. Whatever the chosen strategy, the key structural features enabling the film formation must be maintained in order to achieve the desired properties. Polymer film formation occurs via entanglement of polymer chains and therefore requires polymers of very high molecular weight. [17] The radical polymerization technique enables fast and controlled reaction during which monomers are linked by a carbon-carbon bond into polymers of the required molecular weight range. Polymers obtained by this process include for instance polyacrylates, polyvinylpyrrolidone and their copolymers. Such polymers provide a high level of performances but lack chemical linkages that could enable their biodegradability.

In order to trigger their biodegradability, cleavable linkages can be introduced into the polymer backbone. Alternatively, radical polymerization can be used to grow polyacrylate or PVP segments onto a biodegradable polymer such as cellulose. This process results in a copolymer composed of synthetic and natural polymer segments. Both these synthetic routes are technically feasible. However, the resulting products do usually not reach the performance level of the benchmark polymers. Most importantly, the benefit of these hybrid ingredients in terms of biodegradability is questionable. Indeed, it has been demonstrated that radical polymer segments as short as two to five monomer units already lose ability to biodegrade. [11] Consequently, even if some biobased segments of a biosynthetic hybrid copolymer may biodegrade, short synthetic segments that are persistent will remain.

Polyesters and polyurethanes are synthesized via polycondensation or polyaddition. These polymerization mechanisms typically result in shorter polymer chains in which the monomers are linked to another via cleavable bonds, such as ester, urea or urethane bonds. Because of their low molecular weight polyesters usually lack the mechanical properties to perform well as film forming agents. Although their chain length lies in the same range, polyurethanes in contrast form films of outstanding elasticity. This is due to the unique polyurethane structure, which is schematically depicted in Fig. 4.

Polyurethanes have a segmented morphology alternating soft and rigid segments. The soft segments are usually based on polyester blocks that are well biodegradable. The rigid segments contain urea and urethane linkages that form reversible crosslinks via



hydrogen bonding. These interactions generate a supplementary level of cohesion in between the polymer chains and results in the formation of highly flexible and elastic films. [18] These combined feature results in polymers that can be both biodegradable and deliver properties on the level of benchmark polymers obtained by radical polymerization. **Fig. 5** shows for example the compared performance of typical hair styling film former in a high humidity curl retention test (HHCR). The hair strands were treated with a 2 %-wt solution of polymer, curled around the curler and dried overnight under controlled conditions (23°C and 55% relative humidity). Finally the curls were placed in a high humidity chamber at 30°C and 90% relative humidity. The curl retention, expressed as a percentage of the original curl length, is plotted over time. Under these very harsh conditions, the polyurethanes and the acrylate copolymer provide a significantly better performance than the PVP and VPVA polymers. However, only the Polyurethane-34 and Polyurethane-48 (Baycusan® C 1001 and Baycusan® C 1008 respectively) enable combining these best in class results with high biodegradation rates. Interestingly, building blocks based on renewable resources can also be used to increase the naturality of polyurethanes. For example, the Polyurethane-93 (Baycusan® eco E 1000), based on over 50 % renewable resources, was recently launched for hair care applications. [19]

Conclusion

Besides pressure from consumers who wish for ever more sustainability, public opinion is pushing to reduce or eliminate ingredients of concern from cosmetic products. In particular, non-biodegradable synthetic polymers are facing possible restrictions because of their potential persistence in the environment. Indeed, persistent cosmetic polymers accumulate in water similarly to microplastic wastes. The elements these polymers are made of cannot be recovered or valorized for any other purposes. On the contrary, biodegradable polymers are transformed into CO₂, water and salts by microorganisms. Their carbon and other elements can therefore reenter the biological life cycle, which is in line with the European policy aiming at reducing waste and promoting circular economy. [20]

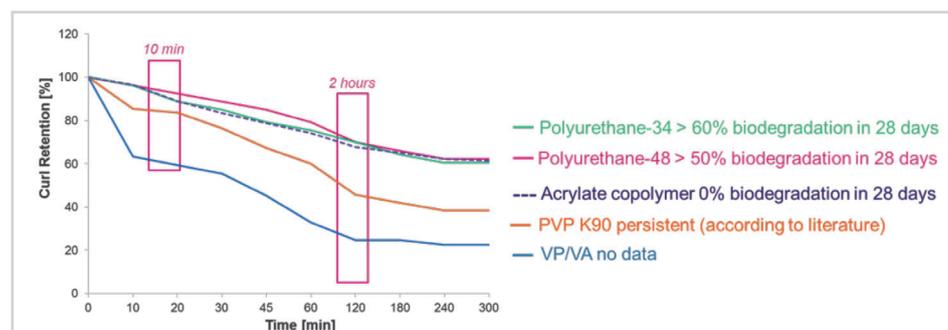


Fig. 5 High humidity Curl Retention (HHCR) curves of representative film formers typically used in hair styling products. Biodegradation values were determined using the OECD 301 standard.

Raw material suppliers are therefore expected to innovate towards a new generation of sustainable polymers. However, combining performance, biodegradability and naturality is far from trivial, especially in case of film forming polymers. Indeed, in most cases the modification of the polymer chemistry required to improve biodegradability or naturality unfortunately goes along with a loss in properties. In this context, polyurethane chemistry offers a unique platform to design new polymers combining biodegradability, naturality and performance. Therefore Covestro, inventor and world leading supplier of polyurethanes, is actively working on the development of new sustainable polyurethanes for the cosmetic industry. Such biobased and biodegradable film formers enable formulators to offer customers eco-conscious and performant products.

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