

The European voice of the adhesive and sealant industry

Brussels, 15 March 2022

Registration of Polymers – the exemption of polyesters

FEICA, the Association of the European Adhesive & Sealant Industry, is a multinational association representing the European adhesive and sealant industry. Today's membership stands at 16 National Association Members, 24 Direct Company Members and 19 Affiliate Company Members. The European market for adhesives and sealants is currently worth more than 17 billion euros. With the support of its national associations and several direct and affiliated members, FEICA coordinates, represents and advocates the common interests of our industry throughout Europe. In this regard, FEICA works with all relevant stakeholders to create a mutually beneficial economic and legislative environment.

Introduction

Polymers are currently exempted from registration under Regulation (EC) No. 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). However, Article 138(2) of REACH foresees a possible further review of REACH to extend the registration requirements to polymers. If the risk posed by certain polymers can be proved, and practical and cost-efficient ways of selecting polymers requiring registration (PRR) can be established, registration requirements under REACH will be extended to polymers.

In principle, polymers without relevant toxicological or ecotoxicological properties will be considered as polymers of low concern (PLC) and exempt from registration obligations. Among others, the PLC concept would in principle also apply to polyester polymers manufactured from predefined monomers under the so-called 'Polyester Exemption'. The polyesters exemption already exists in other jurisdictions such as the United States, Canada and Australia.

In this paper, FEICA would like to:

- support the polyester exemption with scientific data
- suggest updating the list of monomers
- provide some examples of how polyesters are used in adhesives and sealants
- inform about the impact subjecting all polyesters to registration requirements would have on the adhesives and sealants industry

Polyester exemptions in other legislations

The polymer exemption rule was originally promulgated on 21 November 1984 in the United States.¹ Under this exemption, specific polyesters were exempted if derived from reactants included on a list of acceptable polyester reactants ('polyester exemption'). The polyester exemption was upheld under the 1995 Revisions of Exemptions for Polymers while several additional substances were added

¹ <u>TSCA section 5(h)(4) rule granting an exemption for persons who manufacture or import certain polymers, set</u> forth at 40 CFR 723.250.

to the list of acceptable polyester reactants.² Similar exemptions for polyesters have been included in the chemical legislations in Canada, Australia, China and Taiwan.

Justification of the Polyester Exemption

The polyester exemption is, in our understanding, based on the following scientific arguments:

- Polyesters hydrolyse in natural environments over time by reaction with water or in the presence of enzymes, a feature that sets polyesters apart from other polymer classes.³ Hydrolysis of polyesters will ultimately give back their building blocks.⁴ Polyesters manufactured from monomers of negligible hazard will therefore result in non-toxic degradation products. Because of the potential for biodegradation⁵ of the polyesters, certain polyester polymers have been proposed as an alternative to other commonly used persistent polymers in terms of sustainability.⁶
- The United States Environmental Protection Agency (EPA) collected sufficient empirical evidence on polymers to support the polyesters exemption.⁷ For the 1995 TSCA revision, the EPA reviewed over 2,000 polymers submitted as polymer exemption notices in addition to over 10,000 polymers submitted as regular notifications (PMNs). After performing hazard and risk assessments for these polymers, including a review of the available literature and information provided, the EPA has identified polymeric substances that do not pose an unreasonable risk of injury to human health or the environment. Among these polymeric substances, the EPA includes polyesters manufactured from a defined list of monomers. This is the reason why the polyester exemption was also included in 1995 by the EPA in the revised rules of the Exemptions for Polymers.

List of monomers

While FEICA considers the polyester exemption to be scientifically supported, we acknowledge that the list of starting monomers should be updated to eliminate hazardous monomers.

Polyesters eligible for the polyester exemption should be manufactured from a defined list of registered monomers posing no concern to human health or to the environment – in order to safeguard that the eventual hydrolysis products of eligible polyesters will be non-hazardous. To arrive at such a list, existing monomer lists from other jurisdictions can be used as a starting point; however, monomers that have been classified as hazardous as per ulterior data should be removed from the list. Moreover, non-hazardous monomers that are of commercial importance today but were not included in the list at the time should be added to the list.

² Premanufacture Notification Exemptions; Revisions of Exemptions for Polymers; Final Rule. Federal Register / Vol. 60, No. 60 / Wednesday, March 29, 1995 / Rules and Regulations 16316

³ See Annex 1. Hans R. Kricheldorf, Comments on the Hydrolytic Degradation of Polyesters, Statement dated 27 February 2022

⁴ Non-toxic building blocks if the starting materials of the polyester are chosen from a list of non-hazardous monomers and reactants, as intended under the polyester exemption.

⁵ See Annex 2. FEICA paper 'Polyester degrading enzymes in the environment'

⁶ S. M. Satti and A. A. Shah, Polyester-based biodegradable plastics: an approach towards sustainable development, Letters in Applied Microbiology, 2020, 70, 413--430

⁷ Premanufacture Notification Exemptions; Revisions of Exemptions for Polymers; Final Rule. Federal Register / Vol. 60, No. 60 / Wednesday, March 29, 1995 / Rules and Regulations 16316

Examples of polyesters used in adhesives

Polyester-based adhesives are widely used in the adhesives and sealants industry. They display good adhesion to various substrates like ceramics, metals and glass laminates. Polyesters are also produced and used by many small and medium-sized enterprises (SMEs) that sell them to other SMEs to formulate adhesives or use them in-house in the manufacturing of polyester adhesives. Neat polyester polymers are often used as polymeric precursors, a concept that has been brought up as part of the PRR criteria in the ongoing CARACAL polymer subgroup discussions.

Examples of polyester polymers used in adhesives or sealants include adhesives for packaging and food packaging, glass fibre laminates, optical products, furniture, concrete flooring and automobile body repair.

Impact on the adhesives and sealants industry

In a FEICA survey about the number of polymers used by member companies that would fall under the polyester exemption, it was found that the use of polyesters covers a broad range. Some members do not produce or customise polyesters; therefore, the percentage for them would be very low. For other members the percentage of polymers covered by the polyester exemption could reach up to 60%.

Conclusion

FEICA proposes to keep the Polyester Exemption as an EU PLC criterion, considering that polyesters hydrolyse, as discussed above, back to the initial building blocks from an approved list of monomers. FEICA agrees concerning the need to update the list of approved monomers to ensure that no hazardous monomers are included on the list.

Contact

FEICA Regulatory Affairs:

Paula Diaz (p.diaz@feica.eu)

FEICA is registered in the EU Transparency Register with ID no. 51642763262-89

FEICA - Association of the European Adhesive & Sealant Industry Rue Belliard 40 box 10, 1040 Brussels, Belgium Tel: +32 (0)2 896 96 00 info@feica.eu | www.feica.eu

Publication ref.: POP-EX-L03-017

This document has been designed using the best knowledge currently available, and is to be relied upon at the user's own risk. The information is provided in good faith and no representations or warranties are made with regards to the accuracy or completeness, and no liability will be accepted for damages of any nature whatsoever resulting from the use or reliance on this paper. This document does not necessarily represent the views of all member companies of FEICA.

Copyright © FEICA, 2022

Annex 1: Comments on the Hydrolytic Degradation of Polyesters

Prof. Dr. Hans R. Kricheldorf Institut für technische und Makromolekulare Chemie Bundesstr. 45 20146 Hamburg

Comments on the Hydrolytic Degradation of Polyesters

(Hamburg, 27 February 2022)

1. Fundamental properties of polyesters

Polyesters, including polycarbonates, differ from other polymers classes in that they are sensitive to hydrolytic degradation typical for the human environment, meaning oceans, lakes, rivers and any kind of private or technical composting. Polyamides and polyurethanes may be hydrolysed upon heating with strong acids or strong bases, but such conditions do not exist on 99.9% of the surface of the Earth. The most widely used polymers, such as poly(olefins) and vinyl polymers (including polystyrene), but also polyethers, are totally insensitive to hydrolytic degradation. The hydrolytic degradation of polyesters will typically go down to the level of monomers (their building blocks), provided that enough time is available. The rate of hydrolytic degradation of polyesters may vary by a factor of 1 000 or more depending on the chemical and physical parameters discussed below in more detail.

2. Reaction mechanisms of hydrolysis

For the hydrolytic cleavage of ester groups, the following four reaction mechanisms were identified in the first half of the last century:

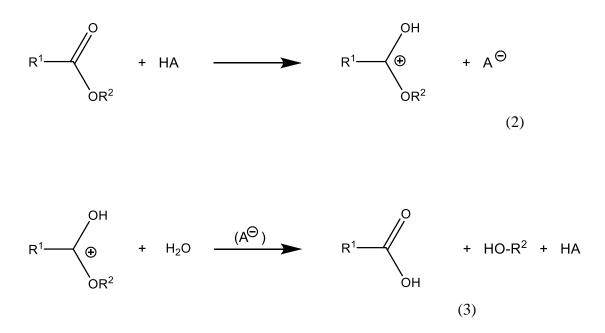
- I. Hydrolysis by neutral water
- II. Hydrolysis catalysed by acids (HA)

- III. Hydrolysis catalysed by bases
- IV. Hydrolysis catalysed by enzymes
- (I) <u>Hydrolysis by neutral water</u>

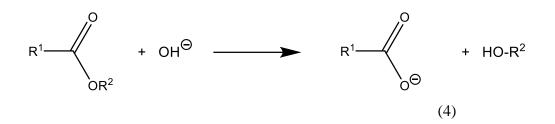
```
R^{1}-CO-O-R^{2} + OH_{2} \rightarrow R^{1}-CO-OH + HO-R^{2} (1)
```

Water reacts as a nucleophile (reagent having a free pair of electrons) with the carbonyl group of the ester (the electrophile), whereupon a carboxylic acid and an alcohol are liberated. Equation (1) is a simplification of the reality. According to Pickett and Coyle (2013), two water molecules cooperate in the hydrolysis of polyesters. The liberated carboxylic acid catalyses the further hydrolysis according to mechanism (II), so that this kind of hydrolytic degradation is autocatalytic. Hydrolysis by neutral water is the slowest of all degradation mechanisms.

(II) <u>Hydrolysis catalysed by acids (HA)</u>



An acidic proton can protonate the carbonyl group of the ester and thus activate the electrophilicity of the ester group, so that it is more sensitive to the attack of water, with the consequence of faster hydrolysis. The rate of hydrolysis increases with acidity and concentration of the acid present in the reaction mixture. The autocatalytic effect, therefore, increases with the progress of the hydrolysis when started with neutral water. The autocatalytic effect is particularly strong for polylactide (Tsuji et al. 2002, Gorassi et al. 2017), but it is also documented for other polyesters (Xi-Lan et al. 2020).



Under alkaline conditions (pH > 7.0, typically > 8.0) the ester group is mainly attacked by the OH anion, which is roughly estimated 10 000 times more nucleophilic than H_20 , so that the rate of hydrolysis is significantly accelerated even when the concentration of the OH anions is low. Furthermore, the alkaline hydrolysis is irreversible in contrast to all other mechanisms because the resulting carboxylate anion cannot take part in the reverse reaction (i.e. esterification). When equal deviations from pH 7 are compared, i.e. pH 5 and pH 9, the alkaline hydrolysis is faster than the acid catalysed hydrolysis.

(IV) <u>Hydrolysis catalysed by enzymes</u>

Almost all living organisms contain esters in the form of lipids. Hence, all organisms contain enzymes (biocatalysts) that are capable of synthesising esters. These enzymes are called lipases, and typically a living organism contains several different lipases with different specificities. Lipases can hydrolyse esters when an excess of water is present. Over the past 50 years numerous individual 'lipases' have been identified and isolated, and part of them are commercial and produced in larger quantities. Greimel et al. (2013) have demonstrated that two commercial lipases are non-specific with regard to the polyester structure and also highly reactive. They enable hydrolytic degradation of various kinds of polyesters down to the level of monomers.

In addition to 'lipases', another group of enzymes has been found capable of hydrolysing polyesters, namely 'hydrolases'. At the current state of research, hydrolases seem to be less efficient than lipases, but further research may change this picture. 'Hydrolases' can even hydrolyse aromatic polyesters, and a total degradation of poly(ethylene terephthalate (PET) by hydrolyses has been demonstrated. Further groups of enzymes that may hydrolyse polyesters are 'esterases' and 'cutinases'. This means that in nature (e.g. in lakes) microorganisms can contribute to the total hydrolysis of polyesters, and microorganisms or isolated enzymes can be used for waste water treatment or for technical composting of polyesters. Recent reviews of enzymes degrading various classes of hydrolytically degradable

polymers in particular polyesters were published by Danso et al. in 2019 and by Satti and Shah in 2020. On the average the mechanisms of hydrolysis obey the following order of increasing efficiency:

neutral $H_2O < acidic H_2O \sim enzymes < alkaline H_2O$.

3. Factors influencing the rate of hydrolysis

The chemical and physical factors that have an influence on the rate of hydrolytic degradation will here be discussed in the following order:

- (A) Chemical structure
- (B) Reaction conditions
- (C) Physical properties of the polyesters
- (D) Bioavailability

Ad (A) The reactivity (electrophilicity) of ester groups towards hydrolysis depends on electronic and steric factors. Electronic means that electronegative substituents in α - or β -position to the ester group enhances the electrophilicity of the CO group. For example, the O-atom in α -position typical for glycolic or lactic acid has the consequence that polyglycolide and polylactide are extraordinarily sensitive to hydrolysis relative to aliphatic polyesters based on adipic or sebacic acid. On the other hand, the π -electrons of aromatic carboxylic acids are delocalised to the CO group and reduce the electrophilicity of aromatic esters significantly. Therefore, textile fibers based on poly(ethylene terephthalate) may be washed at moderate temperatures without being hydrolysed within a few weeks.

Steric factors mean that any kind of alkyl or aryl substituent near the ester group hinders the access of water (or OH anions), and thus, reduces the rate of hydrolytic degradation. This stabilizing effect of branching is valid for branching of diols and also for that of dicarboxylic acids. Hence polyesters of cyclohexane-1,4-dicarboxylic acid are less sensitive to hydrolysis than polyesters of adipic or sebacic acid. Manufacturers which are interested in hydrolytically stable coatings or sealants produce their polyesters from aromatic dicarboxylic acid or cyclohexane dicarboxylic acid in combination with branched diols. In summary, the rate of hydrolysis decreases in the following order:

polylactide > poly(hexamethylene adipate) > poly(ethylene terephthalate) > poly(neopentanediol isophthalate).

The study of Jones and McCarthy (1995) confirms this trend for polyesters. The use of branched diols for stabilisation of poly(ester-urethane)s has also recently been reviewed (Gantrade 2020).

Ad (B) There are mainly three experimental parameters that influence the rate of hydrolytic degradation: temperature, pH and the presence/absence of catalysts. Increasing temperature accelerates almost all chemical reactions including hydrolysis, so that this parameter does not need further discussion. The influence of the pH is evident from the reaction mechanisms (II) and (III) discussed above. The rate of hydrolysis increases dramatically either when the pH decreases from 7 to 1 or when it increases from 7 to 14. Interestingly, oceans contain slightly alkaline water (pH ~7.9-8.2) and thus favor hydrolytic degradation of polyesters more than lakes or rivers containing neutral or slightly acidic water.

Ad (C) A characteristic property of several polyesters such as poly(L-lactide), poly(alkylene adipate)s, or poly(ethylene-terephthalate) and poly(butylene terephthalate) is their semi-crystalline morphology. A general trend for all semi-crystalline polyesters is that the amorphous phase is considerably more sensitive to hydrolysis than the crystalline phase. This difference my amount to a factor of 10. Detailed studies of this aspect were published for polylactides (Gorassi et al. 2017), but the trends found for poly(L-lactide) are also valid for other semi-crystalline polyesters. The polyester chains in the amorphous phase are more mobile than those in the crystalline state, and the amorphous phase contains more free volume, and both parameters favor access and reaction of water.

Hydrolysis is, of course, also favored by pores and flaws in a polyester material. Another important parameter is the surface of a work part (component). It is a general rule across all polyesters that a higher surface area/volume ratio favors hydrolysis. Either the water attacks ester bonds directly on the surface or it penetrates the surface and continues hydrolysis inside the work part. At any rate, a larger surface area eases the hydrolytic degradation. Hence, microparticles of polyester will have a rather short lifetime. The surface of larger work parts or components may be coated by a hydrophobic layer or film, such as silicon oils or hydrolytically stable polymers. Such a surface is, of course, a serious hinderance for rapid hydrolysis until the protecting layer is damaged, e.g. by milling or any other kind of mechanical stress which damages the protecting layer. The influence of various hydrophobic additives on the hydrolytic stability of poly(ester-urethane)s has been reviewed by L. Xi-Lan et al. (2020).

Ad (D) According to the ECETOC, the 'bioavailability' of polymers needs to be distinguished as regards physical availability (as an indicator of exposure potential) and external and internal

bioavailability (ECETOC, 2020). For example, poorly soluble and particulate polymers exhibit reduced physical bioavailability and may result in limited mass transfer in terms of exposure to microorganisms. External bioavailability may be the result of the size of certain polymer molecules that are too large to cross biological barriers such as membranes. The internal bioavailability is a prerequisite for a polymer of a -degradation product to become systemically available and potentially be further degraded (systemic bioavailability).

Polymers that remain bioavailable only externally may physically accumulate and, e.g., cause obtrusion of the gills of fish. In the case of hydrolytically susceptible polyester polymers, biological degradation takes place generally in two stages once physical availability is given. Larger polyester chains destruct into smaller fragments (primary degradation), which are often water soluble and taken up by cells. The polymer shifts from external to internal bioavailable molecules. Enzymes are involved in the hydrolysis, and in the case of some polyesters, chemical and physical processes (e.g. temperature, UV radiation, pH, etc.) also play a role. Variability of physical/chemical environments may explain the differences of degradation kinetics of polyesters in different environmental compartments. It is also known that specificity of enzymes results in differences of hydrolytic efficiencies; hence, competent microorganisms may accelerate primary and ultimate degradation by promoting bioavailability of assessable molecules. In addition to size, the systemic bioavailability of a polymer product is dependent upon further physico-chemical properties, including charge, solubility and partitioning in water and/or biological media, and physical state. Because the degradation of polyester by hydrolysis results in the formation of the monomer or oligomers, the ecotoxic effects of the monomer/oligomer become an important factor for the evaluation of the hazard and risk potential of polyester. Due to their ester bonds, systemic bioavailable oligomeric fragments are broken down further into their monomers until they are mineralised or converted into new biomass (ultimate biodegradation).

Biodegradable polyesters

Over the past 30 years academic research and technical production of biodegradable polyesters have gathered speed stimulated by increasing environmental pollution with 'immortal' plastic.

Biodegradable polyesters are characterized by:

1) Hydrolytic degradation occurs in the natural environment (including the human body) within a few months (when amorphous) or within a few years (when crystalline).

- 2) The hydrolytic degradation is caused by water, and catalysts such as enzymes are not needed.
- The degradation products are non-toxic and can be metabolised by most micro- or macroorganisms.

Excluding the kinetic data, the rules and trends found in those studies are also valid for other polyesters. The review article of Gorarasi et al. (2017) provides all details of interest.

The rates of hydrolysis of the most common biodegradable polyesters decrease in the following order:

Polyglycolide > polylactide > poly(butylene succinate) > poly(butylene adipate) > polycaprolactone.

Oligoesters

All polyesters prepared by polycondensation (i.e. all technically produced polyesters) contain oligomers which may have a linear or cyclic architecture. Linear oligomers are formed in the first stage of a polycondensation, but the fraction of cycles increases with the conversion at the expense of the linear oligomers and polymers. The cyclic oligomers contain more energetically unfavorable conformations than linear chains, which are more reactive, and thus are slightly more sensitive to hydrolysis than linear chains. Furthermore, the hydrolysis of one single ester bond suffices to transform a cyclic into a linear oligomer. The carboxylic groups liberated upon hydrolysis of the cyclics catalyse, in turn, hydrolysis of ester groups via the cationic mechanism (II). Moreover, low oligomers are easily washed out of the polymer and leave free volume that eases migration of water into the polyester. In summary, oligomers favor hydrolytic degradation of polyesters regardless of whether their topology is cyclic or linear.

List of low toxic monomers

In several countries, such as the USA, Canada and Australia, lists of monomers have been compiled that allow for reduced registration requirements for polyesters made only of monomers from this list. These lists were established before the year 2 000 and need to be updated. For example, terephthalic acid is missing as are the monomers liberated from hydrolysis of biodegradable polyesters, such as polylactide, polyglycolide, poly(ε -caprolactone) and poly(butylene succinate). Since lactic acid and succinic acid belong to the metabolism of most living organisms, it is *a priori* clear that dilute solutions of these monomers are not toxic.

Conclusion

Polyesters are a group of polymers which differs from all other groups of polymers in that they can be hydrolysed in any natural environment providing sufficient water. Hydrolysis may proceed just by reaction with water (more rapidly when the pH deviates from 7.0) or in the presence of enzymes (neat or via microorganisms). The rates of hydrolytic degradation may vary by a factor of 1 000 depending on structure and reaction conditions, but finally all polyesters will be hydrolysed down to their (nontoxic) building blocks. Polyesters will, due to their degradation, certainly not contribute to environmental pollution with microplastic particles surviving for hundreds of years. In this connection a recent review of Shen et al. (2020) entitled 'Hydrolysis and Solvolysis as Benign Routes for the End-of- Life Management of Thermoset Polymer Waste' should be mentioned.

References

D. Danso, J. Chow, W. S. Streit, Appl. Environmental Microbiology, 2019, 85 (19), 1-14

ECETOC 2020. Applicability of Analytical Tools, Test Methods and Models for Polymer Risk Assessment. Technical Report No. 133-2 ISSN-2079-1526-133-2 (https://www.ecetoc.org/publications/technical-reports/)

Gantrade : https://www.gantrade.com/blog/hydrolysis-resistant-polyester-polyurethanes

G. Gorassi, R. Pantani, Hydrolysis and biodegradation of Poly(lactic acid) in Synthesis , Structure and properties of Poly(lactic acid), M. L. DiLorenzo and R. Androsch eds., Adv. Polym. Sci. 2017, 279, 119-152

K. Greimel, A. Marold, C. Soahan, R. Feola, A. Temel, T. Schoenbacher, E. Herrero Acero, G. M. Guebitz, Reactive & Functional Polymers, 201373, 1335-1339

T. E. Jones, J. M. McCarthy, J. Coating technol. 1995, 67, 57-65

A. N. Johnson, D. E. Barlow, A. L. Kelly, V. A. Varaljay, W. J. Crooks-Goodson, J. C. Biffinger, Polym. Int. 2021, 70, 977-985

J. E. Pickett, D. J. Coyle, Polym. Degrad. Stabil., 20213 89, 1311-1320

S. M. Satti, A. A. Shah, Letters in Appl. Microbiology, 2020, 70, 413-430

M. Shen, H. Cao, M. L. Robertson, Ann. Rev. Chem. Biol. Eng. 2020, 11, 6.1-6.19

H. Tsuji et al., Polymer, 2002, 43 (6), 1789-1796

L. Xi-Lan, G. Xiu-Fen, S. Jia-Long, S. Guag-Yan, J. Phys. Conference Series 2020, 1635, doi: 10.1088/1742-6596/1635/012109

Annex 2: Polyester degrading enzymes in the environment

Polyesters were identified as naturally occurring polymeric structures in plants, animals and bacteria as early as in the 19th century. They exhibit general properties similar to those of synthetic polyesters and can have molecular weights from 1,000-2,000 g/mol (Spring, 1945). Prominent examples are cutin and suberin, the main components of plant cuticle, and poly-β-hydroxybutyric acid, that is produced by bacteria as an internal energy storage.

Some synthetic polymers, among them polyesters, are susceptible to hydrolysis by catabolic enzymes released by fungi, bacteria and archaea in the environment, and these polymer classes make up 35% of global polymer production (Johnson et al. 2020). Due to high chain length and insolubility of many polyesters in water, microorganisms cannot assimilate larger plastic polymers into their cytoplasm, which is the main site of biochemical processes. For this purpose, microorganisms secrete extracellular enzymes, which result in the breakdown of complex polymers and produce smaller molecules, such as oligomers. This has been suggested for some synthetic polyesters such as polybutylensuccinat or polybutylene-adipat-terephthalate. Abiotic processes, such as purely chemical hydrolysis, can also be involved. With other polyesters, such as polylactic acid, physical factors, e.g., higher temperatures, also have an impact on hydrolysis. The oligomers and monomers resulting from the hydrolysis can usually also be absorbed and utilised by other microorganisms, so that complex microbial communities can settle in the vicinity of the polymers. Where this process of biological degradation takes place it is regardless of environmental compartments (UBA, 2018). In this regard, the microorganisms capable of enzymatic hydrolysis of the polymers are of great importance in all environmental compartments. Hydrolases can be produced by various microorganisms and polyester-degrading microorganisms (including fungi) that are potentially ubiquitous in all environments (Mergaert et al. 1996, Suyama et al 1998, Kijchavengkul et al. 2010). Esterase activities have been frequently reported to act as bioindicators of the biological degradation potential in the environment, among them polymers, (e.g. Regel et al. 2002, Sandoval and Herrera-López 2018). These activities differ in environmental compartments and are potentially highest in soil with the presence of fungi. In fresh and marine waters polyester degradation is generally lower (UBA 2018, Nakayama et al. 2019). Polyester appears not to be degradable under anaerobic conditions (UBA 2018).

The microbial degradation of polyesters such as polybutylensuccinat, polybutylensuccinat /thermoplastic starch, and polylactic acid is described, e.g., in Shah et al. (2014). The hydrolysis of larger polymers like polyesters is the crucial and rate-limiting step in biodegradation (Emadian et al. 2017; Tokiwa et al. 2009). The group of enzymes involved in hydrolysis of polyesters are hydrolases, that represent a structurally, mechanistically and functionally diverse family of enzymes - e.g., esterases, cutinases, lipases, polyhydroxyalkanoate depolymerases and proteinases (Anthonsen 1995, Wackett and Hershberger 2001). The hydrolases differ in their substrate spectrum. They catalyse the cleavage and formation of ester bonds and are widely distributed in animals, plants and microorganisms (Lockrigde et al. 2018, Satti and Shah, 2020). While many esterases show a wide substrate specificity that allows them to access various carbon sources or to be involved in catabolic pathways, others are quite specific (Kijchavengkul et al. 2010, Lockrigde et al. 2018). Lipases and also cutinases are activated at hydrophobic interfaces such as polyesters. Hence, these hydrolases can also accommodate longer fatty acid chains than can esterases and remain active in non-aqueous solvents. Esterases are typically but not exclusively reactive with short-chain water-soluble polyesters

(Gricajeva *et al.* 2021). A considerable number of esterases (carboxyl- or carbohydrate esterases) have been discovered in microorganisms (Anthonsen *et al.*, 1995, Armendáriz-Ruiz, *et al.* 2018). Polyesterases catalyse the breakdown and modification of natural and synthetic polyesters by releases of acyl, aryl or alkyl groups attached by ester linkage to carbohydrates.

Some polyester polymers have been suggested as a solution to the current plastic waste problem because of the potential of these polymers for biodegradation compared with the potential of polymers based on C-C linkages. Such polyester polymers also lead polymers in general in terms of sustainability (Satti and Shah, 2020). As an example, alternative to polyethylene (PE) mulch films, polyester-based biodegradable plastic mulches have been produced and are intended to be tilled into soil at the end of their use where indigenous microorganisms biodegrade them by activity of hydrolases (Yamamoto-Tamura et al. 2015). It was shown that polymer breakdown takes place over time by a complex synergy of abiotic (water, pH, weathering, UV, etc.) and biotic (microbes, enzymes) factors. The impact of degradation products on soil ecology and ecosystem functions has been discussed critically by, e.g., Witt et al. (2001) and Satti and Shah (2020). For example, there are various studies demonstrating polyester-based mulches to be safe from ecotoxicology from the stand-point indicated by various standardised tests that have been applied (Muroi et al. 2016, Briassoulis and Degli Innocenti 2017, Palsikowski et al. 2018, Meng et al. 2019). Another example that testifies to the ubiquitous presence of polyester degradation is the discovery of bacteria that are able to hydrolyse poly(ethylene terephthalate) (PET) via a novel hydrolase type, the 'PETase' (Yoshida et al 2016, Zadjelovic et al. 2020). Researchers have also identified other hydrolases, like 'PETase', produced by thermophilic organisms. These findings initiated intensive research on the mechanisms and optimisation of enzymatic activities for commercial and sustainability purposes (Johnson et al. 2020, Gricajeva et al. 2021).

Although many polyester polymers may be generally uncritical when reaching the environment (see above), there are also some complementary reports. First, some esterases are typically reactive only with short-chain water-soluble polyesters degradation that may depend on environmental conditions, and 'biodegradable' polymers may not degrade fast in all environmental compartments (UBA 2018, Nakayama et al 2019, Johnson et al 2020). Second, because the rate of polyester degradation decreased with the increase in the chain length of the polymer (Kupczak *et al.* 2021), the formation of microplastics, for example, may influence organisms and properties in the long term. **Therefore, current concerns in our knowledge regarding long-term use of biodegradable plastics can be circumvented only where their degradation products are considered as not harmful to the environment and are degradable themselves.**

References

Anthonsen H.W. 1995. Lipases and esterases: a review of their sequences, structure and evolution. Biotechnol. Annu. Rev. 1, 315-371

Armendáriz-Ruiz M., Rodríguez-González J.A., Camacho-Ruíz R.M. and Mateos-Díaz J.C. 2018. Carbohydrate Esterases: An Overview. In: Sandoval G. (eds) Lipases and Phospholipases. Methods in Molecular Biology, vol 1835. Humana Press, New York, NY. https://doi.org/10.1007/978-1-4939-8672-9_2

Briassoulis D., and Degli Innocenti F. 2017. Standards for soil biodegradable plastics. In Soil Degradable Bioplastics for a Sustainable Modern Agriculture. ed. Malinconico M., Berlin, Heidelberg: Springer, Berlin Heidelberg. pp. 139–168

Emadian S.M.; Onay T.T. and Demirel B. 2017. Biodegradation of bioplastics in natural environ-ments. In: Waste management (New York, N.Y.) 59, S. 526-536. DOI: 10.1016/j.wasman.2016.10.006

Gricajeva A, Naddab A.K and Gudiukaite R. 2021. Insights into polyester plastic biodegradation by carboxyl ester hydrolases. J Chem Technol Biotechnol2022;97: 359–380

Kijchavengkul T.; Auras R.; Rubino M.; Selke S.; Ngouajio M and Fernandez, R.T. 2010. Biodegradation and hydrolysis rate of aliphatic aromatic polyester. In: Polymer Degradation and Stability 95 (12), S. 2641-2647. DOI: 10.1016/j.polymdegradstab.2010.07.018.

Kupczak M., Mielanczyk A. and Neugebauer D. 2021. The Influence of Polymer Composition on the Hydrolytic and Enzymatic Degradation of Polyesters and their Block Copolymers with PDMAEMA. Materials, 14, 3636 (https://www.mdpi.com/1996-1944/14/13/3636)

Johnson A.N., Barlow D.E., Kelly A.L, Varaljay V.A., Crookes-Goodson W.J. and Biffinger J.C. 2020. Current progress towards understanding the biodegradation of synthetic condensation polymers with active hydrolases. Polym Int2021;70: 977–983

Lockridge O., Quinn D. M., Radić Z. 2018. Esterases. In Biotransformation (Vol. 10-15, pp. 277-307). Elsevier Inc.. https://doi.org/10.1016/B978-0-12-801238-3.01970-X

Meng K., Ren W., Teng Y., Wang B., Han Y., Christie P. and Luo Y. 2019. Application of biodegradable seedling trays in paddy fields: impacts on the microbial community. Sci Total Environ. 656, 750–759

Mergaert, J.; Swings, J. Biodiversity of microorganisms that degrade bacterial and synthetic polyesters. 1996. J. Ind. Microbiol. 17, 463-469.

Muroi F., Tachibana Y., Kobayashi Y., Sakurai T. and Kasuya K.-I. 2016. Influences of poly (butylene adipate-co-terephthalate) on soil microbiota and plant growth. Polym Degrad Stabil 129, 338–346

Nakayama A., Yamano N., Kawasaki N. 2019. Biodegradation in seawater of aliphatic polyesters.PolymerDegradationandStabilityVolume166,Pages290-299https://doi.org/10.1016/j.polymdegradstab.2019.06.006

Palsikowski P.A., Roberto M.M., Sommaggio L.R., Souza P.M., Morales A.R. and Marin-Morales M.A. 2018. Ecotoxicity evaluation of the biodegradable polymers PLA, PBAT and its blends using Allium cepa as test organism. J Polym Environ26, 938–945

Regel R.H., Ferris J.M., Ganf G.G., Brookes J.D. 2002. Algal esterase activity as a biomeasure of environmental degradation in a freshwater creek, Aquatic Toxicology, Vol 59, 3–4, 24, 209-223

Sandoval, G; Herrera-López, E. J. 2018. Lipase, Phospholipase, and Esterase Biosensors (Review) Methods Mol Biol, Vol. 1835, pp. 391-425

Satti S.M. and Shah A.A. 2020. Polyester-based biodegradable plastics: an approach towards sustainable development. Letters in Applied Microbiology70, 413--430©2020

SPRING F., 1945. Naturally Occurring Polyesters. Nature 155, 272. <u>https://doi.org/10.1038/155272b0</u>

Shah A.; Kato S.; Shintani N.; Kamini N.R. and Nakajima-Kambe T. 2014: Microbial degradation of aliphatic and aliphatic-aromatic co-polyesters. In: Applied microbiology and biotechnology 98 (8), S. 3437-3447. DOI: 10.1007/s00253-014-5558-1.

Suyama, T.; Tokiwa, Y.; Oichanpagdee, P.; Kanagawa, T.; Kamagata, Y. 1998. Phylogenetic affiliation of soil bacteria that degrade aliphatic polyesters available commercially as biodegradable plastics. Appl. Environ. Microbiol., 64, 5008-5011.

Tokiwa Y.; Calabia Benaventurada P.; Ugwu C.U. and Aiba S. 2009. Biodegradability of plastics. In: International journal of molecular sciences 10 (9), S. 3722-3742. DOI: 10.3390/ijms10093722.

Umweltbundesamt (UBA). 2018. Gutachten zur Behandlung biologisch abbaubarer Kunststoffe

Burgstaller M., Potrykus A., Weißenbacher J, Kabasci S., Merrettig-Bruns U., Sayder B. TEXTE 57/2018 Projektnummer 93711 UBA-FB 002676

Wackett L.P and Hershberger C.D, 2001. Biocatalysis and Biodegradation: Microbial Transformations of Organic Compounds. ASM, Washington, DC

Witt U.; Einig T.; Yamamoto M.; Kleeberg I.; Deckwer W.-D; Müller R.-J. 2001. Biodegradation of aliphatic-aromatic copolyesters. Evaluation of the final biodegradability and ecotoxicological impact of degradation intermediates. In: Chemosphere 44 (2), S. 289-299. DOI: 10.1016/S0045-6535(00)00162-4.

Yamamoto-Tamura K., Hiradate S., Watanabe T., Koitabashi M., Sameshima-Yamashita Y., Yarimizu T. and Kitamoto H. 2015. Contribution of soil esterase to biodegradation of aliphatic polyester agricultural mulch film in cultivated soils. AMB Express 5:10

Yoshida S., Hiraga K., Takehana T., Taniguchi I., Yamaji H., Maeda Y. et al., 2016. Science 351:1196–1199.

Zadjelovic V., Chhun A., Quareshy M., Silvano E., Hernandez-Fernaud J.R., Aguilo-Ferretjans M.M. *et al.*, 2020. Potential of Serratia plymuthica IV-11-34 strain for biodegradation of polylactide and poly(ethylene terephthalate) Environ Microbiol 22:1356–1369