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FEICA comments on the degradation 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 15 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 of relevant toxicological or ecotoxicological properties will be subject to registration as foreseen under an upcoming REACH amendment. Polymers without such hazards will be exempt from registration obligation (Polymers of Low Concern [PLC] concept). One such exemption is the so-called 'Polyester Exemption', under which certain polyesters manufactured from predefined monomers will not require registration. This paper intends to address the Polyester Exemption and to provide some background on the degradation of polyesters.

How do polyesters degrade?

Degradation of polyesters happens through their hydrolysis, that is, cleavage of chemical bonds by the addition of water.[1] This process will give back reactants, either as such or as smaller chains at first that are then successively hydrolysed to the reactants as well. The reason for this is that polyester formation is a reversible chemical reaction; in the presence of water, this reaction can be reversed[2].

This hydrolysis can take place within very different time frames: depending on the polyester type, hydrolysis rates may differ by at least a factor of 100, making some polyesters hydrolyse very slowly

[1] (a) Müller, R.-J., Biological degradation of synthetic polyesters—Enzymes as potential catalysts for polyester recycling, Process Biochemistry 41 (2006) 2124-2128 - https://doi.org/10.1016/j.procbio.2006.05.018; (b) Müller, R.-J., Biodegradation behaviour of polymers in liquid environments, in: Catia Bastioli (ed.) Handbook of Biodegradable Polymers, De Gruyter 2020, 23-43; (c) Herzog, K., Müller, R.-J., Deckwer, W.-D., Mechanism and kinetics of the enzymatic hydrolysis of polyester nanoparticles by lipases, Polymer Degradation and Stability 91 (2006) 2486-2498; (d) Lindsay N. Woodard and Melissa A. Grunlan, Hydrolytic Degradation and Erosion of Polyester Biomaterials, ACS Macro Lett. 7(8) (2018) 976–982, DOI: 10.1021/acsmacrolett.8b00424; (e) Nakajima-Kambe, T., Ichihashi, F., Matsuzoe, R., Kato, S., Shintani, N. Degradation of aliphatic–aromatic copolyesters by bacteria that can degrade aliphatic polyesters, Polymer Degradation and Stability 94 (2009) 1901–1905 (a) Müller, R.-J., Biological degradation of synthetic polyesters—Enzymes as potential catalysts for polyester recycling, Process Biochemistry 41 (2006) 2124-2128 - https://doi.org/10.1016/j.procbio.2006.05.018; (b) Müller, R.-J., Biodegradation behaviour of polymers in liquid environments, in: Catia Bastioli (ed.) Handbook of Biodegradable Polymers, De Gruyter 2020, 23-43; (c) Herzog, K., Müller, R.-J., Deckwer, W.-D., Mechanism and kinetics of the enzymatic hydrolysis of polyester nanoparticles by lipases, Polymer Degradation and Stability 91 (2006) 2486-2498; (d) Lindsay N. Woodard and Melissa A. Grunlan, Hydrolytic Degradation and Erosion of Polyester Biomaterials, ACS Macro Lett. 7(8) (2018) 976–982, DOI: 10.1021/acsmacrolett.8b00424; (e) Nakajima-Kambe, T., Ichihashi, F., Matsuzoe, R., Kato, S., Shintani, N. Degradation of aliphatic–aromatic copolyesters by bacteria that can degrade aliphatic polyesters, Polymer Degradation and Stability 94 (2009) 1901–1905

2 Reversible Polymerization, in: Polymer Properties Database; Reversible Polymerization (polymerdatabase.com)

while for others the hydrolysis will be fast.[3] This range in hydrolysis rates stems from the fact that these rates are strongly affected by the chemical and physical properties of the polyester, e. g. molecular structure, degree of crystallinity, molecular weight and ester group density, as well as by environmental factors such as the temperature or pH value. Polyester degradation is further influenced by an autocatalytic effect (one of the reaction products is also a catalyst for the same reaction) caused by the release of acidic protons due to hydrolysis.

Whilst this process occurs easily in living organisms, there have been doubts about the nature of degradation mechanisms of synthetic polyesters in the environment. Recent scientific work, however, demonstrated that microorganisms present in the environment can hydrolyse polyesters under mild conditions.

In summary, hydrolysis of polyesters in the environment will happen – depending on the properties of the polyesters - on very different time scales and will give back the reactant building blocks. For polyesters that will qualify for the proposed Polyester Exemption, these building blocks will then be the monomers specified on a list of approved starting materials (e. g. the list of approved monomers for food contact materials)[4]. At the same time such monomers are already registered under EU-REACH.

Cyclic Diesters

Common by-products of polyester synthesis are cyclic diesters, which also hydrolyse back to monomers. This has been demonstrated through in vitro degradation studies using both simulants of stomach fluids and liver enzymes. A study, sponsored by FEICA, was able to demonstrate this and serves as an example of biodegradation of such esters in in vitro and in vivo conditions[5]. The study is a bibliographical review of toxicological studies conducted by FEICA members, peer reviewed and complied by a certified European toxicologist. Further information is available from FEICA upon request.

Other jurisdictions

Polyester Exemptions are foreseen in several other jurisdictions as well, such as Australia[6], China[7], Taiwan[8], Canada[9] and the United States[10]. The US EPA comments on the exemption by saying that the EPA 'has had sufficient experience in reviewing polymer exemption notices for polyester polymers‘ and 'does not believe such polymers present an unreasonable risk of injury to human health or the environment'. Accordingly, these polyester polymers continue to be eligible for exemption[11].

Moreover, a provision for polymers permissible for use in food-contact materials manufactured from a positive list of monomers can also be found in the EU Food Contact Regulation. The rationale behind these exemptions is that polyesters without reactive functional groups are considered non-hazardous.

3 F. Bélan, V. Bellenger, B.Mor taigne, J. Verdu, Relationship between the structure and hydrolysis rate of unsaturated polyester prepolymers, Polymer Degradation and Stability, 56 (3) (1997) 301 – 309

4 https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32011R0010

5 https://wall.feica.eu/#/group/4810/file/10151?mc_phishing_protection_id=28396-c691qa4na38luuus3pbg

6 https://www.legislation.gov.au/Details/F2019L01543

7 https://www.cirs-reach.com/China_Chemical_Regulation/New_Polymer_Notification_China_REACH.html

8 https://law.moj.gov.tw/ENG/LawClass/LawAll.aspx?pcode=O0060043

9 https://laws-lois.justice.gc.ca/eng/regulations/SOR-2005-247/

10 https://www.epa.gov/laws-regulations/summary-toxic-substances-control-act

11 https://www.federalregister.gov/documents/1995/03/29/95-7712/premanufacture-notification-exemptions-revisions-of-exemptions-for-polymers-final-rule

Conclusions

FEICA proposes to keep the Polyester Exemption as an EU PLC criterion, considering that polyesters hydrolyze, as discussed above, back to the initial building blocks on an approved list of monomers, e. g. those in the EU Food Contact Regulation[12]. This is also in line with the objective stated by the Commission of 'aligning PLC criteria with other global frameworks'[13].

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

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12 https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32011R0010
13 E. g. 42nd Meeting of Competent Authorities for REACH and CLP, 17 November 2021