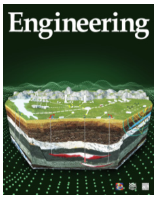
Engineering 14 (2022) 15–18

Contents lists available at ScienceDirect

Engineering

journal homepage: www.elsevier.com/locate/eng



Views & Comments

Reactive Extrusion (REx): Using Chemistry and Engineering to Solve the Problem of Ocean Plastics

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The reality of plastic pollution is no longer under debate: It has invaded our daily lives and is present all around us, with our oceans being no exception. In fact, a seventh "continent" has appeared in the oceans, composed of plastics and microplastics! Newspapers including *Le Monde* in France and *The Guardian* in United Kingdom recently headlined the record rate of microplastic accumulation in the Arctic Ocean. These headlines referred to an article published in *Nature Communications* [1] that reported the finding of up to 12 000 plastic microparticles per liter of water frozen in the sea ice. Given this finding, what future solutions can counteract this particularly insidious pollution?

In this opinion paper, the author wishes to highlight why he feels strongly that reactive extrusion, often referred to as REx, and particularly enzymatic reactive extrusion (e-REx), can effectively contribute to mitigating the impact of plastic waste pollution. The following paragraphs describe the interest in and future contributions of REx technology in the plastics industry. This technology combines the tools of the chemist, such as the synthesis reactor, with those of the chemical and process engineer—in this case, the extruder. Furthermore, biochemistry offers a full range of enzymatic catalysis for the production of polymeric materials and the enzymatic recycling of industrial plastics.

Plastic pollution in oceans mostly originates from three different yet complementary levels: wastewater pathways, road runoff, and mismanaged wastes [2]. The environmental impacts of ocean plastics are not completely understood, and many research activities across the globe are under way to qualitatively and quantitatively identify the deleterious effects of ocean plastics on marine life and on human health via the food chain, which ultimately brings such plastics to our plates. In addition to the environmental destruction triggered by plastic waste accumulation, economic losses have been estimated to be between 0.5 trillion to 2.5 trillion USD annually [3]. The main sources of ocean contamination can be summarized as follows: ① commercial fishing waste, such as old fishing nets; ② consumer products, such as plastic bags, food wrappers, beverage bottles and caps, straws and stirrers, plastic cups and lids, and cigarette butts; and ③ building and construction waste, such as pipes, wires, coatings, and floor tiles.

When discarded in sea water, plastic degrades into smaller fragments under the influence of the sun's ultraviolet rays, exposure to salt, temperature changes, and mechanical wearing from tidal waves over time. Plastic particles smaller than 5 mm across are commonly referred to as microplastics. Because such microplastics are mostly derived from the fragmentation of the previously described (macro)plastic waste, they are designated as *secondary* microplastics. In contrast, *primary* microplastics are industrially produced and are used as is; these include microfibers from synthetic textiles, plastic pellets, and components of road markings, marine coatings, and personal care products. Depending on their density, ocean plastics and microplastics generate huge detriment to marine life in sea water; denser plastics accumulate at the bottom of the ocean, while less dense plastics float on or near to the surface. Since these organic wastes are very resilient and persist in the environment for thousands of years, potential solutions to mitigate ocean plastic pollution are currently being widely sought. Interestingly, Watt et al. [2] at University of Guelph in Canada has published a highly relevant overall scheme summarizing how the negative impacts of ocean plastics can be decreased and what the main potential routes to valorize plastic waste can be (Fig. 1). These views align with those of the current author, who is convinced of the increasing role of REx technology in the plastics industry. The first contribution of REx technology in this industry lies in the strategy of adding value to plastic wastes via upcycling—that is, recycling plastics via (reactive) blending with other materials such as polymers, additives, and fillers and nanofillers to yield novel value-added products. In contrast to downcycling, which refers to conventional recycling via mechanical methods, the upcycling of collected plastic wastes will contribute to a circular bioeconomy, resulting in new families of sustainable products.

A second contribution offered by REx is undoubtedly the production of biobased and biodegradable polymeric materials. One of the main objectives of this opinion paper is to highlight the production of so-called "bioplastics" via REx. Such bioplastics are produced from non-fossil carbon that is directly available from renewable biomass (in a shift from petroleum-based polymers; Fig. 1) and are able to undergo integral biodegradation within just a few months. It is worth pointing out that the term *bioplastics* refers to two types of polymeric materials. The first type consists of bio-sourced plastics derived from biomass, while the second comprises biodegradable (e.g., in compost or in a marine

https://doi.org/10.1016/j.eng.2021.12.009

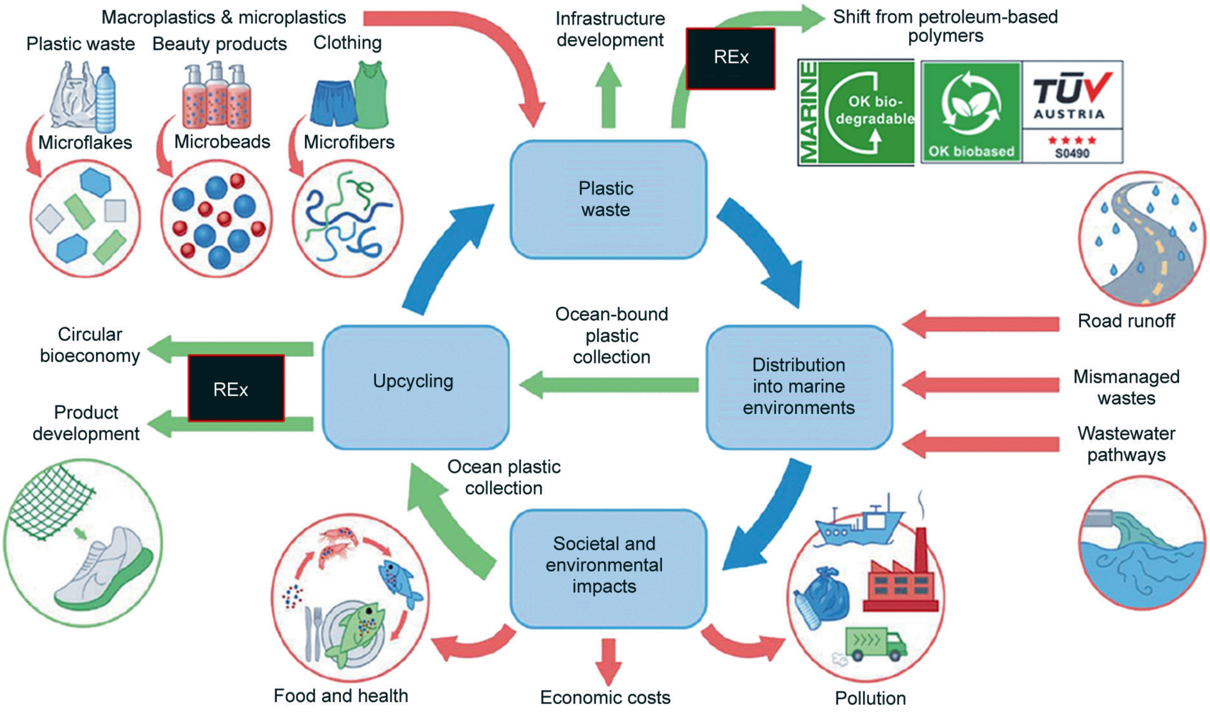

Fig. 1. The life cycle of ocean plastic waste and potential mitigation pathways, including the role of REx. Green arrows show the possibility of reducing the negative impact of ocean plastics and their potential valorization, while red arrows highlight the sources and negative effects of plastic in the oceans. Reproduced from Ref. [2] with permission of the authors, ©2021.

environment) plastics, including those derived from fossil-fuel resources (i.e., petrochemical raw materials). Accordingly, some bioplastics can combine the characteristic features of both types, being both bio-sourced and biodegradable (as demonstrated by the TÜV Austria logos shown in Fig. 1: "OK biodegradable" and "OK biobased").

REx is known to be a very attractive continuous "green" process in polymer processing that includes *in situ* compatibilized melt-blending, filler and nanofiller dispersion (with interfacial compatibilization), and many different chemical reactions such as polymerization and copolymerization, grafting, branching, and chain-functionalization. The use of an extruder to conduct chemical modifications or polymerization reactions has proved to be efficient for low-cost production and processing methods, as it enhances the commercial viability and cost-competitiveness of the materials. The obvious advantages of extrusion polymerization can be summarized as follows: ① a solvent-free melt process; ② continuous processing, such as starting from the monomer and resulting in a polymer or even directly resulting in the finished object; ③ control over residence time and residence-time distribution; and ④ possible integration of other extrusion streams into the polymerization/reaction process.

Both single and twin-screw extruder configurations can be used in REx processes, although twin-screw ones are usually preferred due to the extended control they allow over residence-time distribution and mixing, and their superior heat/mass transfer capabilities. Thanks to these attributes, twin-screw extruders make it possible to tackle more demanding tasks such as dispersing pigments and additives, alloying, homogenizing, reactive compounding, concentrating, devolatilizing, and polymerizing. In a twin-screw extruder, the geometrical configuration of the screws—that is, the modular design and sequential arrangement of the screws, which usually involve kneading blocks, mixing gears, and conveying screw elements—is extremely important. The assembly arrangement of the screw elements determines the residence-time distribution in a twin-screw extruder. Depending on the direction of rotation of the two screws, twin-screw extruders can be categorized as co-rotating or counter-rotating machines, where co-rotating screws have a radial and counter-rotating have an axial shearing and plasticizing effect. Without going into detail, co-rotating intermeshing twin-screw extruders have been found to be more suitable for continuous REx processes. Due to its exceptional characteristic features, REx technology has been adopted for many different chemical reactions involving and/or leading to value-added polymeric materials [4,5], including:

(1) Intensification of polymerization processes via the free-radical, ionic, condensation, or coordination polymerization of monomers or comonomers, providing high-molecular-weight macromolecular materials with almost quantitative yields;

(2) Mitigated degradation of polymers with the possibility of tuning three-dimensional (3D) crosslinking by means of free-radical initiators;

(3) Macromolecular chain chemical functionalization and/or grafting by means of monomer and comonomer oligomerization;

(4) Interchain copolymer formation via *in situ* reactions involving the combination of reactive groups that are available along or at the extremity of polymers to form graft copolymers, for example;

(5) Chain extension or coupling reactions starting from end-functionalized prepolymers/oligomers via polyfunctional coupling agents and/or surface-reactive fillers and nanofillers;

(6) Reactive interfacial compatibilization of immiscible polymer blends and (nano-)filled composite materials.

All these chemical reactions, as performed by REx, have emerged as efficient ways to generate new value-added polymeric materials such as nano-structurized polymer blends, high-performance nanocomposites, and bio-sourced and biodegradable polymeric materials. In the field of bioplastics in particular, REx via twin-screw extruders has been used to produce high-molecular-weight biodegradable aliphatic polyesters such as polylactide

(PLA), polycaprolactone (PCL), and related copolymers by means of fast continuous catalyzed ring-opening polymerization (ROP) [6–8]. Numerous studies have examined the use of REx to produce many other bioplastics, including polysaccharides such as starch, cellulose, and their derivatives; (bio)polyesters such as polyhydroxyalkanoates (e.g., polyhydroxybutyrate-*co*-valerate, PHBV) and polysuccinates (e.g., polybutylene succinate, PBS); polyamides; and polyester amides. The main objective of such studies has always been to tune the physicochemical and thermomechanical properties of the related materials while preserving and even improving their biodegradation ability. The author postulates that it is in this research area that REx technology, as a continuous, solvent-free, "green" process, will pave the way for the industrialization of bioplastics and their related value-added melt-blends and (nano)composites [6–10], which holds the potential to reduce the impact of plastic pollution, particularly in oceans.

To illustrate the huge potential of REx technology, the author would like to emphasize the original combination of two intermeshing co-rotating twin-screws interconnected to each other via a T-shaped configuration (a technology referred to as "t-REx"; see Fig. 2). Interestingly, stereo-complexed PLA-based polyester urethanes (PEUs) have been synthesized by means of t-REx (here, with two intermeshing twin-screw extruders with the same screw diameter (ϕ) of 18 mm) [11]. The process involves two consecutive steps: The first step is the ROP of the lactide (LA) momoner, the cyclic dimer of lactid acid, to yield α,ω-dihydroxyl PLA oligomers, while the second step is a chain extension reaction. An aromatic diamine, 4,4′-diaminodiphenylmethane (MDA), was studied as the initiator for the synthesis of PLA oligomers. It is notable that the same diamine was added as a chain extender in addition to the diisocyanate—that is, diphenyl methane diisocyanate (MDI). Both chain-growth (ROP) and step-growth (chain extension in the presence of MDI/MDA) reactions were promoted by the same catalytic system: an equimolar complex formed between tin(II) 2-ethylhexanoate and triphenyl phosphine ($Sn(Oct)_2–PPh_3$). A single catalytic complex was used and was added only once for the synthesis of the α,ω-hydroxyl PLA precursors; furthermore, the PEUs were produced in bulk (without any solvent) by REx. The "T" configuration proved to be fully adapted for the first step—that is, the ROP of the LA monomers—since the *L* and *D* stereoisomers of LAs, L-LA and D-LA, were separately oligomerized by the ROP in the first section of the principal extruder (length-to-diameter ratio (l/d) = 50) and in the satellite extruder (l/d = 40), respectively (Fig. 2 left). At the "T" joint connecting the two extruders, the poly(*D*-lactide) (PD-LA) and poly(*L*-lactide) (PL-LA) polyesters that were continuously produced in the main extruder and in the satellite extruder, respectively, encountered each other. The concomitant addition of MDA and MDI made it possible for chain extension to take place, along with the stereo-complexation of the as-produced multi-block PLA-based PEUs. Interestingly, due to the inherent stereo-complexation between the PLA blocks of the *D*- and *L*-configurations, these PEUs displayed enhanced thermal stability, resulting in unique melt processability and a significantly higher melting temperature (i.e., at or above 205 °C) [12].

e-REx has also been carried out to produce biodegradable polyesters. For example, conducting an enzymatic ROP via REx at high-shear and high-temperature conditions has been shown to be feasible [13]. Using immobilized *Candida antarctica* lipase B (CALB) as the catalyst at temperatures ranging from 90 to 130 °C, ω-pentadecalactone (PDL) was converted (> 99% monomer conversion) by means of REx for 15 min, yielding only poly(ω-pentadecalactone) (PPDL) with a molecular weight as high as 160 $kg·mol^{-1}$ (Fig. 3).

The addition of enzymes to molten polymeric materials by extrusion is far from trivial, since thermal and shearing constraints are known to have very deleterious effects on enzymatic activity. Very recently, the French company Carbios successfully incorporated precisely designed enzymes in PLA via extrusion [14]. While enzymes are widely used in many everyday applications, including detergents, biofuels, food, textiles, and paper, using them for the degradation of plastic polymers and textiles for industrial purposes had not yet been considered. Carbios developed proprietary enzymes with the ability to break down certain polyesters after use—particularly PLA and related PLA-based materials—via the so-called Evanesto technology (Fig. 4). The true art in this achievement was to preserve enzymatic activity not only during the dispersion of the enzyme within the polyester matrix during the extrusion process, but also throughout the use and application of the resulting PLA formulation. Activation of the enzyme (and therefore polymer degradation) only takes place after use and under specific conditions such as home composting [14]. Carbios is thus the first company to combine the three sciences of enzymology, polymer chemistry, and process engineering so effectively.

As another illustration, polyethylene terephthalate (PET), which is very common in bottles and textiles, can be enzymatically degraded into terephthalic acid and mono-ethylene glycol under rather mild industrial conditions. In one specific case, post-consumer PET flakes were put into contact with the depolymerase enzyme in water at 72 °C and pH 8 (1 m^3 reactor; 200 g PET per liter of water), which resulted in more than 90% conversion into comonomers within 10 h [15]. In other words, after optimization of their microstructure, enzymes can now be used in novel innovative processes such as enzymatic recycling (PET) and the production of home-compostable bioplastics ("enzymatically activated" PLA). Extrapolation to other commercially available thermoplastic materials is currently under way, as announced by Carbios [14].

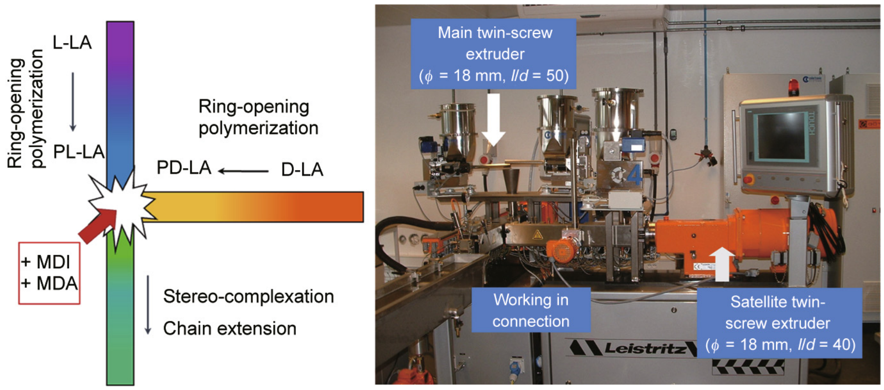

Fig. 2. Continuous production of stereo-complexed PLA-based polyester urethanes by means of t-REx, using a combination of two intermeshing co-rotating twin-screw extruders in a T-shaped configuration. L-LA: *L*-lactide; D-LA: *D*-lactide; PL-LA: poly(*L*-lactide); PD-LA: poly(*D*-lactide); MDA 4,4′-diaminodiphenylmethane; MDI: methane diisocyanate. ϕ: screw diameter; l/d: length-to-diameter ratio.

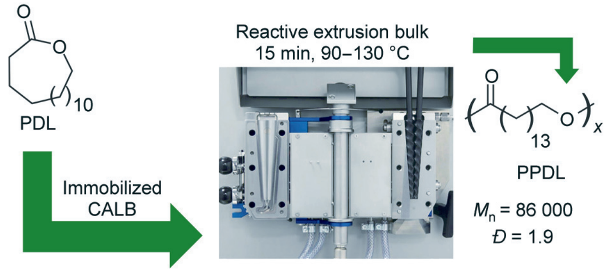

Fig. 3. Production of the biodegradable aliphatic polyester poly(ω-pentadecalactone) (PPDL) via the ROP of ω-pentadecalactone (PDL) by means of e-REx, using immobilized *Candida antarctica* lipase B (CALB) as a catalyst. M_n: the number average molecular weight; $Đ$: dispersity.

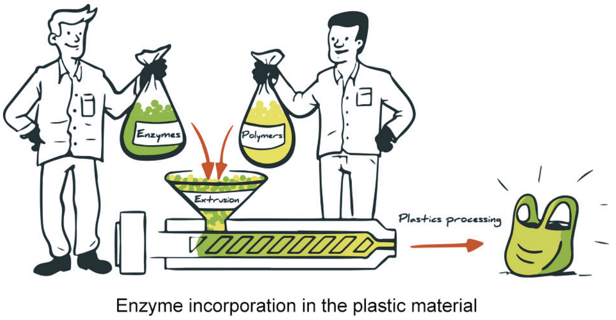

Fig. 4. Sketch of enzyme incorporation in industrial-grade PLA (and related compositions) by means of extrusion processing, leading to "OK home compost" materials. Reproduced with permission by Carbios.

In conclusion, REx and the related configurations of t-REx and e-REx hold enormous potential for reducing and controlling the plastic wastes in our environment. This potential is further confirmed by the very recent development of "active" enzymes trapped within bioplastics such as PLA, as pioneered by Carbios. If enzymes embedded in PLA objects during their production by extrusion can make PLA home-compostable (whereas for decades it has been identified as biodegradable in industrial compost only), it is the author's opinion that it should be feasible to select, design, and produce a depolymerase enzyme that allows PLA to be fully biodegradable in sea water. Other bioplastics can be treated in the same way, which will pave the way for a new era of "enzymatically activated" bioplastics. It is also clear to the author that the combination of REx with novel and rapidly developing technologies such as 3D and four-dimensional (4D) printing [16] and cold plasma surface treatment [17] will enhance the extremely high performance of these technologies and further mitigate the problem of plastic waste pollution.

Acknowledgments

The author warmly thanks all his colleagues and coworkers at Materia Nova, UMONS Innovation Center, for their continuous and dedicated involvement in the field of bioplastics production and characterization as well as materials processing by means of extrusion and reactive extrusion.

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