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Chemical recycling of polyester textile wastes: shifting towards sustainability†

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Amongst all synthetic polymers used in the clothing industry, polyethylene terephthalate (PET) is the most widely used polyester, its fibres representing half the total PET global market (in comparison bottle PET being less than a third). Compared to bottle PET, the recycling of fabric PET fibres represents a challenge, both due to intrinsic structural differences (chain length and crystallinity) and to the presence of various additives (dyes, protection or finishing agents). Effective waste management requires addressing these additives through elimination or recycling processes. This review article aims to give an overview about all the existing means to recycle PET fibres. Textile recycling encompasses primary (closed-loop), secondary (mechanical), tertiary (chemical), and quaternary (incineration with energy recovery) processes. Mechanical recycling faces challenges due to PET's characteristics, including lower molecular weight and additives. Chemical recycling, particularly solvolysis processes (hydrolysis in neutral, acidic, or alkaline media, alcoholysis, glycolysis, aminolysis or enzymatic hydrolysis), offers a more advanced approach and will be described in detail, focusing both on the specific recycling of fibres when available and enlightening the advantages and drawbacks of each method. To discuss the environmental impact of each process, a quantitative analysis was conducted by defining the experimental domain represented by the temperature range and reaction time, and then calculating the energy-saving coefficient, as a green metric adapted to the diversity of textile PET recycling processes and data provided in the literature. This coefficient allows for discussing the relevance of using complex or non-renewable catalysts in processes, the positioning of enzymatic pathways, and the choice of reaction mechanisms applicable to the industry. A prospective approach was employed to identify key criteria for future advancements in green recycling. Subsequently, a comparative analysis of depolymerisation methods will be presented within the context of sustainable development goals (SDGs), green chemistry, and green metrics. Finally, using ε factors, this analysis will facilitate the detection and highlighting of pathways that show the most promise in terms of greening PET recycling.

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1. Introduction

Textile recycling is crucial for reducing the carbon footprint of the industry worldwide. This review aims to discuss the challenges of textile waste recycling, to identify sustainable methods for the environment. Therefore, this review will present the materials used to produce textile fibres, especially polyesters, their properties, and the challenges related to the chemical recycling of these fabrics, which contain various specific additives that must be taken into account in depolymerisation reactions. The depolymerisation methods currently described in the literature will then be presented and detailed. To understand the environmental challenges and obstacles related to a transition to sustainability in textile recycling processes, we will analyse the specific characteristics of this industry, the market, and the volumes involved, and then we will link all this data to sustainable development goals and green chemistry principles. Finally, all depolymerisation methods will be compared using green metrics.

Recycling involves the reuse and reprocessing of used clothing, fabrics and clothing scraps generated during manufacturing. Within the broad spectrum of recycling, and depending

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on the chemical nature of textiles, chemical recycling will be a future solution for producing chemicals to reform new polymers, enabling a true circular economy that limits waste and the environmental impact of this industry.[1] Textiles typically include biodegradable components such as plant fibres (cotton, flax, jute, …), animal fibres (wool, silk, cashmere, …) and alongside non-biodegradable materials like polypropylene, polyethylene, nylon, or other synthetic fibres. Most textile fibres currently on the market are made of polyesters. The modern definition of polyesters includes all polymers containing an ester function in the backbone of their repetition unit, so they can be written as described in Fig. 1.

Such structure allows many different kinds of polyesters and properties. However, only a few polyesters are used in the textile industry (Fig. 2a), and one in particular concentrates the majority of polyester production efforts: polyethylene terephthalate (PET). After initial works on alkyds resins during the second part of 19th century, a major step in polyester history occurred in the 1928–1934 period by Carothers' team for the DuPont de Nemours group, leading to the synthesis of many macromolecules containing esters.[2–4] A few years after, in 1941, Whinfield and Dickson succeeded in forming a polyester from ethylene glycol and terephthalic acid, and PET was born.[5] Soon after this first synthesis, PET fibres were commercialized by the Imperial Chemical Industries (ICI) under the tradename Terylene™.

Then DuPont de Nemours, which previously worked on polyesters, managed to purchase ICI's patent rights in 1945 and created the new polyester fibre Dacron™.[6] In France, this fibre was developed in 1954 by the company Rhodiaceta under the tradename Tergal™. Eastman Chemical followed, and in 1958 created another polyester fibre called Kodel™. Since that date, and until the end of the 1970s, polyester fabrics developed rapidly, with more or less success.[7]

1.1. PET among polyesters

Among industrial polyesters, PET presents three major advantages exploited in three main applications: it is cheap, can be either amorphous (for transparent bottles) or semi-crystalline (for fibres), and finally is well suited for food and beverage storage (for cling films). These three applications represent roughly 98% of virgin PET world consumption in 2014 (Fig. 2b). PET is also the most produced polyester worldwide; as a comparison, polybutylene terephthalate (PBT) is second in terms of global production with 60 times lower tonnage. Indeed, the uses of PBT and other polyesters are mostly focused on other, often more technical, applications which require specific characteristics. Also, other polyesters such as Polyethylene 2,5-furandicarboxylate (PEF) or Polycaprolactone (PCL) are greener alternatives to PET, but they are more expensive and less used currently. Therefore, nowadays polyesters mainly refer to PET.[8,9]

They constitute modern materials that benefit from many technological innovations, both in terms of fibres (chemistry and spinning), and weaving methods. Polyester microfibre development has also contributed to the development of new fabrics and clothing.[10]

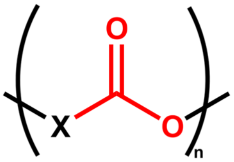

Fig. 1 General structure of polyesters (the spacer X can also include another ester function).

1.2. From PET synthesis and properties to textiles

Polyester synthesis consists mainly of a polycondensation of a carboxylic acid with an alcohol at relatively high temperature and under vacuum (Fig. 2c). While many metallic or organic catalysts suit this reaction, the main industrial catalyst used is antimony trioxide (Sb_2O_3), which presents significant environmental and human health risks, depending on the exposure.[11] For more details about polyesters synthesis, we invite you to read Gubbels *et al.* and Scheirs and Long.[8,9]

With regard to the physicochemical properties, polyester is a thermoplastic polymer which can be fused and remolded, allowing fibres to be produced and recycled. These polyester fibres are manufactured as continuous filaments either from a polymer in the granule form (batch process), or by continuous polymerisation. In the manufacturing process, the molten polymer is immediately solidified and then drawn at a temperature above its glass-transition temperature (T_g = 69 °C.) to improve the polymer chains orientation and increase the polyester fibres strength which are a combination of crystalline and non-crystalline regions. To form fibres, polyester is melt-spun through spinnerets.[12] The resulting fibres are stretched, combined into yarn, and then woven. The hydrophobic nature of the polymer confers water-repellent properties on the fibres. The resulting fabrics are easy to clean, dry quickly, do not crease, and are mildew resistant. Polyester fabrics are also strong, resistant to stretching, shrinking, and abrasion.[13,14] In the 1970s, polyester fabrics were different from those of today, mainly because of the weaving (double knit), and were intended more for inexpensive leisurewear.[7]

The technical qualities and the low production cost of polyester fibres mean that clothing made with this fibre is very present, and constitutes the essential of clothing to be recycled. The numerous additives existing today also are important in the rise of polyester fabrics.

2. The challenges of PET recycling

2.1. Depolymerisation

Depolymerisation reactions are thermochemical methods which require the control of the various reaction stages to optimize recycling efficiency. To limit the environmental impact, catalysts are used to lower temperatures and improve selectivity to obtain monomers from PET.[15] Various strategies have

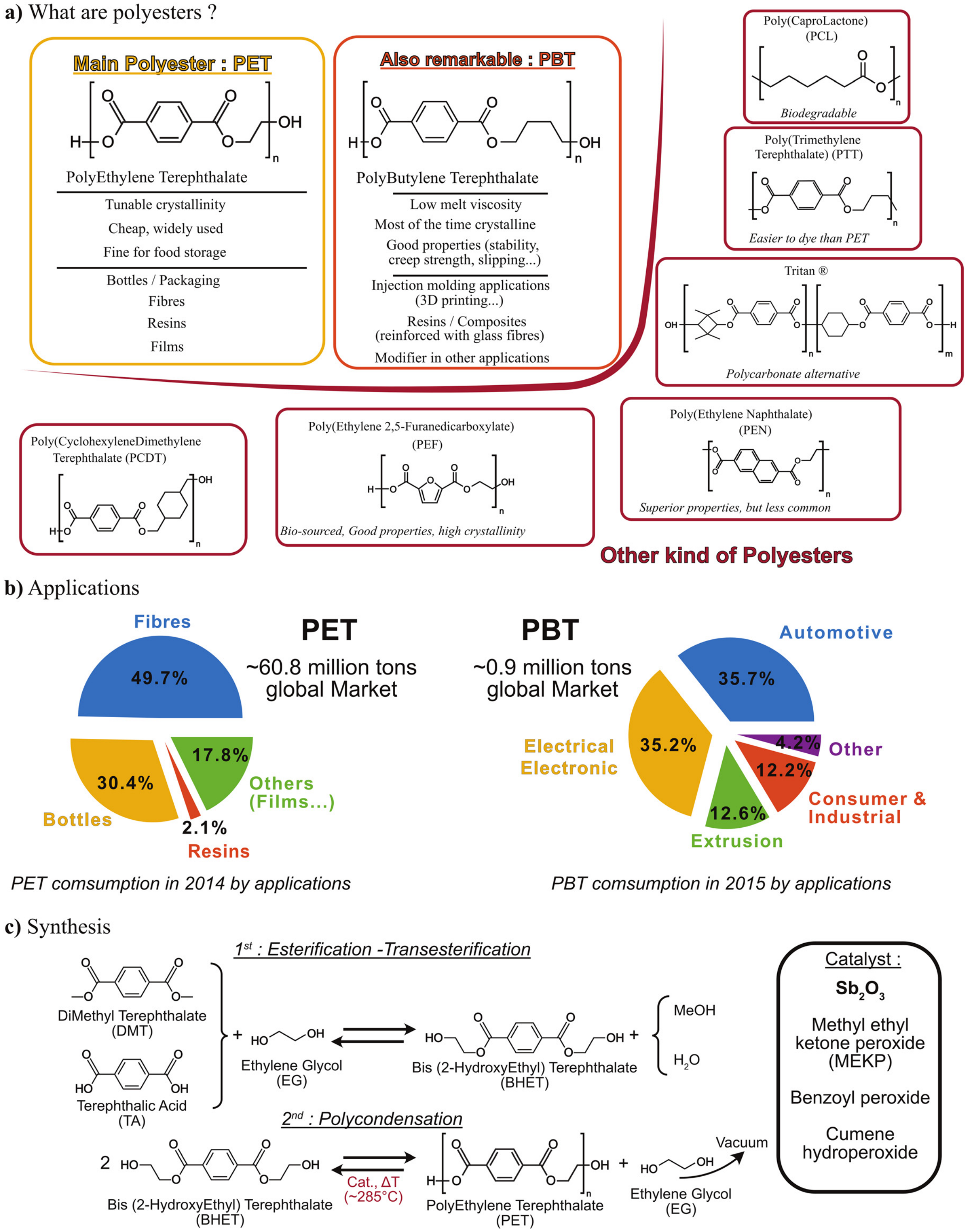

Fig. 2 (a) Some common commercial polyester types. (b) Market share by applications of virgin PET/PBT in 2014/2015 respectively.[8] (c) PET main synthesis from diMethyl therephthalate (DMT) or terephthalic acid (TA).

been developed to lower the reaction temperature and enable depolymerisation at room temperature. But solubilizing polymers often requires the use of solvents with a very high environmental impact.[16] In the case of textiles, depolymerized compounds are commonly used as raw chemical materials, fuels or lubricants, but are rarely reused as precursors for new polymers.[17] This can be explained by the nature of textiles, which contain additives to give them their properties.

2.2. Additives

Whatever the recycling technique, it is necessary to take into account the many additives that may be present in polyester fibres. These additives, if not removed, can affect recycling performance and reduce the quality of recycled products in comparison with bottle grade polyesters.[18] In the textile industry, additives are essential, whether to treat natural or synthetic fibres.[19] These additives provide many features: colouring, protection against ultraviolet light, oil and water repellent, fire resistance, *etc*. In the textile sector, these chemical additives are mainly introduced in the fabric treatment process, such as dyeing and finishing.[20] Also, the additives used are often tenacious, to resist friction and numerous washes. This particularity makes them difficult to eliminate for a recycling process.

Dyes are the most common additives used in the textile industry.[21] In this area, synthetic fibres, including polyesters, are treated in a special way.[22] Polyester is a partially crystalline hydrophobic material, without very reactive functions, for which the traditional dyes of natural fibres (wool, cotton), cannot be used. In this case, special dyes (disperse dyes) must be used, as well as an appropriate dyeing technique.[23,24] Such dyes developed for polymeric targets can represent some health/environmental risks (Fig. 3),[25] are highly water consuming,[26] and might interfere with chemical recycling process if not removed. So that some industries do not include dyed or tinted plastics in their process.[27] The polyester fibres are dyed in the mass by direct dye penetration (Fig. 4), using a carrier, a solvent (swelling) and preferentially operating above the T_g. During the dyeing process, various auxiliaries can be used (fixing agent, stirring agent, dyeing acid *etc.*),[21,22] which are generally removed after rinsing, although some can persist on the fibres. Printed fabrics, especially on polyesters, are more and more common.[28] Printing techniques use suitable inks, but also auxiliaries (thickeners, emulsifiers, fixing agents…) which can persist in the fibre.

Textile finishing consists of using a finishing agent on the fabric, which will modify the surface properties and provide new fabric functions.[29] For example, we can use a water-repellent or oil-repellent finish using an agent that will modify the fibre surface characteristics, so that the fabric will be protected from water (waterproof) or oil (dirt). There are many other agents such as those improving the fastness to rubbing, anti-

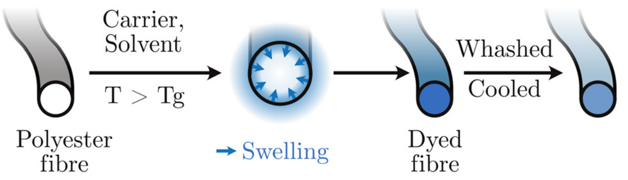

Fig. 4 Representation of the transfer mechanism of dispersed dyes to PET fibres.[24]

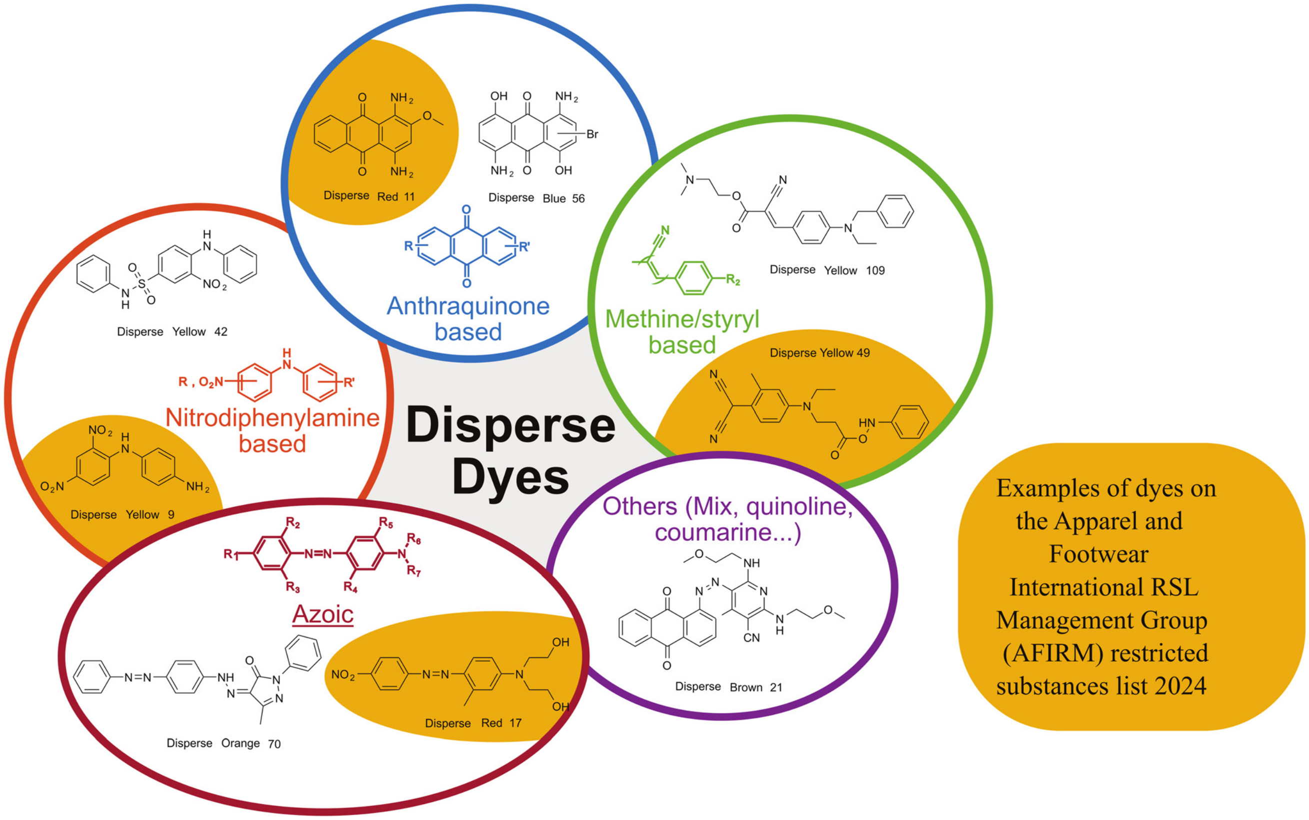

Fig. 3 Disperse dyes families including example of restricted substances.

static agents, anti-slipping agents, anti-creasing agents, agents improving the solidity to light, antibacterial agents, flame retardants, ….[29] As the use of high performance textiles has grown, the need for chemical finishes has grown accordingly. Most of the additives used are bonded to the polyester fibre by weak interactions, but some are covalently bonded, like co-monomers (polyols,[30,31] phthalates…[32–34]). Copolymers with the ethylene terephthalate unit including a brominated or phosphorus part are also used as Flame-Retardant.[35] In all of these cases, the additives will persist in the material regardless of the recycling type. Indeed, fabrics based on polyester fibres are complex mixtures comprising numerous additives of different natures, and in unknown proportions. This complicates recycling, and in particular chemical recycling where some of these additives could interfere. Consequently, an additive (dyes and finishing agents) elimination step (even partial), is recommended before recycling. Also, such a step isolates the additives to treat them separately for their elimination or recycling. Some additives are expensive, or may cause health or environmental problems. Recent innovations include the production of green additives, such as flame retardants derived from bio-macromolecules obtained from lignin,[36] or the introduction of bio-sourced functionalities such as antimicrobials on polyester fabrics.[37]

2.3. Polyesters fibres waste management

Fabrics were conceived to be durable and resistant to degradation. As a consequence, textile fibres are persistent in nature and lead to a pollution estimated to have major ecological and sanitary consequences.[38,39] The alternative to a constant increase in demand for textile production – accompanied by a substantial proportion being released into the natural environment – is dematerialisation, substitution, reuse, material recycling, waste-to-energy transformation, and conversion technologies. These options must be carefully considered to design the best solutions to the environmental challenges imposed by plastic production and general use, and should be considered independently for each application.[40]

Among the solutions cited, recycling is an option. Generally, recycling rates are calculated from collected litter and does not consider mismanaged waste so their constant progression does not reflect a better control of textile-derived plastic pollution. In 2017, Geyer *et al.* estimated that recycling only represented 9% of the plastic ever manufactured while 22% was mismanaged (Fig. 5). This figure could be considered in view of the material recycling rate in Europe which is estimated to have reached 30.6% in 2021.

Little is known about the proportion of synthetic fibres in waste and it varies from country to country. For example, it accounted for 5.8% of the total landfilled municipal solid waste in 2018 in the USA, corresponding approximately to 17 million tonnes (US Environmental Protection Agency). With rapid growth and evolution in fashion trends,[41] textile production and waste generation rates have increased substantially lately,[42] and tonnages are expected to increase by 50% by 2030.[43] It is estimated that synthetic fibres were almost not recycled in 2020.[44] This low score evidences the specificity of fibres recycling.

Synthetic fibres recycling is limited, firstly, because collection, separation, and sorting are very challenging. Sorting is the most important step but contrary to a rather well-organized collection of domestic plastic waste, textiles do not have a dedicated recycling sector. For example, post-consumer textile collection rates are 11% in Italy and 75% in Germany, while some countries do not have textile-recycling systems.[45] As for recycling, less than 1% of total production was recycled in a closed loop (recycled into the same or similar quality applications).[46] Most of the recycled textiles were recycled into other, lower-value applications.[46] Recycling rates do not take into account the number of stages involved to perform recycling, nor the different recycling routes.

Generally speaking, textile recycling covers four distinct processes:

- Primary recycling or closed loop recycling, is when recyclable materials are mechanically processed to create a product that performs a similar function. In this process, textile fibres are reused without a loss of properties. By various mechanical means (crushing, grinding, de-weaving, stretching), fibres can be recovered from textile waste. A second treatment series is then applied (cutting, shredding), depending on the fibre origin and the fabric composition, to obtain recycled materials. The cost of these new fibres and the life cycle assessment of these recycled materials must include the environmental impact of the cutting/shredding and washing operations.

- Secondary recycling is also known as mechanical recycling. It is also a mechanical process, but to make new products. This process will involve more separation and purification stages of textile fibres to produce new materials, but they may not necessarily be reused to produce fabrics. Indeed, the fibre polymers, if not modified in their elemental composition, undergo structural changes, often resulting in a decrease in molecular weight because of chain breakages. If fabrics are composed of different fibre chemical families, for example, natural (like cotton) and synthetic (like polyester), it is necessary to separate the two elements by selectively solubilizing one of the two components or by using enzymes. Treatment processes for additives are often required to eliminate them and make the materials homogeneous (colour, composition). For instance, it is possible to separate cotton from polyester in fabrics through treatment without toxic organic solvents, using ionic liquids to dissolve the cellulose in cotton, isolate the polyester, and produce new cotton fibres through dry-jet spinning.[47]

- Tertiary recycling or chemical recycling is an advanced technology process. The polymer is converted into smaller molecules, through chemical processes, which are used as feedstocks for the production of new polymers, chemicals, or fuels. The chemical processes are tailored to the polymers found in tissues intended for recycling. For polyesters, various catalytic reactions such as hydrolysis, glycolysis, *etc.*, are encountered and will be detailed further in this review. In the

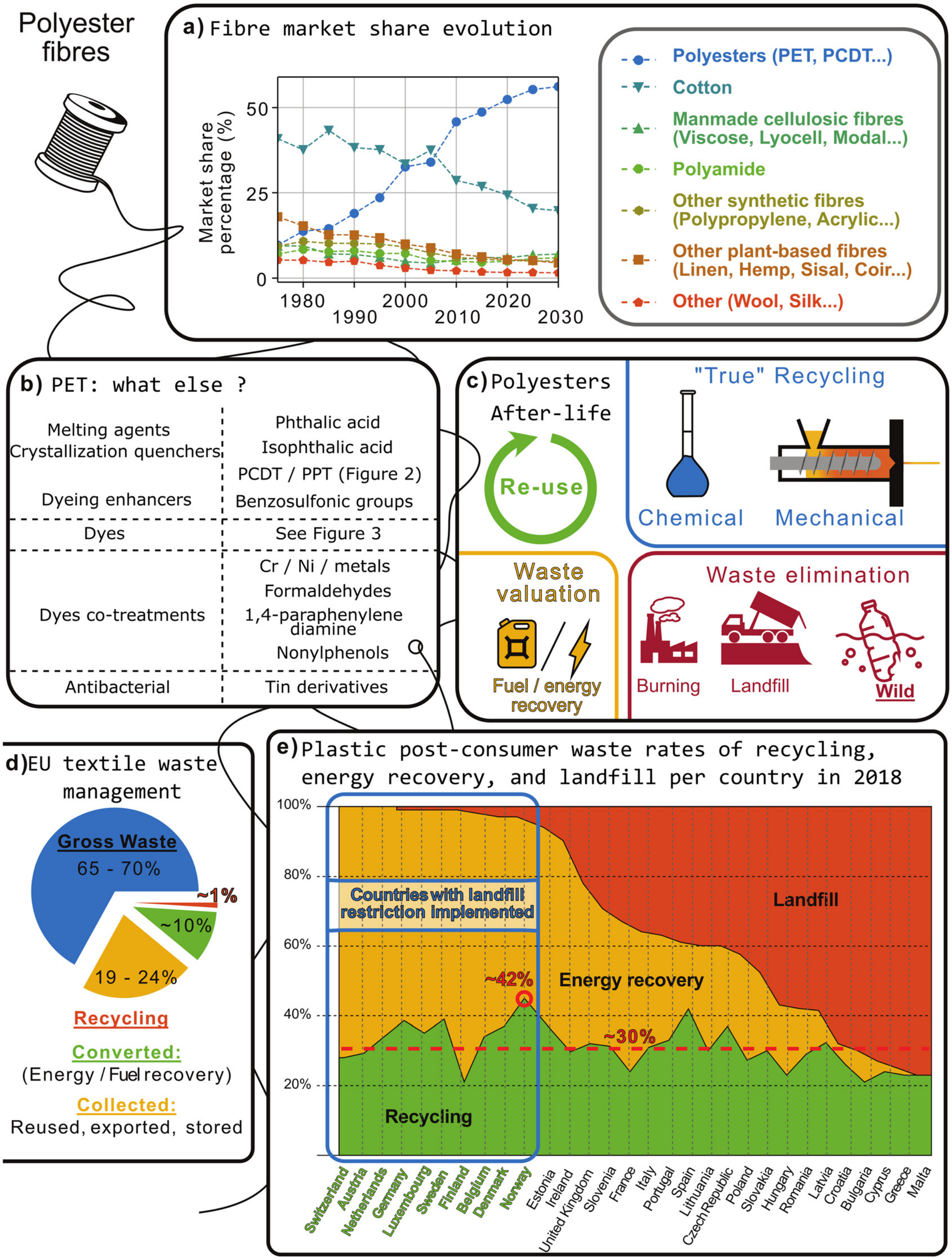

Fig. 5 (a) Previous evolution and prospects of the textile market share according to Textile Exchange.[68] (b) List of additives commonly found in PET fibres. Some are under restrictions according to the country. (c) The different non-storage ending of plastics. (d) Current textile waste management in Europe, gross waste meaning no clear public management and include storage and export.[44] (e) Global plastic management in Europe, including textile and non-textile plastic waste.[69] By comparison with (d), we can observe that textile waste are particularly poorly treated.

pursuit of environmentally-friendly method development, attention should be given to the catalysts involved, solvents, energy consumption, as well as the production of chemical species that may impact the environment.

- Quaternary recycling involves fabric incineration with energy recovery. This route is an alternative to the low recyclability of materials[48] and remains quite common to reduce waste quantity by harnessing the energy contained in the materials.

Synthetic textile recycling routes are typically either mechanical or chemical and less frequently thermal. But in many cases recycling often consists of a combination of the three processes.[49]

For polyester fibres, the first route is abandoned at the industrial scale.[50] Plastic bottles, made of what is called bottle-grade PET, are well engaged in the secondary recycling route. For example, about 50% of PET plastic bottles were recycled in the EU in 2022;[51] this rate meets the average for most industrialized countries.[52] Synthetic fibres are not recycled *via* the mechanical process, because fibre-grade PET presents distinct physico-chemical characteristics: lower molecular weight and intrinsic viscosity. Another reason why synthetic fibres cannot be mechanically recycled is the presence of high levels of additives. Also, the residual presence of other polymers prevents mechanical recycling, therefore the sorting of textile fibres is not well developed in any country.[53]

3. Chemical recycling of polyester fibres

3.1. Global overview

Massive textile production is a major concern for developing eco-friendly recycling technologies. In recent years, global textile fibre consumption reached a record 100 million tonnes in 2016. Within this fibre proliferation, PET has emerged as the leading player, representing over 50% of global consumption in 2018.[54] Alongside this phenomenal sectoral expansion, there has been a significant increase in discarded textiles, leading to major environmental challenges. Indeed, conventional disposal methods, primarily landfilling and incineration, have resulted in significant ecological issues, highlighting the urgent need to find sustainable solutions for managing these textile wastes.[55] PET is a robust, suitable for moulding polymer that can be easily melted to generate new fibres. However, the ductility of PET during a simple mechanical recycling process is significantly altered after three cycles. Consequently, only a small portion of PET is recycled for its original application, with most (50 to 77%) being transformed into fibres used in the production of mixed materials such as carpeting.[56]

Faced with these pressing environmental challenges, alternative chemical, physicochemical, or biocatalytic recycling routes for PET fibres have become an essential solution. These recycling pathways must offer a sustainable alternative to traditional disposal methods, promoting the reuse of these valuable textile resources. Given the quantities of waste generated, chemical recycling of PET emerges as a particularly green promising approach. The nature of the textiles that make up these waste materials will significantly influence the choice of recycling processes to be implemented and their environmental impact. Textile waste is classified into three categories based on the production stage and use: pre-consumer, post-consumer, and industrial waste.[57] To optimize sustainability, textile waste is then recycled at the end of its life to produce new materials or monomers,[58] thus closing the production loop to return to the initial monomers.[59]

Chemical recycling of post-consumer textiles is suitable for various industrial and commercial applications, removing accumulated contaminants in the original fibres, dyes, and all additives, to produce fibres with properties identical to the original ones. Chemical recycling allows for the transformation of the PET chain into monomers (depolymerisation). In some processes, PET polymers can also be randomly broken into shorter chain fragments (oligomers). This PET degradation is achieved either by solvolysis (degradation by solvents) or by pyrolysis (thermal degradation in the absence of oxygen or air, or under vacuum).

Pyrolysis is widely used in industrial settings for the production of gases or fuels as part of the chemical recycling of various plastic waste.[60] However, for PET, this depolymerisation method is less suitable for eco-friendly processes as it primarily generates carbon dioxide and carbon monoxide during the thermal decomposition.[61]

Carbonisation is another thermal valorisation technique of PET with a view to produce carbon materials including activated carbon.[62,63] This technique has recently received much attraction since it can lead to green energy and sustainable environmental applications (batteries, water electrolysis, pollutant remediation, CO_2 capture, *etc.*).[64] PET-containing textiles and blends can also be treated by hydrothermal carbonisation yielding activated carbon with applications to pollutant adsorption and smart textiles conception.[65–67]

Solvolysis, requires water use, alcohols (mainly methanol or ethylene glycol), or amines. The reaction mechanism for PET depolymerisation consists of three nucleophilic substitution steps.[50] Fig. 6 illustrates the reaction pathways for the four most commonly used solvents to carry out this depolymerisation reaction: water (hydrolysis), methanol (methanolysis), ethylene glycol (glycolysis), and amines (aminolysis). The corresponding produced monomers can then be re-used for the synthesis of new PET.

These depolymerized PET waste materials are then regenerated and refined into emerging monomers (or oligomers) or transformed into new products. The regeneration of monomers or oligomers is followed by product purification until it reaches an acceptable quality level, suitable for reproducing PET materials or transforming them into new products.

In this recycling method, the material is first prepared as in the case of secondary recycling, up to cutting it into flakes or pellets. Then, it is chemically processed to produce monomers, oligomers, and mixtures thereof (dimers, trimers, *etc.*), such as bis(2-hydroxyethyl) terephthalate (BHET), terephthalic acid (TPA), glycols, dimethyl terephthalate (DMT), chemicals or fuels, petroleum liquids, and gases.[70] The produced monomers can be processed to create new PET packaging. Regenerated monomers can be mixed with virgin materials to improve quality. Monomer/polymer purification can be achieved through distillation, crystallisation, drying, and some additional chemical reactions.

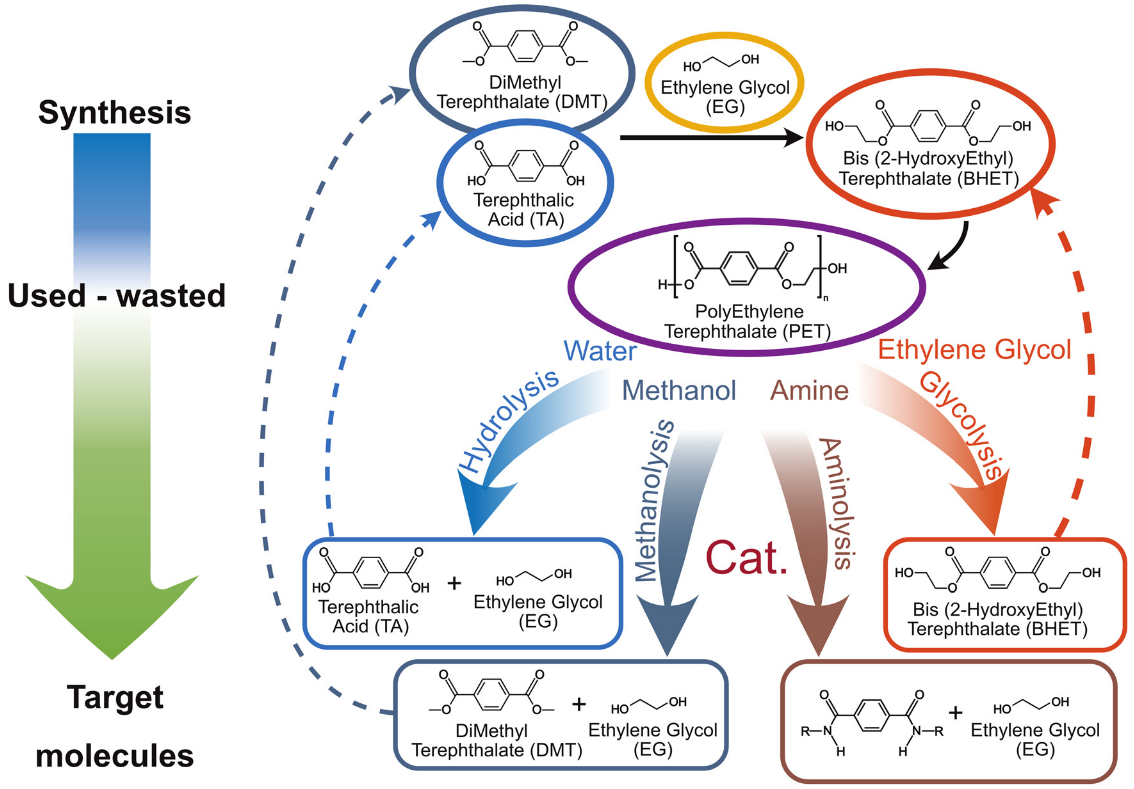

Fig. 6 PET chemical recycling main routes overview.

In the following sections we will describe the different chemical and enzymatic methods used for PET depolymerisation. Most are currently dedicated to PET from bottle origin and have been comprehensively described in this field in many recent reviews. Here we will rather focus on PET issued from textile fibres. Complementary to last reviews on "Polyester fabric recycling", which comprehensively detail the mechanical and technical recycling technologies of textiles[71] and blends containing PET,[72] we aim here at emphasizing the current progresses in greening PET depolymerisations especially if it turns out that fibres have not yet been considered in the general PET recycling. Hydrolysis methods (in neutral, acidic, and alkaline conditions) will be first presented before describing alcoholysis and glycolysis (a peculiar case of alcoholysis). Aminolysis and enzymatic processes will be exposed next. The economic aspects of recycling PET wastes will then be considered by presenting the current industrial approaches developed worldwide.

3.2. Hydrolysis in neutral media

Usually, two strategies are performed for PET hydrolysis in neutral media, uncatalysed or catalysed pathways. Uncatalysed PET hydrolysis achieves PET degradation with only water. Temperature, pressure, PET/water ratio, reaction time, PET source, PET particle size, energy source, and/or water phases are the studied parameters to improve PET conversion and TPA yields. Already, the phase water is important in the efficiency of PET degradation. Best TPA yield was obtained in saturated liquid water compared to compressed liquid or supercritical fluid.[73] Subcritical water conditions were also employed to investigate by NMR the PET depolymerisation chemical pathway. The analysis of PET depolymerisation products and the green metrics indicate the best reaction conditions depending on the interested products.[74] O. N. Onwucha *et al.* developed uncatalysed hydrolysis under neutral conditions offering high hydrolysis yields and the production of large easily filtered TPA crystals and requiring only several water washes.[75] This represents a significant advantage compared to the use of strong acid treatment to precipitate and recover TPA in most catalysed hydrolysis reactions in neutral media. The high TPA yields obtained (85 to 98%) required long reaction times (6 to 24 hours) and high PET/water ratios. This latter requirement is contrary to most of the previous reports.[76–78]

Most of the catalysts used during catalysed neutral PET hydrolysis are metallic however organic catalysts were also developed. The TPA molecule shows efficient catalytic properties on PET hydrolysis with a PET conversion of 100% and TPA yield of 95% at 220 °C with 180 min. It can be easily recovered and reused up to eight times allowing easier product separation in a wastewater free process.[79] Synergistic effects in the presence of other polymers like polypropylene or cellulose were examined. TPA yields increased in their presence at 250 °C for 30 minutes. Different experiments were completed to understand the nature of the chemical interactions at the origin of this synergy.[80] Stanica-Ezeanu *et al.* used common salts like NaCl, $CaCl_2$, $NaHCO_3$ or $KHCO_3$ as catalysts instead of the well-known metal acetate catalysts to hydrolyze PET and obtained similar or better results. They also studied PET kinetic degradation with marine water and estimated the time of waste PET depolymerisation in a marine environment. The depolymerisation rate is controlled by the surface water temperature and not on salt concentrations.[81]

PET depolymerisation under microwave irradiation in water with or without catalyst was also developed. PET depolymerisation can reach 90% with zinc sulfate catalyst at 200 °C and a microwave power of 250 W during 210 minutes and even 100% in pure water at a microwave power of 600 W and 20 bar during 120 minutes.[82,83] Quaternary ammonium polytungstophosphate catalyst ($[(CH_3)_3N(C_{16}H_{33})]_3PW_{12}O_{40}$), a dual functional phase transfer catalyst, exhibits good catalytic performances on PET hydrolysis in neutral media with 100% PET conversion and 93% TPA yield at only 145 °C for 2 h. Moreover, it could be reused without a significant activity decrease for at least three cycles.[84] To improve the catalyst reusability, Yan *et al.* developed Ni/γ-Al_2O_3 which exhibits 97% TPA yield with optimal experimental conditions. It remains active also after three cycles, but it can be regenerated by calcination.[85]

As a major aromatic compound, PET can also be converted back into arenes (toluene and xylene) by a Co/TiO_2 catalyst inducing both depolymerisation and hydrodeoxygenation reactions,[86] or to alkanes with TiO_2 nanoparticle supported Ru catalyst.[87] Catalytic conversion of PET into H_2 fuel in pure water using Ru-5ZnO/mesoporous carbon catalyst was reported. It combines PET depolymerisation and *in situ* aqueous phase reforming.[88]

In summary, PET hydrolysis in neutral media can be achieved with or without a catalyst but often requires high temperatures and reaction times, which represents major disadvantages from the perspective of developing sustainable depolymerisation of PET, particularly in the case of textiles (Fig. 7).

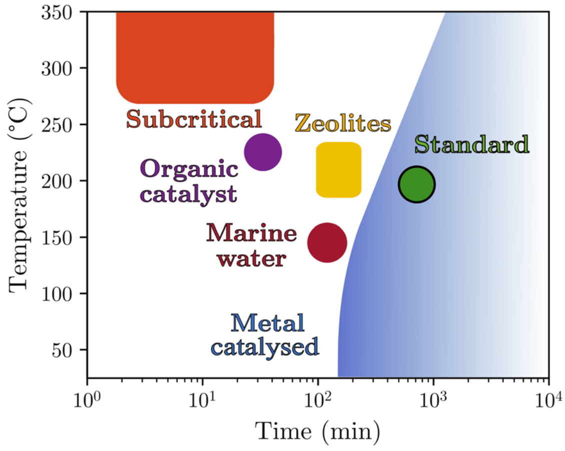

Fig. 7 Classification of hydrolysis methods in neutral media sorted by typical reaction time and temperature.

3.3. Hydrolysis in acidic media

PET hydrolysis in acidic media is a way to recover terephthalic acid and ethylene glycol from waste polymers mainly involving PET bottles, flakes, or powders, and reviewed recently.[89] However, the case of PET textile fibres remains poorly considered, with almost no example of green PET depolymerisation under acidic conditions. In this reaction, the ester bonds in PET are cleaved by water, and hydrolysis is catalysed by acids and H^+ donors.

Although the catalytic aspect of this reaction could at first glance be interesting in a green chemistry approach, it requires large amounts of highly concentrated strong acids at high temperatures. The main acids involved are sulfuric acid,[89] and nitric acid.[90] In the latter case, ethylene glycol is oxidized into more valuable oxalic acid. These processes are costly, difficult to handle, and raise major concerns about recyclability;[91] this could explain why this mechanism has not been preferred over other hydrolytic processes, especially in the case of PET textile fibres. Nevertheless, kinetic studies were performed with these acids to obtain reaction mechanism information.

Hydrolysis in acidic media follows a modified shrinking core model where successive layers are depleted from the bulk PET, starting from the surface.[92,93] The reaction can be monitored using complementary techniques to document both the changes in the polymer crystallinity (using WAXS and DSC) and the molecular alterations occurring during hydrolysis and formation of lower molecular weight species (by ^{13}C NMR).[94] To take into account recyclability concerns, the acid used can be issued from waste batteries.[95]

Besides these harsh conditions, other greener methods have also been considered and developed recently. PET recycling in mixed textiles could be considered in the case of polycotton or cotton-based blends (mixed PET and cellulose fibres) by selective hydrolysis of cellulose in 1 mol L^{-1} aqueous HCl or HNO_3 at reflux for a few hours.[96] PET depolymerisation can also be performed under mild conditions using solid acid catalysts in methanol. This environmentally friendly methanolysis produced dimethylterephthalate (DMT) from PET powder or textile fibres after a 2 h reaction at 160 °C.[97] A very recent promising approach is acetolysis using acetic acid, which has been exemplified with various PET sources including fibres (yarns).[98] This reaction was executed at 280 °C for 2 h leading to terephthalic acid and ethylene glycol diacetate after precipitation. Both components can be reused as is for further PET synthesis, offering a low-carbon process for complete upcycling of waste PET from different sources including textiles.

Other greener approaches were also developed for PET hydrolysis under acidic conditions and recycling, mainly applied on bottles or flakes. Among them, the use of the sulfated TiO_2 solid super acid catalyst in supercritical CO_2,[99] or the use of acidic zeolites under microwave irradiation were proposed.[77] Easily recoverable organic acids are also efficient, such as poly(styrene sulfonic acid) (PSS),[100] *p*-toluenesulfonic acid (PTSA),[101] or even terephthalic acid itself.[79] Such simple organic acids can also be useful in acido-alcoholysis.[102]

Finally, Brønsted acid-based ionic liquids,[103,104] and deep eutectic solvents,[105] represent another green alternative for PET hydrolysis in acidic media. These processes are promising and pave the way for future applications for PET waste textiles degradation and upcycling.

In brief, PET depolymerisation in acidic media often requires the use of strong, concentrated mineral acids (at high temperatures), which do not appear compatible with the development of sustainable processes. Alternative methods using weaker acids or softer acidic conditions still need improvements to consider eco-friendly depolymerisation of PET textile wastes.

3.4. Hydrolysis in alkaline media

Hydrolysis of PET in alkaline media has been widely reported in the literature, mainly involving PET bulk materials, pellets, or bottles.[106,107] In contrast, hydrolysis of PET textile fibres under alkaline conditions remains poorly described, especially when considering a green chemistry approach.

PET depolymerisation by alkalis is based on the nucleophilic cleavage of ester functions, ending in the formation of ethylene glycol and terephthalate salt. In this reaction, the alkali is a reactant and not a catalyst as it is fully consumed. This could appear problematical from the green chemistry perspective, where catalytic processes are preferred over stoichiometric ones.

3.4.1 Mechanism. Different studies have been completed to obtain a description of the mechanism underlying fibrous PET hydrolysis in alkaline media, based on kinetics. The reaction develops in a topochemical way, occurring mainly at the material surface rather than in the bulk. During the process, successive polymer layers of are removed without significant changes in molecular weight distribution in the remaining substrate.[108] This peeling process was first shown of first order with respect to the surface and the hydroxide ions concentration,[109] and was later modelled using a shrinking core model.[110] Microporous hollow fibres are therefore hydrolyzed faster than full ones.[111] As the reaction develops, the material surface properties are modified (increased roughness) and the bulk microstructure of the core polymers is also affected.[112] Moreover, the reaction kinetics depend on the PET fibre types in terms of orientation and crystallinity.[113] The surface-dependent initial mechanism is thought to be because of the very hydrophobic nature of PET, which cannot allow hydrophilic substances such as water and ions from alkalis to diffuse through the bulk of the polymer.

3.4.2 Monitoring the reaction. The reaction progress and the subsequent material properties and structural changes can be monitored using various complementary techniques. In solution, the formation of PET short oligomers and monomers (ethylene glycol EG and ionized terephthalic acid TA) can be classically measured by chromatography (LC-MS) or NMR spectroscopy. Also, the changes in chemical functions occurring during hydrolysis in alkaline media are easily depicted by FTIR spectroscopy, whether at the surface of the remaining fibres or on the reaction products precipitated after acidification. Morphological changes are evidenced by microscopic techniques such as AFM or SEM, while evolution of bulk properties can be followed by DSC (evolution of crystallinity) or tensile tests (changes in mechanical properties).

3.4.3 Complete PET hydrolysis into monomers (ethylene glycol EG and terephthalic acid TA). Complete PET depolymerisation can be useful for the further re-use of EG and TA in new molecular architectures or materials. This hydrolysis is usually performed using concentrated aqueous alkalis at elevated temperatures. Booth *et al.* focused on microplastic fibres which represent a major contribution to water pollution from textiles.[114] They developed a method to get a near-complete (>90%) hydrolysis within 3 h using 10% aqueous NaOH at 90 °C (complete hydrolysis was reached after 24 h). The use of reduced NaOH concentrations did not allow any significant hydrolysis and reducing the temperature considerably increased the reaction times. Stopping the reaction before completion by decreasing the temperature at desired times afforded partially degraded fibres which could be used as reference materials to study the effects and outcomes of environmental contaminants.

Moreover, when different kinds of polymeric materials are engaged together in tissues, the complete selective hydrolysis of PET can be useful to recover other polymer fibres such as cellulose for further recycling. This material recycling approach is an economically and ecologically viable solution,[115,116] as it could potentially be implemented at the industrial scale. In this process, the mixed fabric was treated with 5% aqueous NaOH for 1–24 hours at 90 °C for selective PET hydrolysis and cellulose recovery. The same method was also successfully applied to the selective hydrolysis of PET over PVC in coated woven fabrics.[117]

3.4.4 Partial weak hydrolysis to enhance PET properties for further functionalisation. When the reaction is stopped before completion, partial hydrolysis leads to a mixture containing shorter PET polymer chains with many negative charges. This decreases polymer global crystallinity and induces surface property changes. As initial PET fibres are hydrophobic and only slightly negatively charged, this alkaline pre-treatment enhances PET properties and has therefore often been used to favor further functionalisation. For example, a slight PET alkaline treatment (30 min, 2% NaOH at 98 °C) was used to create enough negative charges to combine it with positively charged biopolymer chitosan and produce a composite material.[118] This method is also useful to favor dyeing,[119] or incorporation of TiO_2 nanoparticles.[106] Moreover, this initial pre-treatment is also accompanied by an increase of PET surface roughness which has been exploited to produce PET fabrics with antimicrobial finish.[120] Selective partial hydrolysis of mixed blends is also a way to favor further selective enzymatic degradation,[121,122] or to produce Janus superhydrophobic PET textiles with uneven wetting properties.[123]

3.4.5 Use of additives and catalysts. Since simple PET hydrolysis in alkaline media requires concentrated alkalis used at high temperature (usually close to 100 °C) for several hours, softener conditions would make this process more economically viable at the industrial level. Green chemistry principles were applied to this reaction using additives or catalysts which could favor the reaction by reducing the duration, temperature, and reactant amount. As an example, PET fabrics pretreatment with aromatic alcohols promotes further hydrolysis,[124] while fatty alcohol 1-decanol was used on full fabrics to enhance wettability and softening thanks to water absorption in the polymer voids during hydrolysis (using alcohols as enhancers is described more in detail in the alcoholysis section).[125] The use of cationic surfactants and polymers during the reaction is also often reported. Their effects seem to depend on their structure. While CTAB had no significant enhancing properties,[108] DBDMAC affected the hydrolysis under alkaline conditions especially at moderate temperature and for PET fibres presenting low crystallinity.[126] Comparing different commercially available surfactants, the cationic ones are more efficient.[109] Another cationic surfactant prepared from diethanolamine was shown to favor hydrolysis of fabrics pretreated with organic solvents.[127] More recently, the use of CTAC as an accelerator to PET hydrolysis in alkaline media has shown its efficiency even at low temperature (80 °C) for 10 min.[128]

Other additives were more efficient then cationic surfactants for improved PET hydrolysis in alkaline media, for instance ionic liquid [BMIM]Cl.[129] Phase transfer catalysts, such as benzyltributylammonium chloride (BTBAC), are also useful and PET hydrolysis can be completed in less than an hour in 10% NaOH solution at 90 °C, allowing selective separation of cotton and PET in mixed textiles.[130] Besides organic additives, inorganic particles were considered for enhancing PET alkaline hydrolysis. TiO_2 particles can favor depolymerisation and promote degradation and breaking load loss of medical textiles,[131] because of the facilitated diffusion of hydroxide ions through the surface defects of polymeric material induced by the particles. Moreover, inorganic Bi_2O_3@N-TiO_2 composite particles were also used as photocatalysts for the enhanced degradation of PET fibre-based microplastics in alkaline media,[132] representing an eco-friendly remediation mechanism.

3.4.6 Alternative processes. Various other approaches were developed to make hydrolysis in alkaline media easier to handle and economically viable. For example, microwave-assisted PET depolymerisation under alkaline conditions enabled significantly shorter reaction times under mild reaction conditions. It is believed that, apart from the local temperature effect, the currents created by the microwaves in the material can increase ion mobilities and favor reactivity.[133] The energy input can also be mechanical. Indeed, solid-state ball milling was efficient for PET quantitative hydrolysis in the absence of solvent or after vapor-assisted aging,[134] offering a new development for more sustainable terephthalic acid production from waste PET. Pushing even more the efforts towards eco-friendly processes, PET recycling under very mild conditions was achieved recently thanks to the development of an intramolecular catalysis of hydrolysis in alkaline media, based on a biomimetic approach.[135] In this later example, the specific activity is increased more than 20 times compared to conventional hydrolysis while reducing the NaOH concentration down to 0.1 M.

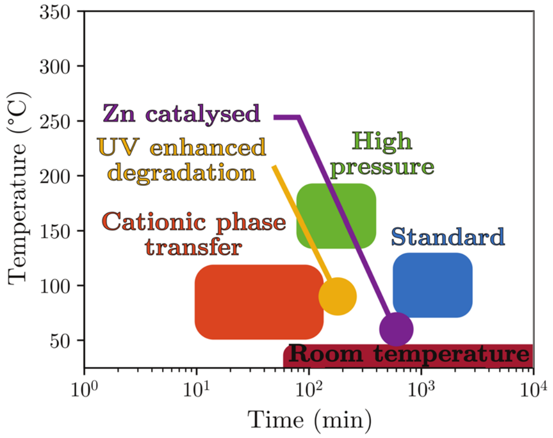

Fig. 8 Classification of hydrolysis methods in alkaline media sorted by typical reaction time and temperature.

It appears from these studies that the depolymerisation of PET in alkaline media has been much more developed than other hydrolytic methods (neutral, acidic). Lower temperatures and reaction times can be reached and eco-friendly methods are being developed, making this approach attractive for future environmentally compatible industrial processes.

3.4.7 NaOH and sustainability. Limiting NaOH (caustic soda) amount in industrial processes was identified as a major criterion to make them economically viable.[115] Indeed, its relatively high cost (500€/ton) is because of the high electrical power needed for production (mainly electrolysis of NaCl brine). Some industries provide now “green caustic soda” guarantying a sustainable electric power source (Westlake Vinnolit© for instance). Other alternatives are the use of less hazardous alkaline earth hydroxides such as $Mg(OH)_2$ or $Ca(OH)_2$, or even calcined banana peel which was involved in the green recycling of waste PET (Fig. 8).[136]

3.5. Alcoholysis

3.5.1 General alcoholysis. Polyester alcoholysis is pretty ancient with the first patents published in the 60′s,[137–139] and have the particularity to include every transesterification reaction with mono or poly alcohol/alcoholate of the polyester (except ethylene glycol which is a particular case). From a general view point, transesterification reactions (Fig. 9) are sensitive to the catalyst, the alcohol used to react, and the stoichiometric ratio.[140]

Early works on model systems showed a greater small alcohols reactivity and in particular methanol in transesterification.[141,142] According to this intuitive result, methanol was the first and most studied non-EG alcohol for PET alcoholysis.

A first important depolymerisation route is the catalyst-free depolymerisation, which is mainly performed under supercritical conditions at typically >220 °C/>6 MPa within tens of minutes.[143–147] While most works focus on methanol, recent

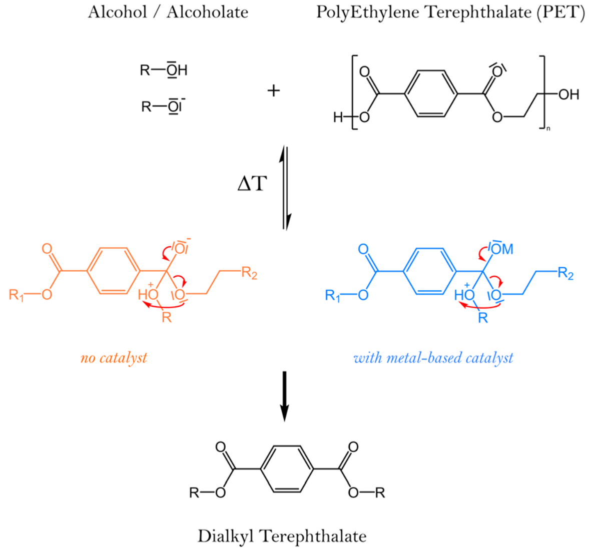

Fig. 9 PET alcoholysis through transesterification with and without catalyst.

studies focused on a greener alternative: ethanol use in pressurized conditions.[148,149] Thus, Lozano-Martinez and co-workers obtained about 94% PET degradation in 30 min at 275 °C/40 bar, and more recently, the effect of adding metal-based catalyst in the process was studied by Yang *et al.* (92% of degradation within 60 min at 270 °C/8 MPa with ZnO/Al_2O_3).[150]

High temperature alcoholysis (>100 °C) in subcritical (but still pressurized) conditions also represents a significant amount of research. Recent efforts demonstrated the possibility to use bio-based catalyst with decent results. Laldinpuii *et al.* demonstrated that bamboo leaf ash use at 200 °C for 2 h allows a decent retrieving monomers yield (78%),[151] and Gangotena *et al.* also used pectin derivatives to obtain an almost full depolymerisation at 160 °C for 4 h.[152] Zeolites can also present nice alternatives to the classical metal-based catalysts, showing similar performances (>90% within 30 min at 200 °C, MgO/NaY catalyst).[153] Ionic liquids also work pretty well in this temperature/time range,[154,155] even focusing originally on fibres waste.[156,157] Thus, Liu *et al.* and Bui *et al.* obtained almost full depolymerisation within 8 h at 180–205 °C. More recent works accelerated the reaction time, with only slightly decreased performances (78% degradation yield in 30 min at 195 °C).[154] Another alcoholysis field working within minutes at relatively high temperature is the microwave-driven depolymerisation.[158] However, this approach gives better results for hydrolysis or glycolysis than methanolysis,[159] and is often coupled with alkaline salt (which will be described later on).[160–162] Some innovative works used bio-sourced fatty alcohol combined with microwave to degrade polyesters.[163]

Low temperature alcoholysis (<100 °C) mainly involved solvent mixture doped with a catalyst. Solvent toxicity, the rarity of the catalyst and the reaction end time are keys factor to compare those methods. The co-solvent choice is critical, and two main molecules seems to be privileged: THF[164,165] and dichloromethane.[18,166] However most of those works exhibit long reaction times (tens of hours), in comparison with high temperature processes, and particularly with microwave-assisted alcoholysis.

3.5.2 Hybrid alcoholysis. Hybrid approaches combining co-solvent, alcohol and hydroxide salts are promising techniques, as both alcohols and hydroxide ions are suitable for PET degradation, and short-chain alcohols can solubilize those salts. One of the first works showed how alcohol/NaOH or alcohol/KOH mixtures with diverse organic solvents can almost fully decompose PET within one hour at 60–80 °C.[167] A similar approach was successfully applied on complex waste mixture by Cosimbescu and co-workers. This work also demonstrated a greater NaOH reactivity in a water/ethanol mixture with PET than in water/ethylene glycol obtaining more than 90% conversion in 2 hours at 80 °C.[168] Some other recent works exhibit shorter reaction times in the same conditions (80 °C, 30 min) by drastically increasing the ethanol amount (90%v), demonstrating the high efficiency of the alcohol/alkaline salt mixture, and suggesting that the reaction is rather driven by the alcoholic transesterification than the hydrolysis in alkaline media.[169,170] Indeed, such alkaline degradation in alcohol plus a co-solvent was studied by Tollini *et al.* and showed a predominance of transesterification in their conditions (70 °C/20 h/CH_2Cl_2 as co-solvent), and also showed the high interest of alcohol in an alkaline mixture for PET degradation.[18]

Going further, both Nikje *et al.* and *Arias et al.* published two works combining alcoholysis, degradation under alkaline conditions, and microwaves, drastically reducing the reaction time (below 5 minutes at the optimum).[160,161,171]

From a textile view point, either alkaline in alcohol or water are more efficient on PET fibres than on other polyester types.[172]

To summarize the chemical processes related to alcoholysis in an experimental domain aimed at identifying their environmental impact, Fig. 10 illustrates the positioning of each through reaction time and operational temperature found in the cited literature. Considering reaction time as a crucial parameter for industrial development, five processes stand out, allowing for short times ranging from 10 to 100 minutes: Hybrid alcoholysis, microwave-assisted alcoholysis, under supercritical conditions, using zeolite or ionic liquid catalysis. Conversely, long reaction times are observed when using bio-based catalysts or co-solvents. Regarding reaction temperatures, high temperatures (>125 °C) are employed for five processes, with only cosolvent-assisted alcoholysis and hybrid alcoholysis conducted at reduced temperatures, in the range of 50 °C to 100 °C. The overall environmental impact can be easily assessed through these two parameters.

Despite some historical limitations (moisture sensitive, high temperature/pressure if no catalyst/co-solvent), alcoholysis recent improvements exhibit competitive reaction times and temperatures, especially when coupled with alkaline salts.

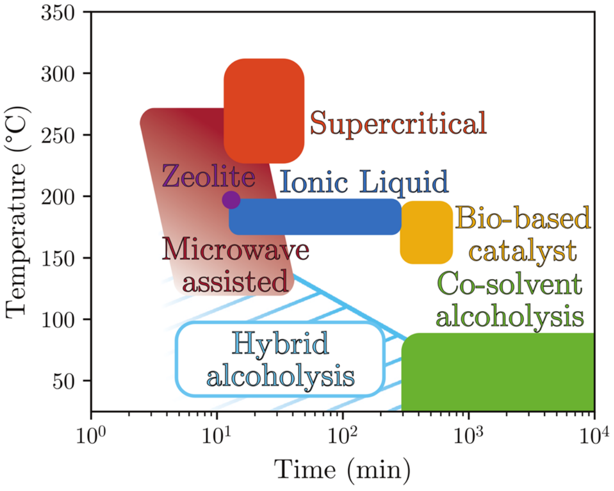

Fig. 10 Classification of alcoholysis methods sorted by typical reaction time and temperature.

Works can still be done to improve sustainability by offering greener co-solvents or reducing the alkaline salt amount used in the reaction; however alcoholysis remains an important approach for a greener recycling of polyester fibres. Indeed some industrial processes have already been developed (see section 4).

3.6. Glycolysis

Glycolysis, which has been patented since 1965, is the most commonly used method for PET recycling.[173] During glycolysis, PET undergoes a transesterification reaction with an excess glycol amount under inert atmosphere and temperatures around 200 °C.

This process leads to the PET depolymerisation and the formation of oligomers and bis-(hydroxyethyl)terephthalate (BHET) (Fig. 6).[174]

While the main focus was on achieving high-purity BHET, the depolymerisation of PET to create oligomers and polyols can have various applications in new materials including epoxy resins, vinyl esters, and unsaturated polyesters.[175–178] Over the years, significant efforts have gone into improving and optimizing the glycolysis process, resulting in its adoption by several industrial companies, including IBM, GARBO SRL, Ioniqa, and Goodyear.[179]

Through extensive research on PET recycling *via* glycolysis, scientists discovered that this process is slow and requires a catalyst for faster reactions. Moreover, without a catalyst, PET depolymerisation towards BHET was not complete and resulted in a mixture of oligomers and monomers. To address these challenges, researchers have focused on increasing the reaction rate and yield of BHET monomers by developing efficient catalysts and optimizing reaction conditions. So far, different methods were used for PET glycolysis, including solvent-assisted glycolysis (use of not eco-friendly organic solvents), supercritical glycolysis (supercritical conditions require very high temperatures and pressures)[180] and the most popular and the greenest process which is the catalysed glycolysis. Kinetics was also studied in the 90′s, showing the important roles of the catalyst and the temperature, which should be maintained relatively high (between 180 °C and 250 °C typically) to achieve full PET depolymerisation.[78,181,182]

Among the catalysts-assisted PET glycolysis, mainly three catalysts families are found in the literature: homogeneous catalysis (including metal salt-based catalysts and organocatalysts), ionic liquid-based catalysts, and heterogeneous catalysts (including zeolites, metal oxides, and other nanoparticles).

3.6.1 Metal salt-based catalysts and organocatalysts. Metal salts were the first catalysts tested in glycolysis PET depolymerisation and are still the most commonly used because of to their easy availability.[183] Metal cation allows the stabilisation of the intermediate species during the transesterification process (Fig. 11). Various reviews list works done to improve and optimize glycolysis processes.[50,184] Most of the studies were performed on PET from bottles. From those works, we can estimate the optimized yield of metal salt-catalysed glycolysis around 80% with a typical temperature ranging between 180 °C and 250 °C. Among these metal salts, zinc, manganese, cobalt, and lead acetate are classically used with a prevalence for Zn salts that exhibits the greatest degree of depolymerisation.[185] If the ethylene glycol/PET ratio reduces slightly over time, one can notice recent improvements on decreasing reaction times with depolymerisation occurring within minutes using $Zn(OAc)_2$ and with the addition of a good solvent for the PET dissolution.[186] Other different optimisations were proposed to make this depolymerisation process more environmentally friendly. Pingale *et al.* showed that microwave assisted depolymerisation with zinc acetate allows very short reaction times compared to conventional heating.[187]

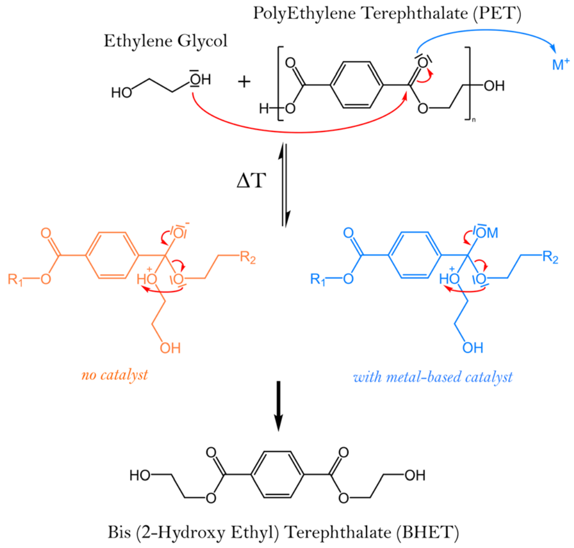

Fig. 11 PET glycolysis through transesterification with and without catalyst.

Composite catalysts of $Zn(OAc)_2$/DBU (DBU stands for 1,8-diazabicyclo[5.4.0]undec-7-ene) were also proposed to stabilize the reactive intermediate and improve yields. Also, to avoid the use of heavy metal salts, more environment-friendly catalysts were proposed using carbonates or bicarbonates.[188,189] Complete depolymerisation was achieved within one hour with sodium carbonate giving BHET yields about 75%. Organocatalysts were also proposed as eco-friendly alternatives to metal salts-catalysts. Fukushima *et al.* showed that TBD (TBD stands for 1,5,7-triazabicyclo[4.4.0]dec-5-ene) facilitates PET depolymerisation thanks to H-bond formation.[190] Moreover with the use of a TBD:MSA protic ionic complex, yields of over 90% BHET were obtained in a solvent-free reaction and the catalyst can be recycled multiple times without losing its activity.[103]

However, conventional glycolysis methods described above, that are commonly used for recycling PET from bottles, are often poorly efficient when it comes to recycling PET from heterogeneous waste textiles.[191] Indeed, PET textile fibres with high crystallinity make it difficult for glycolysis agents to penetrate, so that depolymerisation gradually and slowly takes place from the surface to the bulk. Among metal salts catalysts proposed on fibres, titanium(IV)-phosphate showed greater catalytic activity than $Zn(OAc)_2$ when applied on fibres with respectively 61 and 67% yields. Lei *et al.* proposed a feeding process using tin chloride ($SnCl_2$) that allows a significant increase in the PET fibres conversion of 92.5% and yields of 70.4% compared to 28% and 14.4% respectively with the one-step reaction. In this study, the PET fibres were added stepwise at regular intervals. The authors suggest that this method allows a rapid transformation of PET into a homogeneous system, thereby accelerating the reaction efficiency.[192]

3.6.2 Ionic liquid-based catalysts. More recently, ionic liquids (ILs) were proposed as new eco-friendly catalysts and solvents to perform PET glycolysis. They fully converted PET efficiently with consistent BHET yields in the 75–85% range.[184,193] Wang *et al.* developed efficient and reusable amino acid-functionalised ILs that can reach 75% BHET yield after 50 minutes at atmospheric pressure and at 170 °C.[194] Liu *et al.* obtained Very high yields (85%) using choline-based IL after 4 hours at 180 °C. The increase in the depolymerisation process was attributed to H-bond formation between ethylene glycol and the IL, activating thus the ethylene glycol.[195] Although the depolymerisation temperatures remain substantial and comparable to that of metal catalysts, the major advantage of ionic liquids is the ease of extraction of the final product. As a sub-category of ionic liquids, we can find deep eutectic solvents (DES), which are formed through the interaction between hydrogen bond-acceptor and hydrogen bond donor species.[196] Under optimized conditions, 100% PET conversion was obtained with a 83% selectivity using urea/$ZnCl_2$ deep eutectic solvent.[197]

As with the use of metal salt catalysts, very few examples of glycolysis were performed on PET fibres. In a study with different PET material sources, Bush *et al.* showed that carpet fibres underwent PET full conversion and the greatest efficiency, compared to other PET sources, in BHET production (52%) using Gd salts combined with 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc). These results were attributed to the large polymer surface area, even in the presence of additives and dyes.[198] Liu *et al.* used amino acid ionic liquid catalyst and determined the optimal conditions by response surface methodology (RSM) to obtain 84.5% BHET yields on PET fibres.[199]

3.6.3 Heterogeneous catalysts. For the last fifteen years, heterogeneous catalysts have gained popularity for PET glycolysis because of their excellent catalytic efficiency and their easy separation techniques. Zeolites were first to be tested on PET bottle wastes enhancing the catalytic activity thanks to their mesoporous structures. The BHET yield exceeded 60%, comparable to that of more traditional heavy metal catalysts but the catalyst was much easier to recover.[200] Different types of metal oxide-doped silica nanoparticles (SNPs) were also used for the PET degradation with very high yields obtained with Mn_3O_4/SNPs at 300 °C. This high yield was attributed to the large surface area and the porous structure of the nanocomposite.[201] An original sustainable source of heterogeneous catalysts is calcium oxide derived from eggshells. Similar yields as with metal salts catalysts were obtained (76.4%) on PET bottle wastes.[202] Other matrices were also tested on bottle PET, like polyoxometalates and metal–organic frameworks (MOFs) with BHET yields comparable to those obtained with metal salts.[203] An example of a paramagnetic ionic liquid-coated $SiO_2@Fe_3O_4$ nanoparticles was recently tested by Cano *et al.* showing approximately 100% yield and more than twelve consecutive glycolysis cycles at 180 °C.[204] A similar glycolysis process using ionic liquid as catalyst is currently applied on post-consumer waste by the Ioniqa Company, based on paramagnetic nanoparticles which can be separated using a magnet.

Some recent examples of polyester textile wastes depolymerisation were reported using nanoparticles. Vinitha *et al.* obtained BHET with 90% yield using silver-doped zinc oxide nanoparticles under microwave irradiation for 30 minutes at 180 °C.[205] Guo *et al.* demonstrated that Perkalite F100®, which is an aluminium magnesium layered double hydroxide nanocatalyst, efficiently worked for PET depolymerisation with a BHET yield over 80% after a pre-degradation step.[206] Similarly Mg–Al double oxides nanocatalysts were also used to perform fibre to fibre recycling at 240 °C with a BHET yield of about 80%.[207]

3.6.4 Glycolysis disadvantages/advantages. Glycolysis has the property to generate BHET and oligomers. As it is hard to isolate BHET from other oligomers, emphasis is often placed on PET upcycling rather than fibre-to-fibre recycling (resins in particular).[208–210] The need for relatively high temperatures (>150 °C) whatever the catalyst is a limitation which could impact the sustainability of this method on the large scale. However, the method is considered as less impacted by contaminations in comparison with classical methanolysis for instance, and do not required exotic conditions. For these reasons, PET glycolysis is a well-established approach to recycle PET at the industrial scale.

3.7. Aminolysis

PET solvolysis can occur upon treatment with amines or ammonia, hence providing terephthalamide derivatives. Because of the increased nucleophilicity of amine functions, in comparison to hydroxy groups, the aminolytic process is favored over alcoholysis and thus requires milder operating conditions.

Typical aminolytic depolymerisation reactions are carried out using primary amines at temperatures ranging from 20 °C to 200 °C and generally under atmospheric pressure and neat conditions. The use of homogeneous or heterogeneous catalysts, sometimes combined with microwave irradiation, allows the aminolysis efficiency to improve by reducing the reaction times, reducing operating temperature ranges, and improving monomeric product yields.

Importantly, one must distinguish two main approaches in PET aminolysis. The polymer can be partially degraded, to obtain lower molecular weight fragments, or even only superficially reacted. This allows modification of PET fibres towards different or even improved mechanical and/or physicochemical properties. Conversely, deep aminolysis of PET, *i.e.* complete depolymerisation, leads to the formation of terephthalamide-based monomers. This approach is especially interesting for upcycling, either by transforming the obtained monomers for uses as small molecules or for polymer reprocessing. To date, only superficial aminolysis processes have been developed at the industrial scale, while deep aminolysis still runs only at the laboratory scale.

In a seminal study, Farrow *et al.* carried out partial aminolysis of PET fibres in the presence of aqueous methylamine at room temperature.[211] Starting materials of different crystallinities and orientations were subjected to aminolysis during various times and the weight loss and the crystallinity of the resulting fibres were assessed. From these experiments, the authors concluded that the aminolytic degradation proceeds in three main steps: (1) fast attack at amorphous regions, with small changes in weight and crystallinity; (2) chains scissions leading to an important weight decrease and increase in degree of crystallinity; (3) gradual decrease in degradation rate through a slower attack at both amorphous and crystalline regions. Later, several papers reported on the use of aminolysis (using methyl- to *n*-butylamine) to increase crystallinity of PET fibres to study their morphologies and mechanical properties.[212–215] Overall, these studies showed that aminolytic partial degradation leads to molecular weight and samples weight decreases along with a diminution of mechanical resistance. For instance, Collins *et al.* established a linear relationship between the average molecular weight and the ultimate tenacity of aminolyzed PET fibres.[213] Interestingly, Holmes treated PET fibres either with aqueous or gaseous *n*-butylamine and observed by SEM that surface of water-aminolyzed fibres developed radial cracks while axial cracks appeared in case of gaseous aminolysis. Fibres with axial cracks broke at reduced breaking loads than those presenting radial defects.[212]

Superficial aminolysis methods were developed, mostly using ethylenediamine, to enable surface derivatisation while preventing polymer degradation.[216–220] Hence, it is then possible to easily install various functional moieties onto the surface of PET-based fabrics. For instance, dying, introduction of hydrophilic functions (*e.g.* zwitterionic polymer brushes) for antifouling purpose or of antibacterial groups were achieved. Those modifications did not significantly affect the mechanical properties of the treated fabrics compared to virgin fibres.

Deep aminolysis, *i.e.* complete depolymerisation towards monomers, developed in the 2000′s. Most of the corresponding papers report on catalyst-aided processes, while there are fewer studies dealing with uncatalysed reactions. In 2001, Spychaj *et al.* described aminolysis of PET flakes from bottles in the presence of triethanolamine or polyamines at 210 °C.[221] The maximum depolymerisation conversion was reached after 150 minutes of heating. However, the molecular weight of the products was not characterized (only hydroxyl numbers and viscosity were measured), and it is thus not possible to conclude on the process efficiency as a deep aminolytic degradation. In a more recent study by Hoang and Dang, treatment of flakes with ethylenediamine at 100 °C provided oligomers (tri- to nonamer) that were precisely characterized.[222] Also, the trimer to other oligomers ratio could be tuned *via* modifying the amine/PET ratio, up to quantitative degradation. Quantitative aminolysis to monomers was achieved by Soni *et al.*, by submitting PET flakes to treatment with methyl-, ethyl-, or *n*-butylamine at room temperature during a maximum time of 45 days.[223]

Catalysed aminolysis of PET was extensively studied over the past two decades. Acetate, sulfate, carbonate, and bicarbonate salts of metals such as sodium, potassium, zinc, or lead are among the most used catalysts. In 2003, Goje *et al.* reported the deep degradation of PET powder (50–500 µm particles) in the presence of hydrazine hydrate, DMSO, cyclohexylamine and lead acetate, at 66 °C. Terephthalamide dihydrazide (TPDH) was isolated in a quantitative yield after 3 h and using 127.5 µm particles. The authors claimed that adding cyclohexyalamine to the reaction medium increased the reaction rate, although this effect was not rationalized in the paper. Further studies dealing with hydrazine-mediated aminolysis of PET flakes from bottles in the presence of benign sodium salts as the catalyst were also published. Conventional heating afforded TPDH (85% yield) in 3 h,[224] while microwave heating (domestic microwave oven) led to a similar result in only 5–20 minutes.[225] TPDH is an interesting monomer as it can be further used as starting material to prepare value-added molecules, such as plasticizers for polyvinylchloride (PVC),[226] antibacterial agents,[227] or textile dyes.[228] However, hydrazine hydrate is a very hazardous and toxic compound, which must preclude its use in PET upcycling.

An interesting alternative to hydrazine hydrate is to employ hydroxyamines (*e.g.* ethanolamine) as degradation agents.

Indeed, the obtained monomers are robust, thanks to the amide bonds, and the presence of end hydroxyl groups allows for further functionalisation or polymer reprocessing. Combination of ethanolamine with sodium acetate or bicarbonate furnished excellent yields in bis(2-hydroxy ethylene)terephthalamide (BHETA) monomer, under conventional (170 °C, 8 h) or microwave heating (700 W, 5–7 min), even using PET fibres as starting material.[229–231] Very recently, Pastore and colleagues depicted the synthesis of UV-curable poly(urethane acrylates) from terephthalamide derivatives obtained by NaOAc/microwave-catalysed aminolysis of PET flakes with newly synthesized β-hydroxyamines.[232] Degradation of PET to BHETA was described by Achilias *et al.* under microwave irradiation but without the aid of a catalyst. In this detailed study, the best results were obtained by performing the reaction under irradiation at constant power of 75 W or 100 W, respectively in 20 or 3 minutes.[233]

Fukushima *et al.* reported in 2013 on the use of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as an effective organocatalyst to convert PET flakes to monomers with various primary amines at temperatures ranging from 45 °C to 190 °C.[234] In particular, ethanolamine gave the best result, with a yield of 93% in BHETA by running the depolymerisation at 120 °C for 2 h. Later, Demarteau *et al.* combined TBD with methanesulfonic acid (MSA) to achieve PET aminolysis in a few minutes (8–15 min) at 180 °C with ethanolamine (93%) or *N*-methylethanolamine (87%).[235] The monomer derived from *N*-methylethanolamine-mediated degradation was next used for preparing poly(ester-amide)s. Nica *et al.* derivatized TBD with 4-(methoxycarbonyl)benzoate to prepare a new and effective organocatalyst (M4HPP). Using M4HPP on PET flakes in the presence of ethanolamine or ethylenediamine at 190 °C afforded quantitative yields of monomeric products in only 3–10 minutes.[236] Deep eutectic solvents as well as ionic liquids are known as green catalysts in a range of applications including PET lysis. Musale *et al.* utilized choline chloride·2 $ZnCl_2$ to convert PET flakes to BHETA nearly quantitatively, in refluxing ethanolamine for 90 minutes.[237] When the aminolysis was carried out with diethanolamine and the resulting mixture was treated with 25% hydrochloric acid, terephthalic acid was isolated in 86% yield. The ionic liquid Hmim. TfO was also successfully used with ethanolamine (110 °C, 40 minutes) to afford BHETA in 89% yield.[238]

Tawfik *et al.* studied heterogeneous catalysis of PET aminolysis with dibutyltin oxide (DBTO) to produce BHETA from PET flakes at 62% yield after 4 h of heating in refluxing ethanolamine. With a view to make the process greener, the same authors exposed the PET/ethanolamine/DBTO mixtures to sunlight, keeping the vessel in a sand bath. Quantitative degradation was however achieved after 60 days of exposure.[239] Examples of heterogeneous catalysis by β-zeolites, montmorillonite KSF (clay) and Sn-doped ZnO particles were also reported (in ethanolamine at 150–170 °C), each method providing very good BHETA yields.[240,241]

Besides amine-mediated depolymerisation, ammonolysis, the process using ammonia as the nucleophilic reagent, was also investigated. The reported studies described the use of liquor ammonia, at high (20 bar) or atmospheric pressure and at 40–180 °C, in the presence of a catalyst (zinc acetate or CTAB).[242,243] However, despite high reported yields, the ammonolysis process is scarcely used because the major product, namely teraphthalamide, presents a limited interest, in particular for polymer reprocessing.

In conclusion, aminolysis presents a high potential for PET upcycling and PET fibres functionalisation rather than recycling. The major drawback of this approach is the necessity to use large amounts of eco-unfriendly amines, sometimes under heating at temperatures over 150 °C. These are probably the main reasons why aminolysis is a process restricted so far to the laboratory scale. Despite these limitations, the different reported methods (Fig. 12), and the variety of available amines, including functional ones, offer many possibilities to generate new monomers for polymer chemistry or other applications. The development of new catalysts/eco-friendly processes and the use of more acceptable amines should lead to consider aminolysis of PET textiles suitable for industrial applications.

3.8. Enzymatic PET depolymerisation

As PET is an ester-linked polymer, whole microorganisms or purified enzymes such as esterases could be used to achieve a green and sustainable polymer hydrolysis into its monomers *via* a more environmentally friendly process, therefore avoiding harsh chemicals and/or energy requiring processes.[244]

However, because of its rigid aromatic structure, PET has long been regarded as non-biodegradable. The high stability of the polymer's backbone, its crystallinity (especially in textile fibres) and hydrophobicity are some of the main factors which restrict polymer biodegradability.[245–247]

All these features make them even more difficult to biodegrade than bottle-PET or aliphatic polyesters. Enzymes are sensitive to the polymer-chain flexibility, which relies on the polymer structure (aliphatic or aromatic) or on its crystallinity, which is a limitation for the enzyme active site accessibility.[248]

Some groups have tried to enhance the PET biodegradability by synthesising copolymers with readily hydrolysable aliphatic polyesters (Koshti *et al.*, *i.e.*).[249–251] Nevertheless, it does not address the recycling problem of the already existing PET wastes.

Up to recent years, most of the abundant literature concerning the enzymatic treatment of fabrics, including PET fibres, was for the modification of their surface properties. Enzymes can be efficiently used as competitive alternatives to the chemical surface modification of fabrics (*e.g.* wettability, desizing, scouring, bleaching, dyeing and finishing, for which the existing alternatives use very harsh chemicals whose environmental disposal causes many problems).[252–255]

It is only recently that PET-hydrolases were identified,[256,257] with the first report of a hydrolase from *Thermobifida fusca* less than 20 years ago. Since then, several PET-hydrolases and cutinases (cutine hydrolases) have been described, among which the promising leaf compost cutinase (LCC).

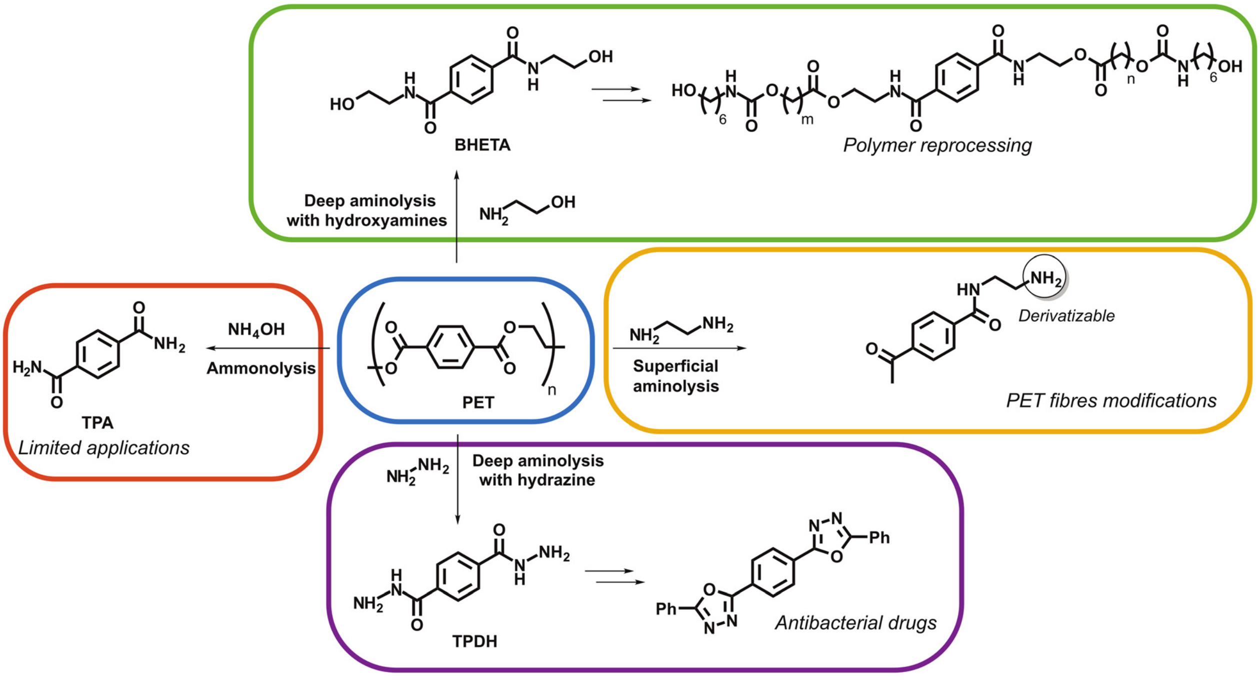

Fig. 12 PET degradation paths using amines.

The limitation for enzyme use lies in the fact that PET has to be hydrolysed at temperatures greater than its glass transition temperature, where the polymer chains become flexible, making them more accessible to the enzyme active sites. That implies the search for thermophilic PET hydrolases.[257]

High crystallinity can also be overcome by using moist-solid reaction mixtures as will be further discussed in the "enzymes in the recycling of textile PET fibres" part.[258]

Aggregation problems have sometimes been reported, which were addressed by cutinases (LCC) glycosylation.[259]

And sometimes the association of two different enzymes was necessary because of incomplete reactions forming both monomers and oligomers which blocked the reaction completion.[260]

Another limitation for enzyme use of is the long reaction times which can hardly be reduced by heating because of the heat sensitivity of PET-hydrolases.

Using computer-aided enzyme engineering, Tournier *et al.* created a modified leaf-branch compost cutinase (LCC) with increased thermal stability that allowed them to achieve a minimum of 90% PET degradation in less than 10 h, which is the best result obtained so far by enzymatic hydrolysis.[261] They also showed that the biologically recycled PET obtained exhibit the same properties as petrochemical PET.

However, these modified enzymes were efficient in the degradation of bottle-PET samples. An on-line biodegradation/recycling of PET bottles in under development.

It would be of great interest to check their efficiency towards the degradation of PET textiles fibres, containing dyes or mixed with other fibre types.

3.8.1 Enzymes in the recycling of textile PET fibres. A synergistic chemo-enzymatic PET hydrolysis from textile waste was developed for the production of high purity TPA (97%) avoiding harsh chemical treatments.[262] A chemical pre-hydrolysis was performed under neutral conditions (T = 250 °C, P = 40 bar), which led to the conversion of PET into 85% TPA and small oligomers. The latter were then hydrolysed in a second step using the *Humicola insolens* cutinase (HiC) yielding 97% pure TPA, therefore comparable with the commercial synthesis grade TPA (98%).

To recycle textile waste, it is sometimes necessary to separate the cotton and PET components. One of the components should be depolymerized or degraded while the other component should be maintained.

Two different strategies are proposed to recycle mixed polyester-cotton textile wastes.

In the first, only the cellulose was enzymatically hydrolysed and the PET fibres were recycled without depolymerisation, which provided a clean and sustainable way of PET separation. The recovered PET from textile waste fibre were re-spun into new fibres by melt spinning.[263]

In the second, alkaline pre-treatment was effective for depolymerizing PET at 70–95 °C temperatures. Three products were obtained from the process: cotton cellulose, TPA, and an aqueous phase containing EG. Terephthalic acid (TPA) can be precipitated by adjusting the aqueous phase pH.[121] However, the separation of TPA and EG was not considered in this study.

Enzymatic hydrolysis does not always require fibre separation thanks to the high substrate enzyme specificity. Also, it allows the depolymerisation under mild and green conditions (*e.g.*, aqueous reaction media, atmospheric pressure, and temperatures up to 65–70 °C).

And despite the recent breakthrough in protein engineering that allowed the elaboration of PET hydrolases such as modified LCC with increased thermal stability and high activity, still these enzymes are not very efficient in the hydrolysis of high-crystallinity PET, such as spun PET fibres compared to bottle PET.[264,265] The necessary melt-amorphisation step of PET prior to the enzymatic hydrolysis is energy demanding and restricts its use to rather clean PET wastes, which is not the case for textile wastes.

High-crystallinity PET (up to 46%) in mixed PET/cotton textiles could be directly and selectively depolymerized to terephthalic acid (TPA) by using a commercial cutinase from *Humicola insolens* under moist-solid reaction conditions (*i.e.*, very high solid loading), with gentle mechanical mixing (mechano-enzymology) instead of standard aqueous solutions, affording up to 30% TPA yield.[266]

The process can be readily combined with cotton depolymerisation through simultaneous or sequential application of cellulase enzymes providing up to 83% glucose yield without any negative influence on the TPA yield, showing the potential for both simultaneous and stepwise depolymerisation of PET and cotton under mild, environmentally benign conditions.

The authors compared terephthalic acid (TPA) production from petrol to that from enzymatic PET depolymerisation, which revealed a 69% lesser energy requirement and 17% lesser greenhouse gas emissions for the latter.

Although enzymatic processes for depolymerizing bottle grade PET are rapidly developing on an industrial scale, they are not easy to transpose to PET textiles. The high crystallinity of PET and the need for prior treatments make this application much more complicated. Due to the high energy inputs on these pre-treatments and the very long reaction times required, the depolymerisation of textile PET by enzymatic processes still requires major improvements to be considered a sustainable route for textile recycling.

4. The economic aspects of recycling polyester wastes

The industrial developments for the chemical recycling of PET are particularly advanced for alcoholysis reactions, and two companies operate in this sector:

- Evonik© has expertise in high temperature depolymerisation using an autoclave.[27] However, they seem to focus on uncoloured bottle recycling, producing high quality monomers, suggesting some limitations because of polyester contaminants. However supercritical ethanol is well suited for multilayer packaging treatment, and therefore offers a wider range of perspectives than only bottle PET.[267] So, it might be possible to use it for fibre treatment.

- Loop© recently patented several processes, based on a hybrid approach of alcoholysis/alkaline in chlorinated solvent.[268,269]

- Glycolysis is also involved: Ioniqa Company has developed a glycolysis process using an ionic liquid as a catalyst, based on paramagnetic nanoparticles that can be separated using a magnet. This process is currently being applied to post-consumer waste.

4.1 Recycled PET market, feasibility and chain sourcing

In any recycling project, it is crucial to assess the commercial potential of products derived from the chemical recycling of PET and their valorisation.[270–272] This approach is essential, and begins with a market analysis based on several points:

1. Understanding the demand dynamics for recycled products, especially in packaging, textiles, and construction sectors.

2. Competitive analysis concerning virgin ingredients used in PET manufacturing, and thus the market share for recycled ingredients, which may entail higher costs.

3. Regulatory considerations, particularly in packaging, that could influence the adoption of PET products derived from recycled ingredients.

4. Market viability assessment, including the availability and reliability of the PET recycling supply chain (collection, sorting, and processing). This aspect is crucial for evaluating the necessary recycling infrastructure.

5. The industrial success of the recycling process will also depend on consumers' perception of the quality, safety, and efficiency of recycled PET products, as well as their environmental benefits. Innovative aspects of recycled products and marketing strategies can further enhance consumer appeal. Educational initiatives can promote the acceptance and adoption of recycled PET. Implementing targeted marketing campaigns can raise consumer awareness and promote the advantages of recycled PET products.

The viability of a recycling industry needs also a fine analysis the sourcing of PET to be recycled. A primary source of PET includes beverage bottles, food containers, and polyester textiles, primarily from post-consumer waste streams. By-products from various industries, such as packaging manufacturers, textile producers, and beverage companies, contribute to a secondary PET supply. Chemical recycling benefits from by-products generated in industrial processes like polyester manufacturing, where PET scrap and off-spec products can also be considered. The supply chain for sourcing PET includes also, waste management facilities, collection networks, logistics and transportation and sorting and cleaning facilities (processes to remove contaminants). Ultimately, the industrial viability of PET chemical recycling will require supportive policies and regulations, to encourage the adoption of recycled PET products. In conclusion, a comprehensive understanding of the market readiness for recycled PET products is essential, identifying both barriers and opportunities for stakeholders to drive sustainable growth and consumer acceptance.

4.2 Scale up of the recycling processes and industrial development

The transition from lab-scale to industrial-scale production for key technologies involves meticulous evaluation of various parameters. Scalability, profitability, regulatory compliance, and technological adaptability all need to be assessed. Comprehensive cost–benefit analyses are imperative to assess economic viability and the potential return on investment. Pilot tests must be carried out to validate scalability and optimize production processes before full-scale implementation. Implementation timeframes and resource requirements must be carefully defined to streamline the transition process. The integration of sustainable practices and environmental impact assessments should be an integral part of the transition strategy.

Cooperation between laboratory and industrial teams is essential for knowledge transfer and skill development. Overall, a systematic and interdisciplinary approach is imperative to successfully move from laboratory to industrial-scale production of key technologies. Leading companies in PET chemical recycling span several countries, including the United States, Germany, Japan, and the Netherlands. Companies like Loop Industries (USA) and APK AG (Germany) specialize in processing PET, addressing both bottles and fiber. Japan's Teijin Limited and Netherlands-based Ioniqa Technologies are prominent in PET fiber recycling. Teijin processes PET fibers for automotive and apparel industries, with an annual capacity exceeding 30 000 tons. Ioniqa employs a proprietary technology to convert colored PET waste into high-grade raw materials.

In the USA, Loop Industries specialize in depolymerisation of PET by methanolysis since 2019, producing high-quality terephthalic esters.[273] They process over 50 000 tons annually, contributing to a circular economy. Meanwhile, in France, companies like Carbios employ enzymatic depolymerisation techniques, focusing on both bottles and fibers, with an annual capacity of 40 000 tons. The economic balance sheet of these companies shows promising growth, driven by increased demand for sustainable solutions and regulatory incentives. Their innovative approach promises sustainability gains and economic viability. All over the world, new companies are being deployed, as Eastman (USA), Itelyum (Italy), Reliance (India), Jeplan (Japan) and much more.[274] Regardless of their interest, these projects demonstrate the feasibility and scalability of chemical recycling of PET. The future of the field looks bright, with investments pouring in and technological advancements paving the way for a greener, more efficient recycling ecosystem.

5. Comparative study

The comparison of chemical recycling methods for textile waste can be conducted according to various sustainability and greenness criteria, which should be defined by linking them to industrial specificities and environmental challenges.

5.1 Sustainable development goals and green chemistry

In 2015, the United Nations released 17 objectives known as the Sustainable Development Goals (SDGs). These SDGs were adopted by all Member States of the United Nations (UN) as part of the 2030 Agenda for Sustainable Development, which outlines a 15-year plan to achieve these goals and improve human well-being by addressing crucial issues of social, environmental, and economic sustainability.[275,276] Regarding the recycling of textile waste, aiming to develop a circular economy, the developed methods primarily reference three objectives. The first, ensuring access to clean water and adequate sanitation (SDG 6), is linked to fabric washing processes, solvents used, and various reactions involved. The second, promoting responsible consumption and production of resources (SDG 12), is related to the possibility of producing new textiles or materials from textile waste. The third, addressing the effects of climate change (SDG 13), is linked to waste valorisation and consumption of fossil and energy resources.

Textile recycling aims to promote a circular economy by organizing the production of materials from waste with equivalent quality over time. In this vein, depolymerisation methods being studied enable the establishment of a long-term supply chain in which today's used garments can become tomorrow's materials. To ensure these three SDGs are met, it is necessary to study the potential environmental impacts of industrial processes implemented in textile recycling. This study is only meaningful in its final industrial application and not at the fundamental stage, which does not consider industrial scales and material and solvent flows. An initial assessment of methods can be made based on SDGs 12 and 13, but publications do not consistently provide all the necessary data for a comparative evaluation. Degradation yields, which characterize the amount of monomer obtained per mass of treated waste, vary from 62% for enzymatic hydrolysis reactions to 100% for many chemical depolymerisation methods. However, many articles do not consistently provide these values (Table S1, ESI†). While it is possible to say that depolymerisation methods align with these goals, it is not possible to classify them qualitatively based on these criteria.

Paul Anastas and John Warner are the pioneers of green chemistry. They developed an approach for designing chemical processes and products that are environmentally friendly.[277] This approach seeks to prevent pollution at its source by limiting the use of harmful substances. The principles of green chemistry emphasize the creation of safer chemicals, the use of catalysts rather than stoichiometric reagents, and the reduction of waste production. According to this approach, pollution prevention should be considered at the molecular level, which involves reducing pollution sources throughout the life cycle of chemicals.[278] The same considerations as previously mentioned using the SDGs should be taken into account to classify depolymerisation methods in terms of the 12 principles of green chemistry. The lack of comprehensive data on degradation yields, in particular, does not allow for a rigorous evaluation.

5.2 Green metrics

The methods allowing PET depolymerisation are quite diverse, as demonstrated in the previous chapter. To compare these methods, a first approach allows positioning them in a 2D experimental domain depicting the reaction time and temperature of all the cited studies. Fig. 13 illustrates this experimental domain. It appears that certain methods have been developed in very broad domains such as hydrolysis in acidic media or aminolysis. In contrast, glycolysis or enzymatic methods are often developed in more restricted temperature and reaction time ranges.

Table S1 (ESI†) provides a summary of the cited methods found in the literature, offering quantitative information on material flows between recycled waste, reaction conditions, and depolymerisation yields for monomer production. To rank the reactions based on the data in this table, it is possible to use green metrics. These indices allow for the quantification of contributions from methodological developments in various principles of green chemistry: atom economy, energy efficiency, waste reduction, and so on. The simplest index that can be calculated to classify different reactions is related to atom economy (AE) published in 1991.[279] AE is calculated based on stoichiometric data but does not take into account solvent use. In the case of solvolysis reactions, this index is therefore not meaningful, as the solvent will have a considerable effect on various depolymerisation reactions. The second index, E factor, described in 1992, calculates the ratio between the waste mass produced and the product mass purified by different reactions.[280] For the calculation of the waste mass generated, a widely used approximation assumes that 90% of the solvents used are industrially recycled, while 10% of the mass of the solvents used becomes waste.

In the case of depolymerisation reactions of textile fibres, this approximation cannot be applied because of the diverse range of methods involved. The production of solvents contaminated with additives, in varying quantities and qualities depending on the recycled fabrics, or the inorganic salts at the end of the hydrolysis reaction, provides no assurance regarding the solvent recyclability. Moreover, in certain reactions, a portion of the solvent is esterified in the depolymerisation process. The combination of these approximations does not allow for a robust classification of depolymerisation methods aimed at recycling PET, especially derived from textile fibres. If calculating the E factor is straightforward to describe a thoroughly validated reaction and has contributed to the success of virtuous reactions,[281,282] it is more complex to implement in the case of depolymerisation reactions. Faced with this challenge, Barnard *et al.* proposed the calculation of an energy economy coefficient (ε) to compare depolymerisation reactions, calculated according to eqn (1):[283]

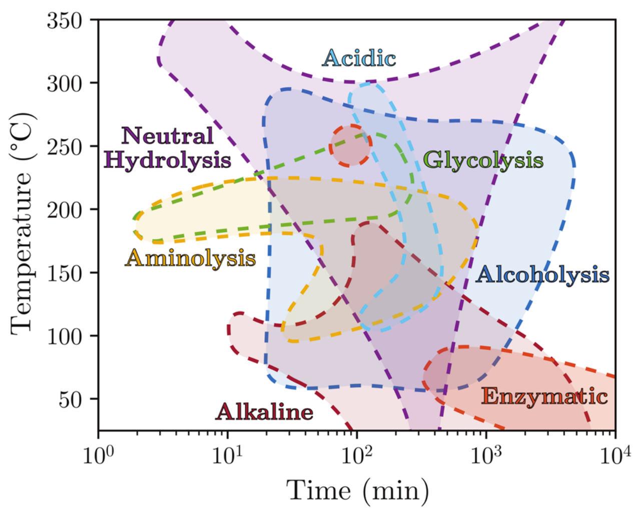

Fig. 13 Global mapping of PET depolymerisation methods sorted by typical reaction time and temperature.

$$\varepsilon = \frac{Y}{T \cdot t} \tag{1}$$

where Y represents the yield of the production of the monomer of interest from the depolymerisation reaction, T is the reaction temperature (°C), and t is the reaction time (min.). The lower the reaction temperature and the shorter the time, the larger ε will be for the same reaction yield. This descriptor, which allows for a simple study of various depolymerisation reactions based on yield and reaction temperature and time conditions, was calculated for all reactions presented in this review. Table 1 provides the values of ε that can be calculated based on the data from the cited publications. For each publication, it includes the optimal conditions under study, *i.e.*, the reaction time and temperature required to achieve the displayed yield of purified monomer in the table.

Fig. 14 provides the classification of the different depolymerisation methods based on the calculated ε from Table 1.

This figure illustrates that two methods stand out significantly from the others, with a ε coefficient of 4.370×10^{-3} and 1.754×10^{-3} °C^{-1} × min^{-1}. The first depolymerisation method, metal salts and organocatalysts-assisted glycolysis enables complete depolymerisation of PET (Table S1, ESI†) with a reaction time of 1 minute at 190 °C with a green Zn acetate catalyst. For this method, the source of PET, whether virgin or post-consumer, is not specified. The second method, a catalysed aminolysis (CA), enables complete depolymerisation of PET with a reaction time of 3 minutes at 190 °C, using a monoamide-ester type catalyst: 1,5,7-triazabicyclo [4.4.0]dec-5-ene (TBD). In this method, the degraded polymer is PET waste obtained from post-consumer bottles.

The depolymerized PET is not derived from textile fibres, for these 2 methods and it should be verified whether these conditions are compatible with the structure of PET in fibres. The following are two methods with an ε coefficient approximately four times lesser. The first is an organocatalyst-assisted glycolysis (MSG), using Ag-doped ZnO nanoparticles, and the second is a mixed alcoholysis (MA) using KOH as a catalyst. While the greater simplicity and greener in sourcing is KOH as a catalyst may provide an advantage to this method, it was only developed for PET derived from bottles. In contrast, the MSG method with Ag-doped ZnO nanoparticles was developed for PET derived from fibres. Both of these methods require reaction times ranging from 15 to 30 minutes and temperatures of 80 or 150 °C.

Table 1 Key parameters of PET depolymerisation reactions including the formed products, yields, and the energy economy coefficient (ε)

Study	Year	Code method	Reaction temperature (°C)	Reaction time (min)	Product	Product yield	ε (°C^{-1} min^{-1})
B. Liu[186]	2018	MSG	190	1	BHET	83.0%	4.370×10^{-3}
S. Nica[236]	2018	CA	190	3	BHETA	100.0%	1.754×10^{-3}
V. Vinitha[205]	2023	MSG	150	15	BHETA	95.00%	4.222×10^{-4}
X. L. Wang[169]	2023	MA	80	30	Terephthalic acid	98.0%	4.083×10^{-4}
V. S. Palekar[238]	2012	CA	110	40	BHETA	89.0%	2.023×10^{-4}
S. Tang[153]	2022	CoAL	200	30	DMT	91.0%	1.517×10^{-4}
D. S. Achilias[233]	2011	μW AA	250	30	BHETA	100.0%	1.333×10^{-4}
P. Lozano Martinez[149]	2021	SCA	275	30	TA/DMT/DMT/DET/EG	94.0%	1.139×10^{-4}
Y. Yang[144]	2002	SCA	250	40	DMT	95.0%	9.500×10^{-5}
R. López-Fonseca[189]	2011	MSG	196	60	BHET	80%	6.803×10^{-5}
H. W. Horn[284]	2012	AT	110	120	BAETA	89%	6.742×10^{-5}
R. M. Musale[237]	2016	CA	170	90	BHETA	97.0%	6.340×10^{-5}
Y. Yang[150]	2023	SCA	270	60	DET	92.0%	5.679×10^{-5}
L. R. Zhang[84]	2013	NH	145	120	TPA	93.0%	5.345×10^{-5}
S. Mishra[90]	2003	ACH	120	140	TPA	87.0%	5.179×10^{-5}
S. Kumagai[117]	2018	ALH	180	120	TPA	100.0%	4.630×10^{-5}
S. Lalhmangaihzuala[286]	2020	MSG	190	90	BHET	79%	4.620×10^{-5}
D. Stanica-Ezeanu[81]	2021	NH	205	120	TA; TPA; TGA	96.0%	3.902×10^{-5}
L. Liu[82]	2005	NH	220	120	TA; TPA; TGA	100.0%	3.788×10^{-5}
F. Quartinello[262]	2017	MCEH	250	90	TA	85.0%	3.778×10^{-5}
M. Imran[201]	2011	MSG	300	80	BHET	90%	3.750×10^{-5}
D. Lei1[92]	2022	MSG	220	90	BHET	70.4%	3.556×10^{-5}
L. Liu[199]	2022	ILG	193,5	125	BHET	84.5%	3.494×10^{-5}
Z. Guo[206]	2018	HCG	240	120	BHET	82.0%	2.847×10^{-5}
Y. Peng[98]	2023	ACH	280	120	TPA + EG diacetate	94.0%	2.798×10^{-5}
B. Yan[136]	2023	ALH	150	240	TPA	100.0%	2.778×10^{-5}
Z. Chen[191]	2023	MSG	250	150	BHET	99.7%	2.659×10^{-5}
S. L. Fávaro[267]	2013	SCA	255	120	DET	80.0%	2.614×10^{-5}
W Yang[79]	2021	NH	220	180	TPA	95.0%	2.399×10^{-5}
T. Yoshioka[92]	1994	ACH	150	300	TPA	95.0%	2.111×10^{-5}
Y. S. Parab[241]	2012	CA	170	240	BHETA	86.0%	2.108×10^{-5}
V. Tournier[261]	2020	EH	72	600	TPA	90.0%	2.083×10^{-5}
N. G. Bush[198]	2023	ILG	180	240	BHET	50.0%	1.157×10^{-5}
S. R. Shukla[231]	2006	CA	170	480	BHETA	91.0%	1.115×10^{-5}
S. Liu[156,157]	2013	ILA	205	480	DBTP	95%	9.654×10^{-6}
A. Peterson[115]	2022	ALH	90	1000	TPA	80.0%	8.889×10^{-6}
P. McKeown[164]	2020	CoAL	100	960	DMT	72.0%	7.500×10^{-6}
C. N. Onwucha[75]	2023	NH	200	1440	TPA	98.0%	3.400×10^{-6}

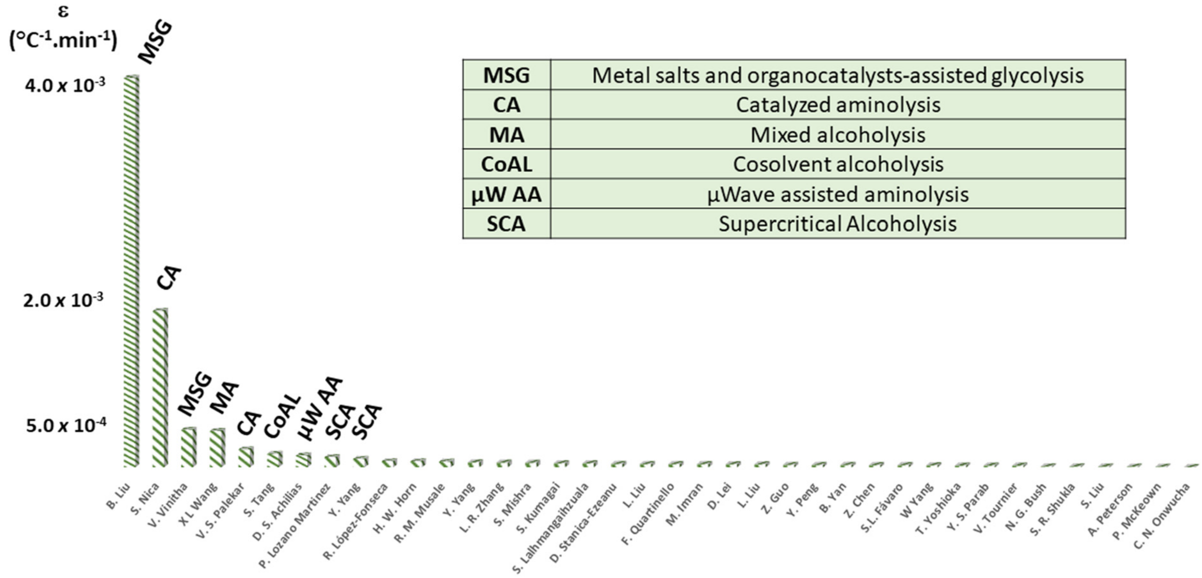

Fig. 14 Classification of depolymerisation methods for the different studies according to the energy economy coefficient ε.

The following 5 methods (CA, CoAL, μW AA, SCA) achieve a calculated ε coefficient ranging between 2×10^{-4} and 1×10^{-4}. It is noteworthy that 2 methods involving the same catalysed aminolysis mechanism exhibit an ε coefficient reduced by a factor of 15. The method using ionic liquids as a catalyst showed a reduced BHETA yield (89%) compared to the one using a monoamide-ester type catalyst (100%). Although the operating temperature is less (110 °C), the time required for depolymerisation and the lesser yield are unfavourable for the green ranking associated with the reaction energy efficiency. All other methods analysed in this review exhibit conditions that are unfavourable in terms of energy efficiency, with an ε factor reduced by a factor of 30 to 3000. Regarding enzymatic or mixed methods (MCEH), often presented as a green process in the literature, the lack of data prevents a comprehensive quantitative assessment. For those with available data, the reduced yield (85%), prolonged reaction time, and greater temperature hinder the achievement of a high energy economy coefficient.

6. Conclusions and perspectives

Recycling of PET, particularly PET from textiles, is an ever-evolving field, as demonstrated by the methods presented previously. The comparative study of the environmental impact of the developed reactions, based on the energy efficiency achieved, enables an objective comparison and provides a foundation for future developments of PET depolymerisation methods derived from textile fibres.

In the realm of chemical recycling, and to minimize the environmental impact of the reactions involved, there is a series of research into new catalysts or new reaction conditions, used to enhance depolymerisation yield and reduce reaction times and temperatures, all aimed at ensuring a high greenness index.[285] Research into new catalysts based on abundant, renewable, and non-toxic resources has shown that PET depolymerisation *via* glycolysis can be complete, in the presence of an excess of ethylene glycol (EG), at a temperature of 196 °C, using sodium carbonate as a catalyst (López-Fonseca 2011).[189] With this catalyst, the reaction time is halved compared to the use of conventional catalysts with a greater environmental impact, such as Mn, Co, Zn, or lead acetate. Organic catalysts, like 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), appear to be "green" candidates for PET depolymerisation *via* glycolysis with a large EG excess.[284] Current research on new organic catalysts continues through theoretical work and extensive use of modeling.[285]

Regarding heterogeneous catalysts based on metal oxides, several systems yield promising results in PET recycling. The primary advantage lies in the ease of catalyst recovery, especially for those formulated at the nanoscale, exhibiting a very large surface area, for example, by impregnating silica nanoparticles[201] or silver-doped ZnO nanoparticles.[205] Other research focuses on the production of new catalytic chemical species from waste valorisation. In PET recycling, a new catalyst produced from orange peel ash, composed of porous materials with a large specific surface area bearing basic sites, shows complete depolymerisation of PET in 90 minutes, with possible catalyst reuse.[286]

In addition to these methods aimed at depolymerizing PET, there is a series of innovative research focused on producing polymer compatibilizers. These are polymers of variable architecture, such as random copolymers, grafted copolymers, and block copolymers, which can interact with conventional PET from recycling to modify their thermoplastic properties, enabling straightforward fusion/moulding to produce new fibres. Often, the method involves creating mixtures of recycled polymers, for example, PET/PE, PET/PP, and producing a new material by adding an agent that makes the mixture compatible.[287,288] As a result, composite fibres were produced from polypropylene (PP) and PET, using a copolymer of PP grafted with acrylic acid (PP-g-AA) as a compatibilizer.[289] An approach to modifying PET chains from textile recycling can also be developed to elongate these chains using different chain extenders. These chain extenders can be oxazolines,[290] organic phosphites,[291] and epoxides.[292] The major advantage of these modifications made to PET chains from textile recycling is to homogenize the average PET molecular weights and produce recycled fibres without altering their crystalline structure, allowing for new recycling cycles at the end of the textile's life.[293]

Finally, PET upcycling is under rapid development with a view to lead to value-added products rather than simple recycling. So far, it has mainly been applied to PET issued from bottles, from packaging, or in pure form and was recently reviewed.[294–299] Different valuable substances can be obtained, among them functional TA and EG derivatives,[300] organic building blocks and bio-products,[301] new polymers such as polyhydroxyalkanoates (PAHs),[302] or other valuable bio-based polymers,[303–305] and membranes.[306] PET upcycling can also produce fuels such as dihydrogen,[307,308] foods (bacterial biomass), or functional materials such as metal–organic frameworks (MOFs) or vitrimers.[309] The processes involved imply biochemical conversions,[301,302] chemical transformations, photocatalysis,[310] and electrocatalysis.[307]

In the case of PET upcycling from textiles and fabrics, examples are currently much rarer. Functional TA derivatives (such as BHET and BHETA) can by produced by direct glycolysis and aminolysis of dyed textiles, catalysed by nanoparticles and under microwave activation.[205] Similarly, valuable phthalic acids were obtained from abandoned banners after thermocatalytic treatment using a metal-based alloy favoring decarboxylation and deshydrogenation reactions.[311] More elaborated products were also directly produced from (dyed) PET textiles, such as (MOFs).[312–314]

The many upcycling developments deployed for bottle PET will certainly be applied soon more largely to textiles, supporting circular economy and reducing environmental pollution.

Author contributions

All authors have contributed equally to the drafting of the manuscript and approve the final version.

Conflicts of interest

There are no conflicts to declare.

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References

1 L. Brivio and F. Tollini, in *Towards Circular Economy: Closing the Loop with Chemical Recycling of Solid Plastic Waste*, ed. D. Moscatelli and M. Pelucchi, Academic Press, 2022, vol. 60, pp. 215–267.

2 J. W. Hill, *J. Am. Chem. Soc.*, 1930, **52**, 4110–4114.

3 W. H. Carothers and J. A. Arvin, *J. Am. Chem. Soc.*, 1929, **51**, 2560–2570.

4 W. H. Carothers, *J. Am. Chem. Soc.*, 1929, **51**, 2548–2559.

5 J. R. Whinfield and J. T. Dickson, *GB Pat*, 578079A, 1941.

6 P. W. Morgan, *J. Macromol. Sci., Part A: Pure Appl.Chem.*, 1981, **15**, 1113–1131.

7 A. Smelik, *Fash. Pract.*, 2023, **15**, 279–299.

8 E. Gubbels, T. Heitz, M. Yamamoto, V. Chilekar, S. Zarbakhsh, M. Gepraegs, H. Köpnick, M. Schmidt, W. Brügging, J. Rüter and W. Kaminsky, *Ullmann's Encyclopedia of Industrial Chemistry*, John Wiley & Sons, Ltd, 2018, pp. 1–30.

9 J. Scheirs and T. E. Long, *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*, Wiley, 2004.

10 B. Henry, K. Laitala and I. G. Klepp, *Sci. Total Environ.*, 2019, **652**, 483–494.

11 C. J. Boreiko and T. G. Rossman, *Toxicol. Appl. Pharmacol.*, 2020, **403**, 115156.

12 R. Hufenus, Y. Yan, M. Dauner and T. Kikutani, *Materials*, 2020, **13**, 4298.

13 S. Grishanov, in *Handbook of Textile and Industrial Dyeing*, ed. M. Clark, Woodhead Publishing, 2011, vol. 1, pp. 28–63.

14 *Handbook of Technical Textiles*, ed. A. Horrocks and S. Anand, CRC Press, 2000.

15 Q. Dong, A. D. Lele, X. Zhao, S. Li, S. Cheng, Y. Wang, M. Cui, M. Guo, A. H. Brozena, Y. Lin, T. Li, L. Xu, A. Qi, I. G. Kevrekidis, J. Mei, X. Pan, D. Liu, Y. Ju and L. Hu, *Nature*, 2023, **616**, 488–494.

16 S. Zhang, W. Xu, R. Du, W. An, X. Liu, S. Xu and Y.-Z. Wang, *Chem. Eng. J.*, 2023, **470**, 144032.

17 L. T. J. Korley, T. H. Epps, B. A. Helms and A. J. Ryan, *Science*, 2021, **373**, 66–69.

18 F. Tollini, L. Brivio, P. Innocenti, M. Sponchioni and D. Moscatelli, *Chem. Eng. Sci.*, 2022, **260**, 117875.

19 R. M. Darbra, J. R. G. Dan, J. Casal, A. Àgueda, E. Capri, G. Fait, M. Schuhmacher, M. Nadal, J. Rovira, V. Grundmann, D. Barceló, A. Ginebreda and D. Guillén, in *Global Risk-Based Management of Chemical Additives I: Production, Usage and Environmental Occurrence*, ed. B. Bilitewski, R. M. Darbra and D. Barceló, Springer Berlin Heidelberg, Berlin, Heidelberg, 2011, pp. 83–107.

20 R. H. Barker, *Environ. Health Perspect.*, 1975, **11**, 41–45.

21 N. N. Mahapatra, *Textile Dyes*, WPI Publishing, 2016.

22 J. Wang, W. Cheng, Y. Gao, L. Zhu and L. Pei, *Polymers*, 2019, **11**, 520.

23 M. Clark, *Handbook of textile and industrial dyeing*, Woodhead Publishing Limited, 2011.

24 A. Ketema and A. Worku, *J. Chem.*, 2020, **2020**, 6628404.

25 Apparel and Footwear International RSL Management (AFIRM) Group, Restricted Substances List, https://afirm-group.com/wp-content/uploads/2024/04/2024_AFIRM_RSL_2024_0404_EN.pdf.

26 L. R. Manea, A.-P. Bertea and A. Bertea, *IOP Conf. Ser.: Mater. Sci. Eng.*, 2020, **877**, 12062.

27 D. Dilba, Long live plastic, https://elements.evonik.com/Research-and-Innovation/long-live-plastic/.

28 M. Y. Soliman, H. A. Othman and A. G. Hassabo, *J. Text. Color. Polym. Sci.*, 2021, **18**, 247–252.

29 W. D. Schindler and P. J. Hauser, *Chemical Finishing of Textiles*, Woodhead Publishing, 2004.

30 B. C. Goswami, R. D. Anandjiwala and D. Hall, *Textile Sizing*, Taylor \& Francis, 2004.

31 M. M. Houck, R. E. Menold and R. A. Huff, *Probl. Forensic Sci.*, 2001, **46**, 217–221.

32 B. J. Holland and J. N. Hay, *Polymer*, 2002, **43**, 1797–1804.

33 D. M. Connor, S. D. Allen, D. M. Collard, C. L. Liotta and D. A. Schiraldi, *J. Appl. Polym. Sci.*, 2001, **81**, 1675–1682.

34 B. Li, J. Yu, S. Lee and M. Ree, *Polymer*, 1999, **40**, 5371–5375.

35 E. L. Lawton and C. J. Setzer, *Flame-Retardant Polymeric Materials*, Springer US, Boston, MA, 1975, pp. 193–221.

36 A. Shukla, V. Sharma, S. Basak and S. W. Ali, *Cellulose*, 2019, **26**, 8191–8208.

37 V. Sharma and S. Wazed Ali, *Sustainable Chem. Pharm.*, 2022, **27**, 100645.

38 M. MacLeod, H. P. H. Arp, M. B. Tekman and A. Jahnke, *Science*, 2021, **373**, 61–65.

39 C. M. Rochman, M. A. Browne, B. S. Halpern, B. T. Hentschel, E. Hoh, H. K. Karapanagioti, L. M. Rios-Mendoza, H. Takada, S. Teh and R. C. Thompson, *Nature*, 2013, **494**, 169–171.

40 I. Paul-Pont, J.-F. Ghiglione, E. Gastaldi, A. Ter Halle, A. Huvet, S. Bruzaud, F. Lagarde, F. Galgani, G. Duflos, M. George and P. Fabre, *Waste Manage.*, 2023, **157**, 242–248.

41 K. Niinimäki, G. Peters, H. Dahlbo, P. Perry, T. Rissanen and A. Gwilt, *Nat. Rev. Earth Environ.*, 2020, **1**, 189–200.

42 F. Uddin, *Textile Manufacturing Processes*, IntechOpen, Rijeka, 2019.

43 N. Šajn, Environmental impact of the textile and clothing industry. What consumers need to know, https://www.

europarl.europa.eu/thinktank/en/document/EPRS_BRI(2019)633143.

44 J. Janmark, K.-H. Magnus, M. Strand, N. Langguth and S. Hedrich, *McKinsey Co.*, 2022, **76**, https://www.mckinsey.com/industries/retail/our-insights/scalingtextile-recycling-in-europe-turning-waste-into-value.

45 D. Watson, A. K. Aare, S. Trzepacz and P. Christine Dahl Petersen, *Eur. Cloth. Action Plan*, 2018, **89**, http://www.ecap.eu.com/wp-content/uploads/2018/07/ECAP-Textile-collection-in-European-cities_full-report_with-summary.pdf.

46 A. Morlet, R. Opsomer, S. Herrmann, L. Balmond, C. Gillet and L. Fuchs, *Ellen MacArthur Found.*, 2017, 1–150.

47 S. Haslinger, M. Hummel, A. Anghelescu-Hakala, M. Määttänen and H. Sixta, *Waste Manage.*, 2019, **97**, 88–96.

48 R. Kumar, *Mater. Today Proc.*, 2021, **37**, 2382–2386.

49 G. Sandin and G. M. Peters, *J. Cleaner Prod.*, 2018, **184**, 353–365.

50 L. Bartolome, M. Imran, B. G. Cho, W. A. Al-Masry and D. H. Kim, *Material Recycling - Trends and Perspectives*, InTech, 2012, pp. 65–84.

51 A. Grant, V. Lahme, T. Connock and L. Lugal, *Zero Waste Eur.*, 2022, https://zerowasteeurope.eu/library/how-circular-is-pet/.

52 N. A. Rorrer, S. Nicholson, A. Carpenter, M. J. Biddy, N. J. Grundl and G. T. Beckham, *Joule*, 2019, **3**, 1006–1027.

53 A. M. Al-Sabagh, F. Z. Yehia, G. Eshaq, A. M. Rabie and A. E. ElMetwally, *Egypt. J. Pet.*, 2016, **25**, 53–64.

54 R. Geyer, J. R. Jambeck and K. L. Law, *Sci. Adv.*, 2017, **3**, e1700782.

55 T. Thiounn and R. C. Smith, *J. Polym. Sci.*, 2020, **58**, 1347–1364.

56 A. Rahimi and J. M. García, *Nat. Rev. Chem.*, 2017, **1**, 46.

57 S. Cuc and M. Vidovic, *Oper. Supply Chain Manag. An Int. J.*, 2014, **4**, 108–115.

58 I. Boustead, Eco-profiles of the European Plastics Industry - Polyethylene Terephthalate (PET) (Bottle grade), https://www.inference.org.uk/sustainable/LCA/elcd/external_docs/petb_31116f00-fabd-11da-974d-0800200c9a66.pdf.

59 J. M. Garcia and M. L. Robertson, *Science*, 2017, **358**, 870–872.

60 L. Dai, N. Zhou, Y. Lv, Y. Cheng, Y. Wang, Y. Liu, K. Cobb, P. Chen, H. Lei and R. Ruan, *Prog. Energy Combust. Sci.*, 2022, **93**, 101021.

61 J. M. Encinar and J. F. González, *Fuel Process. Technol.*, 2008, **89**, 678–686.

62 R. Blanchard and T. H. Mekonnen, *J. Environ. Chem. Eng.*, 2022, **10**, 108810.

63 S. Sharifian and N. Asasian-Kolur, *J. Anal. Appl. Pyrolysis*, 2022, **163**, 105496.

64 Z. Chen, W. Wei, B.-J. Ni and H. Chen, *Environ. Funct. Mater.*, 2022, **1**, 34–48.

65 G. Duman, *J. Water Process Eng.*, 2021, **43**, 102286.

66 E.Ü Parmakoğlu, A. Çay and J. Yanık, *AATCC J. Res.*, 2023, **10**, 133–143.

67 A. Khan, M. Awais and M. Mohsin, *Biomass Convers. Biorefin.*, 2023, 1–16.

68 S. Opperskalski, A. Franz, A. Patanè, S. Siew and E. Tan, *Text. Exch.*, 2022, 1–118.

69 PlasticEurope, Plastics – the Facts 2020, https://plasticseurope.org/knowledge-hub/plastics-the-facts-2020/.

70 A. B. Raheem, Z. Z. Noor, A. Hassan, M. K. Abd Hamid, S. A. Samsudin and A. H. Sabeen, *J. Cleaner Prod.*, 2019, **225**, 1052–1064.

71 R. B. Baloyi, O. J. Gbadeyan, B. Sithole and V. Chunilall, *Text. Res. J.*, 2023, **94**, 508–529.

72 S.-L. Loo, E. Yu and X. Hu, *J. Environ. Chem. Eng.*, 2023, **11**, 110482.

73 P. Pereira, P. E. Savage and C. W. Pester, *ACS Sustainable Chem. Eng.*, 2023, **11**, 7203–7209.

74 A. Jaime-Azuara, T. H. Pedersen and R. Wimmer, *Green Chem.*, 2023, **25**, 2711–2722.

75 C. N. Onwucha, C. O. Ehi-Eromosele, S. O. Ajayi, M. Schaefer, S. Indris and H. Ehrenberg, *Ind. Eng. Chem. Res.*, 2023, **62**, 6378–6385.

76 M. J. Kang, H. J. Yu, J. Jegal, H. S. Kim and H. G. Cha, *Chem. Eng. J.*, 2020, **398**, 125655.

77 C.-Y. Kao, B.-Z. Wan and W.-H. Cheng, *Ind. Eng. Chem. Res.*, 1998, **37**, 1228–1234.

78 J. R. Campanelli, M. R. Kamal and D. G. Cooper, *J. Appl. Polym. Sci.*, 1994, **54**, 1731–1740.

79 W. Yang, R. Liu, C. Li, Y. Song and C. Hu, *Waste Manage.*, 2021, **135**, 267–274.

80 S. Mahadevan Subramanya, Y. Mu and P. E. Savage, *ACS Eng. Au*, 2022, **2**, 507–514.

81 D. Stanica-Ezeanu and D. Matei, *Sci. Rep.*, 2021, **11**, 4431.

82 L. Liu, D. Zhang, L. An, H. Zhang and Y. Tian, *J. Appl. Polym. Sci.*, 2005, **95**, 719–723.

83 W. L. Zhang, X. N. Shi, X. Zhang, C. H. Han and D. Zhang, *Adv. Mater. Res.*, 2012, **550–553**, 792–797.

84 L. Zhang, J. Gao, J. Zou and F. Yi, *J. Appl. Polym. Sci.*, 2013, **130**, 2790–2795.

85 M. Yan, Y. Yang, F. Chen, D. Hantoko, A. Pariatamby and E. Kanchanatip, *Environ. Sci. Pollut. Res.*, 2023, **30**, 102560–102573.

86 S. Hongkailers, Y. Jing, Y. Wang, N. Hinchiranan and N. Yan, *ChemSusChem*, 2021, **14**, 4330–4339.

87 R. Li, W. Zeng, R. Zhao, Y. Zhao, Y. Wang, F. Zhang, M. Tang, Y. Wang, X. Chang, F. Wu and Z. Liu, *Nano Res.*, 2023, **16**, 12223–12229.

88 H. Su, Y. Hu, H. Feng, L. Zhu and S. Wang, *ACS Sustainable Chem. Eng.*, 2023, **11**, 578–586.

89 H. Abedsoltan, *Polym. Eng. Sci.*, 2023, **63**, 2651–2674.

90 S. Mishra, A. S. Goje and V. S. Zope, *Polym. React. Eng.*, 2003, **11**, 79–99.

91 S. H. Park and S. H. Kim, *Fash. Text.*, 2014, **1**, 1.

92 T. Yoshioka, N. Okayama and A. Okuwaki, *Ind. Eng. Chem. Res.*, 1998, **37**, 336–340.

93 T. Yoshioka, T. Motoki and A. Okuwaki, *Ind. Eng. Chem. Res.*, 2001, **40**, 75–79.

94 G. M. de Carvalho, E. C. Muniz and A. F. Rubira, *Polym. Degrad. Stab.*, 2006, **91**, 1326–1332.

95 R. K. Al-tamimi, M. N. Khalaf, M. Sabri and L. Sabri, *J. Mater. Environ. Sci.*, 2011, **2**, 88–93.

96 C. Costa, A. Viana, C. Silva, E. F. Marques and N. G. Azoia, *Waste Manage.*, 2022, **153**, 99–109.

97 B. Ye, R. Zhou, Z. Zhong, S. Wang, H. Wang and Z. Hou, *Green Chem.*, 2023, **25**, 7243–7252.

98 Y. Peng, J. Yang, C. Deng, J. Deng, L. Shen and Y. Fu, *Nat. Commun.*, 2023, **14**, 3249.

99 X. Li, H. Lu, W. Guo, G. Cao, H. Liu and Y. Shi, *AIChE J.*, 2015, **61**, 200–214.

100 H. Abedsoltan, I. S. Omodolor, A. C. Alba-Rubio and M. R. Coleman, *Polymer*, 2021, **222**, 123620.

101 W. Yang, J. Wang, L. Jiao, Y. Song, C. Li and C. Hu, *Green Chem.*, 2022, **24**, 1362–1372.

102 L. Kárpáti, G. Szarka, M. Hartman and V. Vargha, *Period. Polytech., Chem. Eng.*, 2018, **62**, 336–344.

103 C. Jehanno, I. Flores, A. P. Dove, A. J. Müller, F. Ruipérez and H. Sardon, *Green Chem.*, 2018, **20**, 1205–1212.

104 A. S. Amarasekara, J. A. Gonzalez and V. C. Nwankwo, *J. Ion. Liq.*, 2022, **2**, 100021.

105 A. N. Paparella, S. Perrone, A. Salomone, F. Messa, L. Cicco, V. Capriati, F. M. Perna and P. Vitale, *Catalysts*, 2023, **13**, 1035.

106 S. Hashemizad, M. Montazer and A. Rashidi, *J. Appl. Polym. Sci.*, 2012, **125**, 1176–1184.

107 R. Chen, S. Deng, T. Cui, S. Duan, Q. Jia and L. Zhang, *Prog. Rubber, Plast. Recycl. Technol.*, 2024, **40**, 77–97.

108 M. J. Collins, S. H. Zeronian and M. Semmelmeyer, *J. Appl. Polym. Sci.*, 1991, **42**, 2149–2162.

109 A. M. Grancarić and N. Kallay, *J. Appl. Polym. Sci.*, 1993, **49**, 175–181.

110 S. Kumar and C. Guria, *J. Macromol. Sci., Part A: Pure Appl. Chem.*, 2005, **42**, 237–251.

111 W. Tsen, K. Hsiao and Y. Shu, *J. Appl. Polym. Sci.*, 2009, **113**, 1822–1827.

112 H. Tavanai, *J. Text. Inst.*, 2009, **100**, 633–639.

113 Y. Kawahara, T. Yoshioka, W. Takarada, T. Kikutani and M. Tsuji, *J. Fiber Sci. Technol.*, 2016, **72**, 9–16.

114 A. Sarno, K. Olafsen, S. Kubowicz, F. Karimov, S. T. L. Sait, L. Sørensen and A. M. Booth, *Environ. Sci. Technol. Lett.*, 2021, **8**, 250–255.

115 A. Peterson, J. Wallinder, J. Bengtsson, A. Idström, M. Bialik, K. Jedvert and H. de la Motte, *Sustainability*, 2022, **14**, 7272.

116 J. Bengtsson, A. Peterson, A. Idström, H. de la Motte and K. Jedvert, *Sustainability*, 2022, **14**, 6911.

117 S. Kumagai, S. Hirahashi, G. Grause, T. Kameda, H. Toyoda and T. Yoshioka, *J. Mater. Cycles Waste Manag.*, 2018, **20**, 439–449.

118 T. Kaurin, T. Pušić and M. Čurlin, *Polymers*, 2022, **14**, 3088.

119 J. M. Kang, M. G. Kim, J. E. Lee, J. W. Ko, I. J. Kim, J. Y. Lee, D. J. Lee, S. I. Ko, D. H. Jung and S. G. Lee, *Polymers*, 2020, **12**, 1243.

120 N. Prorokova, A. Chorev, S. Kuzmin, S. Vavilova and V. Prorokov, *Chem. Chem. Technol.*, 2014, **8**, 293–302.

121 A. Boondaeng, J. Keabpimai, P. Srichola, P. Vaithanomsat, C. Trakunjae and N. Niyomvong, *Polymers*, 2023, **15**, 1964.

122 E. Gholamzad, K. Karimi and M. Masoomi, *Chem. Eng. J.*, 2014, **253**, 40–45.

123 S. Youn and C. H. Park, *Text. Res. J.*, 2019, **89**, 959–974.

124 E. S. Kim, C. H. Lee and S. H. Kim, *J. Appl. Polym. Sci.*, 2009, **112**, 3071–3078.

125 J. H. Lee, S. H. Park, K. W. Oh, C. H. Lee and S. H. Kim, *Polym. Int.*, 2012, **61**, 657–663.

126 S. Niu, T. Wakida, S. Ogasawara, H. Fujimatsu and S. Takekoshi, *Text. Res. J.*, 1995, **65**, 771–775.

127 S. M. Gawish, S. Mosleh and A. M. Ramadan, *J. Appl. Polym. Sci.*, 2002, **85**, 1652–1660.

128 I. Čorak, A. Tarbuk, D. Đorđević, K. Višić and L. Botteri, *Materials*, 2022, **15**, 1530.

129 R. M. Musale and S. R. Shukla, *J. Text. Inst.*, 2017, **108**, 467–471.

130 A. Palme, A. Peterson, H. de la Motte, H. Theliander and H. Brelid, *Text. Cloth. Sustain.*, 2017, **3**, 4.

131 M. Rahman and G. C. East, *Text. Res. J.*, 2009, **79**, 728–736.

132 D. Zhou, L. Wang, F. Zhang, J. Wu, H. Wang and J. Yang, *Adv. Sustainable Syst.*, 2022, **6**, 2100516.

133 V. Ramopoulos, *Energy-efficient, scalable and modular industrial microwave applicator for high temperature alkaline hydrolysis of PET*, KIT Scientific Publishing, Karlsruhe, 2023.

134 V. Štrukil, *ChemSusChem*, 2021, **14**, 330–338.

135 S. Zhang, Y. Xue, Y. Wu, Y.-X. Zhang, T. Tan and Z. Niu, *Chem. Sci.*, 2023, **14**, 6558–6563.

136 B. Yan, S. Zhang, M. Zhang, Y. Yu, T. Qin, L. Tang, Y. Liu, W. Wu and Q. Mei, *Chem. Eng. J.*, 2023, **474**, 145697.

137 H. Gruschke, W. Hammerschick and H. Medem, *US Pat*, 3403115A, 1968.

138 R. Lotz, G. Wick and C. Neuhaus, *US Pat*, 3321510A, 1967.

139 E. Heisenberg, E. Siggel and R. Lotz, *US Pat*, 3037050A, 1962.

140 J. Otera, *Chem. Rev.*, 1993, **93**, 1449–1470.

141 P. R. Fehlandt and H. Adkins, *J. Am. Chem. Soc.*, 1935, **57**, 193–195.

142 G. B. Hatch and H. Adkins, *J. Am. Chem. Soc.*, 1937, **59**, 1694–1696.

143 M. Goto, H. Koyamoto, A. Kodama, T. Hirose and S. Nagaoka, *J. Phys.: Condens. Matter*, 2002, **14**, 136–144.

144 Y. Yang, Y. Lu, H. Xiang, Y. Xu and Y. Li, *Polym. Degrad. Stab.*, 2002, **75**, 185–191.

145 T. Sako, T. Sugeta, K. Otake, N. Nakazawa, M. Sato, K. Namiki and M. Tsugumi, *J. Chem. Eng. JAPAN*, 1997, **30**, 342–346.

146 Q. Liu, R. Li and T. Fang, *Chem. Eng. J.*, 2015, **270**, 535–541.

147 M. Genta, F. Yano, Y. Kondo, W. Matsubara and S. Oomoto, *Mitsubishi Heavy Ind. Ltd., Tech. Rev.*, 2003, **40**, 1–4.

148 K. Yu, J. Liu, J. Sun, Z. Shen and J. Yin, *J. Supercrit. Fluids*, 2023, **194**, 105837.

149 P. Lozano-Martinez, T. Torres-Zapata and N. Martin-Sanchez, *ACS Sustainable Chem. Eng.*, 2021, **9**, 9846–9853.

150 Y. Yang, F. Chen, T. Shen, A. Pariatamby, X. Wen, M. Yan and E. Kanchanatip, *Process Saf. Environ. Prot.*, 2023, **173**, 881–892.

151 Z. T. Laldinpuii, V. Khiangte, S. Lalhmangaihzuala, C. Lalmuanpuia, Z. Pachuau, C. Lalhriatpuia and K. Vanlaldinpuia, *J. Polym. Environ.*, 2022, **30**, 1600–1614.

152 P. A. Gangotena, S. Ponce, Á. Gallo-Córdova, D. A. Streitwieser and J. R. Mora, *ChemistrySelect*, 2022, **7**, e202103765.

153 S. Tang, F. Li, J. Liu, B. Guo, Z. Tian and J. Lv, *J. Environ. Chem. Eng.*, 2022, **10**, 107927.

154 M. Ma, S. Wang, Y. Liu, H. Yu, S. Yu, C. Ji, H. Li, G. Nie and S. Liu, *J. Appl. Polym. Sci.*, 2022, **139**, e52814.

155 T. T. Le Bui, D. A. Nguyen, S. V. Ho and H. T. N. Uong, *J. Appl. Polym. Sci.*, 2016, **133**, 1–11.

156 S. Liu, L. Zhou, L. Li, S. Yu, F. Liu, C. Xie and Z. Song, *J. Polym. Res.*, 2013, **20**, 310.

157 S. Liu, Z. Wang, L. Li, S. Yu, C. Xie and F. Liu, *J. Appl. Polym. Sci.*, 2013, **130**, 1840–1844.

158 A. Kržan, *J. Appl. Polym. Sci.*, 1998, **69**, 1115–1118.

159 M. N. Siddiqui, H. H. Redhwi and D. S. Achilias, *J. Anal. Appl. Pyrolysis*, 2012, **98**, 214–220.

160 M. M. A. Nikje and F. Nazari, *Polimery*, 2009, **54**, 635–638.

161 M. M. A. Nikje and F. Nazari, *Adv. Polym. Technol.*, 2006, **25**, 242–246.

162 D. S. Achilias, in *Microwave-assisted Polymer Synthesis*, ed. R. Hoogenboom, U. S. Schubert and F. Wiesbrock, Springer International Publishing, Cham, 2016, pp. 309–346.

163 H. Beneš, J. Slabá, Z. Walterová and D. Rais, *Polym. Degrad. Stab.*, 2013, **98**, 2232–2243.

164 P. McKeown, M. Kamran, M. G. Davidson, M. D. Jones, L. A. Román-Ramírez and J. Wood, *Green Chem.*, 2020, **22**, 3721–3726.

165 J. Tang, X. Meng, X. Cheng, Q. Zhu, D. Yan, Y. Zhang, X. Lu, C. Shi and X. Liu, *Ind. Eng. Chem. Res.*, 2023, **62**, 4917–4927.

166 D. D. Pham and J. Cho, *Green Chem.*, 2021, **23**, 511–525.

167 L.-C. Hu, A. Oku, E. Yamada and K. Tomari, *Polym. J.*, 1997, **29**, 708–712.

168 L. Cosimbescu, D. R. Merkel, J. Darsell and G. Petrossian, *Ind. Eng. Chem. Res.*, 2021, **60**, 12792–12797.

169 X.-L. Wang, W.-L. An, R. Du, F. Tian, Y. Yang, X. Zhao, S. Xu and Y.-Z. Wang, *J. Environ. Chem. Eng.*, 2023, **11**, 109434.

170 X.-L. Wang, W.-L. An, F. Tian, Y. Yang, X. Zhao, P.-P. Xu, S. Xu and Y.-Z. Wang, *ACS Sustainable Chem. Eng.*, 2020, **8**, 16010–16019.

171 J. J. R. Arias and W. Thielemans, *Green Chem.*, 2021, **23**, 9945–9956.

172 H. İ İçoğlu, *Tekst. ve Konfeksiyon*, 2022, **32**, 57–64.

173 J. T. Macdowell, *US Pat*, 3222299A, 1965.

174 H. Yue, Y. Zhao, X. Ma and J. Gong, *Chem. Soc. Rev.*, 2012, **41**, 4218–4244.

175 U. R. Vaidya and V. M. Nadkarni, *J. Appl. Polym. Sci.*, 1989, **38**, 1179–1190.

176 U. R. Vaidya and V. M. Nadkarni, *J. Appl. Polym. Sci.*, 1988, **35**, 775–785.

177 U. R. Vaidya and V. M. Nadkarni, *Ind. Eng. Chem. Res.*, 1988, **27**, 2056–2060.

178 U. R. Vaidya and V. M. Nadkarni, *J. Appl. Polym. Sci.*, 1987, **34**, 235–245.

179 K. Ghosal and C. Nayak, *Mater. Adv.*, 2022, **3**, 1974–1992.

180 M. Imran, B.-K. Kim, M. Han, B. G. Cho and D. H. Kim, *Polym. Degrad. Stab.*, 2010, **95**, 1686–1693.

181 J.-W. Chen and L. Chen, *J. Appl. Polym. Sci.*, 1999, **73**, 35–40.

182 D. Gintis, *Makromol. Chem., Macromol. Symp.*, 1992, **57**, 185–190.

183 S. N. Tong, D. S. Chen, C. C. Chen and L. Z. Chung, *Polymer*, 1983, **24**, 469–472.

184 S. C. Kosloski-Oh, Z. A. Wood, Y. Manjarrez, J. P. de los Rios and M. E. Fieser, *Mater. Horiz.*, 2021, **8**, 1084–1129.

185 S. Baliga and W. T. Wong, *J. Polym. Sci., Part A: Polym. Chem.*, 1989, **27**, 2071–2082.

186 B. Liu, X. Lu, Z. Ju, P. Sun, J. Xin, X. Yao, Q. Zhou and S. Zhang, *Ind. Eng. Chem. Res.*, 2018, **57**, 16239–16245.

187 N. D. Pingale and S. R. Shukla, *Eur. Polym. J.*, 2008, **44**, 4151–4156.

188 D.-T. Van-Pham, Q.-H. Le, T.-N. Lam, C.-N. Nguyen and W. Sakai, *Polym. Degrad. Stab.*, 2020, **179**, 109257.

189 R. López-Fonseca, I. Duque-Ingunza, B. de Rivas, L. Flores-Giraldo and J. I. Gutiérrez-Ortiz, *Chem. Eng. J.*, 2011, **168**, 312–320.

190 K. Fukushima, O. Coulembier, J. M. Lecuyer, H. A. Almegren, A. M. Alabdulrahman, F. D. Alsewailem, M. A. Mcneil, P. Dubois, R. M. Waymouth, H. W. Horn, J. E. Rice and J. L. Hedrick, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 1273–1281.

191 Z. Chen, H. Sun, W. Kong, L. Chen and W. Zuo, *Green Chem.*, 2023, **25**, 4429–4437.

192 D. Lei, X.-L. Sun, S. Hu, H. Cheng, Q. Chen, Q. Qian, Q. Xiao, C. Cao, L. Xiao and B. Huang, *Ind. Eng. Chem. Res.*, 2022, **61**, 4794–4802.

193 H. Wang, Z. Li, Y. Liu, X. Zhang and S. Zhang, *Green Chem.*, 2009, **11**, 1568–1575.

194 Q. Wang, X. Yao, S. Tang, X. Lu, X. Zhang and S. Zhang, *Green Chem.*, 2012, **14**, 2559–2566.

195 Y. Liu, X. Yao, H. Yao, Q. Zhou, J. Xin, X. Lu and S. Zhang, *Green Chem.*, 2020, **22**, 3122–3131.

196 A. P. Abbott, G. Capper, D. L. Davies, H. L. Munro, R. K. Rasheed and V. Tambyrajah, *Chem. Commun.*, 2001, **1**, 2010–2011.

197 Q. Wang, X. Yao, Y. Geng, Q. Zhou, X. Lu and S. Zhang, *Green Chem.*, 2015, **17**, 2473–2479.

198 N. G. Bush, C. H. Dinh, C. L. Catterton and M. E. Fieser, *RSC Sustain.*, 2023, **1**, 938–947.

199 L. Liu, H. Yao, Q. Zhou, D. Yan, J. Xu and X. Lu, *ACS Eng. Au*, 2022, **2**, 350–359.

200 S. R. Shukla, V. Palekar and N. Pingale, *J. Appl. Polym. Sci.*, 2008, **110**, 501–506.

201 M. Imran, K. Lee, Q. Imtiaz, B.-K. Kim, M. Han, B. G. Cho and D. H. Kim, *J. Nanosci. Nanotechnol.*, 2011, **11**, 824–828.

202 I. Yunita, S. Putisompon, P. Chumkaeo, T. Poonsawat and E. Somsook, *Chem. Pap.*, 2019, **73**, 1547–1560.

203 Q. Suo, J. Zi, Z. Bai and S. Qi, *Catal. Lett.*, 2017, **147**, 240–252.

204 I. Cano, C. Martin, J. A. Fernandes, R. W. Lodge, J. Dupont, F. A. Casado-Carmona, R. Lucena, S. Cardenas, V. Sans and I. de Pedro, *Appl. Catal., B*, 2020, **260**, 118110.

205 V. Vinitha, M. Preeyanghaa, M. Anbarasu, B. Neppolian and V. Sivamurugan, *Environ. Sci. Pollut. Res.*, 2023, **30**, 75401–75416.

206 Z. Guo, K. Lindqvist and H. de la Motte, *J. Appl. Polym. Sci.*, 2018, **135**, 46285.

207 Z. Guo, M. Eriksson, H. de la Motte and E. Adolfsson, *J. Cleaner Prod.*, 2021, **283**, 124579.

208 B. Shojaei, M. Abtahi and M. Najafi, *Polym. Adv. Technol.*, 2020, **31**, 2912–2938.

209 G. P. Karayannidis and D. S. Achilias, *Macromol. Mater. Eng.*, 2007, **292**, 128–146.

210 D. Paszun and T. Spychaj, *Ind. Eng. Chem. Res.*, 1997, **36**, 1373–1383.

211 G. Farrow, D. Ravens and I. Ward, *Polymer*, 1962, **3**, 17–25.

212 S. A. Holmes, *J. Appl. Polym. Sci.*, 1996, **61**, 255–260.

213 M. J. Collins, S. H. Zeronian and M. L. Marshall, *Macromol. Sci., Part A: Pure Appl.Chem.*, 1991, **28**, 775–792.

214 M. S. Ellison, L. D. Fisher, K. W. Alger and S. H. Zeronian, *J. Appl. Polym. Sci.*, 1982, **27**, 247–257.

215 J. R. Overton and S. K. Haynes, *J. Polym. Sci., Polym. Symp.*, 1973, **43**, 9–17.

216 E. Lorusso, Y. Feng, J. Schneider, L. Kamps, N. Parasothy, T. Mayer-Gall, J. S. Gutmann and W. Ali, *Nano Sel.*, 2022, **3**, 594–607.

217 E. Lorusso, W. Ali, M. Leniart, B. Gebert, M. Oberthür and J. S. Gutmann, *Polymers*, 2020, **12**, 6.

218 J. Zhou, M. Li, L. Zhong, F. Zhang and G. Zhang, *Colloids Surf., A*, 2017, **513**, 146–152.

219 V. Popescu, A. Muresan, O. Constandache, G. Lisa, E. I. Muresan, C. Munteanu and I. Sandu, *Ind. Eng. Chem. Res.*, 2014, **53**, 16652–16663.

220 T. Ohe and Y. Yoshimura, *Sen'i Gakkaishi*, 2012, **68**, 253–258.

221 T. Spychaj, E. Fabrycy, S. Spychaj and M. Kacperski, *J. Mater. Cycles Waste Manag.*, 2001, **3**, 24–31.

222 C. N. Hoang and Y. H. Dang, *Polym. Degrad. Stab.*, 2013, **98**, 697–708.

223 R. K. Soni, S. Singh and K. Dutt, *J. Appl. Polym. Sci.*, 2010, **115**, 3074–3080.

224 N. George and T. Kurian, *Prog. Rubber, Plast. Recycl. Technol.*, 2016, **32**, 153–168.

225 Y. S. Parab, N. D. Pingale and S. R. Shukla, *J. Appl. Polym. Sci.*, 2012, **125**, 1103–1107.

226 R. K. Soni, K. Dutt, A. Jain, S. Soam and S. Singh, *J. Appl. Polym. Sci.*, 2009, **113**, 1090–1096.

227 V. S. Palekar, A. J. Damle and S. R. Shukla, *Eur. J. Med. Chem.*, 2009, **44**, 5112–5116.

228 V. S. Palekar, N. D. Pingale and S. R. Shukla, *Color. Technol.*, 2010, **126**, 86–91.

229 G. M. M. Sadeghi, R. Shamsi and M. Sayaf, *J. Polym. Environ.*, 2011, **19**, 522–534.

230 N. D. Pingale and S. R. Shukla, *Eur. Polym. J.*, 2009, **45**, 2695–2700.

231 S. R. Shukla and A. M. Harad, *Polym. Degrad. Stab.*, 2006, **91**, 1850–1854.

232 G. Pastore, R. Giacomantonio, G. Lupidi, F. Stella, R. Risoluti, E. Papa, R. Ballini, F. Sarasini, J. Tirillò, E. Marcantoni and S. Gabrielli, *Front. Chem.*, 2023, **11**, 1234763.

233 D. S. Achilias, G. P. Tsintzou, A. K. Nikolaidis, D. N. Bikiaris and G. P. Karayannidis, *Polym. Int.*, 2011, **60**, 500–506.

234 K. Fukushima, J. M. Lecuyer, D. S. Wei, H. W. Horn, G. O. Jones, H. A. Al-Megren, A. M. Alabdulrahman, F. D. Alsewailem, M. A. McNeil, J. E. Rice and J. L. Hedrick, *Polym. Chem.*, 2013, **4**, 1610–1616.

235 J. Demarteau, I. Olazabal, C. Jehanno and H. Sardon, *Polym. Chem.*, 2020, **11**, 4875–4882.

236 S. Nica, M. Duldner, A. Hanganu, S. Iancu, B. Cursaru, A. Sarbu, P. Filip and E. Bartha, *Rev. Chim.*, 2018, **69**, 2613–2616.

237 R. M. Musale and S. R. Shukla, *Int. J. Plast. Technol.*, 2016, **20**, 106–120.

238 V. S. Palekar, R. V. Shah and S. R. Shukla, *J. Appl. Polym. Sci.*, 2012, **126**, 1174–1181.

239 M. E. Tawfik, N. M. Ahmed and S. B. Eskander, *J. Appl. Polym. Sci.*, 2011, **120**, 2842–2855.

240 V. Vinitha, M. Preeyanghaa, M. Anbarasu, G. Jeya, B. Neppolian and V. Sivamurugan, *J. Polym. Environ.*, 2022, **30**, 3566–3581.

241 Y. S. Parab, R. V. Shah and S. R. Shukla, *Curr. Chem. Lett.*, 2012, **1**, 81–90.

242 A. Mittal, R. K. Soni, K. Dutt and S. Singh, *J. Hazard. Mater.*, 2010, **178**, 390–396.

243 K. P. Blackmon, D. W. Fox and S. J. Shafer, *US Pat*, 4973746A, 1990.

244 L. Shi and L. Zhu, *ChemBioChem*, 2024, **25**, e202300578.

245 C. Liu, C. Shi, S. Zhu, R. Wei and C.-C. Yin, *Biochem. Biophys. Res. Commun.*, 2019, **508**, 289–294.

246 S. Jaiswal, B. Sharma and P. Shukla, *Environ. Technol. Innov.*, 2020, **17**, 100567.

247 F. Kawai, T. Kawabata and M. Oda, *Appl. Microbiol. Biotechnol.*, 2019, **103**, 4253–4268.

248 M. T. Zumstein, D. Rechsteiner, N. Roduner, V. Perz, D. Ribitsch, G. M. Guebitz, H.-P. E. Kohler, K. McNeill and M. Sander, *Environ. Sci. Technol.*, 2017, **51**, 7476–7485.

249 R.-J. Müller, I. Kleeberg and W.-D. Deckwer, *J. Biotechnol.*, 2001, **86**, 87–95.
250 D. Kint and S. Muñoz-Guerra, *Polym. Int.*, 1999, **48**, 346–352.
251 R. Koshti, L. Mehta and N. Samarth, *J. Polym. Environ.*, 2018, **26**, 3520–3529.
252 T. Brueckner, A. Eberl, S. Heumann, M. Rabe and G. M. Guebitz, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 6435–6443.
253 M. Alisch-Mark, A. Herrmann and W. Zimmermann, *Biotechnol. Lett.*, 2006, **28**, 681–685.
254 G. Fischer-Colbrie, S. Heumann, S. Liebminger, E. Almansa, A. Cavaco-Paulo and G. M. Guebitz, *Biocatal. Biotransform.*, 2004, **22**, 341–346.
255 G. M. Gübitz and A. C. Paulo, *Curr. Opin. Biotechnol.*, 2003, **14**, 577–582.
256 R. Müller, H. Schrader, J. Profe, K. Dresler and W. Deckwer, *Macromol. Rapid Commun.*, 2005, **26**, 1400–1405.
257 F. Kawai, *Catalysts*, 2021, **11**, 206.
258 S. Kaabel, J. P. D. Therien, C. E. Deschênes, D. Duncan, T. Friščić and K. Auclair, *Proc. Natl. Acad. Sci. U. S. A.*, 2021, **118**, e2026452118.
259 A. N. Shirke, C. White, J. A. Englaender, A. Zwarycz, G. L. Butterfoss, R. J. Linhardt and R. A. Gross, *Biochemistry*, 2018, **57**, 1190–1200.
260 A. Mrigwani, B. Thakur and P. Guptasarma, *Green Chem.*, 2022, **24**, 6707–6719.
261 V. Tournier, C. M. Topham, A. Gilles, B. David, C. Folgoas, E. Moya-Leclair, E. Kamionka, M.-L. Desrousseaux, H. Texier, S. Gavalda, M. Cot, E. Guémard, M. Dalibey, J. Nomme, G. Cioci, S. Barbe, M. Chateau, I. André, S. Duquesne and A. Marty, *Nature*, 2020, **580**, 216–219.
262 F. Quartinello, S. Vajnhandl, J. Volmajer Valh, T. J. Farmer, B. Vončina, A. Lobnik, E. Herrero Acero, A. Pellis and G. M. Guebitz, *Microb. Biotechnol.*, 2017, **10**, 1376–1383.
263 X. Li, Y. Hu, C. Du and C. S. K. Lin, *Waste Biomass Valorization*, 2019, **10**, 3763–3772.
264 J. Shimizu and T. Kikutani, *J. Appl. Polym. Sci.*, 2002, **83**, 539–558.
265 Y. Fu, W. R. Busing, Y. Jin, K. A. Affholter and B. Wunderlich, *Macromolecules*, 1993, **26**, 2187–2193.
266 S. Kaabel, J. Arciszewski, T. H. Borchers, J. P. D. Therien, T. Friščić and K. Auclair, *ChemSusChem*, 2023, **16**, e202201613.
267 S. L. Fávaro, A. R. Freitas, T. A. Ganzerli, A. G. B. Pereira, A. L. Cardozo, O. Baron, E. C. Muniz, E. M. Girotto and E. Radovanovic, *J. Supercrit. Fluids*, 2013, **75**, 138–143.
268 H. Essaddam, *US Pat*, 10640442B2, 2020.
269 H. Essaddam, *US Pat*, 10087130B2, 2018.
270 K. Locock, J. Deane, E. Kosior, H. Prabaharan, M. Skidmore and O. Hutt, The Recycled Plastics Market: Global Analysis and Trends, https://publications.csiro.au/publications/publication/PIcsiro:EP19308.
271 W. D'Ambrières, *F. Actions Sci. Reports*, 2019, **19**, 12–21.
272 F. S. Yildizhan, Engineering Plastics: Market Analysis and Recycling Methods, *SciOpen Prepr.*, 2021, DOI: 10.14293/S2199-1006.1.SOR-.PPOYUPU.v1, https://www.scienceopen.com/hosted-document.
273 A. McNeeley and Y. A. Liu, *Ind. Eng. Chem. Res.*, 2024, **63**, 3400–3424.
274 H. Dijkstra, P. van Beukering and R. Brouwer, *Mar. Pollut. Bull.*, 2021, **162**, 111880.
275 Y.-J. Cai and T.-M. Choi, *Transp. Res. Part E: Logist. Trans. Rev.*, 2020, **141**, 102010.
276 A. Halpaap and J. Dittkrist, *Curr. Opin. Green Sustainable Chem.*, 2018, **9**, 25–29.
277 P. T. Anastas, *Chem. Rev.*, 2007, **107**, 2167–2168.
278 T.-L. Chen, H. Kim, S.-Y. Pan, P.-C. Tseng, Y.-P. Lin and P.-C. Chiang, *Sci. Total Environ.*, 2020, **716**, 136998.
279 B. M. Trost, *Science*, 1991, **254**, 1471–1477.
280 R. A. Sheldon, *Chem. Commun.*, 2008, 3352–3365.
281 R. A. Sheldon, *ACS Sustainable Chem. Eng.*, 2018, **6**, 32–48.
282 R. A. Sheldon, *Green Chem.*, 2017, **19**, 18–43.
283 E. Barnard, J. J. Rubio Arias and W. Thielemans, *Green Chem.*, 2021, **23**, 3765–3789.
284 H. W. Horn, G. O. Jones, D. S. Wei, K. Fukushima, J. M. Lecuyer, D. J. Coady, J. L. Hedrick and J. E. Rice, *J. Phys. Chem. A*, 2012, **116**, 12389–12398.
285 C. Jehanno, M. M. Pérez-Madrigal, J. Demarteau, H. Sardon and A. P. Dove, *Polym. Chem.*, 2019, **10**, 172–186.
286 S. Lalhmangaihzuala, Z. Laldinpuii, C. Lalmuanpuia and K. Vanlaldinpuia, *Polymers*, 2020, **13**, 37.
287 I. A. Ignatyev, W. Thielemans and B. Vander Beke, *ChemSusChem*, 2014, **7**, 1579–1593.
288 C. P. Papadopoulou and N. K. Kalfoglou, *Polymer*, 2000, **41**, 2543–2555.
289 X. Si, L. Guo, Y. Wang and K. Lau, *Compos. Sci. Technol.*, 2008, **68**, 2943–2947.
290 G. P. Karayannidis and E. A. Psalida, *J. Appl. Polym. Sci.*, 2000, **77**, 2206–2211.
291 B. Jacques, J. Devaux, R. Legras and E. Nield, *Macromolecules*, 1996, **29**, 3129–3138.
292 P. Raffa, M.-B. Coltelli, S. Savi, S. Bianchi and V. Castelvetro, *React. Funct. Polym.*, 2012, **72**, 50–60.
293 W.-J. Wu, X.-L. Sun, Q. Chen and Q. Qian, *Polymers*, 2022, **14**, 510.
294 W. Yang, *Appl. Comput. Eng.*, 2023, **7**, 229–233.
295 Z. Jia, L. Gao, L. Qin and J. Yin, *RSC Sustain.*, 2023, **1**, 2135–2147.
296 A. Kulkarni, G. Quintens and L. M. Pitet, *Macromolecules*, 2023, **56**, 1747–1758.
297 K. Chan and A. Zinchenko, *J. Cleaner Prod.*, 2023, **433**, 139828.
298 J. Mudondo, H.-S. Lee, Y. Jeong, T. H. Kim, S. Kim, B. H. Sung, S.-H. Park, K. Park, H. G. Cha, Y. J. Yeon and H. T. Kim, *J. Microbiol. Biotechnol.*, 2023, **33**, 1–14.
299 L. G. Schaerer, R. Wu, L. I. Putman, J. M. Pearce, T. Lu, D. R. Shonnard, R. G. Ong and S. M. Techtmann, *Trends Biotechnol.*, 2023, **41**, 184–196.

300 Y. Ogiwara and K. Nomura, *ACS Org. Inorg. Au*, 2023, **3**, 377–383.

301 J. Diao, Y. Hu, Y. Tian, R. Carr and T. S. Moon, *Cell Rep.*, 2023, **42**, 111908.

302 P. Liu, Y. Zheng, Y. Yuan, Y. Han, T. Su and Q. Qi, *Waste Manage*, 2023, **172**, 51–59.

303 T. Tiso, T. Narancic, R. Wei, E. Pollet, N. Beagan, K. Schröder, A. Honak, M. Jiang, S. T. Kenny, N. Wierckx, R. Perrin, L. Avérous, W. Zimmermann, K. O'Connor and L. M. Blank, *Metab. Eng.*, 2021, **66**, 167–178.

304 P. Ranganathan, Y.-H. Chen, S.-P. Rwei and Y.-H. Lee, *Mater. Today Chem.*, 2022, **26**, 101101.

305 Y. Zhang, F. Tian, C. Liu, X. Liu, Y. He and Z. Wu, *J. Cleaner Prod.*, 2024, **434**, 140048.

306 S. Hussain, M. H. Wadgama, A. L. Khan, M. Yasin and F. H. Akhtar, *ACS Sustainable Chem. Eng.*, 2023, **11**, 726–732.

307 H. Zhou, Y. Ren, Z. Li, M. Xu, Y. Wang, R. Ge, X. Kong, L. Zheng and H. Duan, *Nat. Commun.*, 2021, **12**, 4679.

308 H. Su, T. Li, S. Wang, L. Zhu and Y. Hu, *J. Hazard. Mater.*, 2023, **443**, 130120.

309 L. Fabrizio, R. Arrigo, M. T. Scrivani, M. Monti and A. Fina, *Polymer*, 2023, **266**, 125618.

310 L. Fan, L. Chen, H. Zhang, W. Xu, X. Wang, S. Xu and Y. Wang, *Angew. Chem., Int. Ed.*, 2023, **62**, e202314448.

311 C. Park, H. Lee, N. Lee, B. Ahn and J. Lee, *J. Hazard. Mater.*, 2022, **440**, 129825.

312 J. G. D. Dutra, M. H. de Souza Santana, Y. Ko, M. J. Lis, F. M. Bezerra, M. P. Moises and J. P. Hinestroza, *Mater. Circ. Econ.*, 2022, **4**, 24.

313 Y. Ko, T. J. Azbell, P. Milner and J. P. Hinestroza, *Ind. Eng. Chem. Res.*, 2023, **62**, 5771–5781.

314 A. K. Nason, R. T. Jerozal, P. J. Milner and J. Suntivich, *ACS Sustainable Chem. Eng.*, 2023, **11**, 18–22.