

Plastic pretreatment: The key for efficient enzymatic and biodegradation processes

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ABSTRACT

In recent years, enzymatic degradation and biodegradation have attracted great interest in the recycling of plastic waste. Compared to other recycling techniques, they have numerous advantages such as mild reaction conditions both in terms of temperature and pressure and the prevention in the use of toxic solvents. The monomers formed during the degradation processes can result in chemicals with high added value, which can be purified and reused at an industrial level. Unfortunately, numerous factors, both environmental and related to polymer's nature, influence enzymatic degradation and biodegradation, making them very complex processes. An effective way to increase degradation consists in subjecting the plastic material to pretreatments of various kinds, capable of inducing modifications in the polymer and making it more susceptible to the action of microorganisms or enzymes. This review has the objective of analyzing the literature of the last 15 years, to identify the most efficient pretreatments on the base of the polymer's chemistry, also considering technical-economic aspects.

1. Introduction

According to recent data, the production of plastic material in the world reached about 390.7 million tons in 2021 [1], where almost the totality (90.2 %) resulted fossil based. Polyolefins (as high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), polypropylene (PP), polystyrene (PS)), polyethylene terephthalate (PET), poly(vinyl chloride) (PVC), and polyurethanes (PU) are among the most required polymers on the market. The management of this enormous quantity of end-of-life materials, represents a great challenge, which requires the development of increasingly efficient and cost-effective recycling techniques. Alongside traditional recycling methods such as mechanical, chemical, and thermochemical [2–4], enzymatic degradation (ED) and biodegradation

(BD) are gaining considerable interest in recent years [5–7]. According to Vert et al. [8] the term biodegradation refers to "degradation caused by enzymatic process resulting from the action of cells". For this reason, "in vitro activity of isolated enzymes cannot be considered as biological activity" and it is defined enzymatic degradation. ED and BD appear to be promising and greener strategies for converting plastic waste into carbon dioxide (CO₂), monomers, and value-added compounds (VAC) [9]. ED and BD have significant advantages over traditional recycling techniques. First, the reaction conditions are milder both in terms of pressure (ambient) and temperature (the optimum temperature for most enzymes is 37 °C) than thermochemical processes such as pyrolysis (500 °C) [10] or gasification ($T > 800$ °C) [11]. This results in considerable energy savings. Ruthi et al. (2023) [12] showed that it is possible to biodegrade plastic material at very low temperature. They isolated

Abbreviations: BHET, Bis(2-hydroxyethyl) benzene-1,4-dicarboxylate; CA, Cellulose acetate; CDA, Cellulose diacetate; DMT, Dimethyl benzene-1,4-dicarboxylate; EG, Ethane-1,2-diol or ethylene glycol; HDPE, High-density polyethylene; HTL, Hydrothermal liquefaction; LDPE, Low-density polyethylene; LLDPE, Linear low-density polyethylene; MHET, 4-((2-Hydroxyethoxy)carbonyl)benzoic acid; NL_{CH4} kg_{VS}⁻¹, Biomethane potential unit of measure, expressed as the volume of dry methane gas under standard conditions (273.15 K and 101.33 kPa) per mass of volatile solids (VS) of substrate added; PA, Polyamide; P34HB, Poly(3-hydroxybutyrate-co-4-hydroxybutyrate); PBAT, Poly(butylene adipate-co-terephthalate); PBS, Poly(butylene succinate); PBSe, Poly(butylene sebacate); PBSe, Poly(butylene succinate-co-butylene adipate); PC, Polycarbonate; PCL, Poly(ϵ -caprolactone); PET, Poly(ethylbenzene-1,4-dicarboxylate) or polyethylene terephthalate; PHB, Polyhydroxybutyrate; PLA, Poly(lactic acid); PP, Poly(propene); PPC, Poly(propylene carbonate); PS, Polystyrene; PU, Polyurethane; PUR, Polyurethane rigid foam; PVA, Poly(vinyl alcohol); PVC, Poly(vinyl chloride); TPA, Benzene-1,4-dicarboxylic acid or terephthalic acid; TPS, Thermoplastic starch; VS, Volatile solids.

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microbial strains from the plastsphere of cold terrestrial environments and examined their ability to degrade plastic material (PE, dispersed PU, poly(butylene adipate-co-terephthalate) (PBAT) and poly(lactic acid) (PLA) at 15 °C. Agar clearing tests indicated that 19 strains had the ability to degrade PU; PBAT was degraded by 12 strains and PLA by 5. No strain was able to break down PE. So, the identified microbes could represent a valuable resource for the development of efficient and sustainable plastic-waste recycling at very low temperatures.

Among the advantages of ED and BD there are also the conditions of the reaction environment: reactions are carried out in water at physiological pH, unlike what happens in some chemical recycling processes in which dangerous solvents are required. For example, methanolysis of PET [13], commonly applied to scrap bottles, fiber wastes, films and plant wastes, involves the degradation of PET by methanol at high temperatures (180 °C and 280 °C) and high pressures (2 to 4 MPa). The main products are dimethyl benzene-1,4-dicarboxylate (DMT) and ethane-1,2-diol (EG). The most important disadvantages of methanolysis are the high costs associated to the use of catalysts (such as zinc acetate, magnesium acetate, cobalt acetate, and lead dioxide) [14], high pressures and temperatures during the process, the separation and refining of mixture's reaction products (glycols, alcohols, and phthalate derivatives) [15]. Similar considerations can be made for PET glycolysis [16]. Remarkable, recycling plants that operate through enzymatic degradation on an industrial scale are already present. The French company *Carbios* (Clermont-Ferrand) uses an innovative enzymatic technology to recover all PET waste, including waste that cannot be recovered using current recycling technologies such as textile. Their process is based on the use of an improved PET hydrolase that achieves, over 10 h, a minimum of 90 % PET depolymerization into monomers, with a productivity of 16.7 g/(L·h) of terephthalate [17]. Over time the company has filed many patents, here we reported Patent No: US 10,124,512 B2 as an example [18]. This patent relates "a biological method for depolymerizing at least one polymer of a plastic product and recovering the resulting monomers".

At present, great attention is paid to the study of biodegradable polymers as substitutes for fossil polymers in many applications [19]. According to Vert et al. [8] the term biodegradable is a "qualifier for macromolecules or polymeric substances susceptible to degradation by biological activity by lowering of the molar masses of macromolecules that form the substances". Typical examples are polylactides, polyhydroxybutyrate (PHB) and PBAT. Specific conditions in terms of humidity, oxygenation, pH, and presence of metals are required to ensure biodegradation. According to the officially recognized ISO 14855 method, a polymer to be defined as biodegradable, must degrade for at least 90 % to the basic components within six months and in the presence of an environment rich in CO₂ [20]. In particular, the European standard EN 13432 defines the four minimum requirements that packaging has to meet in order to be processed by industrial composting [21].

Despite the advantages described above, ED and BD of plastic material are very complex processes which are influenced by numerous environmental factors (pH, moisture, temperature) and polymer's characteristics [9,22] (e.g., polymer molecular weights, degree of crystallinity, functional groups, crosslinking, and the presence of additives in the polymer formulation). For example, in highly crystalline polymers, enzymes have difficulty accessing the polymer bonds to be cleaved and their catalytic activities result very low, hindering their application in commercial processes. As described in literature, an effective way to increase ED or BD consists in subjecting the plastic material to pretreatments of various nature, capable of inducing modifications in the polymer, which make it more susceptible to attack by microorganisms or enzymes [23]. Classic types of pretreatments are thermal and thermochemical, oxidative, chemical, mechanical [24]. The purpose of this review is therefore to examine the literature of the last 15 years (2008–2023) relating to possible pretreatments to be carried out on plastic materials, to increase their ED or BD. Some technical-economic

considerations related to the degradation processes have been carried out in accordance with the available data.

The main database used for bibliographic research in this review was Scopus, using the keywords "plastic AND pretreatment AND biodegradation" and "plastic AND pretreatment AND enzymatic AND digestion".

As highlighted by the graphs in Fig. 1, the topic covered in this review is extremely recent and the largest number of published articles belongs to the last 3 years (2020–2023).

The papers were then selected considering those most relevant to the topic of the review. This work was not limited to fossil polymers, but biodegradable plastics widely used in packaging were also considered.

Fig. 2 shows the distribution of the selected literature by type of polymer. As can be seen from the graph, the most studied polymer is PET, followed by polyolefins and biodegradable polymers. PU and other polymers such as polyamides, polycarbonate, aliphatic polyesters represent a small percentage.

2. Mechanisms of biodegradation and enzymatic degradation of plastics

The degradation of plastic material can be performed using microorganisms or enzymes. Microorganisms may be a microbial community such as those present in soil or compost, or a single strain of bacteria or fungi [25]. These adhere to the polymer surface forming a biofilm [26]. According to Elahi et al. [27], microorganisms then secrete extracellular enzymes, which adsorb to the polymer surface, causing the depolymerization of smaller fragments in the form of oligomers, dimers, and monomers [28]. Some of them diffuse within the microorganisms and are assimilated as a source of carbon and nitrogen, for their growth. From an industrial point of view, the monomers thus obtained can be chemicals with high added value. They can be purified and reused for re-synthesis of the original material (closed-loop processes) or for their bioconversion into different products (open-loop processes) [29].

In the aerobic biodegradation, oxygen is used in the process as an electron acceptor. The reaction by-products are water, H₂O and CO₂. In anaerobic biodegradation, bacteria use nitrate, sulfate, iron, manganese, and CO₂ as electron acceptors in place of oxygen, to convert large organic compounds into smaller molecules. In this case the reaction by-products are CH₄, H₂O, and CO₂.

As mentioned previously, enzymes can be used in vitro abiotic conditions. Enzymes are proteins that act as biological catalysts by accelerating chemical reactions. In living organisms, they perform essential functions in processes such as metabolism, gene expression, cell division, immune system reactions, and others [30]. Enzymes are classified according to the type of catalyzed reactions and are divided into 7 different classes as shown in Fig. 3: oxidoreductases, transferases, hydrolases, lyases, isomerases, ligases, and translocases.

Enzymes are very specific, and their activity and function depend on several characteristics, including their amino acid sequence, three-dimensional structure, stability, and interactions with other molecules. Their application depends on the nature of the substrate and the type of bonds to be cleaved [30]. Enzymes could be extracted from microorganisms as e.g., laccase from actinomycete *Rhodococcus ruber* [31] but also from mammalian cells such as lipase from *Porcine pancreas* [32] or from plants such as papain from *Carica papaya* [33]. Detailed information on the classification, nomenclature and description of enzymes can be found in the BRAunschweig ENzyme DAtabase (BRENDA) [34].

BD and ED of a plastic material can be monitored through various techniques, for example measuring the change in the chemical and physical properties of the polymer such as: molecular weight distribution [26], tensile strength, particle sizes but also change in functional groups and change in surface topography. BD can be monitored also evaluating CO₂ production and O₂ consumption [35].

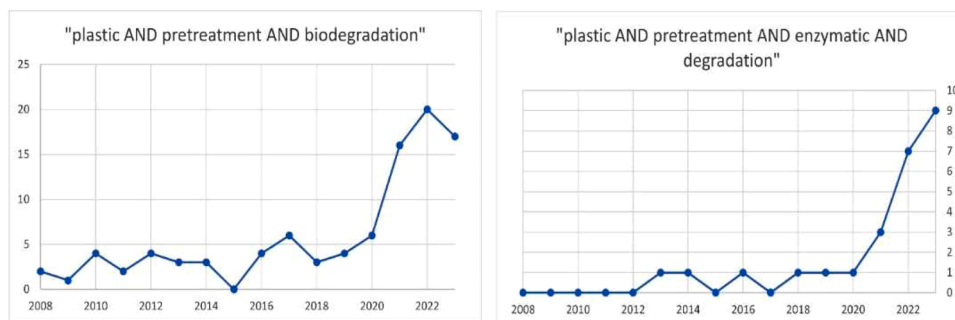


Fig. 1. Number of articles published for each year from 2008 to 2023 relating to pretreatments on plastic material to increase BD or ED. Data from Scopus (December 3rd, 2023).

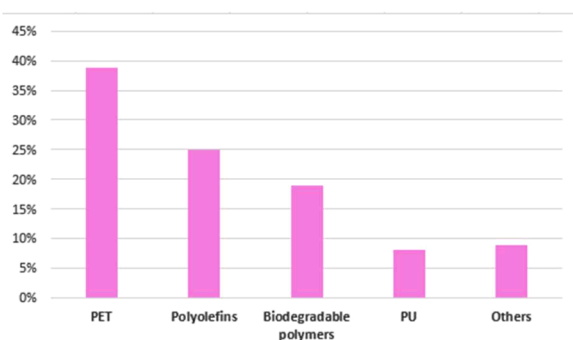


Fig. 2. Distribution of the selected literature by type of polymer.

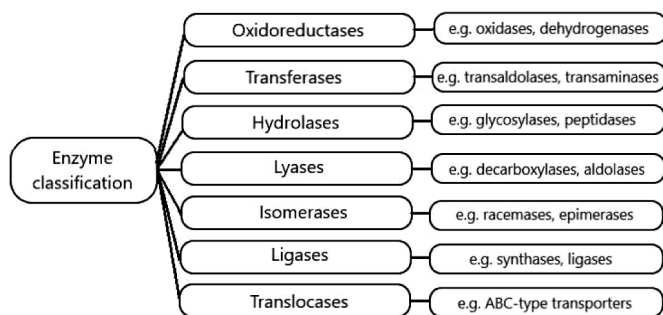


Fig. 3. Enzyme classification with some examples. Figure adapted from Vandenberghe Porto de Souza et al. [30].

3. Factors affecting biodegradation and enzymatic biodegradation

The biodegradation of plastic material is influenced by numerous factors, not only linked to the environmental conditions such as temperature, pH, oxygen, UV-radiation, moisture but also to the chemical-physical properties of the polymer itself, as schematically reported in Fig. 4. As described by some authors, most of these factors also influence ED [36–38].

Some of these factors are examined in more detail below.

The degree of crystallinity (X_c) appears among the most determining factors in the degradation of a polymer. The amorphous regions of the polymer present loosely packed chains and are permeable to water. Since water is required both to support the hydrolytic process and for the viability of the microbes, the amorphous region is more susceptible to biodegradation than the crystalline region [39]. Maurya et al. [38], examined in their review various factors affecting the hydrolysis rate of PET showing that PET with a lower X_c is easily degradable than PET with a high X_c . This is because a highly crystalline PET exhibits high tensile

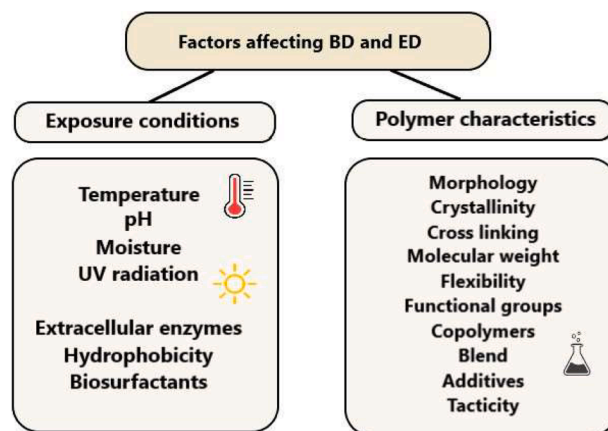


Fig. 4. Environmental conditions and chemical-physical properties affecting BD and ED. Figure adapted from Kijchavengkul and Auras [22].

strength and greater compactness and so it is difficult for the enzyme to access the ester bond.

In the work of Thompsen et al. [40], the effect of X_c on degradation was evaluated for PET samples using two different kinds of engineered, thermostable PET degrading enzymes: LCC_{ICCG}, a variant of the leaf-branch compost cutinase, and DuraPETase, a variant from the *Ideonella sakaiensis* PETase. X_c was varied via isothermal crystallization at 115 °C. Crystallinity affected the enzymatic product release rate that ceased at $X_c = 22\text{--}27\%$ for the LCC_{ICCG} and at $X_c \sim 17\%$ for the DuraPETase.

Another important factor affecting degradation is the hydrophilicity of the surface. An increase in the hydrophilicity of the polymer leads to greater vulnerability to enzymatic action and makes it more biodegradable [39]. Park et al. [41] studied the effect of polymer hydrophilicity in improving biodegradability of aliphatic polyesters (adipic acid or sebacic + 1,4-butanediol) introducing amide group (1,4-butanedi-amine) by copolymerization. The enzyme used for degradation was a lipase obtained from *Aspergillus oryzae*. The study showed that the addition of an appropriate amount of hydrophilic monomers (10–20 %) enhanced the degradability of aliphatic polyesters due to an easier accessibility of water molecules. According to the study, however, further increasing the level of amide content, there is a decrease in ED, probably due to the change in molecular structure.

However most synthetic polymers are hydrophobic and water insoluble, this makes the interaction between the hydrophilic enzyme and the hydrophobic surface of the polymer very complex. The addition of surfactants can be a strategy to increase the biodegradability of the polymer [42]. Furukawa et al. [43] showed that pre-incubation of a low-crystallinity (3–5 %) PET film with a thickness between 150–200 μm, with anionic surfactants for 1 h, prior to initiating the ED, improve

PETase activity of a 120-fold factor. The binding of surfactants to the film makes the surface negatively charged, thus attracting the cationic PETase.

The surface area exposed by the polymer to moisture and enzymes also affects biodegradability. The higher the surface area, the higher the biodegradation rate. Chinaglia et al. [44] explored the role of particle size on biodegradability, using poly(butylene sebacate) (PBSe) as polymer. Plastic pellets of PBSe were milled and sieved into different particle sizes, obtaining samples, with different specific surface areas (i.e., 33, 89, 193, and 824 cm²g⁻¹). These samples were tested for biodegradation in soil for 138 d. 1 g of test material was mixed with 200 g of soil in a 1 L hermetically sealed glass jar. A double dose of test material (2 g) was also tested for the powder fractions: 500 μm–700 μm and 50 μm–75 μm. A beaker with 30 mL of 0.5 M KOH was inserted into each jar. This solution allowed the trapping of the CO₂ produced during the process. The CO₂ was then titrated with 0.3 N HCl using a Mettler Toledo potentiometric titrator (T50). The study showed a correlation between biodegradation rate and the available surface, described by a double reciprocal regression model as in enzymatic kinetics model.

Another factor to consider is the molecular weight of the polymer. As the length of the polymer chain increases, the number of bonds that the enzyme must break increases. Moreover, polymers with a high molecular weight are characterized by low permeability in cellular membrane making them less susceptible to microorganisms attack. Bacteria in fact require the substrate be assimilated through the cellular membrane and then further degraded by cellular enzymes [39]. This process is easier for monomers, dimers, and oligomers [45].

Also, the presences of additives influenced biodegradation of polymers. Organometallic initiators used in radical synthesis and catalysts, might act as microbicides, and retard the degradation [46]. The presence of plasticizers can also influence the biodegradation process. The temperature at which the glassy state makes a transition to rubbery state in a polymer is called glass transition temperature (T_g). Polymers with high T_g are glassier and rigid, therefore little vulnerable to chain fracture. From an industrial point of view, the T_g can be lowered by adding plasticizers, thus making the polymer more easily processable. For example, cellulose acetate (CA), has a high glass transition temperature and cannot be processed in the molten state as raw material because it decomposes before melting [47]. The presence of additives in suitable concentrations not only facilitates the workability of the polymer but also improves its biodegradation. As shown by Phuong et al. [47] pure CA, completely biodegrades in 200 d of testing after reinoculation (the inoculum consists of stabilized and mature compost (> 20 weeks) derived from the organic fraction of municipal solid waste (MSW).

If a 30 % of plasticizer based on triacetin or triacetin-diacetin is added to the sample, biodegradation is completed in 46 d.

4. Plastic pretreatments

The “term” pretreatments, refers to all those processes of physical, chemical, or thermochemical nature (Fig. 5), capable of modifying the properties of a polymer and making it more susceptible to the action of microorganisms or enzymes.

Different types of pretreatments identified in literature of the last 15 years are categorized and commented below.

4.1. Oxidative pretreatments

Oxidative processes are widely used as environmentally friendly methods for the removal of organic pollutants, such as those present in wastewater [48,49]. Considering plastic as an organic pollutant, these types of processes were extended to the pretreatment of end-life plastic materials and/or microplastics, to degrade their surface and make it more rough and colonizable by microorganisms [50]. These processes include photo-oxidative degradation with UV, gamma ray, ozonation and use of oxidizing agents. Each of these pretreatments is summarized in Table 1 and described in detail below.

4.1.1. UV pretreatment

This type of pretreatment belongs to the family of photodegradation processes. Photodegradation can occur both in the presence (photo-oxidative degradation) or in absence (photolysis) of oxygen, leading to a chemical modification of the polymer: rearrangement, chain scission and cross linking [51]. UV pretreatment involves exposing the plastic to ultraviolet radiation (225–325 nm) [23] under controlled conditions, using UV lamps, UV chambers or even simulating natural aging conditions by alternating UV radiation with sprays of H₂O to create humidity. When plastics are subjected to highly energetic radiation, the polymer chains are broken, and radical species are obtained. These radical species undergo various reactions (e.g., the removal of hydrogen atom or the recombination of radicals) to promote chain scission and/or cross-linking [23]. The scission of polymeric chains involves a reduction of the molecular weight, and consequently a variation of the mechanical and optical properties (yellowing) of the polymer [51]. Depending on the type of bonds present in the chain, each polymer will undergo photodegradation at different wavelengths, for example PE at about 300 nm, while PP around 370 nm [52]. In the case of PE, the hydroperoxide group (—CH—OOH) is the primary oxidation product of photo-degradation and is both photolytically and thermally unstable [53]. It decomposes to produce two radicals (C—O· and H—O·), each of which can participate in a chain reaction process. In the oxidized sample, it is possible to observe the presence of the carbonyl group, which, being photolabile, can lead the sample to further biodegradation. So, UV pretreatment in polyolefins, decrease the hydrophobicity of the polymers, introducing on the surface C=O and —OH groups, that makes the exposed polymeric chain more prone to BD and ED [54].

Artham and Doble [55] investigated the biodegradation of Lexan™ polycarbonate (PC) resins films before and after UV pretreatment, with different fungal strains (*Engyodontium album* MTP091, SF1; *Penicillium* spp. MTP093, SF3; *Phanerochaete chrysosporium* NCIM 1170, SF2). PC films (60 × 10 mm) with weight average molecular weight, M_w of 57, 800, were subjected to UV light (UVC >300 nm wavelength) for 10 d. UV pretreatment leads to a reduction in number average molecular weight, M_n , of 24 % (determined with GPC). Incubation of treated and untreated PC was carried out for 12 months at 30 °C and 200 rpm. For the PC sample pretreated with UV and incubated with the SF2 strain for

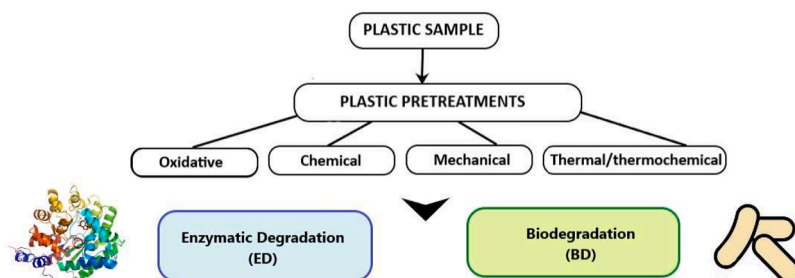


Fig. 5. Different types of pretreatments of plastic material.

Table 1
Oxidative pretreatments methods.

Feedstock	Pretreatment	Molecular weight variations after pretreatment	Microorganism/ Enzyme	Year	References	High value-added products
Lexan™ PC resin films (thickness=0.125 mm)	UV light (UVC >300 nm) for 10 d	Initial M_w PC resin= 57800 After pretreatment UV= 24 % reduction of M_n	<i>Engyodontium album</i> MTP091, SF1; <i>Phanerochaete chrysosporium</i> NCIM 1170, SF2; <i>Penicillium spp.</i> MTP093, SF3;	2010	Artham and Doble [55]	Not discussed
PET films (thickness=250 μm)	UV light (250 nm) for 14 d	Initial M_n PET films= 35000 g/mol M_n PET films after UV treatment= 29000 g/mol Not discussed	LC-cutinase	2020	Falkestain et al. [56]	Not discussed
HDPE, PS and PET films (thickness= 0.12 mm, 2 mm and 0.24 mm)	UV light (245 nm) for 72–120 h at two different distances (24 and 12 cm)	Not discussed	<i>Penicillium raperi</i> , <i>Aspergillus flavus</i> , <i>Penicillium glaucoroseum</i> and <i>Pseudomonas spp.</i>	2021	Taghavi et al. [57]	Not discussed
LDPE and PP (thickness= 20 μm)	Gamma rays 0–1000 kGy for LDPE and 0–100 kGy for PP.	M_w LDPE Control=27114.40 g M_w LDPE-1000 KGy =25953.74 g M_w PP Control= 63826.34 g M_w PP Control-100 KGy= 59020.00 g	<i>Aspergillus sp.</i> , <i>Paecilomyces lilacinus</i> from <i>H. brunonis</i> and <i>Lasiodiplodia theobromae</i> from <i>Psychotria flavida</i>	2015	Sheik et al. [59]	Not discussed
¹⁴ C-PS films	Ozonation	Not discussed	<i>Penicillium variabile</i> CCF3219	2017	Tian et al. [61]	Not discussed
PEU films (thickness= 0.5 mm)	Chemical pretreatment: 10 % H ₂ O ₂ and 0.05 M CoCl ₂	Not discussed	Papain	2000	Hsu and Huang [63]	Not discussed

one year, a weight loss of 5.4 % and a 40 % reduction in M_n , were recorded while an increase in surface energy, oxygen content, and reduction in methyl index indicated the oxidation of PC. The differences observed in the amount of degradation between treated and untreated samples indicate that UV pretreatments enhance biodegradation, increasing surface energy probably by creating new hydrophilic functional groups. The enhancement in biodegradation is however strain specific.

Falkestain et al. [56] carried out a study about the influence of UV irradiation as a potential pretreatment method for ED of PET with the enzyme LC-cutinase. PET films with a thickness of 250 μm were irradiated for 14 d using a 1-kW xenon arc lamp with a cut-off in the UV region at ~ 250 nm. The M_n value before and after pretreatment was estimated by ¹H-NMR spectroscopy and is respectively equal to 35000 and 29000 g/mol. Enzymatic digestion was carried out for 24 h at 70 °C in K₂HPO₄/Cl (1 M, pH = 8.0) under agitation (1000 rpm). In this case the degradation of UV-treated PET films resulted in significantly lower weight losses (41.0 ± 1.3 %) compared to the untreated sample (57.9 ± 2.4 %). This phenomenon was explained thanks to ¹³C-CP/MAS experiment. The evidence indicated an increased crystallinity because of UV exposure and so a reduced accessibility for the enzyme.

Taghavi et al. [57] studied the effect of UV pretreatment on three different plastic samples, HDPE, PS and PET, with different colors and thickness (0.12 mm, 2 mm, and 0.24 mm respectively). The samples were irradiated in a closed metal chamber at 245 nm, for 72 and 120 h at two different distances (24 and 12 cm) from the UV light source. The four different microbial strains used in this study were *Penicillium raperi*, *Aspergillus flavus*, *Penicillium glaucoroseum* and *Pseudomonas spp.* The study showed that the better conditions for UV-pretreatment were a long irradiation time (120 h) and a short distance to UV source (12 cm). These conditions resulted in greater roughness, hydrophilicity, and more significant loss of physical and molecular weight promoting the biodegradation of the two tested polyolefins. After 45 d of incubation time the degradation efficiency is 7.8 % for PE and 5.13 % for PS. UV pretreatment, on the other hand, proved ineffective for PET, whose degradation remained below 1 % even after 90 d of biodegradation.

Pretreatment with UV radiation is therefore very effective against extremely recalcitrant polymers such as polyolefins and polycarbonates, but it is totally ineffective for PET. On an industrial scale, there are already technologies that exploit the UV radiation approach such as those related to the disinfection of water. Disadvantages of this technology can be those linked to the long pretreatment times required, which can lead to high energy consumption. Recent studies [58] have

also highlighted how high-intensity (~2 kW) commercial UVC disinfection devices influence the composition and concentration of gasses and particles in indoor air and can have adverse effects on human health. Furthermore, the disposal of exhausted lamps could become an environmental concern.

4.1.2. Gamma ray pretreatments

Sheik et al. [59] studied the use of gamma rays as pretreatment of LDPE and PP film (thickness = 20 μm). Films were cut into strips and irradiated at different doses of gamma radiation (0–1000 kGy for LDPE and 0–100 kGy for PP) and the M_w was determined by viscometric measurements. Films were incubated for 90 d with strains of fungi from two endemic plants, *Psychotria flavida* and *Humboldtia brunonis*. Irradiation with gamma rays produced carbonyl groups on the polymer's surface and caused a reduction in the M_w of the polymers as shown in Table 1 at row 4. Pretreated LDPE inoculated with *Aspergillus sp.*, *Paecilomyces lilacinus* from *H. brunonis* and *Lasiodiplodia theobromae* from *Psychotria flavida* showed, both, a decrease in intrinsic viscosity and average molecular weight. That indicated fungal efficiency in plastic degradation. Only *L. theobromae* from *P. flavida* could degrade irradiated PP films. Although it is a very efficient pretreatment, the doses of gamma rays used in the experiments are very high compared to the doses commonly used in the materials processing industry (10–30 kGy for sterilization). For this reason, this energy-intensive pretreatment cannot be easily scale up to an industrial scale.

4.1.3. Ozonation

Ozone (O₃) is an extremely strong oxidizing agent, widely used to sterilize food, drinking water and surfaces. Exposure of polymers to ozone causes a degradation of the polymer chains and the introduction of oxygen-containing functional groups [60] on the surface, that increase polymer's hydrophilicity. Ozen et al. [60] demonstrated that ozone treatment caused significant changes in mechanical and oxygen barrier properties of LLDPE and biaxially oriented nylon films. An increase in the treatment time, caused a decrease in oxygen permeability for both film types. In particular, the 24 h treatment with O₃ resulted in a 40±50 % decrease in O₂ permeability for both films.

Tian et al. [61] studied ozonation as pretreatment for a subsequent mineralization of ¹⁴C labeled PS films by the fungus *Penicillium variabile* CCF3219 for 16 weeks. Ozonation of the samples was performed using an ozone generator. The films were insufflated at a rate of 5 L/min for 3 h (i.e., equivalent to 17 g of O₃ in total). Then samples were incubated in liquid medium at pH=7.5 and 24 °C on a rotary shaker (120 rpm) for 16

weeks. During the incubation time, ^{14}C was captured to calculate the mineralization of ^{14}C -PS, instead solid samples were analyzed by means of SEM, FTIR and GPC. FTIR analysis showed that ozonation pretreatment generate $\text{C}=\text{O}$ (1796 cm^{-1}) on the surface of PS. After incubation with *P. variable* for 16 weeks, the intensity of this peak decreased slightly, indicating that the $\text{C}=\text{O}$ groups were consumed by the fungus. Moreover, GPC analysis showed a reduction in the molecular weights of the ozonated PS after incubation. Based on these data ozonation pretreatment could be a potential approach for degradation of PS waste and remediation of PS-contaminated sites.

According to a report of the United States Environmental Protection Agency (EPA) [62] the use of O_3 can present some disadvantages as the intrinsic need of corrosion-resistant materials (e.g., stainless steel) and the associated risk for workers because it is an extremely reactive and irritating gas. In addition, the use of O_3 in water disinfection is expensive and energy intensive [62]. These issues can also arise in the use of O_3 for the pretreatment of polymers and must be carefully evaluated.

4.1.4. Chemical oxidation

Chemical oxidation involves exposing the polymer to reagents, capable of oxidizing the polymer's lateral chains. One of the first studies using this pretreatment is that of Hsu and Huang [63], in which two different poly(ether)urethanes (PEU), one chain extended with 1,4-butanediol (PEU A) and the other with 2-butene-1,4-diol (PEU B) were synthesized and then oxidized, with the aim to convert the ether bonds to ester. In this way the polymers could be made more attackable by an esterase. The oxidative pretreatment was carried out using 10 % H_2O_2 and 0.05 M CoCl_2 . The PEU samples were immersed in this solution at $37\text{ }^\circ\text{C}$ for 1 week. The solution was changed every 3 to 4 d. Samples were then immersed in papain solution. Papain was prepared to a concentration of 140 U/mL in the enzyme activating medium containing 0.05 M cysteine-HCl, 0.01 M EDTA and $6 \cdot 10^{-4}$ M 2-mercaptoethanol at $\text{pH}=6.2$. Samples were incubated at $37\text{ }^\circ\text{C}$ for 1 month, changing the solution every 3 or 4 d. The degradative effect on surfaces was examined by ATR, optical microscopy, and XPS. The increase in the O/C atomic ratio determined by XPS for the samples pretreated and subjected to enzymatic digestion, confirmed that oxidative pretreatment increases the susceptibility of PEU to enzymatic hydrolysis by papain. The increase may be related to the interaction between papain molecules and the oxidized surface. Of the two types of polyurethanes tested, the one containing 2-butene-1,4-diol was more resistant to oxidation and therefore less susceptible to enzymatic degradation (O/C atomic ratio PEU A: 0.32; O/C atomic ratio PEU B: 0.29).

4.2. Chemical pretreatments without oxidizing agents

Non-oxidizing chemical pretreatments can also be performed to reduce the molecular weight of the polymers and change their morphology (Table 2).

Giraldo-Narcizo et al. [64] studied the enzymatic degradation of NaOH pretreated post-consumer PET bottles, using PETase as enzyme. Samples about $1 \times 1\text{ cm}^2$ were immersed into a 10 M NaOH solution for 24 h at room temperature and then washed with distilled water, vacuum dried and weighed. Untreated and pretreated samples were immersed in 200 μL glycine-NaOH buffer (50 mM, $\text{pH}=9.0$) with purified enzymes (2 mg enzyme/g PET) at $30\text{ }^\circ\text{C}$ for 1–6 d. DSC analysis on pretreated sample show a reduction in crystallinity from $3.70 \pm 0.05\%$ to $27.68 \pm 0.34\%$ after alkali pretreatment. This reduction in crystallinity increased the catalytic activity of the enzymes facilitating the enzyme's access to chemical bonds. Moreover, NaOH treatment modify the surface of the substrate that becomes rougher. According to the authors the method was less energy intensive than other pretreatment methods and used cheap chemical products (i.e., NaOH).

Excellent biodegradation results have been obtained after alkaline pretreatment also on biodegradable polymers such as PLA, PBAT, thermoplastic starch (TPS), poly(butylene succinate-co-butylene

adipate) (PBSA), cellulose diacetate (CDA), poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P34HB), poly(butylene succinate) (PBS), poly(ϵ -caprolactone) (PCL), poly(vinyl acetate) (PVA), poly(propylene carbonate) (PPC) by Jin et al. [65]. Alkali pretreatment was performed on polymers powder (particle sizes $< 425\text{ }\mu\text{m}$) using solutions with different NaOH concentrations (1, 3, 5 %wt). Samples were exposed for 24 h at $25\text{ }^\circ\text{C}$. The anaerobic digestion experiment was carried out in triplicate under thermophilic ($55 \pm 2\text{ }^\circ\text{C}$) conditions with a substrate to inoculum ratio of one on a VS basis. The inoculum used was anaerobic sludge collected from the biogas station in Tongzhou District, Beijing. The biodegradability values for 5 % NaOH-pretreated CDA, 3 % NaOH-pretreated P34HB, 5 % NaOH-pretreated PBS, 5 % NaOH-pretreated PBSA, 3 % NaOH-pretreated PCL, 5 % NaOH-pretreated PLA, and 3 % NaOH-pretreated PVA were 85.2 %, 96.7 %, 5.8 %, 88.7 %, 98.7 %, 99.1 %, and 13.8 %, corresponding to increases of 1752.2 %, 13.2 %, 607.3 %, 190.8 %, 6.9 %, 6.6 %, and 15.0 %, respectively ($P < 0.05$). However, the study highlighted how pretreatment with NaOH has no effects on PBAT (0 % biodegradation before and after alkaline pretreatment) and on PPC (0 % biodegradation before and after 90 % alkaline pretreatment). Moreover, although the biodegradation values of PBS and PVA were improved by NaOH pretreatment, their degradation properties were still poor.

Kalia and Dhanya [66], pretreated LDPE waste bags with xylene and then carried out a biodegradation with *Lysinibacillus fusiformis*. LDPE waste bags of $30\text{ }\mu\text{m}$ and $50\text{ }\mu\text{m}$ thickness were cut into uniform pieces of $1 \times 1\text{ cm}^2$ and then were subjected to xylene treatment by boiling for 15 min. Samples were washed with ethanol and dried in a hot air oven at $60\text{ }^\circ\text{C}$. Xylene treatment fragmented the polymer and converted it into a powder. The incubation of LDPE samples with *Lysinibacillus fusiformis* was performed in a rotatory incubator shaker at $30\text{ }^\circ\text{C}$ and 180 rpm for 30 d. According to the authors, fragmentation resulted in changes in the molecular weight distribution and morphology of the LDPE, although details have not been reported. The treatment helped to increase the availability of LDPE to microorganisms improving the bacterial growth on the samples. The biodegradation efficiency of isolated *Lysinibacillus fusiformis* was enhanced of about 12 % and 2 % respectively in $30\text{ }\mu\text{m}$ and $50\text{ }\mu\text{m}$ thick LDPE bags.

Krainara et al. [67] studied pretreatment of PET and PLA wastes (PET bottle, PLA cup, and PLA film) with deep eutectic solvent prepared by mixing choline chloride (ChCl) and glycerol (Gly) in a molar ratio of 1:2. The plastic samples were pretreated with ChCl:Gly-DES through a dip-coating method. The bacterial strains *Chitinophaga jiangningensis* EA02, *Nocardioides zeae* EA12, *Stenotrophomonas pavanii* EA33, *Gordonia desulfuricans* EA63, *Achromobacter xylosoxidans* A9 and *Mycolicibacterium parafortuitum* J101 were used to prepare a bacterial consortium. Samples pretreated with DES show increased surface wettability and biofilm formation, indicating that DES increases the hydrophilicity of the plastic and promotes the attachment of bacteria to the plastic surface. The combined action of DES pretreatment and bioaugmentation with a plastic-degrading bacterial consortium led to improved degradation of the samples in aqueous media at room temperature, in traditional laboratory-scale composting and pilot-scale composting.

4.3. Other pretreatments with chemicals

As previously mentioned in paragraph 3, pretreatment of the plastic material with surfactants can facilitate enzymatic attack [43]. Furukawa et al. [43] incubated low crystallinity PET films with different anionic surfactants (sodium alkylsulfate ($-\text{SO}_4^-$), alkylsulfonate ($-\text{SO}_3^-$) or carboxylate ($-\text{COO}^-$)). PET films were pre-incubated in buffer (50 mM bicine, $\text{pH}=9.0$) with the surfactants at $30\text{ }^\circ\text{C}$ for 1 h. The reaction was initiated by adding 500 nM PETase and incubating at $30\text{ }^\circ\text{C}$ for 1h. The anionic surfactant charged the surface of the polymer negatively attracting the cationic PETase. Moreover, the surfactant adsorbed on PET induces a net orientation of the active site of the enzyme towards the surface, resulting in a more efficient hydrolysis. The presence of

surfactant improves PETase activity 120-fold. After 36h at 30 °C, the film thickness decreased by 22 % (Table 2).

Bertolacci et al. [68] studied the melt-blending of LDPE sheets with fatty acids or triglycerides (either pure oleic acid, OA, or vegetable oil) in ratio 1:5 or 1:10 OA: LDPE. After 5 melting/solidification cycles, thin films were produced by compression molding at 140 °C for 10 min with 3 tons applied load. Fatty acids reduced the dense packing among the polymeric chains and converts the inert LDPE in a softer material suitable for microbial colonization by fungal mycelia. Then incubation with *Agrocybe aegerita* mycelium was performed at 26 °C and 70–80 % RH. Samples were incubated for one month. This fungal mycelium was able to oxidize polyethylene chains as shown by the presence of carbonyl peak in the ATR spectra of incubated samples. This work demonstrates how the synergistic effect of the pretreatment with the employment of an oxidizing fungal mycelium strain, results in a substrate oxidation fourfold higher than the best results reported in literature, laying the bases for the development of biocatalytic recycling processes.

4.4. Mechanical pretreatment

Mechanical pretreatments have been extensively studied since the past for lignocellulosic biomass, to separate lignin, cellulose and hemicellulose and make them accessible to the reagents. This pretreatment has proven to be an efficient method for altering the chemical-physical properties of solid phases and for this reason it is widely used in bio-refineries [69].

The mechanical force applied to a solid sample acts at the molecular level, causing chemical reactions in the solid state by the applied shear stress, breaking symmetry that destabilizes bonds and making them prone to reaction [70]. A chemical reaction induced by the direct absorption of mechanical energy is called a mechano-chemical reaction [71].

The effects of the mechanical action are numerous and concern:

- the creation of irreversible structural defects such as point defects, amorphous regions, dislocations, grain boundaries
- the reduction in the crystalline size due to the high impact force arising from the milling process
- the production of radicals, creation of active sites and oxidation

The grinding has thus received considerable interest as a pretreatment of waste plastic materials for a subsequent ED (Table 3).

Table 2
Pretreatments methods with different types of chemicals.

Feedstock	Pretreatment	Molecular weight variations after pretreatment	Microorganism/ Enzyme	Year	References	High value-added products
PET bottles	NaOH 10 M, 25 °C, 24 h	Not discussed	PETase	2023	Giraldo-Narcizo et al. [64]	MHET and TPA
P34HB, PBS, PCL, PPC, PVA, PLA, PBAT, TPS, PBSA and CDA	NaOH 1 %, 3 %, and 5 %, 25 °C, 24 h	Not discussed	Anaerobic digestion - inoculum from anaerobic sludge	2023	Jin et al. [65]	Not discussed
LDPE waste bags (30 µm and 50 µm)	Boiling in xylene for 15 min	Not discussed	<i>Lysinibacillus fusiformis</i>	2022	Kalia and Dhanya [66]	Not discussed
PLA films (thickness = 0.043 ± 0.003 mm) PLA cup (thickness = 0.254 ± 0.006 mm) PET bottles (thickness = 0.125 ± 0.003 mm)	Coating of plastic with ChCl:Gly-DES, 30 h at 30 °C.	Not discussed	Bacterial consortium: <i>Chitinophaga jiangningensis</i> EA02, <i>Nocardioides zeae</i> EA12, <i>Stenotrophomonas pavanii</i> EA33, <i>Gordonia desulfuricans</i> EA63, <i>Achromobacter xylosoxidans</i> A9, <i>Mycolicibacterium parafortuitum</i> J101	2023	Krainara S. et al. [67]	Not discussed
Low-crystallinity PET film (thickness = 200–150 µm)	Pre-incubation with anionic surfactants	Not discussed	PETase	2018	Furukawa et al. [43]	TPA, MHET, and BHET
LDPE sheets (thickness 1.0 mm)	Melt-blended with fatty acids (ratio 1:5 or 1:10)	Not discussed	<i>Agrocybe aegerita</i> mycelium	2022	Bertolacci et al. [68]	Not discussed

Kawai et al. [72] studied ED of different kinds of PET samples (films, packages, and bottles) using micronization as pretreatment. All the samples were cut into pieces and further homogenized in water. Then amorphous PET pellets were milled into powder particles using different blending systems with or without prefreezing with liquid nitrogen. ED was performed at different temperature (63–70 °C) with shaking at 110 rpm for 3 d using engineered cutinase Cut190. The reaction mixture for PET hydrolysis contained 100 mM HEPES–NaOH buffer (pH=8.5 and 9.0), 2.5 mM CaCl₂, 24 % glycerol, and approximately 2 µM Cut190 derivative. The study demonstrated how an increase in the surface area of the samples promotes the hydrolysis reaction by the enzyme which proceeds through two distinct steps: endo-type scission of a polymer chain and exo-type hydrolysis of depolymerized fragments. In addition to the pretreatment, the presence of a cationic surfactant as dodecyltrimethylammonium chloride (C₁₅H₃₄ClN) plays a fundamental role. In fact, it facilitates the binding between the enzyme, which has a negatively charged surface and the surface of the polymer.

The enzymatic digestion reaction can be carried out directly in ball milling jars as described by Kaabel et al. [73]. PET powder of 36 % of crystallinity was weighed into a 15 mL PTFE or stainless-steel jar, charged either with ZrO₂ or stainless-steel ball(s), with cutinase from *Humicola insolens* preparation (300 µL, 1.95 mg protein) and buffer (150 µL). The milling was carried out at a frequency of 30 Hz for 5 min. The resulting solids were analyzed by HPLC in three steps: 1) post milling, 2) after milling followed by 3 d aging at 55 °C and 3) after milling followed by 7 d aging at 55 °C. These reaction conditions provide a reaction medium that is closer to the natural setting of enzymes like cutinases, which are secreted in the environment by microorganisms. The reaction with an enzyme percentage of 3 % leads to a TPA yield of 50 %.

Despite the plethora of studies available on mechanical pretreatment of biomass, only few studies are available on polymers, specifically on PET. According to some authors [64], the pretreatment of plastic material with ball milling is extremely energy-intensive and cannot be applied on a large scale because of the reduction in size is caused by frictional forces that are generated in the jar.

4.5. Thermal and thermochemical processes

Thermal and thermochemical pretreatments involve heating of plastic samples at given temperature and/or pressure conditions to modify the chemical-physical properties of the polymer or induce chemical reactions which increase its biodegradation.

Table 3
Mechanical pretreatments on PET samples.

Feedstock	Pretreatment	Molecular weight variations after pretreatment	Microorganism/ Enzyme	Year	References	High value-added products
PET samples: • films (thickness= 0.25 mm) • packages (thickness= 0.6 mm) • bottles	Micronization	Not discussed	Engineered cutinase Cut190	2022	Kawai et al. [72]	MHET, BHET, TPA
High crystalline PET (36 %)	Ball milling	Not discussed	Cutinase from <i>Humicola insolens</i>	2021	Kaabel et al. [73]	TPA, MHET, EG

4.5.1. Thermal pretreatment

In the study of Pantani and Sorrentino [74] biodegradation of PLA was examined altering the X_c with annealing at 105 °C. PLA pellets were injection moulded at 200 °C, with an injection pressure of about 70 MPa and a packing time of 40 s. The injection-moulded samples resulted fully amorphous. To increase the X_c some samples were kept in an oven at 105 °C for 8 h. In this way, X_c of about 30 % was reached, which is the maximum achievable for PLA. Biodegradation tests on PLA samples were carried out using compost coming from a municipal composting plant and homemade respirometric system, as assessed by ASTM D 5338 and ISO 14855 standards. The study revealed how the amorphous sample presented a deeper degradation, making it extremely fragile. On the contrary crystallinity reduces the degradation rate of PLA. The study also evaluated the effect of milling on biodegradation. A third sample was prepared by milling the crystalline PLA to a characteristic dimension of 0.2 mm. For this sample the rate of degradation increases toward that of the amorphous sample, confirming how the reduction in size favors biodegradation with the same X_c (Table 4).

Rad et al. [75] investigated biodegradation of LDPE and PVC amorphous microplastics (particle dimension: 250–425 μm) by *Achromobacter denitrificans* from compost. Samples were pretreated with a saturation stream of a small steam boiler under a pressure of 11 psi, at 110 °C and for 10 h. This treatment led to the incorporation of O_2 into the polymer matrix which increased the activity of bacteria. Results showed that about 12.3 % and 6.5 % weight loss, and 326.4 and 112.32 mg L^{-1} of extracellular protein were obtained in bacterial flasks with PVC and LDPE, respectively. Consequently, thermo-oxidative pretreatment was considered a suitable strategy for improving microplastics biodegradation.

4.5.2. Thermochemical pretreatments

Thermochemical pretreatments have also been studied within our research group to increase the biodegradability of rigid polyether PU foam (PUR) [76]. These polymers are particularly recalcitrant to biodegradation as shown in other study [77]. Its structure and chemical composition were determined through ATR analysis and solid-state ^{13}C -NMR. PUR foam was then subjected to hydrothermal liquefaction (HTL) ($T = 350$ °C, reaction time: 20 min) using either ultra-pure water or KOH as a basic catalyst (1.12 g). Enzymatic digestion was then performed on: bulk foam sample, hand milled foam sample and on the organic fractions obtained from the both HTL experiments. The enzyme used in this study was a lipase extracted from *Candida rugosa*. Samples were incubated at 37 °C and $\text{pH}=7.2$ for 1 week under orbital agitation.

Table 4
Thermal pretreatments.

Feedstock	Pretreatment	Molecular weight after pretreatment	Microorganism/ Enzyme	Year	References	High value-added products
PLA pellets	Annealing at 105 °C and milling for one sample	Not discussed	Compost	2013	Pantani and Sorrentino [74]	Not discussed
LDPE and PVC amorphous microplastics	Saturation stream of a small steam boiler ($P = 11$ psi, $T = 110$ °C, time= 10 h)	Not discussed	<i>Achromobacter denitrificans</i> from compost	2022	Rad et al. [75]	Not discussed

The study demonstrated that enzymatic digestion does not occur on the PU bulk and is difficult to achieve on the powdered material, because it occurs at the interface between the enzyme-containing solution and the insoluble plastic material. Moreover, the presence of non-polar surfactants at the polymer's surface prevents the enzyme from reaching the surface of the polymer. Thermochemical pretreatment fragmented the polymer into oligomers, which are therefore more easily accessible to the enzyme and more easily biodegradable as shown by the HPLC-UV-Vis analysis. In this work, we demonstrate that HTL pretreatment in subcritical conditions, carried out for short times, can be an effective method for a subsequent enzymatic valorization of PUR (Table 5).

Thermochemical treatments are also efficient for the ED of textile fibers. Quartinello et al. [78] studied the ED of Wellman PET fibers with a viscosity of 0.62 dL/g. PET fibers were hydrolyzed in a stainless-steel reactor at two different temperatures (180 and 250 °C), two different reactions time (60 and 90 min) and with and without the addition of zinc acetate as catalyst. When temperature and pressure were increased to 250 °C and 39 bar, respectively, the polymer was completely reduced in powder. White powder was made for an 85 % of TPA, while the remaining 15 % was made by PET oligomers. An enzymatic hydrolysis was carried out on these oligomers, using *Humicola insolens* cutinase (HiC) at different concentrations. The incubation was carried out at $\text{pH}=7$, for 24 h at 50 °C and under orbital shaking. The study demonstrated that the highest amount of soluble TPA (6.5 mM) was obtained after 6 h of incubation when 1 or 2 mg/mL of HiC were applied without further addition increase up to 24 h of incubation. Hydrolysis with a subsequent enzymatic digestion allows to obtain TPA with 97 % purity which is comparable to synthesis-grade TPA (98 % pure). Instead, when chemical pre-hydrolysis of PET was performed in the presence of zinc acetate as a catalyst, a negative influence on enzymatic hydrolysis was observed.

4.6. Study of combined pretreatments on the same type of polymer

In some studies, different types of pretreatments have been compared for the same type of polymer (Table 6). For example, Arkatkar et al. [79], studied biodegradation of PP films (1.5 × 1.5 cm and 0.05 mm thickness) in vitro in minimal medium with four different soil cultures (*Pseudomonas azotoformans*, *Pseudomonas stutzeri*, *Bacillus subtilis* and *Bacillus flexus* separately) for 12 months at $\text{pH}=7$ and temperature of 35–37 °C, under aerobic conditions at 180 rpm. PP films were pretreated:

Table 5
Thermochemical pretreatments.

Feedstock	Pretreatment	Molecular weight after pretreatment	Microorganism/ Enzyme	Year	References	High value-added products
PUR	HTL ($T = 350\text{ }^{\circ}\text{C}$, $P = 22\text{ MPa}$, $t = 20\text{ min}$)	Not discussed	Lipase from <i>Candida rugosa</i>	2022	Gallorini et al. [76]	Variously substituted quinolines and 4,4'-methylenedianiline
PET fibers	Hydrolysis at 180 and 250 °C, for 60/90 min, with or without ZnAc	Not discussed	<i>Humicola insolens</i> cutinase (HiC)	2017	Quartinello et al. [78]	TPA

- 1) Chemically with Aquaregia for 3 d (PP-ART) or with Fenton's reagent (Fe(II) salt, at pH=5.5, drop wise addition of H₂O₂) for 7 d (PP-FRT)
- 2) Thermally at 100 °C for 8 d in a hot air oven (PP-TT)
- 3) Short UV pretreated (PP-SUV) at 225 nm for 6 d

The FTIR spectroscopy performed on the samples after pretreatment showed the formation of carbonyl groups both on the chemically pretreated samples and on those pretreated by photodegradation. The formation of ester carbonyl groups was observed on the thermally pretreated and UV pretreated sample. The presence of these bonds indicates a surface oxidation, which allows an easier attack by microorganisms. All four microorganisms tested behaved differently in the presence of different pretreated films. *P. azotoformans* and *B. subtilis* were able to produce biosurfactant and form biofilm on the polymer surface with comparatively higher carbohydrate and protein than the other two organisms. *P. stutzeri* was not found to have any effect on the polymer and it wasn't able to growth on its surface. *B. flexus* did not produce biosurfactant but it was able to degrade chemically pretreated PP films. Moreover, it oxidized unpretreated PP more when compared to other three organisms. Thus, it can be concluded that out of the four microorganisms screened, *B. flexus*, was able to biodegrade pretreated PP films showing a synergistic effect between pretreatment and biodegradation. Highest weight loss (2.5 %) was observed in the case of short UV treated polymer exposed to *B. flexus* after one year.

Falah et al. [80] investigated the potential of microalgal species *Chlorella vulgaris* to remediate pretreated plastic waste. PET films were pretreated by different processes:

- 1) Physical treatment (UV and temperature, i.e., 100 °C for 48 h)
- 2) Chemical pretreatment (90 % concentrated nitric acid, for 5 d at ambient temperature)

The incubation of samples with *Chlorella vulgaris* was carried out under light illumination for 1 month at room temperature. As shown by the study, pretreatments had a marked effect on the cracking and alteration of plastic polymer, which helped to grow microbial species on cracked surfaces. FTIR analysis has highlighted how pretreated samples showed a greater number of functional groups than the original PET which helped algal species to biodegrade plastic structure. GC-MS analysis revealed that the microbial specie could produce biodegradation products which were likely to be found in the structure of PET, including bis(2-ethylhexyl)phthalate, a toxic biodegradation product coming from phthalic acid.

Balasubramanian et al. [81], investigated the influence of physical (heat and UV), chemical (citric acid and potassium permanganate/hydrochloric acid, KMnO₄/HCl), and biological (microbial) treatments in different combinations to enhance HDPE degradation. HDPE film was exposed to heat at 50 °C for 72 h. For photodegradative pretreatment HDPE was alternatively subjected to exposure to UV (312 nm) and humidity for 5 cycles day⁻¹ separated by 1 h intervals at 50 °C, during which water is condensed on the HDPE surface. The overall pretreatment time is 60 h The HDPE film was also chemically pretreated immersing it into a solution of KMnO₄/HCl at concentration of 0.25–0.5 mol/L at 45 °C for 8 h. Another kind of pretreatment was realized submerging HDPE in 10 % citric acid for 8 h at 45 °C. These

pretreatments were combined in different ways to maximize the biodegradation. The pretreated HDPE samples were aseptically inoculated with *A. terreus* MF12 for 30 d of incubation at 30 °C for microbial treatments. The combination of pretreatments that gave the best results is that: UV treatment + KMnO₄/HCl + citric acid + heat treatment. In fact, the degradation rate was enhanced from 9.4 ± 0.1 % to 20.8 ± 0.1 %. Environmental factors (physical and chemical) therefore play an important role to initiate the degradation of HDPE and support the *A. terreus* MF12 to degrade HDPE.

Cazaudehore et al. [82], investigated how to enhance PLA biodegradation rate under mesophilic anaerobic digestion, performing different kinds of pretreatments:

- 1) Mechanical pretreatment using liquid N₂ and a centrifugal mill at a screen size of 2 mm.
- 2) Thermal and chemical pretreatments in 35 mL pyrex glass tubes heated in a heat system with magnetic agitation. Different temperatures (70, 90, 120, and 150 °C) and different residence times (1, 6, 24, and 48 h) were tested. After thermal treatment, samples were subjected to a chemical treatment with calcium hydroxide, Ca(OH)₂ and phosphoric acid, H₃PO₄ at concentrations of 5 % w/v. Finally an optimization of the Ca(OH)₂ concentration (0.5, 1.25, 2.5, and 5 % w/v) was performed at 70 and 90 °C for 48 h. As shown by the authors mechanical pretreatment of PLA samples improved their biodegradation rate but did not affect the ultimate methane potential (430–461 NL_{CH4} kg_{VS}⁻¹). Thermal and thermo-acid pretreatments exhibited a similar trend for PLA solubilization. This becomes >60 % w/v at very high temperature (120 and 150 °C). Instead, thermo-alkaline pretreatment improved PLA solubilization at lower temperature (70 and 90 °C) and it increased the methane potential. The most suitable condition of pretreatment was at 70 °C for 48 h in the presence of 2.5 % w/v Ca(OH)₂, resulting in a methane potential of 381 NL_{CH4} kg_{VS}⁻¹ and a biodegradation yield of 73 % in 30 d.

5. Concluding remarks

As highlighted by the studies reported in this review, the choice of an appropriate pretreatment for a plastic material can remarkably improve its degradation carried out via microorganisms or enzymes. In the case of polyolefins (PE, PP, PS) but also PC, photodegradation pretreatments are very effective [55,57]. By breaking the polymer chains, UV radiation introduces radical species, which in turn promotes further cleavage reactions, reducing the molecular weights of the chains and leading to a modification of mechanical properties. The introduction of polar functional groups, such as —OH and C=O, increases the polarity of the surface favoring the interaction between the hydrophobic polymer and the microorganism/enzyme. The operating conditions typically used for photooxidative pretreatment are irradiation in the near UV (245–300 nm) for periods of time from a minimum of 3 to a maximum of 14 d. As described by Balasubramanian et al. [81] the photodegradation pretreatment can be followed by further pretreatments such as chemical and thermal ones, to increase the efficiency of the biodegradation. However, UV pretreatment is time consuming, and the disposal of UV lamps can be an environmental problem. Polyolefins can also be pretreated with high dose gamma rays (from 0 to 1000 kGy) [59]. Although this pretreatment is very effective, the associated energy consumption is

Table 6
Thermochemical pretreatments.

Feedstock	Pretreatment	Molecular weight after pretreatment	Microorganism/ Enzyme	Year	References	High value-added products
PP films (thickness=0.05 mm)	Aquaregia for 3 d or Fenton's reagent for 7 d Thermally pretreated at 100 °C for 8 d UV pretreated (PP-SUV) at 225 nm for 6 d	Not discussed	<i>Pseudomonas azotoformans</i> , <i>Pseudomonas stutzeri</i> , <i>Bacillus subtilis</i> and <i>Bacillus flexus</i>	2010	Arkatkar et al. [79]	Not discussed
PET bottles	UV and $T = 100\text{ }^{\circ}\text{C}$ Chemical pretreatment (90 % concentrated HNO_3 , for 5 d at ambient temperature)	Not discussed	<i>Chlorella vulgaris</i>	2020	Falah et al. [80]	TPA
HDPE films (thickness 40 μm)	50 °C for 72 h Exposure to UV (312 nm) and humidity for 5 cycles day^{-1} (60 h tot) KMnO_4/HCl at concentration of 0.25/0.5 mol/L at 45 °C for 8 h 10 % citric acid for 8 h at 45 °C.	Not discussed	<i>A. terreus</i> MF12 separately and consortia	2014	Balasubramanian et al. [81]	Not discussed
PLA NaturePlast	Milling Thermal treatment at different T and for different time $\text{Ca}(\text{OH})_2$ and H_3PO_4 (5 % w/v).	Not discussed	Mesophilic anaerobic digestion	2022	Cazaudehore et al. [82]	CH_4

very high therefore the process is not industrially scalable. In the case of PS, a successful pretreatment is ozonation performed for 3 h with a flow of 5 L/min. Being a strongly oxidizing agent, O_3 can induce surface oxidation of the material, making it more hydrophilic [61]. Pretreatments with O_3 are extremely energetic and require the use of special anti-corrosives steels. For LDPE, non-oxidative pretreatments were also carried out such as boiling in xylene for 15 min [66] or blending with fatty acids, for example oleic acid [68]. These pretreatments induce changes in the structure of the polymer or significantly decrease the binding of the chains, favoring the permeation of microorganisms into the substrate.

PET is certainly the most studied polymer. In all the studies reported excepted for that of Taghavi et al. [57], enzymatic digestion is carried out with the enzymes cutinase or PETase, in some cases suitably engineered. UV irradiation has proved to be an extremely ineffective pretreatment for this kind of polymer because it involves an increase in the X_c of the polymer, making it less subject to biodegradation [56,57]. PET, on the other hand, can be subjected to chemical treatment, such as basic hydrolysis with NaOH. This reduces the X_c of the polymer, making it more accessible to the enzyme [64]. Another type of pretreatment involves the incubation of PET with anionic surfactants to make the surface negatively charged and thus capable of attracting positively charged enzymatic species, even orienting the active site of the enzyme towards the surface of the polymer [43]. PET also lends itself to mechanical pretreatments which involve a reduction of the dimensions and an increase of the surface area available for the enzyme [72,73]. Thermochemical pretreatments can also be carried out on PET in an autoclave which allow the polymer to be degraded by 85 % in its constituent monomers. Remaining low molecular weight oligomers can be further subjected to enzymatic digestion [78]. Pretreatments with deep eutectic solvent have also proven to be very effective on PET [67].

Biodegradable polymers have been studied in anaerobic digesters or in compost by exploiting communities of microorganisms. Chemical pretreatments with 5 % NaOH are efficient for polymers such as PLA, TPS, PBSA, CDA except for PBAT [65]. Specific studies have been carried out on PLA, now widely used in packaging. Pretreatments such as annealing of the polymer at 105 °C, hinder biodegradation, as they increase the X_c of the polymer [74]. An efficient pretreatment for PLA consists in heating it at 70 °C for 48 h in the presence of 2.5 % w/v $\text{Ca}(\text{OH})_2$. This leads to a very high subsequent methane potential and a biodegradation yield of 73 % in 30 d [82]. Even in the case of PLA, the treatment with a deep eutectic solvent made it possible to increase

biodegradation [67].

Finally, for PUR foams thermochemical treatments such as HTL represent an excellent pretreatment. This approach produces oligomers with a lower molecular weight that are more easily attacked by the enzyme and allows the recovery of relevant precursors for the chemical industry [76].

Surely one aspect that emerges from this review is the lack of global homogeneity in the operating conditions used by the authors, both in terms of the type of feedstock used for the same type of polymer, and in terms of enzyme/microorganism used for degradation. This does not allow a direct comparison between the different studies on the same type of polymer and uniquely define the best type of pretreatment.

Most of the studies reviewed do not report information regarding the change in molecular weight before and after the pretreatment process. Therefore, it is not easy to discern if pretreatment results in a major reduction in molecular weight acting itself as a recycling process. In our opinion some types of pretreatments such as those of a mechanical, chemical and thermochemical nature cause great reductions in the molecular weight of the polymer. In any case, pretreatment even if it reduces molecular weight, is still propaedeutic to facilitate subsequent enzymatic degradation or biodegradation, making these processes faster and often more selective in obtaining high value-added products.

Finally, there aren't technical assessments relating to the economic feasibility of the processes. To bring these processes at an industrial scale, it is necessary to: reduce pretreatment and degradation times (for example through a detailed knowledge of the degradation mechanisms [83]); enable simultaneous enzymatic digestions of mixed plastic materials [84]; evaluate the BD and ED of commercial plastic composites; evaluate the effects of additives used in plastic on BD and ED [84]. Further studies are therefore necessary to optimize processes and calculate LCA, for a systematic and scientific evaluation of the environmental impacts caused by this type of recycling.

CRediT authorship contribution statement

Benedetta Ciuffi: Data curation, Investigation, Writing – original draft, Methodology, Writing – review & editing. **Emiliano Fratini:** Writing – review & editing, Methodology. **Luca Rosi:** Conceptualization, Methodology, Project administration, Resources, Supervision, Writing – review & editing, Data curation, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data reported in this review were collected from the scientific literature.

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