REVIEW

Recycling of polyamides: Processes and conditions

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Abstract

Polyamides (PA) are a family of engineering thermoplastics used in a wide range of applications including automotive, building, construction, separation processes, textiles, and so forth. This is related to their good properties (mechanical and thermal) which can also be modified by additives, other polymers (blends and multilayers) and fillers (composites). But these complex systems (several components) make the final materials more difficult to recycle. In this review, basic statistics on the production rate of polyamides are presented and the different recycling methods are reported to compare their advantages and limitations with respect to economics and technical analyses. The discussion includes biological, chemical, mechanical, physical, and thermal treatments to reintroduce, as much as possible, the parts after their end-of-service. Finally, a general conclusion on the current state of PA recycling is presented with several openings for future developments to satisfy the concept of circular economy and general sustainability.

KEYWORDS
circular economy, nylon, polyamide, processing, recycling, sustainability

1 | INTRODUCTION

Polyamides (PA), commonly called Nylons (commercial name from Dupont), are a family of semicrystalline thermoplastics typically made from petroleum-derived feedstock. They belong to the category of engineering plastics due to their high melt temperature combined with excellent mechanical properties. Polyamides can be melt processed into various shapes including membranes, films, and mostly fibers (fabrics). Naturally formed PA can also be found in proteins.[1]

Polyamide 6.6 (PA6.6) was first developed by a research team around W.H. Carothers at Dupont in the 1930s and presented to the public in 1938 as the first commercially successful thermoplastic polymer for application in toothbrushes. The ε-caprolactam based PA6 (Nylon 6)

was first developed by Paul Schlack at the German IG Farben in 1938. Nowadays, PA are used in several applications and industries such as electronics or automotive,[2] food packaging,[3] or pavements such as carpets.[4] Consequently, large amounts of PA waste are generated each year and their recycling becomes of high importance.

Although several books and review articles have been separately published on polyamides/Nylons (polymerization, modification, processing, characterization, and so forth),[5] structures (fibers, films, foams, blends, (nano)composites, membranes, multilayers, and so forth),[6] history,[7] as well as plastics recycling,[8,9] almost nothing is available in the literature on the combination of both subjects[10] or the information is outdated.[11] This is now highly important to account for these issues within the concepts of sustainable development and circular economy to manage the

important amount of waste generated after their end-of-life (EoF) or end-of-service (EoS). The society is now aware of the basic "3R" which are reduce, reuse and recycle, but they must be applied to all materials.

The concept of "reduce" can generally be applied to materials, energies and wastes. So, this is always the first option to select for any production. Then, it must be determined if the waste can be "reused" in the same or similar application with/without slight modifications/transformations. Although some studies have been published on reusing polyamides/Nylon, especially fibers[11] and membranes,[12] they are not complete to represent the whole range of applications. Even today, there is still not enough applications developed to reuse all the waste that is generated, so another option (complementary and not in competition) must be investigated which is recycling.

Nylons are commonly used plastics with a current global market of more than 8 million tons per annum, which is expected to grow at the rate of 2.2%, reaching up to 10.4 million tons, equivalent to 47.0 billion USD by 2027. PA6 and PA6.6 account for about 2/3 and 1/3 of the world PA production,[13] with about 5 and 2.5 Mio t of production each. Half of the PA6 is produced in China, 1 Mio t in the rest of Asia and 0.6–0.8 Mio t in Europe and the Americas. The production of PA6.6 is more equally distributed over the four geographic regions.[13] About 7% of the polymer fibers used worldwide are PA, with the largest share of about 80% being polyesters.[13] Currently, polyamide 12 (PA12) is the most widely commercialized material for additive manufacturing (AM) technologies based on polymers.

Today, with a transition toward a more "natural" economy, biobased materials are getting more attention and this is also the case for PA. Nevertheless, far less than 0.5 Mio t worldwide of PA are produced from biobased resources, representing about 10% of the biobased and biodegradable production.[14]

PA are identified as the resin identification code (RIC) 7, which is the category of "*all other plastics*" (ASTM D7611). Since it is mixed with several other resins, there is very limited recycling performed and this commingled blend of polymers mostly goes to energetical recycling or being disposed in landfill (solid residues). For example, only 9% of PA carpet fibers are recycled in the US, while 18% are energetically disposed and 73% are landfilled.[15] Nevertheless, due to its high technological importance, a small number of companies are dedicated to postconsumer PA recycling such as BASF within its "Ultramid Ccycled" program.[16] Companies molding recycled feedstock PA are mainly in the high-end and lifestyle segment. For example, the company *Bureo* mechanically recycles fishing nets made from PA into skateboards and sunglasses.[17] *Econyl* follows a similar target of recycling PA waste of fishing nets, carpets and similar products into high-end

products.[18] It is estimated that 10% of the debris found in the oceans, especially fishing nets, are PA fibers.[19] Nevertheless, some companies are now looking to start PA recycling. This is done by either using recycled PA for their productions or by recovery of their own products when returned to them (extended producer responsibility, EPR).

On a more technical side, waste management should follow the concept of waste hierarchy which is a tool developed to protect the environment by making some priorities/choices. The waste management hierarchy proposes the order of action to manage these wastes. A simplified version is presented in Figure 1 based on the subjects included in this review.

Plastics recycling can be defined as the process of recovering scrap or used plastics and reprocessing the materials into useful products. Different recycling methods have been proposed depending on the way the material is transformed. Nevertheless, different classifications have been proposed mainly depending on the origin of the material.

Primary recycling (also called closed loop recycling) is performed on waste of known history. The materials have a known composition since they never left the production site and is referred as post-industrial origin. On the other hand, when the materials were shipped and used, they become of postconsumer origin. Their recycling can be classified based on the transformation methods such as: biological, chemical, mechanical, physical, and thermal recycling as described next.

Biological recycling (biorecycling or composting) includes all the processes (aerobic and anaerobic) for which microorganisms (bacteria, enzymes, fungi, microbes, and so forth) are acting (digestion) to break down the materials into smaller pieces and/or lower molecular weights. Although it is considered as the main origin of the microplastics (MP) found in air, land, and sea (oceans), it is also the most environmentally friendly method when complete decomposition is achieved to produce CO_2, CH_4, H_2O, and salts.

Chemical recycling (also call tertiary recycling) is based on chemical reactions degrading (depolymerization) the plastics wastes into low molecular weight compounds (oligomers and/or monomers). These molecules can be more easily processed and purified to be reused/transformed into useful products. Chemical recycling is interesting because the purified molecules can be repolymerized to produce the same resin (monomer recycling) or can be part of other reactions to produce value-added materials (feedstock recycling). Theoretically, the depolymerization/repolymerization cycle can be performed indefinitely which is interesting in terms of life cycle assessment (LCA).

Mechanical recycling (also call secondary recycling) refers to the transformation of waste plastics via mechanical methods such as grinders, pulverizers, extruders, and

FIGURE 1 The concept of waste hierarchy to manage the end-of-service parts.
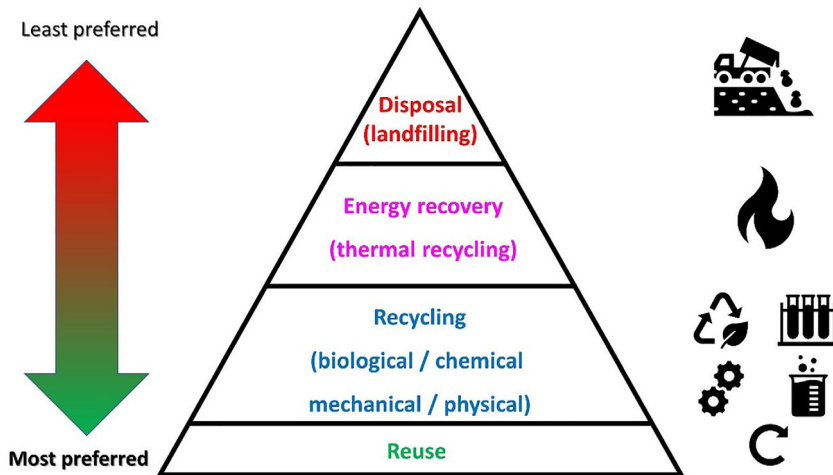
so forth. These methods are usually of low processing costs, generate less residues and require less energy. On the other hand, it is more difficult to handle contaminations and they are known to degrade the polymer chains (scission, oxidation, and so forth) every time they are recycled.

Physical recycling mostly represents processes where the material is dissolved into a solvent or combination thereof for easier separation and treatment. In solution, the molecules can be separated using a specific solvent for each resin (especially useful for polymer blends). It is also possible to remove contamination (fillers) by filtration and get a purified material by solvent removal (precipitation). This process is highly efficient for mixtures of materials (blends and composites) and is believed to operate without modifying/degrading the polymer molecules which is interesting for their reintroduction into production lines.

Thermal recycling (also called quaternary recycling) refers to the conversion of materials into monomers or energy (recovery). For polyamides, monomer recovery targets to break only the amide bonds via thermal cracking to get back the monomer. By contrast, energy recovery is usually done via incineration/combustion and is mainly performed on plastics wastes of low quality and/or mixtures difficult to sort/separate. Since most plastics are organic compounds with high heat energy, burning them can generate steam and electricity (cogeneration). Although not well perceived by the public, this option should only be done as a last resort (see Figure 1) since possible harmful/toxic chemicals (halogens, NO_x, SO_x, heavy metals, and so forth) are produced needing special treatment (purification) before their release into the atmosphere/environment, thus increasing the processing costs.

Recycling of PA is very important since their production is highly energy intensive. For example, the production of PA6.6 requires 163 MJ/kg of polymer, while the value is "only" 54 MJ/kg of polymer for polyethylene terephthalate (PET).[9] Another example of high carbon footprint is that PA6 generates 6.7 tCO_2-eq per ton of polymer. Therefore, it is worth to recover/reuse/recycle the materials as much as possible.

The main objective of this review is to present a general and current overview of the situation for the recycling of polyamides/Nylons. This is done by reporting the main results obtained on recycling methods including biological, chemical, mechanical, physical, and thermal processes. The review ends with a general conclusion on the current situation with openings for future works.

1.1 | Classification of polyamides

Chemically, two different types of linear PA can be found. The first one is based on "lactam," while the second is based on "diacid + diamine." The lactam type is synthesized via ring-opening polymerization from a lactam, for example ε-caprolactam for PA6 as shown in Figure 2. The industrial synthesis of ε-caprolactam uses petroleum-based feedstock, starting with the hydrogenation of benzene and subsequent oxidation to cyclohexanone and converted with hydroxylamine to cyclohexanone oxime. The final monomer ε-caprolactam is obtained by a Beckmann rearrangement.

The "diacid + diamine" type PA are synthesized by a polycondensation reaction of a diacid and a diamine. A typical example combines hexamethylenediamine and adipic acid to form PA6 as shown in Figure 3. Another route to obtain "diacid + diamine" type PA uses a Schotten–Bauman reaction to create the amide group via the polycondensation of a diamine and a diacyl chloride, resulting again in the desired PA leading to PA6.10 and the production of HCl[20] (Figure 3).[21]
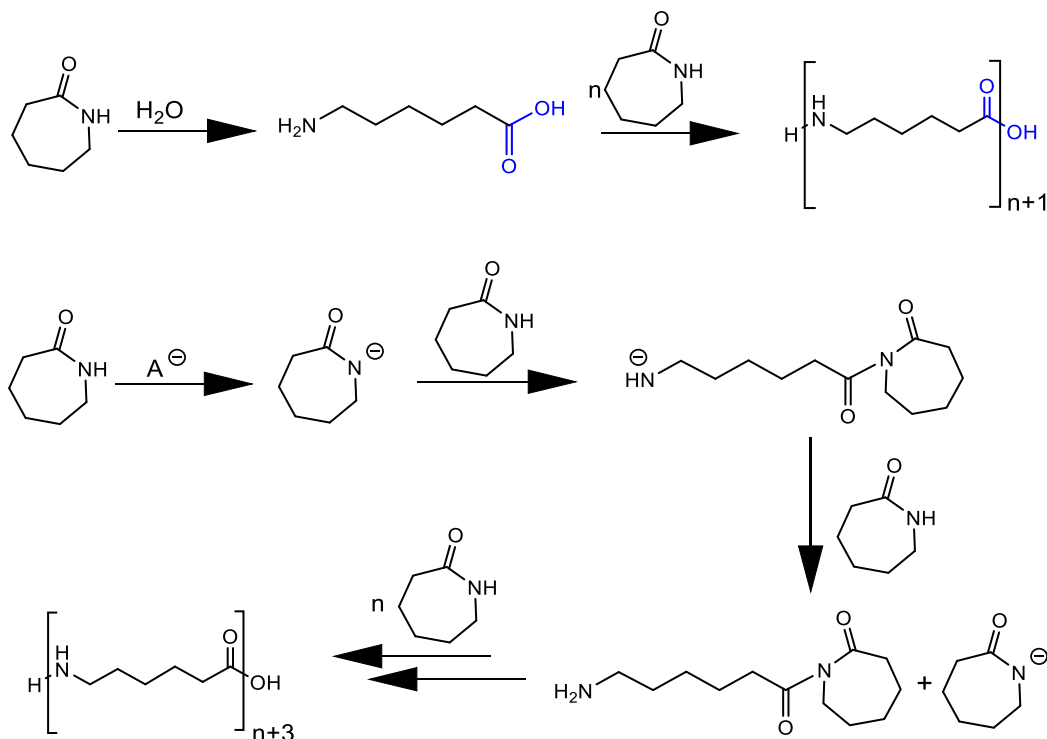
FIGURE 2 Synthesis of PA6 via a combination of polycondensation and ring opening polymerization, as well as ring opening polymerization of caprolactam with a strong, nonnucleophilic base catalyst A^-.
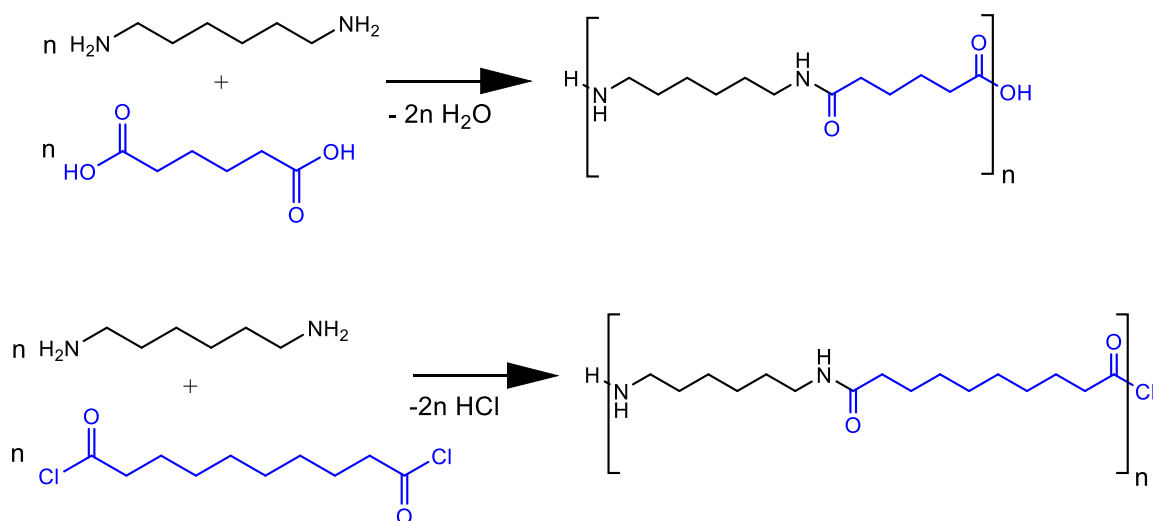

FIGURE 3 Synthesis of PA6.6 via the polycondensation of hexamethylenediamine (six carbons) and adipic acid (six carbons) and of PA6.10 via the reaction of hexamethylenediamine (six carbons) and sebacoyl chloride (10 carbons).

Different types of PA can be produced based on the chemicals used. So, a nomenclature was imposed to determine their composition which can be easily understood. The first number stands for the number of carbons in the diamine, while the second indicates the number of carbons in the diacid or diacyl chloride. The difference between PA6.6 and PA6.10 can be seen in Figure 3. In all cases, the main advantage is that the reaction is very fast,

irreversible, can be performed at room temperature and allows to build high molecular weights. Interfacial polymerization can also be used to produce fibers.

Another advantage of PA is related to the high number of planar amide (–CO–NH–) groups which are very polar, forming multiple hydrogen bonds among adjacent polymer chains and creating a regular and symmetrical structure. This is especially interesting if all the amide

TABLE 1 PA grades and their repetitive unit, their melt, and glass transition temperature and their Young's modulus for dried materials.[24]

PA grade	Repetitive unit	T_m (°C) (dry)	T_g (°C) (dry)	E-modulus (GPa) (dry)	Biobased Synthesis routes
PA4.6		295	80	3.3	✓25
PA4.10		250	70	2.88	✓26
PA6 Nylon 6		220–225	63	2.6–3.2	✓27
PA6.6 Nylon 6.6		255–260	45	2.7–3.3	
PA6.9		210	58	–	
PA6.10		210–220	49	2–2.4	63% ✓26
PA6.12		218	46	2.1	
PA10.10		191		1.8	✓26
PA11		198	46	1.0–1.4	✓26
PA12		178	37	1.3–1.6	✓26

bonds are in the *trans* configuration supporting crystallization making excellent fibers. But the level of crystallinity depends on the PA type (chemical structure) and the processing conditions (mainly cooling rate).

1.2 | Properties of polyamides

Polyamides belong to engineering plastics and some grades, such as PA4.6, can be considered as high-performance plastics due to their high impact strength, excellent sliding and frictional behavior, and their thermal properties. PA typically have high melting temperatures due to the high number of hydrogen bonds between the amide groups. The highest values are around 300 °C for PA4.6 (low number of carbons in a repeating unit) and decreasing with monomer length down to about 180 °C for PA12.

Polyamides are highly hygroscopic, thus absorb water acting as a plasticizer in the amorphous regions between crystalline domains with increased chain mobility.[22] The humidity level highly influences (negatively) the mechanical properties (lower Young's modulus with increasing water content), as well as the glass transition temperature.[23] Moreover, absorbed water makes PA prone to degradation via hydrolysis, especially at higher temperatures during processing. The tendency to absorb water typically decreases with increasing number of carbons in the repeating unit; that is. the polymer and its properties get closer to polyethylene (PE). Similarly, the melting and glass transition temperature, as well as the Young's modulus, decrease with increasing carbon: amide group ratio: from 5:1 for PA6 to 11:1 for PA12. Table 1 lists some of the most common PA grades, as well as their chemical repeating unit, melt, and glass transition temperature and their Young's modulus for the dried material. The table also indicates if biobased production is possible.

Based on the information available, the following sections present the current situation of PA recycling from the different options available: biological, chemical, mechanical, physical, and thermal processes. For each case, the most important information is presented and discussed in terms of processing steps, equipment used, and conditions applied. A comparative table for each method is also included for easy referral.

2 | BIOLOGICAL RECYCLING

Biological recycling is associated with a more "natural" way to obtain materials from the original parts after their EoS. Different options are investigated, but the most

important are related to compost and marine (ocean) degradation. When performed under uncontrolled conditions (in the nature), the degradation usually leads to the production of microplastics defined as particles in the range of 1–5 mm.[28] These particles can be recuperated and introduced into standard processing streams. But in general, the size reduction occurs slowly under the action of enzymes, fungi, and bacteria.

In the past, polyamides were seen as stable materials with negligible degradation due to environmental attacks. This is why the material was highly used to perform composting/biodegradation studies in the form of bags, films, filters, gauzes, membranes, nets, meshes, permeable/porous plates, trays, and so forth. But today, several reports on PA biodegradation are available. Although neat PA seems to be highly stable, this is not the case when blended (physical mixing) or copolymerized (chemical modification) with other polymers, especially biodegradable ones such as polylactic acid (PLA) and polycaprolactone (PCL).

Okada et al.[29] performed a complete study by investigating the enzymatic degradation of eight different copolymers of amide and ester under soil burial and activated sludge using porcine pancreas lipase (PPL) and papain (PAP). Their results showed that the degradation rate depended on the PA molecular structure. In particular, shorter methylene chain lengths degraded faster in PPL than in PAP.

Then, Tercjak et al.[30] followed the biodegradation of PA11/PHBV (polyhydroxybutyrate-*co*-hydroxyvalerate with different V content) blends for 25 weeks in compost. Using mass loss and melting enthalpy, it was observed that the level of biodegradation was proportional to the amount of PHBV in the blend, but the rate of mass loss decreased as the polymer crystallinity increased.

Similarly, Hashimoto et al.[31] studied the biodegradation of AB and ABA block copolymers based on PA4 (A) and polyoxymethylene (B) in a composting soil. It was observed that increasing the B content decreased the biodegradation rate which was determined via mass loss and humidity absorption.

On the other hand, Friedrich et al.[32] performed an extensive experimental study on the effect of 58 fungi on the biodegradation of PA6. For the conditions investigated, a wood degrading fungi (white rot *Bjerkandera adusta*) was more efficient by transforming fibers into small fragments (particle size reduction). It was observed that the PA6 molecular weight was decreased by 67% (16.9 to 4.5 kDa) over 60 days leading to lower melting points and broader melting endotherms which are easy to detect via differential scanning calorimetry (DSC).

To determine the behavior of PA in oceans, Sudhakar et al.[33] investigated the effect of four marine bacteria

(*Bacillus cereus, Bacillus sphaericus, Brevundimonas vesicularis,* and *Vibrio furnissii*) on the biodegradation of both PA6 and PA6.6. Under specific conditions (marine salt media, 35 °C and pH = 7.5), *B. cereus* was the most effective as the average molecular weight decreased by 31%–42% for both PA over 3 months. Once again, lower melting temperature and fusion enthalpy via DSC confirmed the degradation results. Overall, it was found that both oxidation and hydrolysis were involved in the degradation steps.

For copolymers, Michell et al.[34] studied different structures (block and random) based on PA6 and PCL with a range of total molecular weight (6.5–64.6 kDa). Biodegradation was performed in composted soil containing organic waste and enzyme concentrates at 20–30 °C. Weight loss was followed for a period of 50 days and faster degradation rates were obtained for random copolymers, especially when the PCL content was above 30%. Once again, higher crystallinity led to slower biodegradation since the morphology is more compact: the molecules are less mobile and more difficult to access.

As a comparative study, Tachibana et al.[35] investigated the effect of one bacteria (*Stenotrophomonas* sp.) and one fungus (*Fusarium* sp.) on the biodegradation of PA4 with different molecular weight (1.3–30 kDa) to compare with PA6 (37 kDa). Under the selected conditions (25 °C), PA6 did not significantly degraded for a period of 1 week, while significant PA4 degradation occurred over the same period. But most importantly, *Stenotrophomonas* sp. was more efficient as it generated higher biochemical oxygen demand.

Different microplastics (PA, PE, PET, and PP) were investigated when placed inside sewage sludge used as soil amendment.[36] The composting was done over 200 days and different physico-chemical methods were used to follow the materials behavior as a function of time. Composition and particle size was followed, but the final conclusion was that the latter decreased with time without clear confirmation of proportion modification.

The effect of biopolymer (PCL and PLA) addition (as compatibilizing agents) on PA6/PP (30/70) blends was investigated by Amantes et al.[37] The specimens (20 mm × 15 mm × 3 mm) were buried in soil at room temperature for up to 140 days with constant compost humidity. Using morphological and mechanical analyses, a slight initial degradation was observed (short time), but limited biodegradation occurred due to the good homogeneity of the ternary blends produced.

Cañado et al.[38] investigated the recyclability of different microplastics (marine plastics waste) for 3D printing. In particular, they compared bio-PA with recycled PA6.6 (MP) collected from the ocean (fishing nets). A complete LCA was performed (cradle-to-grave) and the results showed that the recycled PA (even if slightly degraded in the ocean) was environmentally better than the bio-PA and virgin PA.

Finally, Buchholz et al.[39] produced a list of hydrolytic enzymes (about 50) for plastics degradation. Although several of them were shown to be active for PET and PUR, very few are known for PA. Their results led to the Plastics-Active Enzymes Database (PAZy) which is open access (https://pazy.eu).

Based on the open literature, Table 2 presents an overview of the works reporting on PA biodegradation under environmental conditions. It can be seen that the number of studies is very limited, especially on neat PA. Unfortunately, the composition of the compost is not always given to get a full comparison and all the conditions are not completely reported, especially for earlier studies (before 2010).

3 | CHEMICAL RECYCLING

Tertiary recycling, sometimes referred to as chemical recycling, uses chemical processes to break down the polymers into value-added commodities. Depolymerization reaction, converting polymers into their corresponding monomers, is the first stage for carrying out chemical recycling. The polymerization reaction of monomers to polymers is typically a thermodynamically favored process dissipating heat and yielding a thermodynamically stable polymer. Consequently, the depolymerization reaction is thermodynamically unfavored and requires significant energy input for an efficient progress of the reaction. Polymer chains break-up can be done via two processes. In chemical recycling, depolymerization is supported not only by heat, but also by other chemical compounds. In pyrolysis, the polymer is decomposed with heat either into its monomers or into pyrolytic oils and gases.

The monomers obtained can then be used as a feedstock to produce fuels or to repolymerize new polymers. A major challenge in the chemical reactivity of Nylons is their resistance to solvents and reagents due to the numerous and strong intermolecular hydrogen bonding interactions between the polymer chains. For complete PA depolymerization into the constituent monomers, extreme reaction conditions and long reaction times are usually required, which can also lead to undesired side products making the purification steps more complex and tedious. Such processes often prove to be economically unviable due to the low yields of recovered monomers. In contrast to other physical and mechanical recycling, the properties/quality of the new materials are not coupled to the properties/quality of the virgin

TABLE 2　Overview of the information available on the biological recycling of PA.

PA grade	Other materials	Conditions	Reference
PA	Polyester	Soil burial Activated sludge Enzyme	29
PA11	PHBV	Compost	30
PA4	Polyoxyethylene	Soil burial	31
PA6	–	Fungi	32
PA6/PA6.6	–	Marine bacteria	33
PA6	PCL	Compost	34
PA4/PA6	–	Bacteria Fungi	35
PA	–	Sewage sludge (MP)	36
PA6	PP + PLA/PCL	Soil burial	37
PA6.6	–	Ocean (MP)	38
PA	–	Enzymes	39

Abbreviations: MP, microplastics; PA, polyamide; PCL, polycaprolactone; PHBV, polyhydroxybutyrate-*co*-hydroxyvalerate; PLA, polylactic acid; PP, polypropylene.

feedstock and allows (via the repolymerization) new products with better or specifically targeted properties (upcycling).

Here, different chemical recycling strategies are presented, starting with hydrolysis and ammonolysis, followed by other techniques such as microwave heating, the use of catalysts or ionic liquids (IL).

3.1 | Hydrolysis

The most natural approach to hydrolyze PA is adding HCl for water hydrolysis. However, this results in a slow degradation process.[40] Using low acidity organic acids, such as acetic, propanoic and butanoic acid at 100 and 120 °C, was found to highly increase the degradation speed of PA11, by up to a factor of two, compared with HCl in water.[40] This is explained by the faster diffusion of the organic acids into PA11, thus speeding up the degradation.

A major strategy for the hydrolysis of PA is to melt the polymer in sub- or super-critical water,[41] in primary such as methanol[42,43] or secondary or tertiary alcohols such as 2-butanol, cyclohexanol or *tert*-butyl alcohol,[44] in a hydrocarbon-water mixture,[45] in water with catalyzed with solids acids,[46] or via oxidative degradation with NO_2 in supercritical CO_2[47]; that is at high temperature and high pressure. The decomposition products are then soluble in the super- or sub-critical media. Using alcohols instead of water allows to not only recover the monomer, but also to use recycled PA as a feedstock to produce other molecules such as ω-hydroxyalkanoic acid derivatives[43] or for upcycling to more valuable chemical compounds such as 1,6-hexanediol.[48] In addition, alcohols allow to reach the super- or sub-critical conditions at much lower temperatures and pressures.[44] Using supercritical water (sc-H_2O), PA6.6 was completely decomposed without any oligomers present after 30 min at 380 °C and 28 MPa, but yielded only 8.5 wt% adipic acid without hexanediamide. On the other hand, cyclic products such as cyclopentanone (6 wt%) and cycloheptylamine (52 wt%) as well as CO_2 were produced due to a decarboxylation reaction of the carboxylic acid monomer.[41] Under supercritical conditions, water has an acidic-type catalysis effect on PA6.6 decomposition and hypo-decomposition of hexanediamine, while the adipic acid showed similar effects to supercritical water. Kamimura et al.[44] found that using primary and secondary alcohols and super-critical conditions on the decomposition of PA6 had significantly higher ε-caprolactam yield above 95% when secondary alcohols, such as s-butanol, isopropanol, cyclohexanol, or *tert*-butanol, were used at lower temperature and pressure compared with supercritical water. To avoid the degradation of the reactor, the use of solid acids is of interest. For example, Wang et al.[46] showed that the reaction can be speeded up with α-Al_2O_3 or zeolite Hβ-25 at 345 °C compared with the hydrolysis without catalyst, resulting after 30 min of reaction time in about 60% ε-caprolactam, 35% oligomers and the rest being unreacted PA6.

In subcritical water, PA6 was completely decomposed into water-soluble monomers and oligomers after 45 min at 345 °C and 9 MPa.[49] The targeted product of ε-caprolactam was obtained with a maximum yield of up

TABLE 3 Overview about the chemical recycling methods, polymer decomposed, recycling conditions, and the yield obtained.

Recycling method	Catalyst/reactive species	PA grade	Pressure	Temperature	Time	Degree of depolymerization	Yield/monomer recovery	Reference
Hydrolysis	Fivefold ethylene glycol, 2 wt% $(NH_4)_2HPO_4$			190 °C	1.5 h	Liquid product		40
	Boiling glycol	PA6		197 °C		Oligoamides		55
	Supercritical H_2O		28 MPa	380 °C	30 min	100%	8.5 wt% adipic acid	41
	Subcritical H_2O			345 °C	75 min	100%	89%	49
	Subcritical H_2O, 3% $H_3PW_{12}O_{40}$	PA6		300 °C	55 min	>95%	59%	51
				300 °C	85 min	>95%	78%	
	H_2O + 1.25 HCl/amide mol ratio	PA6.6		200 °C Microwave heating	10 min	100%	90% adipic acid and 86% hexamethylene diamine	52
	H_2O + 2.5 HCl/amide mole ratio	PA11 PA12 PA10.10		200 °C Microwave heating	10 min	100%	89–97%	52
	H_2O and H_3PO_4	PA6		200 W/ 100 mL water Microwave heating	20 min	>95%	>90% ε-amino-caproic acid	54
	5 mol% DMAP, 5 equiv. Ac_2O	PA6		250 °C Microwave heating	15 min	100%	78% N-acetylcaprolactam	56
Ammonolysis	$La(Otf)_3$	PA6.6	1 bar NH_3	200 °C	20 h	68%	–	57
Ionic liquids	[emim][BF4] DMAP	PA6		300 °C	60 min	–	55%	58
	P13-TFSI DMAP	PA6		300 °C	6 h	–	86%	59
Metal complex catalyst	Ru pincer complex	PA6, PA12	70 bar H_2	150 °C	48 h	80%	24–26% yield of 6-amino-1-hexanol	60
	Ln^{NTMS}	PA6		280 °C	30 min	>95%	95%	61
	Nb_2O_5 and $RuWO_x$/ $MgAl_2O_4$	PA6.6, PA10.10 PA11 PA12	6 bar NH_3 and 50 bar H_2	200 °C	16 h	100%	62% primary amines, 36% secondary amines	62

to 89% after hydrolysis for 75 min. The rapid hydrolysis of PA6 waste and scrap textiles to ε-caprolactam (CPL) was found to deliver about 90% of CPL at 300 °C, a water:PA6 mass ratio of 11:1 and a reaction time of 60 min.[50] Furthermore, it was observed that PA6 textiles were easier to degrade compared with virgin PA6. However, the virgin PA6 had a 50% higher M_w and M_n, thus more bonds needed to be hydrolyzed.

Chen et al.[51] studied the use of a hydrothermal diamond anvil cell reactor at 513, 553, 583, and 603 K. They found that the addition of 3% of phosphotungstic heteropoly acid (HPA, $H_3PW_{12}O_{40}$) as a catalyst can improve PA6 hydrolysis to obtain high yield ε-caprolactam compared with low temperature subcritical water. At 573 K, the PA6 was nearly completely decomposed after 55 min with a 59% yield of ε-caprolactam. The kinetics studied revealed a decrease in apparent activation energy with 3% HPA from 86.6 to 77.4 kJ/mol, indicating accelerated PA6 degradation with HPA.

Instead of conventional heating, microwave radiation can be applied which was shown to be more effective.[52,53] Depolymerization of several aliphatic polyamides, such as PA6.6, PA11, PA12, or PA10.10 and some containing glass fibers (GF), was done to generate the monomers using microwave radiation, water and HCl,[52,53] or water and H_3PO_4[54] as catalyst (hydrolysis). Using an excess of HCl compared with amide bonds of 25% yielded for PA6.6 after 5 min to a degree of conversion of 99.7% and 100% after 10 min. For the other PA, 2.5 times HCl excess was necessary to achieve 100% conversion within 15–20 min. Although the GF were nearly completely recovered (∼97%–99%), the monomers were only recovered between 71% and 97%; for example for PA6.6 it was 90% adipic acid and 86% hexamethylene diamine. This underlines the importance of this method as most chemical recycling approaches for PA6.6 resulted in low yields as reported in Table 3 due to monomer degradation (e.g., decarboxylation) during the depolymerization step.[63] Alberti et al.[56] reported on PA6 depolymerization into *N*-acetylcaprolactam using 4-dimethylaminopyridine (DMAP) as catalyst in acetic anhydride (Ac₂O) under microwave irradiation at 220–260 °C. The maximum *N*-acetylcaprolactam yield (above 95%) was obtained using 5 mol% DMAP and 5 equiv. Ac₂O for 15 min at 250 °C. From the reaction mixture, *N*-acetylcaprolactam could be distilled after AcOH and Ac₂O removal with a high yield (78%). Most importantly, the process was found to be highly suitable for the depolymerization of PA6 commodities such as a hammock, screw anchors and thread.

3.2 | Glycolysis

The glycolysis of PA6 in boiling ethylene glycol (EG) was one of the first chemical degradation process of PA6

studied,[55] resulting in oligoamides with amino- and hydroxyl end groups (no monomer recovery). Kim et al.[64] reported a severe M_n and M_w reduction of PA6.6 during glycolysis after 4 h at 275 °C. However, no further decomposition reaction occurred due to the equilibrium glycolysis reaction under a closed system. Consequently, glycolysis can be more considered as a degradation reaction. Therefore, it is not suitable for an efficient chemical recovery of monomers without a catalyst as the monomer yield is too low. Finally, Datta et al.[65] described the successful glycolysis of PA6.6 using up to fivefold addition of EG and 2 wt% of diammonium hydrogen phosphate as catalyst at 190 °C, yielding a low molecular weight liquid product after 1.5 h.

3.3 | Ammonolysis

During ammonolysis, polyamides are decomposed into their monomers in the presence of NH_3 with and without additional H_2. The NH_3 can be either in liquid or gaseous form. The ammonolysis of PA6.6 is described at high temperatures (320 °C) while using a catalyst (e.g., Lewis acid) gives a yield of about 40%,[66] or a metal complex catalyst as described later.[62] A recent work proposed a decomposition route for PA6.6 under mild conditions by using $La(OTf)_3$ as a Lewis acid catalyst and 1 bar of NH_3 in a simple glycol solvent at 200 °C for 20 h, giving a degree of depolymerization of up to 68%.[57]

3.4 | Catalytic depolymerization and ionic liquids

Another approach to depolymerize PA, especially PA6, is by using IL combined with high temperatures which is schematically shown in Figure 4.[67] Using IL has a substantial advantage as the monomer can be directly recovered via distillation from the reaction. The use of 1-methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide (PP13-TFSI, Figure 5) as an IL solvent and DMAP as catalyst yielded at 300 °C a monomer conversion of 86% after 6 h. Without the use of a catalyst, they reported less than 1% conversion if either EG or triethylene glycol (TEG) was used, as well as only 55% monomer yield for PP13-TFSI and no effect for 1-methylimidazole (NMI) as catalyst. Furthermore, they reported only 43% monomer yield if 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF4]) was used as an IL without a catalyst. A similar study with PA12 showed much less recovery efficiency for its monomer (laurolactam) using 5% DMAP as catalyst and PP13-TFSI as IL at 300 °C and 6 h with a yield of about 10%.[59]

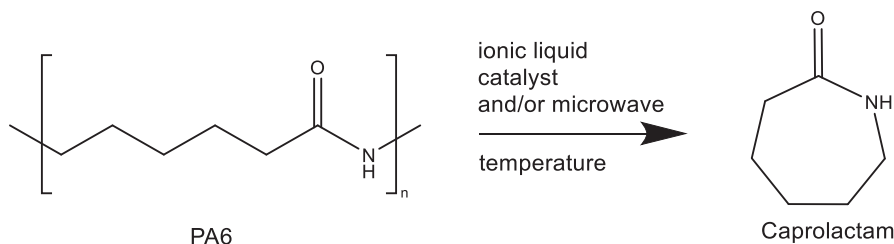**FIGURE 4** Depolymerization of PA6 with ionic liquids under high temperature.

PA6 → ionic liquid catalyst and/or microwave temperature → Caprolactam

FIGURE 5 Structure of ionic liquids: [emim][BF4] (left) and P13-TFSI (right).

[emim][BF4]   PP13-TFSI
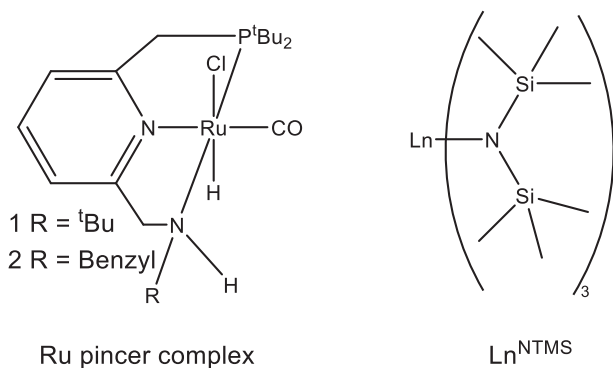

1 R = ^{t}Bu
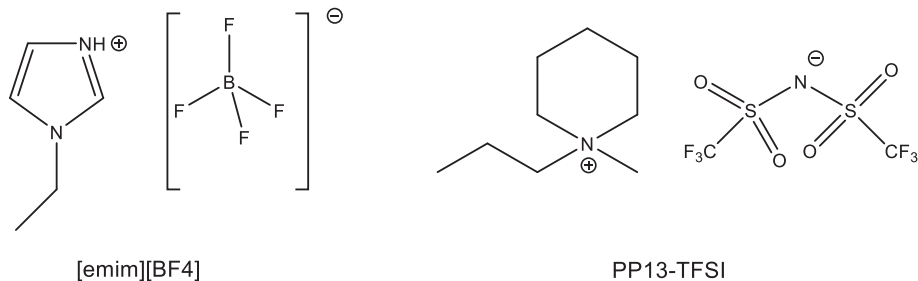2 R = Benzyl

Ru pincer complex   Ln^{NTMS}

FIGURE 6 Examples of Ru-pincer and Ln^{NTMS} catalysts.

The combination of ILs, high temperatures and microwave radiation allowed to further increase the yield from depolymerizing PA6 while speeding up the reaction time.[58] The use of ([emim][BF4]) as IL, DMAP as catalyst (10 wt%), 300 °C and 60 min reaction time, let to a monomer recovery of 55%. The monomer could be easily separated from the IL with an aqueous work-up due to the hydrophilicity of the IL. Within the concepts of a circular economy with an efficient waste management, the recovery of the IL was also studied, yielding recovery rates of about 85% after each use. Overall, DMAP salts and PP13-TFSI seemed to be the most efficient.[68]

3.5 | Metal complex catalyst

Recently, a series of organo-metal (pincer-type) complex catalysts for the depolymerization of PA via hydrogenation to form alcohols and amines have been developed.[69] They are catalysts based on ruthenium,[70] iron,[71] and manganese.[72]

Kumar et al.[60] developed a ruthenium pincer catalyst for the hydrogeneration of PA6 as shown in Figure 6. Using the catalyst, PA6 could be hydrogenatively depolymerized at only 150 °C with 70 bar of H_2. Using dimethyl sulfoxide (DMSO) as a solvent for a PA6 with a molecular weight of 11 kg/mol, 2 mol% of catalyst, 8 mol% KOtBu, 70 bar of H_2, and 150 °C (oil bath temperature) for 48 h, depolymerization degrees of about 77% to 80% of PA6 were found, with a 24%–26% yield of 6-amino-1-hexanol; the remaining being dimer-tetramer oligomers. The authors assumed a deactivation of the catalyst over time to hinder full conversion, thus a second addition of catalyst and 8 mol% KOtBu to the initial depolymerization product and another 72 h under the same conditions as before, yielded 99% PA6 depolymerization into 37% 6-amino-1-hexanol and a mixture of oligomers. The same depolymerization procedure was applied on PA6 and PA12, as well as self-synthesized PA, reporting depolymerization degrees beyond 80% within one depolymerization cycle except for PA6 (77%). A similar approach was used on a technical grade PA6.6 in tetrahydrofuran, yielding up to 80% depolymerization at 200 °C and 100 bar H_2.[73] Using an ammonolysis-hydrogenation process, a bicatalytic system based on Nb_2O_5 and $RuWO_x/MgAl_2O_4$ was described at 200 °C in cyclopentyl methyl ether as a green solvent with the addition of NH_3 and H_2 at comparably lower pressures.[62] Complete depolymerization of PA10.10, PA11, and PA12 into α,ω-diamine monomers and oligomers was achieved at 6 bar NH_3 and 50 bar H_2 after 16 h, but only low PA6.6 conversion was achieved due to its low solubility in the solvent under the reaction conditions. For PA10.10, PA11, and PA12, the diamine monomer yield was about 20%, 45%, and 40%, respectively. This approach was shown to be very robust

against common (processing) additives and impurities in the polymers, such as plasticizers, antioxidants, and fillers, with only sulfur-containing compounds needed to be removed to avoid degradation of the Ru-catalyst.

A solvent-free catalytic route was proposed by Wursthorn et al.,[61] using lanthanide-organic catalysts, based on the finding that Ln^{NTMS} catalysts (see Figure 6) efficiently activate amide bonds in the deoxygenative reductions of amides with pinacolborane.[74] The addition of 1 mol% tris[bis(trimethylsilyl)amido] lanthanide complexes (Ln^{NTMS}) to a PA6 melt at 240 °C was reported to efficiently catalyze the depolymerization of PA6 into ϵ-caprolactam with about 90% selectivity conversion. Higher yields (up to 95%) were achieved at higher temperatures (280 °C) after only 30 min of reaction time. It was also observed that the catalytic activity scales with the lanthanide ion size, thus the largest La^{3+} exhibited the highest activity. Another reported advantage is the catalyst compatibility with other commodity plastics such as PE, PP, and PET.

Based on the literature available, Table 3 presents an overview of the different chemical recycling methods for PA, including the conditions (pressure, temperature, and time) as well as the possibility to use catalysts. For each method, the best degree of depolymerization, as well as the maximum yield of monomer recovery, is also reported.

To simplify chemical recycling and to incorporate circularity directly into the material design, Cywar et al.[75] developed a PA made of ϵ-caprolactam and pyrrolidone, where the PA can be depolymerized with 93%–98% into the monomers at 290 °C using a Lewis acid (ZnCl$_2$) after 18 h. Chemical recycling can be applied to more complex polymer systems such as multilayer films or multicomponent carpet wastes. The objective is to only decompose the PA part as in PA/polyolefin (PO) multilayers films which are usually glued together by polyurethane (PU),[76] or use a microwave assisted selective hydrolysis of PA from multicomponent carpet wastes,[77] offering an advantage over other processes such mechanical recycling.

4 | MECHANICAL RECYCLING

Mechanical recycling techniques, as most of the recycling techniques, start with a size reduction step using multishaft shredders and cutters, which primarily cut, chop, shatter, and grind the waste parts into small pieces followed by sieving and feeding into a processing equipment (melt processing). These methods can directly produce raw materials. They are considered as fast, easy to scale-up and not directly producing CO$_2$ and other waste gases, but they consume high amount of electrical energy.
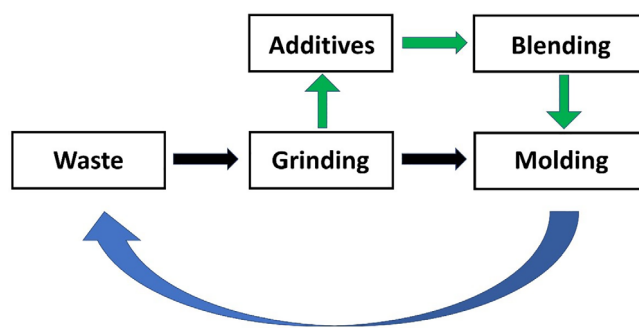

FIGURE 7 General overview of the steps involved in mechanical recycling.

Figure 7 presents an overview of the steps involved with mechanical recycling. The black arrows indicate the direct recycling of the materials which is low costs but usually leads to downcycling, while the green arrows are associated with possible improvements of the recycled products for upcycling purposes generating added-value.

An early study on the mechanical recycling of different engineering plastics (ABS, PA, PC, and PMMA) was published by Liu and Bertilsson.[78] The material originated from waste car parts were first grinded (knife mill). The material was dried and extruded in a corotating twin-screw extruder (240 °C and 200 rpm) before being injection molded (T_{inj} = 240 °C and T_{mold} = 50 °C). To improve the properties of the final parts, additives such as impact modifiers (styrene maleic anhydride) and stabilizers (phenolic antioxidant and metal deactivator) were added (2–5 phr). The PA fraction was determined to be PA6 and PA6.6 and acted as a contaminant which was found to be incompatible with the other polymers and should be separated before blending.

Kowalska et al.[79] recycled postconsumer carpets based on PAN:PA6.6 (80:20) to compare with PP samples. After carpet defibring, the materials were blended with PP or LDPE as the matrix to produce sound absorbing screens.

Bernasconi et al.[80] studied the recycling of PA6.6 with 35 wt% GF. After grinding, the samples were compounded via extrusion before being injection molded. In particular, the ratio between virgin and recycled materials was investigated (0%, 25%, 50%, and 100% recycled). The samples were characterized in terms of GF length distribution, as well as tensile and fatigue mechanical solicitation. In all cases, limited properties loss (less than 5%) were observed up to 50% recycled content, but the 100% recycled materials gave lower values (down by 14%). Based on these results, micromechanical modeling was performed to predict the properties.[81]

Casado et al.[82] investigated the recycling of railway fastener. The samples were produced via injection

molding ($T_{inj} = 290\ °C$ and $P_{inj} = 80$ bar) and composed of PA6.6 reinforced by 35 wt% short GF. After grinding, the parts were injection molded again to perform close-loop mechanical recycling up to three cycles. Samples were also produced from 50/50 mixture of each cycle with the virgin compound. From the results obtained, negligible properties loss (less than 10%) were observed for the range of conditions investigated, with the exception of the impact strength which decreased by 13% for the third cycle. Properties loss were directly related to variation in GF length which are broken during processing.

Ferreira et al.[83] investigated a complex polymer blend by recycling PET fibers (different origin) with PA fibers (waste tires). To improve on the blends properties (compatibilization), reactive extrusion was performed using a trans-reaction catalyst (tin(II) 2-ethylhexanoate). The materials were extruded with different PA wt% (0, 25, 50, 75, and 100) in an extruder at $40\ °C$ with a temperature profile between $250\ °C$ (feed) and $270\ °C$ (die). The results showed that using 25%–50% PA was the best for the conditions studied. Following this study, the same group performed more experiments by characterizing the recycled PA fibers which was found to be a blend of PA6 and PA6.6 with rubber particles.[84] To improve on the properties, surface modified (organosiloxane) E GF were added. The GF content was fixed at 5, 10, and 30 wt% with different PET content (0%, 50%, 75%, and 100%) using 0.1% of catalyst. In this case, the compounds were extruded (single screw) at 60 rpm with a temperature profile between $220\ °C$ (feed) and $250\ °C$ (die) before being injection molded ($P_{inj} = 6$ bar and $T_{inj} = 260\ °C$). As expected, the highest GF content (15%) gave the best mechanical properties, but the presence of rubber particles (recycled tire origin of PA) was found to interfere with the overall performances. Once again, the 75% PET (25% PA) was found to give the best properties.

Colucci et al.[85] investigated the mechanical recycling of PA6.6 reinforced with 30 wt% carbon fibers (CF) from commercial pellets (TORAYCA®). The sample were aged using different UV radiation (10 cycles of 8 h following UNI EN ISO 4892-3), temperature and moisture cycles to simulate degradation for automotive applications. Closed-loop recycling was performed by grinding, aging and injection molding ($P_{inj} = 80$–90 bar and $T_{inj} = 280\ °C$) of the samples for their characterization. The results showed that mechanical recycling generated limited degradation on the pristine sample, but aging led to significant properties losses, especially viscosity.

Production residues, offcuts from PA6-GF (67 wt%) composite sheets, were valorized via mechanical recycling of these post-industrial residues (PIR).[86] The material was grinded (single shaft mill) and processed via twin-screw extrusion ($270\ °C$ and 350 rpm) to produce pellets of different contents before being injection molding. In the extrusion step, virgin PA was added via a side-stuffer to control the final GF content (20, 30, and 40 wt%). Before injection molding, the material was dried for 5 h at $80\ °C$. From the results obtained, a wide range of tensile and impact properties were observed which was directly related to the final GF content and fiber length which decreased due to recycling.

To recycle multilayer film waste, Pinzón Moreno and Saron studied the LDPE/PA6 (78%/22%) packaging systems.[87,88] Using mechanical recycling, the blends were compatibilized using 2.5 wt% of maleic anhydride grafted polyethylene (MAPE) and stabilized (0.15 wt% of Songnox 21B FF). The recycled materials were also combined with virgin PA. The raw materials were grinded, dried and compounded in a single-screw extruder at 80 rpm with a temperature profile between $180\ °C$ (feed) and $240\ °C$ (die). After pelletization, all the samples were injection molded ($P_{inj} = 70$ bar and $T_{inj} = 240\ °C$) for a complete set of characterization (DSC, melt flow rate, morphology, and tension). Since both polymers are highly incompatible, poor properties were obtained even when MAPE was added, unless the PA content was kept below 20 wt%, except for the elongation at break which substantially decreased for all PA content.

Lesiak et al.[89] investigated the recycling of shredded carpet waste from automotive applications. The material was composed of PA6 (24%) with chalk (28%), PET (7%), and PP (8%) and blended with LLDPE to produce recycled compounds from 10% to 100% LLDPE by 10% interval. The blends were performed on a counter-rotating twin-screw extruder at 40 rpm with a temperature profile between 100 and $180\ °C$. Finally, the samples were injection molded ($P_{inj} = 80$–120 MPa, $T_{inj} = 170\ °C$ and $T_{mold} = 30\ °C$) for characterization (morphology, tension, and TGA). For the conditions tested, good properties were obtained up to 50% of recycled content.

Pietroluongo et al.[90] also investigated automotive residues (radiator parts over 10 years old) based on PA6.6 reinforced with 35.7 wt% short GF. The original material was compared with up to three close-loop mechanical recycling including grinding and injection molding ($P_{inj} = 100$ bar and $T_{inj} = 285$–290 °C) to characterize the morphological, mechanical, and rheological properties. As expected, the properties are slightly decreasing with the number of recycling loop, mainly because of GF break-up during both processing steps (grinding and injection).

Finally, Demets et al.[91] presented a molecular investigation on the recycling of four PO (HDPE, LDPE, LLDPE, and PP) with three nonpolyolefins (NPO) (PA6, PET, and PS). All materials were of different origin, but
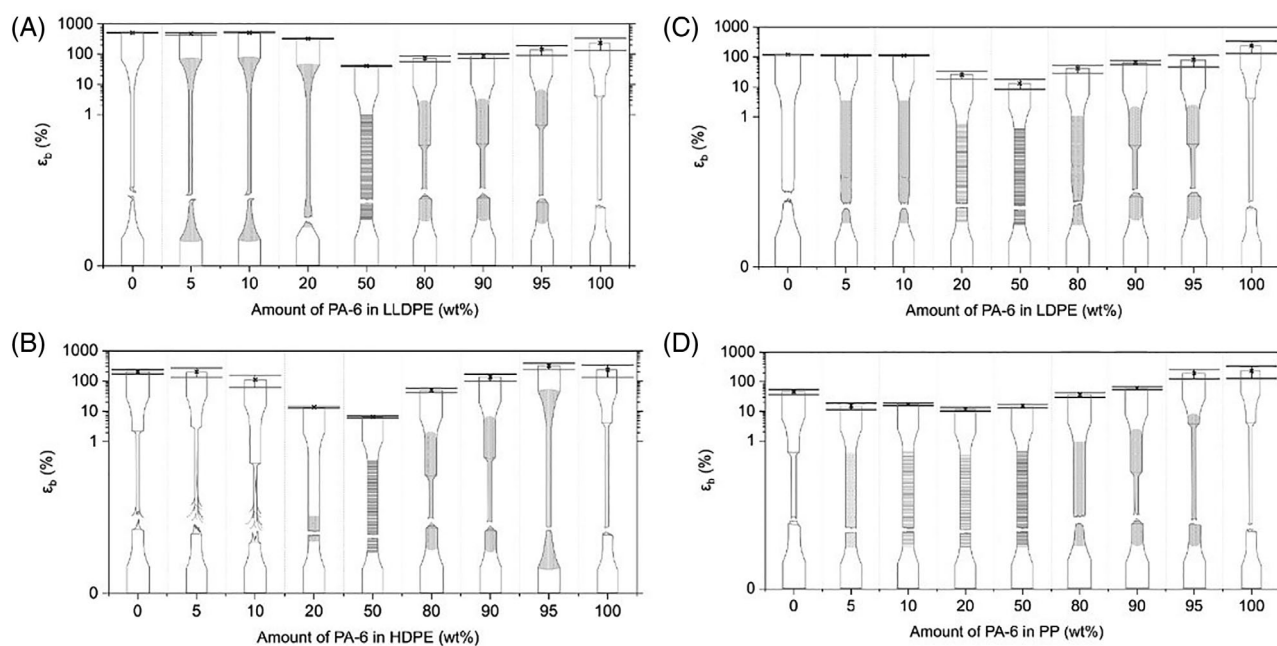
FIGURE 8 Effect of nonpolyolefin (NPO) content in (A) LLDPE, (B) LDPE, (C) HDPE and (D) PP on the elongation at break of PA6. The necking behavior is controlling the deformability of this recycled system.[91]

TABLE 4 Overview of the information available on the mechanical recycling of PA.

PA grade	Other materials	Processing method	Reference
PA6, PA6.6	ABS, PC, PMMA	EXT, INJ	78
PA6.6	PAN	INJ	79
PA6.6	GF	INJ	80
PA6.6	GF	INJ	81
PA6.6	GF	INJ	82
PA	RUBBER	EXT	83
PA6, PA6.6	RUBBER	–	84
PA6.6	CF	INJ	85
PA6	GF	EXT, INJ	86
PA6	ABS, PC, PET, PP, PTFE	–	92
PA6	PTFE, PU	–	93
PA6	LDPE, MAPE	EXT, INJ	87
PA6	LDPE, MAPE	EXT, INJ	88
PA6	PP, CHALK	EXT, INJ	89
PA6.6	GF	INJ	90
PA6	HDPE, LDPE, LLDPE, PP	INJ	91

Abbreviations: ABS, acrylonitrile-butadiene-styrene; CF, carbon fibers; EXT, extrusion; GF, glass fibers; HDPE, high density polyethylene; INJ, injection molding; LDPE, low density polyethylene; LLDPE, linear low density polyethylene; MAPE, maleic anhydride grafted polyethylene; PA, polyamide; PAN, polyacrylonitrile; PET, polyethylene terephthalate; PMMA, polymethyl methacrylate; PP, polypropylene; PTFE, polytetrafluoroethylene; PU, polyurethane.

the PA6 was from films and injection molded samples. Each binary blend was performed using a range of minor phase concentration (0, 5, 10, 20, and 50 wt%). The samples were injection molded at 275 °C for PA6-NPO blends with a mold temperature of 40 °C. All the samples were characterized using DSC, morphological and mechanical properties in tension. For tensile properties, significant differences were observed depending on the PO resin
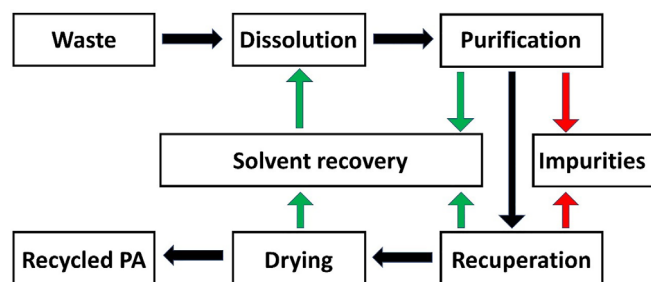
FIGURE 9 General overview of the steps involved in physical recycling.

used as reported in Figure 8. Overall, the differences were related to the samples' morphology and crystallinity which was controlled by the system's rheology and the distribution of the minor phase. A clear difference between the behavior of low crystallinity (LLDPE and LDPE) and high crystallinity (HDPE and PP) resins was observed.

From the literature found on the subject of PA mechanical recycling, Table 4 presents an overview of these works in terms of the polymer systems studied and the processing methods used, usually after a washing, drying and size reduction step.

5 | PHYSICAL RECYCLING

The process involves several steps to dissolve the matrix which involves mass transfer by diffusion and convection. A typical overview of the steps is presented in Figure 9. The black arrows indicate the general path of the materials, while the green arrows are related to the environmentally friendly aspects of reducing the residues associated to the solvents used. The red arrows indicate the possible presence of contaminants which must be accounted for a complete circular economy analysis such as LCA.

Several solvents can be used to dissolve PA depending on the grade. The most common are: formic acid (FA), phenols, trifluoro-ethanol, α-cyanohydrin, hexamethylphosphoric triamide, phenol: tetrachloroethane (1:1).[94] Some preliminary calculations can also be done using the concepts of Hansen or Hildebrand solubility parameters.[95] A review on the selection of solvents (dissolution) and antisolvents (precipitation) for different polymers was presented by Zhao et al.[96]

One of the first paper reporting on the physical recycling of PA was the work of Zagouras.[97] They proposed a step-by-step strategy to separate via selective dissolution a mixture of polymers taken from food packaging and municipal waste. FA was used to remove the Nylons and

a techno-economic analysis was performed to conclude that the removal order should be PE, PVC, PP, PS, and then the other polymers (cellulose, NR, PA, PAN, PB, PET, PI, and PU). Nevertheless, the order highly depends on the relative amount of each component in the waste stream, as well as their financial value which are both related to when the evaluation is done (time variation).

Griffith et al.[20] combined a selective dissolution of PA in FA (88% aqueous solution) at 40 °C. The original material was carpet waste also containing PP, SBR, and $CaCO_3$. The PA (powder) was recovered via antisolvent precipitation using super-critical carbon dioxide ($scCO_2$) also at 40 °C with pressures between 84 and 125 bar.

Kartalis et al.[98] studied the separation of two different systems. The first one was a mixture (model system) of PA6 and PA6.6. In this case, DMSO at 110–130 °C was used to dissolve PA6, while FA at 160–180 °C was selected to dissolve the PA6.6 fraction. Both polymers were recovered using methyl ethyl ketone as the antisolvent. Based on the results obtained (optimum conditions), a second system was investigated which was a mixture of a PA (PA6 and PA6.6) with HDPE and EVA (three-layered bottles). Using the same solvent/antisolvent, their main conclusion was that the polymer solution in the solvent must be carefully controlled because the solution can become too viscous to be pumped and filtered. So values below 0.15 kg/L were recommended. A similar study was presented by Papaspyrides and Kartalis,[99] but using polymer concentrations up to 0.3 kg/L. In both cases, physical recycling via dissolution/precipitation did not significantly modified the physicochemical properties of both PA.

Busquets-Fité et al.[100] studied model nanocomposites systems based on different polymers. In particular, inorganic metal oxide nanoparticles (NP) (SiO_2, TiO_2, and ZnO), multiwall carbon nanotubes (MWCNT), and nanoclays of Montmorillonite were dispersed in PA6, as well as PP and EVA for comparison purposes. The compounds were submitted to accelerated aging to simulate their use and get EoF materials to recycle. For PA6, the material was dissolved in FA (95%) and the separation was done via centrifugation followed by drying. The results showed that for aged and unaged PA6 samples, low NP recovery (43%–60%) was observed, with the exception of ZnO (almost zero).

Yin et al.[101] investigated the recovery of textile fibers/fabrics. The postconsumer materials was a mixture of Spandex (polyether-polyurea copolymer) and PA6. After a pretreatment (washing and drying), the Spandex fibers were removed by dissolution in N,N-dimethyl formamide (DMF), which was recovered by solvent evaporation to produce a cast film. The PA6 fraction was recovered by separation from the polymer solution.

Lv et al.[102] studied textile fibers based on cotton (cellulose) and PA6 obtained from tailor shops. In this case, an IL 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) was used to extract the cotton. The parameters studied were the waste fabrics ratio (1–3 wt%), temperature (90–120 °C), and time (40–120 min). The PA6 fraction was filtered out from the polymer solution, washed and dried. For the conditions studied, the Nylon recovery was stated to be above 39%.

For a more complex situation, Chandrasekaran et al.[103] studied different e-wastes. Two systems were investigated: PA/PC (cellular phones) and PA/PC/ABS/PMMA (general electronics). Although the latter was treated via pyrolysis, the former used selective dissolution to separate all the components. The parts were washed with soap/water and methanol before grinding (size reduction) and magnetic separation was applied to remove all the metals. Then, PC was dissolved in dichloromethane for 30 min at 38 °C or N-methyl-2-pyrrolidone for 45 min at 80 °C. The undissolved PA was filtered from the solution. A complete characterization of the recycled polymers combined with an environmental analysis was performed to account for contamination effects.

In the field of composites, Knappich et al.[104] investigated the recycling and recovery of PA6 reinforced with CF to compare with epoxy (EP) and PUR. A series of nine Creasolv solvents were used to determine the best one based on their chemical nature (polar protic, nonpolar, nonpolar aprotic and polar aprotic). The PA6-CF samples were produced by automated tape-laying and only some polar protic solvent were able to dissolve the samples for temperatures between 140 and 180 °C, while the dissolution time (from 3 h to about 1.4 h) decreased with increasing temperature.

Tao et al.[105] investigated a biobased polyamide (PA109) dissolved in superheated water (sH$_2$O). It was found that a minimum temperature of 170 °C was necessary to completely dissolve the polymer, but also partial hydrolysis occurred which increased with temperature and time (1–12 h) up to a point for which complete hydrolysis occurred (100% oligomers) at 280 °C. This hydrothermal process was found to be more environmentally friendly since a green solvent was used.

Önal et al.[106] studied the recycling of different permanent magnets bonding systems using IL. Four different polymers were detected in their samples: PA6, PA12, poly-p-phenylene sulfide (PPS) and epoxy (EP). Both PA were removed by dissolution in IL containing coordinating anions (acetate, chloride, and dialkylphosphate), while PPS was dissolve in 1-chloronaphtalene and triphenylbenzene at high temperature. For PA, tributylethylphosphonium diethylphosphate ([P$_{4442}$][Et$_2$PO$_4$]) was used at 165 °C for 12 h. The polymers were precipitated by water addition and filtered out.

Gong et al.[107] separated PA6 from PU (Spandex) from waste textile fibers. In their case, DMF was used to dissolve the PU fraction using a range of temperature (30–110 °C), time (10 min to 10 h) and liquid: solid ratio (5:1 to 30:1) the undissolved PA6 was recovered by suction (vacuum) followed by washing and drying, while PU was precipitated using water. The results showed that PU dissolution in DMF was easy (very fast) and no significant differences were observed between the processing conditions over the range investigated.

Rietzler et al.[108] studied the recycling of textile waste composed of PA6.6 (50%) with merino wool fibers (50%). The solvent used was a molar mixture (CEW) of water (25%) with 62.5% ethanol (EtOH) and 12.5% calcium chloride dihydrate (CaCl$_2$). The dissolution was performed by adding 5 g of fibers into 85 g of CEW at room temperature under mechanical mixing for 60 min. The PA6.6 fraction was recovered by water addition and filtration. The PA6.6 was found to have sustained negligible degradation during the process, but it must be carefully washed to remove residual calcium which might disrupt hydrogen bonds after reprocessing.

To remove dyes from textile fibers and recover uncolored (white) materials, Mu and Yang[109] used different solvents for PA6.6, as well as PET and cotton. Different number of treatment (cycles) were applied for each system. For PA6.6, three cycles (100 °C with a solid: liquid ratio of 1:5) was shown to remove 100% of the initial dye (acid blue 40) content. In this case, both the polymer and dye can be recovered for future uses.

To recycle multilayered packaging, O'Rourke et al.[76] used the solvent targeted dissolution-precipitation method to separate PA from PO bounded by PU adhesives. A range of temperature (80–200 °C) and time (1–5 h) was investigated to completely separate the layers. In this case, different glycols were selected as solvents: EG, diethylene glycol, TEG, and tetraethylene glycol. Different samples composed of oriented polyamides were bounded with solvent-free polyurethane (sf-PU) to PE films or cast polypropylene which were recovered using different solvents. For PA recovery, the best conditions were 150 °C for 3 h in EG.

To compare the systems investigated, Table 5 presents the composition of the original materials with the solvent used. For binary blends, the PA or the contaminant can be dissolved and recovered via different methods (evaporation, precipitation, and so forth) after filtration (purification).

6 | THERMAL RECYCLING

During pyrolysis (thermal recycling), the polymers are decomposed into lower molecular weight compounds, where in general two different products are targeted. First energy recovery via fuels such as pyrolytic gas and

TABLE 5 Overview of the information available on the physical recycling of PA.

PA grade	Other materials	Solvent	Reference
PA	Municipal waste	FA	97
PA	PP, SBR, $CaCO_3$	FA	20
PA6, PA6.6	EVA, HDPE	DMSO, FA	98
PA6, PA6.6	MMT, MWCNT	DMSO	99
PA6	SiO_2, TiO_2, ZnO	FA	100
PA6	Spandex	DMF	101
PA6	Cellulose	IL	102
PA	ABS, PC, PMMA	DCM, NMP	103
PA6	CF	Creasolv	104
PA10.9	–	sH_2O	105
PA6, PA12	–	IL	106
PA6	PU	DMF	107
PA6.6	Wool fibers	$CaCl_2/EtOH/H_2O$	108
PA6.6	Dyes	DMSO, DO, IP, TMO	109
PA	PO, PU	EG	76

Abbreviations: ABS, acrylonitrile-butadiene-styrene; CF, carbon fibers; DMF, dimethyl formamide; DMSO, dimethyl sulfoxide; EG, ethylene glycol; EVA, ethylene vinyl acetate; FA, formic acid; HDPE, high density polyethylene; IL, ionic liquids; IP, isopropyl alcohol; MMT, montmorillonite; MWCNT, multiwall carbon nanotubes; NMP, *N*-methyl-2-pyrrolidone; PA, polyamide; PC, polycarbonate; PMMA, polymethyl methacrylate; PO, polyolefins; PP, polypropylene; PU, polyurethane; SBR, styrene-butadiene rubber; sH_2O, superheated water.
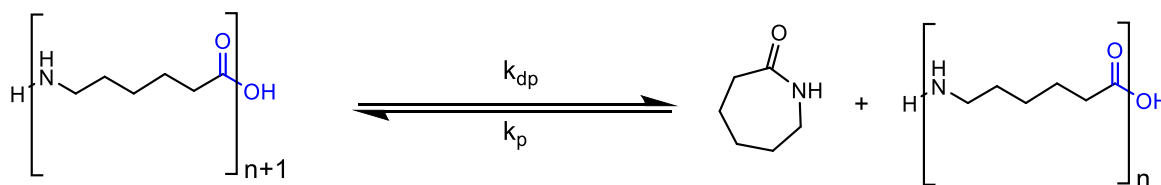

FIGURE 10 Depolymerization of PA6 into the monomer ε-caprolactam and shorter polymer by thermal degradation.

pyrolytic oil, and second as monomers recovery. During the polymerization process, energy is gained, resulting in a thermodynamically stable polymer. Above the ceiling temperature, enough energy is available to reverse this process and the monomer can be recovered as shown in Figure 10.

During pyrolysis of PA, toxic HCN, CO, CO_2, and NH_3 can be produced,[110] where the nitrogen containing compounds can be further converted into NO_x in the presence of O_2. In the case of textiles, pyrolysis offers an upcycling opportunity instead of being disposed in landfill.[111] However, pyrolysis to pyrolytic oils or gas results in an economic value lost since ε-caprolactam is derived from fossil feedstocks as described in section 1.

6.1 | Energy recovery

Simple incineration of PA results in a combustion energy of 30.2 MJ/kg,[112] which is about 10 MJ/kg less than crude oil. In general, incineration allows to recover the chemically bound energy in PA. However, the production of PA is highly energy intensive. For example, the production of PA6.6 requires 163 MJ/kg of polymer. Thus incineration has a very low efficiency and other recycling methods are much more favorable.

To create pyrolytic fuels, high temperature and heating rate are of high importance to avoid crosslinking of the material leading to a solid char-like material. Pannase et al.[113] reported the thermal degradation of PA6 under different heating rates to obtain pyrolytic oils, with a maximum oil recovery of 88% in a closed mixed bed reactor at a heating rate of 10 K/min at 600 °C, compared with 87% at 550 °C using a slower heating rate of 5 K/min. Moreover, the oil yield was found to highly depend on the temperature, as lower temperatures yielded less oil, but a higher gas fraction. On the other hand, much higher heating rates or temperatures resulted in a gel-like fraction; that is chemical crosslinking of a remaining part

TABLE 6 Overview of the different thermal degradation processes available for the conversion of polyamides for monomer recovery.

Recycling method	Catalyst/reactive species	PA grade	Pressure	Temperature	Time	Yield / monomer recovery	Reference
Thermal degradation— monomer recovery	Heating within 20 ms	PA6		500 °C		Exclusively monomer	115
	NaOH	PA6	0.004 bar	250 °C	270 min	90.5%	116
	5 wt% KOH, α-Al	PA6		360 °C	60 min	85%	117
	NaOH and KOH	PA6		350 °C		98.4%	118

of the material. The oil fraction was found to consist of alkanes, alkenes and aromatic compounds, while the gas was composed of low molecular weight hydrocarbons with H_2, CO, and CO_2 from the decarboxylation of the carboxylic acid groups created in the process.

6.2 | Monomer recovery

During chemical recycling, the target is to decompose the polymer chains into their monomer units. The primary polyamide chain scission occurs either at the peptide C(O)–NH or at adjacent bonds, such as the alkyl-amide NH–CH_2 bond which is relatively the weakest in the aliphatic chain.[114] As shown from the comparison in Table 6, the thermal degradation for monomer recovery is only suitable for PA6 (and maybe all the caprolactam types in general), which can be polymerized via ring opening polymerization from ε-caprolactam being ring-opening-polymerization, not as polycondensation; that is no water addition is needed for the monomer recovery.

For the monomer recovery via PA pyrolysis, cyclic monomeric products are targeted for the polylactam type PA (PA6, PA11, and PA12), while for the diacid + diamine type PA (PA6.6, PA6.10, and PA6.12) linear products are obtained. However, due to structure difference between the polylactam type and diacid + diamine type, different products can be obtained. For PA6, end-biting of a terminal amine on a carbonyl group results in the desired cyclic monomer, but also dimers, trimers and tetramers are reported. In addition, β-C-N hydrogen transfer can occur, where an amide bond is split resulting in two chains with one containing a terminal double bond and the other one having a terminal amide group. In a further step, the amide group can eliminate water resulting in a terminal nitrile group.[119]

Using pyrolysis coupled with mass spectroscopy, a different mechanism for PA6.6 was revealed with significant amounts of secondary products. However, PA6.6 intramolecular end-biting results in terminal isocyanide, cyclic oligomers, and cyclopentanone,[119] as well as other cyclic side products.[120] In addition, adipic acid tends to eliminate CO and H_2O and to undergo cyclization.[114,120] A remaining gel-like crosslinked portion is often found and explained by first the reaction of two terminal amine groups to a secondary amine and NH_3. Second, the secondary amine further reacts with the terminal carboxylic acid groups of other PA, resulting in a tertiary amine, and therefore crosslinking.[121] Similarly to PA6 and PA6.6, PA12 mainly produces cyclic pyrolysis products, while PA6.11[122] and PA6.12 decompose into several side products. For example, PA6.12 decomposes, among others, into caprolactam, toluene, undecane nitrile, lauryl lactam, and traces of cyclic products.[123]

The polylactam type PA was found to tend to reequilibrate to monomeric or oligomeric cyclic products. For example, Lüderwald et al.[124] found intensive thermal degradation for the pyrolysis of PA6 at 390 °C in an ion source of the mass spectrometer, mainly resulting in cyclic oligomers. Furthermore, the comparison of works from different groups showed that sample size and heating rate played important roles for the generation of side products. For example, using thin PA6 films and a quasi instantaneous heating (less than 20 ms) to reach a degradation temperature of 350–550 °C was found to result exclusively in the monomer recovery,[115] but slower heating rates resulted in additional cyclic dimers, trimers, and tetramers.[125] From the pyrolysis of PA6, higher monomer recovery was also observed for higher temperatures when the sample contained teabag waste,[126] leading to recovery as high as 59% at 500 °C.

Similar to chemical recycling, efficient monomer recovery under pyrolysis can be enhanced by adding a catalyst. For example, sodium hydroxide (NaOH) addition resulted in a 90% caprolactam yield at 250 °C under vacuum (0.004 atm) for 270 min.[116] Czernik et al.[117] reported caprolactam recovery of up to 85% within 60 min at 360 °C using 5 wt% potassium hydroxide (KOH) supported on α-alumina as catalyst. The apparent activation energy (E_a) for the formation of ε-caprolactam is around 205 kJ/mol, while the use of a mixture of bases, such as NaOH and KOH, was found to significantly lower

the apparent activation energy by nearly 100 kJ/mol (113 kJ/mol) resulting in an excellent monomer conversion of 98 wt% at 350 °C.[118] Other catalysts, such as phosphoric acid,[118] can also decrease the apparent activation energy by about 50 kJ/mol compared with the noncatalyzed reaction. They can also change the reaction order (from first to second order) with an activation energy of around 163 kJ/mol.[118]

Table 6 present a comparison of the works available on the thermal recycling of polyamides. It can be seen that a wide range of conditions were investigated. Nevertheless, mainly works on PA6 were found.

7 | CONCLUSION

In this review, the main recycling methods (biological, chemical, mechanical, physical, and thermal) were presented, discussed and compared for the specific case of polyamides/Nylon (PA). A comparison between each method showed that each technique has advantages and limitations as reported in a recent review by Uekert et al.[127] for different polymers (PE, PET, and PP). Their analysis also included an economic and environmental comparison.

In general, mechanical recycling outperforms on all aspects, but produces materials of lower quality (higher contamination content). Chemical recycling can generate high purity materials, but performs less on the environmental issues (solvents). This is also a problem for physical recycling. Thermal recycling consumes high amounts of energy (economic constraint) and the different products are difficult to separate. Finally, biological treatments are very limited for polymers in general (even more for PA due to its high stability) because specific conditions must be used needing long processing time (still not technically and economically viable). Nevertheless, developments are still under way to improve on the current technologies which can be seen as complementary instead than being in competition depending on the origin of the material and its composition.

But before recycling a part, it is always better to try to reuse it (see waste hierarchy, Figure 1). A typical example was the work of Morón-López et al.[12] who converted EoF reverse osmosis membranes into biofilm reactor membranes.

Another important step to improve the final quality of mechanical recycling is by removing contaminations. To this end, a series of two papers were published reporting on magnetic levitation.[92,93] PA6 was investigated with ABS, PC, PET, PP, and PTFE, as well as PU. The idea is to place grinded particles of the recycled materials in a liquid bath (paramagnetic medium) and a two-stage

process is applied. In the first bath, 2.5 M $MnCl_2$ is dissolved in 80:20 vol. H_2O:EtOH, while the second stage is composed of 1.0 M $MnCl_2$ in water. Then, applying different vertical magnetic field is able to separate the resins due to differences in density/buoyancy (polymer vs. solution) and lift-force (magnetic). In all cases, the resin purity achieved was over 96%. The method is automatic and continuous for easy industrial scale-up, especially for waste electrical and electronic equipment and end-of-life vehicle.

In conclusion, several methods have been developed to recycle PA under different compositions and structures: blends, multilayers and (nano)composites. Unfortunately, not much information has been found on PA foams[128] and biobased-PA,[129] as well as the effect of different additives such as flame retardants, antioxidants, stabilizers and plasticizers.[130] Another subject of high interest would be to investigate into more details crosslinked PA.[131] In addition, most of the literature focused on aliphatic polyamides (PA6 and PA6.6). It would of high interest to investigate other types of PA, including aromatic polyamides and polyphthalamides.[132] Finally, other processing methods than extrusion and injection should be investigated. For example, rotational molding and AM (3D printing) are examples where PA are used for several applications.

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