

Chemical aspects of polymer recycling

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ABSTRACT

Since recycling of polymers is a preferred means of reducing unwanted wastes and land-filling activity, and recovering monomers or other materials of economic value, tertiary methods of recycling (chemical recycling) have been critically reviewed, giving special attention, in each case, to the chemical basis of the particular recycling pathway and its potential applicability. Recycling issues of each of the widely used commodity polymers – polyesters, polyamides, polyurethanes, epoxies, poly(vinyl chloride), polystyrene, and polyolefins – have been discussed individually, giving attention to both conventional and unconventional methods of perceived high potential, such as enzymatic degradation, ionic liquids mediation, microwave irradiation, and treatment in super critical liquids as well as super fluids. In addition, novel emerging methods undergoing greater study at present, such as cross-alkane metathesis (CAM), tandem hydrogenolysis/aromatization, vitrimer-based recycling, and dynamic covalent bonding are also highlighted.

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1. Introduction

The world's mounting plastics waste problem has several dimensions to it — social, technical, and economic. While plastics left lying around after use do not disappear from view and such post-consumer waste as foam cups, detergent bottles, and discarded film is a visual annoyance, the disposal of post-use plastics in landfills, rivers or oceans, besides signifying an economic loss, poses a major environmental concern, because they may take centuries to degrade and disappear naturally. Incineration of plastic waste to produce heat may be a possible way of plastics disposal, but that way also the organic content would totally be destroyed and converted only to CO₂, H₂O, and possibly some harmful gases. Recycling is an alternate method to above types of disposal. It not only protects the environment, but also helps to convert the potential resource to useful products.


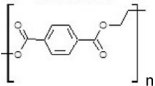

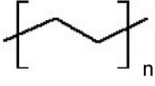

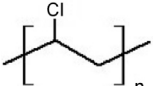

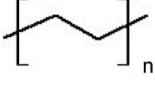

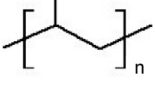

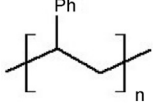


According to the type of product from the recycling process and the percentage of the economic value recovered, the following broad classification of recycling technologies is commonly made: (1) *primary recycling* (reprocessing of plastics waste into the same or similar types of product from which it has been generated); (2) *secondary recycling* (processing of plastics waste into plastics products with less demanding properties); (3) *tertiary recycling*

(recovery of chemicals from waste plastics); and (4) *quaternary recycling* (recovery of energy from waste plastics). Among these recycling methods, tertiary recycling, in which the waste plastic material is converted to chemicals and fuels is gaining increased attention worldwide, while the most desirable way of tertiary recycling is, obviously, to break plastics down to original monomers or larger polymerizable units or fragments from which polymers or other useful products can be made [1,2].

Since it is chemistry that brought plastics into the world, it is reasonable to look again into chemistry for possible ways of taking plastics apart so as to generate monomers and/or reusable smaller units. In terms of chemistry, waste plastics in the recycle stream can be classified as thermoplastic or thermosetting types. While most thermosetting plastics which are crosslinked can be decomposed only by pyrolysis to produce fuels and hydrocarbon feedstocks, or incinerated for energy recovery, polymers comprising thermoplastic solids are either addition polymers, for which the synthesis reactions are essentially not reversible, or step-growth condensation polymers, such as polyesters, polyamides, and polyurethanes which are formed by condensation reactions. Thus, while polyesters, polyamides or polyurethanes can be depolymerized and recycled into plastics, depolymerization of addition polymers needs pyrolysis or such severe chemical attack that usually creates a wide spectrum of species of different sizes, offering little in the way of winning desirable products in economically viable yields.

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Table 1
SPI code, polymer name and structure.

SPI Code	Polymer	Structure
 PETE	Polyethylene terephthalate (PET or PETE)	
 HDPE	High density polyethylene (HDPE)	
 V	Polyvinyl chloride (PVC or V)	
 LDPE	Low density polyethylene (LDPE)	
 PP	Polypropylene (PP)	
 PS	Polystyrene (PS)	
 OTHER	Other plastics (PC, PU etc.)	

It should also be emphasized that while recycling strategies are dictated essentially by the aforesaid chemical reactivity differences and different plastics have different properties, there are a host of other practical considerations ranging from collection and sorting to pretreatment (since waste plastics may have contaminations, adhesives, colorants, etc.) that influence the choice of recycling method adopted in practice. Thus, for better recycling each type of plastic must first be sorted. While there are many different methods of sorting plastics that have been used and are being studied for optimization, in the present review, however, the main

focus will be on chemical aspects of processes that can be used to harvest polymerizable units or other high value chemical species from different types of waste plastics that have been sorted and cleaned.

The vast majority of plastics (~87%) in use are thermoplastics and they fall into six categories described by SPI (Society of Plastics Industry) codes 1–6, which were established to help sort plastics materials for different recycling pathways. While all plastics are not equal with respect to ease of recycling, the most easy-to-handle favorites are polyethylene terephthalate (PET) and high-density

polyethylene (HDPE). These are the most commonly recycled plastics and have SPI code identification numbers “1” and “2”, respectively. In using the recycling code developed by SPI for containers, the “chasing arrows” triangle is being used more widely for recycling by the public. The numbers and letters are described in Table 1. Thus, for example, a clear, relatively less flexible soda bottle has a “1” within the “chasing arrows” and underneath it “PETE”, both signifying that the bottle is made of poly(ethylene terephthalate) polymer. Similarly, a colorless, somewhat hazy container has a “2” and “HDPE”, both indicating that the bottle is made out of high-density polyethylene (HDPE). Again, a brownish, clear medicine container has a “5” and the letter “PP” on its bottom, signifying that the bottle is made of polypropylene. Ready identification of some common items is thus easy.

Plastics bearing SPI numbers “1” and “2” are amenable to traditional *mechanical recycling*, in which the plastics can be simply sorted, cleaned, shredded, melted, and then re-extruded into plastic pellets for use in new products. However, this does not happen with other polymers having higher SPI code numbers (Table 1). Recycling these polymers presents a much greater challenge and has led to researches in “advanced recycling”, also called “chemical recycling”, which refers to several different processes based on existing and emerging technologies.

Multiple types and mixes of plastics can undergo chemical recycling to create multiple high-value products including monomers. In brief, chemical recycling has the potential of producing a higher quality output from a lower quality, contaminated waste plastics. The current review aims to highlight existing methods of chemical recycling as well as contemporary academic efforts to develop new methods for recycling some of the most abundantly produced plastics, specifically, condensation polymers such as polyethylene terephthalate (PET), polyamides (PA), polyurethanes (PU), and some large-tonnage commodity plastics made by addition polymerization, namely, polyethylene (PE), polypropylene (PP), poly(vinyl chloride) (PVC), and polystyrene (PS).

2. Recycling of Poly(Ethylene terephthalate)

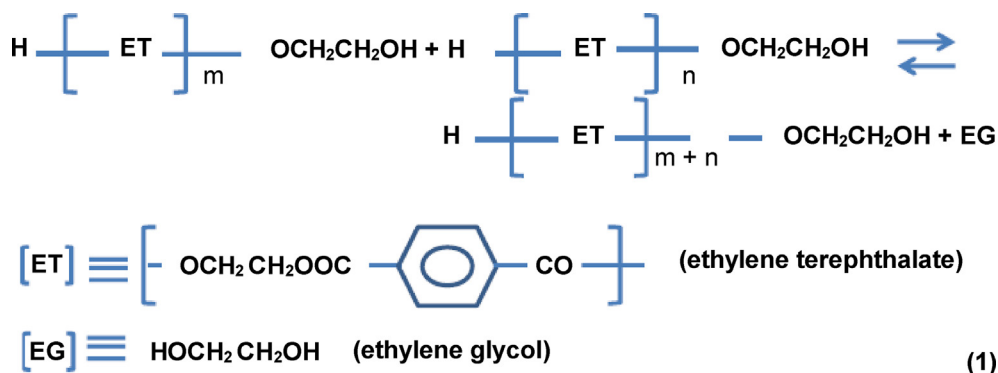
The largest use of poly(ethylene terephthalate) (PET) is in the fiber sector with PET film and PET bottles representing only about 10% each of the total PET volume produced annually. A large percentage of the total PET output comprising films, plastics, and fibers

is recycled by various methods and for several applications, which makes PET one of the largest in volume of recycled polymers in the world. Contributing to this is the suitability of PET for practically all recycling methods, which include direct reuse of uncontaminated discarded plastic by shredding, heating and remolding (often termed “closed loop recycling”), reuse after modification, recovery of monomers and other low-molecular-weight intermediates via depolymerization, and also incineration [2]. Any particular recycling method is selected on the basis of the quality of the waste and scrap, the economy of the process, and the convenience of the operation.

Contamination of post-consumer PET (POSTC-PET) is the major cause of deterioration of its physical and chemical properties during reprocessing. POSTC-PET is contaminated with many substances: (1) acid-producing contaminants, such as poly(vinyl acetate) and PVC; (2) water; (3) coloring contaminants; (4) acetaldehyde; (5) other contaminants, such as detergents, fuel, pesticide, etc. stored in PET bottles. The most harmful substance to the POSTC-PET recycling process is acetic acid, which is produced by the degradation of poly(vinyl acetate) closures, and hydrochloric acid produced by the degradation of PVC. The acids act as catalysts for the chain scission reactions during POSTC-PET melt processing. Thus the presence of PVC, even as little as 100 ppm, would increase POSTC-PET chain scission [3]. Water is known to reduce the molecular weight (MW) during POSTC-PET recycling through hydrolysis reactions at the processing temperature (280°). Moisture contaminants should be below 0.02% to avoid such MW reduction [1]. Acetaldehyde is present in PET and POSTC-PET, as it is a by-product of PET degradation reactions. Acetaldehyde being highly volatile, it can be minimized by processing under vacuum or by drying. Stabilizers such as 4-aminobenzoic acid, diphenylamine, and 4,5-dihydroxybenzoic acid are added to PET in order to minimize the generation of acetaldehyde during processing [4].

2.1. Direct reuse

This method, which is a primary recycling method, called variously as manual recycling, recycling by re-extrusion, or melt recovery, is used for relatively pure PET waste such as cleaned consumer bottles or in-house waste. The method is based on the same principles as the original equilibrium polycondensation reaction:



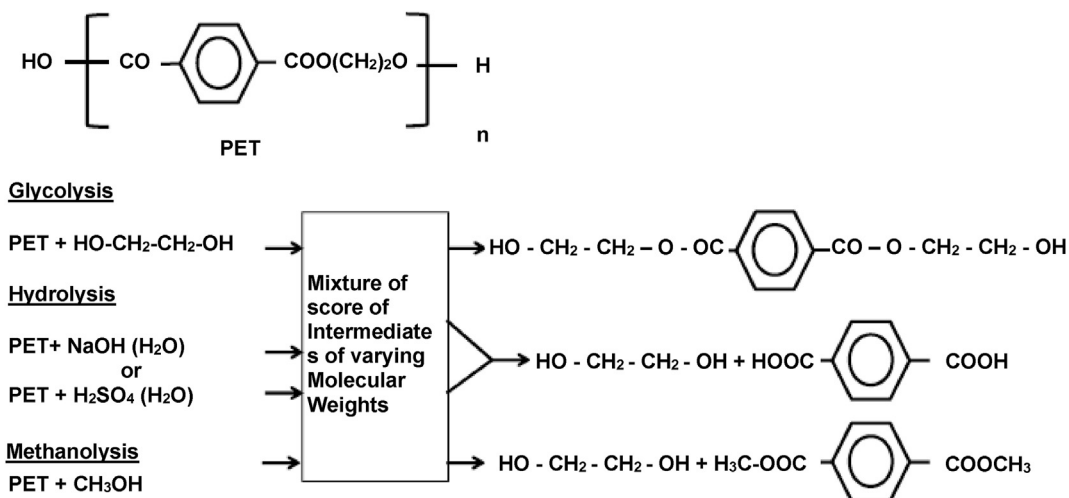


Fig. 1. PET degradation by glycolysis [6].

As polymer build-up and polymer degradation take place in the melt simultaneously, the reaction conditions have to be controlled very carefully in order to obtain the desired molecular weight and molecular weight distribution for the end use. In theory, this seems rather simple; in practice, however, a large amount of determining parameters (temperature, environmental atmosphere, holding time in a melt state, amount of impurities, type of used catalysts, stabilizers, etc.) have to be kept under control.

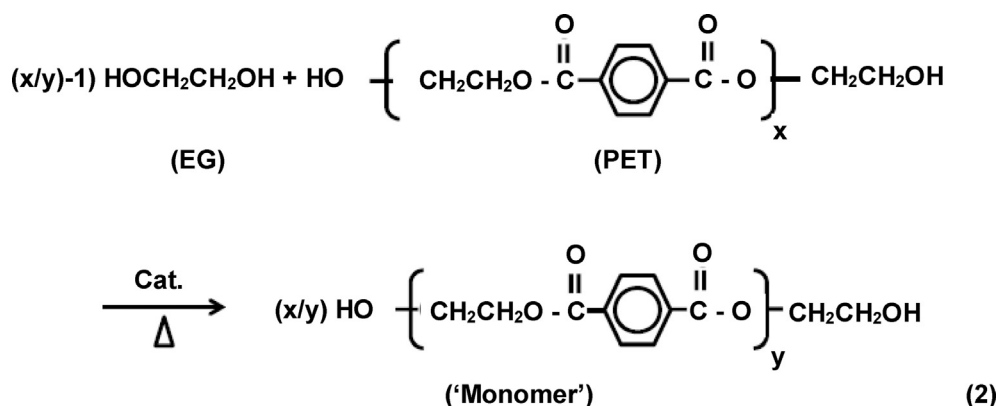
A significant problem with recycling of PET by the re-extrusion method is that the mechanical properties of the recycled material are greatly reduced with each reuse, as revealed by the strain-at-break property (i.e., the percent of length that a sample can be stretched before it breaks). For example, it is 42% for virgin PET but only 0.7%

products that can be isolated. The principles of chemical processes involved in these methods are schematically represented in Fig. 1.

Hydrolysis and methanolysis of PET regenerate the starting monomers. Thus, terephthalic acid (TA) along with ethylene glycol (EG) are obtained by hydrolysis, while methanolysis yields EG and dimethyl terephthalate (DMT) among other products. Stop-ping short of complete depolymerization, glycolysis degrades long polymer chains (with typical repeat sequences of 150 units) into short-chain oligomers (repeat sequences of 2–10 units) having hydroethyl end groups.

2.2.1. Glycolysis

The addition of EG and PET reverses the polymerization reaction. This can be stoichiometrically represented by



(typically) after the fifth cycle of re-extrusion [5]. For this reason, tertiary recycling via chemical decomposition processes has received significant attention by researchers [2].

2.2. Chemical recycling

For chemical recycling or reuse after modification, POSTC-PET waste having a higher degree of contamination can be used and technological processes based on decomposition by either glycolysis, methanolysis, or hydrolysis can be employed [1]. These yield

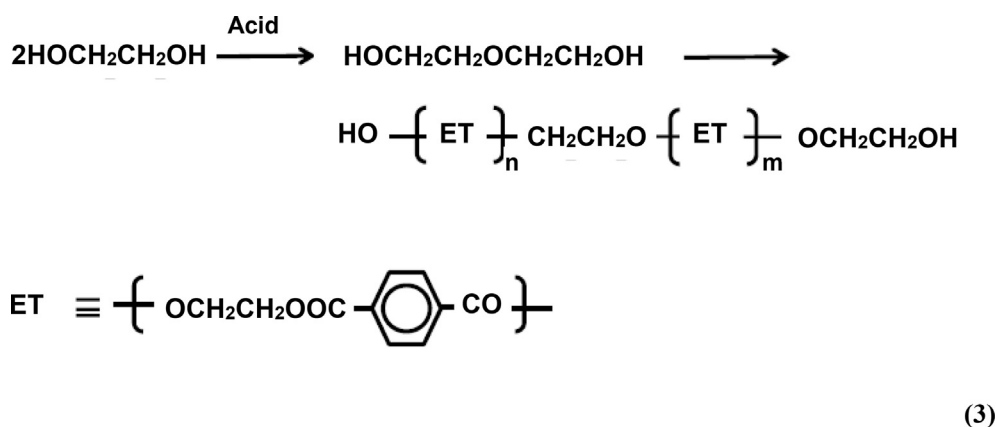
where x = average number of repeat units in polymer and y = average number of repeat units in 'monomer'. When $y = 1$, monomer = dihydroxyethyl terephthalate (DHET).

Glycolysis thus represents a compromise between regeneration of starting ingredients by methanolysis or hydrolysis and direct melt recovery [7]. It is less costly than the former and more versatile than the latter. The resultant, easily filtered, low viscosity 'monomer' can be repolymerized to a useful higher molecular weight product.

In a batch process, a molten 'monomer' heel is left in the reactor to allow the feed-stock/glycol mixture to reach optimum reaction

temperatures. In a continuous process, some of the molten 'non-omer' is recycled to a stirred reactor to accomplish the same function. High glycol/terephthalate (G/T) ratios lead to more complete glycolysis but lower the maximum temperature, increasing the reaction time. A ratio of 1.7–2.0 is a practical compromise [3]. An ester exchange catalyst as zinc or lithium acetate is usually added to increase the rate of glycolysis. Reaction temperatures of 220–240 °C and times of 60–90 min are typical. The reactor is operated under a positive pressure to prevent formation of an explosive mixture of air and glycol vapors.

A major side reaction is the production of ethers (see Eq. 3). Since this reaction is acid catalyzed, it can be minimized by adding a buffer such as sodium acetate or by adding water. Lithium acetate catalyst also produces less ethers than zinc acetate. Some other side reactions are the formation of aldehyde, cyclic trimer of ET, and dioxane. Oxidation of glycol ends produces aldehydes that lead to colored compounds.



While glycolysis reactions are very useful for the recycling of PET, a challenge has been the immiscibility of PET with the polyols. In an effort to address this problem, Liu et al. [8] conducted a careful study on the role of different solvents in the conversion of PET to dihydroxyethyl terephthalate (DHET). Thus, dimethylsulfoxide (DMSO), among many solvents screened, proved to be most effective for co-solvation of EG and PET, thereby producing an increase in the yield of DHET to 82% (as compared to only 20% without DMSO) at 190° and atmospheric pressure.

Much research has also been conducted in the area of catalyst development. While zinc acetate, as mentioned above, has been the primary catalyst used in the glycolysis of PET, Troev et al. [9] have recently developed a titanium (IV) phosphate catalyst for the glycolysis of PET with EG, DEG, or 1,2-propylene glycol. This catalyst needed shorter reaction times compared to previous catalysts and provided higher yields and selectivity for DHET with shorter reaction times. While titanium is advantageous as it is non-toxic, the catalyst could not be recycled efficiently. To overcome this drawback, Wang et al. [10] used sustainably produced organocatalysts, such as urea, in place of transition metal catalysts. Urea proved to be an effective catalyst giving 100% conversion of PET with 74% selectivity for DHET under the reaction conditions of m(PET waste): m(ethylene glycol): m(urea) = 1 : 4: 0.1, atmospheric pressure at 160 °C for 2.5 h. Moreover, urea could be recycled several times without loss of activity or selectivity for DHET.

Ionic fluids, which have emerged as promising green chemistry tools owing to their attractive features, such as, high thermal stability, nonvolatility, electrochemical stability and low flammability,

besides having strong solvent power for both organic and inorganic compounds, have also been explored as a catalyst for the glycolysis of PET [11,12]. An example is 1-butyl-3-methylimidazolium hydroxide ([Bmim]OH), which was used by Yue et al. [12] to catalyze PET glycolysis, leading to 100% conversion of PET and DHET selectivity of 72%, compared to only 11% PET conversion in the absence of an ionic fluid. These workers also employed a Lewis acidic liquid such as ([Bmim]ZnCl₃), to achieve 100% conversion and improved DHET selectivity of 84% with a catalyst loading of only 0.16 wt%.

Deep eutectic solvents also have been used to catalyze glycolysis of PET. Thus, Wang et al. [13] reported that under the optimum conditions of ethylene glycol (20 g), catalyst (n(urea)/n(ZnCl₂), 4/1, 0.25 g), PET (5 g) and atmospheric pressure at 170 °C for 50 min, the conversion of PET and selectivity of DHET were 100% and 85%, respectively. On the other hand, using a combination of 1,3-dimethylurea (1,3-DMU) with 5 wt% Zn(OAc)₂, Liu et al. [14] was able to achieve 100% conversion of PET with 82% selectivity for

DHET at 190 °C in only 10 min. The high selectivity was attributed to relatively mild reaction conditions owing to the acid-base synergistic effects between 1,3-DMU and Zn(OAc)₂. The catalyst was recycled up to five times without any loss in activity, though the zinc content was found to decrease by 25% after five cycles, thereby limiting further recycling ability of the catalyst.

While the main thrust of PET recycling efforts has been on the depolymerization of PET to synthesize DHET as a monomer feedstock, an emerging area of interest now is the use of the products of chemical recycling of PET as feedstocks for other polymer formulations. If other glycols, such as diethylene glycol, propylene glycol, butylene glycol, and dipropylene glycol are substituted for ethylene glycol, the corresponding oligomers are formed. For example, the alcoholysis of PET with diethylene glycol (DEG) proceeds according to the reaction shown in Fig. 2(a). The alcoholysis consists of transesterification and depolymerization of PET resulting in oligomers. Using a small excess of the glycol, the oligoesters obtained have mainly two hydroxyl groups, i.e., oligoester diols are formed (Fig. 2(b)), which can be used as a diol component in the synthesis of value-added products. A few examples from literature are cited below.

Atta et al. [15] prepared an epoxy resin by reacting the aforesaid oligoester diol with epichlorohydrin and new diacrylate and dimethacrylate vinyl esters were synthesized by the reaction of the terminal epoxy groups with acrylic acid and methacrylic acid, respectively. These vinyl esters were then used as cross-linking agents for unsaturated polyester resins diluted with styrene. The resulting products found application in coating on steel.

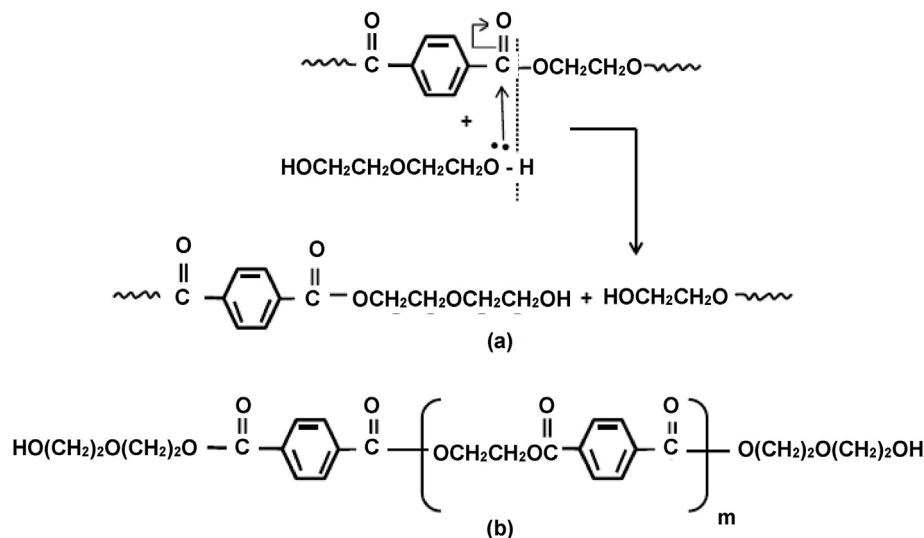


Fig. 2. (a) The glycolysis of PET with diethylene glycol (DEG). (b) The structure of oligoester diols resulting from the glycolysis of PET with DEG.

In a new application, Karayannidis et al. [16] reacted the oligoester diol from PET- DEG reaction with maleic anhydride, phthalic anhydride, and propylene glycol to form unsaturated polyester resins, which were then mixed with styrene and cured using benzoyl peroxide/amine initiator system to carry out the reaction at ambient temperature. The mechanical properties (tensile strength and elongation at break) of the resins were found to be comparable with those of the general purpose resin.

Karayannidis et al. [17] also converted the hydroxyl end-groups of PET-DEG glycolysate into methacrylate end-groups using methacryloyl chloride [CH₃C(=CH₂)C(=O)Cl] as the methacrylating agent. The dimethacrylated oligoesters were applied as potential raw materials for the production of UV-curable formulations, used as enamel paints, or coatings for metallic surfaces in the automotive industry.

Polyurethanes can be synthesized from the aforesaid oligoester diols. Thus, Vaidya and Nadkarni [18] showed that oligoesters obtained by the glycolysis of PET with DEG or higher glycols can be polymerized with aliphatic diacids, such as adipic acid to give polyester polyols with low acid number and then cured with polymeric 4,4'-diphenylmethane diisocyanate to produce polyurethane rigid foams and elastomers. Additives to control luster, color, and so on can be added in the usual manner before and after polymerization.

Desai et al. [19] synthesized polyol blends by reacting PET waste with plant-derived starch and then esterified the so-formed oligomers with fatty acids, available as high-volume waste products from other industries. These esterified PET products were used to synthesize polyurethanes that exhibited tunable variation of properties such as adhesion, flexibility, and chemical resistance as a function of PET products present in the formulation.

Amaro et al. [20] found that oligomers produced by the glycolysis of PET with DEG using Ca/Zn stearate catalyst at 250 °C for only 20 min are effective as secondary plasticizers in PVC formulations resulting in improved thermal stability and flexibility of the PVC product. The plasticizer migration also decreased greatly as compared to traditional PVC plasticizers, such as di(2-ethylhexyl) phthalate (DEHP), which leach out with time.

2.2.2. Methanolysis

PET waste obtained in the form of film, bottles, and fibers can be very conveniently converted into its raw materials dimethyl terephthalate (DMT) and ethylene glycol (EG) by methanolysis. The process involves heating the PET waste with methanol at high

temperatures (180–280 °C) and pressures (20–40 atm) in the presence of a catalyst, most commonly zinc acetate [21]. The crude product contains not only DMT and EG but also other alcohols and phthalate derivatives. DMT is recrystallized from the EG-methanol molten liquor, and distilled to obtain polymerization-grade DMT. Also EG and methanol are purified by distillation. Eastman Kodak has been using such a process for recycling of x-ray films for several decades and it has also improved the process, e.g. by using superheated methanol vapor to allow the use of even more impure PET waste. Important factors that have to be dealt with in this process are avoiding coloration due to aldehyde formation and minimizing the formation of ether glycols. In a recent development, Tang et al. [22] demonstrated that DMT recovered from methanolysis of PET could be exploited as starting material for the synthesis of gasoline and jet fuel.

2.2.3. Ammonolysis

PET wastes can be converted via ammonolysis to para-phenylenediamine, which is a basic raw material for the high-modulus fiber kevlar or for high-value hair dyes. The chemical basis for this process is a modified Hoffman rearrangement. The synthesis may be done via three stages, as shown in Fig. 3.

In the first step, granulated PET is suspended in ethylene glycol and treated with gaseous ammonia at 100–149°. In this reaction, the ethylene glycol also acts as a catalyst. The product terephthalimide (I) is suspended in water and chlorinated vigorously with chlorine gas. The resulting terephthalic bis-chloramide (II) is treated with NaOH solution to obtain paraphenylenediamine (III). An important aspect of this process is that the paraphenylenediamine so obtained is completely free from its ortho and meta isomers and its production cost is much less than the market price. ICI reported an alternative single-step process for the conversion of PET to para-phenylene-diamine by ammonolysis in the presence of hydrogen gas.

2.2.4. Aminolysis

Aminolysis can be used to depolymerize PET, yielding diamides of terephthalic acid (TA). The process requires an amine (which is often toxic or expensive) and re-action temperatures are usually in the range of 20–100 °C. In a study carried out by Teotia et al. [23], in which four different amines — methylamine, ethylenediamine, ethanolamine, and butylamine — were reacted with PET, high

conversion of PET into lower molecular weight oligomers was obtained at ambient temperatures and pressures, but this required reaction times ranging from 10 to 85 days. Soni et al. [24] also carried out aminolysis of PET with a variety of amines and achieved complete decomposition of PET to the diamide after 45 days of reaction. Later, Hoang et al. [25] showed that ethylenediamine was more effective as it depolymerized PET to a range of oligomers after only 17 h at 100 °C. However, several catalysts, such as dibutyl tin oxide, sodium acetate, and cetyltrimethylammonium bromide have shown promise for shorter reaction times and improved selectivity [26].

Tawfik et al. [26] subjected POSTC-PET bottle wastes to an aminolysis process with ethanolamine as a degradative agent in the presence of one of the aforesaid catalysts and using sunlight as the source of energy. They utilized the end product [bis (2-hydroxyethylene) terephthalamide] (BHETA) as an ingredient in anticorrosive paints for the protection of steel structures.

The product BHETA obtained by aminolytic degradation of POSTC-PET wastes has also potential for other useful applications. Thus, Shamsi et al. [27] synthesized novel polyurethanes based on PET waste-derived BHETA, 1,4-butanediol, ether-type polyol, and various molar ratios of hexamethylene diisocyanate.

2.2.5. Hydrolysis

A chemical process that has shown great promise for recycling PET by depolymerization into its monomeric units (TA and EG) is hydrolysis. It is the only method that leads to the monomers TA and EG. There are three different types of hydrolysis that have been studied in detail: neutral, acidic, and alkaline.

Neutral hydrolysis [28] uses only water or steam at high temperatures (200–399 °C) and elevated pressures (1–4 MPa). High depolymerization rates are obtained when the reaction occurs at temperatures close to that of the polymer melting point and by using high pressure systems. For example, Mancini and Zanin [29], studying the reaction of POSTC-PET flakes with water at the molar ratio 1:91, obtained depolymerization extents of 1.7, 8.2, and 99% at 135°, 170°, and 205 °C, respectively, each after a reaction time equal to 6 h and at the corresponding autogenous pressures of 4.0, 7.5, and 13.5 atm. However, it may be mentioned that, besides having relatively slow rate of reaction and requiring large ratios of water: PET, the process generally produces low-purity monomers.

Microwave irradiation is reported to enhance the rate of neutral hydrolysis of PET. It is considered to happen due to increase in the rate of diffusion of water into PET matrix by the effect of structure relaxation, as compared to the state of conventional heating [30]. Thus, complete degradation of PET was achieved in only 30 min at 223–232 °C and pressure of 2.3–3.0 MPa under the microwave heating condition [30].

The rate of hydrolytic depolymerization is enhanced considerably by the presence of proton donating inorganic acids – HCl, H₂SO₄, HNO₃, H₃PO₄. For acid hydrolysis, however, the most common acid used is H₂SO₄, the rate being strongly dependent on temperature. In one example, studying the decomposition of POSTC-PET flakes with 7.5 M aqueous solution of sulfuric acid, Mancini and Zanin [31] obtained 80% conversion in 4 days at 100 °C and 90% in 5 h at 135 °C. Analyzing the results of their study, they also concluded that the hydrolysis occurred preferentially at chain ends and was controlled by the diffusion of acid into the polymer structure. Although the yields obtained from this method are generally high, the rigorous requirement of corrosion resistance of the equipment makes profitability questionable. Moreover, the simultaneous recovery of TA and EG, requiring the use of ecologically undesirable halogenated solvents, is difficult and not economical.

2.2.6. Depolymerization in supercritical fluids

Above its critical point, a supercritical fluid has a high density as in the liquid state and high kinetic energy as in the gaseous state. The reaction rate in supercritical fluids is thus expected to be higher than in the liquid state conditions. PET is thus found to depolymerize quickly by solvolysis in supercritical water or supercritical methanol [32]. The main products of PET depolymerization in supercritical methanol are dimethyl terephthalate (DMT) and ethylene glycol (EG), as shown in Fig. 4. The depolymerization is carried out typically at temperatures between 543 and 603 K under pressures of 0.1–15 MPa for a reaction time of 3–60 min. For example, at 573 K, sample/methanol ratio 1/5 (by wt), and reaction pressure 14.7 MPa, DMT yield is reported to be 98% in 30 min [33]. It has been suggested that random scission of polymer chain takes place predominantly in the heterogeneous phase during the initial stage of PET depolymerization in supercritical methanol producing oligomers, whereas specific (chain end) scission to monomers

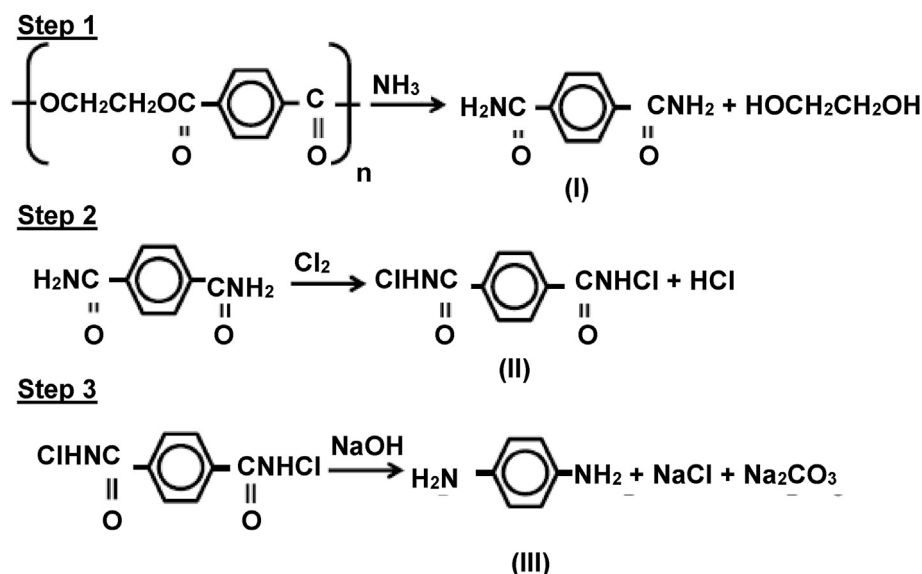


Fig. 3. Synthesis of paraphenylenediamine by ammonolysis of PET.

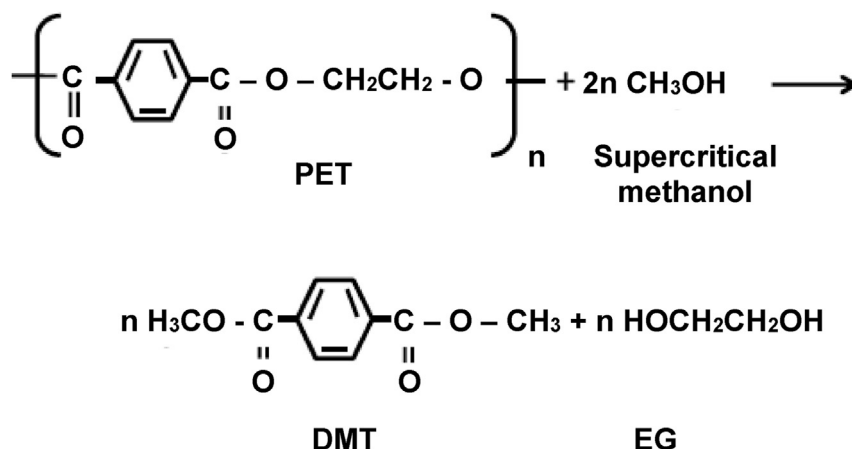


Fig. 4. Main reaction of PET depolymerization in supercritical methanol.

proceeds predominantly in the homogeneous phase during the final stage.

2.2.7. Enzymatic depolymerization

In 1977, Tokiwa and Suzuki [33] reported that some lipases, which are extracellular enzymes that usually cleave esters in oils and fats, are also able to attack ester bonds in some aliphatic polyesters and can depolymerize such materials. Aliphatic polyesters, however, exhibit only limited useful properties for many applications. Aromatic polyesters, such as PET and PBT, which are widely applied because of their excellent properties, are not attacked by hydrolytic enzymes. This led to the development of aliphatic-aromatic polyesters as biodegradable plastics that present a compromise between biodegradability and material properties. Later, Müller et al. [34] isolated a hydrolase (TfH) from *Thermofibida fusca*, which is able to depolymerize the aromatic polyester PET at a high rate, in contrast to other hydrolases, such as lipases. They demonstrated that commercial PET can be effectively hydrolyzed by an enzyme at a rate that does not exclude biological recycling of PET. The effective depolymerization of PET with the enzyme TfH results in water soluble oligomers and/or monomers that can be reused for synthesis. In contrast, a microbial treatment of PET may not be appropriate for recycling purposes, since monomeric and oligomeric depolymerization products would be consumed by the microorganisms involved or inhibit their action or growth [34].

It is likely that the degradability of PET with hydrolases such as TfH strongly depends on the polymer crystallinity and the temperature at which the enzymatic degradation takes place [34]. The effective enzymatic PET hydrolysis will thus be expected to occur only below a certain critical degree of crystallinity. However, for bottle manufacture polyesters with low crystallinity are usually preferred for high transparency, thus increasing the susceptibility of PET to enzymatic attack.

One reason for the high activity of TfH hydrolase towards PET may be the high temperature (55°) optimum, which is a result of its origin from a thermophilic microorganism. However, the activity differences between TfH and other lipases may also be due to differences in the structure of the enzymes, possibly enabling TfH to attack less mobile segments and degrade PET at a significantly high rate.

3. Recycling of polyamides

Polyamides (PAs) are a group of crystalline polymers which are commonly represented by two commercial products, i.e. polyamide

6 (nylon 6) and polyamide 6,6 (nylon 6,6). Blends of two different types of polyamides, such as PA6/6 or PA6/12 are other attractive alternatives. The world demand for polyamides is increasing year by year because of its wide use in various applications by the automotive, electrical, electronic, construction, packaging, and other industries. The problem of recycling and disposal of a growing volume of polyamide waste has therefore attracted greater attention.

3.1. Mechanical recycling

Mechanical recycling by melt extrusion is the easiest way to recycle polyamides, though, in practice, the use of costly waste separation and cleaning is a significant impediment to the process. Moreover, repetitive melt processing can lead to severe degradation of the polymer with consequent deterioration of all the properties, though molecular weight increase may also occur as a result of condensation and *trans*-reactions [35,36]. The degradation rate of polyamide is much faster in the presence of water as it induces depolymerization reaction, having also a synergistic effect with thermomechanical degradation. In this case, careful drying is a necessary step before the melt operation. This increases the costs of recycling. The drying step can be avoided, however, by adding an antioxidant that is able to remove moisture as well from the melt. A typical example of such an antioxidant is Sandostab P-EPQ (Clariant), a high molecular weight phosphonite compound, which has been found to be effective (at 500 ppm) for nylon 6 molding [37].

3.2. Chemical recycling

Since polyamides contain polar amide groups in the main polymer chain and hence can react with decomposing agents, they are amenable to chemical recycling for recovery and reuse of monomers. The typical decomposing agents are water or steam (hydrolysis), ammonia (ammonolysis), and glycols (glycolysis). The products of decomposition are oligomers or small chemical compounds, the preferred ones being caprolactam and hexamethylenediamine, which can be utilized in the synthesis of new polyamide or other polymers.

3.2.1. Hydrolysis

Polyamide waste can be decomposed in water at temperatures of 150–240 °C and pressures of 100–700 psi. Nemade et al. [38], studying the hydrolysis in an autoclave at 240 °C and 700 psi, determined the velocity constant for 99.99% depolymerization to

be $2.936 \times 10^{-2} \text{ min}^{-1}$. Iwaya et al. [39] investigated the influence of reaction temperature, time, and water density on the hydrolytic decomposition of polyamide using nylon 6. The reaction was carried out at temperatures between 300 and 400 °C under pressures of up to 35 MPa for reaction times of 5–60 min. The main products of hydrolysis by sub- and supercritical water were found to be ϵ -caprolactam and ϵ -aminocaproic acid. Based on experimental results it was concluded that nylon 6 is decomposed into ϵ -aminocaproic acid by hydrolysis followed by cyclodehydration to ϵ -caprolactam or decomposition further to lower molecules.

The rate of decomposition is accelerated by the presence of inorganic acids (HCl, H₂SO₄, H₃PO₄). Wang and Zhang [40] examined the hydrolysis of polyamide 6 in subcritical water replacing the traditionally utilized homogeneous acids with H-form zeolites. The study led to the conclusion that the temperature and reaction time are the decisive factors of depolymerization by hydrolysis and that the amount of water used does not affect the depolymerization of nylon. They concluded from their study that hydrogen bonds are first broken, which is followed by the formation of oligomers as a result of a nucleophilic substitution reaction between water and the carboxyl groups.

Patil and Madhamshettiwar [41] determined the optimum condition for depolymerization of nylon-6,6 by acid hydrolysis in HCl. They obtained a maximum depolymerization of 99.9% into hexamethylenediamine (HMD) for nylon-6,6 waste of average molecular weight 27,000 using 6 wt% powdered waste in 5 N HCl at 80 °C and time of reaction 120 min under reflux. The reaction rate constant under these conditions was determined to be $7.32 \times 10^{-3} \text{ min}^{-1}$.

A promising novel method described in the literature is the hydrothermal treatment of waste plastics. The method was also applied to aliphatic polyamides [42,43]. The study conducted by Wang et al. [42] revealed that above 160 °C, PA 6 dissolves fully in the superheated water and hydrolysis takes place producing an oil that contains caprolactam among other products. The hydrolysis results in a significant reduction in molecular weight of polyamide and it recrystallizes on cooling.

3.2.2. Glycolysis

Many workers have studied the depolymerization of polyamides by glycolysis. In order to study the mechanism of glycolysis, Kim et al. [44] used *N,N*-hexamethylene- bis(hexamide) as a model compound for polyamide PA 6,6 and characterized the glycolysates using GPC, GC-MS, and FTIR analysis. The glycolysis was carried out at a temperature of 275° and [PA 6,6]/[EG] molar ratio of 1:2. From this study, they proposed a mechanism that involves the formation of hexamethylenediamine, esters, and another primary amine.

According to the mechanism, oligomeric compounds with hydroxyl and/or amine end groups are formed at the beginning of the process, while in the final stage, a mixture of low-molecular-weight products, specifically unreacted ethylene glycol, hexamethylenediamine (HMD) or a compound with β -hydroxyethylester end-groups can be obtained. In the case of amino-glycolysis, on the other hand, the obtained oligomeric compounds can have amine end-groups derived from triethylenetetramine used as a decomposing agent along with EG. In both glycolysis and aminoglycolysis, however, esters and primary amines can also be obtained.

A new approach to chemical recycling of polyamide was explored by Datta et al. [45]. They synthesized polyurethanes with intermediates recovered from glycolysis and amino-glycolysis of nylon 6,6 using, respectively, ethylene glycol (EG) and a mixture of EG and triethylenetetramine (TETA) as the decomposing agents. The method did not require the use of elevated pressure and was carried out at 190° in the presence of diammonium hydrogen phosphate as catalyst. Poly(ester urethane)s were then synthesized

by means of a one-step method through reaction between 4,4'-diphenylmethane diisocyanate (MDI), 1,4-butanediol (as a chain extender) and a mixture of polyol with glycolysates prepared in a previous step. The glycolysates were mixed in an amount of 10 wt% with a commercial polyol. In order to partially bond-free amine groups, 1 wt% of orthophosphoric acid was added per glycolysate used. The reaction was done at 60 °C in the presence of 0.3 wt% of DABCO [N₂(C₂H₄)₃] as a catalyst. The reaction mixture was cured in a metal mold at 70 °C and then seasoned in an oven at 100 °C for 24 h.

3.2.3. Alcoholysis

While decomposition of polyamide-6 in supercritical water gives a complex mixture of depolymerized products due to the high reactivity of supercritical water, supercritical alcohols having milder properties produce more selective depolymerization to simpler products. Researches of Kamimura et al. [46], however, revealed that the use of simple primary alcohols, such as MeOH and EtOH, gives rise to complex mixtures containing many side products and, hence, poor yield of caprolactam, but the use of primary alcohols with longer alkyl chains give much better yield of caprolactam, which improves still further with the use of secondary and tertiary alcohols, the observed yields (shown in parentheses) of caprolactam from decomposition of nylon 6 in super- or sub-critical alcohols at 370 °C for 1–4 h being, thus, MeOH (14%), EtOH (36%), ProH (35%), BuOH (47%), C₁₈H₃₇OH (55%), C₁₂H₂₅OH (61%), iPrOH (91%), sec-BuOH (96%), and tBuOH (95%). Simple concentration of the reaction mixture afforded caprolactam in very pure form.

3.2.4. Ammonolysis

Polyamides can be depolymerized by heating in ammonia to obtain useful monomeric products. As early as 1969, a British Patent [47] disclosed a process for converting polyamides into monomeric compounds containing nitrogen. The process comprises heating the polyamide with ammonia in the presence of hydrogen and a hydrogenation catalyst, the quantity of ammonia employed being at least *n* moles per mole of polyamide, where *n* is the average number of amide groups in each molecule of polyamide. Examples described the production of (a) hexamethylenimine and hexamethylene- 1,6-diamine (HMD) from nylon-6,6 and (b) hexamethylenimine, HMD, and N-(6- aminohexyl)-hexamethylenimine from nylon-6 polymer.

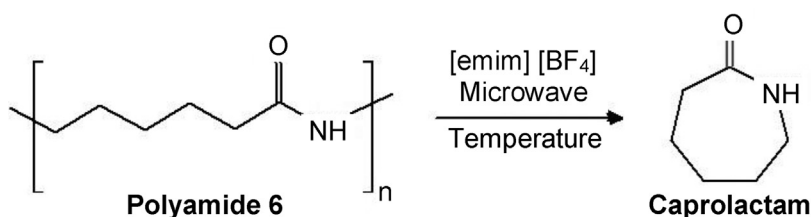
A subsequent US Patent [48] disclosed a process for preparing a mixture of monomers suitable for conversion to HMD by reacting nylon-6,6 or a mixture of nylon-6,6 and nylon-6, with at least 1 equivalent of ammonia per amide group of the polymer at a temperature between 250 and 400 °C and at a pressure of at least 100 psig in the presence of (NH₄)₂HPO₄ as catalyst, the ratio of nylon-6,6 to nylon-6 in the mixture being from 1:9 to 9:1 on a weight basis. The monomer products generally included HMD, 5-cyanovaleramide, adiponitrile, caprolactam, 6-aminocaproamide, and 6-aminocapronitrile.

Studying the process of ammonolysis for polyamide mixtures of nylon-6 and nylon- 6,6, Kalfas [49], however, proposed that the depolymerization mechanism involves amide link breakage and amide-end dehydration (nitrilation) reactions, as also ring addition and ring opening reactions for cyclic lactams in nylon-6. On the basis of this mechanism, he was able to develop a kinetic model for the ammonolysis of nylon mixtures.

3.2.5. Ionic liquids mediation

Being nonvolatile and capable of withstanding relatively high temperatures, ionic liquids have been employed as medium for depolymerization of polyamides with promising results. However, the nonvolatility of the solvent also brings in a serious separation

problem where the used ionic liquid and the products of polymer decomposition are both hydrophobic, as the ionic liquid cannot be separated from the products by extraction while distillation also cannot be used to separate the solvent. To enable extraction following depolymerization, Kamimura et al. [50] chose hydrophilic ionic liquids that should be removed by liquid-liquid extraction. While the solubility of ionic liquids would readily be controlled by changing their counter-anion, it could also change their reactivity very significantly. The authors chose BF_4 anion as it provides high ionicity and would also be expected to provide high reactivity for the depolymerization reaction [51]. Polyamide (mol. wt. 22,000) was thus found [50] to undergo efficient depolymerization when heated with the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ($[\text{emim}][\text{BF}_4]$) under microwave irradiation at 300 °C for 60 min:



(4)

Small amounts of *N,N*-dimethylaminopyridine (DMAP) were added as catalyst to promote the depolymerization effectively. The product caprolactam was separated in 55% yield by simple extraction, thereby avoiding distillation and saving on energy. The ionic liquid was reused several times.

4. Recycling of polyurethanes

Though most polyurethane (PU) plastics are cross-linked polymers, they cannot be regarded as ordinary thermosetting plastics, owing to their chemical structure and physical domain structure. Thus, in contrast to typical thermosetting plastics, various methods are available today for recycling PU scrap and used parts, which can be grouped under *mechanical recycling*, *chemical recycling*, and *energy recycling*. The first two recycling methods are preferred since in this way material resources are replenished. After multiple uses the material can finally be used for energy recovery by high-temperature combustion or gasification.

Among several processes described for material recycling of PU, *thermopressing* and *kneader process* have attracted much attention. By the thermopressing process [52], granulated or powdered PU wastes can be converted into new molded parts, while in the kneader process a thermomechanical operation causes partial chemical breakdown of PU polymer chains that can be subsequently cross-linked by reacting with polyisocyanates. Hydrolysis, glycolysis, and ammonolysis are important chemical recycling processes for PU wastes.

4.1. Thermopressing process

Thermopressing [52], or molding by heat and compression, is a direct method of material recycling that is designed such that elastomeric, cross-linked polyurethanes can be recycled in much the same way as thermoplastic materials. A water-blown flexible PU foam being actually a poly(urethane-co-urea), the principle of

thermopressing is based on the realization that polyurethane and polyurea granules are capable of flowing into each other and building up new bonding forces under the influence of high temperature (185–195 °C), high pressure (300–800 bar), and strong shearing forces. The granules generally used for this purpose have a diameter of 0.5–3 mm. They completely fill the cavities of a mold and so moldings with new geometries can also be made.

Unlike injection molding of thermoplastics for which a cold mold is used, in the thermopressing process, the mold is kept constantly hot at a temperature of 190 ± 5 °C and no release agent is used for demolding. This relatively simple technique will permit 100% recycling of PU reaction-injection molded (RIM) objects. Because of the use of granulated feed, the produced molded parts

lack surface smoothness and thus should be used preferably in those areas where they are not visible. Examples of application are wheel boxes, reserve wheel covers and similar other covers, mudguard linings, glove boxes, and casings.

4.2. Kneader process

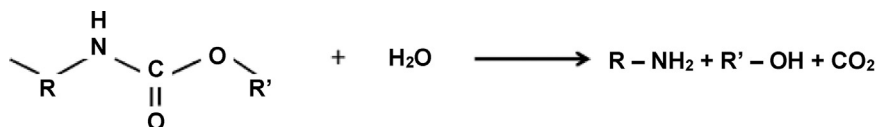
The basic of a kneader recycling process [52] is a thermomechanical degradation of polymer chains to smaller-size segments. The hard elastic PU is thereby converted into a soft, plastic (unmolten) state, which is achieved with a kneader temperature of 150 °C and additional frictional heating. This leads to temperatures above 200 °C and causes thermal decomposition into a product that is soft at 150–200 °C but becomes brittle at room temperature, enabling it to be crushed to powder in a cold kneader or roller press. The resulting powder can be easily mixed with a powder form polyisocyanate (e.g., Desmodur of Bayer) and molded into desired shapes by compression molding at 150 °C and 200 bar pressure.

Partial breakdown of PU network in the kneader results in highly branched molecules with many functional groups necessitating addition of polyisocyanate in relatively high concentration for subsequent cross-linking to produce molded articles. The process thus yields products of high hardness (with Shore up to 80) and high tensile strength (30 MPa), but small elongation at break (6–8%).

Among the various material recycling methods for PU scrap and wastes, the thermopressing and kneading processes are especially significant, because these simple processes render the recycling of cross-linked PU products equivalent to that of thermoplastic products. Lack of surface smoothness and some reduction in mechanical properties are to be tolerated. However, good values of E-modulus, structural rigidity, and hot and cold impact resistance permit use of the molded components of recycled PU in many applications, e.g., in unsighted parts of automobiles, instruments, and machineries.

4.3. Hydrolysis

Hydrolysis of PU waste results in the formation of polyethers and polyamines that can be used as starting materials for producing foam. In this process, powdered PU waste is reacted with superheated steam at 160–190 °C and the polymers get converted in about 15 min to a liquid heavier than water. The liquid is a mixture of toluene diamine and propylene oxide (polyether diol), the former accounting for 65–85% of the theoretical yield. The reaction appears to be simple and proceeds according to the general equation:



(5)

It is necessary to completely separate the amines from polyether polyols. This complete separation is necessary if the amines are to be used to produce new isocyanates. The recovered polyether can be used in formulations for making PU foam, preferably in admixture with virgin polyether.

A continuous hydrolysis reactor utilizing a twin-screw extruder has been designed [53] that can be heated to a temperature of 300 °C and has a provision for injection of water into the extruder at a point where the scrap is almost in the pulp state. Polyurethane scrap in powder form is fed into the extruder and residence time is adjusted to 5–30 min. Separation of the two components, polyether and diamine, in the product may be effected by fractional distillation, by extraction with a suitable solvent, or by chemical means. The PU foams made from these recycled products can be used in several applications, one example being protection boards for construction sites. Hydrolytic recycling has not, however, found much application, since virgin raw materials are cheaper than the regenerated products.

It should be noted that hydrolysis is usually always a side reaction [54] to chemical recycling of polyurethanes, since any PU foam contains absorbed water (between 5 wt% in viscoelastic foams and 0.5 wt% in aged rigid foams). Water will react as side reactions giving undesired products, especially primary aromatic diamines, such as 4,4'-diaminodiphenylmethane (MDA) or 2,4- and 2,6-tolylene diamines, which are carcinogenic substances. Though numerous patents on PU alcoholysis have appeared, none however has seen larger scale application.

4.4. Glycolysis

Extensive studies have been made on glycolytic degradation of PU wastes. In a glycolytic process, powdered PU waste is suspended in a short-chain glycol such as diethylene glycol or dipropylene glycol or mixtures thereof and heated to a temperature of 185–219 °C in nitrogen atmosphere. The glycolysis reaction takes place by way of transesterification of carbonate groups in PU [Fig. 5]. The reaction product is predominantly a mixture of glycols and does not need any further separation of the components, unlike in the hydrolytic process. The reaction is performed either in batch reactors or with specially designed reactors in a continuous way by using extruders or extruders coupled with a tandem of reactors [54]. A special process is the split-phase process in which, after glycolysis, the glycol is distilled off the mixed polyols. The cost of producing such recycled polyol is reported to be low enough to make the process economically viable. The mixed polyols resulting from glycolytic degradation of PU waste is, however, suitable mainly for the production of hard foam, such as insulating foam for houses.

4.5. Ammonolysis

Chemical recycling of PUs by ammonolytic cleavage of urethane and urea bonds under supercritical conditions has been described [55]. It is well known that a number of low-boiling materials provide enhanced solubility and reactivity under supercritical conditions. Ammonia has a critical point at 132.45 °C and 112.8 bar (11.28 MPa) with a density of 0.235 g/cm³. Being able to act as hydrogen bond donor and acceptor, it provides good solubility for PU and dissolves their hard segment domains, thus enabling a

homogeneous reaction. Ammonia is also a reagent having greater nucleophilicity than, for example, water or glycol is; since it is added in a huge molar excess compared to the urethane or urea groups of the materials to be cleaved, the equilibrium is shifted towards the ammonolysis products. The stoichiometry of ammonolysis reaction of a polyetherurethane is shown in Fig. 6.

The typical reaction parameters of an ammonolysis process are temperature of 139 °C, pressure of 140 bar, and reaction time of 120 min. The ammonolysis reaction transforms derivatives of carbonic acid into urea. Ether bonds as well as hydroxy groups are inert towards ammonia under the reaction conditions applied. Hydroxy compounds like polyols and diol chain extenders that do not contain ester groups are recovered as such. The C=O fragments of urethane and urea functional groups are converted to unsubstituted urea.

After ammonolysis, ammonia is evaporated and can be reused after liquefaction, while degradation products of polyurethane hard segments (i.e., amines and chain extenders) and urea are removed by extraction. The pure polyol is left in the reactor. It can be removed mechanically or by extraction with liquid ammonia in which it is soluble. The recovered amines can be converted to the corresponding isocyanates and can be reused, along with polyols, in the same applications as before.

5. Recycling of Poly(vinyl chloride)

Aside from polyolefins, poly(vinyl chloride) (PVC) and some other chlorine-containing polymers belong to the most widely applied thermoplastic materials. There are many applications of rigid and plasticized PVC. In the building sector, for example, very large amounts are used for pipes, profiles for windows, floor coverings, roofing sheets, and so on. By the end of the life-time of these articles, large amounts of scrap are produced. It is of economic and environmental interest to recycle this PVC waste as much as possible. Disposal of PVC by incineration has its special problems as, due to the high chlorine content of PVC, its incineration yields large amounts of HCl gas in addition to the possibility of formation of toxic dioxines and furans. On the other hand, it is a great advantage that many sources produce large amounts of PVC scrap of the same origin and with similar composition, which simplifies the re-use possibilities from a logistic point of view.

PVC is known to degrade in two steps when heated. At lower temperatures (220–350 °C), HCl and small amounts of benzene are formed. As dehydrochlorination (elimination of HCl) takes place, polyene structures are formed, giving rise to discoloration:

6. Recycling of polystyrene

Polystyrene (PS) is a natural transparent thermoplastic that is available in both forms — solid (SPS) as well as expanded (EPS). PS is the eighth largest tonnage polymer made in the world with global production capacity (in 2018) of 16 million tons, which underlines the importance of its end-of-life disposal issues. PS can be recycled by mechanical, chemical, and thermal methods. High-impact PS (HIPS) is particularly suitable for mechanical recycling since its properties are not significantly affected even after multiple processing of up to nine times. EPS is, however, recycled only after volume reduction by heating, pressing, pulverizing or dissolving in a solvent.

6.1. Mechanical recycling

Polystyrene is reclaimed from waste plastics for reuse. In a patented process [58] for reclamation of PS from wastes for recycling, a reusable solvent having a low boiling point and high rate of vaporization is used to remove PS from solid contaminants by dissolution and the PS is recovered in a solid form by volatilization of the solvent, the maximum temperature in the recovery section being 190 °C. Propyl bromide or an environmentally safe mixture thereof such as with isopropyl alcohol is mentioned as the preferred solvent.

In another patented process [59], suggested for recycling EPS, dialkyl carbonates are used for removing the PS from insoluble components. The polymer is then selectively precipitated with a nonsolvent or a blend of nonsolvents. Pure PS is thus recovered for subsequent processing.

Dibasic esters also have been used for the recovery of PS polymer from PS foams [60]. Thus when an aqueous solution of dibasic

ester selected from the group of dimethyl glutarate, dimethyl adipate, and dimethyl succinate, and a surfactant is applied to PS foam, a gel-type substance is formed which may be applied as a water-proofing agent or recycled into PS foam.

An innovative way of recycling PS waste has been described [61] in which extract from citrus peel is used to convert PS waste objects into submicron aligned fibers. The hydrophobic-oleophilic PS fabric produced from the latter is used as an effective sorbent of oil.

6.2. Chemical recycling

Post-consumer PS can be used to derive styrene and other polymerizable units or chemicals by various processes, which include catalytic degradation, controlled thermal depolymerization, cracking thermal depolymerization, and depolymerization in super-critical fluids.

6.2.1. Catalytic degradation

One of the attractive chemical recycling processes for PS is catalytic degradation [62], which yields styrene monomer with high selectivity at a relatively low temperature. Thus over Fe–K/Al₂O₃ at 400 °C, the yields of oil and styrene monomer from the degradation of PS waste were obtained as 92.2 and 65.8 wt%, respectively, with activation energy as 138 kJ/mol. The selectivity to styrene monomer, however, decreased in the presence of MgO in the catalyst.

Studying the degradation of PS on solid acids and bases viz., MgO, CaO, BaO, K₂O, SiO₂/Al₂O₃, aluminosilicate zeolite ZSM-5, and active carbon as catalyst, Ukei et al. [63] reported that solid bases were more effective than solid acids for the degradation of PS into styrene. This was attributed to differences in the degradation mechanism of PS over solid acids and bases. Among the solid bases

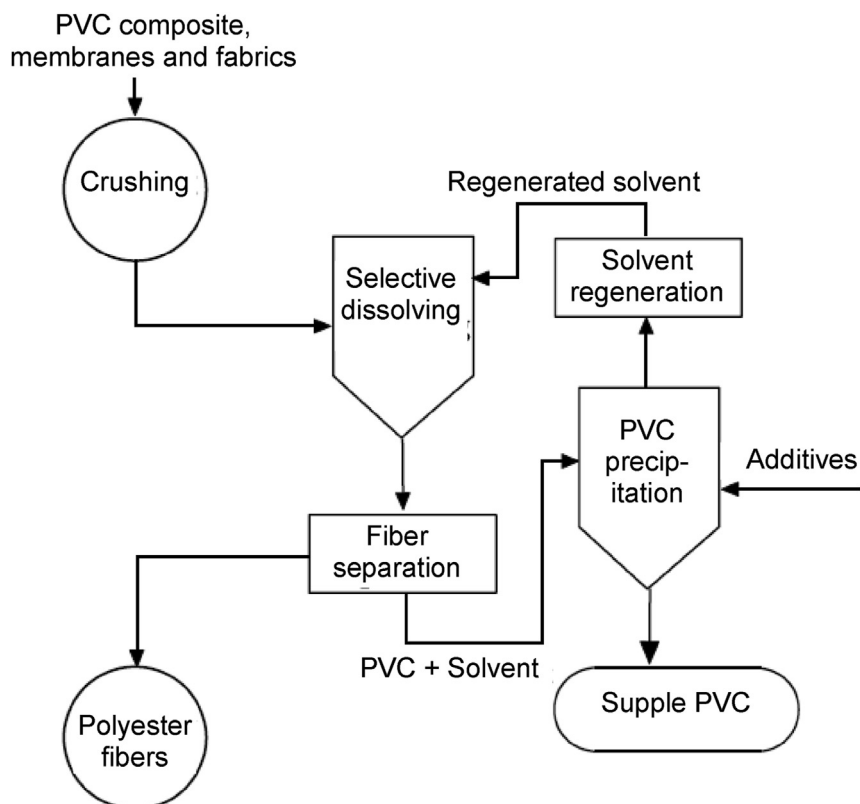


Fig. 7. Texyloop process for recycling PVC.

employed, BaO was found to be the most effective catalyst producing ~90 wt% conversion of PS into styrene at 350 °C.

6.2.2. Controlled thermal depolymerization

Controlled thermal depolymerization (plastic to monomer and other small units) exists for PS because it contains some activated bonds that are easier to break. The companies Agilyx (USA) and Pyrowave (Canada) have developed new processes for such depolymerization, though very little information is made available. The Agilyx process can revert polystyrene back to monomeric styrene, toluene, and ethylbenzene and can select for different products by tuning the time, temperature, and pressure of the pyrolysis process.

Pyrowave, on the other hand, applies catalytic microwave depolymerization (CMD) at a commercial scale for recycling post-consumer contaminated PS. The process is said to produce rather high levels of monomer, less amounts of dimer and trimers, and almost no higher chains. One of the differences of CMD from other conventional pyrolysis processes is the heating rate which is faster in CMD because energy is transferred on a volumetric basis, whereas other conventional approaches are much slower because the heating occurs on a conduction/convection basis. It has also been shown [64] that the Arrhenius ratio E_A/RT in a microwave environment is lower by a factor of 4–6 compared to the same ratio obtained by conductive/convective heating, which could contribute to the different degradation behavior observed in CMD. The possibility of the decrease in the Arrhenius ratio being due to a significantly higher local temperature caused by resonance between the microwave electrical field and the molecular structure of the polymers being decomposed has been explored [64].

6.2.3. Cracking thermal depolymerization

Cracking thermal depolymerization of PS can, in principle, produce monomers for plastic production or fuel and whether the output will be the former or the latter depends on the input and the process parameters. As an example, the results of an isothermal pyrolysis study of Kim et al. [65] can be cited. The isothermal pyrolysis of PS was conducted in a relatively low temperature range of 370–400 °C using a stirred tank of batch-type with respect to the liquid phase and open system with respect to the gas phase. The main liquid products of pyrolysis were found to be single and double aromatic ring species: styrene, α -methyl styrene, toluene, 1,3-diphenyl propane, and 1,3-diphenyl butene. The yield of styrene, however, was much larger than any other product and amounted to ca. 70% by weight.

The liquid product of the cracking thermal depolymerization of PS can be re-polymerized to produce polymer. However, the different aromatic compounds included in the fraction may act as chain transfer agents, lowering significantly both the average molecular weight and the T_g of the polymer produced.

The thermal degradation of random copolymers of styrene, such as, HIPS, SAN, and ABS, produces more complex liquid products than the homopolymer of styrene, as the process involves more complex mechanisms. Thus, studying the thermal degradation of HIPS, SAN, and ABS, at low temperatures and in air, Gupta and Nambiar [66] found that while the dominant process in the degradation of HIPS is random chain scission due to weak links, in SAN it is intermolecular chain transfer. On the other hand, the degradation in ABS is initially random scission due to weak links and then mainly intermolecular chain transfer. The IR spectra revealed that during degradation, the labile links are attacked by O_2 and peroxidic free-radicals are produced, which are responsible (via hydrogen abstraction or auto-oxidation of olefinic links) for the formation of aliphatic ketonic or peroxy-ester structures, and for isomerization and cyclization.

6.2.4. Depolymerization in supercritical fluids

Reactions are conducted in supercritical fluids to take advantage of good heat and mass transfer that promotes faster reaction and higher conversion. PS was found to depolymerize in supercritical benzene, toluene, and xylene at 310–370 °C and 6.0 MPa pressure with high conversion in a short reaction time, forming monomer, dimer, and other products [67]. Supercritical toluene was found to be more effective than other solvents in this respect, producing 77 wt% conversion in 20 min at 360 °C.

Degradation of polystyrene was studied by Hwang et al. [68] in supercritical *n*-hexane at reaction temperature ranging from 330 °C to 390 °C and pressure ranging from 30 bar to 70 bar. PS rapidly degraded in the temperature range 350–390 °C, the degree of degradation rising to >90% and the selectivity for styrene rising to 65% in 90 min at 390 °C. With rising temperature, the amount of high-molecular-weight product decreased but that of oligomers increased in the degradation product.

In a study of PS degradation in supercritical acetone, the total conversion was found [69] to increase rapidly with rise of temperature from 270 to 290 °C. The yield of styrene was the highest among aromatic products when the weight ratio of acetone to PS was fixed at 11.2, which was equivalent to acetone density 0.406. The yields of styrene and diphenylbutene (equivalent to dimer of styrene) attained maximum values at a temperature between 280 and 290 °C.

Polystyrene undergoes depolymerization in supercritical water producing small units of aromatic hydrocarbons. Kwak et al. [70] studied the degradation of PS in both sub- and supercritical water at reaction temperatures ranging from 370 °C to 420 °C and pressures of 240–320 bar. At 370 °C where water is in a subcritical state, the degradation attained equilibrium conversion of ca. 80 wt% in about 5 min, whereas at 380 °C and 390 °C, where water is in a supercritical state, the degradation attained the equilibrium conversion of 100 wt% in 15 and 3 min, respectively. The degradation products contained monomer, dimer, and trimer of styrene, toluene, ethyl benzene, isopropyl benzene, triphenyl benzene, among others. The selectivity for styrene products decreased with increase of reaction time, whereas that of benzene and other derivatives increased because of the difficulty of decomposing the benzene and phenyl radicals. A first order kinetic behavior was observed for PS degradation in supercritical water like that in supercritical acetone and *n*-hexane.

7. Recycling of polyolefins

Although they are formed from olefins, polyolefins such as polyethylene or polypropylene are not olefinic, since paraffinic molecules result from the polymerization of olefins. These long-chain hydrocarbon polymers are extremely inert and there is no simple way to transform them, especially at moderate temperatures, into useful products. Thermo-chemical conversion is an attractive route to produce fuels from these waste plastics, thus diverting them from landfills. Unlike biofuels, these are non-acidic and non-corrosive due to the absence of water and oxygen, and have high calorific value, comparable to fossil fuels. One thermo-chemical conversion process is pyrolysis which is a thermal degradation method in the absence of air/oxygen. Larger polymeric chains are broken in the process into smaller hydrocarbons, producing a wide distribution of hydrocarbons that changes with both temperature and reaction time. For example, large amounts of gaseous products are formed as the temperature reaches approximately 700 °C [71].

Pyrolytic conversion may also not be economically feasible since it requires high energy input. Economics can be improved, however, through the use of a catalyst in the process. Besides reducing

the reaction temperature, and hence energy consumption by lowering the activation energy required for pyrolysis, the choice of catalyst may also affect significantly the yield and product selectivity of the process. In a hydrocracking process [72], in which catalytic pyrolysis is carried out in the presence of hydrogen at moderate temperatures, the cleavage of carbon-carbon bond in heavy plastic molecules occurs with simultaneous or successive hydrogenation of unsaturated molecules formed during the process, resulting in reduced amounts of olefins, aromatics, and coke. The process is also advantageous from the energy perspective as cracking is an endothermic reaction, while hydrogenation is exothermic.

Degradation of polyolefins by thermal pyrolysis, whether catalytic or non-catalytic, is essentially a high-energy process and results in a rather wide distribution of products. However, recent research efforts have provided an exciting pathway to satisfy the needs of a new low-energy process for polyolefin degradation with product control and higher efficiency. Thus, utilizing a tandem catalytic *cross-alkane metathesis* (CAM), based on a sequence of dehydrogenation/hydrogenation reactions conducted by two catalysts, the new process [73] leads to waxes and liquid fuels as recycled products. Another research effort reported very recently has led to the development of a novel one-pot low-temperature catalytic method to convert various grades of polyethylene directly to liquid aromatics over a simple Γ -alumina supported platinum catalyst [74].

7.1. Thermolysis/reactive distillation

Thermal pyrolysis usually refers to thermal depolymerization of melted polymer under inert atmosphere into lower-molecular-weight compounds that vaporize and reduce the melt volume. The vapors from such pyrolysis of polyethylene contain a wide distribution of molecular fragments with an average molecular weight that is a function of the volatility of the products at the reaction conditions employed, such as temperature and amount as well as surface area-to-volume ratio of the melt.

Non-catalytic thermolysis of polyethylene and direct distillation is usually reported to produce less than 5% of the charge as liquid product at moderate temperatures (generally less than 500 °C), the main product being a wax that is volatile at the reaction temperature. In contrast, a significantly high yield of liquid distillate is obtained when the thermolysis is coupled with reflux distillation [75]. Thus from LLDPE and HDPE the reaction products were found [75] to consist of linear alkanes and alkenes ranging from six carbon-atom species up to approximately 30–35 carbon atoms. The high yields of liquid product were attributed to the fact that all of the volatile products were passed through a distillation column by a purge gas before they were collected in the product stream. Higher boiling point fractions would thus be condensed inside the distillation column and returned to the charge with only the lighter fractions being able to escape into the product stream. This is in agreement with the finding of Seth and Sarkar [76], who compared the effects of degradation with and without reflux on the MWD of the product using simulation and solving the governing population balance equation for the polymer degradation.

7.2. Catalytic pyrolysis

Catalytic pyrolysis is a potential option to convert waste polyethylene and polypropylene back into useable fuels and raw materials for the chemical industry. A large number of heterogeneous catalysts have been investigated, including zeolites, both fresh and spent FCC-based zeolites, various silica-alumina systems and clay-based catalysts. Excellent reviews on these can be found in the

literature [77]. The most widely used catalysts are zeolite-based, such as HZSM-5, H β , and zeolite HY.

One of the aim of the on-going research in plastic waste to fuel conversion is to develop a good catalyst for an energy-saving pyrolysis process to maximize both plastic conversion and target selectivities. To give a notable example, the work of Almustapha et al. [78] with sulfated zirconia (SZ) may be cited. It is a super acid solid due to Brönsted and Lewis acid sites, has large surface area and mesoporosity, and has the potential to promote primary cracking of polyolefins into oligomers at moderate temperatures. Thus the catalyst with 10 wt% SZ was found to reduce the onset temperature of degradation of HDPE from above 330 °C–187 °C and produce 98% conversion at 380 °C in 30 min. The liquid yield obtained was 38 wt % with a composition of 16 wt% paraffins, 2 wt% olefins, 5 wt% naphthenes, and 58 wt% aromatics. The carbon number distribution of the liquid was C₇–C₁₂ which is within the gasoline range, and gaseous products ranged from methane up to different isomers of pentane, mostly paraffinic and naphthenic.

7.3. Hydrocracking

Hydrocracking of a polymer generally occurs in the presence of a bifunctional catalyst in a stirred autoclave at moderate temperatures and relatively high pressure, typically 300–450 °C and 2–15 MPa cold hydrogen pressure. The catalyst must have a cracking function as well as a hydrogenation-dehydrogenation (H-DH) function. A typical hydrocracking catalyst thus has an acidic support with metal impregnated on it, the former being responsible for cracking and isomerization reactions and the latter having the H-DH function. The acidic support is usually an amorphous oxide such as silica-alumina, crystalline zeolite such as HZSM-5, a strong solid acid such as sulfated zirconia, or a combination of these materials, while the metal can be a noble metal (Pd or Pt), Group VIA metal (Mo or W), or Group VIIIA metal (Co or Ni). Munir et al. [72] provides an elaborate list of research works carried out on direct liquefaction of plastic material by hydrocracking on various types of catalysts and under different conditions.

A hydrocracking process can be used directly on the plastic or in a two-stage process where the plastic material is first pyrolyzed (thermally or catalytically) and then subjected to hydrotreatment. Although not cost-effective, the two-stage process has the advantage that the fuel product after the second stage can be directly used in an automobile engine [72].

7.4. Tandem catalysis

As mentioned earlier, two new processes have been developed recently that use different catalytic processes in tandem to achieve efficient and controlled degradation of polyolefins into utility products. These are *tandem catalytic cross-alkane metathesis* [73], referred to, in short, as the CAM process and tandem hydrogenolysis/aromatization or THA process [74].

The CAM process evolved from the presumption that PE being alkanes, though with ultra-long molecules, could undergo chain cleavage and new distribution of alkane products by alkane metathesis with light alkanes under appropriate conditions. This indeed was achieved by a process developed by Goldman et al. [79] and Huang et al. [80]. It involves three steps: (1) dehydrogenation of PE and an externally added light alkane, such as hexane, on a catalyst, resulting in the formation of alkenes; (2) alkene metathesis on a metathesis catalyst; and (3) catalytic hydrogenation of the newly formed alkenes. The process is shown schematically in Fig. 8. First, the dehydrogenation catalyst Ir removes hydrogen from both PE and the light alkane in a sealed system to form unsaturated species and Ir–H₂. The olefin metathesis catalyst then scrambles

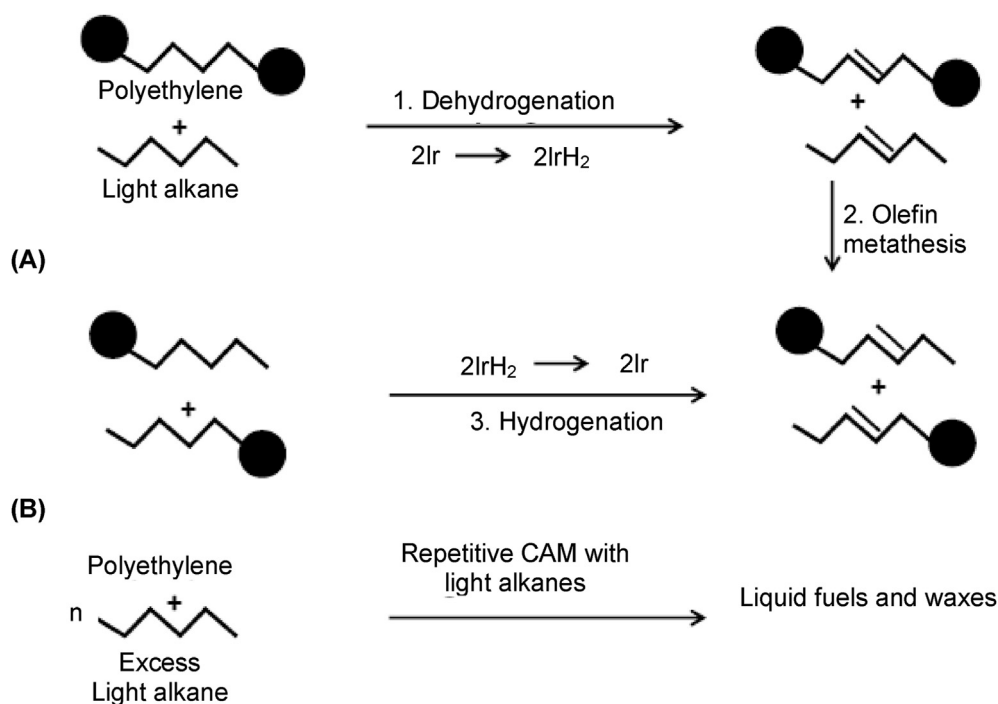


Fig. 8. (A) The three steps in the CAM process for polyethylene. (B) The overall conversion in the CAM process. (After Ref (81)).

the alkenes, effectively resulting in a breakdown of PE chains, since the chain length of PE reduces every time an internal double bond of PE scrambles with a double bond of the light alkane. Finally, the newly formed alkenes are hydrogenated with Ir–H₂, yielding saturated alkanes. After multiple cycles of such CAM with light alkanes, added in large excess, PE will be converted to short hydrocarbons suitable for transportation oils. A dual catalyst system containing a supported “pincer”-ligated iridium complex [81], which is a dehydrogenation/hydrogenation catalyst and Re₂O₇/γ-Al₂O₃ [82], which is an olefin metathesis catalyst, proved to be robust and effective for the CAM process.

Zhang et al. [74] recently described a tandem catalytic process for upcycling polyethylene to long-chain alkylaromatics. Thus, tandem catalytic conversion, in one pot, by platinum supported on γ-alumina was found to convert various polyethylene grades in high yields (up to 80 wt%) to low-molecular-weight liquid/wax products, in the absence of added solvent or molecular hydrogen, with little production of light gases. The major components were valuable long-chain alkylaromatics and alkyl naphthenes (average-C₃₀, dispersity 1.1). The high yield of liquid aromatics is particularly promising, since such compounds find widespread application as surfactants, lubricants, refrigeration fluids, and insulating oils, and their manufacture from waste polyethylene could displace fossil fuel-based routes.

8. Conclusions

While the plastics recycling activity, driven by consumer, economic, and legislative pressures, is all but certain to increase, the key variables in the rate of growth are the plastics industry's ability to develop an economical material-collection infrastructure and to improve the methods for handling and processing of contaminated scrap so as to identify and sort them with speed and accuracy. For major polymer types, various methods have been developed for recycling as raw material for the same plastic or other plastics or products of economic value. Thus the present review discusses both

the existing as well as new pathways emerging in the field of plastics recycling.

The tertiary or chemical recycling methods of major commodity plastics have been discussed, focussing on the chemical issues involved in them. Chemical means such as glycolysis, methanolysis, and hydrolysis, which are good at unzipping mainly the condensation polymers, such as polyester, nylons, and polyurethanes, are highlighted. Unconventional, but promising novel methods, such as supercritical fluid mediation, ionic fluid treatment, microwave irradiation, enzymatic decomposition, and tandem catalysis, are also discussed in the context of chemical recycling of polymers, both condensation and addition types.

Pyrolysis as a means of recycling has high potential for heterogeneous waste plastics which cannot be economically separated. Pyrolysis is favoured because of the high rates of conversion into oil and generation of gaseous products of high calorific value that may be used as a fuel in the process. However, the embodied energy that can be recovered by combustion is far less than that used in pyrolysis and in the original manufacturing of the plastic. Moreover, depolymerization by pyrolysis at temperatures above 400 °C, with or without a catalyst, generates highly complex and difficult-to-separate mixtures of gas, hydrocarbons, and char, which is a drawback. Though somewhat more selective degradation can be achieved at lower temperatures via catalytic hydrocracking or catalytic alkane metathesis, the economics of these processes may not be attractive. In this context, the novel solar driven reforming of plastics reported by Uekert et al. [83] is significant. For demonstration, they carried out efficient photoreforming of three common polymers – polylactic acid, PET and PU – using inexpensive CdS/CdOx quantum dots in aqueous alkaline solution. Operating at ambient temperature and pressure, the visible light-driven, noble metal-free photoreforming process is found to generate pure H₂, while the waste polymer is converted into useful organic products, such as formate, acetate, and pyruvate.

With the growing realization that the problem of plastics waste, its disposal and recycling is an unavoidable consequence of the

nature of chemical make-up of polymers that have been created in the laboratory, there is now increasing effort to develop new polymers which would facilitate closed-loop recycling and circular economy, similarly to what now applies currently to PET.

It is recognized that closed-loop polymers are critical to sustainability efforts world-wide and their integration into the global materials' ecosystem depends on maintaining high value for recovered materials at the end of products' life, as also on reducing the cost and energy intensity of depolymerizing plastics, for which, however, lowering the energy barrier to bond cleavage is critical. Potential solutions to these problems have emerged from recent advances in catalysis [84] and dynamic covalent chemistry [85]. Particularly significant is the advent of dynamic covalent copolymers known as 'vitrimers', proposed as sustainable replacements for non-recyclable thermoset plastics. As vitrimers undergo associative bond-exchange reactions in the solid state, it allows cross-linked materials to be thermally processed and recycled like thermoplastics while maintaining high cross-link density.

A vitrimer-based recycling approach mentioned above does not, however, emphasize a return to the original monomers and a re-entry to the supply chain, thereby largely limiting reformulation opportunities. In comparison, new plastics based on dynamic covalent diketoenamine bonds allow recovery of monomers from common additives even in mixed plastic streams [86]. Thus, poly(diketoenamine)s or PDKs, signifying high potential for closed-loop recycling, have been shown to "click" together from a wide variety of triketones and aromatic or aliphatic amines, yielding only water as a by-product, while PDKs are also capable of hydrolyzing in strong aqueous acid (0.5–5.0 M H₂SO₄) at ambient temperature to yield pure and reusable triketones. It must however be emphasized that while circular use of polymers will help to preserve finite natural resources besides addressing end-of-life issues, to replace currently available commercial polymers, depolymerizable polymers being developed would need to match or exceed the properties of the current ones that we are so familiar with.

Declaration of competing interest

There are no conflicts to declare.

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The author devotes this paper to the 85-th anniversary of Prof. Stoyko Fakirov with the best wishes for a good health and further contributions to the polymer science.

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