Chemical Recycling of Poly(ethylene terephthalate)

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This paper reviews the state of the art in the field of chemical recycling of poly(ethylene terephthalate) (PET). Advantages of the chemical recycling of PET, the theoretical basis of the ester bond cleavage, and a wide spectrum of degrading agents and final products are presented. Chemical processes applied in polymer recycling are divided into six groups: methanolysis, glycolysis, hydrolysis, ammonolysis, aminolysis, and other methods. Numerous possibilities for the utilization of waste PET as a very useful raw chemical material are described on the basis of literature. A comparison of chemical recycling methods is carried out. The following aspects were taken into consideration: (i) flexibility in utilizing a variety of waste types, (ii) conditions necessary for degradation including safety requirements, (iii) economic aspects, and (iv) product versatility. A total of 108 references including 46 patents are cited in this paper.

1. Introduction

Poly(ethylene terephthalate) (PET) is a saturated polyester of terephthalic acid and ethylene glycol. The growing interest in PET recycling is due to the widespread use of packaging made of this polymer—mainly as bottles. Since the middle of the 1970s, first in the USA and Canada and subsequently in Western Europe, increased quantities of PET are used for the production of soft drink bottles, and a further increase in its application in this area is predicted. The overall world consumption of PET currently amounts to about 13 million tons, of which 9.5 million tons is processed by the textiles industry, 2 million tons is used in the manufacture of audio and video tapes, and 1.5 million tons is used in the manufacture of various types of packaging—mainly bottles and jars. PET bottles are characterized by high strength, low weight, and low permeability of gases (mainly CO_2) as well as by their aesthetic appearance (good light transmittance, smooth surface). A very important feature of PET, decisive in the choice of its wide application in the manufacture of packaging for the food industry, is that it does not have any side effects on the human organism.

PET does not create a direct hazard to the environment, but due to its substantial fraction by volume in the waste stream and its high resistance to the atmospheric and biological agents, it is seen as a noxious material. Ecological as well as economic considerations advocate the introduction of wide-scale PET recycling, similar to the recycling of traditional materials such as glass, paper, or metals.

The recycling of waste polymers including PET can be carried out in many ways. A very attractive form of recycling of used polymer materials is the so-called, "materials recycling", which consists of the collection, disintegration, and granulation of waste polymer and then their recirculation into production. This PET recyclate can be used to make products which do not have to meet very high quality standards. For many reasons, this form of recycling can be effectively applied only to a part of all polymer wastes.

Among other methods of polymer recycling, chemical recycling, applied above all in the case of postconsumer condensation polymers, which are very vulnerable to solvolytic chain cleavage, is of great interest. Polyamides, polyurethanes, and polyesters belong to this group of polymers. The availability of a wide spectrum of degrading (depolymerizing) agents and a large variety of products, e.g., monomers for polymer and resin syntheses and other additives for polymeric materials, are some of the advantages of PET chemical recycling (Paszun et al., 1993).

Therefore, in recent years one can observe a growing interest in the use of PET waste for low-tonnage production of specialized products such as raw materials for the syntheses of saturated and unsaturated polyesters (Ostrysz et al., 1990; Vaidya and Nadkarni, 1990; Rebeiz et al., 1992; Watanabe et al., 1992; Rebeiz, 1993; Kim et al., 1995; Pepper, 1995), polyurethanes (Vaidya and Nadkarni, 1990; Tersac et al., 1991; Lee et al., 1995), coating materials (Sayre et al., 1993; Pilati et al., 1996; Toselli et al., 1996), and additives (Wang et al., 1991; Bai et al., 1993; Dupont and Gupta, 1993; Ostrysz et al., 1995; Paszun and Spychaj, 1995).

This paper is a review of chemical recycling methods of PET waste.

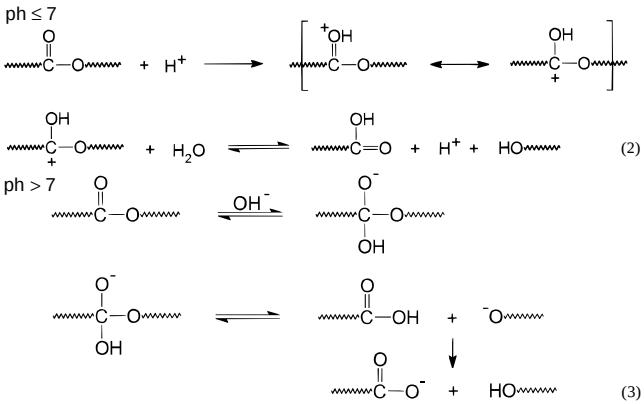
2. Theoretical Basis of Ester Linkage Solvolysis

Generally, the solvolytic reactions of polymers consist of the cleavage of the C−X bonds of the polymer chain, where X is a heteroatom (O, N, P, S, Si) or halogen. In the case of the solvolytic reaction of polymers containing heteroatoms in the main chain, the chain is degraded in accordance with the scheme

(1)

where YZ is the solvolytic agent, e.g., water, alcohol, acid, or alkali.

The dominant mechanism of degradation in an acidic and neutral environment is different from the mechanism of degradation in an alkali environment. This is shown in the scheme of hydrolytic cleavage of the ester bond (Schnabel, 1981).



Poly(ethylene terephthalate) is very vulnerable to chemical degradation. From the point of view of the chemism of the reactions, they can be divided into four

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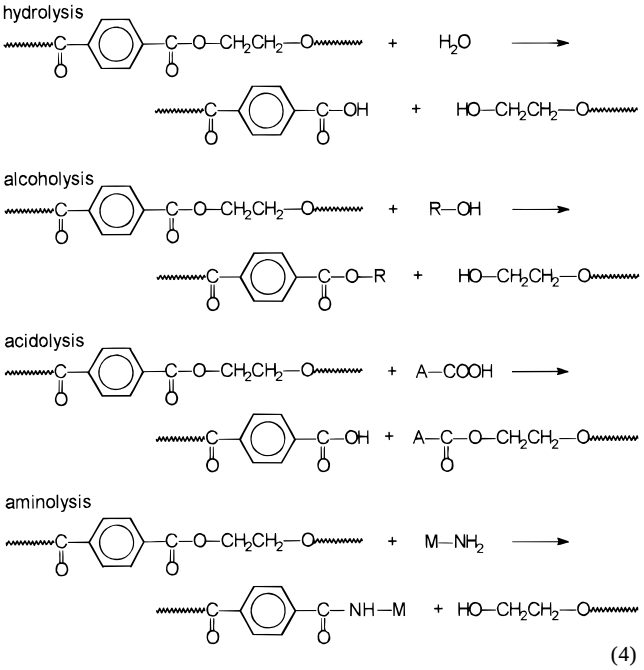


(4)

The reactions schematically presented actually are much more complicated, and the formation of byproducts should be taken into account.

3. Chemical Recycling Methods

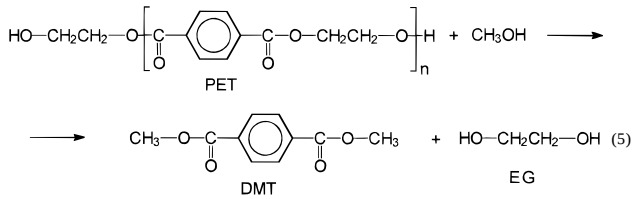
Chemical recycling processes for PET were implemented nearly parallel to the manufacture of the polymer on a commercial scale. This is confirmed by numerous patents starting from the 1950s. Initially, chemical recycling found an application as a way to utilize wastes arising in the PET production cycle (technological wastes and polymer from unsuccessful batches). In time, a change in the PET consumption structure, as well as public awareness, caused the emphasis to be laid on the recycling of postconsumer waste.

Historical and practical reasons cause processes of chemical degradation of waste PET to be usually divided as follows: (i) methanolysis, (ii) glycolysis, (iii) hydrolysis, (iv) ammonolysis, (v) aminolysis, (vi) other processes.

Methanolysis and glycolysis are mainly applied on a commercial scale. In recent years there has been an increase in interest for the production of oligomeric intermediate products from waste PET of specialized components for the chemical industry.

Some new technologies appearing in the chemical processing of PET waste cannot be classified in any one of the aforementioned classification groups. In this paper they will be presented as a separate group: other methods of chemical recycling.

3.1. Methanolysis. This process consists of the degradation of PET by methanol at high temperatures and under high-pressure conditions. The main products of PET methanolysis are dimethyl terephthalate (DMT) and ethylene glycol (EG), which are raw materials necessary for the production of this polymer.



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The methanolysis process is used by large PET manufacturers such as Hoechst (Brandrup, 1975), Eastman (Mush et al., 1992), and DuPont (Firm booklet, 1992) as well as lesser manufacturers (Kapelanski et al., 1995). The possibility of locating an installation for methanolysis, in the polymer production line, is one of the advantages of this method. In this way, waste PET arising in the production cycle is utilized and the monomers recovered are used in the manufacture of full value polymer. A schematic diagram of such an installation is shown in Figure 1.

Methods for the conduction of methanolysis have similar basic parameters, e.g., pressures of 2−4 MPa and temperatures of 180−280 °C (Lotz et al., 1967; Marathe et al., 1980; Michel, 1992; Socrate and Vosa, 1995). The polymer degradation takes place with the release of ethylene glycol. The reaction is catalyzed by typical transesterification catalysts such as zinc acetate, magnesium acetate, cobalt acetate, and lead dioxide; however, the most commonly used is zinc acetate (GB Patent, 1957; Dimov and Terlemezyan, 1972). There are known examples of using arylsulfonic acid salts as the catalyst for methanolytic degradation of PET (GB Patent, 1958). After the termination of the reaction, it is necessary to deactivate the catalyst. Otherwise, in subsequent stages of the process, there could occur possible DMT losses as a result of transesterification with ethylene glycol. The DMT obtained is precipitated from the postreaction mixture after its previous cooling and then is centrifuged and crystallized.

Both continuous and batch methods can be applied in methanolysis. The principal elements of the installation used in the batch method of methanolysis are autoclave, crystallizer, centrifuge, and a system for the melting and distillation of the DMT obtained (Marathe et al., 1980). The continuous method requires a much more complicated apparatus, where the necessity to continuously supply a high-pressure reactor with raw materials remains a problem. In a two-stage, continuous process developed for Hoechst (Gruschke et al., 1968), waste PET, after melting at temperatures of 265−285 °C, is collected in a liquid state in the technological tank and then fed to the reactor. Methanol, preliminarily heated to the reaction temperature, e.g., 190−210 °C, is introduced into the autoclave, equipped with a mixer, at a weight ratio to PET of 4:1. The average residence time of reagents in the first reactor is 7−13 min, and the reaction proceeds in 70−90%. The reaction stream is next introduced into the second autoclave at a slightly lower temperature, close to the bottom, where it slowly rises toward the outlet, which is located in the upper part of the reactor. The impurities having a higher density than the reaction mixture settle at the bottom, from where they can be removed. The reaction stream then leaves the second autoclave, and its pressure is reduced to 0.3 MPa. It is then directed to a mixer, in which it is cooled to about 100 °C. After further reduction of pressure and further cooling, the DMT is precipitated and then purified.

In accordance with another continuous depolymerization technology, waste PET is introduced into the reactor in the form of an aerosol with an inert gas (i.e., nitrogen) and methanol vapors (Lotz et al., 1967). Earlier, the polyester scraps are melted using overheated steam and then after solidification are pulverized into dust of 1 mm particle size. The temperature of the flow reactor is maintained at 250−300 °C. It is essential for the reaction to run in an oxygen-free atmosphere,

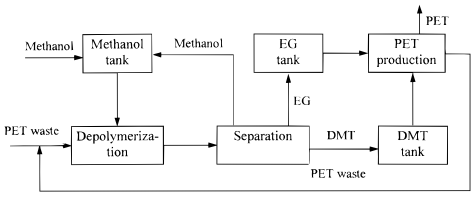


Figure 1. Flowsheet of the methanolysis process in the PET production line.

and the turbulent flow of substrates through the reactor should be preserved.

Eastman Kodak Co. possesses a patent describing the process and optimum properties of PET methanolysis (Debruin et al., 1995) in a three-stage installation consisting of a dissolver, a depolymerization reactor, and a rectifying column. The polyester stream is directed into the dissolver, where, due to the action of the molten polymer from the reactor and liquid from the rectifying column, the polyester's chain length is reduced. The polyester is then depolymerized in the reactor by overheated methanol. The depolymerization products are separated in the rectification process into a gas phase containing the monomer components and into a liquid oligomerized phase.

Another approach to the methanolysis has been presented in the patent specification concerning a continuous, two-stage process of terephthalic acid (TPA) reclamation from polyterephthalate waste (Socrate and Vosa, 1995). The polymer wastes are first subjected to the action of overheated methanol (240−260 °C) in a weight ratio of methanol−PET of 3−5:1. The product of the first step is then hydrolyzed by water or steam at temperatures of 110−150 °C, as a result of which TPA is obtained.

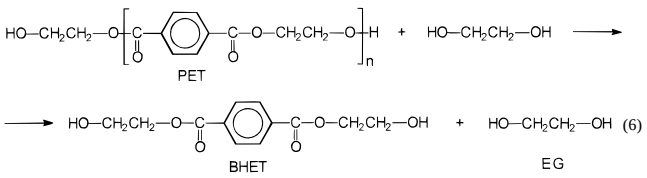
There are solutions proposing a combination of high-temperature PET methanolysis with the esterification of TPA or with the products of *p*-xylene oxidation (GB Patent, 1959). Polyester waste is introduced at a weight fraction of 20−30% in relation to TPA, which results in an increased process yield.

It has been observed that the yield of PET to DMT methanolysis processes does not exceed 90% (Marathe et al., 1980). Studies conducted have shown that, after methanolysis and the separation of DMT, dissolved methyl(hydroxyethyl) terephthalate (MHET) remains in the filtrate. It has been found that the filtrate usually contains, depending on the reaction parameters, 11−22% of MHET. This TPA derivative can be nearly quantitatively transformed into DMT by heating under pressure, during a period of 0.5−2 h without the addition of catalysts. The best results are obtained by performing the same operation in the presence of catalysts such as sodium carbonate, sodium bicarbonate, calcium hydroxide, and sodium hydroxide. It seems to be most advantageous to introduce a second catalyst to the methanolysis process which allows a considerable increase of the yield without the need of introducing an additional stage. The presence of MHET is disadvantageous during subsequent distillation of the EG formed.

Because of the increased interest in the production of polymer blends containing PET, the need to develop methods to chemically recycle such systems appeared. This is particularly justified in the case of polycondensation polymer blends. Sato and Sumitani (1995) have patented a method of methanolysis of polymer blends containing the segment alkylene-2,6-naphthalene dicarboxylate and the segment alkylene terephthalate. This allows the recovery of dimethyl esters of the corresponding dicarboxylic acid and glycol.

Substantial amounts of waste EG usually contaminated by degraded polyester are formed during PET depolymerization processes. It may be recovered by distillation in recycling installations and introduced back into the system. However, residue from glycol rectification is also present. It contains about 80 wt % of bis(hydroxyethyl) terephthalate (BHET), 5 wt % of EG, diglycols, and ethylene polyglycols as well as other derivatives of TPA and EG. The residue from EG rectification has a greasy consistency and is environmentally harmful. A method has been developed in which residue from EG rectification is utilized in PET methanolysis processes (Mikolajczyk et al., 1985), through its introduction into the reactor along with an appropriate transesterification catalyst. This method causes an increase of about 10% in the yield of the PET methanolysis process and significantly increases the size of the DMT crystals, which, in turn, has an advantageous effect on the efficiency of their release from the postreaction mixture.

3.2. Glycolysis. The second most important method in the chemical processing of PET waste is glycolysis. This process is used widely on a commercial scale. The result of deep glycolysis by EG is primarily bis(hydroxyethyl) terephthalate, which similarly to DMT is a substrate for PET synthesis (Jadhav and Kantor, 1986):



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In appropriate preselected conditions partial PET glycolysis can be performed, resulting in lower oligomers of chain lengths dependent on process conditions.

According to A. G. Zimmer (Mush et al., 1992), the glycolyzate product of low viscosity and defined average molecular weight is more suitable for purification and subsequent recycling than the PET waste melt.

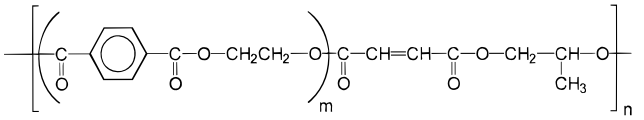
PET degradation is carried out most frequently using ethylene glycol, (Fujita et al., 1985, 1986; Baliga and Wong, 1989; Vaidya and Nadkarni, 1989; Nevrekar and Steth, 1990; Chen et al., 1991; Johnson and Teeters, 1991; Tersac et al., 1991), diethylene glycol (Ostrysz, 1969; Vaidya and Nadkarni, 1989; Johnson and Teeters, 1991), propylene glycol (Vaidya and Nadkarni, 1987b, 1989; Kim et al., 1995), and dipropylene glycol (Johnson and Teeters, 1991; Kim et al., 1995). Research concerning this process has been mainly conducted from the point of view of the utilization of the products obtained; very few works have been devoted to the description of the kinetics of glycolysis reactions (Baliga and Wong, 1989; Chen et al., 1991; Campanelli et al., 1994a; Lee et al., 1995).

The process is conducted in a wide range of temperatures 180−250 °C (Ostrysz, 1969, 1970; Grigsby et al., 1985; Hallmark et al., 1985; Vaidya and Nadkarni, 1987b; Baliga and Wong, 1989; Chen et al., 1991; Morita and Okasaka, 1994), during a time period of 0.5−8 h. Usually, 0.5% by weight of catalyst (most often zinc acetate) in relation to the PET content is added. Results of research on the catalytic influence of NaCl, urea, and BHET on the process are given by Nevrekar and Sheth (1990). The best results were achieved when BHET was used as the catalyst.

Much attention has been devoted to glycolysis by EG. In this system, the effect of the reaction parameters, i.e., temperature (190−240 °C), pressure (0.1−0.6 MPa) and PET to EG ratio on the reaction rate (Chen et al., 1991) has been investigated. It has been observed that the rate of the reaction is proportional to the square of the EG concentration at constant temperature, pressure, and PET concentration.

PET glycolyzates find application in the manufacture of unsaturated polyester resins (Vaidya and Nadkarni, 1987a,b, 1990; Ostrysz et al., 1990; Rebeiz, 1993, 1995; Rebeiz et al., 1992, 1993; Kim et al., 1995; Pepper, 1995), polyurethane foams (Speranza et al., 1984; Carlstrom et al., 1985; Grigsby et al., 1985; Hallmark et al., 1985; Vaidya and Nadkarni, 1988, 1990; Tersac et al., 1991), and polyisocyanurate foams (Carlstrom et al., 1985; Fujita et al., 1985; Hallmark et al., 1985; Baliga and Wong, 1989; Vaidya and Nadkarni, 1989; Nevrekar and Sheth, 1990; Chen et al., 1991; Johnson and Teeters, 1991).

One of the first methods of the synthesis of unsaturated polyester resins (UPR), in which a product of partial PET glycolysis was used, was developed by Ostrysz et al. (1964). The product of partial PET glycolysis was applied together with maleic anhydride and propylene glycol so as to obtain an unsaturated polyester with the following structure:



(7)

After dissolving the synthesized polyester alkyd in styrene, UPR resin was obtained. During the following years The Industrial Chemistry Research Institute in Warsaw developed technology for the production of UPR with built-in segments of oligo(ethylene terephthalate) obtained as a result of partial PET waste glycolysis with propylene glycol in ratios 0.25−1.0 mol/mol of PET at a temperature of 200 °C (240−250 °C) and a reaction time of 2 h (Ostrysz, 1969, 1970). Due to difficulties in obtaining a glycolyzate with reproducible properties, a new type of unsaturated polyester has been evolved, containing ethylene−diethylene diester obtained as a result of PET degradation by diethylene glycol as its terephthalic part. This resin was used in the production of polyester molding compounds (Nowaczek et al., 1992).

In recent years, there is an increased interest in the manufacture of UPR, utilizing PET waste. In one of the patents (Pepper, 1995), PET glycolysis products undergo a reaction with maleic anhydride and subsequently a reaction with (di)cyclopentadiene. The polyesters obtained have wide possibilities of application, e.g., for gel coats, casting marble, bath fixtures, car elements, etc.

Interesting research results on the synthesis and viscosity of UPR obtained by polycondensation of PET glycolysis product (with propylene or dipropylene glycol) and maleic anhydride have recently been published by Kim et al. (1995). It has been observed that the molecular weights of UPR increase with an increase of PET content in the reaction system or an increase of the dicarboxylic acid/glycol ratio as well as in the case of the application of dipropylene glycol instead of propylene glycol in the same conditions of glycolysis.

Methods of synthesis of cross-linked polyesters have also been developed; PET glycolyzate and dimethyl glutarate were used as raw materials (Penczek, 1996), and the products are subsequently used in polyurethane production. The syntheses of poly(ester polyols) containing polyterephthalate segments for the production of some types of polyurethanes require, in the case of direct utilization of pure terephthalic acid, the solution of the problem of TPA sublimation. This can be avoided with simultaneous ecological advantages, by using oligomeric products of PET glycolysis, which subsequently react with adipic acid (Ostrysz et al., 1982; Vaidya and Nadkarni, 1988; Tersac et al., 1991; Lee et al., 1995). The kinetics of this reaction have been described by Vaidya and Nadkarni (1988). Such poly(ester polyols) in reaction with diphenyl methanediisocyanate (MDI) (Vaidya and Nadkarni, 1988; Lee et al., 1995) or toluene-2,4-diisocyanate (TDI) (Lee et al., (1995) enable the manufacture of polyurethanes with various properties.

Another approach was described by Speranza et al. (1984), who presented a method of manufacture of stable clear poly(ester polyols) from the product of PET glycolysis reacted with alkylene oxides, e.g., propylene oxide. Poly(ester polyols) obtained during the reaction of PET with alkylene oxides, in the presence of a catalyst (Brennan, 1984), are used in the production of polyurethane or polycyanurate foams as an admixture to the traditional polyols, thus obtaining materials with enhanced fire resistance.

PET waste can be an excellent raw material for the production of new polyesters using the transesterification process with the application of an oligomer of the following formula:

$$H[O(CH_2)_mOCO\text{-}p\text{-}C_6H_4CO]_nO(CH_2)_mOH \quad (1)$$

($m = 2-6$; $n = 1-3$), followed by the polycondensation of the reaction mixture under reduced pressure (Watanabe et al., 1992).

In some works biphenols are used for PET degradation, e.g., Bisphenol A (Wang et al., 1995) at temperatures of 190−230 °C, in autoclave conditions. The influence of the process parameters and the reaction mechanism composed of the six elementary equilibration reactions was investigated.

3.3. Hydrolysis. The next method of PET waste chemical processing is hydrolysis to TPA and EG. A growing interest in this method is connected with the development of PET synthesis directly from EG and TPA, which eliminates methanol from the technological cycle. The process can be performed as (a) acid hydrolysis, (b) alkaline hydrolysis, and (c) neutral hydrolysis.

3.3.1. Acid Hydrolysis. Although the application of other concentrated mineral acids (e.g., phosphoric or nitric acid) is permissible, acid hydrolysis is performed most frequently using concentrated sulfuric acid (Brown and O'Brien, 1976; Pusztaszeri, 1982; Sharma et al., 1985). In these patent specifications of PET recycling processes using the acid hydrolysis method, concentrated sulfuric acid (minimum 87 wt %) was used. This allowed the process to take place in a pressureless apparatus. According to Pusztaszeri (1982), it runs without an outside heat energy supply, whereas other methods require heating of the reaction mixture (Brown and O'Brien, 1976; Sharma et al., 1985). The reaction runs for up to 5 min under atmospheric pressure. In the first stage, the ground PET waste is mixed with sulfuric acid of a concentration not less than 87 wt % at temperatures of 85−90 °C (Sharma et al., 1985), 60−93 °C (Brown and O'Brien, 1976), or room temperature

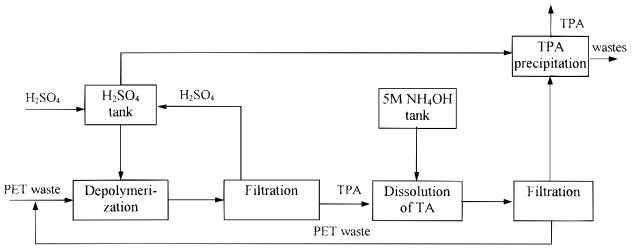


Figure 2. Flowsheet of installation for the acidic hydrolysis of PET.

(Pusztaszeri, 1982). As a result of dissolution and PET degradation to TPA and EG, an oily, viscous liquid is obtained. It is introduced into an aqueous solution of sodium hydroxide, in order to neutralize TPA and raise the system's pH to 7.5−8 (Brown and O'Brien, 1976). According to Pusztaszeri (1982), the postreaction mixture was first diluted with cool water, and then alkali was added to obtain a level of pH 11. The solution obtained has a dark coloration and contains TPA in the form of sodium salt soluble in water, sodium sulfate, EG, and sodium hydroxide as well as a small amount of insoluble impurities, which are filtered off using traditional methods. If there is such a need, it is possible to remove the coloration of the filtrate using ion-exchange columns. The next stage of the process is the acidification of the solution to pH 0−3 (Pusztaszeri, 1982), 2.5−3 (Brown and O'Brien, 1976), or 6−6.5 (Sharma et al., 1985), using acid (e.g., sulfuric or hydrochloric) in order to reprecipitate TPA. After filtering, washing off with water, and drying, TPA of a purity >99% was obtained.

EG was recovered from the remaining filtrate through extraction with organic solvents, e.g., trichlorethylene (Brown and O'Brien, 1976). Another method for EG recovery is based on the introduction into the filtrate of sodium sulfate so as to obtain a saturated solution—then EG salting out takes place, forming a separate organic layer. Calcium oxide in quantities equivalent to the ratio of sodium sulfate and sulfuric acid content is added and simultaneously mixed into the aqueous layer obtained in the first variant. The precipitated calcium sulfate is separated by filtration or centrifugation. The remaining aqueous solution of sodium hydroxide can then be recycled back into the process.

A substantial drawback of PET hydrolysis by concentrated sulfuric acid is the high corrosivity of the reaction system and the generation of large quantities of waste inorganic salts and aqueous wastes. Yoshioka et al. (1994) conducted a minimization trial of the last two inconveniences. Diluted solutions of H_2SO_4 (<67.7 wt %) were used for this purpose; the sulfuric acid can be recovered and reused in the process. However, this requires the prolongation of reaction time to 1−6 h, and the process runs at much higher temperatures ∼ 150 °C; also the high pressure apparatus used should have a large volume due to the necessity to use an excess of diluted acid. After the reaction, PET residue and TPA were filtered off, the deposit obtained is treated with 5 M NH_4OH in order to transform TPA into a soluble salt, and then PET is filtered out. Terephthalic acid was precipitated with the filtrate containing H_2SO_4, obtained earlier. A flowsheet of the installation based on this concept is shown in Figure 2.

3.3.2. Alkaline Hydrolysis. Alkaline hydrolysis is usually carried out with the use of an aqueous solution of NaOH of a concentration of 4−20 wt %. The reaction proceeds slowly; therefore, amines with the dissociation constant $K > 10^{-5}$ can be used to accelerate the process. The process runs for 3−5 h at temperatures of 210−250 °C, under pressures of 1.4−2 MPa (Alter, 1986).

Pitat et al. (1959) have patented a method of PET alkaline hydrolysis by an 18 wt % solution of NaOH. The most advantageous results are achieved at a PET−NaOH weight ratio of 1:20, at about 100 °C in 2 h. Sodium salt of terephthalic acid formed in the reaction is relatively well-soluble in aqueous solutions of alkaline hydroxides; however, by maintaining the concentration of NaOH at a constant level of 18 wt %, it is possible to achieve its complete precipitation. After separation it is dissolved in a small amount of water so as to obtain a nearly saturated solution. After acidification, TPA is precipitated from the solution, filtered off, rinsed, and dried. Other than TPA, EG formed during the reaction remains in the aqueous phase. This is recycled into the process after its enrichment in NaOH. The EG content in a solution increases, and therefore its recovery by vacuum distillation becomes feasible. An aqueous alcoholic solution instead of an aqueous solution of alkaline hydroxide should be used in order to decrease the solubility of TPA sodium salt in the reaction mixture. The process can be run either in high pressure conditions or in pressureless conditions as well as in conditions using lower hydroxide concentrations (Pitat et al., 1959).

Lazarus et al. (1967) described a process allowing the recovery of TPA and other monomeric components from PET/polyamide 6 polymeric mixtures. In the first stage, the mixture is heated in an aqueous solution of sodium or potassium hydroxide; most favorable results are achieved at temperatures of 210−250 °C under autogenic pressure. Technologically the most advantageous is a weight ratio of the polymer mixture to water within a range of 1:2 to 1:3. If hydroxide solutions of a concentration of 3−10 wt % are used, then the reaction time amounts to 3−5 h. The quantity of alkali used is dependent on the polyester content of the polymer mixture. After the termination of the reaction, the mixture is filtered in order to remove the insoluble residue, and then a strong mineral acid is added so that the dicarboxylic acid being formed is released. The generated caprolactam and EG are separated by distillation or are salted out using NaCl.

A significant reduction of TPA impurities generated in alkaline processes of PET hydrolysis can be achieved by introducing an additional stage consisting of the oxidation of impurities and thereby converting them into insoluble forms (Rollick, 1995). The process can be additionally improved through the application of quaternary ammonium hydroxide or nonionic surface-active agents which accelerate the depolymerization reaction. After the hydrolysis is finished, the postreaction mixture is diluted and the precipitate is separated; the remaining solution is supersaturated with air. The precipitated hardly soluble impurities are filtered off, and the filtrate is subsequently acidified in order to separate TPA.

Very good results of PET alkaline hydrolysis are achieved using an aqueous ammonia solution at 200 °C. In this case a solution of TPA diammonium salt is formed, from which, after filtration and acidification with sulfuric acid, TPA of high purity (99 wt %) is obtained (Datye et al., 1984).

An interesting solution is the alkaline hydrolysis of a mixture of PET waste and methyl benzoate formed

as a byproduct of the oxidation of *p*-xylene to TPA (Kozlov et al., 1984). In the first stage PET is treated with methyl benzoate at temperature of 190−200 °C. The mixture obtained undergoes hydrolysis by an aqueous solution of alkali-metal hydroxide with a concentration of 2−7 wt % for 30 min at temperatures of 95−100 °C. The process allows the recovery of TPA and benzoic acid with yields of 87−95% and 84−89%, respectively.

Treatment processes based on partial PET alkaline hydrolysis are widely used in the polyester fiber industry. The effect of such processes on the mechanical properties of fibers (Namboori and Haith, 1968; Ellison et al, 1982; Filipowska and Kubacki, 1985), oligomer content and change of the molecular weight distribution (Filipowska and Kubacki, 1985; Collins and Zeronian, 1992), or loss of fiber mass (Ellison et al., 1982; Collins and Zeronian, 1992) has been investigated. From the point of view of research on PET chemical recycling, an interesting relationship between PET mass loss, reaction time, and the concentration of the NaOH aqueous solution used (Namboori and Haith, 1968), as well as between oligomer contents and the molecular weight distribution of degraded PET (Collins and Zeronian, 1992) has been observed. Collins and Zeronian (1992) have demonstrated that NaOH solutions in methanol react with PET significantly faster than analogous aqueous solutions.

Namboori and Haith (1968) have compared the reactivity of NaOH aqueous solutions, as well as solutions of sodium *tert*-butoxide in *tert*-butanol, sodium isopropoxide in isopropyl alcohol, sodium methoxide in methanol, and sodium ethoxide in ethanol with PET. They have demonstrated that, of the above-mentioned solutions, sodium ethoxide in ethanol is the most reactive and an aqueous solution of sodium hydroxide is the least reactive.

In the recycling of PET to terephthalates of alkali metals or alkaline-earth metals, a process described by Benzaria et al. (1994) may be crucial. The depolymerization is carried out in a mixer−extruder with the use of solid NaOH at temperatures of 100−200 °C. After the distillation of EG from the postreaction mixture under reduced pressure, a corresponding salt of terephthalic acid in the form of a powder is obtained. In this method the necessity of separating the glycol and water mixture is eliminated, which is undoubtedly its essential advantage. The degree of polyester saponification achieved a level of about 97%.

3.3.3. Neutral Hydrolysis. Neutral hydrolysis is carried out with the use of water or steam. In spite of this, the pH of the postreaction mixture amounts to 3.5−4.0, which according to Michalski (1993) is caused by the formation of TPA monoglycol ester during the reaction. The process usually runs at a pressure of 1−4 MPa at temperatures of 200−300 °C (GB Patent, 1960; GB Patent, 1984, Mandoki, 1986; Rosen, 1991; Royall and Harvie, 1993; Campanelli et al., 1994b). The ratio by weight of PET to water is from 1:2 to 1:12. Launay et al. (1994) have described the process' kinetics at temperatures of 100 °C, whereas Campanelli et al. (1992) have described the application of the process in PET recycling. It has been confirmed that PET hydrolysis proceeds significantly faster in the molten state than as a solid; therefore, it is advantageous to carry out recycling using this method at temperatures higher than 245 °C.

The application of common transesterification catalysts is possible; however, the recommended ones are alkali-metal acetates (Kozlov et al., 1984). Michalski (1990) has conducted studies on the influence of polymer synthesis catalysts contained in commercial PET, i.e., the first stage (transesterification), the acetates of calcium, manganese, and zinc; the second stage (polycondensation), antimony trioxide as well as the stabilizers blocking transesterification (added between the first and second stage), i.e., phosphorus compounds. Michalski's investigations have proved the accelerating action of the transesterification catalysts. No inhibiting effects of stabilizers were observed, and in some cases their action had an accelerating effect. Campanelli et al. (1994b) have described the catalytic effect of zinc catalysts at temperatures of 250−265 °C. They have found the rate constant to be about 20% greater than in the uncatalyzed system. The catalytic effect of zinc salt as well as sodium salt is attributed to the electrolytic destabilization of the polymer−water interface in the hydrolysis process.

During the PET hydrolysis, monoester of glycol and terephthalic acid is formed as a byproduct. It dissolves well in water at temperatures of 95−100 °C; at these temperatures TPA is practically insoluble. Owing to this, the separation of TPA from the postreaction mixture does not create any problems (Michalski, 1987a). Using statistical methods, it has been proved that appropriate control of reaction conditions limits to not more than 2% the quantity of monoester obtained (Doerr, 1986; Michalski, 1987a).

The neutral hydrolysis method is exempt from the primary drawbacks characteristic for acid or alkaline hydrolysis. The formation of substantial quantities of inorganic salts difficult to dispose of is avoided; also problems connected with the corrosion of apparatus due to the use of concentrated acids and alkalis do not occur. An undoubted advantage of neutral hydrolysis is its high ecological purity, and therefore growing interest in this technology can be expected. Its drawback is that all mechanical impurities present in the polymer are left in the TPA; thus, the product has a considerably worse purity than the product of acid or alkaline hydrolysis. Consequently, a much more sophisticated purification process is necessary. Possible product contaminations are removed by filtration of the solution of TPA dissolved in caprolactam or in an aqueous solution of sodium hydroxide (Michalski, 1987a). The crystallization of TPA from caprolactam makes it possible to obtain a product with a purity of at least 99% (Michalski, 1987b). During the hydrolysis of PET a substantial volume of diluted EG is generated, which can be recovered through extraction or by distillation.

An effective five-stage process of neutral hydrolysis of PET to EG and TPA of a purity required for the synthesis of the new polymer has been patented by Tustin et al. (1995). PET is hydrolyzed at temperatures of 200−280 °C. After cooling the postreaction mixture to 70−100 °C, the solid product of the process is filtered and dried at temperatures of 25−199 °C. EG is recovered from the filtrate as a result of two-stage distillation. The solid product of hydrolysis is heated with water at temperatures of 310−370 °C, and after cooling TPA is obtained. The purity of the recovered TPA and EG allows their application in the production of high-quality homo- and copolymers and does not exclude their use in the manufacture of bottles and fibers.

Kamal et al. (1994) have presented an efficient process of continuous hydrolysis in which they have used a twin-screw extruder as a reactor. Using this

method, it is possible to obtain in an efficient manner PET oligomers containing 2−3 repeating units. Those products with end carboxyl groups have higher melting temperatures in comparison with virgin PET, while those with one carboxyl group and one or two hydroxyl groups have lower melting points. It has been demonstrated that utilization of cold or even hot water in the process does not give a satisfying degree of depolymerization. There is a difference when high-pressure saturated steam of temperatures close to that of molten PET is injected into the reaction zone of the extruder. The maintenance of adequate high pressures requires the application of suitable throttling systems, allowing the control of backleakage of the postreaction mixture from the extruder.

3.4. Aminolysis. Deep aminolysis of PET yields corresponding diamides of TPA and EG. There are no known reports concerning the utilization of this process on a commercial scale in PET recycling. However, it is known that partial aminolysis has found its application in the improvement of PET properties (Collins et al., 1991), in the manufacture of fibers with defined processing properties.

In the majority of PET aminolysis processes described, the polymer was in the form of powder or fibers. The reaction was usually carried out using primary amine aqueous solutions, most frequently methylamine (Overton and Haynes, 1973, Awodi et al., 1987; Popoola, 1988; Collins et al., 1991), ethylamine (Ellison et al., 1982; Collins et al., 1991), and ethanolamine (Collins et al., 1991) in the temperature range of 20−100 °C. Anhydrous *n*-butylamine was also applied as an aminolytic agent at a temperature of 21 °C (Collins et al., 1991). Most of these investigations have been focused on selective PET degradation by an aqueous solution of methylamine so as to determine its morphology. The presumption was that, under the influence of primary amine aqueous solutions, the amorphous region would first undergo rapid degradation, and subsequently a significantly slower attack would take place on the crystalline regions (Farrow et al., 1962).

3.5. Ammonolysis. TPA amide is produced by the action of anhydrous ammonia on PET in an ethylene glycol environment. This can be converted into terephthalic acid nitrile and further to *p*-xylylenediamine or 1,4-bis(aminoethyl)cyclohexane (Blackmon et al., 1988). Very good results were obtained from the ammonolysis of PET waste from postconsumer bottles; the process was carried out under a pressure of about 2 MPa in a temperature range of 120−180 °C for 1−7 h. After the reaction was completed, the amide produced is filtered, rinsed with water, and dried at a temperature of 80 °C. The product has a purity of not less than 99%, and the yield is above 90% (Blackmon et al., 1988).

A low-pressure method of PET ammonolysis, in which the degradation agent is ammonia in an ethylene glycol environment (Ind. Patent, 1985), is also known. The process is catalyzed by zinc acetate in a quantity of 0.05 wt %, conducted at a temperature of 70 °C and a ratio of PET−NH_3 of 1:6. TPA amide was produced with a yield of about 87%.

3.6. Other Methods of Chemical Recycling. In recent years many processes have been developed based on new directions of waste PET chemical recycling. They are characterized by the specific treatment of a problem. Most of these processes are for low-tonnage production of substrates for the plastics and the coatings industry. It is possible to obtain valuable products which are competitive pricewise to their equivalents manufactured through conventional synthesis methods. These technologies are safe and low-waste or practically no waste is formed, sometimes less complex than the traditional ones. In this paper these processes are grouped in a separate chapter in spite of the fact that they are sometimes more developed versions of methods already described. Possibly they could be classified to one of them.

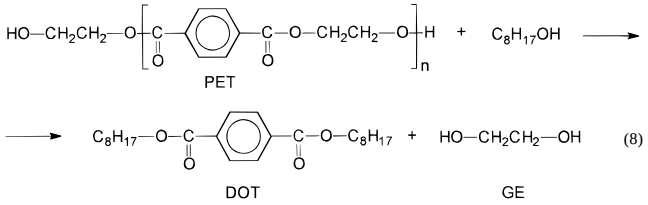
3.6.1. Coating Materials. The use of PET chemical recycling products for the manufacture of coating materials is described more and more frequently. This concerns, among others, the transesterification of PET by esters of higher glycols and carboxylic acids (Schaaf and Zimmermann, 1989) as well as esters of pentaerythritol with fatty acids (Kato and Shibata, 1985). The reactions were conducted at temperatures of 200−300 °C.

PET waste was used in the manufacture of alkyd resins used in water thinnable paints. The products obtained from the reaction of PET with a mixture of fatty acids of large linoleic acid and trimethylolethane were used in the preparation of water-dispersible coating compounds (Sayre et al., 1993). Trimethylolpropane reacted with PET at a temperature of 230 °C for a time period of 45 min. This gives a mixture of oligomers which are next subjected to a reaction with isophthalic and fatty acids and then with trimellitic anhydride (Toselli et al., 1996). The reaction took place without the addition of a catalyst because it was concluded that the catalysts present in commercial PET assure a satisfactory reaction rate.

Products of PET degradation by trimethylolpropane and pentaerythritol can be used in the manufacture of high solids paints (Pilati et al., 1996). In the first stage, PET waste is depolymerized by trimethylolpropane and pentaerythritol at temperatures of 230−240 °C for a period of 45 min. The final paint compositions contain 30−50 wt % of PET degradation products.

PET waste can be used in the production of terephthalic electroinsulation lacquers (Ostrysz et al., 1986). For this purpose PET is heated in a mixture of triol and glycol at temperatures of 230−260 °C to obtain a homogeneous solution. The process is continued under a reflux condenser until the polyester softening temperature is established below 60 °C (1−4 h). The next stage is the addition of a transesterification catalyst, e.g., zinc chloride, heating at temperatures of 220−250 °C, and distilling off of low molecular products of degradation, until the required softening temperature of polyester (about 60−100 °C) is achieved.

3.6.2. Plasticizers. Dioctyl terephthalate (DOT) is created in the transesterification reaction of PET with 2-ethylhexanol and used as a PVC plasticizer (Wang et al., 1991; Dupont and Gupta, 1993; Ostrysz et al., 1995).



(8)

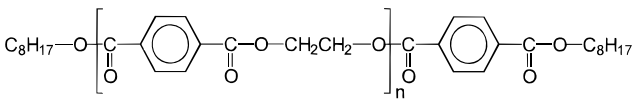
The actual product is a mixture of DOT and small quantities of octyl (2-hydroxyethylene)terephthalate and terephthalate oligoesters and can be described by the

Table 1. Advantages and Disadvantages of the Chemical Recycling Methods of Poly(ethylene terephthalate)[a]

	chemical recycling methods					
aspects of evaluation	methanolysis	glycolysis	hydrolysis	aminolysis	ammonolysis	other methods
1. flexibility in utilizing a variety of wastes	low: well-defined industrial wastes (−)	medium (±)	medium (±)	medium (±) ?	medium (±)	low or medium (±)
2. degradation conditions	high parameters; $t \leq 300$ °C; $p \leq 4$ MPa; separation, purification of the products (−)	$t \leq 280$ °C (+)	acidic, $t \leq 100$ °C; alkaline, $t \leq 250$ °C; neutral, $t \leq 300$ °C; $p \leq 4$ MPa (±)	$t \leq 100$ °C (+)	$t \leq 200$ °C; $p \leq 2$ MPa (±)	$t \leq 330$ °C (+)
3. safety conditions	high requirement (−)	conventional (+)	high requirement (−)	medium (±)	medium or high (−)	conventional (+)
4. corrosive and/or toxic media	toxic methanol (−)	(+)	strong acids or alkalis (±)	amines (±)	ammonium (±)	(+)
5. economic aspects (including advisability of purification of the main product)	for large-scale installations (yes) (+)	for small or medium installations (no) (+)	(yes) (±)	?	(yes) (±)	(yes or no) (±)
6. product versatility	low: DMT, EG (−)	high: oligomeric mixtures (+)	low: TPA, EG (−)	?	low: TPA diamid, EG (−)	low or high (±)
remarks	industrially applied; large installations	commercially applied; small or medium installations	commercially applied high-purity TPA; large amounts of inorganic aqueous wastes	?	high-purity TPA diamide	some may be commercially applied

[a] Scale of evaluation: (+) positive, (−) negative, (±) intermediate.

formula (Ostrysz et al., 1995):



(9)

PVC plasticized with this product have parameters at least similar to the parameters of dioctyl phthalate modified polymer.

3.6.3. Other Products. Chemical processes of PET recycling being investigated in the authors' laboratory have allowed the synthesis of solid cross-linking monomers. The methods are based on the controlled degradation of PET using allylamine and/or allyl alcohol (Paszun and Spychaj, 1995; Spychaj and Paszun, 1995).

An interesting method of recycling waste PET is based on polymer degradation in a coal−tar pitch environment, and the products obtained are utilized in the manufacture of polyurethane of an inferior quality, designated for the production of putties and sealing compounds for the building industry (Polaczek et al., 1987). Pulverized foil waste or PET fibers are mixed in batches with coal−tar pitch and heated at temperatures of 130−330 °C. The most advantageous effects are obtained in the case of mixtures containing not less than 30 wt % of coal−tar pitch. Heating of the mixture proceeds for 15−60 min. An inert gas stream, e.g., nitrogen, carbon dioxide, or argon, is passed through the polymer melt. After termination of the reaction and cooling, products with softening temperatures within the limits of 30−230 °C are obtained.

A method allowing the application of PET waste in phenol/formaldehyde molding compounds is known (Penczek and Ostrysz, 1995). The method is a development of previously described hydrolysis; however, in contradiction to the typical hydrolysis processes carried out in order to produce terephthalic acid and ethylene glycol, only a partial degradation of PET is performed. A high tolerance of impurities and a complete lack of waste characterize that process. PET waste is dissolved in phenol, to obtain a polymer solution of high viscosity. In order to reduce the viscosity, a small amount of water and a catalyst is added into the system and then heated so that partial PET hydrolysis occurs. The next stage consists of the polycondensation of phenol with formalin, in conditions characteristic for standard novolac resin synthesis. Possible mechanical impurities of PET are not a hindrance because the powder fillers are subsequently added to the molding compound system.

Another application is the manufacture of PET of high molecular weight, which is obtained as a result of prepolymer polycondensation. For instance, Karayannidis et al. (1993, 1995) have undertaken investigations into the polycondensation of PET with $M_n = 20\,300$ derived from postconsumer bottles separated from PE and PP impurities. The PET waste before polycondensation was dissolved in benzyl alcohol, phenol/tetrachloroethane mixture (60/40% w/w), *o*-chlorophenol, trifluoroacetic acid, a mixture of trifluoroacetic acid/dichloromethane (50/50% v/v), and nitrobenzene and then precipitated with methanol so as to obtain material with high surface development. PET prepared in such a way was polycondensized in a solid state, under reduced pressure at a temperature of 230 °C for 8 h. In spite of the fact that the best solvent appeared to be the system trifluoroacetic acid/dichloromethane, the highest molecular weight of about 60 000 was observed in the case of the polycondensation of polymer dissolved in *o*-chlorophenol and nitrobenzene.

4. Conclusions

Degradation (depolymerization) of polymer chains to different degrees takes place during chemical recycling of PET. Therefore, chemical products obtained have many applications.

Generally, the economic viability of a given method of chemical recycling is decisive in its application. This is connected with the processing capabilities of installations, specifics of the technology used (temperature, pressure) and the chemical agent (corrosive and/or toxic character, special labor safety requirements), methods of separating the products (if necessary), and their further application and purity. All these factors, as well as others such as the cost of purchase and transportation of waste polymer, have an influence on the final price of the product obtained from PET recycling. The scattering and high volume to mass ratio of PET waste from postconsumer packaging (bottles, foil) limit the area from which the transport of raw materials is financially viable. It often happens that the price of products obtained from the chemical recycling of PET is higher than that if these products were manufactured in the classical way, i.e., as a result of direct synthesis.

Table 1 contains a relative evaluation of the chemical recycling methods described in this paper. The following factors were taken into account: flexibility in processing different types of PET waste, degradation conditions and the types of chemical agents used, safety and economic aspects, and the application versatility the products obtained.

According to our evaluation, PET waste recycling is economically most viable in the case of (a) degradation in very large quantities of defined industrial polymer waste, specially waste occurring at the place of manufacture, and (b) manufacture of special products of low or medium tonnage, i.e., polyols often used in situ in the synthesis of polyurethanes, unsaturated polyester resins, saturated polyesters, paints, and additives for various applications (usually through glycolysis).

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