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Polyethylene Terephthalate Waste Recycling and Application Possibilities: a Review

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This paper presents a review of works that cover PET post-consumer waste recycling and application during last twenty years. It is shown that physically recycled PET can be used in the blends with other polymers, such as high and low density polyethylene, polycarbonates, polyvinyl chloride, etc. The compatibilizers and other additives often are used to obtain valuable blends of recycled PET with virgin or other plastics. Molecular weights of blended polymers must be similar to obtain the compatible blends of recycled PET with other plastics, therefore, additional processes are needed for the lowering average molecular weights of the polymers.

Chemically recycled PET by esterifying the polyester with an excess of reactant such as diols, diamines, alcohols, or water can be used as starting ingredients for synthesis of other polymers. A focus on the production of oligoesters coming from the glycolysis of PET waste that have been introduced as a starting material in the manufacture of polyurethanes, unsaturated polyesters and saturated polyester plasticizers is done. A possibility of new application of acrylate/methacrylate PET oligomers for UV curable coatings, useful for wood surfaces, paints and other applications is decribed.

Keywords: polyethylene terephthalate, waste, physical and chemical reprocessing, glycolysis.

1. INTRODUCTION

The consumption of plastics in Western Europe is of 38 million tonnes per year, the majority of which are used in the production of plastic packaging, household and domestic products, electrical and electronic goods [1]. There is also significant consumption of plastics for the building and construction industry and automotive industry. The two main types of plastics are thermoplastics, which soften when heated and harden again when cooled, and thermosets, which harden by curing and cannot be re-moulded. About 80 % of plastics used in Western Europe are thermoplastics [2].

For many waste landfills is the largest route for disposal throughout the countries of Europe. For some countries, including Lithuania, more than 60 % of municipal solid waste is disposed of to landfill [3]. Plastics make up high proportion of waste that volume and range used increases dramatically. Although plastics make up between 5 wt.% and 15 wt.% of municipal solid waste it comprises 20 % – 30 % of the volume [2]. Most plastics are non-degradable and take a long time to decompose, possibly up to hundreds of years – although no-one knows for certain as plastics have not existed for long enough, when they are landfilled.

It is estimated that only about 50 % of the plastics produced in Western Europe each year are available for collection and recycling [1 – 3]. According to the experts from Kaunas University of Technology in Lithuania plastics reach about 82 thousands tones of municipal solid waste in 2004. It comprised about 24 kg for one inhabitant [4]. Waste recycling in Lithuania increases constantly and during 2000–2006 it ranges between 20 – 35 thousand tonnes per year [5].

According to the Environmental Protection Agency (EPA) "recycling" is considered to be processing of waste to make new article. There are divided three distinct approaches to the recycling of post-consumer plastic materials [6, 7]: 1) it could be reused directly; 2) undergo physical reprocessing, for example, grinding, melting and reforming; 3) be subjected to chemical treatment, when components are isolated and reprocessed for use in manufacture. A new widespread nomenclature of recycling was adopted by EPA. Primary recycling involves the use of pre-consumer industrial scrap and salvage, while physical reprocessing refers as secondary recycling and chemical processing as tertiary recycling [6]. Pre-consumer industrial scrap and salvage is the recycling of clean, uncontaminated single-type waste. The recycled scrap or waste is either mixed with virgin material to assure product quality or used as secondary grade material [6, 8, 9]. Reuse could be considered as "zero order". In simply reuse, the plastic article remains intact and is reused in its original form. However, plans for reuse of plastic bottles could include a limit on the number of use cycles a bottle will undergo, an expiration date for the use of such articles, a visual inspection system for gross contamination and damaged bottles [7]. A fourth operation of plastic waste management is the recovery of its energy content by incineration (combustion). Incineration, aimed at the recovery of energy, is currently the most effective way to reduce the volume of organic material, that, owing to a lack of other recycling possibilities, may then end up disposed of in landfills. Plastics, either thermoplastic or thermosetting, are actually high-yielding energy sources [6].

There are six main plastics which arise in municipal solid waste – high density polyethylene, low density

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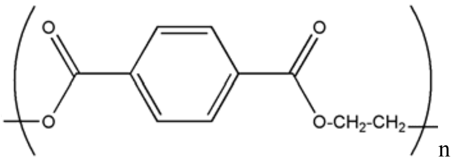
polyethylene, polyethylene terephthalate, polystyrene, polypropylene and polyvinyl chloride.

Polyethylene terephthalate (PET) is thermoplastic polyester widely used in application as diverse as textile fibres, films, bottles and other moulded products [10]. The majority of the world PET production is for synthetic fibers (in excess of 60 %) with bottle production accounting for around 30 % of global demand. One of the main reasons for the widespread use of PET is their possibility of producing a number of different grades over a broad range of molecular weights in a single multiproduct polymerization plant [11].

Depending on PET processing and thermal history, it may exist both as an amorphous (transparent) and as a semi-crystalline (opaque and white) material. Its monomer can be synthesized by the esterification reaction between terephthalic acid and ethylene glycol with water as a byproduct, or the transesterification reaction between ethylene glycol and dimethyl terephthalate with methanol as a byproduct [11]. Polymerization is through a polycondensation reaction of the monomers (done immediately after esterification/transesterification) with ethylene glycol as the byproduct (the ethylene glycol is recycled in production). Chemical structure of PET is shown in Scheme 1.



Scheme 1. Chemical structure of PET

Over the recent years, the amount of different products from PET has been particularly increasing, resulting in the greater quantities of household polymeric waste. For example, in Lithuania companies produce about 10 thousand tonnes of PET containers per year, while in Western Europe it is significantly higher [4].

However, the huge amounts of PET products (bottles, spinning, packaging films) cause serious environmental pollution. Commonly, PET content reaches about 12 % in municipal plastic waste [2]. In fact, the separation of PET bottles from municipal waste represents one of the most successful examples of polymer recycling. Numerous ways of recycling disposable beverage bottles are available, including methods of chemical recycling, such as hydrolysis, aminolysis, glycolysis, etc., or physical recycling by re-melting.

Plastic recycling is very important for the least two main reasons: *firstly*, to reduce the increasing volumes of plastic waste and *secondly*, to generate value-added materials from low cost sources by converting them into valuable materials. The demand to expand grade uses of recycled plastics led to the research into alternative processing methods in order to produce higher value products.

In this article recent studies in the field of physical and chemical reprocessing of PET are reviewed with a focus on new trends of glycolysis reactions. The application possibilities of PET recycled products are described, also.

2. RECYCLING OF PET

A driving force for PET recycling is that PET products have a slow rate of natural decomposition [12]. PET is a non-degradable plastic in normal conditions as there is no known organism that can consume its relatively large molecules. Complicated and expensive procedures need to be operated in order for PET to degrade biologically [13].

Many researchers reported that in order to achieve successful PET recycling, PET flakes should meet certain minimum requirements [13 – 16]. Examples of the minimum requirements for the post-consumer PET flakes are summarized in Table 1. The major factor affecting the suitability of PET flake for recycling is the level and nature of contaminants present in the flakes.

Table 1. Minimum requirements for post-consumer PET flakes to be reprocessed [13, 16]

Property	Value
Viscosity coefficient [η]	> 0.7 dl·g^{-1}
Melting temperature T_m	> 240 °C
Water content	< 0.02 wt.%
Flake size	0.4 mm $< D <$ 8 mm
Dye content	< 10 ppm
Yellowing index	< 20
Metal content	< 3 ppm
PVC content	< 50 ppm
Polyolefin content	< 10 ppm

Nevertheless, PET recycling is problematic in all countries. For example, in the United States alone, there are over 20 000 plastic recycling programs and 10 000 of them recycle only PET bottles. However, according to National Association of Plastic Container Resources (USA) the volume of PET plastic bottles recycled is markedly lower to that wasted (Fig. 1).

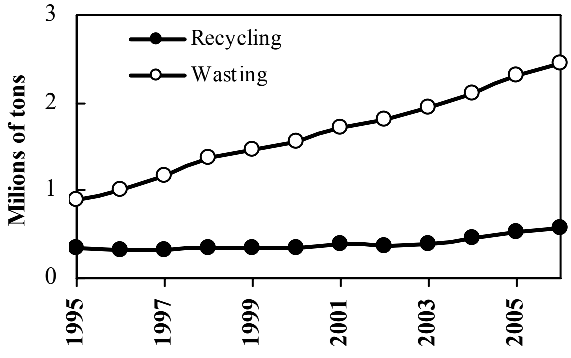


Fig. 1. PET plastic bottles recycling and wasting in USA, 1995–2006 (according to “2006 Report on Post Consumer PET Containers Recycling Activity”. National Association for PET Container Resources, 2007)

In Lithuania 24 companies recycle plastic waste. The joint stock companies such as “PET Recycling”, “Polivektris”, “Plastiksė”, “Veeka”, “Ecoservice”, and V. Puidoko company provide PET waste recycling.

Numerous methods of recycling disposable beverage bottles and other containers made of PET or blends of PET with other materials have been reported in [6, 13 – 18]. These include reprocessing with virgin resin, blending and compatibilization, recycling through solutions and chemical reactions [15].

There are three main factors, which must be considered regarding the issue of PET recycling: *first*, the collection of the waste; *second*, the recycling process itself; and *third*, whether or not there is a market of the end product of recycling. The third factor is the most important.

2.1. Applications of physically reprocessed PET products

In physical recycling the separated PET waste is processed by the end user by being granulated or pelletised, melted or partially melted and extruded to form the end product. The basic polymer is not altered during the process. Prior to melting and reforming the polymer, the ground, flaked, or pelletized plastics is washed to remove contaminants. Different plastics may also undergo different reforming conditions, such as different processing temperatures, the use of vacuum stripping, or other procedures, that could influence contaminant levels. Recycled PET is more sensitive to thermal and hydrolysis degradation than virgin PET [15]. Besides, recycling of PET gave rise to a decrease in the melt viscosity, average molecular weight, thermal and mechanical properties of the material because of the hydrolytic chain scission and thermomechanical degradation undergone during processing [13]. Therefore, to produce a plastic with the desired qualities additional antioxidants, processing aids or other additives may need to be added to the recycled resin [5, 7, 9].

The recycled PET may be added to virgin plastic during the process. A. Oromiehie and A. Mamizadeh [17] have processed and modified the mixture of virgin grade PET (V-PET) and recycled grade (R-PET) with and without modifier by different extrusion methods, and then characterized the physical, thermal and mechanical properties of the modified PET. The variation of intrinsic viscosity was in accordance the proportion of the two components in the blended samples (R-PET/V-PET). It was shown that the molecular weight decreases when the percentage of recycled PET is increased. These properties were improved by adding compatibilizer to the blend [17].

Polymer blends have always been considered to be interesting combinations for obtaining new high-performance polymeric materials without synthesizing fully new polymers especially when the properties of two or more polymers are synergistically combined [19]. It is also one of the most important routes of polymer recycling because it makes the sorting step much simpler during recycling operation. Unfortunately, most polymers are immiscible. Hence, their blends show poor mechanical properties and unstable morphology. These problems can be overcome by using various kinds of compatibilizers. Some cases of blends formation with or without compatibilizers will be reviewed.

The thermal and mechanical properties of blends of PET with polycarbonate (PC) prepared in a twin-extruder by melt blending in the absence and presence of stannous octoate as a transesterification catalyst has been investigated on the whole composition range by S. Mbarek with co-workers [20]. PET/PC blends exhibited enhanced tensile properties in comparison to neat components for compositions of PET higher than 50 % and these properties are improved by the addition of a transesterification catalyst. The PET/PC blend containing 20 wt% of PC, prepared with stannous octoate, showed the smallest size of the dispersed phase because of transesterification reactions that generate copolymer molecules at the interface between the immiscible polymers. The melting temperature of PET was decreased with the increase of the PC content in the blends extruded in the presence of the catalyst. Also, the temperatures of the cold crystallization of PET were higher than those of similar blends without catalyst. Both features gave rise to better moulding properties because of a shortening of the cooling time [20].

Melted in a co-rotating twin-screw extruder PET waste and a polyolefinic elastomer with and without compatibilizer blends were studied by K.P.Chaudhari and D. D. Kale [21]. The blends were characterized for mechanical, thermal and rheological properties as well as for morphological characteristics. The impact strength of PET waste was increased by blending with polyolefinic elastomer using poly(ethylene-*co*-acrylic acid) as a compatibilizer. Other mechanical properties were not significantly affected. The impact strength increases as the amount of polyolefinic elastomer in the blend increases. Due to the presence of elastomer, the crystallization of PET waste is hindered. The blends are easily injection mouldable and extrudable [21].

A possibility of recycling high density polyethylene (HDPE) and PET mixed scrubs, in the proportion usually found in the post-consumer waste, by compatibilization of blend through the addition of poly[ethylene terephtalate)-co-(ε-caprolactone)] copolymer as emulsifying agent is shown in [22]. The copolymer was synthesised by polycondesation of low molecular weight poly(ε-caprolactone) precursors, previously end-capped with reactive isocyanate groups, and oligomers of PET obtained from PET waste. HDPE/PET blends of 70/30 wt.% with and without the addition of the compatibilizer were prepared in a single screw mixer – extruder. The effect of compatibilizer was evaluated by studying the thermal, dynamic-mechanical and mechanical properties and the morphology of the blends. The compatibilizer was found to be a good emulsifying agent from a morphological point of view.

Particularly in the case of blends of semi-crystalline polymers, as HDPE and PET are, many factors beside emulsification play important roles in the final performance of the material. It is possible that, while poly(ε-caprolactone) segments of poly[ethylene terephtalate)-co-(ε-caprolactone)] copolymer properly emulsify PET domains to the HDPE matrix, its low strength is unable to firmly entangle the two phases, so the mechanical continuity of the material during elongation is not assured [22].

M. Kaci *et al.* [23] used the terpolymer of ethylen-butyl acrylate-glycidyl methacrylate as compatibilizer for low density polyethylene (LDPE) and PET blends. It was shown that the addition of compatibilizer effectively changed the morphology of both the virgin and waste blends of LDPE/PET. A reduction in the size of PET inclusions in LDPE matrix and strong interfacial adhesion strength between the two polymers indicated the effective interfacial activity of the ethylen-butyl acrylate-glycidyl methacrylate terpolymer. The application of ethylen-butyl acrylate-glycidyl methacrylate terpolymer induced a decrease in the Young‘s modulus and a slight increased of the elongation at break. Its efficiency was found particularly in impact strength – the concentrations of 5 pph and 10 pph were sufficient to change brittle blends into highly impact resistant materials. The mechanical properties of the waste blends present comparable values to those of the virgin blends [23].

Composites of polyethylene and aluminium may be obtained from the recycling of post-consumer packaging. The components of the composite are LDPE, aluminum and an ethylene-methacrylic acid random copolymer. Therefore, Lopes and co-workers showed that ethylene-methacrylic acid random ionomer present in the composite changed completely the morphology of the blend with PET comparing to the non-compatibilized PET/LDPE blend [24]. The main morphological characteristics observed in the polyethylene and aluminium blends, which were evidences for compatibilization, were the strong interfacial adhesion, the better dispersion of the dispersed phase and the high stability against coalescence in post-processing. Such morphology features comparable to those of the ionomer/PET blends, resulted from the strong interactions between the acrylate groups of ethylene-methacrylic acid random and the ester groups of PET. Authors claim that, in respect to the mechanical properties, PET/polyethylene and aluminium blends present elongation at break and impact resistance similar to the PET/LDPE blends and Young‘s modulus values superior to PET/LDPE and PET/ethylene-methacrylic acid copolymer random blends. These results reflected the predominant influence of aluminium particles in the mechanical properties over the polymeric phase morphology [24].

The motivation of the work of S. Fakirov *et al.* [25] on the modification of recycled PET waste was to manufacture micro-fibrillar reinforced composites comprising of an isotropic matrix from a lower melting polymer, reinforced by micro-fibrils of a higher melting polymer. LDPE (matrix) and recycled PET (reinforced material) from bottles were melt blended in different ratios and extruded, followed by continuous drawing, palletizing and injection moulding. Experimental studies showed that the extruded blend was isotropic but becomes highly oriented after drawing, being converted into a polymer-polymer composite upon injection moulding at temperatures below the melting temperature of PET. The mechanical properties of micro-fibrillar reinforced composites show impressive results, regarding tensile elongation and impact strength. The authors concluded that: 1) micro-fibrillar reinforced composites approach can be applied in the industrially relevant conditions using various blend parameters and 2) micro-fibrillar reinforced composites represents an attractive alternative for recycling of PET as well as other polymers.

The effect of hygrothermal aging in high humid conditions on the microstructure and thermomechanical properties of recycled PET and its short glass fibres composites was discussed in [26]. Hydrolysis process during aging decreases molecular weight of the recycled PET, so marked reduction of tensile strength and apparent fracture toughness was observed. Process causes an increase in the crystallinity content, a reduction of plastic deformation of the recycled PET matrix and a weakening of the fibre-matrix for PET composites.

The investigation of the possibilities for the use of recycled PET in powder form as a filler in the polyvinyl chloride matrix was reported by G. Akovali and E. Karababa in [27]. To enhance the degree of interaction and compatibility, the surface of powdered PET was modified at various plasma conditions. Studies of mechanical, thermal properties and surface energy showed that it is possible to improve the properties and in some surface modification cases can even lead to synergetic results.

Mechanical and morphological properties of PET bottle waste blends with maleic anhydride modified styrene butadiene rubber (SBR-*g*-MAH) were studied in [28]. PET/SBR-*g*-MAH blends showed homogeneous dispersions, high adhesion between dispersed and matrix phase and improved mechanical properties. It was supposed that PET-*g*-SBR graft copolymers were generated during the melt processing and acted as compatibilizers [28].

PET waste grinded into high dispersity particles can be used as filler in the adhesive composition. R. Barkauskas *et al.* [29 – 31] determined that such filler not only improves adhesion properties of polychloroprene adhesive, but also decreases its viscosity and improves wetability properties .

2.2. Chemical recycling of PET

PET is chemically processed by total depolymerization into monomers or partial depolymerization into oligomers and other products [13, 32]. The monomers are then re-polymerized and the regenerated or reconstituted polymer is formed into new article. Regenerated monomer, polymer, or both may be blended with virgin materials. The regeneration process may involve a variety of monomer/polymer purification steps in addition to washings, such as distillation, crystallization, and additional chemical reaction [6, 7].

Different recycling processes for chemical reprocessing or chemolysis of PET waste are available and most of them consist of esterifying the polyester with an excess of reactant such as diols, diamines, alcohols, or water. PET conversion products are used as monomers for further synthesis of PET, polyurethanes, polyvinyl chloride, or polyesters. Table 2 summarizes the most popular chemical methods to treat PET wastes. Scheme 2 shows some possible chemical routes for recycling PET polymers.

G.P. Karayannidis and D.S. Achilias [33] define *hydrolysis* as the method of PET waste recycling by the reaction of PET with water in an acid, alkaline or neutral environment, leading to total depolymerization to its monomers terephthalic acid and ethylene glycol. The reaction time ranges from a few to 30 minutes at high temperature and under high pressure, and requires no additives, such as catalyst or neutralizer [34 – 40].

Methanolysis is the degradation of PET by methanol at high temperatures and high pressures with the main products being dimethyl terephthalate and ethylene glycol. The dimethyl terephthalate produced can be purified and used to create new PET [13, 35, 41 – 43]. Methanolysis is relatively tolerant to the contents of impurities in the input materials.

Aminolysis of PET proceeds under the action of amine and terephtalamide is obtained. Depolymerisation of the PET waste using different amines such as allylamine, morpholine, hydrazine, and polyamines can be implemented [44 – 46].

Glycolysis reaction is the molecular degradation of PET polymer by glycols, in the presence of trans-esterification catalysts, mainly metal acetates, where ester linkages are broken and replaced with hydroxyl terminals. PET waste can be depolymerized by glycolysis to obtain oligomeric diols and polyols, or glycolyzed into its monomeric units, bis(2-hydroxyethyl) terephthalate or dimethyl terephthalate [47 – 51]. Bis(2-hydroxyethyl) terephthalate can be used as a substrate to create PET and other polymers [34].

The focus mainly on new trends of glycolysis reactions, as this process is more advantageous from the economical point of view than other kinds of chemolysis is made. The companies such as “Eastman Kodak“, “Goodyear“, “Du Pont“, “Zimmer“ use mainly glycolysis for PET recycling [31].

The glycolysis of PET has been found to depend on the reaction conditions represented in the glycolysis time, glycolysis temperature, catalyst concentration and glycol concentration. Ch.-H. Chen *et al.* [48, 52] found that the sequence of the main effects on the glycolysis conversion of recycled PET is in the following descending order: *catalyst concentration>glycolysis temperature>glycolysis time*.

In recent publications [53, 54] it have been shown that changing the glycol concentration at constant time, temperature and the catalyst concentration, the produced glycolysis products were significantly different in their functionality and molecular weights. K. Troev *et al.* [55] introduced a novel catalyst for the glycolysis of PET. This catalyst was synthesized by the reaction of $TiCl_4$ with triethyl phosphate (C_2H_5) P(O). It was found that the depolymerization of PET fibers proceeds faster in the presence of titanium (IV) phosphate compared with traditional metal acetate salts known in this area.

C.-H. Chen [56] studied the factors affecting the glycolysis reaction in detail. These include time, temperature and the amount of Mn-acetate catalyst used. The best glycolysis condition to reach 100 % conversion would be conducted at temperature of 190 °C, time $t = 1.5$ h, and a catalyst concentration of 0.025 mol per 100 kg of PET. The author also derived a prediction equation of glycolysis and described the effect strength of these parameters on the course of the glycolysis reaction. S. Mishra and A. S. Goje studied the kinetics of the glycolysis of PET waste powder with ethylene glycol under variable conditions covering the effect of the external pressure [57], temperature, particle size, reaction time and catalyst type and concentration [58]. The authors proposed a kinetic model and estimated the values of the rate constant and the reaction activation energy.

2.3. Applications of the glycolysis products of PET waste

Polyurethane Industry. In the PET recycling procedure obtained oligoesters can be further reacted with aliphatic diacids to form polyester polyols that can be used as a starting material in the polyurethane industry [59 – 61]. Rigid polyurethane foams prepared from the product of PET degradation with triethanolamine can be considered as insulation materials [62].

Glycolyzed PET oligoesters can be reacted directly as a polyol component with diisocyanate compounds to build up a urethane group [47-51].

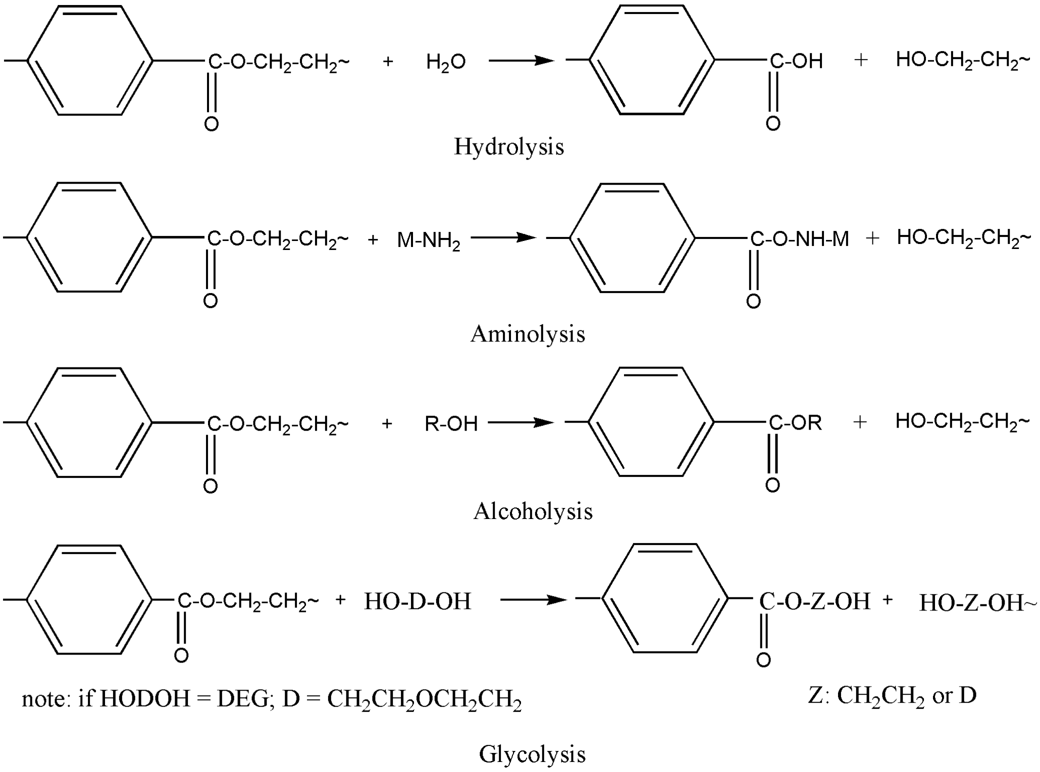
O. Mercit *et al.* [63] have synthesized new urethane oil varnishes from glycolyzed PET waste. The depolymerization products of PET by ethylene glycol, diethylene glycol, polyethylene glycol-200 and glycerin were transesterified with the glycolyzed products of soy bean oil and glycerin.

The product of this step was linked together with toluene diisocyanate to yield urethane varnish oil that was diluted with white spirit to about 60 % solid. Different glycolysis products were obtained by glycolyzing PET with different diol compounds and hence the urethane varnish oils finally obtained showed a broad spectrum of physical properties that are matching and, in some instances, are better than those of commercial grades.

Recently O. Saravari *et al.* [64] depolymerized waste PET bottles by propylene glycol using zinc acetate as a catalyst. The glycolyzed product, consisting of oligomeric diols with a number-average molecular weight range of 240 – 1107 was obtained. It was further reacted with palm oil and tolylene diisocyanate to obtain urethane oils at hydroxyl to isocyanate ratios from 1:1 to 1:0.8, with and without methanol acting as a blocking agent. It was found that all the synthesized urethane oils were yellowish transparent liquids of low molecular weights. A lower isocyanate content or the presence of a blocking agent results in higher viscosity, higher molecular weight, and

Table 2. Common PET depolymerisation treatments for recycling

Treatment	Reactant	Reactions Products	References
Hydrolysis	Water	Terephtalic acid and ethylene glycol	42 – 40
Methanolysis	Methanol	Dimethyl terephthalate and ethylene glycol (1,2-etandiol)	41 – 43
Aminolysis	Amine	Terephtalamide	44 – 46
Glycolysis	Ethylene glycol	Bishydroxyethyl terephthalate and ethylene glycol	40, 47 – 51



Scheme 2. Chemolysis reactions of PET [6, 32, 49]

shorter drying time. The films of all synthesized urethane oils exhibit good hardness, excellent flexibility, and high impact strength. They also show excellent water resistance, good acid resistance but only fair alkali resistance. Moreover, these prepared urethane oils had better adhesion compared with those of the commercial urethane oil [64].

As a new motivation, PET waste was depolymerized with a number of special diols and used for the synthesis of novel block copolymers [65, 66]. N. Kizilcan *et al.* [65] based his new idea on synthesizing di-isocyanate terminated oligomers from glycolyzed PET waste and then reacting this product with an excess of tert-butyl hydroxyperoxide to obtain macro-initiators with di-peroxide terminal groups. A series of different macro-initiators were prepared by varying the diol involved in the step of the PET glycolysis. These macro-initiators were then incorporated in the free radical polymerization with styrene monomer to prepare novel block copolymers. G.O. Atici *et al.* [66] synthesized new block copolymers through redox polymerization of the monomers by using appropriate polymeric diols as reducing agents and Ce(IV) as the oxidant in an aqueous medium. Oligoester diols coming from depolymerizing PET waste were introduced as reducing agents in these redox polymerization reactions, where the resulting polymers were suggested to have chain ends of the corresponding reducing agent moiety and hence affected the final physical properties of the resulting copolymers. The process is commercially important, first because it converts a waste material to a value-added product, and second, because it gives polyester polyols that have terephthalate-repeating units, which overcomes the problem of sublimation arising from direct use of terephthalic acid as a starting material in the polyol synthesis.

Unsaturated Polyesters. Unsaturated polyester resins are used extensively as a matrix for fiber-reinforced composites that replace conventional structural materials like steel and wood in a variety of engineering applications. Fiber-reinforced plastics are composed mainly of cross-linkable polymeric materials and reinforcing fibers. These cross-linkable polymeric materials are most commonly unsaturated polyesters or epoxy resins. The reinforcing fibers are mainly carbon, glass, aramid, ultra-high molecular-weight polyethylene, boron, quartz, or ceramic and hybrid combinations [6]. These high-performance composites offer excellent chemical resistance, weather-ability, high strength to weight ratio and ease of fabrication. Unsaturated polyester can be synthesized for this purpose from virgin material [67] or from recycled products of PET waste [68]. Unsaturated polyester resin synthesized from PET waste is also applied in making polymer concretes and polymer mortars [69] and was more recently applied for synthesizing modified unsaturated polyesters with improved curing thermal profiles [70] and improved mechanical properties [71]. V. Pimpan [72] studied the synthesis and curing characteristic behaviour of unsaturated polyester resins from post-consumer PET bottles. The author investigated the effect of the glycol type (ethylene glycol, propylene glycol and diethylene glycol) on both uncured and cured polyester resins. The type of glycol had a significant effect on the characteristics of glycolyzed products and the uncured and cured resins. The preparation of unsaturated polyesters also depended on the glycol type. The results showed that the type of bottle did not affect the properties of the synthesized unsaturated polyester resins, therefore, no separation of bottles is needed.

Acrylate/Methacrylate-Terminated Oligoesters. With increasing regulatory pressure to reduce solvent emissions, many coating processes have adopted radiation curing, using either ultraviolet or electron beam irradiation [6, 73]. Radiation cured formulations can be made using liquid monomers that polymerize upon ultraviolet or electron beam irradiation. Such coating processes are intrinsically green, since they do not use any volatile organic solvents that would give rise to air pollution. Specific application areas include printing inks, and metal and wood coatings. Acrylates are the most commonly used monomers and irradiation initiated free radical processes lead to curing. These formulations typically include an acrylate terminated urethane oligomer, a multi-functional acrylate for cross-linking and mono-acrylate reactive diluents [6].

Investigations show [6, 73] that PET waste can be processed to give radiation curable oligomers. PET waste was converted to either acrylate or methacrylate-terminated PET oligomers by a two-stage process, first glycolysis with diethylene glycol followed by reaction with either acryloyl chloride or methacryloyl chloride [74]. The oligomers were viscous oils that could be blended with commercial radiation-curable oligomers, cast into films and cured by UV irradiation. The films had Young's moduli in the range of 1-3 GPa and tensile strengths of 4 MPa – 40 MPa [73]. These results raise the possibility of converting waste PET into high value-added radiation-curable oligomers for coatings applications [6].

CONCLUSIONS

Different recycling processes for physical and chemical reprocessing of PET waste are available. Physically recycled PET is widely used in the blends with other polymers, while chemically recycled PET can be introduced as starting ingredients for synthesis of many other polymers.

The compatibilizers and other additives often are used in order to obtain valuable blends of recycled PET with virgin plastic or other plastics. However, molecular weights of blended polymers must be similar to obtain the compatible blends of recycled PET with other plastics. Otherwise additional processes are needed for the lowering average molecular weights of the polymers.

Oligoesters coming from the glycolysis of PET waste can be utilized as a starting material in the production of polyurethanes, unsaturated polyesters and saturated polyester plasticizers. The glycolysis products of PET waste open the potential for the market to apply for UV curable coatings, useful for wood surfaces, paints and other applications.

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