



Polyester the Workhorse of Polymers: A Review from Synthesis to Recycling

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ABSTRACT

In this age of polymer, polyester still conquered the leading position amongst the other manmade polymers. Polyester has become the focus of interdisciplinary research and received considerable attention due to their unique chemical and physical properties as well as their potential applications. Also, we accomplished from the recent researches that polyester is involved either in one or the other form in many works. Thus we show our deliberation to make a platform for those researchers who show interest in work on polyesters, where they find enough basics related to polyesters and its current scenario. In this framework, this review provides the extractive information's about the polyesters, which covers from to its development, chemistry, application fields up to the methods of recycling used in present scenario.

Keywords: Polyesters, Chemistry, Applications, Recycling, Present scenario.

INTRODUCTION

Human history is tied to the way of using the existed or created materials for the development of living standards. This makes possible the progress of mankind from the Stone Age, through the bronze, iron, and steel ages into its current age, the age of polymers. Due to the versatile and tailored made properties, polymers have found a ready market in a large number of areas. Today it is difficult to envision the world without them. From morning to night, bathroom to bedroom, dining hall to the kitchen, living room to office, classroom to laboratory, polymers invade every sphere of life. So we can say that polymer products are the ubiquitous legacy of our age.

Polymers have been with us since the beginning of life and those such as DNA, RNA, proteins, and polysaccharides play crucial roles in plant and animal life. The first polymers used were natural products, especially cotton, starch, proteins, and wool as materials for providing clothing, decoration, shelter, tools, weapons, writing materials and other requirements. The "polymer" term was first coined by a Swedish chemist Jöns Jacob Berzelius in 1833 to describe organic compounds, which shared identical empirical formulas but which differed in overall molecular weight. Berzelius is also credited with originating the chemical terms "catalysis," "isomer," and "allotrope," although his original definitions differ dramatically from modern usage [1]. The word polymer derived from Greek poly and meros, meaning many and parts, respectively. Instead of polymer, many scientists prefer to use the word macromolecule or large molecule or giant molecule [2]. Throughout the nineteenth century, chemists worked with macromolecules without having any clear understanding of their structure. The first truly synthetic polymer to be used on a commercial scale was a phenol-formaldehyde resin; commercially known as Bakelite developed in the early

1900s by the Belgian-born chemist Leo Baekeland [3]. Other polymers were also developed commercial about the same time which is listed chronologically in Table 1. The concept of polymers being mixtures of molecules with long chains of atoms connected to one another seems simple and logical today but was not accepted until the 1930's when the results of the extensive work of the German scientist Hermann Staudinger, finally became appreciated. He received the Nobel Prize in Chemistry in 1953 for attributing the remarkable properties of polymers. Prior to Staudinger's work, polymers were believed to be colloidal aggregates of small molecules with quite nonspecific chemical structures. World War II led to a significant advance in polymer chemistry [4].

Table 1: Chronological development of commercial polymers

No.	Years	Developed Polymers	Inventors	Reference
1	Before 1800	Cotton, Flax, Wool and Silk fibers; glass and cement; leather and cellulose sheet; Natura rubber, gutta-percha, balata and shellac	--	
2	1839	Vulcanization of rubber; Polymerization of styrene (Metastyrol)	Charles Goodyear; Eduard Simon	[5,6]
3	1845	Cellulose esters	Christian Friedrich Schönbein	[7]
4	1846	Nitration of cellulose	Christian Friedrich Schönbein	[7]
5	1851	Hard rubber (Ebonite)	Nelson Goodyear	[8]
6	1869	Celluloid (solid, stable nitrocellulose)	John Wesley Hyatt	[9]
7	1887	Pneumatic tyre	John Boyd Dunlop	[10]
8	1891	Viscous rayon fiber	C.F. Cross and E.J. Bevan	[11]
9	1897	Poly (phynylenesulfide)	P. Genvresse	[12]
10	1901	Glyptal	Watson Smith	[13]
11	1903	First tubeless tyre.	P.W. Litchfield	[14]
12	1908	Cellulose acetate Photographic film	Eastman Kodak	[15]
13	1912	Poly (vinyl Acetate)	Fritz Klatte	[16]
14	1919	Urea-formaldehyde resin	Hanns John	[17]
15	1924	Cellulose acetate fibers	Camille and Henry Creysuf	[18]
16	1926	Alkyd polyester	R.H. Kienle	[19]
17	1927	Poly (vinyl chloride)	Benjamin Franklin Goodrich	[20]
18	1928	Nylon	Wallace Carothers	[21]
19	1929	Thiokol (polysulfide polymers)	Joseph C. Patrick and Nathan Mnookin	[22]
20	1930	polyethylene	Friedrich and Marvel	[23]
21	1931	Polymethylmethacrylate (PMMA)	Rowland Hill and John Crawford	[24]
22	1931	Neoprene	Wallace Carothers	[21]
23	1934	Epoxy resin	Schlack	[25]
24	1937	Polystyrene	Staudinger	[26]
25	1937	Buna-S and Buna-N	Bock, Konrad, and Tschunkur	[27]
26	1938	Melamine formaldehyde resins	I.G. Ferben, Henkel, CIBA	[28]
27	1940	Butyl Rubber	Robert Mckee Thomas	[29]
28	1941	Terylene	John Rex Whinfield and James Tennant Dickson	[30]

29	1942	Unsaturated Polyester	Ellis	[31]
30	1943	TEFLON	Roy J. Plunkett	[32]
31	1945	SBR (GR- S)	–	[33]
32	1947	Cyanoacrylate	Alan Ardis	[34]
33	1953	Polyester fibers	John Rex Whinfield and James Tennant Dickson	[35]
34	1957	Polycarbonate	A. Einhorn	[36]
35	1960	Polyimide	Du Pont Scientists	[36]
36	1970	Poly (butylene terephthalate) (Hytrel)	Du Pont Scientists	[37]
37	1986	Dendrimers synthesized	D. Tomalia.	[38]
38	1991	Carbon Nanotube	Iijima; NEC Lab	[21]
39	1993	M5 (PIPD) Fiber	Sikkema and Lishinsky	[39]
40	1998	Marketing of Zylon (PBO) Fiber	Toyoba	[39]
41	2007	Nylon 4, T	DSM Engineering Plastics	[39]

In this age of polymer, polyesters are the most consumable polymer among the other manmade polymers for satisfying the need of the growing population and its living standards. Polyesters have conquered the leading position and become the focus of interdisciplinary research, also received considerable attention due to their unique chemical and physical properties as well as their potential applications in form of fiber, film, resin, laminates, etc. On the other hand, due to the Petro-based and count as noxious materials because of its non-biodegradability, polymer scientists face a dilemma for polyesters production and disposal. So polyester and its recycling are proven the hot research fields for the polymer scientists, environmental and waste management researchers. Extensive successful attempts had been made in the past to overcome the stated dilemma of polyesters. This review provides comprehensive information's about the journey of polyesters, from its development, chemistry through advanced developments to the recycling, at present scenario.

POLYESTERS

Historical perspective

Now a day, Polyesters are one of the most economically important and widely used classes of polymers among the polycondensation polymers. The 'Polyesters' is a term used for polymeric material having ester groups in the polymeric main chain of macromolecules instead of ester groups in the side chain of macromolecules, as in the case of poly (vinyl acetate), poly (methyl methacrylate), Or Cellulose triacetate, etc. Since time immemorial, the use of natural polyester has been in vogue to mankind. The reports show that the shellac (Natural polyester) was used in the mummies embalming by ancestors of Egyptians and as a molding resin for phonographic records [40,41]. The journey of synthesizing synthetic polyesters has been known since the late eighteenth century as a resinous form, the exact composition of which remained unknown. Earlier reports of these types of polyester resin show that Berzelius was the first scientist who synthesized first polyesters of polybasic acids and polyvalent alcohol by reacting tartaric acid and glycerol in 1847[41]. Many other efforts had been made at the same time those from Berthelot, who obtained a resin by reacting glycerol and camphoric acid in 1853 [42] and Van Bemmelen, who made glycerides of succinic acid and citric acid in 1856. The first commercially important polyester was alkyd resins, developed for the coating, varnishes, and paints applications. Alkyd resins are essentially polyester of phthalic anhydride, glycerol, and monocarboxylic unsaturated fatty acids. Alkyd resin was first marketed in 1929 by the General Electric Company of the USA, with the trade name of Glyptal®.

However, the modern history of polyesters began with the work of the Carothers in 1930s. He proved the macromolecular theory of Staudinger by experimental studies on the reaction between aliphatic dibasic acids and diols and recognized the relationship between the degree of polymerization, conversion, functionality and gel point. Carothers and co-workers made a large number of aliphatic polyesters ranging in different molecular weights, those from Carothers and Arvin, Who synthesized polyesters having a molecular weight 4000 by reacting octadecanoic acid with PDO in 1929 [43] and Carothers and Hill, who synthesized 3G18 and Super polyester having 12000 and up

to 25000 molecular weight, respectively in 1932 [44]. Although it is generally thought that works on aliphatic polyesters by Carothers and co-workers were not suitable for commercial applications due to its low melting point and sensitivity to hydrolysis. J. R. Whinfield and J. T. Dickson were greatly influenced by the works and their limitations of Carothers and initiated works on the stiffening of the polyesters chain. They were successfully synthesized high melting point polyesters by reacting terephthalic acid and aliphatic diols, which was the first aromatic polyester as poly(ethylene terephthalate) in 1941 [45]. PET was introduced commercially in 1953 as a textile fiber and thereafter as a film. Follow the invention of PET, many other aromatic polyesters were evaluated and patented such as Poly(trimethylene terephthalate) PTT, Poly (butylene terephthalate) PBT, Poly (1,4-cyclohexylene dimethylene terephthalate) PCT, Poly (ethylene 2,6-naphthalate) PEN.

The commercialization of maleic anhydride in 1933 became accountable for the development of the unsaturated polyesters. The new type of thermosetting resin was obtained by dissolving unsaturated polyesters in an unsaturated monomer such as styrene. Unsaturated polyesters found its first application as Glass-Reinforced Polyesters (GRPs) during World War II, but the technology was widely commercially available only in the mid-1950s. The period of the 1970s and 1980s were proven paramount for the research on block copolymers and high performance wholly aromatic polyesters. During the 1990s increasing environmental concern and demanding of biodegradable polymers has resulted in a rehabilitated interest in aliphatic polyesters, such as poly(lactones) and poly(lactides), or copolyesters containing aliphatic moieties [46-48]. New polyester polymers have been very recently or are soon commercially introduced for the varying application in the field of fiber, film, and biodegradability. Also recently hyperbranched polyesters reported and find application as crosslinker, additives, and surfactants. So we can say that polyester synthesis is still a very active field.

Classification

Polyesters are broadly classified into two types, namely: (i) thermoplastic polyesters and (ii) unsaturated polyesters than became cross-linked thermosets. Thermoplastic polyesters can be further classified into six types: (i) Linear aromatic polyesters, which is further sub-classified based on the type of aromatic moiety present in the polyester main chain. They are (a) phthalates and (b) naphthalates, which are mouldable, film-forming and fiber-forming polyesters. Polyethylene terephthalate (PET), polybutylene terephthalate (PTT), polybutylene terephthalate (PBT) belong to the phthalate group while Polyethylene naphthalate (PEN), polytributylene naphthalate (PTN) and polybutylene naphthalate (PBN) are considered under naphthalates group. (ii) Elastomers, which are block copolyesters containing both the stiff and flexible parts. (iii) Engineering plastics, which are strong, stiff, tough and highly crystalline. (iv) Aliphatic polyesters which are found to be biodegradable and biocompatible. (v) Liquid Crystalline Polyesters (LCP). (vi) Biodegradable polyesters such as Poly (hydroxyl alkenoates). The growing need to find a sustainable, environmentally friendly replacement for petroleum-based materials is fuelling the development of bio-based polyesters from renewable resources. Amongst the most promising of these are vegetable oil-based polyesters. The traditionally and most widely used modified oil-based polyesters classified in to three categories based on the content of oil, (i) short oil polyesters, which contain 40% oil based on the total weight of the resin, (ii) medium oil polyesters, which contain 40%-60% oil based on the total weight of the resin, (iii) long oil polyesters, which contain more than 60% oil based on the total weight of the resin [49-51].

Polymerization processes

Many reactions can be used for the synthesis of polyesters [52-54], but the most valuable synthesise methods, because of their range and utility, are reviewed.

Step-growth polycondensation

It is a conventional polymerization method. In this method, Polyester is formed by the polycondensation of dicarboxylic acids or certain of their functional derivatives with diols or their functional derivatives. Water and methanol are the byproducts of this method, based on the reactant used namely dicarboxylic acid or its dimethyl ester. Compounds of antimony, germanium, titanium, and aluminum are most commonly used as a catalyst in the polycondensation reaction. From that, antimony based catalyst and titanium-based catalyst are generally used at a dosage level of 300 ppm and 20 ppm, respectively. As result polyester prepared from titanium-based catalysts contain lesser amounts of residual catalysts. In the synthesis of aromatic polyesters, Enzyme protease from *Bacillus licheniformis* can also be used as a catalyst for the transesterification of DMT and diol [55-57]. The overall reaction time for step-growth polycondensation processes is long and usually varies from 5 to 10 hours, but the previous study on the polymerization kinetics shows that under variations of reaction conditions, such as faster stirring, high temperature and uses of various additives like TPA can decrease the reaction time [58-60].

Ring-opening polymerization

It is a novel manufacturing method. Polyesters can be prepared by ring-opening polymerization using cyclic oligomers. Many studies on the conversion of cyclic oligomers to high molecular weight linear polymer by ring-opening polymerizations have been reported. Ring-opening polymerization offers several potential advantages, comprise (a) higher polymer molecular weights can be more easily achieved (100,000–300,000 g/mol), (b) no byproduct formation and (c) it allows processing by various techniques, such as pultrusion, resin transfer molding, melt filtration, or reaction injection molding. Various transesterification catalysts are used in ring-opening polymerizations for the synthesizing high molecular weight polyesters, amongst that organotin and organotitanate compounds are most effective catalysts [61-63]. Table 2 shows detailed reaction conditions of the ring-opening polymerization using by various investigators [64-69].

Table 2: Reaction conditions for ring-opening polymerization

Temperature (°C)	Time (Min.)	Catalyst	Molecular weight/Intrinsic Viscosity	Polymer	Reference
293	10-15	Antimony trioxide	32,100 g/mol	PET	[64]
285	10	Titanium(IV) isopropoxide	38,900 g/mol	PET	[65]
230	10	Cyclic stannoxane	0.51 dl/g	PET	[66]
190	20	Cyclic stannoxane, Tetrakis(2-ethylhexyl)-titanate	445,000 g/mol	PBT	[67]
300	120	Dibutyltin oxide	0.66 dl/g	PTT	[68]
275	15	Dibutyltin oxide	0.28 dl/g	PBN	[69]
300	25	Titanium (IV) propoxide	0.24 dl/g	PEN	[69]

Polyaddition reaction

Polyaddition is a unique and successful method for the synthesis of reactive polymer. Polyesters can be prepared by the polyaddition reaction of diepoxides to diacids. Polyaddition of bis (cyclic ethers) such as bisoxiranes and bisoxetanes with bis (aryl esters) and diacyl chlorides such as terephthaloyl chloride (TPC), Isophthaloyl chloride (IPC), sebacoyl chloride (SCC), and adipoyl chloride (APC) give polyesters with reactive chloromethyl groups at their side-chain [70,71]. This reaction is catalyzed by amines, quaternary ammonium, antimony trioxide, antimony pentachloride, Ph3As. Another related reaction is the polyaddition reaction of carbon suboxide (C₃O₂) and glycols giving polymalonates, and of bisketenes with diols, yielding polyesters. Lastly, polyesters are produced by alternating step-polyaddition reactions of cyclic anhydrides of dicarboxylic acids with diepoxides, as well as by their reaction cyclic carbonates or sulfates and dioxans. Formation numerous side reactions during the polyaddition reaction restricted the use of it for synthesis at the same level (linear polyester). These polyesters are used as composites, blends, laminates and biodegradable polymers [72-75].

Poly (ethylene terephthalate) (PET) is the most commercially succeed long-chain polymer belonging to the generic family of polyesters. It was the first artificial fiber developed by Whinfield and Dixon having trade name Dacron and Terylene, in UK. Dacron polyester plant went into operation in 1953. PET is also known as polyethylene glycol terephthalate, ethylene terephthalate polymer, poly (oxy-1, 2-ethanediylloxycarbonyl- 1, 4-phenylene dicarbonyl), terephthalic acid-ethylene glycol polyester and 2GT. The formation of PET consists of two main reactions namely: (i) esterification and (ii) polycondensation. The esterification reaction is conducted in excess of MEG. The first step produces a prepolymer which contains bis (hydroxyethyl terephthalate) (BHET) (or) dimethylene glycol terephthalate and short-chain oligomers and by-products namely water (or) methanol depending upon the raw material used namely PTA or DMT respectively. The mixture then reacts further, distills out excess ethylene glycol and forms the PET as shown in Figure 1. At this stage, the PET is a viscous molten liquid. It is extruded, and water quenched to form a glasslike amorphous material [76,77].

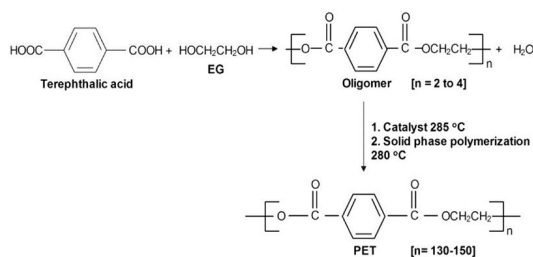


Figure 1: PET formation

Physical and chemical properties of PET

As a thermoplastic polyester resin, PET exhibits interesting physical and chemical properties. Figure 2 shows the repeating unit of PET having a physical length of about 1.09 nm and a molecular weight of 192. PET having relatively high thermal stability compared to other aliphatic polymers such as polyolefin or polyamide because the presence of aromatic ring coupled with short aliphatic chain, which makes the polymer stiffer. PET is insoluble in water and it desires sufficient drying to minimize the drop in intrinsic viscosity (IV) during processing, due to hygroscopic nature. It is very difficult to polymerize higher intrinsic viscosity (IV) polymer in the melt-phase because of the thermal degradation reactions [78]. It is an amorphous glass-like material in its purest form. Its crystallinity can be enhanced by adding modifying additives or by heat treatment of the polymer melt 80. Commercial PET has a melting temperature (T_m) of between 255°C and 265°C and for more crystalline PET is 265°C. T_g of virgin PET varies between 67°C and 140°C. The thermal transitions and crystallization of virgin PET with a focus on reversing crystallization and melting have been analyzed by several researchers. An interesting phenomenon was reported in which the virgin PET experiences multiple endothermic transitions during thermal analysis. It was reported that this phenomenon is attributable to morphological and structural re-organization. As the temperature increases, better crystal structures are achieved because of the re-organization of the less perfect crystals. Virgin PET is well known for having very slow crystallization rate. The highest crystallization rate takes place at 170°C, or 190°C. Cooling PET rapidly from the melt to a temperature below T_g can produce an amorphous, transparent PET. Semi-crystalline PET can be obtained by heating the solid amorphous PET to a temperature above T_g where 30% crystallinity can be achieved. The rate of crystallization of virgin PET depends greatly on temperature and reaches its maximum at a temperature of 150-180°C. The rate of crystallization also depends on other factors such as MW, the presence of nucleating agents, the degree of chain orientation, the nature of the polymerization catalyst used in the original production of PET and the thermal history [79-84].

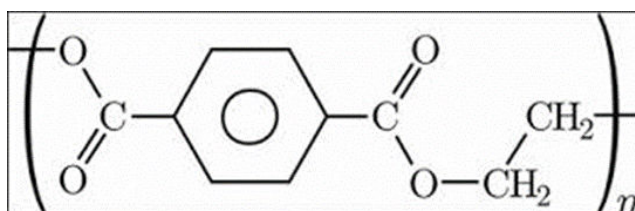


Figure 2: PET repeating unit

Significance of poly (ethylene terephthalate) PET and issues

Polyester consumption has increased substantially in fibers and molding resins due to the strong demand for textile applications, as well as in food packaging and bottle markets for glass replacement. The overall world production of polyesters was 25-30 million tons in 2000, this value increased to 55 million tons in 2012 and it is expected to grow by 4.5% per year, that mostly consisted of poly (ethylene terephthalate), because of its low cost, excellent tensile strength, chemical resistance, clarity, processability, reasonable thermal stability, and wide range of applications. Poly (ethylene terephthalate), more commonly known as 'polyester' in the textile industry and generally referred to as PET in the packaging industry. The PET bottle was patented in 1973 by Nathaniel Wyeth and began to be used popularly for the production of disposable soft drink bottles in the 1980s. In 1987, more than 700 million pounds of PET were consumed in their production. These developments resulted in a diversity of industrial applications,

leading to increased consumer demand for PET, and many global companies produced PET with different trade names as listed in Table 3 [85,86].

Table 3: PET with different trade names

PET	Trade Name	Company
	Dacron	DuPont
	Encron	American Enka Corp
	Hostphan	Hoechst
	Teijin-Tetoron	Teijin Ltd
	Terylene	ICI Fibres Ltd
	Melinar	ICI
	Mylar	DuPont

Two PET grades now dominate the global market, i.e. fiber grade PET and bottle-grade PET. These standard grades differ mainly in molecular weight or intrinsic viscosity (IV), respectively, optical appearance and the production recipes. The latter differ in the amount and type of co-monomers, stabilizers, and metal catalysts, as well as colorants. Textile fiber-grade PET has a molecular weight of 15,000-20,000 g/mol, which refers to an intrinsic viscosity between 0.55 and 0.67 dL/g. PET fiber-grades for technical yarns such as tire cord has high molecular weights, with an intrinsic viscosity above 0.98 dL/g. Bottle-grade PET appears 'glass-clear' in the amorphous state. The average molecular weight ranges from 24,000 to 36,000 g/mol, which refers to an intrinsic viscosity between 0.75 and 1.00 dL/g. The standard bottle grade has an intrinsic viscosity of 0.80 dL/g. Other PET grades are manufactured for packaging films, as well as for the production of video and audiotapes. These PET types are often standard grades with an intrinsic viscosity of 0.64 dL/g. To reduce the sticking tendency of the final product, solid additives such as SiO₂ or clay with specific particle sizes and particle-size distributions are incorporated [87-89].

Along with the widespread application of PET is the inevitable creation of large amounts of PET waste. PET does not have any side effects on the human body and does not create a direct hazard to the environment, but due to its substantial fraction by volume in the waste stream and its high resistant to the atmospheric and biological agents, it is seen as noxious material. With such a large consumption, the effective utilization of PET waste is of considerable commercial and technological issues for the researchers.

RECENT WORK TO POLYESTERS

Bio-based alternatives for biodegradable polyesters

The improvement of the physical properties of aliphatic polyesters has become a challenging task for the last few years. As improving the mechanical properties with modular biodegradability, the introduction of aromatic units appeared to be interesting as a first strategy for the synthesis of polyesters. In this way, aromatic-aliphatic polyesters such as poly (butylene succinate-co-terephthalate) (PBST), poly(ethylene succinate-co-terephthalate) (PEST) and poly(butylene adipate-co-terephthalate) (PBAT) have received much interest from many research groups and were produced on an industrial scale. For example, BASF, DuPont and Eastman Chemical have developed copolymers, sold under the trade names Ecoflex (PBAT), Biomax (PBST/PEST) and Eastar Bio (PBAT) [90]. Utilization of bio-based feedstocks as a substitute for conventional petrochemical routes, for producing aliphatic monomers, namely 1,4 butanediol, ethanediol, succinic acid, and adipic acid, have been recently practiced. On the other hand, the replacement of petrochemical terephthalic moieties still remains a challenge in aromatic aliphatic copolyesters. The production of bio-based terephthalic acid has been recently described from isobutene and limonene, but these processes are still far from meeting the industrial requirements [91-93]. 1,4: 3,6-dianhydrohexitols or 2,5-furan dicarboxylic acid (FDCA) is a promising alternative to petrochemical terephthalic moieties and used as a rigid monomer in synthesis of polyesters [94-97].

An isomannide, isosorbide, and isoidide, are rigid diol derivatives of the 1,4:3,6-dianhydrohexitols, which obtained by the double dehydration of the associated sugar. Amongst them, isosorbide (or dianhydro-1,4:3,6-D-glucitol) is currently produced on an industrial scale and one of the most promising rigid and biobased comonomers for

polycondensation and especially for the modification of aliphatic and aromatic polyesters. In a similar manner, 2,5-furan dicarboxylic acid (FDCA) recently gained much interest in polycondensates such as PET, PBT, and PTT [95-98]. The previous works of Noordover et al. show the utilization of isosorbide, they reported the polyesterification of isosorbide and succinic acid with several diols to produce oligomers for bio-based coating applications. In these studies, 1,4-butanediol was not evaluated as a comonomer of isosorbide and only the synthesis of low molar mass reactive oligomers was reported [98-100]. In a more recent work of Lavilla et al., shows the synthesis of high Tg poly (butylene succinate) polyesters modified by copolymerization with bicyclic D-mannitol. In that study, interesting semi-crystalline copolyesters that degrade faster than PBS was obtained [101]. The use of furan monomers has been recently reported in several research papers and patents for the synthesis of aromatic- aliphatic polyesters such as poly(butylene succinate-co-furanoate) (later designated PBSF) [102], poly(ethylene succinate co-furanoate) [103,104], poly(butylene sebacate-co-furanoate) or poly(butylene adipate-co-furanoate) [105]. The synthesis of aliphatic block copolyesters with controlled structures, based on lactide, menthide, α - methylene- γ -butyrolactone, and carvone, all derived from renewable resources, have been recently discussed. Their synthesis is rather straightforward and their potential application as biodegradable thermoplastic elastomers appears economically viable [106-112].

A significantly growing interest is to design a new strategy for the development of biodegradable polymer, due to limited fossil fuel reserves, the rise of petrochemicals price and strict environmental laws. As biomaterial and due to biodegradability, aliphatic polyesters are growing research in the field of biodegradable polyesters. In fact, a number of synthetic polyesters have been found to be biodegradable, and several aliphatic polyesters, are now produced on a semi-commercial scale by a number of companies that make biodegradable plastics [106-111]. Polylactide (PLA), polyglycolate (PGA), polycaprolactone (PCL), poly(3-hydroxybutyrate) (PHB), polyhydroxy valerate (PHV) and their copolymers poly(butylene succinate) (PBSu), poly(ethylene succinate) (PESu), poly(propylene adipate) (PPAd), etc. [112-116], are the most used aliphatic polyesters for a wide variety of applications such as packaging materials, medical products and mulch films, in an effort to solve the problems related to plastic waste accumulation. The degradation of aliphatic polyesters proceeds by one or several mechanisms including chemical hydrolysis, microbial, enzymatic and thermal degradation. However, the majority of polyesters is degrading by enzymes such as lipases, which are only active after conformational changes induced by adsorptive binding at the substrate surface. First investigations on the enzymatic attack on synthetic polyesters with lipases were done already by Tokiwa and Suzuki [117]. Detailed and systematic studies on the influence of polyester specific parameters on the biodegradation with lipases were also reported by Marten et al. [118,119]. In a recent study, the degradation of several aliphatic and aromatic polyesters with lipases from *Candida cylindracea* (CcL) and *Pseudomonas* sp. (PsL) was investigated [120]. Figure 3 shows the enzymatic hydrolysis process of aliphatic polyesters. To avoid the effect of several factors on aliphatic polyester degradation, nanoparticles with diameters 50-250 nm were prepared by Dimitrios N. Bikiaris [121]. This is very important since it was found that the degradation rate of the enzymatic polyester hydrolysis can be increased significantly by applying nanoparticles instead of films. Polyester hydrolysis in the form of films lasted from some hours to many days while the polyester nanoparticles were totally hydrolyzed within some minutes.

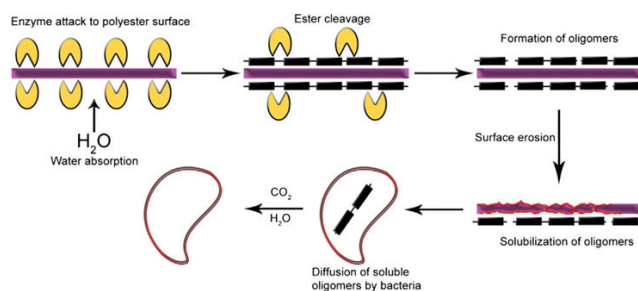


Figure 3: Enzymatic hydrolysis of PET

Branched and hyperbranched polyesters

It is widely documented that a high degree of branching in a polymer backbone provides enhanced solubility, lower viscosity, and lower crystallinity, for the case of symmetric chains that readily crystallize than a linear polymer of equal molecular weight. Polyesters offer good mechanical and thermal properties and high chemical resistance at relatively low cost. However, the processing of some polyester is limited due to insufficient melt strength and melt viscosity. Thus, many researchers have focused on modifying polyesters for enhanced melt strength and melt viscosity by introducing long chain branches into the polyester backbone. The most common method for synthesizing

branched polyesters is via the addition of small amounts of tri- or tetra functional comonomer to the polymerization. Manaresi et al. first reported the synthesis of branched PETs from Dimethyl Terephthalate (DMT) and ethylene glycol (EG) using a trifunctional branching agent, trimethyl trimester. Intrinsic viscosities and the extents of reaction by end-group analysis were reported, even though Manaresi et al. did not report the absolute molecular weights of the polymers [106]. Later on Weisskopf et al. synthesized high molecular weight branched PETs using different trifunctional agents and Trimethylolpropane (TME) and trimesic acid as multifunctional comonomers [108]. In a similar manner Yoon et al. also synthesized branched PETs using TME as a branching agent at concentrations from 0.04 to 0.15 mol% and titanium isopropoxide as the catalyst for the polycondensation reaction [108]. Recently, Hudson et al. studied branched PETs based on various branching agents such as benzene-1,2,4,5-tetracarboxylic acid, dipentaerythritol, and tripentaerythritol, with the end-capping reagent benzyl alcohol. To study the influence of branching on the solution and melt properties, they characterized polymers using FTIR and ¹H NMR spectroscopy, light scattering, dilute solution viscometry and melt rheology [109]. Moreover, by Timothy et al., various long-chain branched polyesters and the influence of branching on polyester properties for new high-performance applications was reviewed [110].

As an important class of hyperbranched polymers, aromatic hyperbranched polyesters have attracted increased interest and are intensively studied because of their excellent thermal stability, chemical resistance, and mechanical properties. Based on the literature survey we resolve that the technique used to synthesize the HBPEs can be divided into two categories: (1) polycondensation of AB₂ monomers; (2) polymerization of two types of monomers or a monomer pair, such as A₂+B₃ monomers, A*+B₃ monomers, and AA*/A₂*+B₂ monomers. We are not reviewing in detail the developments in synthesis, modifications, and applications of aromatic hyperbranched polyesters, because of avoiding the repetition of the work, as it is recently reported by Xinli Zhang in his review [111].

RECYCLING OF POLYESTERS

For more than 100 years, polyester products have revolutionized the way we live. Polyethylene terephthalate (PET) is a particularly notable example of it. This is just because of its large volume applications, such as textile fiber for apparel, industrial fibers in tyre cords, safety belts and bags, bottles and containers for liquid packaging, technical textiles including non-wovens, audio/videotapes, X-rays and photographic films, thermoforming and engineering resins often in combination with glass fiber. Moreover, it is also used for microwaves food trays and food packaging films due to its inherent properties and having excellent barrier capacity against oxygen and carbon dioxide. This widespread uses, particularly in the textile and packaging sectors, generate tones of PET waste to the environment which leads to waste disposal management difficulties. PET accounts for 8% by weight and 12% by volume of the global solid waste [122,123]. Incineration helps produce energy but has a problem with emission of the toxic fumes and gases. On the other hand landfilling of PET waste is not preferred because of space constraints and land pollution. While recycling processes are the best ways to economically reduce PET waste. Thus, the current scenario demands a simple, eco-friendly and economical route for recycling PET wastes that may otherwise disrupt the balance of the ecosystem due to their non-biodegradable nature. It should be pointed out that, PET could be thought of as a noxious material because of its substantial volume and slow biodegradability. Nonetheless, it does not create a direct hazard to the environment. Thus the recycling of PET does not only serve as a partial solution to the solid waste problem but also contributes to the conservation of raw petrochemical and energy [124,125].

Types, sources, and management of PET waste

“Process waste” and “post-consumer waste” are the two types of PET waste. Polymerization, pelletizing, melt spinning and annealing are such operations where process waste is generated in the form of chips, fibers, and filaments. String waste from spinning, drawn waste, undrawn waste and crimped fiber are the other forms of the fiber waste. It is possible to prevent or minimize the contamination of process waste through machinery design, as in automatic recycling of the edge-trim waste in PET film manufacture and through well-defined shop-floor practice for house-keeping and production oppression. While the post-consumer PET waste is available from used textile products, recycled bottles, injection-molded articles, photographic and x-ray films. The used garments made from polyester fibers and filament would potentially be a major source of PET waste since man-made fiber still represents almost 75% of the annual PET consumption. The quantity of generation of waste from photographic and x-rays film with injection-molded plastics are limited, thus incineration may be the best option for the disposing [125-127].

Establishment of an effective system for collection, accumulation, and transport to waste reprocessing plants is the prime need for recycling post-consumer PET waste. PET can be recycled by practically all known recycling methods. Physical recycling is one, which includes direct conversion of fiber or fabric waste into secondary textile products by

textile reprocessing, blending of waste with virgin polymer and thermal reprocessing of granules or flakes for further processing into useful products. While chemical recycling is the technique where waste is depolymerized for the recovery of monomers, oligomers or producing chemical precursors for value-added polymeric products. Amongst these, chemical recycling is of great interest because of the wide range of depolymerizing agents and a large variety of products [123,128,129].

Physical vs. chemical recycling

Compared to chemical recycling routes, the physical recycling of PET is relatively simple, requires low investments, utilizes established equipment, is flexible in terms of feedstock volume and has a little adverse environmental impact. Despite the positive incentives to recycle PET mechanically, there are a number of barriers, and these include: (a) Paper labels and label adhesives (based on polyvinyl acetate/ethylene vinyl acetate) cause the PET to discolor and lose clarity. (b) PET containing residual moisture degrades readily when reprocessed, if not dried. (c) Thermal and oxidative degradation products cause yellowing and diminish the mechanical properties of PET. (d) Collection, sorting, and separation costs are high because of the low-bulk density of PET bottles and the stringent requirement to have well-sorted feedstock. (e) PVC liners in bottle caps are problematic for the PET recycling process. PVC and PET have almost the same density and are difficult to separate from each other. PVC releases hydrochloric acid during PET reprocessing, reducing the commercial value of recycled PET. Thus, it is very difficult to recycle complex and contaminated PET wastes mechanically [130,131]. Recycled PET obtained from mechanical recycling plants exhibits relatively low and heterogeneous intrinsic viscosity values. On the other hand, chemical recycling is an accepted PET recycling method that follows the principles of “sustainable development”. The fact that chemically recycled PET is well suited for food-contact applications has increasingly attracted researchers to the various hemolysis possibilities. Chemical recycling methods are opening newer pathways for using PET waste as a precursor in generating pure value-added products for various industrial and commercial applications. However, chemically recycled PET is more expensive than virgin PET because of its raw material cost, capital investment, and scale of operation. The chemical recycling is carried out either by (i) solvolysis or by (ii) pyrolysis, where solvolysis includes Hydrolysis, Aminolysis, Ammonolysis, Methanolysis, and Glycolysis. Amongst these, glycolytic and aminolysis depolymerization of PET wastes has more commercial significance.

Recycling by glycolysis

Glycolysis is the simplest and oldest method of PET depolymerization. It is a commercial PET recycling method practiced by renowned companies worldwide such as DuPont, Goodyear, Shell Polyester, Zimmer and Eastman Kodak. The glycolysis reaction is the molecular degradation of PET polymer by glycols, in the presence of transesterification catalysts, where ester linkages are broken and replaced with hydroxyl terminals. Glycolysis of PET was first described in a patent in 1965. The glycolysis of waste PET proceeds through at least three stages, from oligomers to monomer through dimer [132]. Studies on the kinetics of PET glycolysis have shown that glycolysis without a catalyst is very slow and complete depolymerization of PET to BHET cannot be achieved. Thus, research efforts have been directed toward increasing the rate and BHET monomer yield by developing highly efficient catalysts and other techniques and optimizing the reaction conditions such as temperature, time, PET/EG ratio and PET/catalyst ratio.

Solvent-assisted glycolysis

As a name suggesting that in this technique solvent is used as a reaction medium for the degradation of PET by glycols. The attempt had been by Guclu et al. [133], in which they added “Xylene” as a solvent in the zinc acetate catalyzed PET glycolysis reaction. Results show that the obtained yield of BHET was higher than the process without xylene. The main objective of Xylene was initially to provide homogeneity to the PET-glycol mixture. At temperatures between 170°C and 225°C, EG dissolves sparingly in Xylene while it dissolves readily in PET. Meanwhile, the glycolysis products are soluble in Xylene. Therefore, as the reaction progressed, the glycolysis products moved from the PET-glycol phase to the Xylene phase, shifting the reaction to the direction of depolymerization. Further investigations may have been prevented by the reason that organic solvents are harmful to the environment and massive use of these solvents is not a very attractive idea.

Supercritical glycolysis

Supercritical glycolysis involves the degradation of PET by ethylene glycol at a temperature and pressure above the critical point of ethylene glycol. The use of supercritical conditions has been explored earlier in PET hydrolysis and methanolysis, but only recently for glycolysis. Supercritical glycolysis has a considerably shorter reaction time with

high throughput due to the high solvent density, solubility, high kinetic energy, and high diffusion and reaction rates of the supercritical ethylene glycol. Imran et al. [134] investigated the glycolysis of PET with EG under supercritical and subcritical conditions with a PET: EG ratio of 1:16. The results show that compares to the subcritical process, the BHET-dimer equilibrium was achieved much earlier in supercritical condition and a maximum BHET yield of 93.5% was reached in 30 min. The main advantage of the use of supercritical fluids in a reaction is the elimination of the need for catalysts, which are difficult to separate from the reaction products. It is also environmentally friendly. While disadvantages of the method include the high temperature and pressure needed to carry out the process.

Microwave-assisted glycolysis

The high reaction temperature and reaction time are the main characteristics of conventional glycolysis. Overcome this issue, organic chemists applied microwave heating. The use of microwave heating offers many advantages over conventional heating such as instantaneous and rapid heating with high specificity without contact with the material to be heated. Thus, extremely short reaction time coupled with substantial energy conservation can be attained. The first successful method was developed by Krazan for depolymerizing the PET bottle by microwave irradiation [135]. In addition to this Shukla et al. [136] had made an attempt of depolymerization by microwave irradiation in the presence of various catalysts like zinc acetate, sodium carbonate, and bicarbonate. The results show that the reaction time drastically reduced from 8 h to 35 min, and the yield of BHET increased using microwaves as the heating source. The comparative yields of BHET using different catalysts are presented in Figure 4 which shows that carbonate and bicarbonate catalysts can be proven as a potential replacement to the metal catalysts. Similarly, there were other attempts had been by Chaudhary et al., and Benes et al. [137-139]. In which utilization of castor oil as a replacement to diol in depolymerization of PET waste by microwave irradiation is the center of the work of the bens et al. [138].

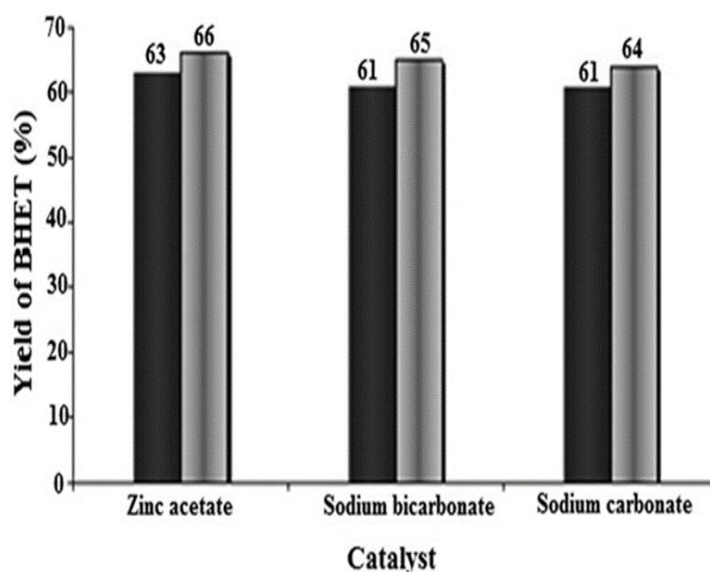


Figure 4: Catalyst for glycolysis

Depolymerizing agents, catalysts and applications of glycolyzed products

Different depolymerizing agents and catalyst attempted for glycolysis were, ethylene glycol [139-145], diethylene glycol [146-148], propylene glycol [149], di propylene glycol [147-149], SOFA [150,151], starch derived glycol glycoside [152], castor oil [138] in presence of various catalysts such as metal salts, non-toxic metal salts, recoverable catalyst, and high surface area catalyst. Among this depolymerization using ethylene glycol in the presence of different catalysts was most practiced. The optimum glycolysis conditions of PET with EG in the presence of various catalysts under ambient pressure conditions are summarized in Table 4. Converting products of glycolysis reaction find an application in the synthesis of various value-added products. The attempted filed in which they utilized are shown in Figure 5 [152-170].

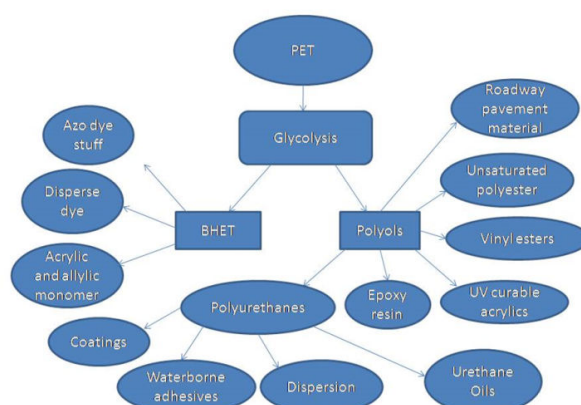


Figure 5: Glycolysed product utilization

Table 4: Optimum conditions of PET glycolysis reactions with EG in the presence of various catalysts

PET:EG ratio (w/w)	Reflux time (h)	Reaction temp (°C)	Catalyst (w/w of PET)	Yield of BHET (%)	References
1:5	3	196	1% zinc acetate	85.6	[131]
1:6	8	196	0.5% zinc acetate 0.5% sodium Bicarbonate 0.5% sodium carbonate	63 61 61	[161]
1:18	6	190	1% zinc acetate	87	[163]
1:14	8	197	0.5% zinc chloride	74	[162]
1:7.6	8	196	1% sodium carbonate	70	[164]
1:4	3	180	10% urea	78	[165]
1:6	8	196	1% Y-zeolite/1% β-zeolite	65	[167]
1:10	2	190	5% [bmim]OH	71	[167]
1:4	8	180	80% [bmim]Cl	78	[168]
1:11	2	190	1.25% [bmim]ZnCl ₃	84.9	[169]
0.96:5	3.5	190	0.7% TBD	78	[170]

CONCLUSION AND FUTURE DIRECTIONS

This review outlined polyesters, with the emphasis on history, synthesis, recent works, and its recycling. There can be no doubt that polyesters will continue to be one of the most important classes of the polymer. Polyesters have been manufactured by conventional and novel polymerization processes. The major disadvantage of the conventional polymerization method for PET is a long polymerization time. However, a novel manufacturing method, namely ring-opening polymerization (ROP) of cyclic oligoesters, offers advantages over the conventional polymerization method. Higher polymer molecular weight can be achieved in shorter reaction times under atmospheric pressure, and no by-product is generated. Recent developments in the field of polyesters show that bio-based resources can potentially prove as a substitute for conventional petrochemical routes, because of what polyester has a high physical, chemical properties, and more environmentally friendly today. So that polyesters have become the focus of interdisciplinary research. PET is the workhorse of the polyesters and found an application in the various field due to

its unique physical, chemical properties, and easy processibility. Because of what, world production and consumption increase dramatically in past decades. Recycling of PET is become a necessity due to its non-biodegradability and consciousness. PET enjoys the advantage of easy reprocess ability and recyclability. Publications review as reported above indicates that many scientific findings were made in the field of recycling of PET, and we resolve that most of the attempts had been made on bottle grade PET waste. There was a mere investigation had found to recycle the fiber grade PET waste. Also, few attempts had made in recycling PET waste by utilizing biomaterial as a replacement to petroleum diols. So that researchers can make an attempt to recycle FG-PET and also used the various biomaterials in recycling practice.

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