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Engineering and Specialty Thermoplastics: Polyethers and Polyesters

State-of-the-art, New Challenges and Opportunities

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1.1 Introduction

Polyethers and polyesters are oxygen containing polymers. These polymers in general contain functional groups of ethers (polyethers) or esters (polyesters) in the main chain of the macromolecule; they may be saturated or unsaturated. Thermoplastic polymers generally refer to a class of plastic used in a variety of markets and applications especially in the transportation sector, including automotive exterior and interior fascia. They are usually injection molded into the desired article though there is increasing use of sheet and profile extrusion/thermoforming and other processes. These useful characteristics have, in the past two decades, led to extensive commercial development and use of a variety of polyethers. Poly(propylene oxide) has become the basis of the large scale, world-wide development of "one-shot" polyurethane foam rubber, for mattresses, furniture, cushions, padding, etc. Linear poly(2,6-xylenol) is made on a large scale as an engineering plastic with important combination of properties, such as high glass transition temperature, good

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thermal stability, good electrical properties, excellent adhesion and ready solubility in common organic solvents.

Polyethers are usually more elastic than polyesters. Polyethers and polyesters may enter into chemical reactions at the end functional groups, with an increase in molecular weight; unsaturated polyethers and polyesters undergo cross-linking to form three-dimensional structures. Polyesters are hydrolyzed in the presence of acids and alkalies, whereas polyethers are considerably more resistant to hydrolysis. The properties of polyethers and polyesters determine their uses. For example, low-molecular-weight unsaturated polyethers and polyesters are used as components for adhesives, paints, and varnishes, and also for impregnation. High-molecular-weight polyesters are used in the manufacture of plastics (for example, polycarbonates), films, and fibers. The highly diverse properties of polyethers and polyesters depend on chemical composition, structure, and molecular weight, and also on the presence of functional groups (—OH and —COOH).

1.2 Polyesters Synthesis

Polyesters are polymers obtained by condensation reaction of difunctional reactants and are characterized by the presence of ester functions (-COO-) along the chain. Table 1.1 shows the types, nature of the repeating unit and manufacturing methods of different types of polyesters. Polyesters are prepared from chemical resources found mainly in petroleum and are manufactured in fibers, films and objects with simple or complex shapes. Linear polyester can be classified into three classes: aliphatic, partly aromatic and aromatic polymers. Aliphatic polyesters are obtained from aliphatic dicarboxylic acids (or esters) and aliphatic diols. Partly aromatics are obtained from aromatic dicarboxylic acids (or esters) and aliphatic diols and aromatic polyesters have all ester functions attached to aromatic rings. Polyesters as thermoplastics may change shape after the application of heat. While combustible at high temperatures, polyesters tend to shrink away from flames and self-extinguish upon ignition. Polyester fibres have high tenacity and E-modulus as well as low water absorption and minimal shrinkage in comparison with other industrial fibres.

The general structure of linear polyesters is as follows:

$$H{-}[{-}OAO{-}CO{-}A'{-}CO{-}]_n{-}OH$$

Table 1.1 Methods and examples of some polyesters.

Type of Polyesters	Repeating Units	Examples	Manufacturing Methods
Aliphatic	Homo-polymer	Polyglycolide or Polyglycolic acid (PGA)	Polycondensation of glycolic acid
		Polylactic acid (PLA)	Ring-opening polymerization of lactide
		Polycaprolactone (PCL)	Ring-opening polymerization of caprolactone
	Copolymer	Polyethylene adipate (PEA)	
		Polyhydroxyalkanoate (PHA)	
Semi-aromatic	Copolymer	Polyethylene terephtalate (PET)	Polycondensation of terephthalic acid with ethylene glycol
		Polybutylene terephthalate (PBT)	Polycondensation of terephthalic acid with 2,3-butanediol
		Polytrimethylene terephthalate (PTT)	Polycondensation of terephthalic acid with 1,3-propanediol
		Polyethylene naphthalate (PEN)	
Aromatic		Vectran	Polycondensation of 4-hydroxybenzoic acid and 6-hydroxy-naphthalene-2-carboxylic acid

In this A is a hydrocarbon radical and A′ is an organic or inorganic acid radical (for example, polyethylene terephthalate, nucleic acids). They are prepared by polycondensation of glycols with dibasic acids or their anhydrides, or hydroxy acids. Branched polyesters (for example, alkyd resins) or cross-linked polyesters are produced by using polyhydric alcohols (more than two OH groups; for example, glycerol, and pentaerythritol and various polyols).

1.3 Polyethers

In each of these polyethers, the ether link is part of the "backbone" of the polymer chain. The ether linkage makes an important contribution to the physical properties and chemical stability on which the utility is based.

1.3.1 Aromatic Polyethers

The phenyl ether polymers are a class of polyethers containing aromatic cycles in their main chain. The examples include: polyphenyl ether (PPE) and poly (p-phenylene oxide) (PPO).

1.4 Individual Polyethers and Polyesters and Their Application

1.4.1 Poly (Phenylene Oxide)

PPO is one of the most important engineering plastics first synthesized by Hay *et al* in 1959 by the oxidative polymerization of 2,6-dimethylphenol using copper(I) chloride/pyridine catalyst under oxygen (1–4). Poly(phenylene oxide) (PPO) is a thermoplastic, linear, noncrystalline polyether commercially produced by the oxidative polymerization of 2,6-dimethylphenol in the presence of a copper-amine catalyst. PPO has become one of the most important engineering plastics widely used for a broad range of applications due to its unique combination of mechanical properties, low moisture absorption, excellent electrical insulation property, dimension stability and inherent flame resistance. PPO finds applications in automotive instrument panels, internal decoration and exterior decoration parts. Typical applications include wheel covers, fenders, doors and exterior vertical body panels. In these applications, they offer good processibility, PPO also finds wide range of applications in electrical and electronic components, mechanical appliances. These include color TV output transformer, air conditioning electric control boxes, deflection yoke, bobbins and fly back transformer. The flame retardance, low moisture absorption and excellent electrical properties of PPO contribute the wide applications in the electric field. PPO is also used for the manufacture of office equipment such as photocopying machines stand, base, middle box, bottom box, flap, fax machine shell, bearing, photocopier toner, computer plug-ins, printer etc. The high stiffness, impact strength, heat resistance, dimension stability and color ability are the required properties from PPO in these applications. Other applications include fluid handling and water pump housings, IC trays and food packaging, building and construction.

1.4.2 Polyether Ether Ketone

Poly (ether ether ketone) (PEEK) is a highly aromatic semi-crystalline thermoplastic. It is one of the highest performing polymers due to its good properties. In 1962, Bonner in DuPont suggested the Friedel-Crafts catalyzed polymerization of diphenyl ether and aromatic diacid chloride or phosgene to yield PEK, which was subject to significant branching or crosslinking problems (5). PEEKs are lightweight engineering plastics well-suited for exterior applications in aerospace contacting with atmospheric particulates and chemicals, while interior applications demand the durability, flammability and low smoke toxicity properties of PEEK. In automobile applications, PEEK can be a lightweight, high performance metal replacement solution for longer lasting applications. PEEK offers excellent mechanical performance at high temperatures and can replace metals and other polymers due to its unique combination of outstanding wear performance, processing flexibility, and excellent chemical resistance including all automotive fluids. Its applications include piston units, seals, washers, bearings, transmission, braking and air-conditioning systems, actuators, gears and electronics/sensors. Due to its environmental and regulatory advantages as they readily meet the demands of lead-free solder processes while being fully recyclable and naturally flame retardant without the need for toxic additives, PEEK also found applications in mobile phones, circuit boards, and audio speakers to printers, copiers, sensors and connectors via an exceptional combination of benefits including wear resistance, processing flexibility, dimensional stability, low out gassing and moisture absorption, and high temperature resistance. In energy applications such as finding and recovering oil in offshore reserves or deepwater horizons, PEEK is a vital link in the exploration, development and delivery process, ranging from seismic surveys to refining for longer-life parts and reduced maintenance downtimes. PEEK resins, coatings and films can be made to conform to FDA requirements and are considered safe for repeated use in food contact. PEEK has been proven to maintain mechanical and chemical properties past 3,000 hours in high-pressure steam. It has outstanding stability upon exposure to radiation and will withstand most chemicals and gasses. These properties enable applications of PEEK in medical OEMs as biocompatible polymers for devices. For example, the biocompatible Invibio® PEEK from Victrex Plc provides a wide-range of solutions for human implantation, and blood, bone or tissue contact of 24 hours or more. PEEK also established applications in some key semiconductor applications include CMP rings, LCD carriers, FOUPs, wafer carriers, wafer effectors, wafer wands, equipment components, dry and wet etch parts, and IC transport/testing parts such as high heat matrix trays and IC test sockets. In addition, PEEK films, e.g. APTIV ™, are featured in applications such as aerospace films, loudspeaker diaphragms, voice coil bobbins, high performance labels, pressure-sensitive adhesive tapes, printed circuit substrates and more. PEEK in either a liquid or powder form, e.g. VICOTE®, as a high-temperature performance coating, is applied to industrial parts, bearings, glass fiber, molds, energy piping, or automotive parts to improve the overall wear and life of their applications.

1.4.3 Poly(Ethylene Terephthalate)

PET production grew rapidly and during the two last decades. PET has become a material of choice in various applications. Annual global production at the end of the 1990s was approximately 24 million tones. Currently, annual production is close to 60 million tones (6–8). Poly(ethylene terephthalate) (abbreviated PET or PETE) is a semi-aromatic thermoplastic polyester obtained by condensation reaction of difunctional reactants and well-known for more than 60 years. PET is commonly produced by esterification reaction between terephthalic acid and ethylene glycol with water as a byproduct or by transesterification reaction between ethylene glycol and dimethyl terephthalate with methanol as a byproduct. In order to obtain high molar masses polymers, solid-state polymerization is carried out. PET is one of the most important industrial polymers because of its excellent properties as tensile impact strength, chemical resistance, processability, clarity, thermal stability and others. The main applications of PET are fibers for textiles, films and bottles. PET materials were manufactured using extrusion, injection molding and blow molding techniques. PET finds a lot of applications. In packaging field, PET finds a lot of applications due to easy machineablility, high strength, dimensional stability over a broad temperature range, crystal clarity, printability, moisture and solvent resistance, barrier against oxygen and water vapor. In electrical applications, PET is finds uses in motors, wires, cables, transformers and high-voltage distribution equipment, hermetic applications with refrigerator and air conditioner motosr. PET is also used in digital imaging, overhead transparencies, printing and pre-press films, color proofing, printing plates etc.

1.4.4 Poly(Butylene Terephthalate)

Synthesis, properties and application of thermoplastic polyester, poly(buthylene terephthalate) (PBT), are well documented in literature. The advantages and disadvantages of two synthetic routes–from dimethyl terephthalate (DMT) and terephthalic (TPA) have been discussed widely. The reaction conditions of the DMT route, as the main industrial synthetic route, are described elsewhere. Blending of PBT with other polymers is a powerful route for obtaining materials with improved property/cost performances. A wide variety of nanoparticles, such as clays, carbon nanotubes and others, are often used for enhancement of physical, mechanical and thermal properties of PBT nanocomposites. PBT is a semi-crystalline thermoplastic polymer designed to perform in applications requiring high strength and toughness with very low creep even at elevated temperatures. It exhibits minimal moisture absorption and is resistant to many chemicals, oils, greases and solvents. The properties of PBT are strongly dependent on the crystalline portion and on the resulting morphology after processing. As a strong and light, weather, heat and chemical resistant thermoplastic polyester, PBT can be used in numerous applications: electronic and communications equipment, computers, televisions, kitchen and household appliances, industrial equipment, lighting systems, gardening and agricultural equipment, medical devices, food handling systems, pumps, bobbins and spindles as well as automotive parts in both 'under-the-hood' and exterior applications. Examples of the latter include fender extensions, cowl vents and door handles, vacuum actuators, air-conditioning valves, hydraulic transmission parts, molded-on wire connectors, lamp socket inserts and rectifier bridges. Today, most keyboard caps are made from PBT. Unmodified PBT is also used in optical fiber buffer tubes and some electrical connectors. However, the vast majority of PBTs are blended with many other ingredients to give a balance of properties for different applications. PBT is typically used in 'high temperature' applications. Industrial filters for hydraulic oil and automotive filters for diesel engines are a few typical examples. The usage of PBT in automotive filters is very popular compared to traditional poly(propylene) (PP), as PBT filters last longer and allow higher vehicle mileage between oil changes. Blood filtration is another application area, since PBT is a good candidate for use as a filter - thanks to its outstanding wettability and fine fiber size. Leukocyte filters for filtering erythrocytes and thrombocyte concentrates as well as whole blood are becoming more important in daily hospital use. An illustration of a typical blood filter used during open-heart surgery can be found in literature. PBT can be effectively sterilized, which renders it suitable for other medical applications. PBT monofilaments have been used in certain tire and hose reinforcements, as well as in paintbrushes and toothbrushes. Industrial weaving products have also been made from thermoplastic polyesters such as PBT, although it is not typically used in textile applications due to its perceived high price. Further, PBT is widely used to form electrical connectors. As a result of dimensional stability and good electrical properties, PBT permits automated soldering. Another specialist field is its application as light-wave cables. In industry, PBT polymers are used for valves, brackets, water meter components, casings, and replacements for metals in many types of load-bearing parts. Since they are light, colorful and easy to mould with good friction properties, PBT polymers are also used in hair dryers, pocket calculations and pen barrels. Iron and toaster housings, cooker/fryer handles, hair drier nozzles and food processor blades can all be made of PBT. PBT, through its many blended products, can be tailored to suit numerous applications. Nowadays, a broad range of pure and modified

PBT grades are available, as well as a whole spectrum of PBT blends, with numerous applications. In general, the properties of pure polymers do not always meet the demands for the application of the customer. Often, the bulk properties have to be modified to make polymer suitable for some specific application. Nowadays, a broad range of pure and modified PBT grades are available, as well as a whole spectrum of PBT blends that are widely applied in the automotive and electric/electronic industries [9–13].

1.4.5 Polyesters Containing Cyclohexanedimethanol Units

Aliphatic and aromatic polyesters and copolyesters containing cyclohexanedimethanol units have received a lot of attention. Thermal and mechanical properties as well as thermal and chemical stability of these polymers have already been studied with special reference to the polyester structure. Compounding, processing, recycling and applications of these polyesters and copolyesters are reported. These polymers also find applications in the field of polymer blends and composites. Thus aliphatic polyesters and copolyesters are produced to generate biodegradable or biocompatible objects, as it is the case of poly(1,4-cyclohexylenedimethylene fumarate), with application in the manufacture of bioresorbable bone cement composites. Polyoxaesters of 1,4-CHDM are a new class of synthetic absorbable polyesters with potential surgical applications as suture coatings, or adhesion prevention barriers. The PCT polyester, due to its crystalline nature, finds applications in the textile industry to produce fibers suitable for high temperature applications. PCT fibers can be used for pillows, cushions, bed pads, carpets, nonwoven materials etc. The high HDT of PCT makes it usable in a wide range of injection molded components for electrical, electronics, automotive, appliance, and other industrial and domestic products. Typical parts made of PCT include circuit board connectors, automotive connectors (headers), lamp sockets and relays. Both indoor and outdoor refrigerated vending machine covers, windows for recreational vehicles, windshields for snowmobiles, tinted hoods for pay phones, and helmets for bicycles and motorcycles are application examples of Polyesters cyclohexanedimethanol ($PE_{70}C_{30}T$). Exceptional attributes, as excellent ductility, biocompatibility, clarity, sterilizability and chemical resistance have led it to be used in a number of medical applications. It has been shown that thin sheets $PE_{70}C_{30}T$ foams have excellent sound absorption which opens its use in the field of acoustic isolations. Other applications are shrink labels or credit cards to the point that more than 75% of credit cards in the word are made of this polymer.

1.4.6. Liquid Crystal Polyesters

Liquid crystal to liquid crystalline polymer to polyester (LC polyester) is a long way travelled by researchers due to its unique characteristics, such as, chemical inertness, thermal stability, very high strength etc. Later, it opened many possibilities of processing such as, blending composite making, polymer dispersed liquid crystal making and as a result the innovative commercial utilization has followed a rapid track. They have wide applications in following areas: fibers, rods, sheets, composites used in mechanical and chemical industries; chip carriers, connectors, switches used in electronics; connectors, couplers, buffers used in fiber optics; interior components, brackets in aerospace; and so on. LC polyester fibers have high strength and stiffness and are lightweight. Fabrics of LC polyester fibers (such as Vectran fibers) have been used as ballistic garments, helmets, and military flak jackets. Excellent cut/tear resistance and thermal insulation also make LC polyesters fibers desirable for protective gloves and clothing. Large-diameter melt-extruded LC polyester rods have been used to replace steel wire and even used as strength members in optical cable applications. This is because LC polyester rods have the following characteristics: lightweight and flexible, excellent tensile properties, which prevent optical fibers from breaking during the lay down process, very small negative coefficient of thermal expansion, which minimize the external stress, good chemical resistance, and almost zero water regain.

1.4.7 Polylactide

The production of durable functional products without using petroleum based raw materials is a focus of much academic research today but it is also prioritized by many industries. Many questions still remain concerning the use, production and properties of bio-based and/or degradable polymers and whether or not they are more environmentally friendly than oil-based products. Polylactide is a bio-based compostable thermoplastic that is considered as one of the most promising materials for replacement of traditional volume plastics. The properties of polylactide can be tuned to resemble polystyrene, poly(ethylene terephthalate) or polyolefins by controlling the stereochemistry, by copolymerization or blending. Polylactide and its copolymers are among the most well-known and studied bioresorbable biomedical materials and have been used in biomedical applications since 1980s. The applications include resorbable sutures, implants and supports in human body such as bone screws and plates, stents, drug delivery devices and tissue engineering. Polylactide has been shown to have good or satisfactory biocompatibility and degrades in the body to non-harmful natural metabolites i.e. lactic acid. The degradation time in the body can be modified over a wide span ranging from less than one year to several years depending on the L/DL composition, porosity and degree of crystallinity. In packaging applications PLA is suitable for cups, bottles, films and containers. Applications include rigid thermoforms such as trays and lids, bottles for water, milk or oil, clamshells for food packaging, shrink wraps for packaging, candy and flower wraps, disposable salad cups and cold drink cups. Polylactide is also highly resistant to ultraviolet light and is, thus, suitable for outdoor applications. The fiber applications include shirts, furniture textiles, carpets, pillows, wipes, beddings, table clothes, curtains, mattresses, underwear and sports' clothes. Polylactide has high potential in agricultural applications such as mulch films either in pure form or blended with other polymers such as thermoplastic starch. In addition polylactide is used in compostable yard bags and dog poop bags. Lactic acid based hot-melt adhesives have also been developed. Foamed PLA could be used as structural protective foams, loose-fill packaging and insulation material as an alternative for expanded polystyrene (EPS). While packaging is currently the high volume application for PLA, in the future it is predicted that approximately half of PLA production would go to textile fibers and fabrics. Other important future applications are predicted to be in transportation and building, electrical appliances and electronics.

1.4.8 Thermoplastic Copolyester Elastomers (TPEEs)

Thermoplastic copolyester elastomers are multiblock copolymers built up from so-called short crystallizable hard segments and long flexible segments. Owing to such chemical structure, TPEEs exhibit unusual combination of thermoplastic and elastomeric behavior. Physical and mechanical properties of these copolymers strongly depend on the chemical composition and the molecular structure of both hard and soft segments. By variation of the hard to soft segment ratio, the length of the soft segments and the degree of crystallinity of the hard segments, TPEEs ranging from soft to the relatively hard elastomers could be obtained. Thermoplastic copolyester elastomers are a class of polymeric materials that combine many of the properties of both thermoplastics and rubbers. In commercial application, TPEEs could replace a variety of conventional materials, such as metal, leather and rubber. Since the strength of TPEEs is 2 to 15 times higher than chemically cross-linked elastomers, they could replace composites of rubber with metal, glass and fabric without reinforcement. The automotive industry is the main end user of TPEEs, being applied in boots and bellows, air duct and air bag covers. The TPEEs resistance to oil and chemicals, together with their flexibility and abrasion resistance, make them suitable for application in many types of cable jacketing and hose, both as tubes and covers. Taking advantage of their mechanical strength combined with environmental resistance, TPEEs can be used in the fiber optics technology for cable jackets. In addition, various types of powdered TPEEs are used as protective coatings on metal parts of all sizes and complexities. They may also be applied by such techniques as fluidized-bed coating, electrostatic deposition, flame spray, and plasma spray. These thermoplastic elastomers are also widely used, both with and without tensile-reinforcing cords, as power transmission belts and roll covers, and in a wide range of molded goods, such as diaphragms, gaskets, seals, O rings, plugs and pads. TPEE films are also applied as laminates for the carpet underlay. Important application of TPEEs is in medical devices owing to their compatibility with human blood and tissue, as well as inherent resistance to radiation used for sterilization. For example, biodegradable TPEEs based on PBT and PEO under trade name PolyActive could be used in tissue engineering scaffold, bone replacement, wound dressing, artificial skin and as drug release carrier, due to mechanical properties similar to native cartilage.

1.4.9 Polycarbonate (PC)

Polycarbonate (PC) has good insulating properties. As a result, today the major application of PC is for the production of housings for power tools, connectors, and, more in general, for electrically insulating and electronic devices. Polycarbonate is tough and impact-resistant (the second property in the list). Hence it is used in hard-hats, helmets and in sports. For the same reason, it finds application as stiffener in polymer blends with PBT and PET and with ABS plastic. Polycarbonate is transparent. It is used in the car industry for lenses. As discussed previously, high molar-mass PC (with M_n= 50000 M_w=100000 gram/mol) is more expensive than low molar-mass PC (with M_n= 6000 M_w=12000). In compact-disc (and DVD) manufacturing, the upper face is usually made of an inexpensive polycarbonate or made of a copolycarbonate. The face is covered by a very thin metal layer (usually Al) which reflects diode-laser light. The metallic layer must be protected by a plastic layer (this constitutes the lower face). It is made of polystyrene (or other commodity plastic). Polycarbonates (PC) were prepared more than a century ago by reacting hydroquinone or resorcinol with phosgene in pyridine, but the crystalline polymers produced were brittle and difficult to process. Due to the high engineering performance of PC polymer, they find extensive uses in mechanical, electrical, chemical and thermal fields. The thermo and photo oxidative behaviours, the hydrolytic stability and the consequent modification on PC have been studied. Diepens and co-workers (14) have prepared unstabilized bisphenol A polycarbonate (BPA-PC) films and investigated different studies using UV and IR spectroscopy.

1.5 New Challenges and Opportunities

The green synthesis of polyesters and polyethers from renewable resources using new nano catalyst systems is one of the challenging tasks. Metal alkoxide bonds are key players in the catalytic reactions involving the ring-opening polymerization (ROP) of cyclic esters to give polyesters and in the copolymerization of epoxides and carbon dioxide to give polycarbonates. Polyesters have continuously found new and interesting applications, in many cases without any substituting alternative. The application opportunities of polyesters including high-performance materials are still not exhausted.

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