

Handbook of Engineering and Specialty Thermoplastics

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Handbook of Engineering and Specialty Thermoplastics

Volume 3
Polyethers and Polyesters

Sabu Thomas and Visakh P.M.



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Poly(ethylene terephthalate)

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Abstract

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. Annual world PET production is around 60 millions tons. PET materials were manufactured using extrusion, injection molding and blow molding techniques.

Keywords: Thermoplastic, polyester, poly(ethylene terephthalate), PET, polycondensation, films, fibers, bottles, thermal properties, mechanical properties, chemical stability, processing, recycling, blends, nanocomposites, surface modification.

4.1 Introduction and History

Polyesters are polymers obtained by condensation reaction of difunctional reactants and are characterized by the presence of ester functions (-COO-) along the chain. 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 in three classes: aliphatic, partly aromatic and aromatic polymers. Aliphatic polyesters are obtained from aliphatic dicarboxylic acids (or esters) and aliphatic diols. Partly aromatic are obtained from aromatic dicarboxylic acids (or esters) and aliphatic diols and aromatic polyesters have all ester functions attached to aromatic rings (1).

The history of thermoplastic polyester goes back to 1929 with the pioneering work of Carothers. The first aromatic polyester of importance is poly(ethylene terephthalate) commonly abbreviated PET (or PETE) and was prepared by Whinfield and Dickson. In 1941, they created the first polyester fibers called Terylene and first manufactured by Imperial Chemical Industries (ICI). PET was produced commercially in 1953 as fiber for textile industry (Dacron) by Dupont using modified nylon technology. Dupont polyester research rapidly leads to a whole range of trademarked products as Mylar, a strong polyester film.

PET production grew rapidly and during the two last decades, PET is 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 closed to 60 million tones (1–3).

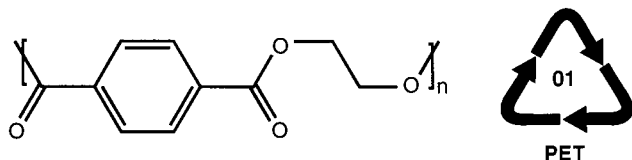
Depending on its processing and thermal history, this polymer can be transparent, in its amorphous state; or translucent in its semi-crystalline state. PET can be semi-rigid or rigid depending on its thickness. With excellent barrier (CO_2 permeation) and mechanical properties, PET is becoming the polymer of choice for food and beverage packaging applications, even replacing traditional materials such as metals or glass. Furthermore, polyester and modified polyesters are found in many applications such as fibers, automotive parts, architectural glazing and window films.

An other important thermoplastic polyester is poly(butylene terephthalate) (PBT), PBT has better processability than PET with lower melting temperature.

4.2 Polymerization and Fabrication

Poly(ethylene terephthalate) is a linear partly aromatic polyester with a repeating unit $\text{C}_{10}\text{H}_8\text{O}_4$ presented below (Scheme 4.1).

In this scheme is also presented the plastic identification code (PIC) of PET.



Scheme 4.1 Chemical structure of poly(ethylene terephthalate) and PET identification code.

PET could be synthesized in two steps: prepolymerization followed by polycondensation steps. For the prepolymerization step, two main procedures were used in industry:

- Esterification reaction between terephthalic acid and ethylene glycol
- Transesterification reaction between dimethyl terephthalate and ethylene glycol

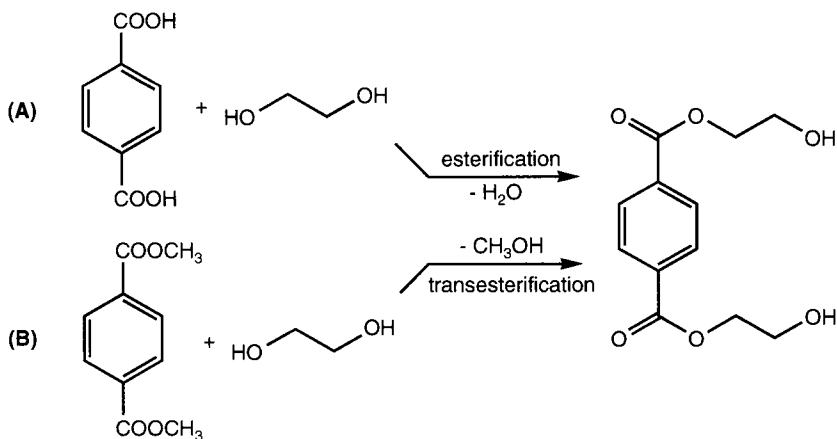
4.2.1 First Step: Prepolymerization

This prepolymerization could be performed via transesterification or direct esterification

- The monomers for transesterification reaction are dimethyl terephthalate and ethylene glycol (Scheme 4.2 (B)). An excess of ethylene glycol is used and the temperature should be 150–210 °C. When the reaction medium reaches the temperature, catalyst is added. Typical catalysts for transesterification reaction are derived-metal compounds based on Ti, Mn, Ge, Ca, Zn, Sn... The catalyst amount represents 0.05–0.5 % of the total mass of the reaction medium. Antimony oxide historically emerged as the catalyst of choice. Germanium oxide is also used but although it is a more active catalyst than antimony, the high cost of the germanium excludes its common used in commercial production of PET. During the reaction, methanol is formed and is collected by distillation in order to displace the equilibrium of the reaction.

When distillation of methanol ceases, the reaction is completed and bis-(2-hydroxyethyl) terephthalate is obtained (2,3).

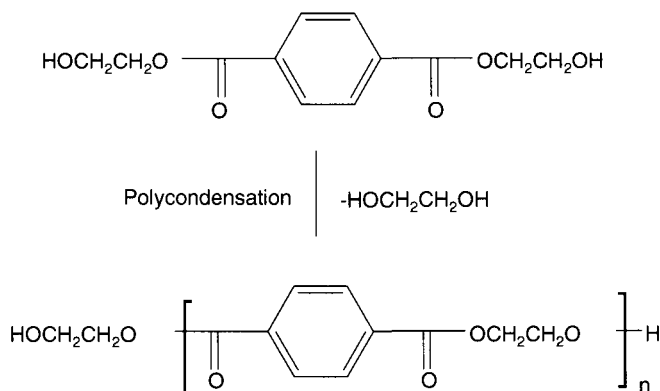
- The monomers for direct esterification reaction are terephthalic acid and ethylene glycol (Scheme 4.2 (A)). In this case, the reaction medium is heterogeneous because terephthalic acid is hard to dissolve in ethylene glycol. However, the use of small monomer feed ratio and high reaction temperature are useful to enhance the solubility. Water formed during the reaction was collected to estimate the reaction conversion. Addition of a catalyst is not necessary since the acid group of terephthalic acid self-catalyze the reaction. But, when concentration of acid groups decrease, metal catalysts could be employed to maintain the reaction rate (2).



Scheme 4.2 Preparation of bis-(2-hydroxyethyl) terephthalate by direct esterification (A) and transesterification (B) reaction.

4.2.2 Second Step: Polycondensation

Bis-(2-hydroxyethyl) terephthalate obtained during the first step is heated between 280 °C and 300 °C under vacuum (10–50 Pa). Ethylene glycol is formed and is eliminated as by-product. Polymers with polymerization degree closed to 100 are classically obtained. The reaction time including the two steps is long and usually varies from 5 to 10 h. Reaction time could be reduced by high temperature



and the addition of a metal catalyst as Sb_2O_3 , $\text{Sb}(\text{OAc})_3$, $\text{Ti}(\text{OC}_4\text{H}_9)_4$ or GeO_2 is necessary. Diethylene glycol ($\text{HO}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$) could be generated during this reaction and incorporated in the polymer (1-4).

4.2.3 Solid-State Polymerization

Solid-state polymerization allows obtaining high molar mass (> 30,000 g/mol number average molar mass) and high viscosity polymer without the need of high reaction temperature that can produce degradation reactions. The solid-state polymerization is carried out around 220–230 °C, between the glass transition temperature and the crystalline melting temperature of PET allowing chain mobility and residual monomers diffusion in the polymer. PET obtained by solid-state polymerization had higher melting point and higher crystallinity than conventional PET (2).

Commercial PET obtained via polycondensation reaction contains small quantities of low molar masses cyclic molecules with high molar mass linear macromolecules. The cyclic oligomers could create problems during PET processing but removal of cyclic oligomers is not currently practiced in industry.

Main commercial names and suppliers of PET are Arnite (DSM), Crastine (Du Pont), Dacron (Invista), Hostaphan Films (Mitsubishi), Impet (Ticona), Melinex (Dupont), Mylar (Du Pont Teijin Films), Petra (BASF), Pocan (Bayer), Raditer (Radici group), Rynite (Dupont), Tergal (Tergal Industries), Terylene (ICI).

4.3 Solid-State Properties

4.3.1 Mechanical Properties

Mechanical properties of PET depend on its final form and hence on the fabrication process (see section 4.6). PET materials can be obtained under the form of amorphous or semi-crystalline films, oriented films or fibers. The simplest way to evaluate the mechanical property of a material is the establishment of stress-strain curves (Figure 4.1). From these curves, it is easy to obtain the Modulus of elasticity (or Young's Modulus), the strength to break (σ_r) and the strain to break (ϵ_r). These values are collected in Table 4.1 for amorphous, semi-crystalline and glass fiber reinforced PET material (film obtained by injection).

Oriented films are obtained by extrusion (for a temperature around 250 °C) through a flat die. After the die the film is amorphous with a σ_r of 30 MPa and a ϵ_r of 500 %. After monoorientation by stretching σ_r increases up to 500 MPa but the film is very brittle.

On the other hand, after biorientation and thermal treatment, a film with good mechanical properties is obtained ($E = 3\text{--}4.2$ GPa and ϵ_r of 70–130 %).

These films present excellent resistance to biological agents and are autoextinguishable. Their main applications are in the electric field (condenser, insulation, etc) and sterilizable packaging. They don't need to be plasticized.

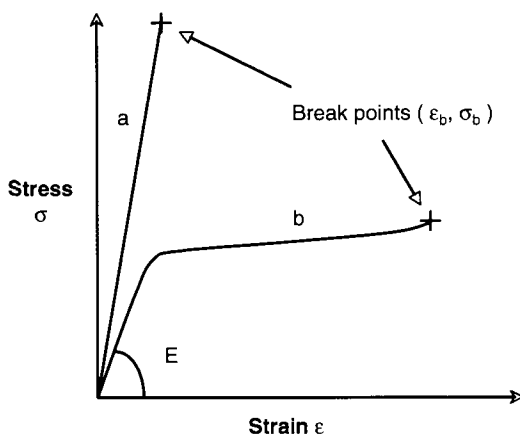


Figure 4.1 Typical stress-strain curves for (a) brittle polymer and (b) softer polymer that yields to stress.

Table 4.1 Mechanical properties of amorphous and semi-crystalline PET.

PET sample	Amorphous		Semi-crystalline	
	Non-loaded	Loaded with 20 % glass fibers	Non-loaded	Loaded with 20 % glass fibers
Modulus of elasticity, E (GPa)	2	5	2.4	5.6
Ultimate tensile strength, σ_r (MPa)	45	114	38.5	138
Elongation at break, ϵ_r (%)	250	3	90	3

Mechanical properties of PET fibers commonly used in the textile field are characterized by high values of both Young's Modulus (2–2.7 GPa) and σ_r and by low ϵ_r values. In the case of normal tenacity PET fibers, σ_r is 3400–6350 MPa with ϵ_r of 19–40 % and for high tenacity PET fibers σ_r increases up to 7300–11550 MPa with ϵ_r values of 10–13 % (5–7).

4.3.2 Thermal Properties

Thermal properties of PET are greatly influenced by the presence of the aromatic benzyl group substituted in 1,4 (para) positions which provides an overall stiffness of the polymer repeating unit. It explains the relatively high thermal stability (for a polymer) of PET. The value of the experimental melting temperature of commercial PET (fibers) is in the range 250 – 265 °C. It is possible to calculate a theoretical value of 292 °C which can be experimentally approached if a correct annealing process is applied (8).

The glass transition temperature (T_g) depends on the polymer chain arrangement: T_g is equal to 67 °C in an amorphous state, 81 °C in a semi-crystalline state and 125 °C in a crystalline and oriented state.

PET is a semi-crystalline polymer but amorphous PET can be obtained by rapid cooling. In fact PET crystallization is slow and 30 % of crystalline phase (triclinic crystal structure) can be obtained to the best. In this amorphous state, PET is transparent and can be

used as film and thin sheet. Light transmission can reach 85 % for films with thickness from 12 up to 125 μm and used as overhead projector transparency, photographic film, etc.

The heat deflection temperature (or heat distortion temperature (HDT)), temperature at which a polymer or plastic sample deforms under a specified load is given below for amorphous and loaded PET samples:

- 65 °C (1.8 MPa) for amorphous PET
- 224 °C (1.8 MPa) for PET with 30 % of glass fibers.

The values of thermal conductivity of PET are in the range 0.15–0.4 W/m.K and the upper working temperature is in the range 115–170 °C.

4.3.3 Gas Barrier Properties

PET films are widely used as packaging material for food, pharmaceuticals, electronics and medical products because of its good mechanical properties. PET is known for its low gases and solvents permeability. However, in order to enhance its barrier properties, many approaches were developed: crystallization, orientation, coating, metallization, copolymerization, incorporation of nanodispersed clay (2).

Classical values of PET film permeability are given below (9).

Permeability to hydrogen, 25°C	$0.4 \times 10^{-13} \text{ cm}^3 \cdot \text{cm cm}^{-2} \cdot \text{s}^{-1} \text{Pa}^{-1}$
Permeability to nitrogen, 25°C	$0.004 \times 10^{-13} \text{ cm}^3 \cdot \text{cm cm}^{-2} \cdot \text{s}^{-1} \text{Pa}^{-1}$
Permeability to oxygen, 25°C	$0.03 \times 10^{-13} \text{ cm}^3 \cdot \text{cm cm}^{-2} \cdot \text{s}^{-1} \text{Pa}^{-1}$

Oxygen permeability is influenced by the crystallinity of polymer because the diffusion of oxygen is affected by more tortuous path through polymer due to increased crystallinity, so that stretching causes the decrease of oxygen permeability. Incorporation of

Table 4.2 Density values of PE.

Amorphous PET	Semi-crystalline PET	PET loaded with 30 % glass fibers
1.30–1.34 g/cm ³	1.50 g/cm ³	1.56 g/cm ³

Refractive index of PET is in the range 1.58–1.65.

additives may also play a role in crystallinity development through their influence on crystallization.

4.3.4 Other Physical Properties

Density values (g/cm^3) of different PET grades are reported in Table 4.2.

4.4 Chemical Stability

4.4.1 Solubility and Chemical Resistance of PET

Chemical resistance of PET to different solvents and chemicals are given in the following table.

PET is insoluble in mostly all organic solvents. However it is possible to obtain PET solutions by using *o*-chlorophenol, trifluoroacetic acid, hexafluoroisopropanol (HFIP) and a mixture of phenol and trichloroethane.

In such solvents, it is possible to establish Mark-Houwink-Sakurada relationships:

$$[\eta] = K M_v^a \quad (4.1)$$

Where $[\eta]$ is the intrinsic viscosity (usually in mL/g or dL/g units), M is the viscosimetric-average molar mass and K and a are

Table 4.3 Chemical resistance of PET to different chemicals.

Chemical	Chemical resistance
Weak acid	Good
Strong acid	Poor
Weak alkali	Poor
Strong alkali	Poor
Organic solvent	Excellent
Alcohols	Good
(aromatic) Hydrocarbures	Poor
Fuels	Good
Halogens	Good
Ketones	Good

parameters depending on solvent and temperature e.g. $a = 0.695$ and $K = 5.2 \cdot 10^{-4}$ (with $[\eta]$ in dL/g in that case) using HFIP as solvent at 25 °C.

By using this kind of equation, it is possible to characterize a polymer by its intrinsic viscosity and to obtain its viscosimetric-average molar mass M_v . It is also possible to obtain the complete distribution of molar mass (DMM) by using Size Exclusion Chromatography and pure HFIP or a chloroform/HFIP 98/2 mixture as a mobile phase (eluent) (10,11).

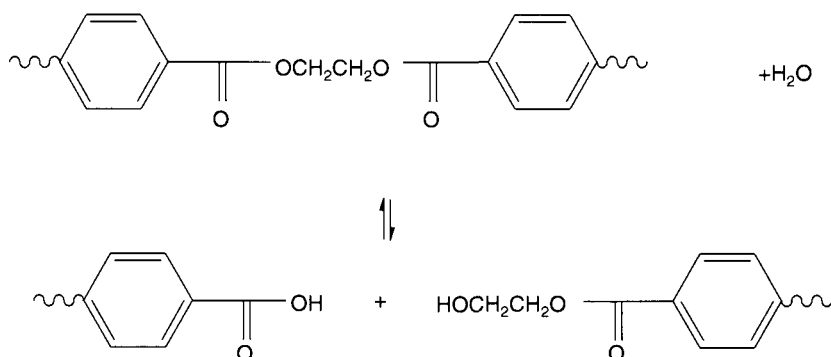
It is important to characterize M_v because it is possible to use PET with relatively low molar mass obtained by solution polycondensation to make fibers or films. For the manufacture of bottles and tire cords, PET obtained by solid-state polymerization possessing a higher molar mass must be used.

In the industry, molar masses are not generally directly obtained. Intrinsic Viscosity (I.V.) or an Index of Viscosity (viscosity measurement at only one concentration) are more often measured and related. These values are dependent on the solvent or mixture of solvents used but very often the conditions of the characterization (solvent, temperature, etc) are not mentioned (12).

4.4.2 Hydrolytic Degradation of PET

PET is a polymer sensitive to hydrolysis. Significant hydrolysis of PET occurs in moist, wet or humid conditions at temperatures above glass transition temperature. It is an important problem associated with many commercial applications. The studies about PET ageing in water or in humid atmosphere are relatively abundant in literature. The hydrolytic degradation induces chain scission. This reaction is reversible and yields to the formation of carboxylic acid and alcohol functions (Scheme 4.4). For high reaction time, this reaction is self-catalyzed by the carboxylic acid functions formed during degradation. PET is a semi-crystalline polymer and the crystalline fraction is very less reactive towards hydrolysis owing to its impermeability to water. Crystalline phase degradation occurs for high reaction time. An increase of the crystallinity at the beginning of the degradation due to plasticization by the moisture was observed (13).

Thominette and Verdu studied the hydrolysis of PET (with M_w equal to 27,000 g/mol) in boiling water. The evolution of molar mass is followed by size exclusion chromatography. It appears that



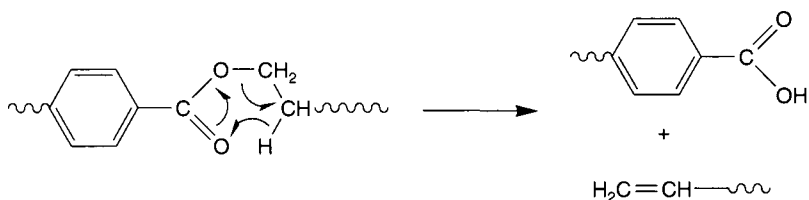
Scheme 4.4 Hydrolytic degradation of PET.

both the average molar mass and the polydispersity index decrease in a pseudohyperbolic way and tend towards asymptotic values equal to 2,000 g/mol and 1.5 for number average molar mass and polydispersity index, respectively. After complete degradation of the amorphous phase, the authors expect that the residual polymer is composed of chains of length equal to the crystalline lamellae thickness. In addition, a weight loss is observed probably due to the elimination of terephthalic acid molecules.

Under acidic or basic conditions, the rate of hydrolysis is enhanced. Under acidic conditions, the hydrolysis involved protonation of the in-chain oxygen atom of the ester function followed by reaction with water to produce hydroxyl and carboxyl end groups compounds. Under basic conditions, the hydroxide anion attacks the carbonyl oxygen atom to produce same compounds. The hydrolysis reaction can be followed by measuring the increase in the concentration of carboxyl ends with time by using classical end group analysis (14,15).

4.4.2 Thermal Degradation of PET

Thermal degradation is degradation produced at elevated temperature without oxygen. Thermal degradation of PET was found to follow a chain scission mechanism leading to carboxyl and vinyl ester ends groups and the molar mass progressively decreased (Scheme 4.5). Degradation rate was prominent only at temperature above the T_g of PET.

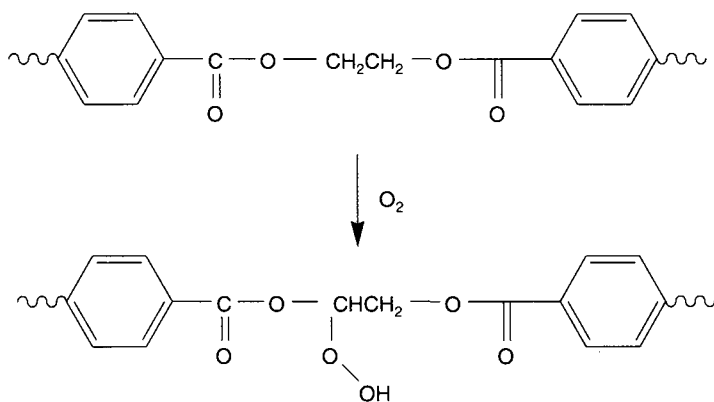


Scheme 4.5 Thermal degradation of PET (ester rearrangement).

The chemical structure of products formed during thermal degradation is function of the temperature. Degradation experiments were performed in the temperature range of 270–370 °C in order to simulate the reactions that take place during the processing of PET. Analysis of reaction products by MALDI-TOF (Matrix Assisted Laser Desorption Ionization – Time Of Flight) mass spectrometry and NMR indicate the formation of cyclic oligomers containing ester and anhydride functions (at about 300 °C). As the heating temperature rises (at about 400 °C), the cyclic oligomers become unstable and formation of oligomers bearing two carboxyl chain ends is observed. Formation of acetaldehyde was detected by ^1H NMR (16,17).

4.4.3 Thermo-oxidative Degradation of PET

Thermo-oxidation occurs at elevated temperature in the presence of oxygen. The thermo-oxidative degradation of PET is a chemical process leading to formation of initiators (hydroperoxides)



Scheme 4.6 Thermo-oxidative degradation of PET.

along the polymer backbone (Scheme 4.6). The mechanism is not completely understood but seems to follow a radical mechanism.

The labile nature of the hydrogens α to the ester groups towards abstraction by oxygen provides the initiation reaction. In the presence of oxygen, the alkyl radical formed rapidly react with oxygen to form a peroxy radical. Then, the peroxy radical abstracts hydrogen atom for polymer chain to form a hydroperoxide (18).

The next step is thermal scission of the hydroperoxide to form an alkoxy macroradical (and HO° species) that may abstract hydrogen atom to form a hydroxyl group. This species can undergo chain scission to form an acid and aldehyde chains ends.

Thermo-oxidative degradation of PET is a complex phenomenon that gives formation of many species. Cross-linking and gel formation could occur.

In industrial applications, PET materials are commonly treated in air at elevated temperature and thermo-oxidative degradation occurs.

4.5 Compounding and Special Additives

Raw polymers are manufactured and delivered in several forms: powders, pellets or flakes.

The material from which plastic objects are made is rarely a pure polymer. Usually it contains a lot of additives: plasticizers for the control of T_g , antioxidants and UV absorbers for extension of life-time, reinforcing materials such as glass fibers (GF) to give strength, and others like fillers, antidegradants, processing aids, surface modifiers, flame retardants, colorants and pigments, biocides and fungicides and coupling agents.

Preparation of these mixtures is called compounding. Compounding of the raw material and additives is a process of mixing.

4.6 Processing

Different kinds of materials and shaped objects can be produced from PET because PET is a thermoplastic polymer possessing a good thermal stability and a good fluidity in the melt. The process used depends on the kind of object desired. PET must be carefully dried before any kind of process to avoid hydrolytic degradation. The level of water content must be below 0.02 % (19,20).

4.6.1 Extrusion

Extrusion is used to obtain simple shaped objects like films, sheets, rods, tubes, etc. The extrusion process is designed to continuously convert a thermoplastic material into a particular form. A polymer under a granular form is thermomechanically treated into a cylindrical chamber containing one rotating screw or two co-rotating screws. After melting, the polymer is forced through a die and solidifies after leaving the die, forming an infinitely long object having a profile that is determined by the shape of the die: circular die, a rod; annular die, a tube; slit die, a film. The final shapes also include pipes, sheets, fibers, profiles, etc. Extruders are also used to feed the blow molding machines that produce bottles and other hollow articles and the melt spinning process to produce fibers.

4.6.2 Injection Molding

Injection molding is used to obtain objects with a complex shape. The polymer preformed mold is delivered to a mold with the desired final shape under pressure by an injector. An injector is a screw rotating in a heated barrel. The screw is operating axially and acts as a piston. The machine works in cycles. First, the feed is melted and compacted in front of the rotating screw. In the second phase, the melt is injected through a gate into the colded mold, where it solidifies. Then the molded article is ejected, and the cycle is repeated. This machine is used to prepare preforms for PET bottles for mineral water and carbonated drinks.

4.6.3 Blow Molding

There are different types of blow molding: extrusion, injection and stretch blow molding (12). Extrusion blow molding is the simplest type of blow molding used for manufacturing a wide variety of container shapes, sizes and neck openings, as well as the production of handle-ware. A piece of hot polymer tube called a parison is transferred from an extruder to between two halves of a mold, which closes around it and pinches one end of the tube. Compressed gas is then injected through the other end and presses the polymer against the mold, where it solidifies. Extrusion blow molds are generally much less expensive than injection blow molds and can be produced in a much shorter period of time. Extrusion blow

molding can be used to process HDPE, PVC, PC, PP and PETG (copolyester). Extrusion blow molding requires relatively small capital investment in equipment.

Injection blow molding can be broken down into three stages.

The first stage is where the melted plastic is injected into a split steel mold cavity. The mold produces a preform parison which resembles a test tube with a screw finish on the top.

For the second stage, the preform is then transferred on a core rod placed inside another cold and usually aluminium blow mold cavity. Air is then injected through the core rod till the preform takes the shape of the cavity.

While still on the core rod, the container is then transferred to a desired location for the third stage, where it is ejected from the machine.

Stretch blow molding is best known for producing PET bottles commonly used for water, juice and a variety of other products. Stretch blow molding has been used since the early 1970's especially for packaging detergent, and has grown in existence with the primary use for making carbonated beverage bottles.

One of the major advantages of stretch blow molding is the ability to stretch the preform in both the hoop direction and the axial direction. This biaxial stretching of material increases the tensile strength, barrier properties, drop impact, clarity, and top load in the container. With these increases it is usually possible to reduce the overall weight in a container by 10 to 15 percent less than when producing a container in another way.

Stretch blow molding is divided into two different categories single-stage and two-stage.

- Single-stage uses the extruder to inject parison into a preform mold where the plastic is rapidly cooled to form the preform. The preform is then reheated and placed in the bottle mold. Then softened parison stretches to about twice its original length. Compressed air is then blown into the stretched parison to expand to the bottles mold. Once the bottle is cooled the mold is opened and the finished bottle is emptied from the mold cavity. This technique is most effective in specialty applications, such as wide mouthed jars, where very high production rates are not a requirement.

- Two-stage stretch blow molding is the same as single-stage, except the preforms are already made. The single-stage process is usually done using one machine, where the two-stage process uses preforms that have already been made and cooled. This allows companies to either make or buy their own preforms. In this process, the machinery involved injection molds a preform, which is then transferred within the machine to another station where it is blown and then ejected from the machine. This process is used for extremely high volume runs of items such as wide mouth peanut butter jars, narrow mouth water bottles, carbonated beverage bottles, liquor bottles, etc (12).

4.7 Applications

4.7.1 PET Fibers

First commercial PET fibers were produced in 1953 by DuPont Company. PET with high molar mass is produced by the methods described below and fibers are obtained by melt spinning. In melt spinning, the fiber-forming substance is melted for extrusion through the spinneret and then directly solidified by cooling. Strong resistance to stretching and shrinking, resistant to most chemicals, quick drying, abrasion resistant, easily washed, characterizes polyester fibers. Most PET fibers are produced in a diameter range of about 10–50 μm (Figure 4.2) (21).

Major PET fibers uses are:

- Every form of clothing
- Home furnishing: carpets, draperies, sheets, pillows, wall coverings, upholstery...
- Other uses: hoses, ropes and nets, cords...

Bicomponent fibers are made by mixing two different polymers, combining the best of both polymers, which provide new possibilities for use. Woven fabrics are manufactured by the regular interlacing of two arrays of yarns fibers at right angles to each other, these being referred to as the warp and weft (Figure 4. 3).

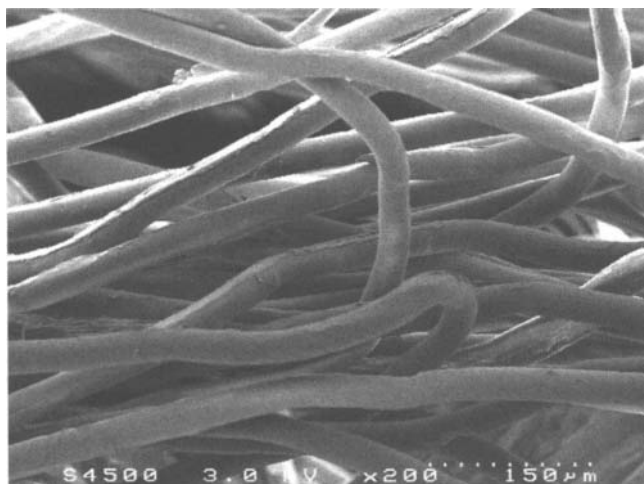


Figure 4. 2 Scanning electronic microscopy of PET fibers (with a diameter equal to 12 μm) (image T. Meylheuc, INRA-AgroParisTech, France).

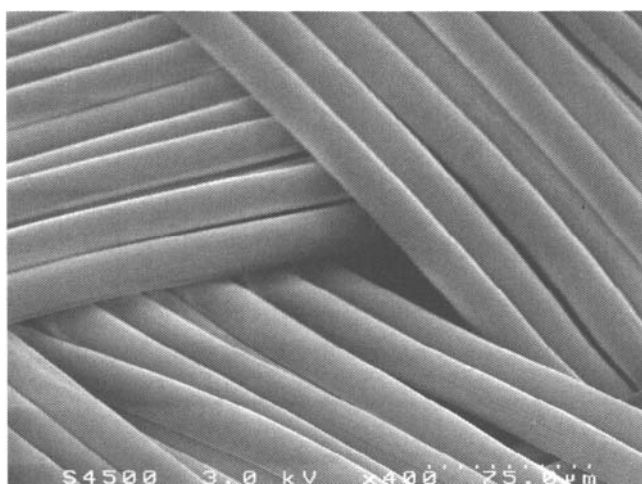


Figure 4. 3 Scanning electronic microscopy of PET fabrics with a thickness of 130 μm and a warp and weft yarns equal to 28 Tex (image T. Meylheuc, INRA-AgroParisTech, France).

4.7.2 PET Films

PET films are manufactured by extrusion (see section 4. 6.1), these films are obtained with various characteristics as thicknesses from one to several hundred microns, visual appearance from optically

clear to opaque, plain and treated surfaces with a variety of effects (such as adhesion and printability).

Applications:

- Packaging: easy machineability, high strength, dimensional stability over a broad temperature range, crystal clarity, printability, moisture and solvent resistance, barrier against oxygen and water vapor...
- Electrical: motor applications, wire, cable, transformer and high-voltage distribution equipment, hermetic applications with refrigerator and air conditioner motor (22)
- Imaging: brilliantly clear nature, smooth glossy surface, non-aging, translucent, opaque or colored (with additives), excellent flatness, digital imaging, overhead transparencies, printing and pre-press films, color proofing, printing plates.

PET track etched membranes are manufactured of thin polymer films irradiated by heavy ion beam (23). Latent tracks of heavy ions in polymer material are treated by chemical ways and as a result, membranes with regular, cylindrical pores with diameter in the range 0.1–3 μm and pore density between 10^5 to 6×10^8 pores/ cm^2 are obtained (Figure 4. 4). Typical applications of PET membranes are analytical methods, water analysis, general filtration (particles and bacteria removal, chromatography sample preparation), micro-organism analysis, blood filtration and microscopy (24)...

4.7.3 PET Bottles

PET bottles replace more and more glass bottles in the food and beverage sector. The reasons are based on several economic and environmental advantages. PET production is less expensive and energy consuming than glass production. The light weight of PET bottles is another advantage.

In 1992, PET has progressively completely replaced another synthetic polymer - polyvinylchloride (PVC) used since 1958 instead of glass - for the packaging of mineral water.

PET plastic has good barrier properties against oxygen and carbon dioxide. Therefore, it is utilized in bottles for mineral water. PET is commonly used to package soft drinks, water, juice,

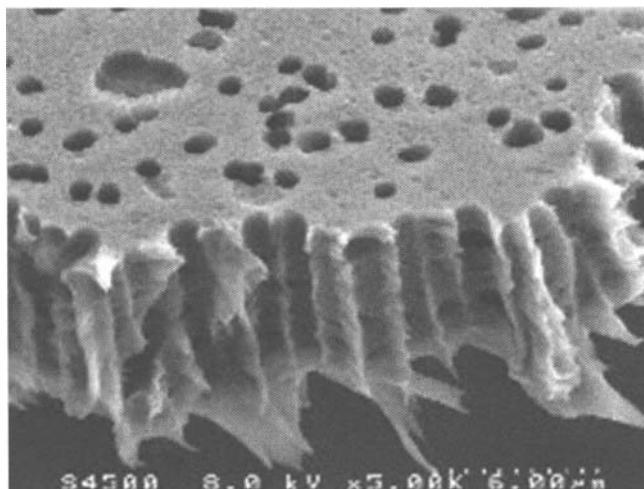


Figure 4. 4 PET track etched membranes with pores diameter equal to 200 nm (image T. Meylheuc, INRA-AgroParisTech, France).

peanut butter, salad dressings and oil, cosmetics and household cleaners (25).

4.8 Environmental Impact and Recycling

4.8.1 Generality about PET Recycling

PET bottles are estimated to take 500–700 years to biodegrade leading to serious plastic pollution problem. PET bottles are fully recyclable however the recycle rate is less than 25 % due to the lack of recycle receptacles (26).

Worldwide, approximately 4.53 million tons of PET were collected in 2007. This gave 3.64 million tons of flake. 2.6 million tons were used to produce fibers, 0.3 million tons to produce bottles, 0.37 million tons to produce APET (amorphous PET) sheets for thermoforming, 0.17 million tons to produce strapping tape and 0.12 million tons for miscellaneous applications.

PET recycling represents one of the most successful and widespread examples of polymer recycling. The recycling of PET waste can be carried out in many ways.

In 2008 45 % of all recovered European PET was used to produce polyester fibers. Fibers are used to stuff anoraks, sleeping bags and soft toys. They are woven into “polar” fleece fabric used for

sweatshirts, jackets and scarves. Such fabrics can contain up to 100 % of recycled material, and a polar fleece jacket uses 25 recycled PET bottles. Polyester fibers are currently being engineered to provide qualities that are similar to upholstery foams. Egg containers and other preformed plastic boxes (such as fruit boxes) account for about 22 % of total recycled PET usage.

Other recycled PET packaging applications include containers for water, soft drinks, juices, toiletries and household products. 22 % of European RPET (recycled PET) was used to make containers (food and non-food) in 2008.

The PET industry is in constant search for new applications for reclaimed material. There are many developing markets for recovered PET:

- Polyurethane foams can be made by using polyester polyols developed from PET flakes
- Engineered resins made from recovered PET can be injection molded to manufacture computer and automotive parts (27).

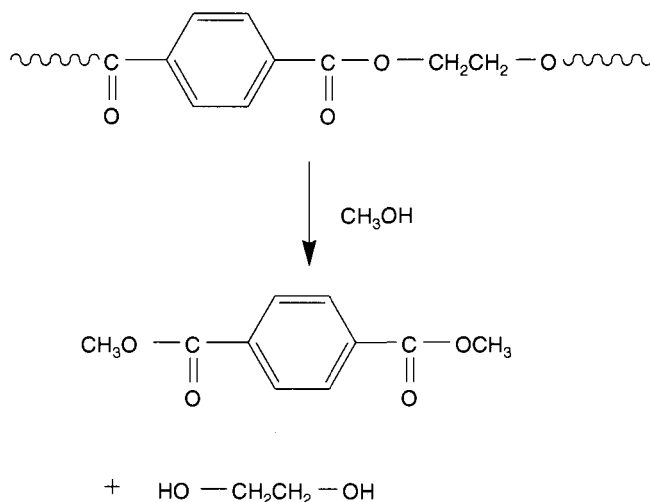
4.8.2 Chemical Recycling of PET

Chemical recycling is a process leading to total depolymerization of PET to the monomers or partial depolymerization to oligomers and other chemicals. The monomers can be polymerized again to regenerate the native polymer. The following paragraphs summarize the main methods used for the chemical recycling of PET: glycolysis, methanolysis, hydrolysis and other methods (28).

4.8.2.1 Methanolysis

Methanolysis is the main process used for chemical recycling of PET. Methanolysis consists of the degradation of polymer by methanol at high temperatures and under high-pressure conditions. The reaction is presented below (scheme 4.7). The products formed are dimethyl terephthalate and ethylene glycol, which are the reactants necessary for the production of PET using transesterification procedure.

Mitsubishi Heavy Industries (MHI) has been developing a chemical PET recycling process using supercritical methanol to



Scheme 4.7 Methanolysis of PET.

depolymerize PET material into its monomers with a short reaction time without any catalyst. Monomers recovered by this process have qualities equivalent to those of the original monomers produced from petroleum. MHI intends to establish an ideal recycling system consisting of a recycle flow from PET bottles to PET bottles (called B to B recycling) while minimizing the consumption of natural resources and the generation of wastes by making this process practicable (29).

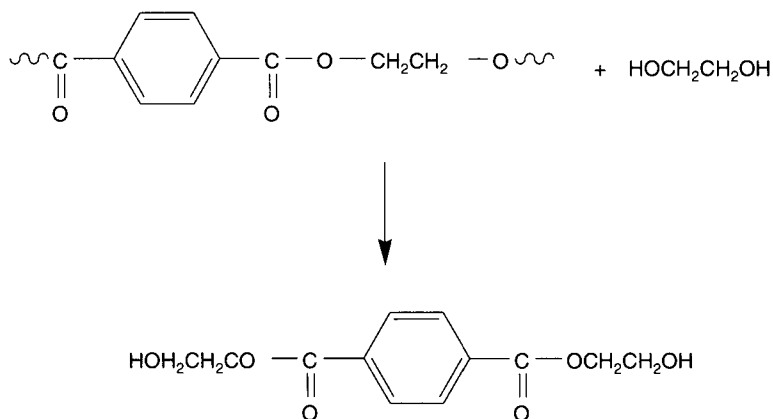
4.8.2.2 Glycolysis

Glycolysis is the second most important procedure for the chemical recycling of PET. This process is largely used on a large scale. The products of glycolysis reaction are bis-(2-hydroxyethyl) terephthalate an ethylene glycol which are reactants for the production of PET using direct esterification or transesterification reactions (Scheme 4.8).

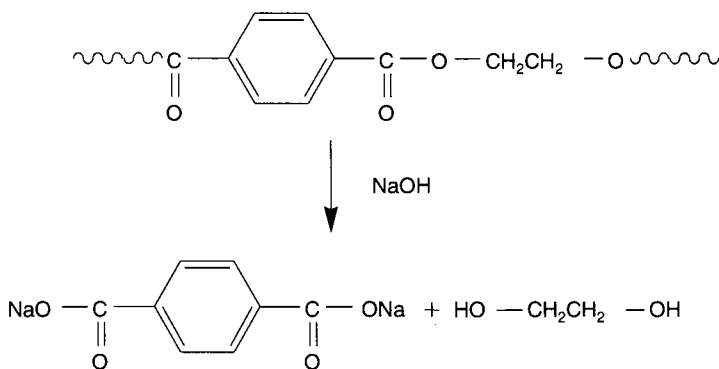
4.8.2.3 Hydrolysis

Another method of chemical PET recycling is hydrolysis reaction using acid, alkaline or neutral conditions.

Alkaline hydrolysis is usually carried out with an aqueous solution of NaOH or KOH (concentration between 4–20 wt%).

**Scheme 4.8** Glycolysis of PET.

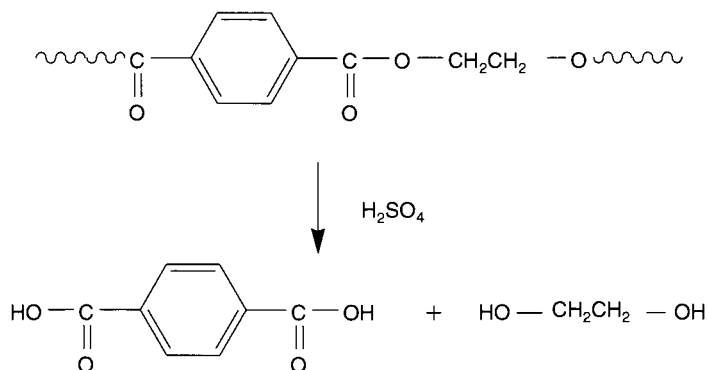
The reaction products are ethylene glycol and the disodium (or dipotassium) terephthalate salt (Scheme 4.9).

**Scheme 4.9** Alkaline hydrolysis of PET.

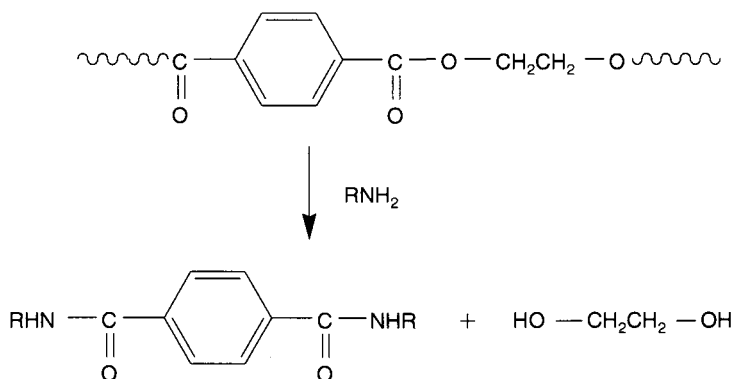
Acid hydrolysis is usually carried out with sulfuric acid. The reaction products are ethylene glycol and terephthalic acid (Scheme 4.10).

4.8.2.4 Others methods

Aminolysis is reaction of PET with an aqueous primary amine solution (as methylamine, ethylamine, ethanolamine) in the temperature range of 20 to 100°C to yield the corresponding diamide and ethylene glycol as presented on Scheme 4.11.



Scheme 4.10 Acid hydrolysis of PET.

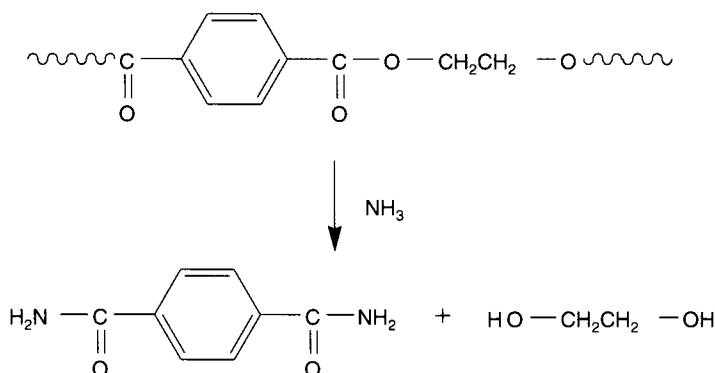


Scheme 4.11 Aminolysis of PET with primary amine (RNH_2).

Ammonolysis is reaction with ammonia to yield terephthal-diamide and ethylene glycol (Scheme 4.12).

4.8.3 Mechanical Recycling

Production of polyester fibers using cleaned bottled flakes as raw material consumes approximately 80 % less energy, and emits 70 % less CO_2 and 40 % less water than the production from petroleum. PET bottles are cut into small pieces, and then cleaned in a hot water process to remove dirt, then sorted and extruded to polyester fibers. Mechanically recycled PET is widely used on consumer products such as: carpets, T-shirts, underwear, fleece and others. During its recycling by extrusion, PET can undergo structural changes. Chain scission or crosslink could occur after several



Scheme 4.12 Ammonolysis of PET with ammonia.

successive extrusions. The global trend depends sharply of the presence or not of oxygen (30).

4.8.4 Recent Developments in PET Recycling

Very recently, possibility for using simultaneous hydrolysis and glycolysis products of waste PET in alkyd resins manufacturing was reported. In this study, waste PET flakes obtained from grinding postconsumer bottles were treated with ethylene glycol and water in the presence of xylene, an emulsifier at 180°C and zinc acetate as catalyst. The reaction products were purified by filtration, extraction, crystallization and resins were prepared by reaction with phthalic acid, glycerine or oil fatty acid (31).

4.9 Recent Developments in Poly(ethylene terephthalate) Based Blends and Composites and Their Applications

4.9.1 PET Blends

The motivations for the preparation of blends based on thermoplastic polyesters (as PET) and other polymers are (32):

- Improve the solvent resistance and processability of amorphous polymers (PC, PS...)
- reduce the mold shrinkage of polyesters associated with their crystallization
- improve toughness

4.9.1.1 PC/PET blends

Polycarbonate (PC) and polyesters blends are phase separated and are obtained without ester exchange reaction. So, the crystallinity of polyester is maintained. These blends combine the characteristics of both polymers. Catalysts could be added to promote ester exchange reaction and yielding to the disappearance of the PET crystallinity.

PC/polyester blends are resistant to hydrocarbons, alcohols, organic acids, inorganic aqueous salts and mild acid or base solutions. PC/polyester blends present superior chemical resistance over polycarbonate. This makes PC/polyester blends suitable for utilizations requiring resistance to intermittent contact with fuels or oils.

These blends find different applications (automobile industries, sporting goods, electrical...) due to their good thermal properties, toughness and chemical resistance (33).

4.9.1.2 PP/PET Blends

Among thermoplastics alloys the combination of PP and PET offers some advantages over the pure components. PET may enhance the stiffness of PP at higher temperatures while the polyolefin could facilitate PET crystallization. Non-compatibilized and compatibilized PET/PP blends were prepared. Main compatibilizers used were PP-acrylic acid copolymer, maleic anhydride modified PP (PP-g-MA), hydrogenated SBS block copolymer (SEBS-g-MA) and linear low-density polyethylene (LLDPE-g-MA) (34).

4.9.1.3 PET/PBT Blends

Commercial grade of PET and PBT were melt blended over the entire composition range using a counterrotating twin-screw extruder. PET and PBT seemed to be miscible over the entire composition range. Transesterification reaction occurs during the melt processing leading to the formation of block copolymers in the initial stage and random copolymers finally. This miscibility results in a single glass transition temperature. PET/PBT blends showed enhanced crystallizability, high elongation and impact strength than PET or PBT alone. The addition of PBT increased the processability of PET (35).

Inorganic nanoparticles (as unmodified or organic modified SiO_2 nanoparticles) are commonly utilized to fill in polymer matrix to prepare PET/PBT nanocomposites which are expected to enhance their stiffness and impact properties (36).

4.9.2 PET and Layered Silicates Nanocomposites

During the last years, much attention has been paid to polymer/layered silicate nanocomposites because remarkable improvements can be expected in mechanical, thermal, flame resistant and physicochemical properties compared to their base polymers or conventional composites (37,38).

PET is a low-cost and high-performance polymer that finds use in a wide variety of applications. Incorporation of nanodispersed clay can have a significant impact on the PET applications, potentially imparting higher flame resistance for textiles, decreasing oxygen permeability in food packaging and increasing the modulus in reinforcement and packaging products.

Several authors reported the preparation of PET/layered silicate nanocomposites. The main procedures used for nanocomposites preparations are melt polymerization, common solvent mixing and *in-situ* polymerization. In most cases, intercalated nanocomposites were obtained.

Intercalated PET montmorillonite clay nanocomposites were compounded via melt-blending in a corotating mini twin-screw extruder. Nanocomposites compounded with 1,2-dimethyl-3-N-hexadecyl imidazolium treated montmorillonite showed higher levels of dispersion and delamination than those with a typical quaternary ammonium salt (39).

Intercalated nanocomposites of PET and layered silicate were prepared with different kinds of cationic surfactants as compatibilizers by a two-step polymerization process: a melt polymerization of bis-(2-hydroxyethyl)terephthalate followed by a solid state polymerization. The obtained nanocomposites showed a higher tensile storage modulus compared with those prepared without compatibilizers (40).

4.10 Recent Advances in Surface Modification of PET Materials

Many methods of surface modification of PET were described. Among them are irradiation with high-energy particles, chemical

treatment by breaking of ester bond and grafting polymerizations. Surface treatments were developed to obtain specific surface properties as:

- Enhanced surface wettability
- Surface functionalization
- Adhesion promotion
- Molecules immobilization
- Non-fouling coating
- Biocompatibility improvement
- Barrier surface coating...

4.10.1 Surface Modification by Physical Treatment

Polymer surfaces could be modified both chemically and physically when they are exposed to a physical treatment like plasma, corona discharge, flame treatment, UV irradiation or electron and neutron beam irradiation (41)...

Plasma treatments were developed in order to modify surface properties of polymers such as adhesivity, hydrophobicity and hydrophilicity. In particular, surface treatments of PET films are of great interest in packaging industry to increase wettability or printability, to enhance optic properties and in biomedical field to improve biocompatibility. By comparison with conventional chemical treatments cold plasma techniques have the advantage of being eco-friendly by keeping bulk properties unchanged. Plasma treatment can be carried out by using chemically reactive (N_2 , O_2 , CO_2 , CF_4 , etc.) or inert (H_2 , Ar, He) gases. This treatment leads to the disruption of the polymer chains by the energetic ions and radiation generated in the plasma as well as to the introduction of functional groups on the polymer surface (42).

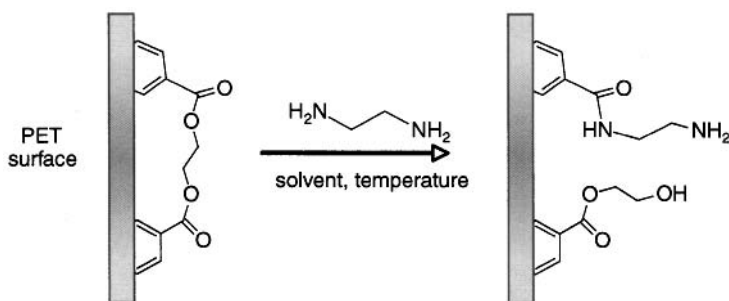
Glycopolymers were recently grafted onto PET fibers by double plasma treatment in order to obtain a surface compatible with biological material. The first step is activation of the PET surface by argon plasma treatment leading to the formation of radicals by scission of the chemical bonds. Then, fibers are exposed to air in order to form (hydro)peroxides functions. The activated fibers are dipped in glycomonomers solutions and dried. A second plasma treatment is applied to polymerize the monomers adsorbed on fibers (43).

4.10.2 Chemical Treatment

In wet chemical surface modification, a material is treated with liquid reagents to generate reactive functional groups on the surface.

Many methods were described for the chemical modification of PET surfaces. Most of them concern chemical breaking of ester bonds by reaction with low molar mass compounds containing hydroxyl or amine groups thus incorporating corresponding functionalities onto the surface. These reactions increase the hydrophilicity of the polymer surface and create anchored functionalities (when difunctional compounds were used) available for subsequent reactions.

Primary amines (as 1,2-diaminoethane, 1,6-diaminohexane or hydrazine) are often used to anchored amino groups on PET surfaces by aminolysis reaction. This reaction yields to the formation of a new amide bond and presence of free amino and alcohol groups on the surfaces according to the following reaction (Scheme 4.13). Amino-containing PET surfaces are potential biomaterial substrate for the covalent attachment of biomolecules as oligosaccharides (44).



Scheme 4.13 Aminolysis reaction of PET surface by reaction with 1,2-diaminoethane (44).

The main problem of these treatments is to find optimal conditions that do not cause severe degradation and significant decrease of mechanical properties of the PET material (films or fibers).

4.10.3 Grafting Polymerization

Grafting from techniques can be used for the modification of polymer surfaces including PET materials. In the *grafting from* approach, the polymerization is directly initiated from initiator-functionalized

surfaces. Controlled and living polymerization techniques are well suited for the preparation of polymer brushes following the *grafting from* strategy (allowing accurate control over brush thickness, composition and architecture) (45).

Recently, we report an approach for the preparation of polymer brushes on different kinds of PET surfaces (films, fibers and fabrics). The PET surfaces were first reacted with 1,2-diaminoethane by aminolysis reaction to incorporate functional groups on the surface. Then, in a second step, atom transfer radical polymerization (ATRP) initiators were grafted by reaction with bromoisobutyryl bromide. Surface-initiated ATRP was performed in bulk using styrene monomer and the adequate catalytic system in the presence of sacrificial initiator. Polymer brushes were obtained with a good controlled of polymerization (46).

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