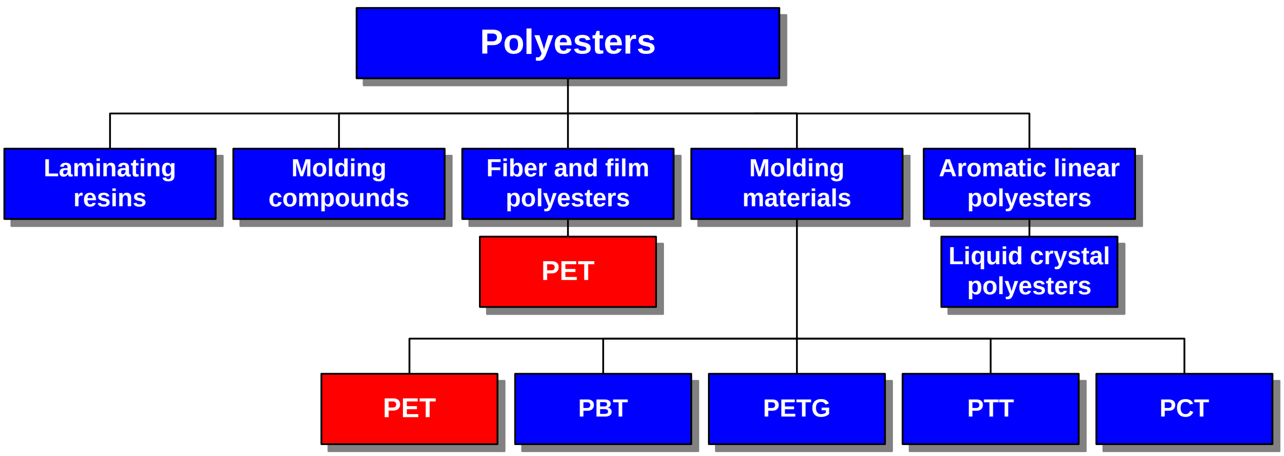
TECHNICAL NEWSLETTER

Focus on PET

Introduction

PET or poly(ethylene terephthalate) belongs to the polyester family of polymers, one of the largest and most diverse of the polymer families. This family of polymers is linked by the common feature of having an ester (-COO-) link in the main chain, but the range of polyester materials is probably the largest of all the polymer families. A basic outline of the main members of the polyester family is given below:



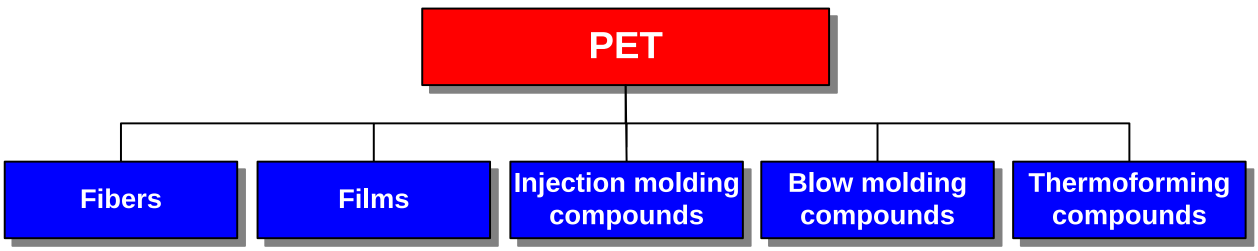
PET in the polyester family.

Members of the polyester family are used for everything from the conventional glass-fiber reinforced polyesters beloved of boat builders to the cutting edge developments in liquid crystal polyesters where the strong rigid linear molecules can be oriented in the melt-phase to be essentially self-reinforcing. This current utility is relatively exciting considering this is one of the oldest of the polymer families.

The first commercial PET polymer was announced in 1941 and followed on from the epic work of Wallace Carothers (the discoverer of nylon of polyamide). The work of Carothers on aliphatic polyesters was extended to cover aromatic polyesters by J.R.Whinfield and J.T.Dickson at the Calico Printers Association in Britain and the result was the development of poly(ethylene terephthalate). PET was initially used as a fiber for fabric production as Terylene™ (ICI) and Dacron™ (DuPont). These were the original “wash and wear” fabrics. Shirt makers and ironers of the world rejoiced and for many years polyester shirts reduced the amount of ironing in the world. Later PET film grades were developed and released as Melinex™ (ICI) and Mylar™ (DuPont) and were used for recording tape, drawing office materials, and decorative packaging materials.

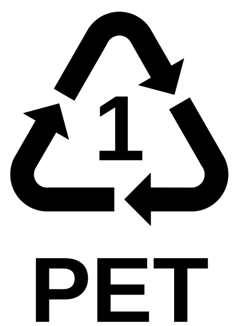
The 1970's saw the development of glass-filled PET materials as engineering polymers and the introduction of the first use of PET as a container material for drinks and other liquids. This application uses injection stretch blow molding to produce the stiff soda or water bottles that are now seen all over the world and represent the largest growth market for PET.

The excellent properties of PET are now driving the development of PET as a thermoformed product for applications, such as bakery products where the exceptional clarity displays the products and for ready-meals where the high heat distortion temperature means that the containers can be used in both traditional and microwave ovens.



The main applications of PET

PET is highly recyclable from bottles and other applications and is given the symbol shown below:



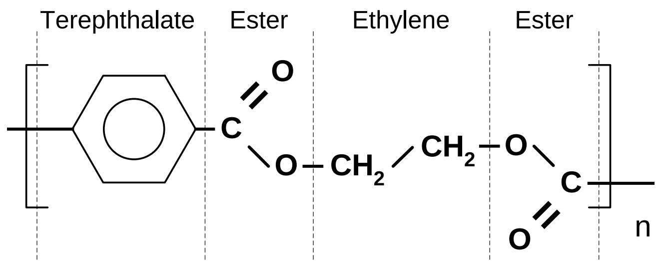
The recycling symbol for PET

The high recyclability of PET has actually led to the introduction of the designation rPET, which stands for recycled PET and there is a great deal of work being carried out around the world into improving the recycling process for PET in order to reduce the costs and enable rPET materials to be recycled into food packaging rather than "down cycled" into carpets, fleeces, or other less critical applications.

Chemical Structure

The monomer for the production of PET is ethylene terephthalate and this consists of the ethylene molecule (-CH_2 - CH_2-), two ester molecules (-COO-), and the terephthalate ring molecule. The only atomic species present in PET are therefore hydrogen, oxygen, and carbon.

Burning PET generates only carbon dioxide (CO_2) and water (H_2O). The structure of the PET monomer is shown below:



The chemical structure of the PET monomer

PET is nominally a linear crystalline plastic but the high T_g of around 80ºC (176F) compared to the melt temperature of 260ºC (500F) means that the actual amount of crystallization can be controlled in the process. Rapid cooling below T_g (using a cold tool of ≈ 50ºC (122F)) produces an amorphous polymer whereas slow cooling (using a hot tool of ≈ 130ºC (266F)) produces a crystalline polymer.

Properties

When PET is produced as an injection molding material it is generally used with glass-fiber reinforcement and has excellent properties. These grades are often used in electrical and electronics applications. PET molding materials are hard, stiff, and strong with good dimensional stability at elevated temperatures particularly if glass filled.

The major current use of PET is as an injection stretch blow molding material that uses special grades with improved clarity, toughness, and barrier properties. These grades also have improved properties to prevent the transfer of any taste to the product. This application uses the properties of the amorphous form of PET and the ability of PET to undergo strain-hardening to further improve the mechanical properties.

The growing use of PET as a thermoformed product for ready meals uses the crystalline form of PET. If PET is stretched and held above T_g the material crystallizes and becomes more opaque and more rigid. This variant is sometimes known as CPET (crystallized PET) and crystallization is often increased by the use of a nucleating agent to promote crystal formation. Therefore, the properties of PET can be varied quite considerably by changing the physical nature of the polymer via the crystallinity as well as by the addition of limited property modifiers, such as fire retardants.

The general properties of PET are typical of other semi-crystalline performance plastics:

- Very good temperature stability
- Good electrical properties
- Good chemical resistance
- Good weathering resistance
- Low coefficient of friction
- Excellent toughness
- High clarity when in amorphous state

Physical and Mechanical

Typical mechanical and thermal properties are given in the Table below:

Property	Approximate Value Natural polymer
Tensile Strength (@23ºC)	**55 – 75 MPa**
Tensile Modulus (@ 1% strain @ 23ºC)	**2 - 4 GPa**
Elongation at Break (@23ºC)	**50 - 165%**
Flexural Strength (@23ºC)	**No Break**
Izod Notched Impact Strength (@23ºC)	**13 – 35 J.m-1**
Coefficient of friction (dynamic)	**0.2 – 0.4**
Heat Deflection Temperature (0.45 MPa)	**115ºC**
Low Temperature Toughness	**¯40 - ¯60ºC**
Glass Transition Temperature	**80°C**
Coefficient of Thermal Expansion (20 – 100ºC)	**7 x 10^{-5}/ºC**
Long Term Service Temperature	**115 - 170ºC**
Melting point	**260ºC**
Specific Gravity (depends on crystallinity)	**1.3 – 1.4**
Water Absorption	**0.07 – 0.10% (50% rh)**
Transparency (depends on crystallinity)	**Transparent**

Thermal and fire

The fire behavior of PET is good and PET can achieve UL 94 HB for most grades and UL 94 V1 for flame retardant grades. The Limiting Oxygen Index (LOI) for PET is approximately 21, which means there must be over 21% oxygen present to support free combustion. Air contains approximately 21% oxygen and therefore a material with an LOI of greater than 21 will probably not support burning in an open air situation. PET is sometimes classed as “self-extinguishing.” As noted above, when PET burns, the only combustion products are hydrogen, oxygen, and carbon. PET can be safely burnt with no noxious gases being produced.

Electrical

Molding grade PET materials have generally good electrical properties although one of the main reasons they are used for these applications is the low viscosity of the melt makes it easy to fill complex and thin sections easily.

Chemical resistance

PET has good resistance to most acids, alkalis, alcohols, greases, and oils. PET is very suitable for food contact and many of the major applications involve food contact. Extensive research into the use of PET for food contact has shown that PET is very suitable for contact with both liquids (mineral water or soda water) and with solid foods, such as bakery goods.

The International Life Sciences Institute (ILSI) report on PET states:

> "*The chemistry of PET is simple and its intrinsic properties do not rely on the presence of additives. It can be recycled, and this is being done on an increasing scale. General toxicity and genotoxicity studies, on PET, its monomers and typical intermediates indicate that this material does not pose a threat to human health. There is a significant body of evidence demonstrating that PET shows no oestrogenic activity. As PET can be used in many packaging forms ranging from wrapping films to bottles, it constitutes a valuable basic packaging material for a variety of foodstuffs.*"[1]

PET has good weathering resistance to sunlight, ozone and ultra-violet light.

Optical

PET has a very high clarity and transmittance of both UV and visible wavelengths when in the amorphous state, although it can have a slight blue tint. The crystalline state is opaque. Transparent PET has a refractive index of 1.60. PET can be colored almost any color using suitable pigments, but the majority of PET used is in the clear format.

Advantages and Limitations

Advantages	Limitations
1. PET bottles and thermoformed trays can be made crystal clear to display the contents.	**1. PET materials are hygroscopic and always need drying before processing.**
2. PET oven trays can withstand microwave and low conventional oven temperatures for reheating of pre-cooked meals.	**2. PET oven trays are only for single-use and should only be used with the packaged product.**
3. PET has very low to negligible odor or taste transfer to the contents of food packaging.	**3. Reuse of reprocessed material requires recrystallization of the material.**

[1] Report on Packaging Materials: 1. Polyethylene Terephthalate (PET) for Food Packaging Applications, ILSI Europe Packaging Material Task Force. ISBN 1-57881-092-2

4. PET containers are tough, stiff, and have excellent barrier properties.	
5. PET bottles are very lightweight and reduce transport costs and increase shelf utilization in supermarkets.	
6. PET is fully recyclable.	

Processing

The high melt temperature needed for molding PET and the hygroscopic nature of the material mean that thorough drying is needed before processing. The presence of even small amounts of moisture at the high processing temperatures needed causes hydrolysis of the PET chains and significant decreases in mechanical properties.

Processing Method	Applicable
Injection molding	**Yes**
Extrusion (fibers and films)	**Yes**
Blow molding (injection stretch)	**Yes**
Thermoforming	**Yes**

PET Grades

PET is produced in a variety of grades depending on the processing method. Specific grades are available for injection molding, extrusion, blow molding, and thermoforming. The majority of material used is a homopolymer, but some grades are copolymers of PET and isophthalic acid. These copolymers have lower melting points, slower crystallization, and therefore improved clarity. This is advantageous for thick walled products where it is difficult to cool the product quickly enough to prevent crystallization.

One specific grade is PETG or glycol modified PET. This uses a copolymer of PET, isophthalic acid, and a glycol complex. The copolymer is irregular in structure and this substantially decreases the crystallinity, resulting in improved impact resistance, excellent gloss, and excellent clarity - key properties for PET bottle production.

Typical Applications

PET is a ubiquitous polymer seen in applications ranging from yacht sails to electrical products. As if that were not enough, there is current research aiming to replace PVC and other polymers with PET blends for building applications. Typical applications are:

- Yacht sails
- Fabrics
- Carpet fibers

- Recording tapes
- Drawing films
- Capacitors
- “Space blankets”
- Soda, water, and juice bottles
- Beer bottles (with additional barrier treatments)
- Reheatable food trays
- Bakery good tray
- Electrical components

Summary

PET is truly one of the most versatile of all the polymer families. Other polymers may be used in more applications, but the uniqueness of PET is the sheer diversity of applications for the single material. One of the major reasons for this is the very controllable crystallization behavior of the material due to the high glass transition temperature. No other material can be controlled to quite the same degree and this makes PET a truly unique family of polymers.

How Zeus Can Help

With a technical inside and outside sales force backed up with engineering and polymer experts, Zeus is prepared to assist in material selection and can provide product samples for evaluation. A dedicated R&D department staffed with PHD polymer chemists and supported by a world-class analytical lab, allows Zeus an unparalleled position in polymer development and customization.

Since 1966, Zeus has been built upon the core technology of precision extrusion of high temperature plastics. Today, with a broad portfolio of engineered resins, advanced polymers, and secondary operations, Zeus can provide turnkey solutions for development and high-volume supply requirements.

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