

Zimmer® Polymer Technology

PBT Polybutylene Terephthalate Process and its Co-Polymers



PBT plant

Introduction

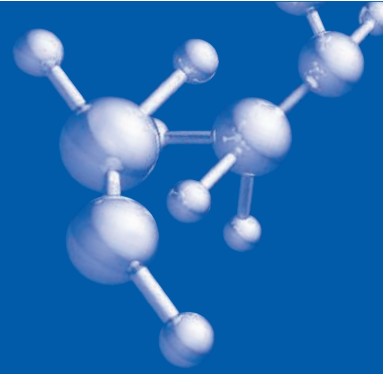
Towards the end of the sixties, polybutylene terephthalate (PBT) emerged on the market as a raw material for synthetic fibers and engineering plastics.

PBT belongs to the group of linear, saturated polyesters such as for instance PET, which is well-known since the 1930s. Zimmer started its R&D activities in the early seventies and developed processes for the production of PBT from DMT or PTA and a commercial spinning process for BCF yarns for carpet production.

Initially, PBT was very expensive due to small production capacities and shortage of 1,4-butanediol (BDO). With enhanced BDO production capacities the price decreased. As acid components, terephthalic acid (PTA) or DMT became readily available*, new applications promoted the market penetration of PBT with steadily rising growth rates.

* for example the BP/Lurgi Geminox® process and new production technologies.

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Comparison of Properties

The general characteristics of PBT lie between polyamide (PA 6, PA 6.6) and PET as shown in the table below. PBT is the main competitor of polyamides. The reasons for this are lower production costs, on the one hand, and the outstanding physical performance and excellent chemical resistance of PBT, on the other.

One major advantage of PBT is its very low water take-up of 0.4 % as compared to that of polyamides which pick up between 2 and 8 % of water. The different behavior of the polymers results in a strong dependence of the physical properties of the polyamides on their moisture content as a function of whether they are applied or stored under dry or wet climatic conditions. PBT, by contrast, does not exhibit this disadvantage.

Also the fast crystallization of PBT is of great importance. It is much faster than that of either polyamides or PET. This leads to low mould temperatures and short cycle times, and therefore to economical processing.

The processability of PBT is excellent due to its relatively low melting point of around 224 °C and the easy flow of the melt which enables injection molding of thin-walled parts with complex shapes.

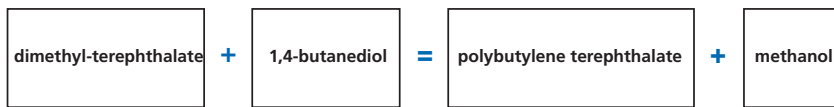
Other remarkable properties are high surface hardness and stiffness, which provide good dimensional stability under heat, a low friction coefficient and, last but not least, an excellent chemical resistance, e.g. against solvents, gasoline, oils, greases, etc. All these properties are of particular importance in the field of engineering plastics.

	PET	PTT*)	PBT	PA 6	PA 6.6
Melting point (°C)	260	228	224	220	265
Glass transition temp. (°C)	70–80	45–55	20–40	40–80	50–90
Density (amorphous) (g/cm ³)	1,335	1,277	1,286	1,110	1,090
Density (crystal) (g/cm ³)	1,455	1,387	1,390	1,230	1,240
Crystallization speed index **)	1	10	15	5	12

*) PTT = polytrimethyl terephthalate, also known as PPT (polypropylene terephthalate)

***) Reciprocal of time from starting point of cooling crystallization temperature to its maximum peak

Polymer comparison



PBT – DMT route

The Zimmer® Process

General features of the PBT process

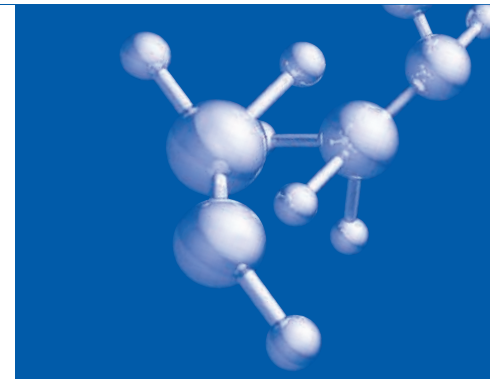
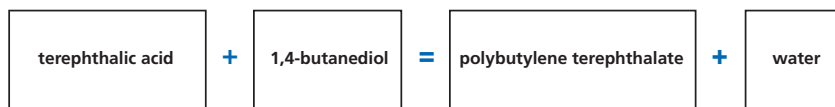
For a long time, DMT and BDO have been the major raw materials used for PBT production. However, Zimmer developed a continuous process for PBT with PTA and BDO as raw materials. The first continuous plant using PTA as raw material was started up in 1997 followed by several single-line plants with a capacity of 200 t/d.

The benefits of PBT produced from PTA compared to PBT from DMT are:

- Less raw material consumption
- Higher polycondensation speed
- No methanol handling
- THF as a highly valuable by-product
- Wide range of raw material suppliers
- Less process stages

US Patent No	
4,499,261	Continuous process with DMT as raw material (Feb 12, 1985)
4,680,376	Continuous process with PTA as raw material (July 14, 1987)
4,877,572	Production of PBT / BCF carpet yarn (Nov 14, 1988)
5,266,601	Process for preparing PBT from PET scrap (Nov 30, 1993)
6,367,235	Method for the production of Polybutylene Terephthalate (April 16, 2002)
EP 1820814	Method for the esterification of terephthalic acid with butanediol (Aug 22, 2007)

Zimmer® patents



PBT – PTA route

Process Design

Process configuration

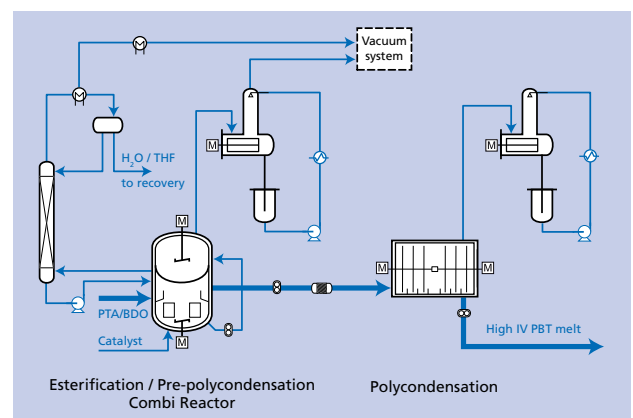
Lurgi is able to offer second-generation plants for high-viscosity and high capacity in one single line. The PTA/PBT process is available in two different configurations. The first process is based on the commercially-proven 3-reactor plant design. The second process (see illustration) uses our production experience for the scale-up and combination of two reactors (esterification and pre-polycondensation) into one (COMBI REACTOR). This development allows reducing the overall investment as compared to the proven 3-reactor process.

Continuous polycondensation (PTA route)

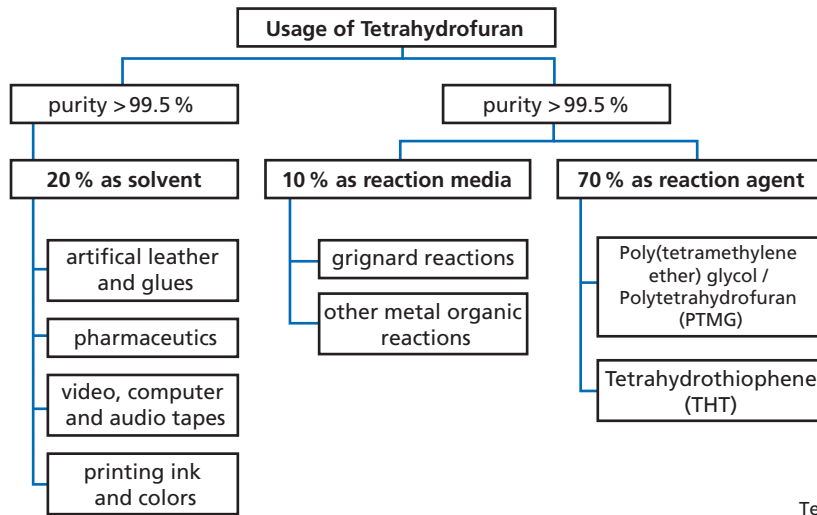
PTA and BDO are mixed and fed into the esterification section. In this section, an intermediate polymer is generated under vacuum and temperature. During this reaction mainly water, THF and BDO are evaporated and separated in a column. THF and water are removed as head product and sent to the THF recovery unit. The BDO is returned to the esterification stage. After esterification is completed, the product is transferred to the pre-polycondensation section where PBT with a low molecular weight is produced under elevated temperatures and further reduced pressure while BDO and THF are separated. This reaction is performed either in two independent reactors or in the new COMBI REACTOR described above.

From the pre-polycondensation section the PBT with low molecular weight is fed to the polycondensation stage where the desired molecular weight is generated. This polycondensation process takes place in a special double-drive disc ring reactor (DD-DRR). A continuous polycondensation DMT route is equally available.

We also offer a batch process for smaller plant capacities. It is more flexible in adapting the product to different market demands and producing special products, i.e. copolymers of minor amounts.



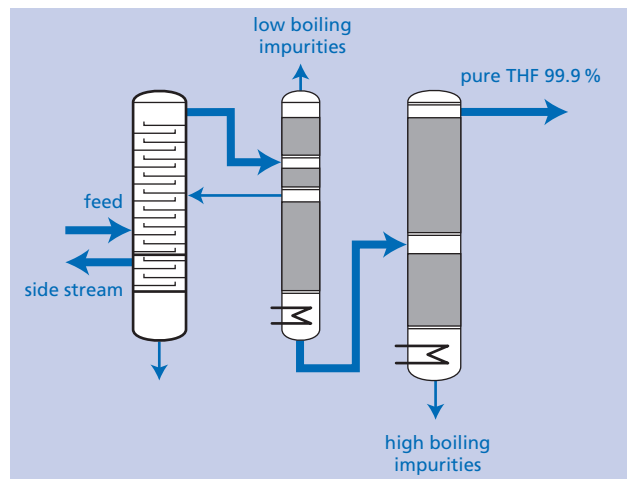
Zimmer® continuous PBT process (PTA route)



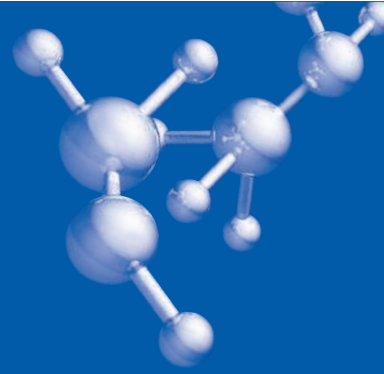
PBT 3-stage THF recovery

Lurgi offers a three-stage THF recovery process. The first stage is a distillation under atmospheric pressure to separate an azeotrope of THF and water (94 % THF) as the column head product while the water leaves the column at the bottom. In the second stage, the azeotrope is shifted by applying a higher pressure to reach a purity of up to 99.5 % THF in the bottoms. The third column serves as a final purification stage to achieve a purity of 99.9 % THF in the column overhead product.

This THF is suited for polycondensation to PTMG, which can be used for thermoplastic elastomers, thermoplastic poly-etheresters, special fibers and thermoplastic poly-etheramides.

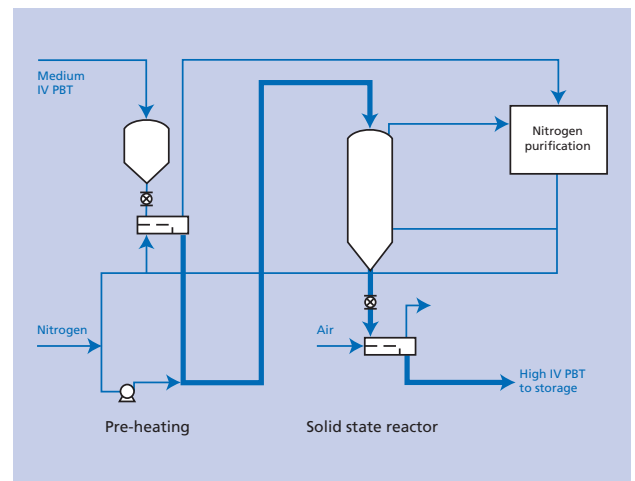


PBT 3-stage THF recovery

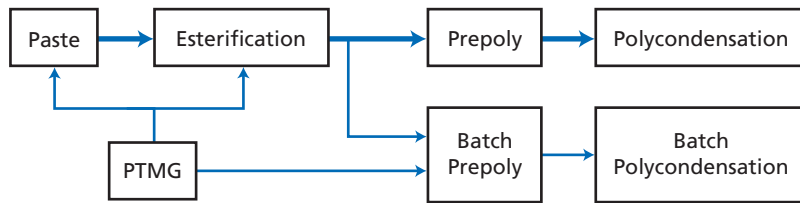


Solid state polycondensation (SSP)

The SSP is used for special applications such as PBT of ultra-high molecular weight ($IV > 1.25$) and polymers with a low THF content. This sophisticated continuous technology was developed by Zimmer. Basically, the crystallized chips continuously pass through a tubular reactor operated in counter-current to an inert gas stream at temperatures well below their melting point thereby leading to higher product viscosity and removing volatile reaction products and impurities by means of the inert gas. For small capacities of up to 30 t/d, specially equipped tumble dryers can be used as discontinuous SSP units.



Continuous solid state polycondensation for PBT



Production of PBT co-polymer TPE-E

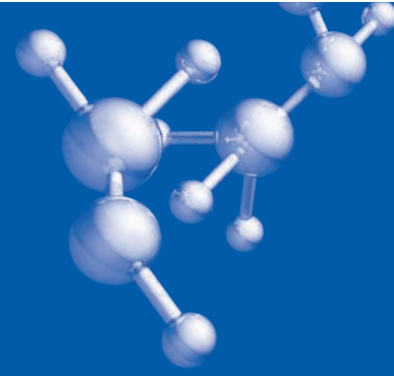
Process for PBT Co-Polymer TPE-E

TPE-E (Thermoplastic Elastomers-Polyester) is a co-polymer of PTA, BDO and PTMG. PTMG is produced by polycondensation of THF to molecular weights of 1,000 to 2,000. The co-polymer is produced by adding PTMG to the esterification stage of the PBT line. Alternatively, a side stream of esterification product is fed to a batch plant.

TPE-E having hard polyester segments and soft polyester segments combines features of engineering plastics and rubber. Other than rubber, TPE-Es are not cross-linked and therefore recyclable.

Advantages of TPE-E:

- Low temperature elasticity
- High temperature mechanical properties
- High temperature stability
- Resistance to grease and oil
- Restricted low hardness range



PBT Application

PBT as engineering plastics

PBT is mainly used in intrinsic viscosities between 0.7 and 1.2 dl/g for injection molding and from 1.1 to 1.5 dl/g for extrusion. For most applications, PBT is not used in the pure form in which it leaves the polycondensation unit but as compounded materials produced by admixing and homogenizing PBT melt with certain additives: glass fiber, talc, flame retardant, pigments, slipping agents, antioxidants, stabilizers, PTMG.

Advantages

- Better mechanical properties
- Higher heat stability
- Lower inflammability
- Better coloring
- Higher UV stabilization
- Improved processability
- Less degradation
- Elastomeric behavior (PTMG)

The main applications for PBT are in the automotive industry, electrical and electronics industry and machinery sector (technical, business and household machines).

PBT as textile for filament and fibers

PBT filaments and fibers are ideal for swimwear, underwear and hosiery.

Advantages compared to PA 6 and PA 6.6:

- High stability to shape
- Excellent bulk and crimp behavior
- High tenacity
- High elasticity and stretching recovery

PBT as carpet yarn (BCF)

For carpet yarn, the following advantages are important:

- High elasticity
- Good pile recovery force
- Good dimensional stability
- Good under wet conditions
- Carrierless dyeable at boiling temperature under atmospheric conditions
- Excellent stain resistance and wool-like feel

PBT BCF carpet yarns can be processed on the same spin-draw-texturing machines as PA.



Highlights of Zimmer® PBT Process

Based on more than 40 years of experience with Zimmer® polycondensation plants Lurgi can offer PBT technology and know-how in a number of variations. The company has built plants featuring continuous and batch PBT process with DMT or PTA as raw material.

With regard to the market requirements the following technologies can be provided:

- Reliable technology for highest quality
- Continuous, single-line polycondensation plants with capacities of up to 360 tons/day at IV 1.25
- 2 or 3 reactor process with PTA as raw material
- BD jet system for vacuum generation
- Solid stating for IVs >1.25 up to 300 tons/day
- THF / water recovery THF purity up to >99.9 WT %
- Integration of PTMG plant from excess THF
- Production of PBT Co-Polymer TPE-E

Moreover, we also offer the new direct butane 1,4-butane-diol (BDO) Geminox® process jointly developed by Lurgi and BP Amoco. This BDO technology will reduce the raw material price further and will make PBT an even more competitive product to PA and PET in future.

Various applications in:

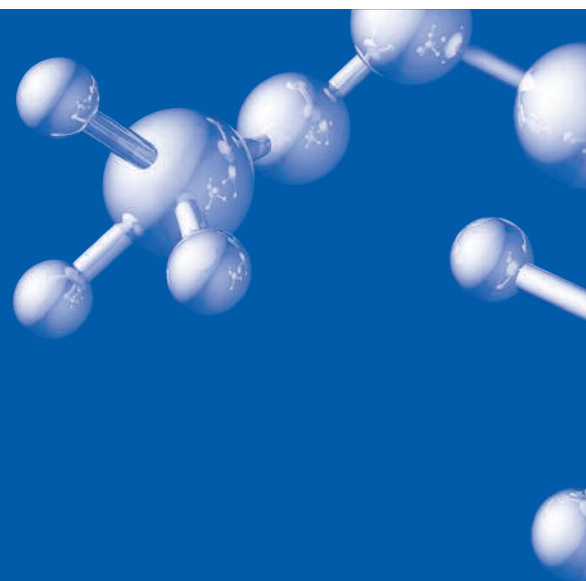
- Automotives
- Telecommunication and electronics
- Household and engineering plastics



Lurgi is a leading technology company operating worldwide in the fields of process engineering and plant contracting. The strength of Lurgi lies in innovative technologies of the future focusing on customized solutions for growth markets. The technological leadership is based on proprietary technologies and exclusively licensed technologies in the areas gas-to-petrochemical products via synthesis gas or methanol and synthetic fuels, petrochemicals, refinery technology and polymer industry as well as renewable resources/food.

Lurgi is a member of the Air Liquide Group

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