The Polyester Resin Family
PET, PBT, PTT, PEN and Modified Polyester
Latest Stage of Development

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About the Consulting Service Dr. THIELE – POLYESTER TECHNOLOGY

This new international technology and consulting service specialising in the field of POLYESTER TECHNOLOGY was established in mid-1999.
A commercial service, the company has expertise in the areas of:Production, technology and design of polyesters

- Polymer processing
- Polyester research and development
- Application
- Structure properties
- Patent support →Polyester Technology, as a scientific consulting firm,

concentrates on monitoring the technical background and driving forces of bulk as well as specialty polyester products, to provide detailed knowledge for the customer. The activities are targeted towards improving management strategy, as well as supporting research and development, production and engineering.
More information is available at: www.polyester-technology.com

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CONTENT

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→ INTRODUCTION

Ladies and Gentleman, At a time when the polyester industry is maturing and in the process of restructuring – from well-known large industrial complexes,

such as DuPont, Hoechst and ICI, toward family-owned production units – the development culture is also changing.
Unlike the fast-growing 1980s and 90s we are now faced with straight and disciplined cost-saving programmes and shrinking research and development facilities.
However, linear polyesters are now the most attractive polymer family, this covers a very wide range of raw materials for textiles, packaging, bottles, film, coatings and engineering plastics in a broad sense. With the introduction of new chemical processes to get access to diols, such as cyclohexanedimethanol, propanediol-1,3 or butanediol-1,4 and dicarbonic acids, including naphthaline dicarbonic acid and diphenyldicarbonic acid, at a reasonably low price the variety of polymer properties is steadily increasing.
More and more, the economies of scale and the degree of integration, from oil via the intermediates to polyester, are finally deciding profit or loss over a longer time scale. Plant capacities of 800t/d are under serious discussion and the PET bottle resin producer especially is heading for the largest single production trains.
PBT, as the second largest market segment after PET resin for bottles, is seeing a time of rapid growth and one is left wondering who and where all the new PBT capacity, due to come on stream during the next two years, will be consumed.

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→General trends in polyester development
Investigating the frequency of worldwide published patents and research papers in the field of linear polyester resins from the last 12 months Polyester Technology found the topic distribution described in Table 1 and 2. ollected in Table 1 are the important research issues, which occur in the statistics with a frequency of approximately 2 per cent or more of the total indexed publications. Table 2 shows the less frequently occurring research issues in the statistics, with a frequency of less than 2 per cent but with more than two hits in total.###############

Table 1: Important and frequently published research issues

Antistatic Modification	3.22 %	Impact Improvement	5.67 %
Barrier Improvement	7.74 %	New Copolyester	3.04 %
BOTTLE PET	2.65 %	Oligomer Reduction	5.48 %
Catalyst	4.54 %	PBT	2.85 %
Chain Extender	2.85 %	PTT	4.54 %
Crystallization / Morph.	6.61 %	PET-Process + Hardware	3.98 %
Engineering Plastic	3.41 %	Plasma Coating	2.40 %
Film BOPET and Process	5.30 %	Recycling general	3.98 %
FR-Modification	6.05 %	Recycling Bottle	5.11 %
Functional PET-Add. + MB	4.17 %	Thermoplastic Elastomers	4.15 %

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Table 2: Polyester research issues with a frequency of less than 2 per cent.

AA Scavenger	0.56 %	LCP	1.32 %
Cyclic Polyester	0.38 %	Nano Additives	1.32 %
Conductive Compounds	0.94 %	Nano Compounds	1.32 %
Foam PET	1.32 %	PET/PEN Copolymers	0.94 %
High Tenacity PET	1.14 %	Softening Agents	0.38 %
Hydrolysis Resistance	0.38 %	TiO_2	0.56 %
IR Absorption Impr.	0.56 %	Tg-Upgrading	1.32 %

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CONCLUSIONS:

Development issues in bottle PET resin, packaging and film 35%
Development issues in engineering plastics, special additives, compounds and masterbatch 33%
Polyester recycling issues 10%
Research in crystallinity and morphology 7%
Miscellaneous 15%
Not included in this statistic investigation are development areas, such as biodegradable co-polyester and PLA

On the one hand: These findings reflect well-known worldwide activity in packaging, especially the introduction of PET in the beer-bottle market, including bottle recycling.
On the other hand: It is surprising to see the high intensity and dynamism in engineering plastic research issues. This justifies the assertion that linear polyesters are becoming an increasingly important raw material in technical applications.

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→ PET: Are melt-phase or solid-state processes gaining the upper hand in PET resin production?

The driving forces of the development of a "NEW GENERATION" PET processing, where the polycondensation occurs without a vacuum and the reaction shifts by over 50 % to solid-phase, are:
 # Significantly lower investment
 # Freedom for further capacity scale up
 # Improved product quality because of low reaction temperature

This new process design has not yet been industrially proven and involves several unknown risks including those listed below:

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Process risks:
 # Long-term consumption and maintenance figures, especially: energy, raw material and nitrogen, for large scale processes remain unknown.

 # Market acceptance in downstream processing

 # Significantly high Sb content is needed, as yet, no specific and antimony-free SSP catalyst has been proven
 # Process risks, including product in-homogeneity

 # High risk of dust creation,

Research tasks:

 # Sufficient catalyst to increase SSP velocity

 # Improvements in particle forming to minimize any dust generation

 # Improvements in the particle handling and conveying systems
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How state-of-the-art technology providers are responding

 # Intrinsic viscosity out of the melt-phase finisher is decreasing stepwise from 0.64 dl/g to 0.58 dl/g and less

 # Decreasing melt-phase viscosity results at the same time as increasing the melt-phase plant capacity significantly, a single unit capacity of 800 t/d is under discussion# Recent patent publication (WO 01 42,334) is claiming a precursor IV out of the melt-phase polycondensation from 0,25–0,40 dl/g, containing more than 7 per cent co-monomer.

 # Finally we predict a stepwise approach of both processes in the near future and there may be a conversion of existing continuous PET plants

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→PBT and its current growth acceleration

Today are four new PBT projects known, these are not coming on stream until 2003/2004

The total new name plate capacity is estimated to be in a range of approximately 600 t/d

The new continuous lines are able to provide PBT in a wide variety of viscosity; for high-IV-grades, no further SSP process is necessary

The new capacity will replace the remaining high-cost discontinuous production lines in operation, which are mostly old converted PET lines and where a further SSP process is necessary to produce high-viscosity PBT

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→PBT – research and development

The availability of BPT, creating better price conditions in the near future, will widen the field of applications and interest in the textile spinning, such as BCF, might even see a revival# As shown in Table 1, there is only a small number of publications and patents that are directly dedicated to PBT developments (2,85 %)
Most of the published patents are aimed at providing improvements in the polycondensation catalyst and the currently used titanium alkoxides.

New compounds and flame-retardant compositions for engineering plastic applications

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→PTT: Specific production requirements

There are two routes to synthesise PTT: the transesterification of dimethylterephthalate (DMT) with propylenediol (PDO) and the esterification route, starting with terephthalic acid (PTA) and PDO; these are similar to the PET process.

It is possible, in general, to convert existing PET production facilities to produce PTT. The industrial introduction takes the same path as PBT did 10 years ago.

The easiest way to produce PTT to use an existing PET batch-plant.

It is necessary to have a separate PDO rectification unit available.

The availability and purity of PDO are key prerequisites for the production of

a pure polymer

 # Both process economy and PTT-polymer quality are strongly dependent on PDO purity. #################

→PTT – properties and applications

 # Polymer properties are similar to those of PBT (see Table 3)
 # PTT films show high elasticity and low water-vapour permeation
 # PTT is a welcome crystallization enhancer for PET within a lower range of addition
 # Most interest and development activity lies in filament and fibre spinning
 # The until today, lower interest in the field of engineering plastics and packaging technology might have bern caused by the limited availability of PTT-standard resins in the market
 # In general, applications and processing are similar to those of PBT

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Table 3: Comparison of some polymer properties of linear polyesters

FIGURE	PTT	PBT	PET	PEN
IV [dl/g]	0.7–1.2	0.85–1.40	0.55–1.00	0.45–0.70
TG [°C]	50–60	30–50	76–80	120–128
TK [°C]	80–120	80–120	130–150	140–170
TM [°C]	226–229	222–232	248–258	265–270
Crystallisation	non	non	1 h at 150°C	1h at 170 °C
Drying temp. [°C]	125	140	160	170
Time [h]	6	6	6	7
Extrusion Zones [°C]	240–270	240–270	280–295	295–305

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→PEN: Waiting for the break through in consumption – a chicken and egg situation.

 # Research and development activities are minor (0.94 per cent)

 # There are some applications in packaging but growth is limited because of the unfavourable price – performance correlation

 # Excellent market niches for high-performance products in film, tire cord and high-barrier bottles

 # PEN molecules in low concentrations are increasingly used as modifiers in PET to improve barrier properties

 # PET-PEN mixtures are difficult to separate during recycling

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→Modified Polyester

 # Growing niche products, such as barrier resins (Co-PET-PEN, PEI and others)
PETG, C-PET, A-PET, FR-PET, EBM-PET take a role in increasing available smaller and redundant production facilities

 # Modified polyester resins have the following properties:

low or no crystallization + low melt temperature
low crystallization + high glass-transition temperature
low crystallization + high melt viscosity
low crystallization + low melt viscosity
high gas barrier for oxygen, CO_2
high gas barrier for water vapour
permanently flame retardant
fast crystallizing
high impact strength and transparency

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→ Modified Polyester

 # New co-monomers are necessary prior to introduction on an industrial scale

 # The problem of new co-monomers is the correlations:

co-monomer price ←→ availability and purity → effect of modification and FDA – STATUS

 # Amorphous CHDM modified polyester resin is now also available from a KOREAN source (continuous operating facility)

 # Low-price imitations of the CHDM modified amorphous polyester are occasionally appearing# The pressure to develop specialties is anti-cyclic to the marketperformance of PET bottle and fibre resin
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→ Summary

 # The major research efforts are still in the field of bottle and packaging resins

→# Research and development is increasingly concentrated on material science issues

 # Development of PET-based polymers for engineering plastics has meanwhile increased to nearly the amount packaging resin

 # For PET resin, the existing processes are approaching stepwise, to

lower molecular weights in the precursor and shifting higher conversion rates to the SSP

 # With new capacity of about 600 t/d in 2003, PBT is seeking a push in production capacity

 # The basis of PTT production is access to low-price, high-quality PDO; production processes are available

 # PEN is mainly for hi-tech and high-performance products; bulk applications are failing because of the high price of raw materials

 # Some of the highly modified polyesters, for example PETG, are on the way to being produced in larger quantities

 # Availability and price of special co-monomers are limiting production and application

 # Specialized polyester producers are providing tailored products
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GLOSSARY of often occurring polyester abbreviations

Co-PET-PEN	Copolyester with 2 – 10 weight per cent NDA
PEI	Polyethylene isophthalate
PETG	Glycol modified polyester, mainly used for CHDM modified amorphous polyester resins
C-PET	Crystallized or fast crystallisable polyester
A-PET	Amorphous polyester, mainly used for cast film
FR-PET	Flame retardant polyester
EBM-PET	Polyester for extrusion blow moulding
PBT	Polybutylene terephthalate
PTT	Polytrimethylene terephthalate
PEN	Polyethylene naphthalate
PLA	Polylactic acid
IPA	Isophthalic acid
NDC	Dimethyl-2,6-naphthalenedicarboxylate
CHDM	Cyclohexanedimethanol
PDO	Propylenediol or propylenediol-1,3
BD-1,4	Buthanediol-1,4
DEG	Diethyleneglycol
PEG	Polyethleneglycol