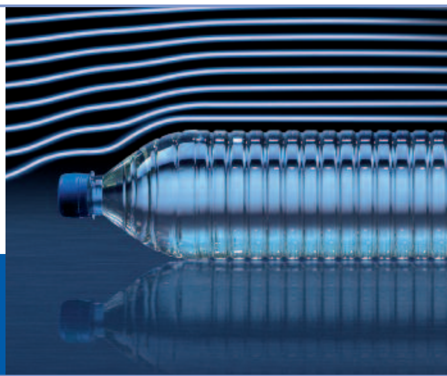
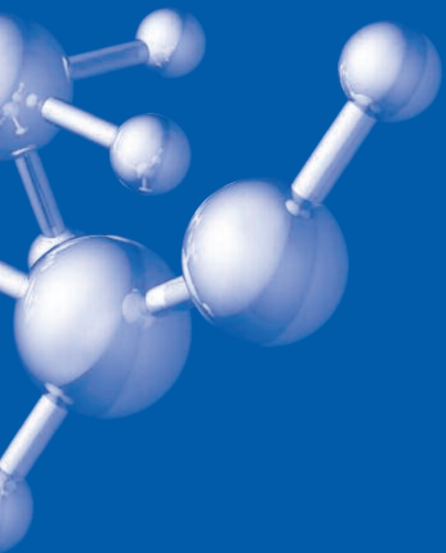
AIR LIQUIDE

Lurgi





Zimmer® Polymer Technology

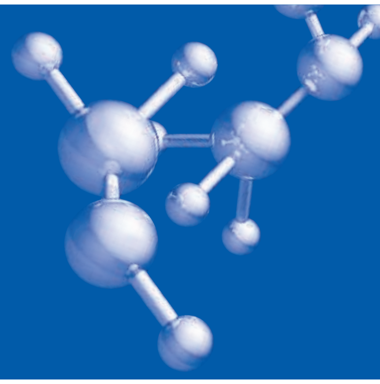
Polyester Packaging

Polyester packaging resin plant

Introduction

PET commands a considerable market share as a raw material for packaging, bottles, films and engineering plastics.

Lurgi builts on long experience of Zimmer® in polyester packaging technology to present a manufacturing process with market leading operating economics and superior product quality.



Market requirements

PET as raw material is required for several applications with different properties transparent packaging – bottles, foils and films.

Most important characteristics PET bottles

- Highly transparency
- Low weight
- Unbreakable / High firmness
- Very good mechanical characteristics
- Good barrier properties
- No taste influence on the filling mediums
- Good form stability
- High recyclability
- Health authorities approval (FDA, EU)
- Economic production

Most important characteristics A-PET films

- Excellent transparency and gloss
- Good mechanical properties
- High form stability easy thermoform
- Good printability
- Non toxic
- Suitable for food packaging including fats
- Low water absorption and gas permeability

PET used for these products are mostly modified by adding co-monomers and additives which influence such properties as

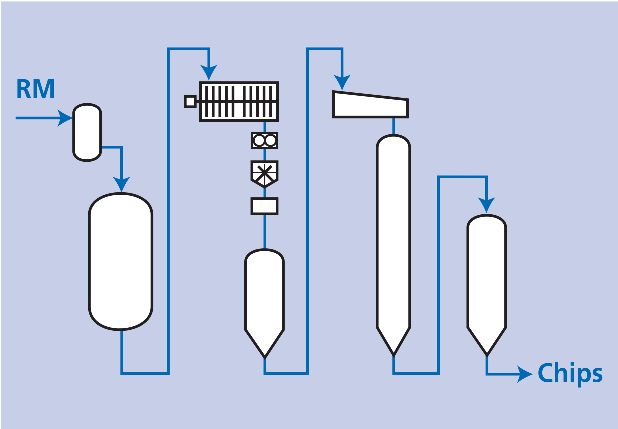
- Clarity
- Colour
- Melt behaviour
- AA reformation
- Crystallinity
- Molecular weight distribution

In general, modified resins for rigid packaging have higher molecular weights than standard PET resins for textile applications.

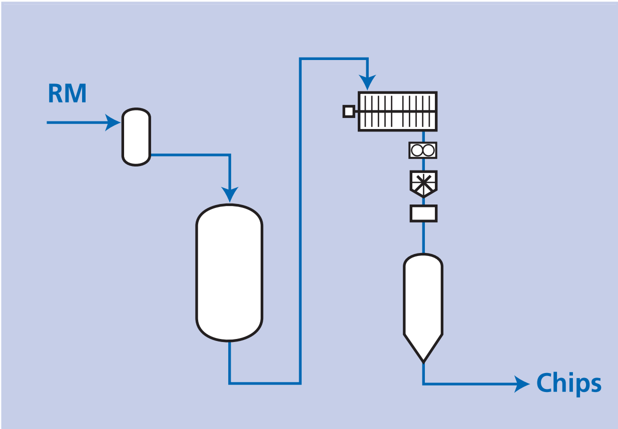
The required viscosities as well as lowest acetaldehyde levels (AA) are reached by the new Direct-high-IV (DHI) technology. Using this new technology operating units of up 1.800 t/d in one line are available.

Direct High Intrinsic Viscosity – process overview

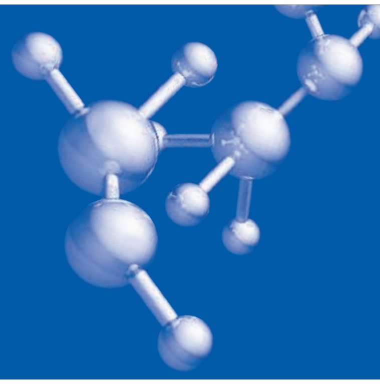
The polymer produced in a standard melt polycondensation process is characterized by high acetaldehyde content (AA) and relatively low intrinsic viscosity (IV). Therefore, solid state polycondensation (SSP) is required as an additional step for the production of bottle grade PET granulate.



Standard polycondensation with SSP



DHI polycondensation



The melt phase process and de-aldehydization (DHI)

As the common PET process, pure terephthalic acid (PTA) or dimethyl terephthalate (DMT) and ethylene glycol (EG) are used for esterification/transesterification and further polycondensation to PET. The DHI process is based on the new 2 stage melt plant design. However, the DHI unit directly produces a high viscosity melt up to 0,86 dl/g Intrinsic viscosity (IV). The melt is routed from the DHI finisher through a flexible melt distribution system where it is continuously filtered and granulated. The granulation system is integrated with a small crystallization section that provides a highly uniform, virtually dust-free granulate. The crystallized high viscosity chips then pass through a dealdehydization unit that reduces the AA content to levels < 1 ppm.

However, Zimmer® DHI technology offers a unique approach to PET polycondensation process. The mode of operation offers many benefits, including greater energy efficiency, minimal reaction by-products, excellent product quality and low AA reformation.

Diols or dicarboxylic acids are added as co-monomers; they are built into the polyester chain to reduce the melting temperature and the crystallization rate of co-PET. This modification is necessary to achieve the required product quality for rigid packaging products.

As an alternative to antimony-based catalysts, a heavy metal-free catalyst/stabilizer system for PET can be used.

Exceeding market requirements

DHI bottle PET resin offers preform producers key advantages compared to conventional standard SSP bottle PET resin.

- Steady and more consistent processability
  - Stable IV and crystallinity
  - Constant humidity
  - Consistent pellet size and shape
  - No contamination (from amorphous chips handling)

- Lower injection cycle times achieved by:
  - Lower heat of fusion (HOF), lower degree of crystallinity, homogeneous IV = reduced energy input
  - Lower AA reformation, more homogeneous AA content across the tool

DHI bottle PET resin also offer bottle producers and fillers key advantages compared to conventional standard SSP bottle PET resin.

- More consistent preforms
  - More consistent polymer properties means more consistent preforms for blowing
  - DHI-based preforms require fewer changes on blowing machine = easier, steadier, lower energy operation
- Wider operating window for blowing process
- Clearer, more transparent bottles
  - Lower thermal stress in processing = better color and clarity, more attractive on the display shelf

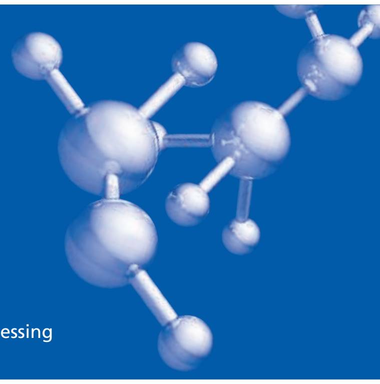
Product Parameter		DHI chips	SSP chips
Acetaldehyde content	ppm	< 1	< 1
Viscosity	dl/g	0.65 – 0.86	0.75 – 0.86
Deviation of viscosity	dl/g	± ≤ 0.01	± ≤ 0.02
COOH end groups	mmol/kg	≤ 40	≤ 40
Melting point*	°C	248 – 252	248 – 252
Color b-value	Hunter Lab	≤1.0	≤1.0
Off-white chips		0	Normally not specified
High-high IV dust content	ppm	0	Normally not specified
Degree of crystallinity**	%	≤ 52	≥ 56
Heat of fusion	kJ/kg	≤ 48	≥ 52
Preform processing temp	°C	~ 265	~ 285

* DSC method, normal copolymer recipes ** Basis: normal IPA; DEG copolymer recipes

Product parameters of DHI chips in comparison to conventional SSP chips

Commercial bottle grade PET chips

DHI chips



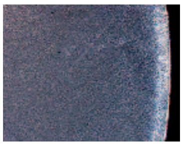
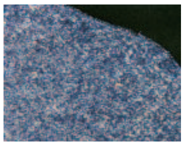
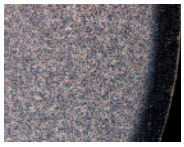
Average preform machine processing temperature (shown in white)

Advantages of DHI technology – downstream processability

A central feature of the DHI process is the direct linking of the granulation step with the crystallization step in order to exploit the latent heat in the granulated polymer. For DHI chips, the direction for latent heat crystallization is from inside-to-outside. For chips passing through conventional crystallization steps found in a SSP, the crystallization direction is from outside-to-inside. This results in a lower, more consistent degree of crystallinity and a lower heat of fusion for DHI chips as compared to any other commercially available bottle grade PET chips.

Having a lower heat of fusion combined with a lower, more consistent degree of crystallinity offers preform producers greater operating flexibility. For example, a producer can operate the preform machine with a lower temperature profile, thereby further reducing energy costs as well as AA rebuild without compromising appearance.
In production trials on commercial scale machines, preforms made from DHI chips were still haze-free at processing temperatures 10°K to 20°K lower than preforms made from conventional SSP chips. This is shown in the photos below.

Clearly, bottle grade PET resin produced using DHI technology offers a range of quality advantages and flexibility for the resin producer as well as the converter.

Typical SSP chip	Low IV chip	High IV Zimmer DHI chip
		
Chip crystallization process from outside to inside	Crystallization process with low IV melt	Latent heat crystallization from inside to out-side
IV 0.80 (dl/g)	IV 0.80 (dl/g)	IV 0.80 (dl/g)
HOF 57 (kJ/kg)	HOF 65 (kJ/kg)	HOF 42 (kJ/kg)
DOC 56 (%)	DOC 64 (%)	DOC 48 (%)

HOF: Heat of fusion
DOC: Degree of crystallization, using graduated measuring column

Analytical results from actual chips samples

AA level variation at perform machine

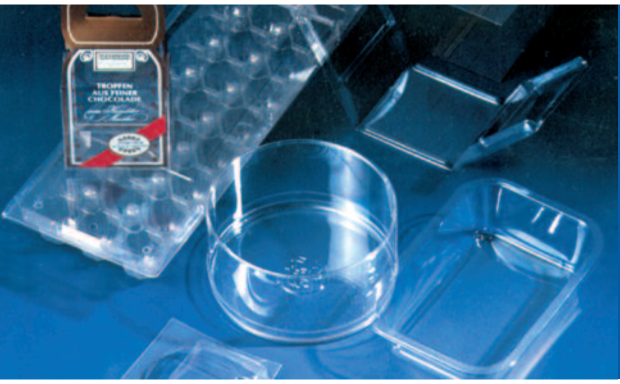
Standard PET (72 cavity mold; 1st quadrant)		
Cav 1	Cav 13	Cav 25
Cav 2	Cav 14	Cav 26
Cav 3	Cav 15	Cav 27
Cav 4	Cav 16	Cav 28
Cav 5	Cav 17	Cav 29
Cav 6	Cav 18	Cav 230

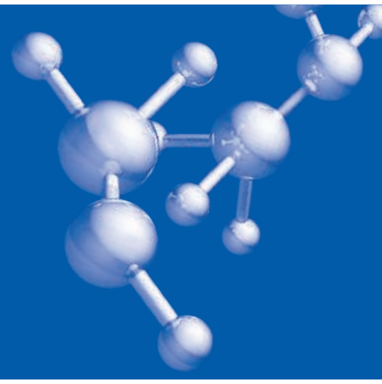
DHI PET (72 cavity mold; 1st quadrant)		
Cav 1	Cav 13	Cav 25
Cav 2	Cav 14	Cav 26
Cav 3	Cav 15	Cav 27
Cav 4	Cav 16	Cav 28
Cav 5	Cav 17	Cav 29
Cav 6	Cav 18	Cav 230

low AA high AA

PET bottle resin application

- Typical polymers used for water
  - Typical polymers used for carbonated water
  - Typical polymers used for flat water
- Typical polymers used for CSD (Coca Cola, Pepsi Cola, Sprite ...)
- Typical polymers used for refillable bottles; 5 Gallon Bottle for Water
- Typical polymers used for hot-fill bottles
- Other applications for PET containers
- A-PET film





PET film application

Product Parameter	Homo/Copo	IV[dl/g]	Preform AA [ppm]
Carbonated Mineral water	copo	0.76 – 0.82	< 2
Flat water	copo	0.70 – 0.82	< 4
CSD	copo	0.76 – 0.83	< 8
Refillable bottle	copo	0.78 – 0.86	< 8 CSD
5 Gallon bottle	high copo	0. 80 – 0.83	< 4 flat water
Hot-fillable bottle: Sports drinks, Ice tea	copo	0.74 – 0.82	< 8
Hot-fillable bottle: Fruit Juices, Baby food, Milk	homo/low copo	0.74 – 0.82	< 8
Edible oil	homo/copo/	> 0.70	< 8
Vinegar	homo/copo	> 0.70	< 8
Cosmetics/Household Pharmaceuticals	homo/copo	> 0.74	–
A-PET film: Blister packs, films, foils	copo/high copo	0.70 – 0.85	–

Homo = Homo-PET (DEG 1.4 ± 0.1 wt-%);
Copo= Co-PET (DEG 1.4 ± 0.1 wt-% + IPA 2.0 ± 0.1 wt-%)

PET packaging applications

DHI economic advantages – lower raw materials cost

By eliminating the SSP, the DHI process also eliminates the losses associated with the SSP step. These losses – including unrecovered EG, dust, spillage and drying – can range from 3 to 6 kilograms per ton of chips product*.
Because the SSP-related losses are not relevant in DHI, raw materials cost per ton of chips product is reduced. Examples of estimated raw materials cost savings** for DHI plants with selected capacities are shown in the table below.

Capacity tons/day	**Estimated savings** Euro/year
440	600 000–800 000
660	900 000–1 200 000
1320	1 800 000–2 400 000

DHI economic advantages – 17 % lower conversion cost

The DHI process eliminates some process steps while combining others. The result is a more labor and energy efficient production process. The chart above shows how several cost-intensive steps are eliminated in a DHI plant as compared to a conventional melt plant with a SSP. Eliminating cost-intensive steps and combining other steps results in a conversion cost savings of 17 %. For this comparison, conversion cost includes utilities, additives and direct manufacturing labor – raw materials PTA, IPA and EG are excluded. Major cost savings are derived from eliminating:

- Re-heat and re-cool cycle in the SSP
- Nitrogen consumption and the related nitrogen purification unit
- Energy-consuming conventional crystallization units
- At least one chips conveying step
- SSP labor, maintenance and other overheads

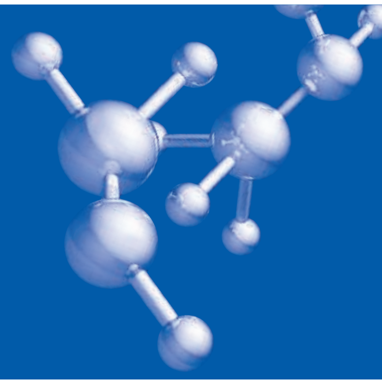
DHI economic advantages – 15 % lower plant investment

Eliminating the SSP and combining other process steps has a significant effect on the plant investment. Specifically, the DHI plant investment will be 15 % lower than the investment in a conventional plant. For this comparison, the plant investment includes process equipment and basic engineering; excluded are land, erection, utilities and off-sites. The investment savings are applicable for capacities ranging from 440 t/d to more than 1800 t/d.

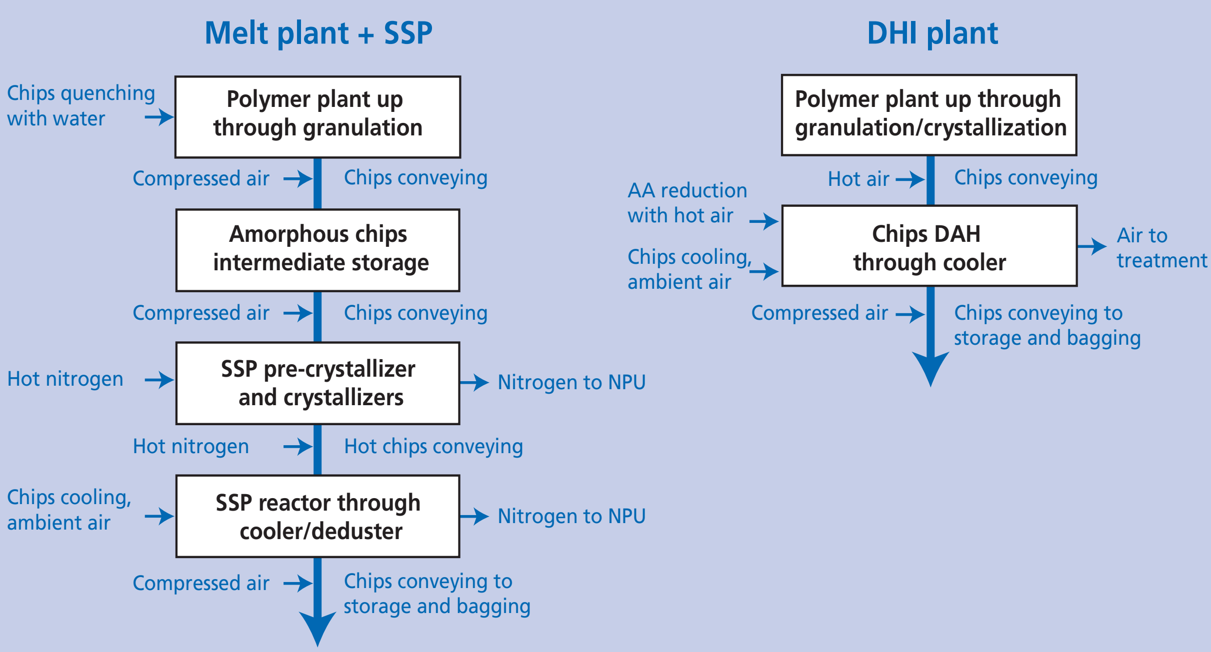
Overall project investment savings are derived from:

- No SSP plant, no nitrogen purification unit
- No intermediate product storage or handling
- Reduced plant footprint and reactor building volume
- Reduced utilities and auxiliary systems

* Common guarantee figures from SSP plant suppliers; actual losses depend on SSP configuration selected
** Includes PTA, MEG and IPA only; prices from PCI, European basis



Conversion comparison



Lurgi is a leading technology company operating worldwide in the fields of process engineering and plant contracting. Based on syngas, hydrogen production and clean conversion technologies for fuels or chemicals Lurgi offers innovative solutions that allow the operation of environmentally compatible plants with clean and energy-efficient production processes.
Its technological leadership is based on proprietary and exclusively licensed technologies which aim to convert all carbon energy resources (oil, coal, natural gas, biomass, etc.) in clean products.

Lurgi is a member of the Air Liquide Group

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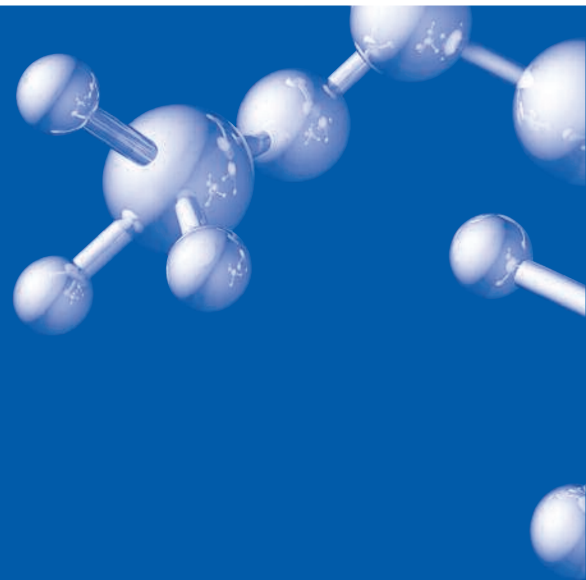

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