

Polyamide for Flexible Packaging Film

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Abstract

PA 6 is a widely used resin for the production of flexible packaging film, in most cases combined with polyolefins as a component of a multilayer structure. It has found numerous applications for its unique combination of properties like mechanical strength, transparency, thermoformability and barrier.

This presentation summarizes the fundamental information about the chemistry and properties of nylon resins, their processing, and the properties and applications of packaging film produced utilizing nylon.

Polyamides may be processed into film by blown or cast film process, oriented or non-oriented. Standard extrusion equipment may be used, however post-treatment by humidification or annealing helps to postcrystallize PA film and to achieve dimensionally stable, ready-to-use film of high quality.

Polyamide for Flexible Packaging Film

fig 1

1. Introduction

Polyamide is widely used for the production of flexible film for packaging of perishable food due to its unique combination of properties:

fig 2:

- mechanical strength
- high heat distortion temperature
- high flexibility and toughness
- good barrier to oxygen, chemicals and aroma substances
- high transparency
- thermoformability

fig 3

In 2002, about 260 000 t of polyamides, mainly PA 6 and copolyamides PA6/66, were used for packaging film worldwide. Multilayer films in combination with PE, PP or EVOH form the major share of the polyamide film market.

fig 4

The term "polyamide" describes a family of polymers which are characterized by the presence of amide groups. Since the first - and still most important - synthetic polyamides, PA66 (Nylon) and PA6 (Perlon), have been developed in 1938/39, they have found wide applications as film, fibers, engineering resins and others. Today, DuPont's original brand name for PA66, "Nylon", is often used as generic name for all synthetic polyamides. However, polyamides have been useful materials long before the development of these synthetic nylon resins as the naturally occurring protein, the polymer of α -aminoacid, the base material of wool and silk, is also to be considered a member of the polyamide group.

2. Chemistry and Properties of Polyamide Resins

fig 5

Polyamides are mostly aliphatic, linear polymers characterized by the presence of the amide group, the condensation product of amine and carboxylic acid, as repeating unit in the polymer chain, separated by hydrocarbon unit.

fig 6

Polyamides may be synthesized either by

- (A) polycondensation of divalent carboxylic acid and divalent amines, or by
- (B) polycondensation of difunctional aminoacids containing both one amine and one carboxylic acid functionality in the same molecule (or their intramolecular ring-shaped condensation products "lactams").

The many different types of polyamides are named according ISO 1874 by the using symbol PA (for polyamide) and:

fig 7

- (A) the number of carbon atoms in the diamine monomer, followed by number of carbon atoms in the dicarboxylic acid (for linear aliphatic polyamides), e.g. PA 66 for the polyamide of hexene diamine and adipic acid or PA612 for the polyamide of hexene diamine and dodecanic diacid, or
- (B) the number of carbon atoms in the aminoacid or lactam monomer (for linear aliphatic polyamides), e.g. PA 6 for the polyamide of caprolactam (aminocaproic acid) or PA12 for the polyamide of laurine lactam

Other monomers are indicated by letters defined in ISO 1874, e.g. I for isophthalic acid or T for terephthalic acid. Copolyamides are designated by listing their monomers separated by a slash, e.g. PA 6/66 for the copolymer of caprolactam, hexene diamine and adipic acid.

Many technically used synthetic polyamides are derived from monomers containing 6-12 carbon atoms; most prevalent are PA6 and PA66. The film sector is dominated by PA6 and the random copolymer PA6/66, mostly due to their relatively easy processing that facilitates coextrusion with lower melting, thermally sensitive polyolefins.

fig 8: important polyamides

	type	monomers	melting temperature	water absorption (in water, 23°C)
PA66	A	hexene diamine (C6) adipic acid (C6)	260°C	8.5%
PA 610	A	hexene diamine (C6) sebacic acid (C10)	220°C	3.3%
PA 612	A	hexene diamine (C6) dodecanic diacid (C12)	215°C	2.8%
PA 6	B	caprolactam (C6)	220°C	9.5%
PA 11	B	aminoundecanic acid (C11)	185°C	1.8%
PA 12	B	aminododecanic acid (C12)	178°C	1.5%
PA 6/66 (85:15)	A,B	copolyamide of caprolactam (85%), hexene diamine and adipic acid (15%)	195°C	10.5%
PA 6I/6T	A	hexene diamine (C6) Terephthalic and Isophthalic acid	T _g = 132°C ^{*)}	1.3%

^{*)} glass transition temperature

The amide groups in the mostly semicrystalline polyamides are capable of forming strong electrostatic forces between the -NH and the -CO - units (hydrogen bonds), producing high melting points, exceptional strength and stiffness, high barrier properties and excellent chemical resistance. However, the amide units also form strong interactions with water, causing the polyamides to absorb water in a range between 2 and 20%. These water molecules are inserted into the hydrogen bonds, loosening the intermolecular attracting forces and acting as a plastisizer, resulting in the exceptional toughness and elasticity well known of polyamides.

3. Film Processing of Polyamide Resins

3.1. Pre-Processing

Polyamide, as a water absorbing polycondensation polymer, is sensitive to moisture. Processing nylon resin with excessive moisture content will result in molecular weight degradation by hydrolysis and the formation of steam bubbles. To prevent this, the moisture levels should be maintained below 0.1 wt%. Most resin producers supply nylon pre-dried and in moisture-proof packaging to ensure the resin stays dry and ready for use. Once this moisture proof packaging is opened, nylon will begin absorbing moisture from the atmosphere, therefore nylon exposure to air humidity after opening the bag must be minimized by rapidly using the resin or by blanketing the resin with dry air or nitrogen. This action is essential for bulk supply of polyamide resin which is of rapidly increasing importance.

fig 9

Only if a polyamide resin absorbs more than the recommended 0.1 wt.%, it should be dried at 80°C utilizing a dry air dryer of dew point below -20°C. Simple hot-air dryers should be avoided as they may actually humidify nylon when ambient humidity levels are high.

3.2. Extrusion

Polyamide can be processed as blown and cast film, and can be used for extrusion coating and the production of biaxially oriented film (BOPA).

Polyamide processes well in a wide variety of standard extrusion equipment. General recommendations for an extruder to process nylon are:

fig 10:

- barrier or 3-zone compression screw
- compression ratio between 3.1:1 and 4:1
- length to diameter (L/D) ratio at least 24:1 or higher
 - 35% feed (preheating)
 - 15% compression (melting)
 - 50% metering (homogenizing)

Polyamides melt at relatively high temperatures and need higher processing temperature than polyolefins. A typical temperature profile for a screw with 5 heat zones for processing polyamide 6 would be (for copolyamide PA6/66, 20°C lower temperatures):

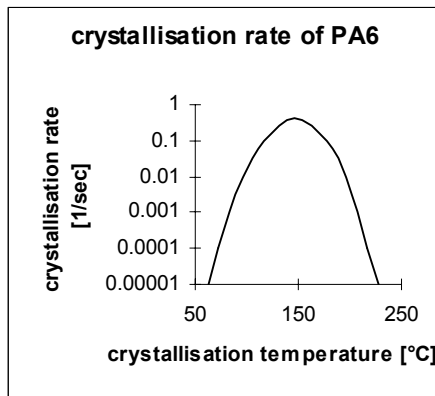
fig 11:

barrel type	film type	throat	zone 1 [°C]	zone 2 [°C]	zone 3 [°C]	zone 4 [°C]	connecting pipe [°C]	head [°C]	melt temperature [°C]
smooth	blown	200	260	258	253	250	250	250	250
gooved	blown	200	240	243	247	250	250	250	250
smooth	cast	200	275	272	268	265	265	265	265
grooved	cast	200	260	255	260	265	265	265	265

3.3. Film Forming

Polyamide is used in both cast and blown film equipment, predominantly for multilayer films. Since nylon is a semicrystalline material, processes that rapidly cool the polyamide film will result in lower crystallinity and therefore provide more transparent, flexible, thermoformable film.

fig 12



For cast films, standard equipment as used for PE or PP is used for multilayer film with polyamide layers. Factors to consider are

fig 13:

- chill roll temperature 20-50°C for high thermoformability
- chill roll temperature 75-85°C for high dimensional stability
- polyamide resins with viscosity number 200-230 cm³/g
- polyethylene resins of MI = 3.0 – 4.0 cm³/10min

Standard blown film equipment is used for producing multilayer films with nylon layers. In general, these topics need to be considered for blown film

fig 14:

- Cooling with ambient air or refrigerated air
- optional IBC Internal Bubble Cooling
- Blow up ratio: 1:1.1 – 1:2.5
- Polyamide with Viscosity Number 200-260 cm³/g
 - predominantly random copolyamides PA6/66
- Polyethylene of MI = 0.8 – 1.0 cm²/10min

A technology already published in the literature in the late 50's but that attracted more attention recently is the extrusion of a tubular film into a cold-water bath, optionally with internal water cooling mandrill. This film forming method provides extremely high cooling rates and produces therefore – even at high specific output - film of even better transparency and thermoformability than rapidly cooled cast film. On the other hand, this tubular film avoids some of the disadvantages of cast multilayer film such as difficult to control layer distribution and hardly recyclable edge trim of significant amount.

fig 15

Biaxially oriented PA film (BOPA) may be produced by both blown film process ("double bubble") and cast film ("tenter frame ") process with simultaneous or sequential orientation, similar to those used for BOPET and BOPP.

fig 16

The production of biaxially oriented nylon film consists of the consecutive steps:

- extrusion of a rapidly quenched, amorphous primary film
- reheating of the primary film
- stretching
- thermofixation/annealing

For some applications such as shrink bags or sausage casing, a controlled level of shrinkability is retained in the film by only partly annealing the film. Such sausage casing film – which has a double function as processing aid for curing the sausage but also as packaging film – is today produced by double bubble BOPA process with up to seven layers of PA, PE and optionally EVOH.

fig 17

3.4. Post-Treatment

A specific property of polyamide, that makes it distinct of most other polymers, is its water absorption

fig 18

When nylon exits the extruder, it will absorb moisture from the atmosphere over time. The absorbed water acts as a plasticizer and lowers the glass transition temperature.

fig 19

This effect drastically increases the elastic properties of polyamide film such as

- flexibility
- elongation at break
- puncture resistance
- impact strength
- thermoformability

fig 20

Polyamide film should therefore be used or converted only after it has been conditioned with water. This may be done by giving the film sufficient time to come to equilibrium with the air humidity – a process which may consume considerable time especially in case of multilayer film where a PA core layer is embedded in polyolefin skin layers. A ready-to-use film may be obtained by in-line humidification by passing the film through a hot-water bath, a steam chamber or a water-spray station.

fig 21

An additional benefit of in-line humidification is the high dimensional stability of film produced utilizing such equipment. Polyamide is a semicrystalline material that crystallizes more or less completely, depending on the type of polyamide and the cooling rate during the film solidification: Rapidly quenched film made by cast film process with very low chill roll temperature or water-cooled blown film is nearly amorphous, whereas blown film cooled with ambient air is highly crystalline. Amorphous or partly crystallized film will postcrystallize and shrink when the film absorbs humidity from the air. Cutting to the desired film width can therefore only be completed once the film is conditioned. By in-line humidification, or even by only in-line reheating to a temperature above the glass transition temperature, the film will immediately postcrystallize and complete its shrinkage process. Such a film can be cut to the desired width immediately without prior conditioning time. This effect was demonstrated by producing a monolayer (50µm) film at 20°C chill roll temperature, the crystallinity of this film (according X-ray scattering) was < 1%. Within 2h of exposure to 23°C/65% rh, this film was shrinking 1-2%. But if the film had passed a second, heated “chill” roll of 80-100°C during the extrusion process, the film remained at its original dimensions when exposed to humid air.

fig 22

The reason for this shrinkage is a solid-state postcrystallisation of the initially amorphous film as soon as the temperature exceeds the polyamide’s glass transition temperature (55°C), or as soon as the absorbed humidity from the air causes the T_g to drop below the ambient temperature. However this postcrystallisation does not affect the beneficial properties that make rapidly cooled film superior to slowly cooled, highly crystalline film:

- high transparency
- high flexibility
- superior puncture and impact resistance
- good thermoformability

fig 23

If film is cooled slowly, it has sufficient time to grow crystals of significant size, spherulites. These scatter and reflect visible light and cause haze – however the addition of a nucleating agent into the PA resin will help to reduce the spherulite size to below 400nm, the wavelength of the visible light, and significantly improve transparency. SEM micrographs show that the spherulites are agglomerates of microcrystals.

fig 24

Rapidly cooled film is optically transparent, however SEM micrographs reveal the same type of microcrystals – after postcrystallisation by exposing the film to humidity. But the microcrystals produced by solid-state postcrystallisation do not agglomerate to form large, visible spherulites.

4. Properties of nylon film

Nylon properties are dominated by the presence of the amide group in the polymer chain, which provides strong intermolecular adhesion via hydrogen bonds. These strong attractive forces between the molecules result in

fig 25

- **high melting point and heat resistance**
- **high mechanical properties (strength, stiffness)**
- **high barrier to oxygen, carbon dioxide and many solvents and aroma materials**

The highly polarity of the amide groups is also responsible for the water absorption of nylon resins. Water molecules inserted into the hydrogen bonds provide superior elastic properties, as

fig 26

- **high puncture resistance and toughness**
- **good thermoformability**

The outstanding feature of nylon is the fact that it provides all these properties simultaneously to the film construction. Nylon is therefore chosen when a complex property portfolio is requested from a film construction.

4.1. Mechanical Properties

Nylon shows exceptionally high strength, toughness and puncture resistance and provides these properties also to multilayer film based on nylon.

As the mechanical properties of nylon film depend on the resin's water absorption. Water acts as a plasticizer for polyamides, lowering its strength and stiffness while increasing its toughness, drawability and elasticity. As film rapidly absorbs moisture – surface layers within minutes, but even PA layers shielded by polyethylene layers from the ambient atmosphere within a few days – only mechanical properties after moisturization into humidity equilibrium are relevant.

4.2. Barrier Properties

fig 27

PA6 has an intermediate oxygen transmission rate (OTR) that increases at higher humidity levels. Its barrier is 2 magnitudes higher than that of polyolefins, but still 10-100x inferior to high-barrier EVOH. In high humidity environment, the EVOH's barrier is reduced even stronger and may achieve the magnitude of special polyamide resins as PA MXD6, the polyamide of m-xylylene diamine and adipic acid.

Nylon shows superior barrier to chemicals of low polarity as hydrocarbon solvents, but also to low polarity aroma substances in food component, as limonene, campher, vanillin and menthol. Only with regard to highly polar chemicals that are readily absorbed by nylon, as water, ethanol or methanol, its barrier is inferior.

fig 28: barrier of various polymer resins, at 23°C, for 25µm film thickness (typical values)

	N2	CO2	C2H6	H2O	Isooctane	limonene	Menthol
25µm film	0% rh	0%rh		85→0%	50%rh	50%rh	50%rh
	cm ³ / m ² d bar	cm ³ / m ² d bar	cm ³ / m ² d bar	g/m ² d	g/m ² d	g/m ² d	g/m ² d
PA6	14	200	0.5	35	0.08	0.012	<0.01
BOPA6	12	150	0.4	30			
LDPE				5	350	60	10
EVOH 44%					0.1	0.012	<0.01

4.3. Thermoformability

fig 29

Polyamide is often used in multilayer structures for its high maximum deep draw depth and its ability to maintain as much barrier layer thickness in the corners of the thermoformed, the areas of deepest draw.

fig 30

In a multilayer film PE-tie-PA-EVOH-PA, the EVOH's drawability is significantly improved compared to a structure where the EVOH barrier layer is not sandwiched between PA layers.

4.4. Sealability

fig 31

An outside layer of PA provides high heat resistance to a multilayer film structure, allowing the processor to operate at a high sealing bar temperature without sticking of the film to the sealing bar surface. Such a film will therefore provide high sealing line speed as well as good seal quality. For this type of film, a well crystallized PA film – by slow cooling or solid-state postcrystallisation – is essential to avoid shrinkage of the film in the seal area, which might result in wrinkles and pinholes.

4.5. Properties of Oriented PA Film

fig 32

Biaxially oriented nylon (BOPA) film is characterized by

- **very high stiffness**
- **very good printability**
- **very high strength**
- **high puncture resistance**
- **low elongation to break**

Its deformation mode under load is dominated by an elastic behavior, rather than the plastic deformation of standard nylon film. Biaxially oriented nylon film is therefore highly suitable for metallisation or coating with inorganic barrier layers as “SiOx”, further it exhibits very good printability due to its high dimensional stability under load.

fig 33

BOPA has a 30% higher oxygen barrier compared to non-oriented cast PA film, a small increase compared to the 3x improvement between BOPET and non-oriented CPET. This is caused by the fact that in case of PA, BOPA film with its stress-induced crystallinity is compared to crystalline CPA film, whereas in case of PET film, the non-oriented baseline is formed by a predominantly amorphous CPET film.

5. Applications

fig 34, fig 35

The wide majority of nylon film is used as a component of coextruded or laminated multilayer film for packaging of food sensitive to oxygen, such as

- **meat**
- **processed meat (sausage, bacon)**
- **smoked fish**
- **cereals**
- **cheese and dairy products**
- **semi-finished meals ("TV dinner")**

Nylon for Flexible Packaging Film

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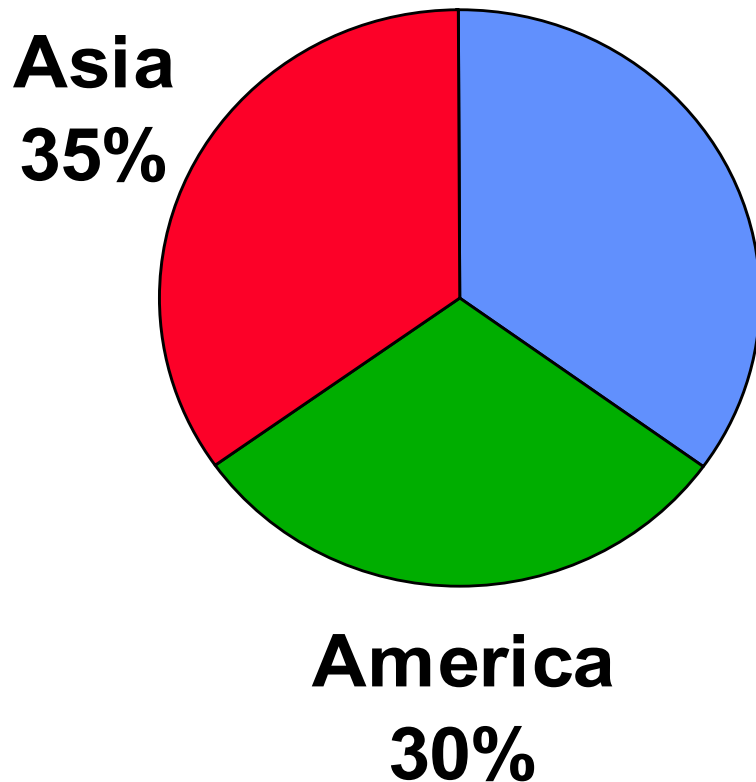


Polyamides are widely used for demanding applications in the packaging field for due to their unique combination of

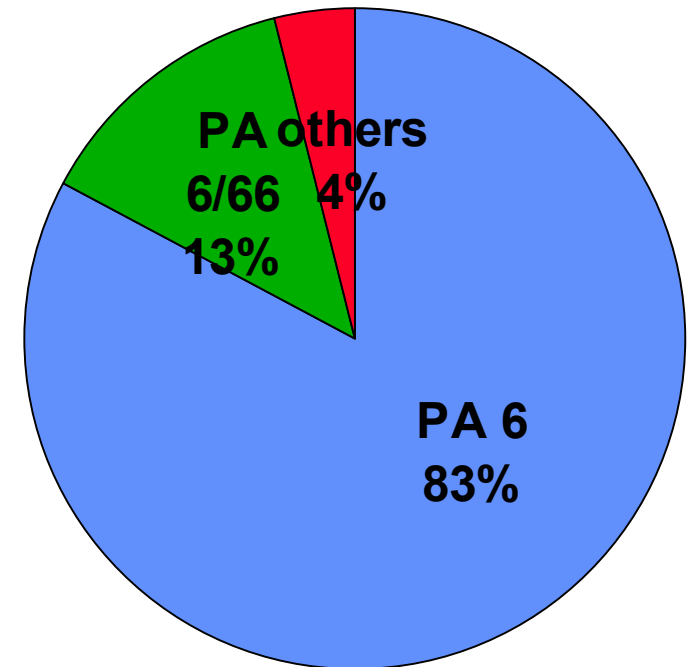
- **mechanical strength**
- **high heat distortion temperature**
- **high flexibility and toughness**
- **good barrier to oxygen, chemicals and aroma substances**
- **high transparency**
- **thermoformability**



PA consumption for film production



Europe
35%



total: 260 kt (2002)

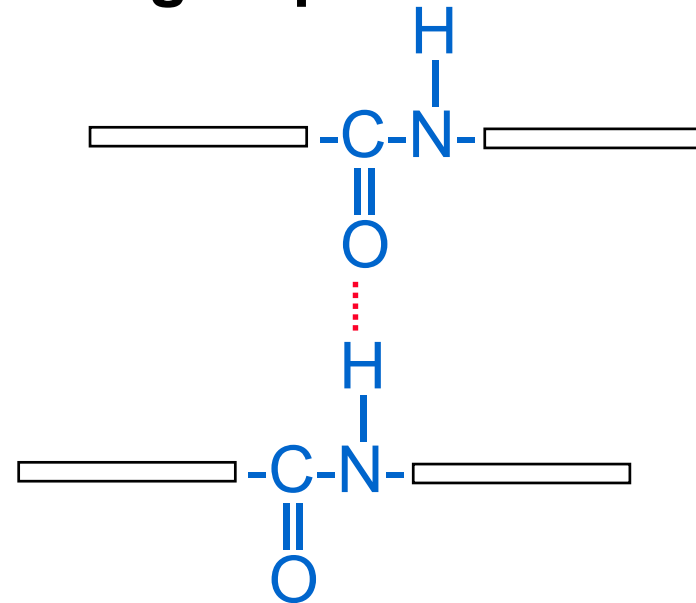
Introduction: What are Polyamides?

- **Synthetic Polyamides were developed in 1938**
 - **Perlon, Polyamid PA6 in Germany**
 - **Nylon, Polyamid PA66 in USA**
- **naturally occurring polyamides are**
 - **proteins**
 - **silk, wool, ..**
- **First applications for fibers, later also for engineering resins and for packaging film**
- **today, Nylon is often used as generic name for PA**

Introduction: What are Polyamides?

- Polyamide properties dominated by **amide** group

- strong interaction
 - with each other
 - with water



- between amide groups, water-repellent hydrocarbons are located

Introduction: What are Polyamides?

polyamides may be synthesized from

type A:



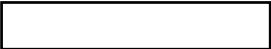
type B:

aminoacid



N = Amine group

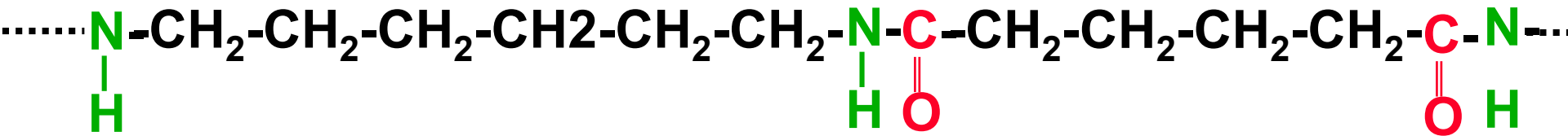
A = Acid group

 = hydrocarbon block

Introduction: Nomenclature of Polyamides

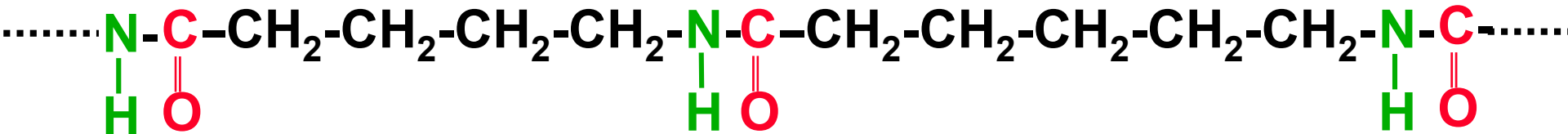
type A:

PA (number of amine carbon atoms) (number of acid carbon atoms)



type B

PA (number of aminoacid carbon atoms)

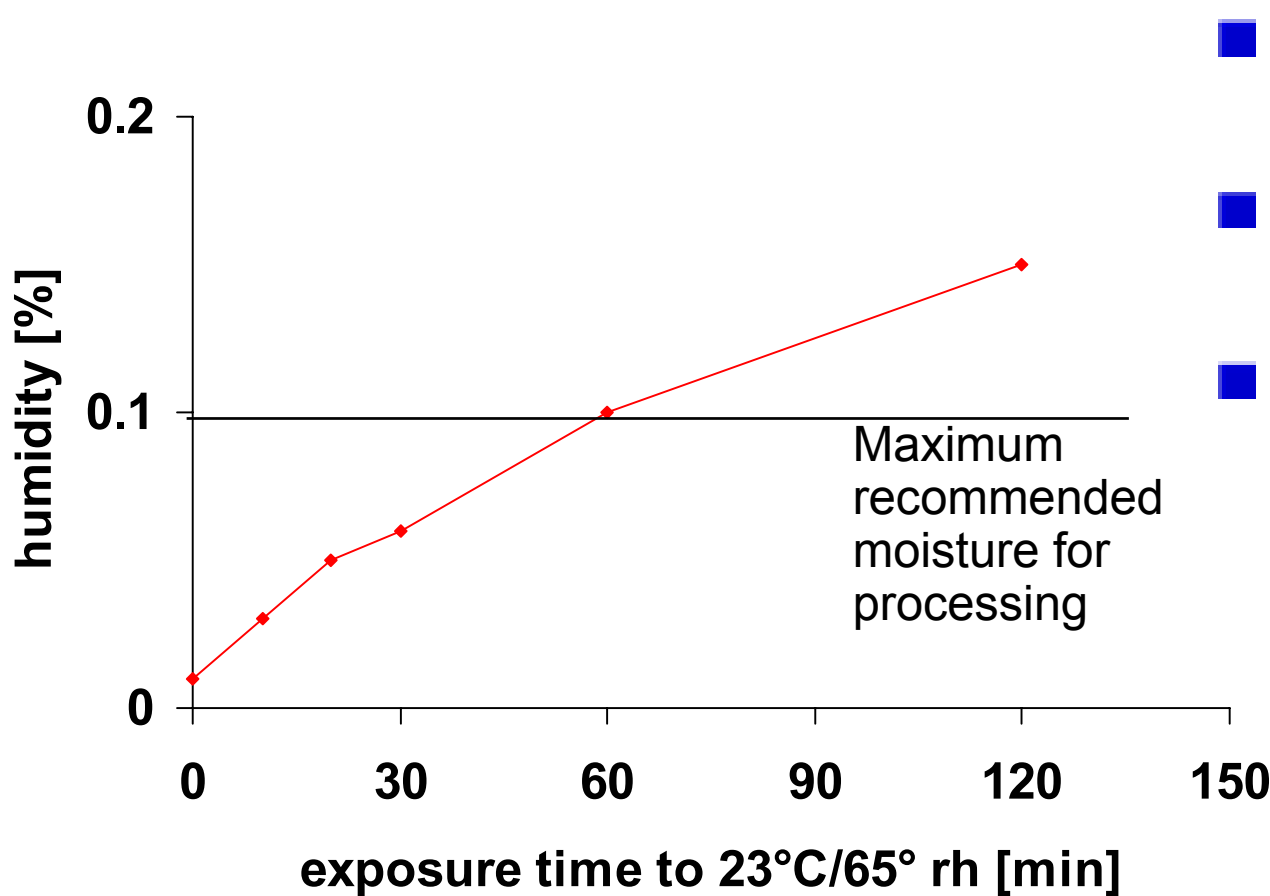


important Polyamides

	monomers	Tm	water absorption
PA 66	hexene diamine, adipic acid	260 °C	8.5%
PA 612	hexene diamine, dodecanic diacid	215 °C	2.8%
PA 6	caprolactame (aminocaproic acid)	220 °C	9.5%
PA 12	laurinlactame	178°C	1.5%
PA 6/66 (85:15)	hexene diamine, adipic acid caprolactame	195°C	10.5%
PA 6I/6T	hexene diamine, isophthalic acid, terephthalic acid	Tg = 132°C	1.3%

PA6 and PA6/66 most important for packaging film

moisture absorption rate of PA 6



- PA typically pre-dried
- keep under dry-air blanket
- drying only with dry-air dryer

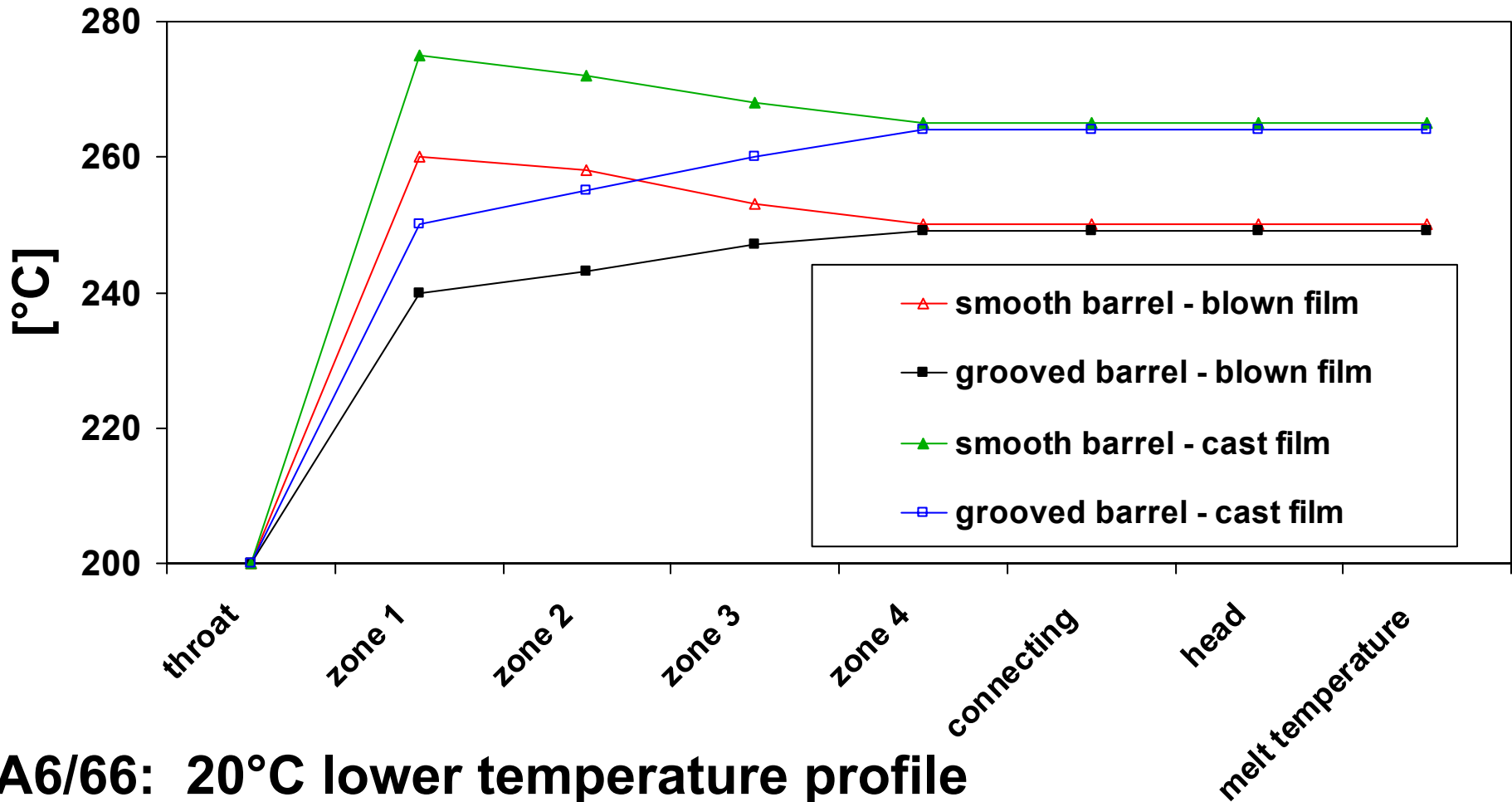
Moisture absorption of a single pellet layer, 65% r.h. / 23°C

Processing of PA : General Recommendations

- barrier or 3-zone screw
- minimum length/diameter of barrel (L/D) 24:1
- compression ratio 3:1(PA6)

Feed	35 %	9 D
Compression	15 %	4 D
Metering	50 %	11 D

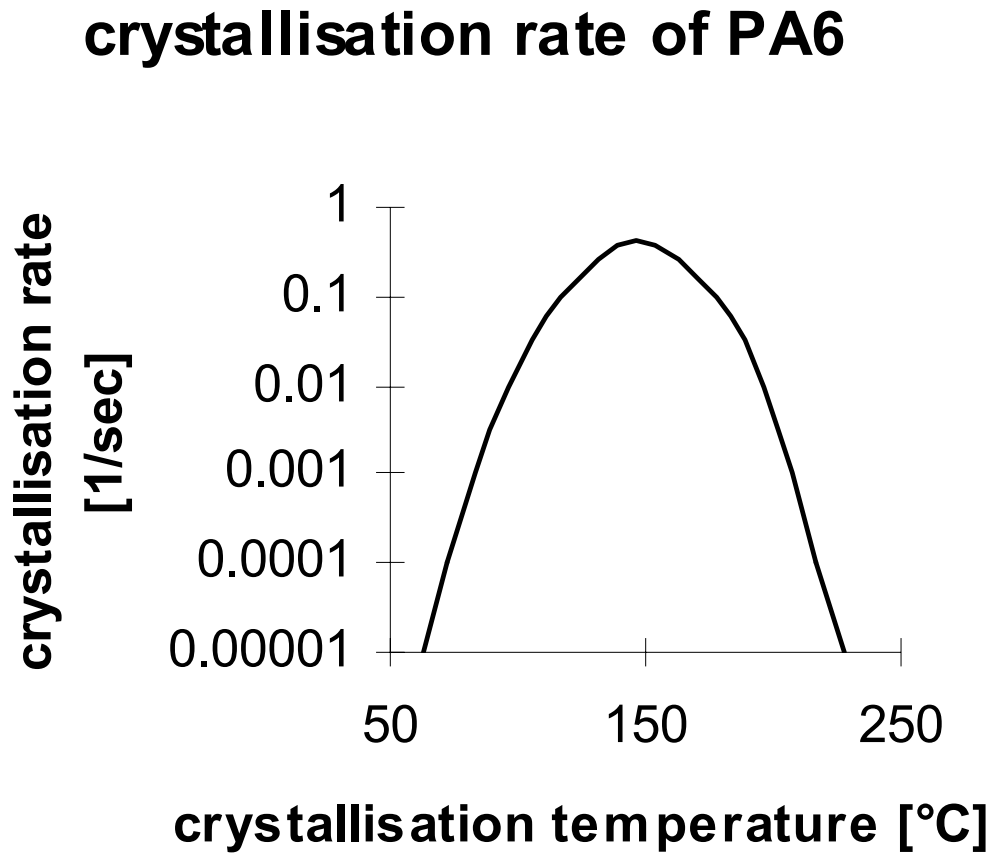
Processing of PA : Temperature Profile



PA6/66: 20°C lower temperature profile

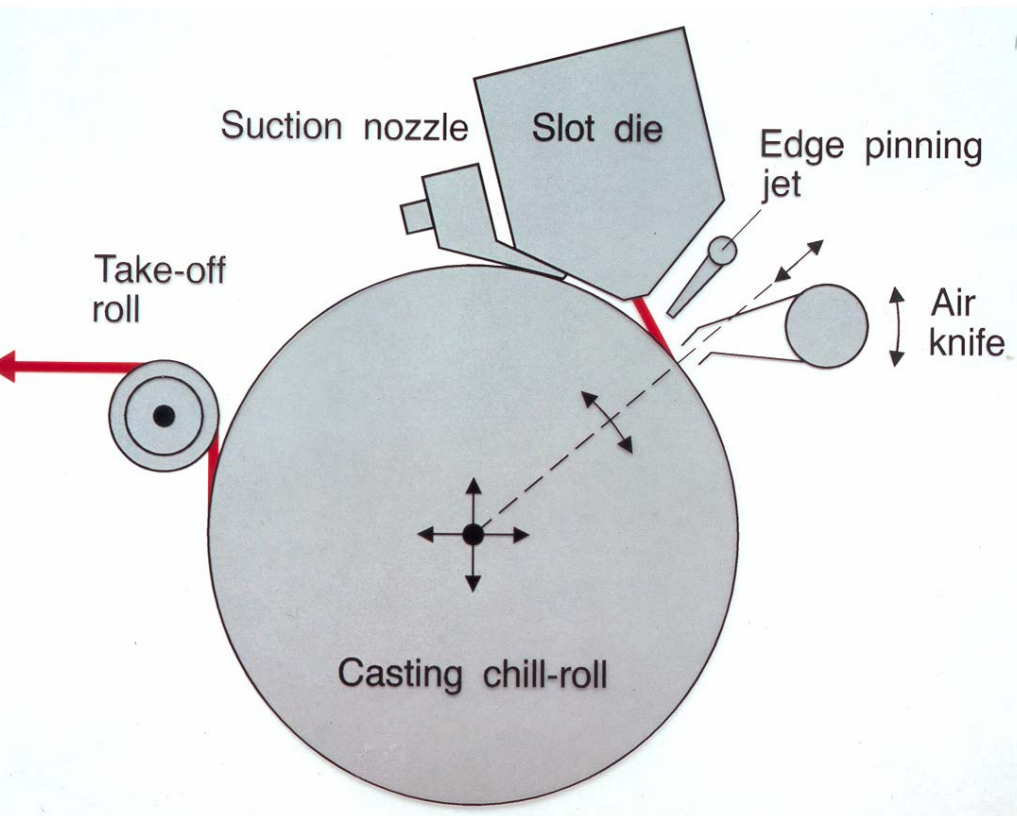
examples for typical temperature profile

Processing of PA : Crystallisation Rate of PA6



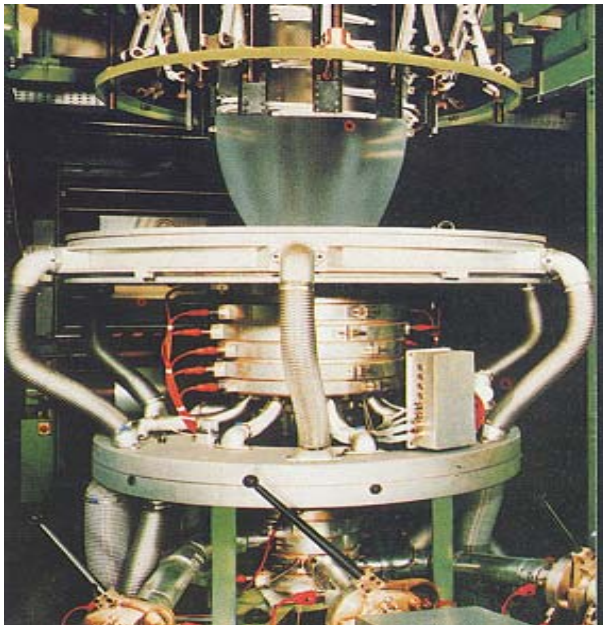
- 180 – 130°C:
moderate
crystallisation rate
- < 80°C:
crystallisation frozen
- rapid cooling:
amorphous film
- slow cooling:
crystalline film

Processing of Polyamide film: Cast Film



- standard cast film equipment
- chill roll 70-85°C : dimensional stability
- chill roll 20-35°C: high thermoformability
- PE (MI = 3-4)
- PA6 (RV3,2-3,6)
- nucleated PA recommended

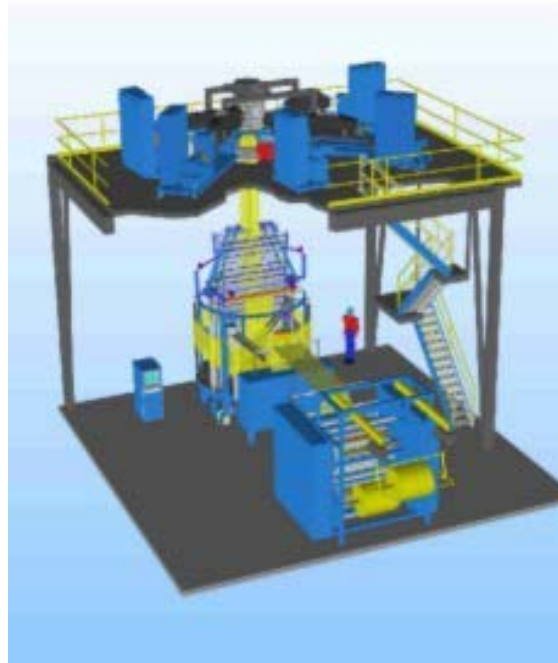
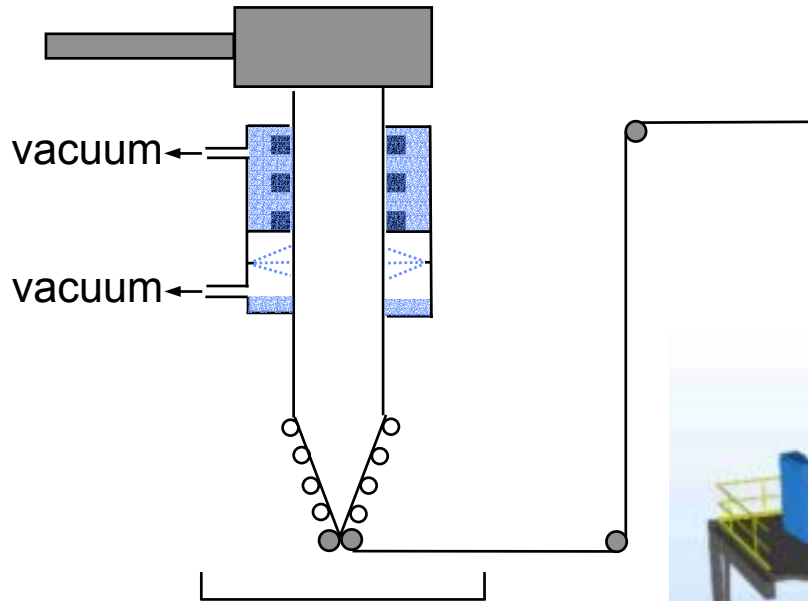
Processing of Polyamide Film: Blown Film



- standard blown film equipment
- air or refrigerated air cooling
- optional IBC

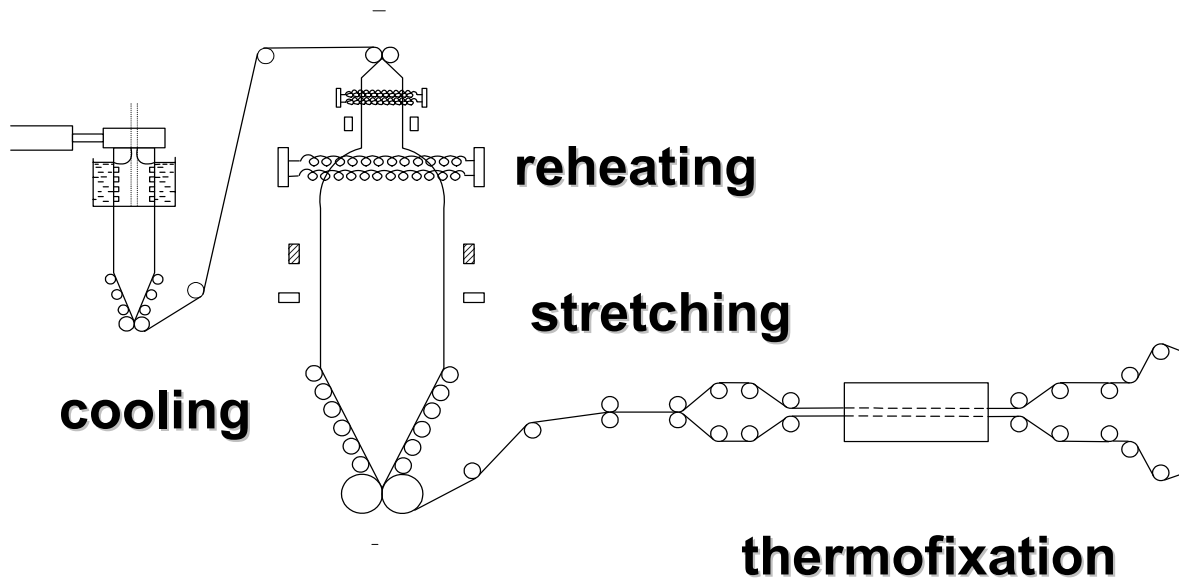
- PE (MI = 0.8 – 1 cm³/10min)
+ co-PA 6/66 (RV 3.2-3.6)
+ PA6 (RV 3.8-4.0)

Processing of PA Film: Water-Quenched Blown Film



- superior thermoformability
- high puncture resistance
- high line speed
- no/little edge trim

Processing of PA Film: Biaxially Oriented PA Film



BOPA film:

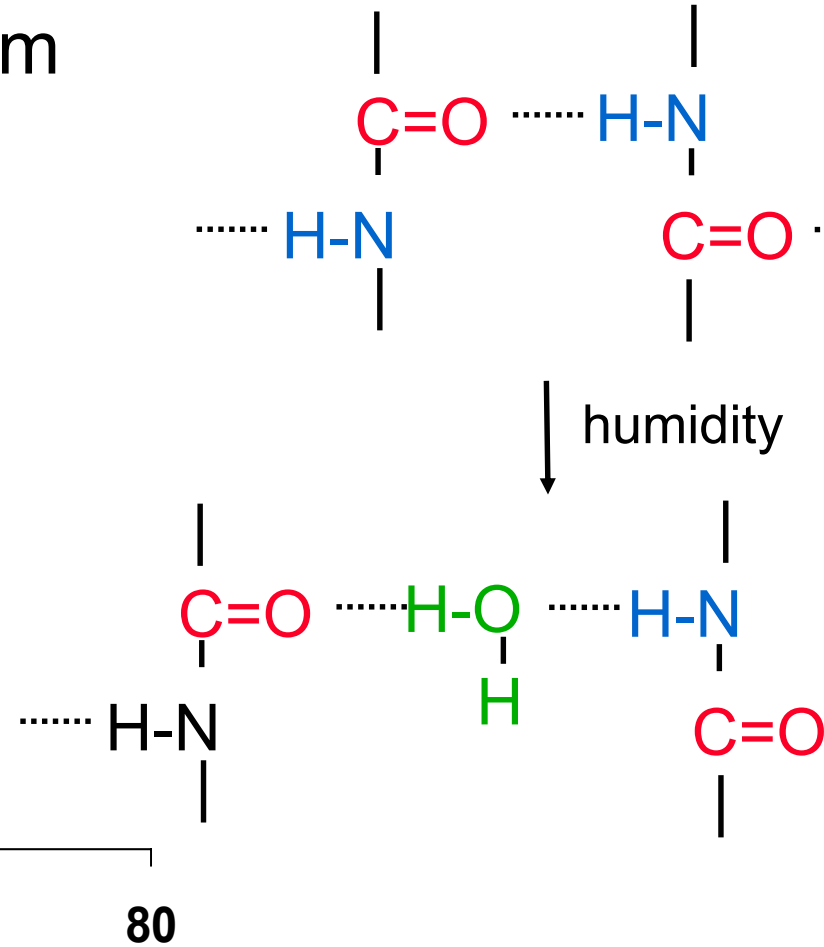
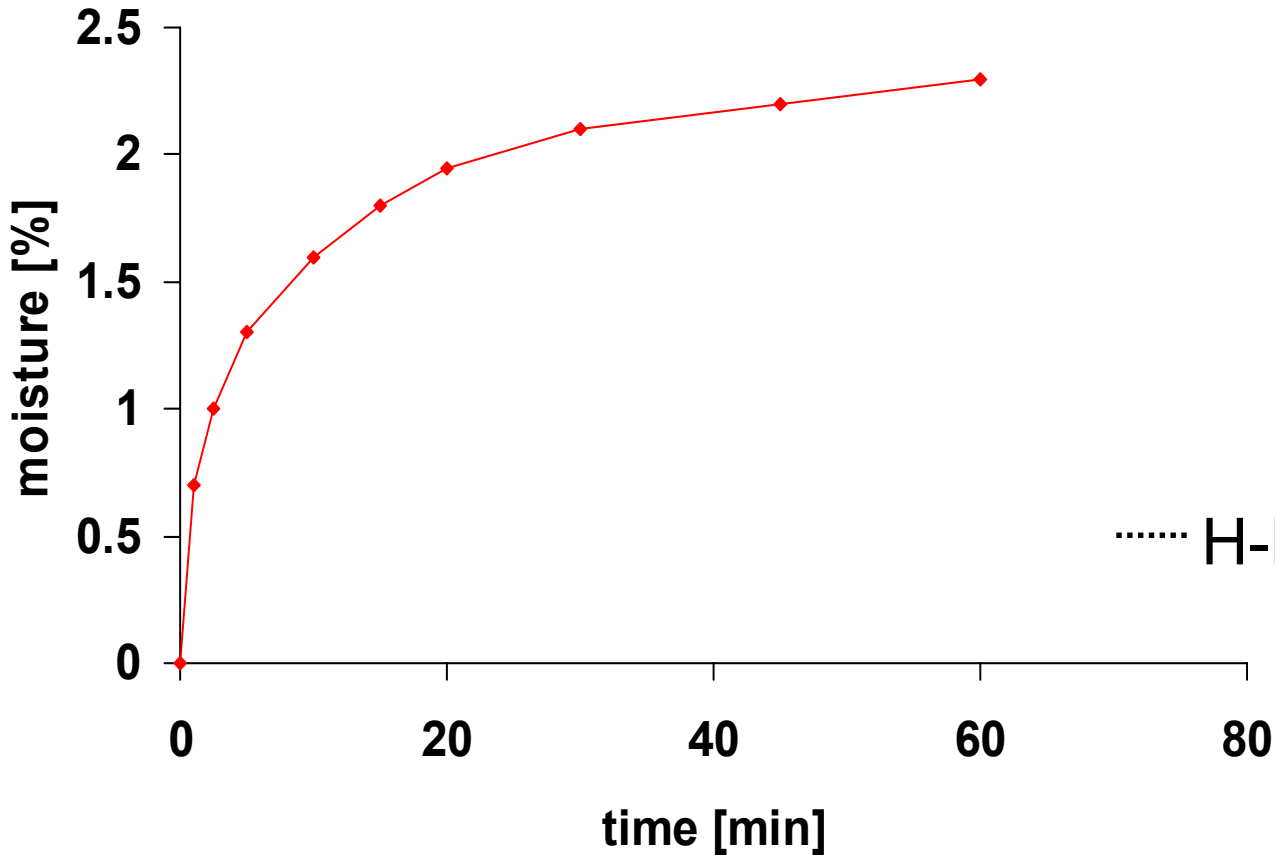
- rapid cooling
 - reheating $>T_g$
 - stretching
 - annealing/
thermofixation
- double bubble process
 - tenter frame - simultaneous
 - tenter frame - sequential

BOPA Sausage Casing



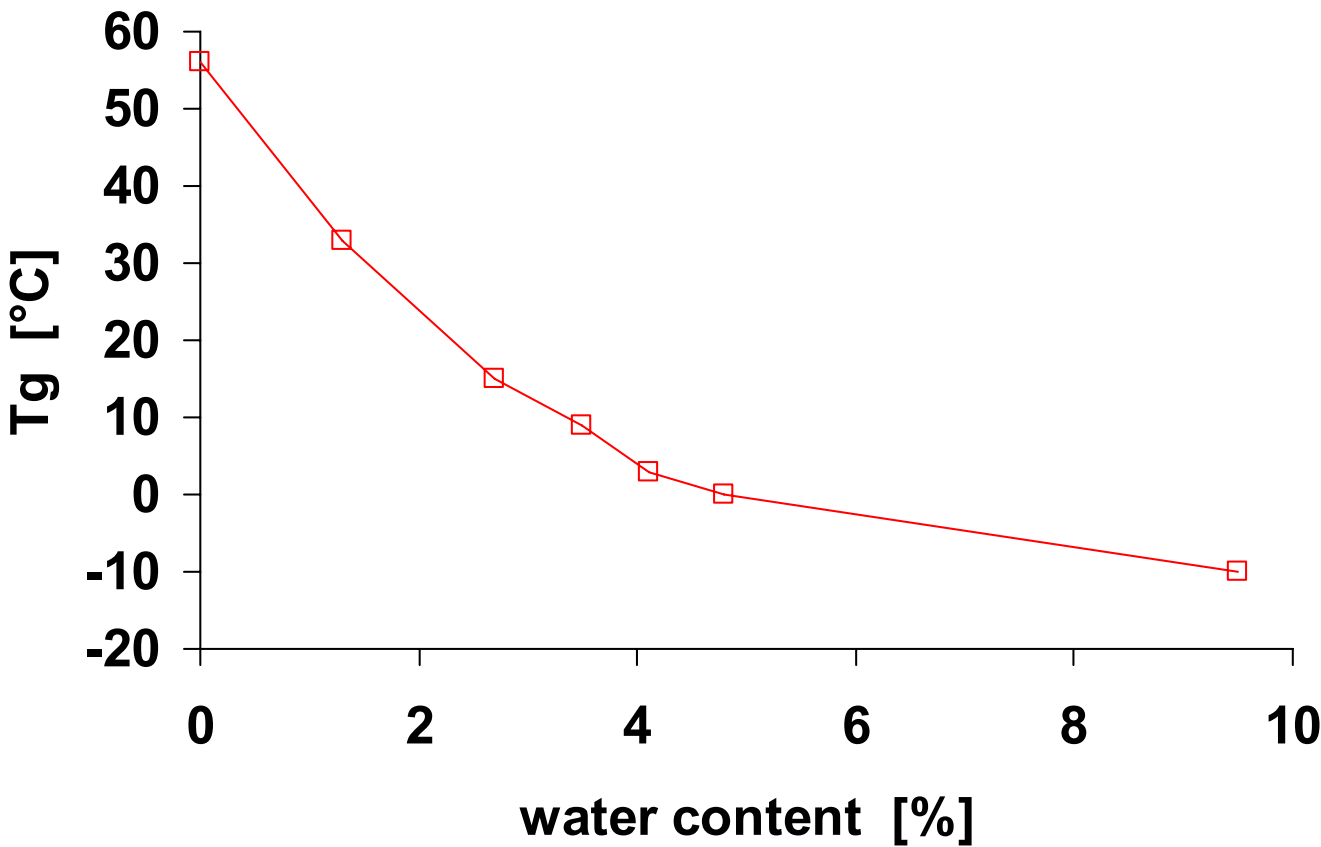
- double bubble process
- monolayer / multilayer
- defined shrinkability
- oxygen barrier
- meat (protein) adhesion
- printability

Moisture Absorption of PA 6 Film



moisture absorption of a 50 μ m PA6 mopnolayer film; 23°C / 65% r.h.

Moisture Absorption of PA 6 Film

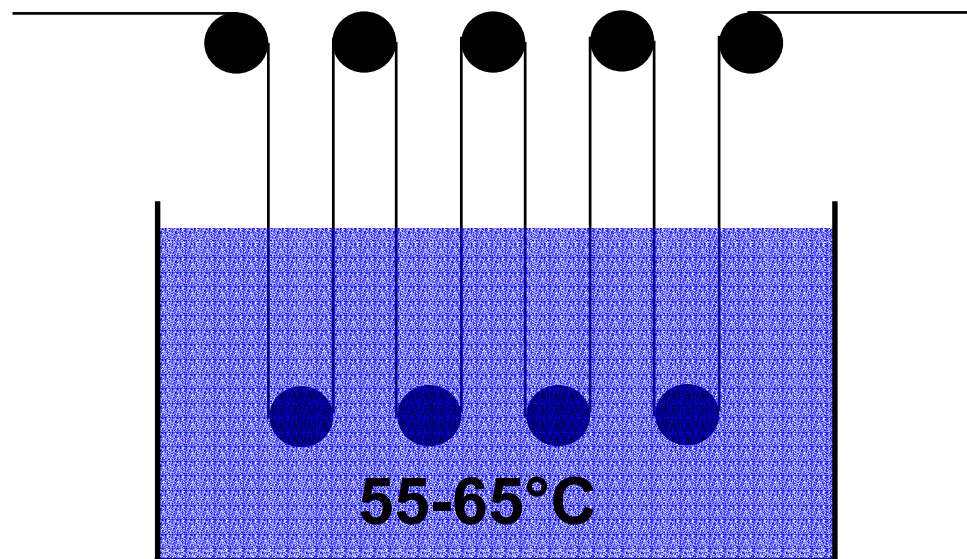
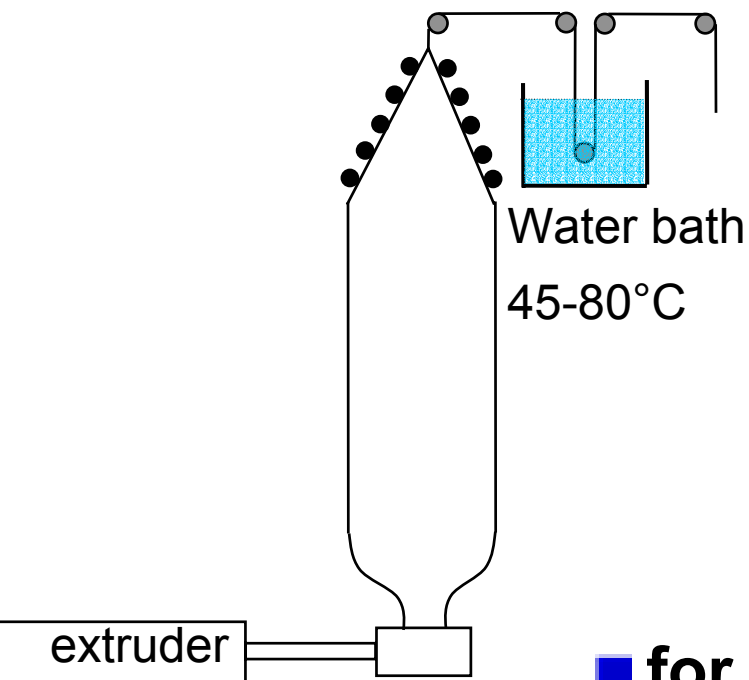


water

- inserted into hydrogen bond
- plasticizer
- lowers Tg
- + flexibility
- + puncture resistance
- + thermoformability

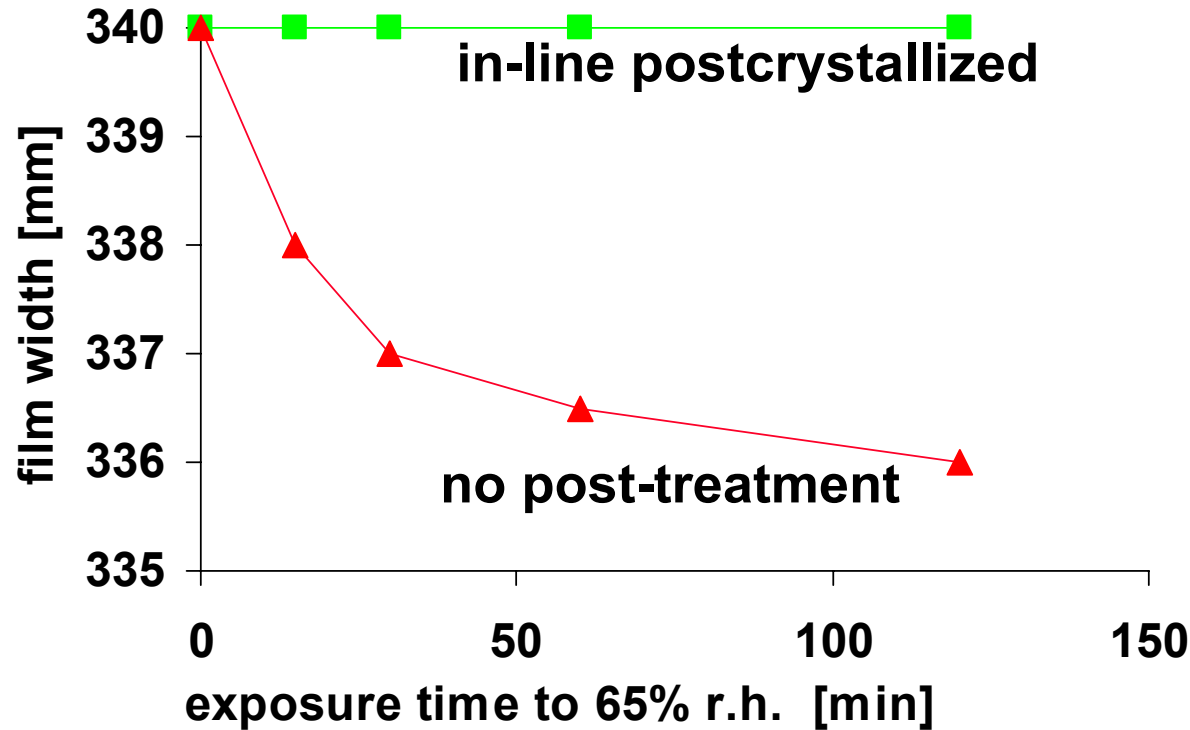
glass transition temperature of 1mm PA6 plates, torsion pendulum

Post-Treatment: In-line Humidification



- for blown or cast film
- water tank or steam tunnel
- film immediately ready to use
- no postshrinkage
- curl reduction of non-symmetric blown film

Post-Treatment: Dimensional Stability

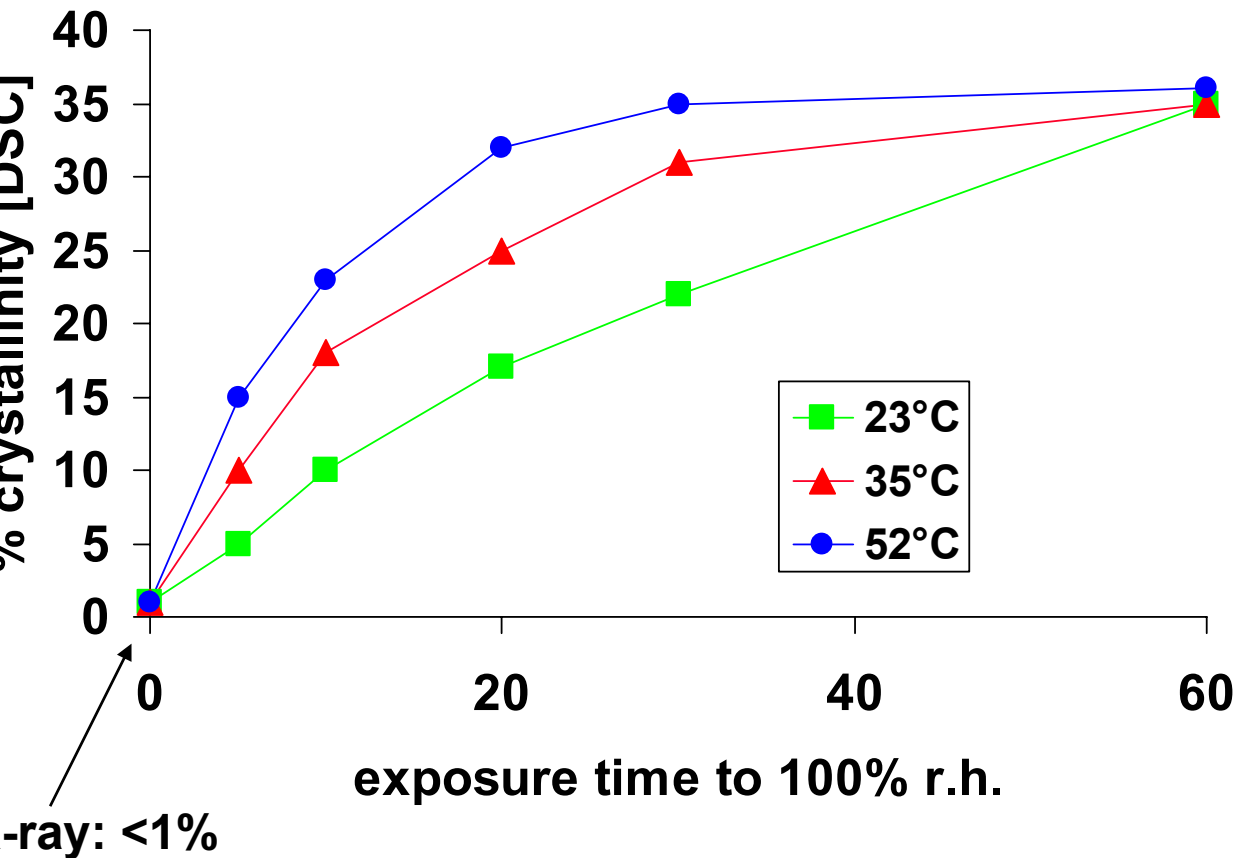


■ rapidly cooled film:
⇒ shrinkage by water absorption

■ in-line humidification or annealing:
⇒ no further shrinkage

dimensions of 50 μ m single layer PA6 film, 20°C chill roll temp

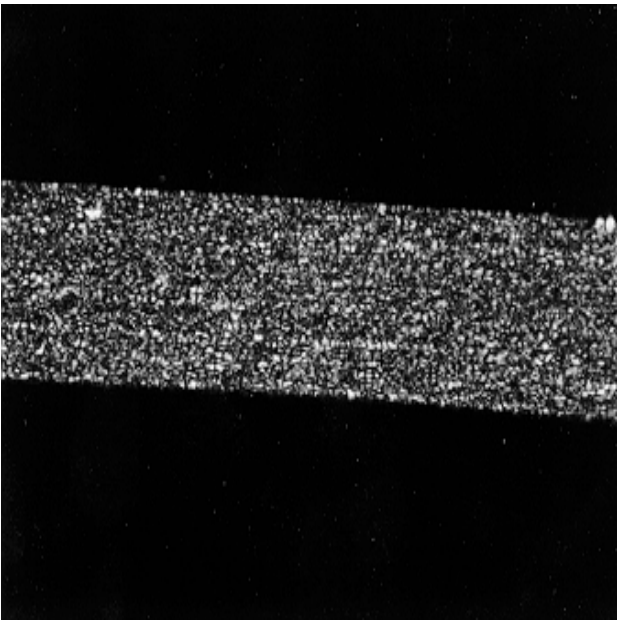
Post-Treatment: Solid-State Postcrystallisation



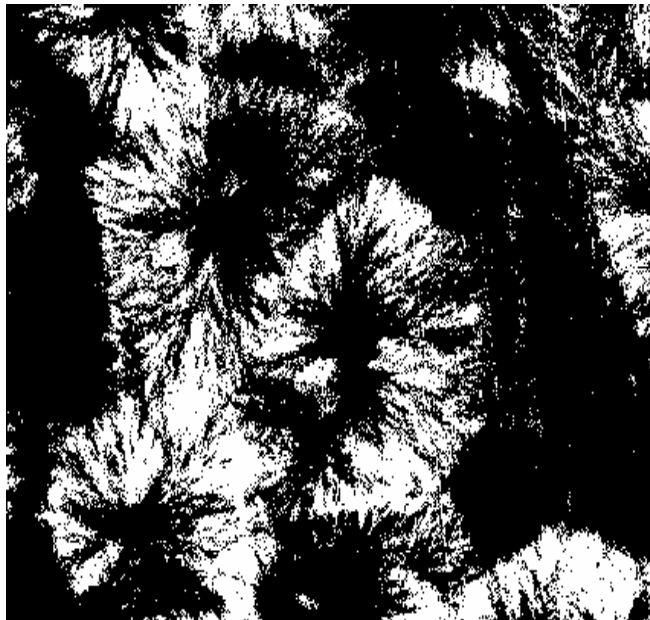
postcrystallisation of 50 μ m single layer PA6 film (20°C chill roll temp) at 100% rh

Post-Treatment: Solid-State Postcrystallisation

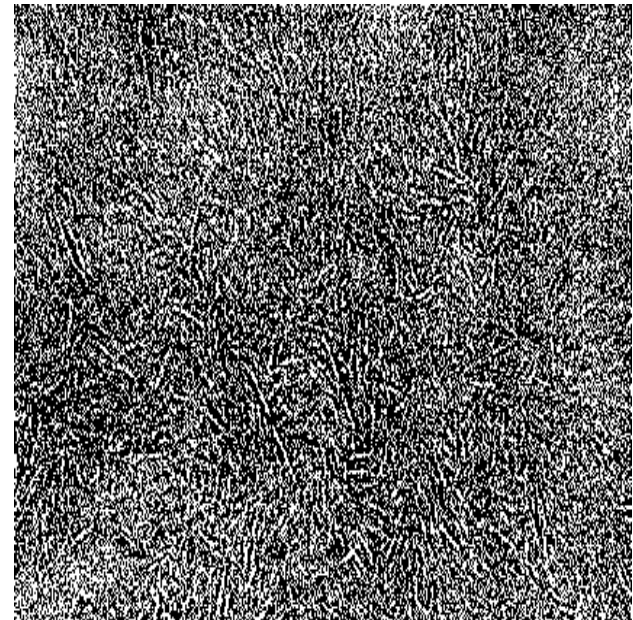
1:640x / light



1:10 000x / TEM



1:212 500x / TEM

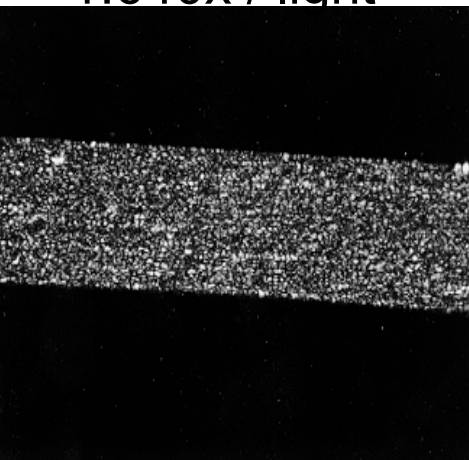


- **visible crystallinity = spherulites**
⇒ **agglomerates of microcrystals**

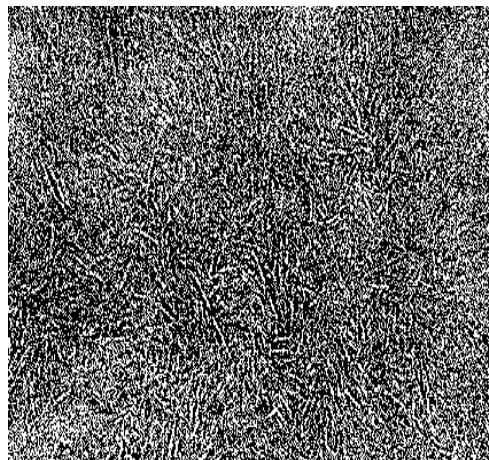
crystallinity of 50 μ m single layer film (130°C chill roll temp); nucleated PA6

Post-Treatment: Solid-State Postcrystallisation

1:640x / light



1:212 500x / TEM

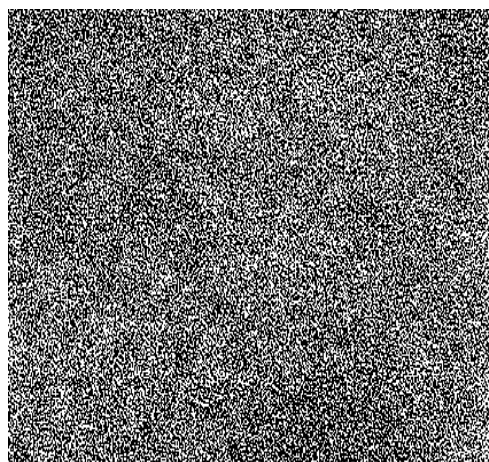
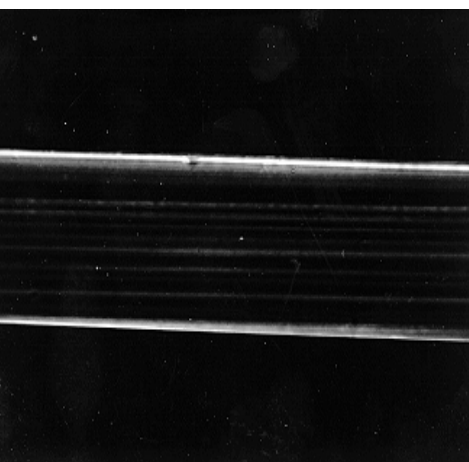


slowly
cooled

X-ray:
34% cryst.

crystalline film:

- spherulites
- agglomerates of microcrystals



rapidly
cooled

X-ray:
25% cryst

„amorphous“ film:

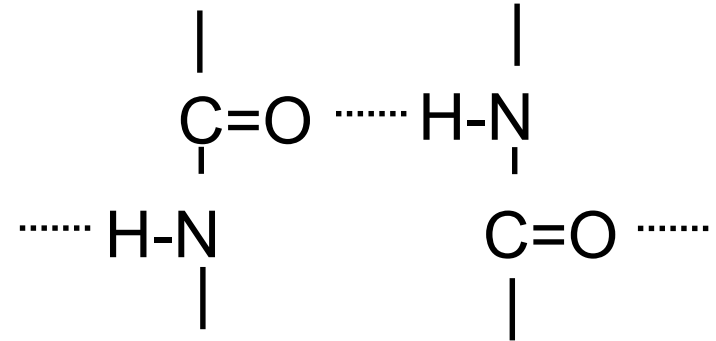
- no spherulites
- microcrystallinity by post-crystallisation

crystallinity of 50µm single layer PA6 cast film (130°C and 20°C chill roll temp)

Properties of Polyamides

amide-amide interactions provide

- high melting point
- high strength
- high stiffness
- good abrasion resistance
- high barrier/resistance to chemicals
gasoline, fat, aroma materials.....
- High oxygen barrier
- good printability
- **water absorption**

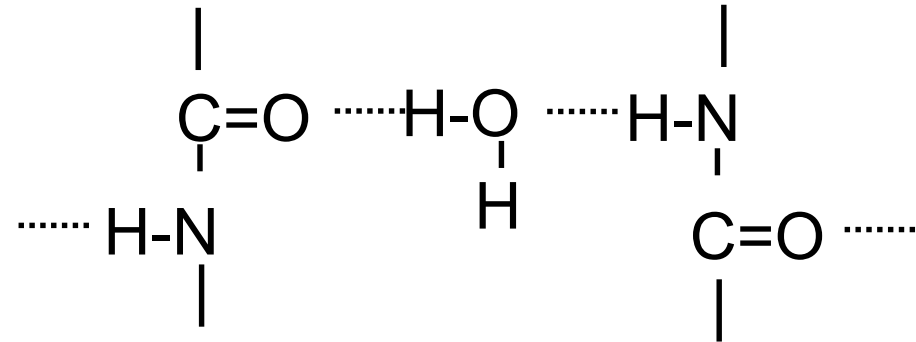


Properties of Polyamides

amide-water interactions provide

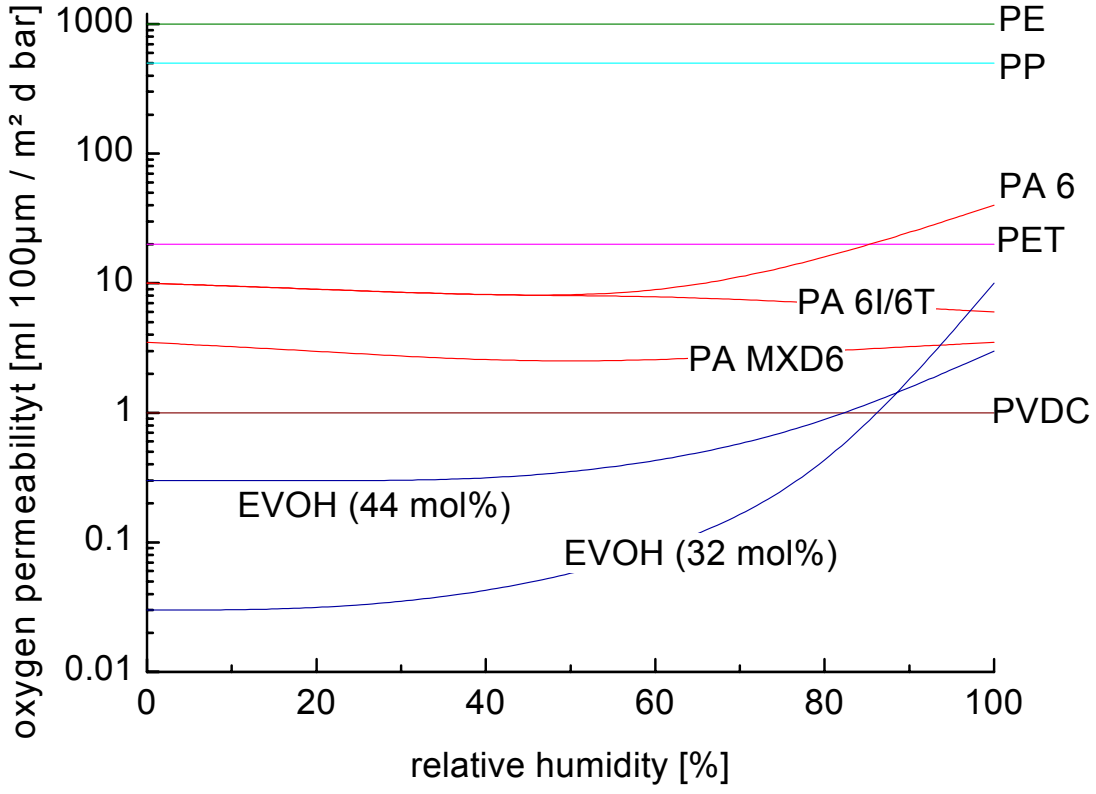
- flexibility and elasticity
- high toughness
- high stiffness
- good thermoformability

⇒ only after water absorption



● polyamide have **simultaneously** advantages in all these properties

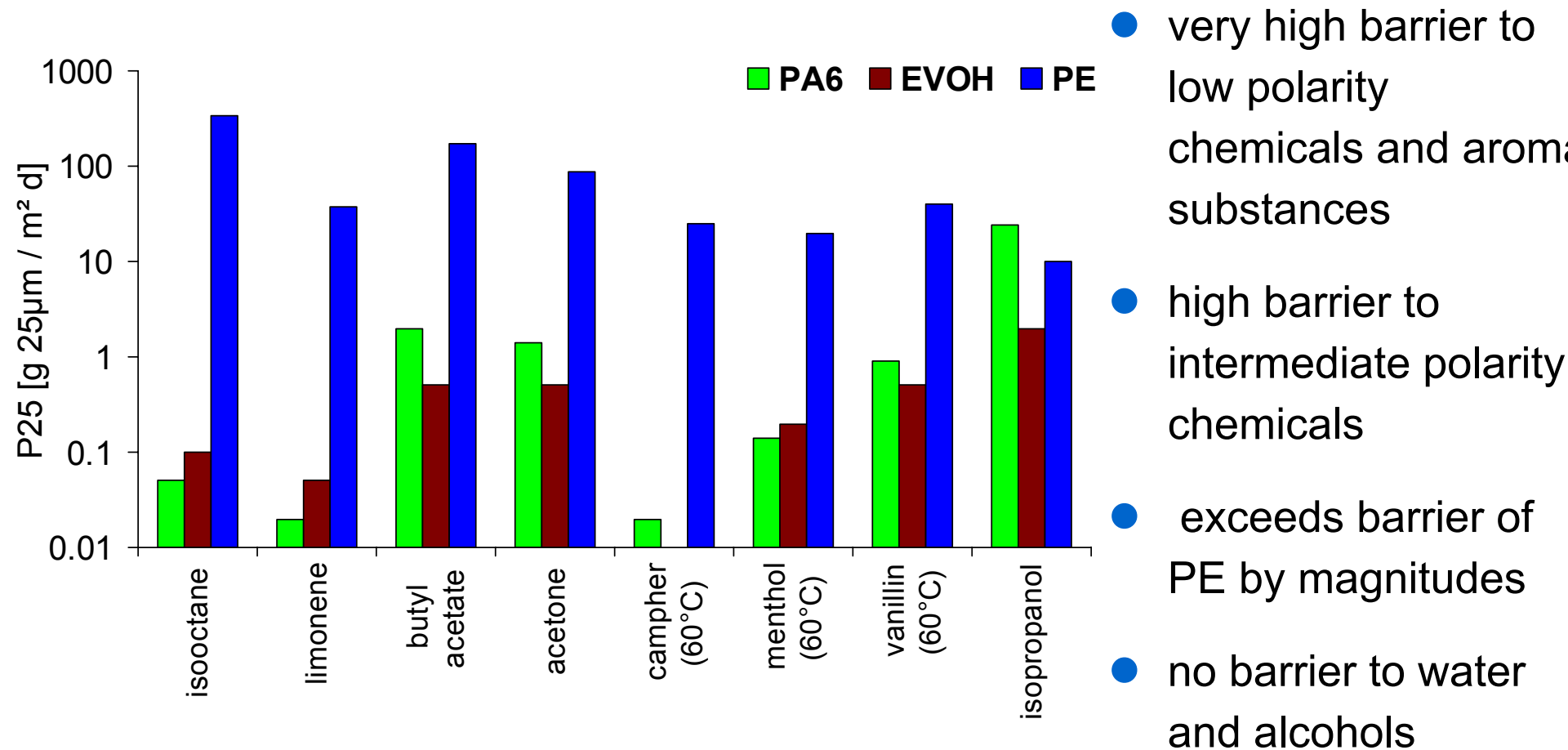
Properties of Polyamide Film: Barrier Properties



- high oxygen barrier of PA6
- some aromatic polymers with even higher barrier
- EVOH very high barrier, but strong reduction at high humidity

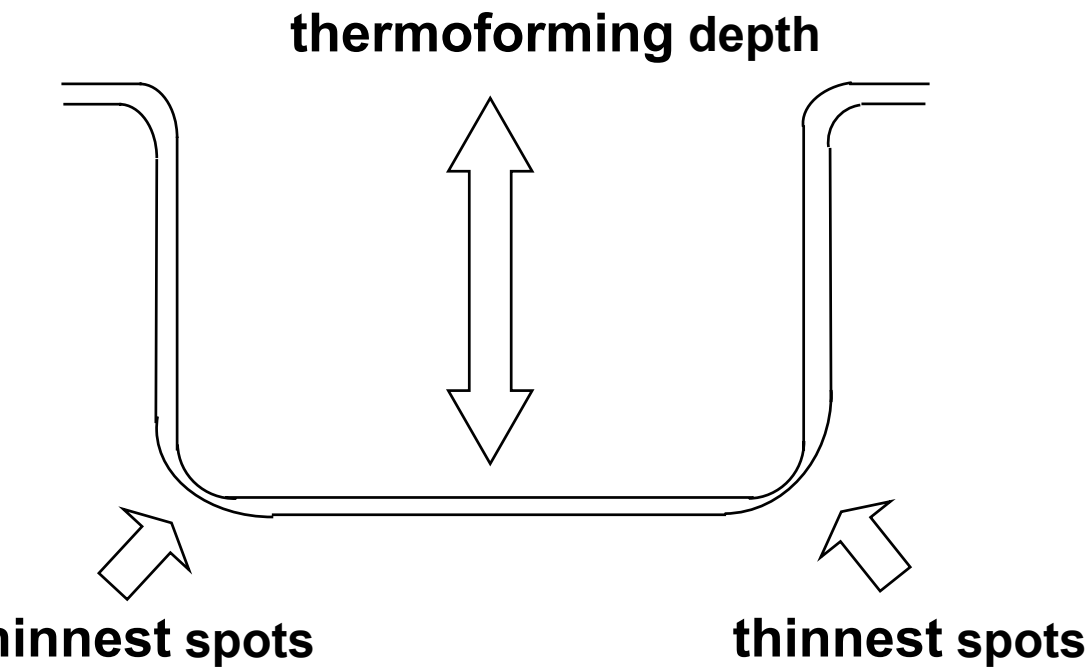
Oxygen barrier for 100 µm of various packaging polymers

Properties of PA Film: Solvent and Aroma Barrier

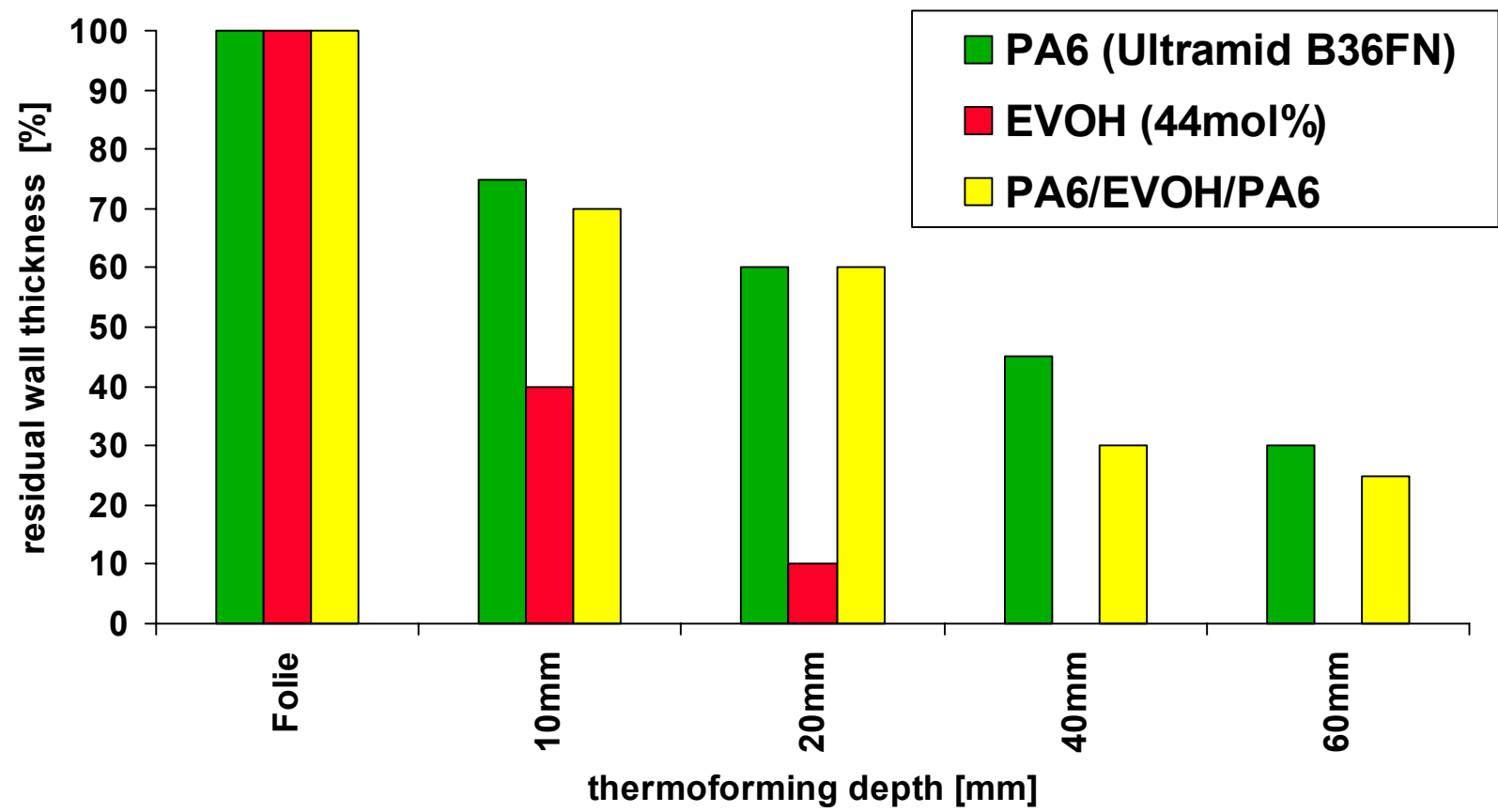


Permeation rate P25 for different solvent molecules at 23°C / 25µm PA6

Thermoforming of Polyamide Film



Properties of PA Film: Thermoforming



residual wall thickness [% of initial thickness of barrier layer] of blown film

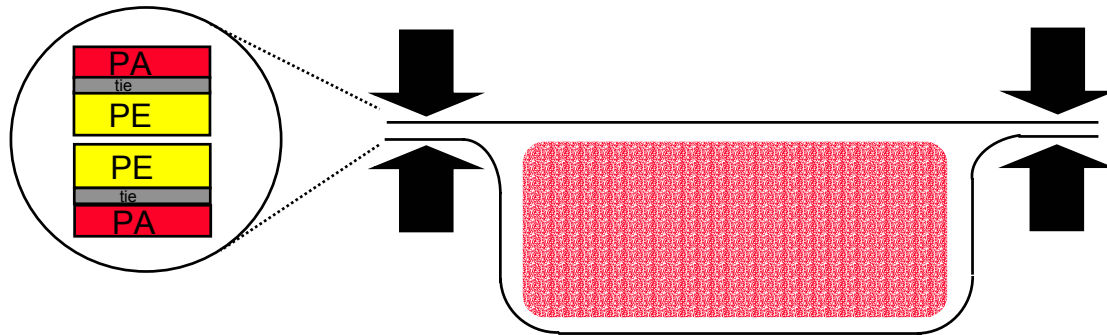
PE/adh/PA(50µm)/adh/PE

PE/adh/EVOH(10µm)/adh/PE

PE/adh/PA(20)/EVOH(8)/PA(25)

thermoforming 120x80mm, 6mm corner radius, 90°C

Properties of PA Film: Heat Resistance



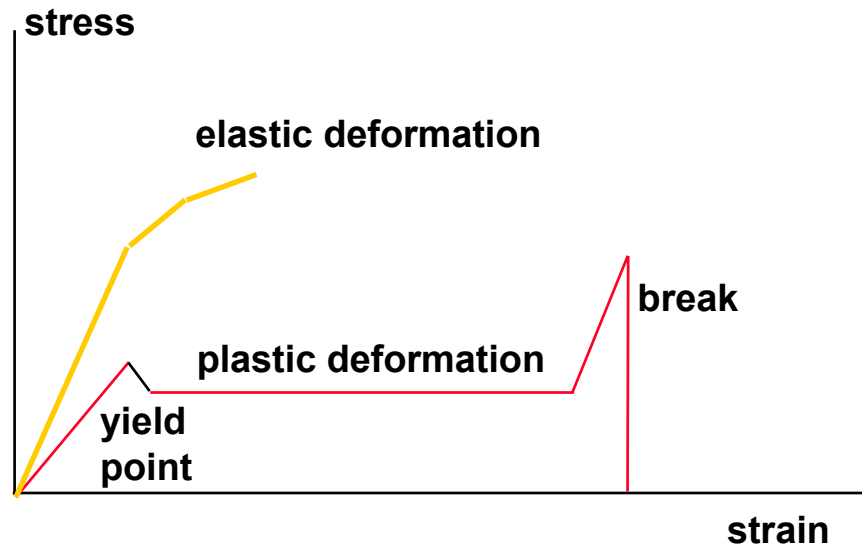
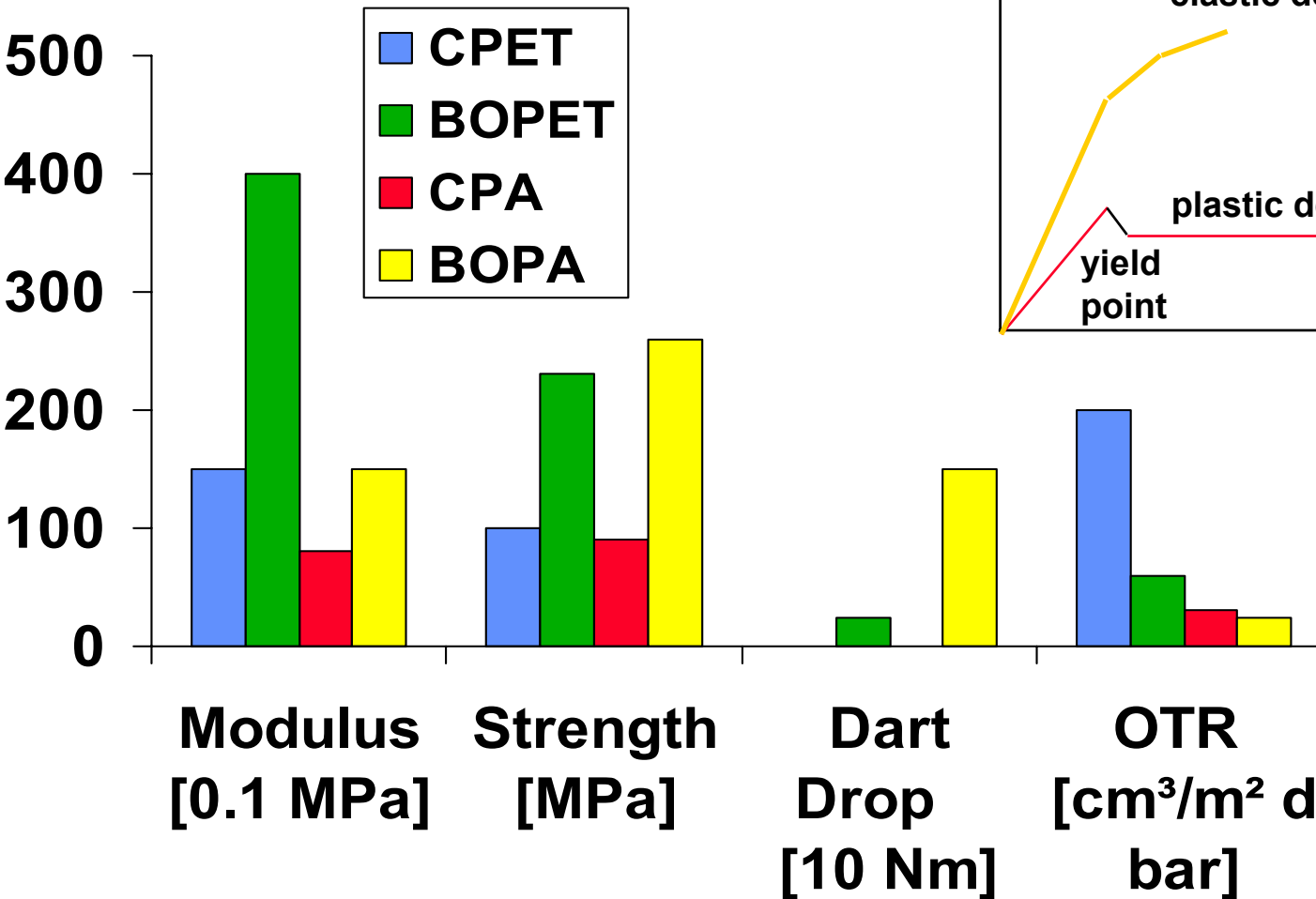
PA skin layer:

- high sealing temperature
- no sticking to sealing bar
- rapid sealing

	T _m [°C]
HDPE	130-135
LDPE, LLDPE	110-125
PP	165
PA6	220
PA66	260 *)
PET	260 *)

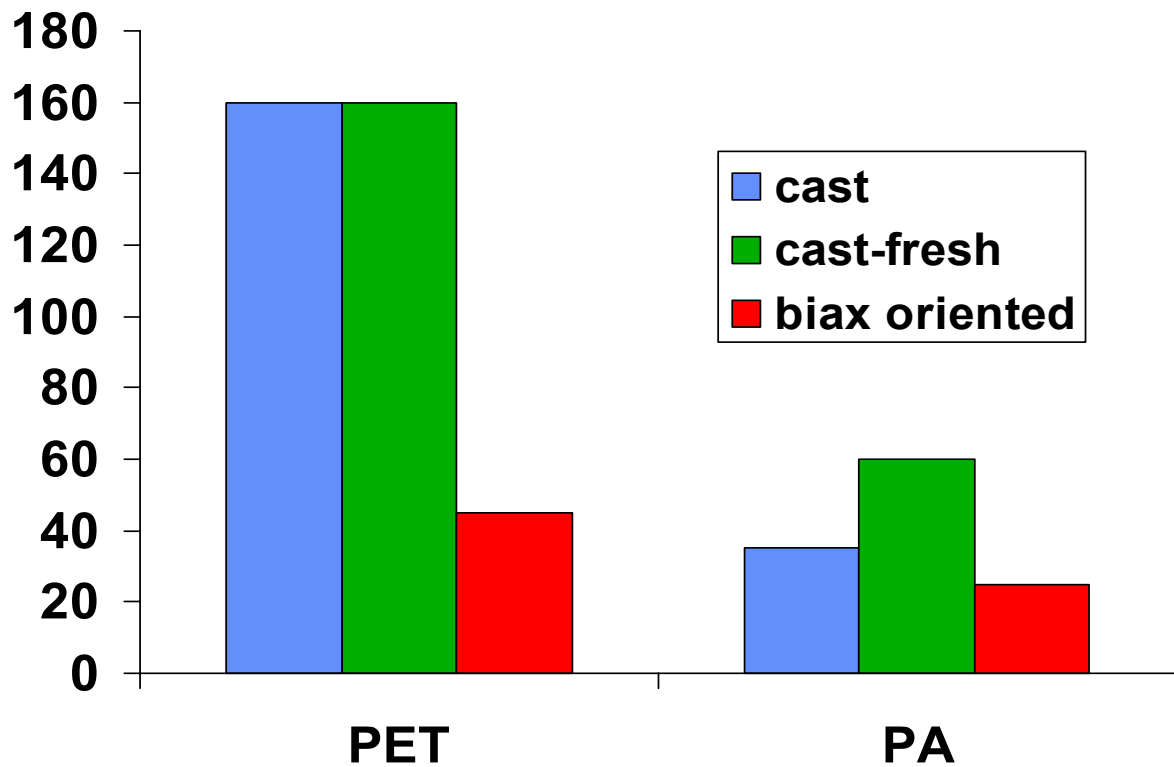
*) processing temperature too high for coextrusion

Properties of BOPA Film



- stiffness
- printability
- metallizable
- puncture resistance

Properties of BOPA Film



■ oriented film:

■ crystalline

■ stress-induced crystallisation

■ cast film

■ CPET: amorphous

■ CPA: crystalline

OTR (0% rh) of 25µm film, cast / cast-dry as moulded / biaxially oriented

Applications

Polyamides is used for packaging film for its

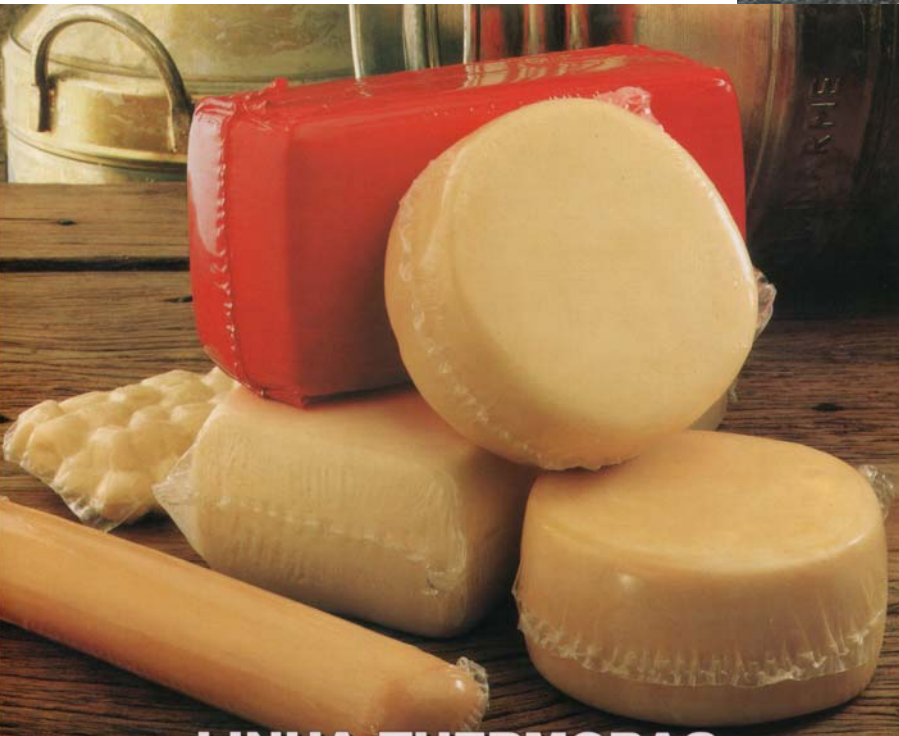
- **mechanical strength and toughness**
- **high temperature resistance**
- **good barrier**
- **thermoformability**

mostly for packaging of oxygen-sensitive food as

- **meat and processed meat**
- **cheese**
- **processed food**



Applications



**TAPPI 2003 European PLACE Conference
Rome, May 12 - 14, 2003**

Adhesion of Aluminium Foil to Coatings - Stick With It !

Günter Schubert,
Hydro Aluminium Deutschland GmbH, Bonn



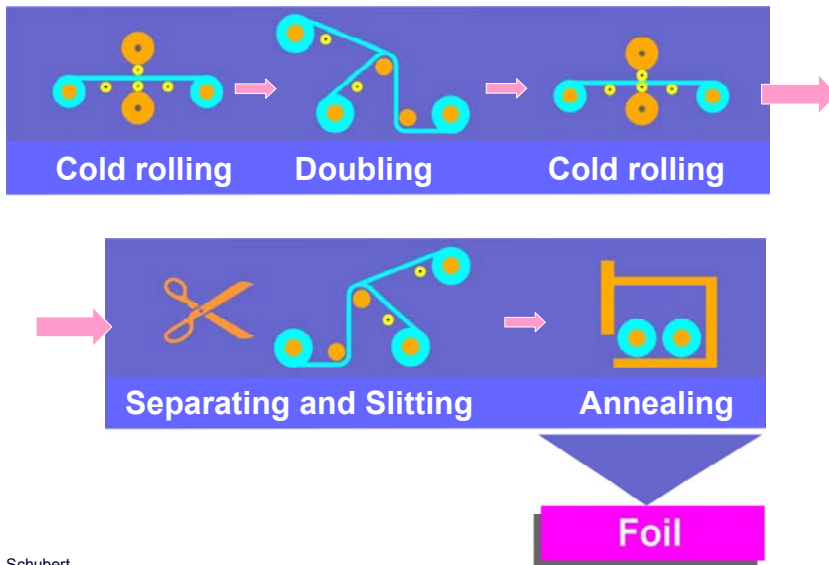
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Structure

- ▶ **Manufacturing Aluminium Foil**
- ▶ **Formation and Composition of Aluminium Foil Surface**
- ▶ **Cases challenging adhesion**
 - **lacquered and extrusion-coated dairy lidding**
 - **adhesive laminates and retorting**
 - **sealant - packaged good interaction**
- ▶ **Conclusions**

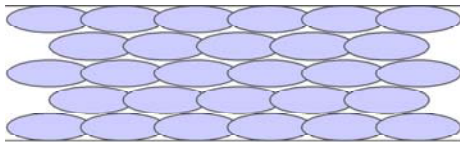
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Cold Rolling of Aluminium Foil

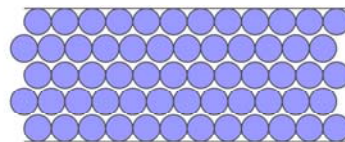
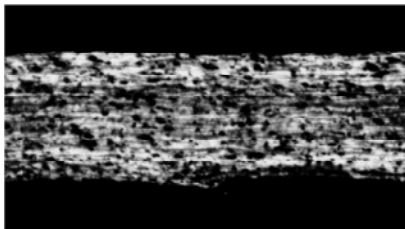


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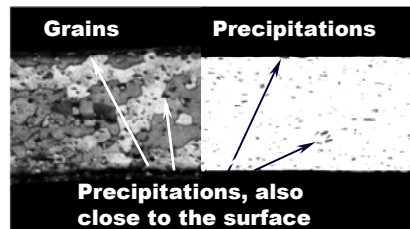
Precipitations and Grain Structure in Non-Annealed and Annealed Foil



Foil after finishing

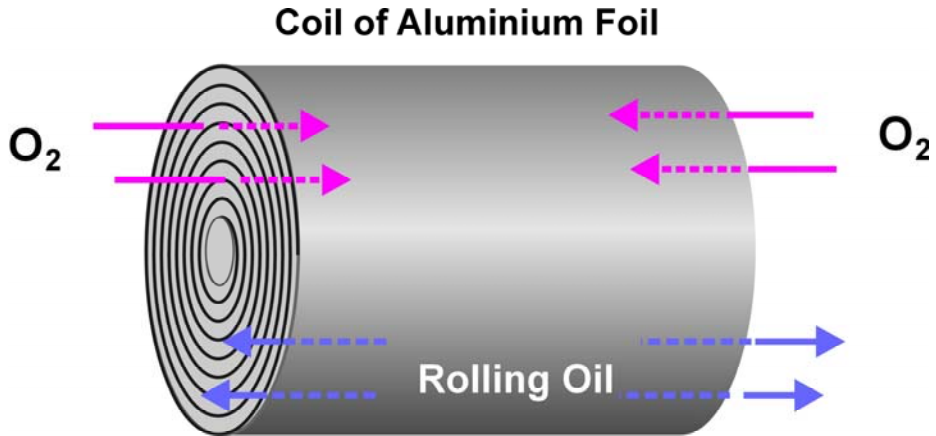


Foil after annealing (soft annealing)



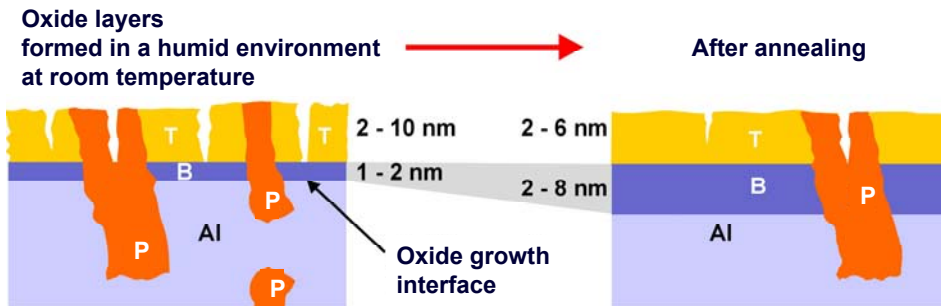
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Coil during annealing



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Oxide Growth during Annealing and Precipitations Embedded in the Surface



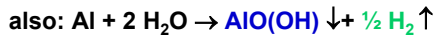
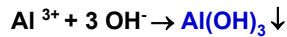
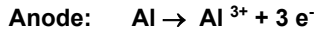
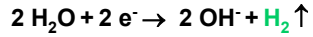
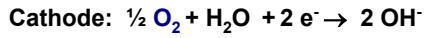
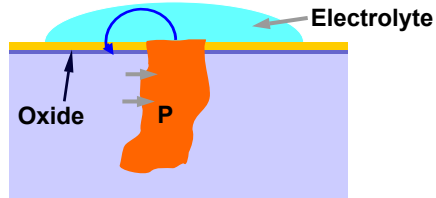
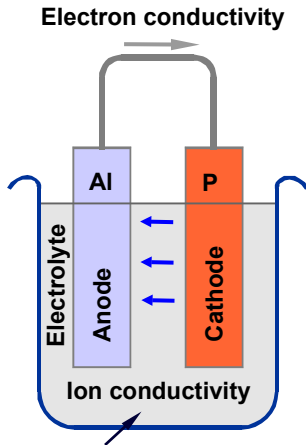
P = Precipitation (like AlFeSi , Al_3Fe)

T = Top layer

B = Barrier layer

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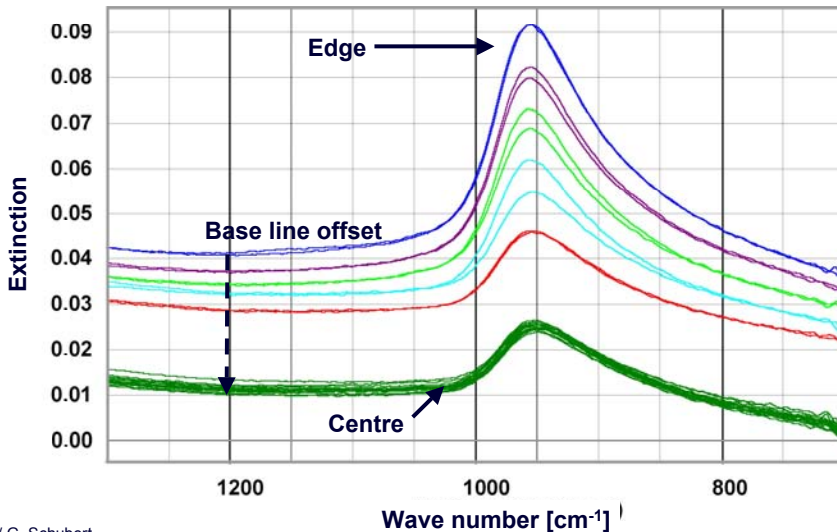
Contact Corrosion Analogon in the Presence of Electrolyte



Reactions depend on the availability of oxygen and water, pH and temperature

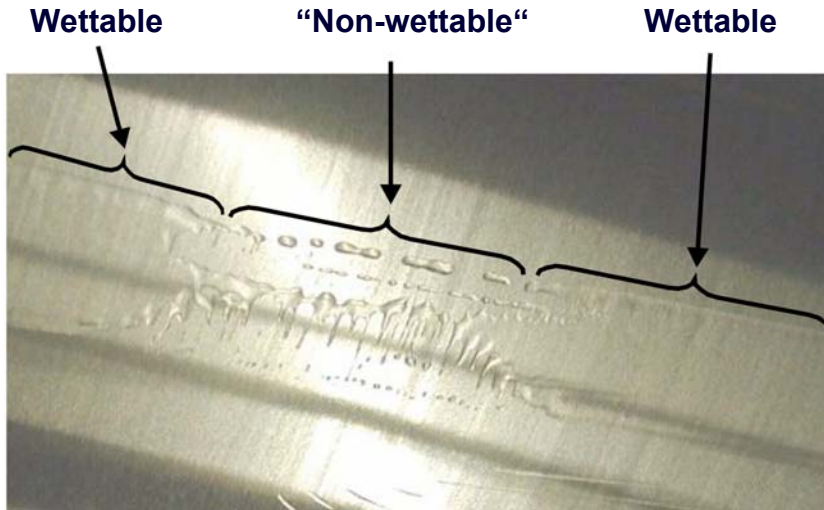
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Oxide Thickness by IR-Absorption



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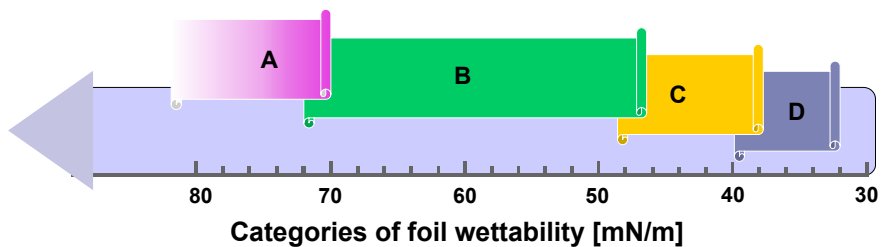
Non-Wettable Width of a Foil Web



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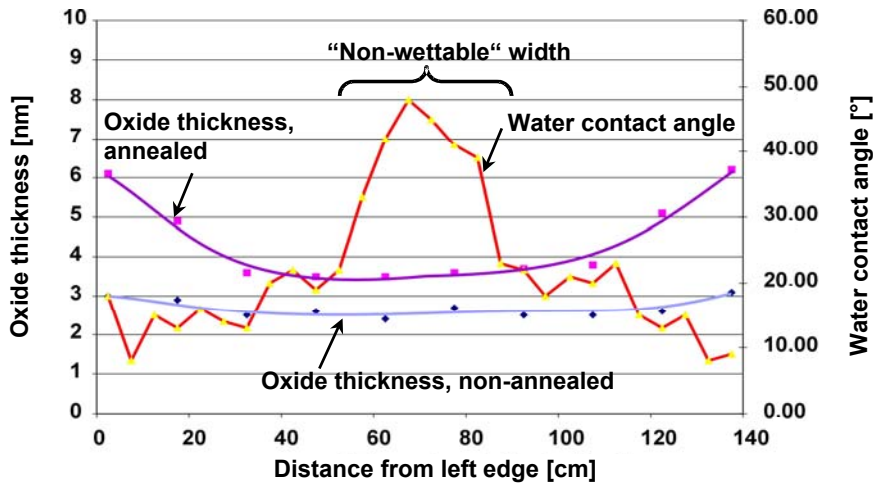
Surface Tension and Wettability Categories for Aluminium Foil (AFCO)

A: Water	100%	72.0 mN/m
B: Water/Ethyl alcohol	90% : 10%	47.0 mN/m
C: Water/Ethyl alcohol	80% : 20%	38.5 mN/m
D: Water/Ethyl alcohol	70% : 30%	33.0 mN/m



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Oxide Thickness and Wettability Profile



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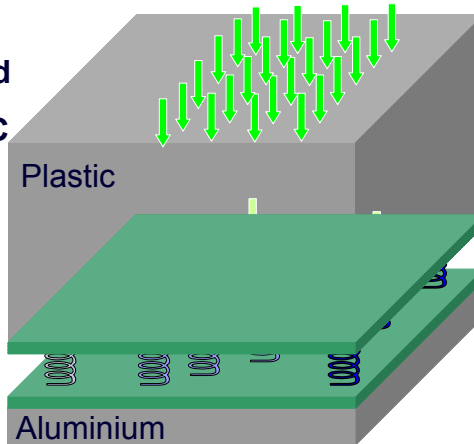
Foil Annealing Requirements

- ✧ Recrystallising grain structure
- ✧ Removing rolling oil
- ✧ Maintaining good unwinding properties
- ✧ Providing homogeneous wettability
- ✧ Providing strong adhesion

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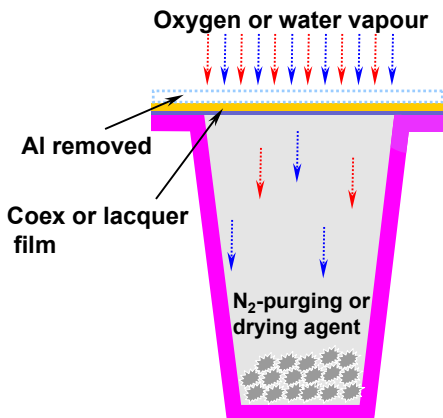
Permeants and Conditions Potentially Affecting Aluminium - Plastic Adhesion

Oxygen **Water**
Acetic acid **Citric acid**
Lactic acid **Vitamin C**
Preservatives **Fat**
Emulsifiers **Salt**
Hot filling
Pasteurising
Retorting
Storage time **Light**



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Permeation Measurements of Dairy Lid Coatings



	Lacquer (5 µm)	Coex-coating (20 µm)
--	----------------	----------------------

WVTR [g/d·m²] @ 20°C/ 100%r.h.

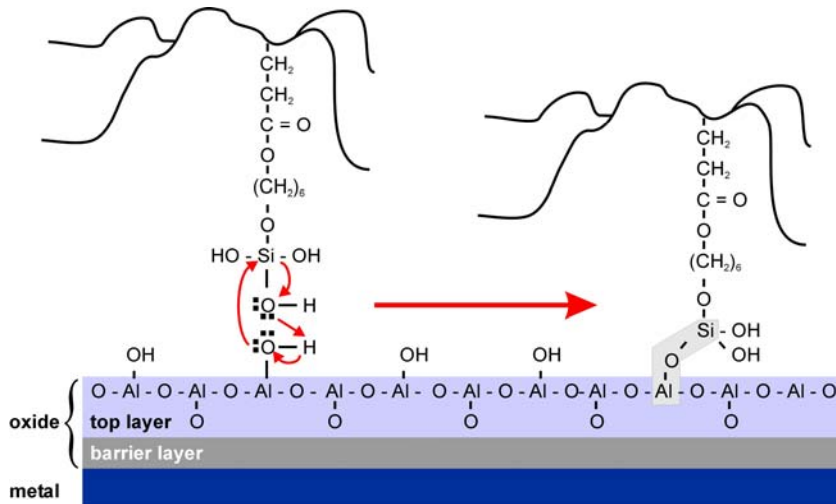
30 **5**

OTR [ml/d·m²·bar] @ 23°C/75% r.F.

380 **7000**

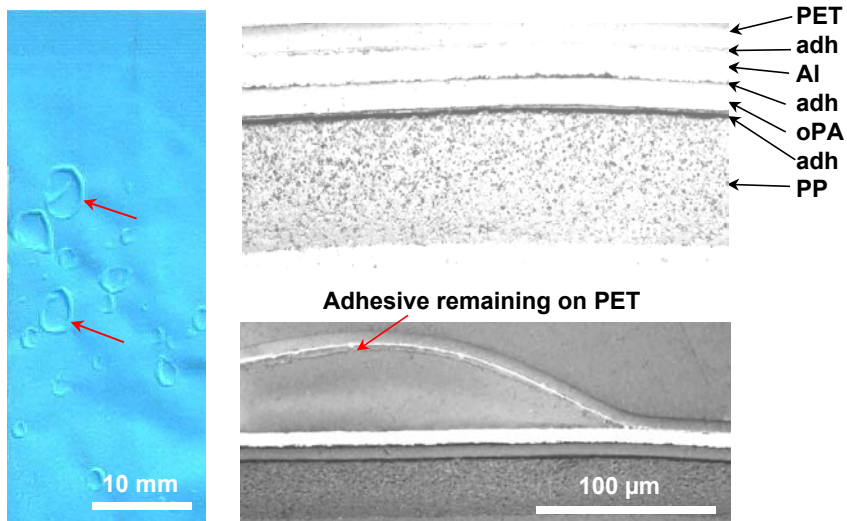
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Interaction Between Silanol and Alumina During Retorting



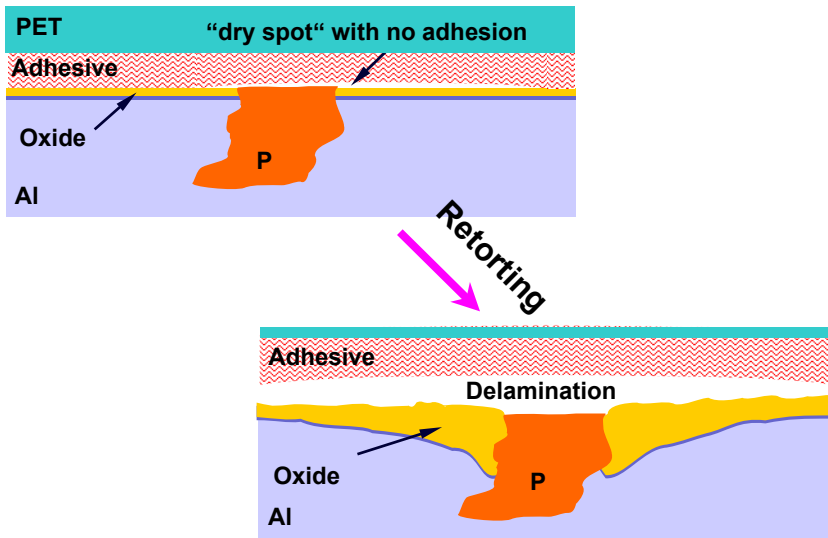
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Bubble Formation in a Retortable Stand-Up Pouch



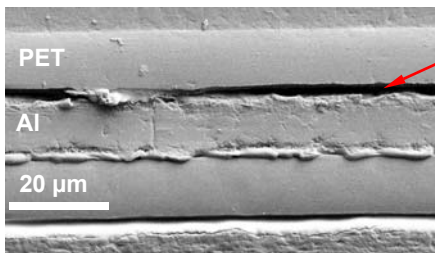
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Bubble Formation During Retorting



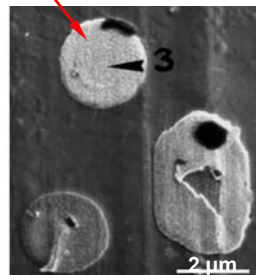
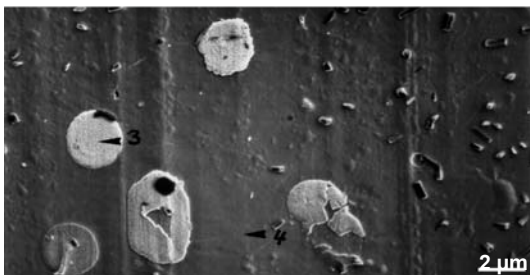
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"Dry Spots" With No Adhesion and Oxide Layer Spots Grown in a Bubble



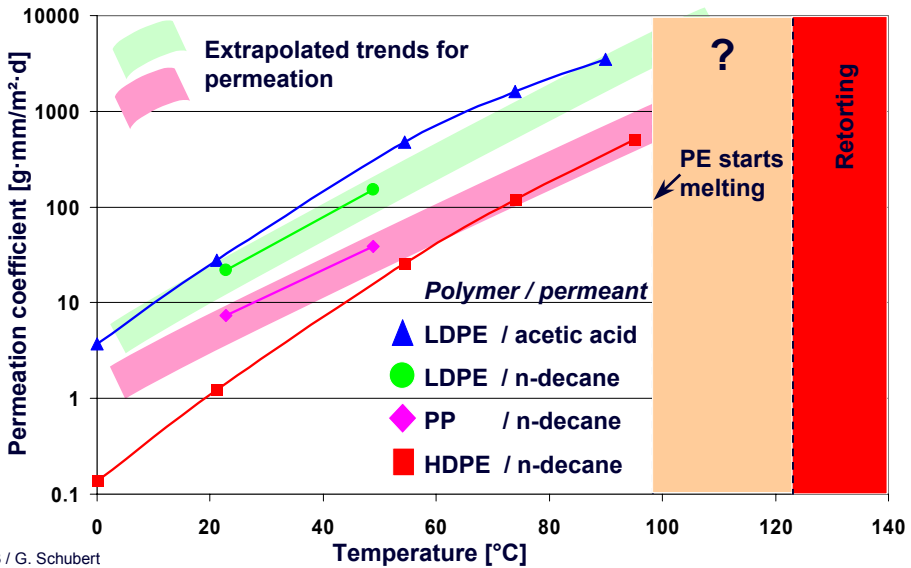
"Dry spot" without adhesion
(before retorting)

Oxide spots
grown during retorting



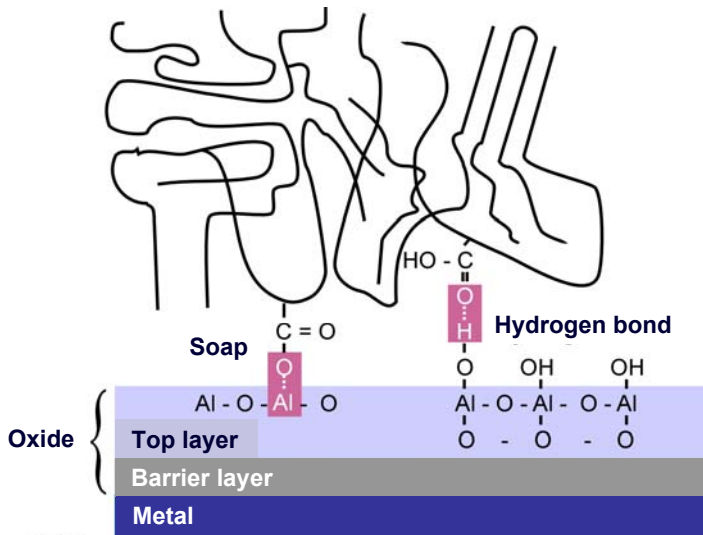
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Temperature Dependence of Permeation Through Plastics



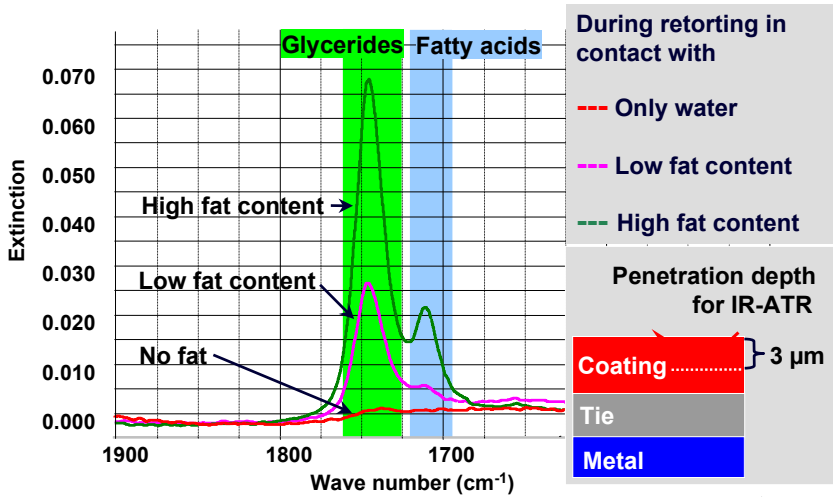
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Bond Formation of Acid Copolymers on Aluminium Foil



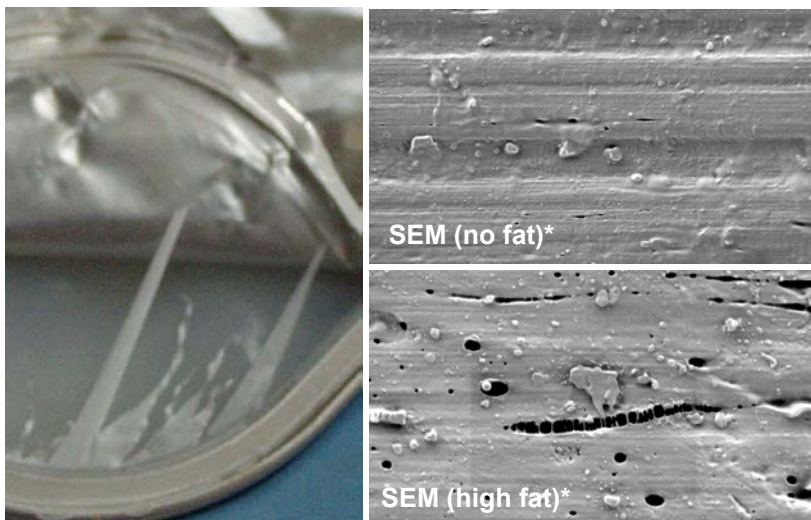
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Fat Absorbed in a Sealant Coating After Retorting (IR)



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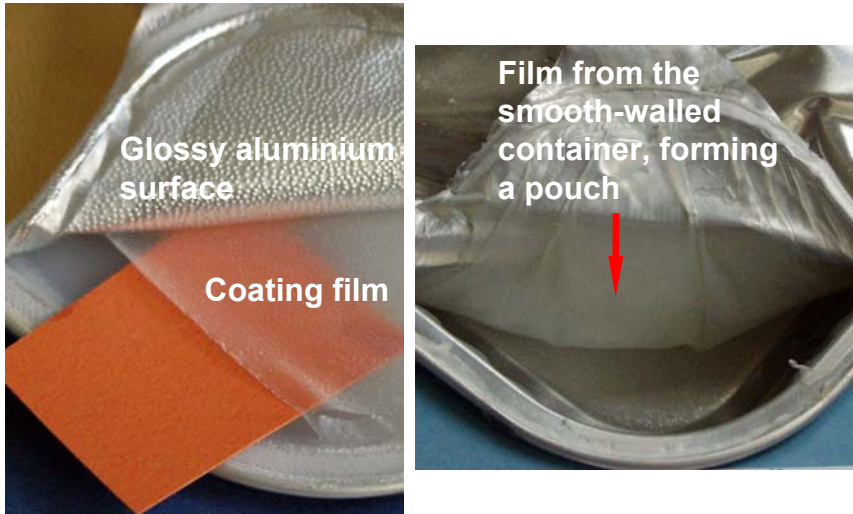
Plastification of Coatings During Retorting



(* specimen extracted)

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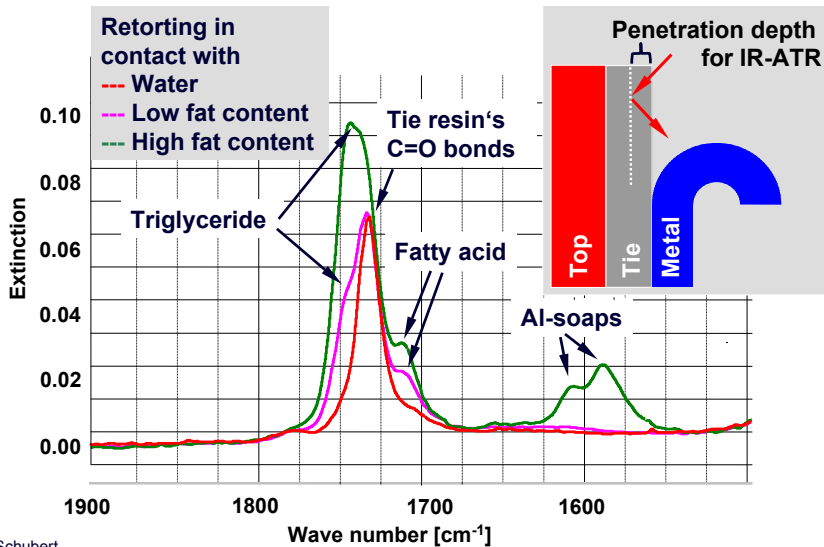
Delaminations During Retorting



Packaged good: Simulant paste with fat and fatty acid

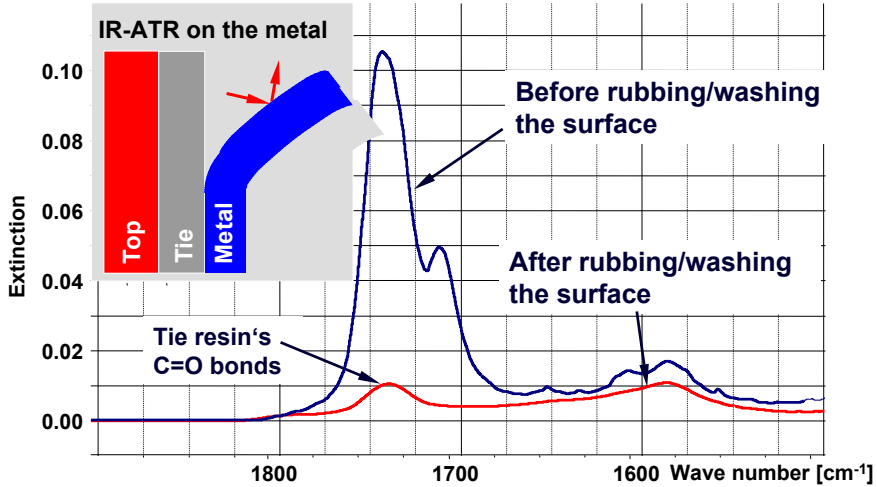
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Species at a Delaminated Aluminium-Plastic Interface after Retorting



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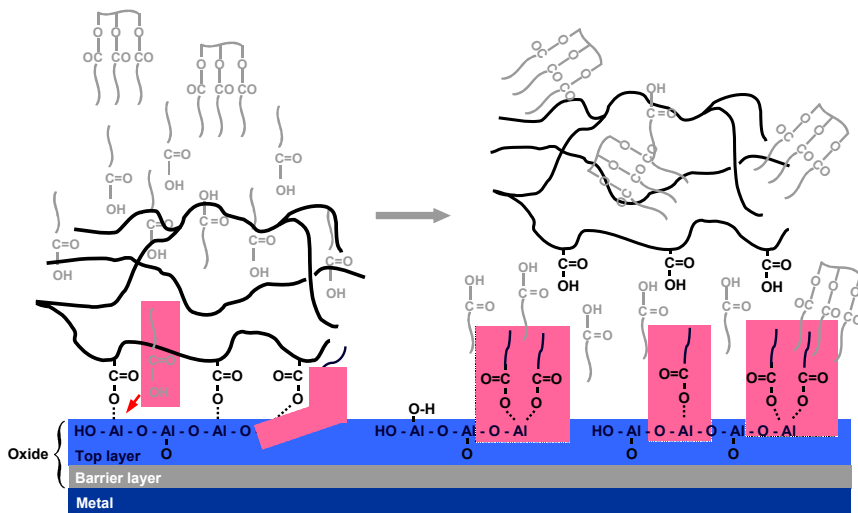
Abrasion Proofness and Bonding of Soap Species to the Aluminium Surface



Aluminium soaps adhere well to the metal surface !

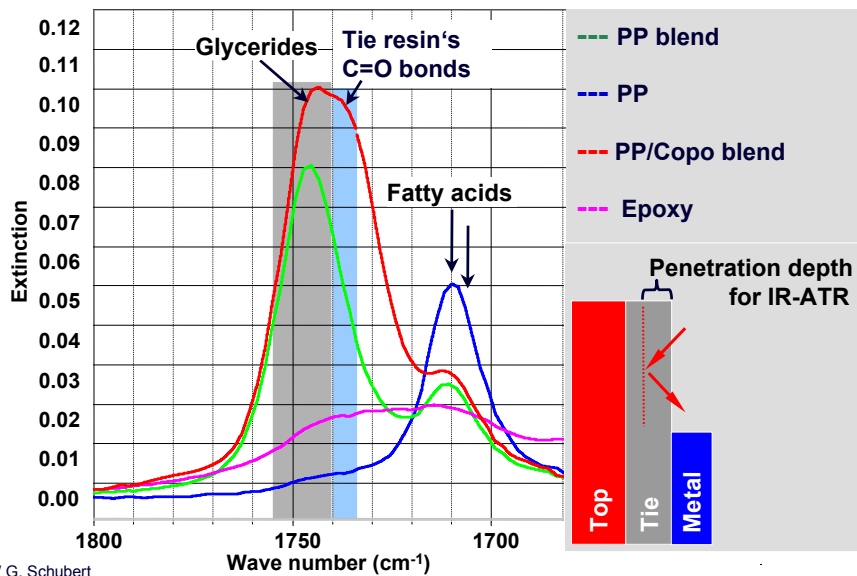
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Adhesion Failure as a Result of Saponification



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Migrated C=O-Species in the Adhering Interface of Different Tie Resins



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14.05.2003

Conclusions

- ✧ The surface of aluminium foil is well-prepared for adhesion, chemical resistance and acts as a barrier
- ✧ Complete spreading of coatings on foil is essential for durability
- ✧ Adhesion to foil can be affected by extreme migration during thermal treatment
- ✧ Under these conditions plastics are not as dense as expected and allow such migration
- ✧ Particular foil applications need a “smart” functional barrier in the coating

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