

# Polyamide for Flexible Packaging Film



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# Polyamide Film: Applications

**Polyamide widely used for food packaging**

- meat, poultry
- cheese
- processed food

**due to its combination of**

- oxygen barrier
- flavor and aroma barrier
- good mechanical properties
- high transparency
- thermoformability
- thermal stability



# What are Polyamides?

- **Synthetic Polyamides were developed in 1938**
  - **Perlon, Polyamid PA6 by IG Farben, Germany**
  - **Nylon, Polyamid PA66, by DuPont, 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**

# What are Polyamides?

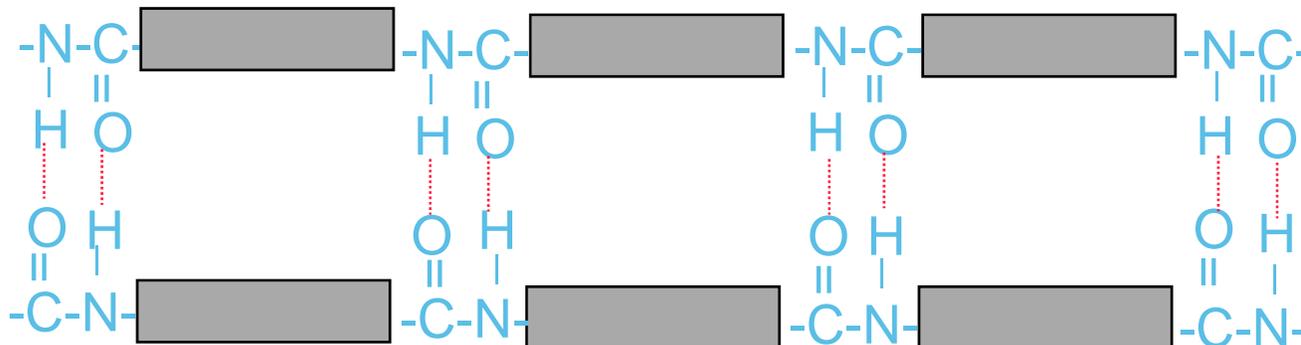
**Polyamides = polymer molecules based on amide group**

⇒ **hydrogen bonds**

⇒ **strong intermolecular interactions / high strength**

⇒ **absorption of water / high toughness**

**between amide groups: water-repellent hydrocarbon segments**



# What are Polyamides?

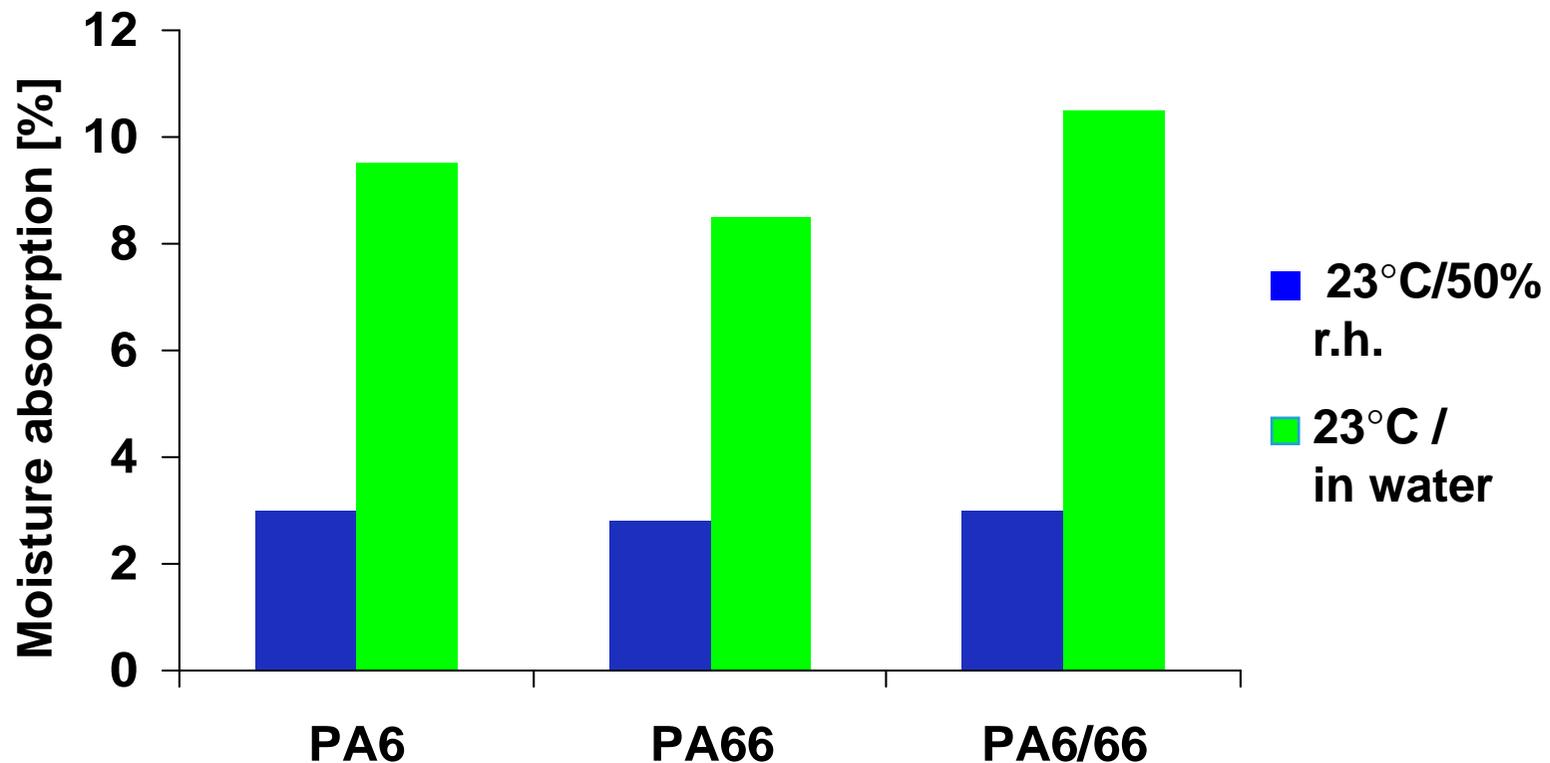
**PA name: PA + number of carbon atoms between amide N**

|                        | <b>Monomers</b>  | <b>Melting Temperature °C</b> |
|------------------------|--|-------------------------------|
| <b>PA66</b>            | <b>hexene diamine (C6), adipic acid (C6)</b>               | <b>260°C</b>                  |
| <b>PA 610</b>          | <b>hexene diamine (C6), sebacic acid (C10)</b>             | <b>220°C</b>                  |
| <b>PA 612</b>          | <b>hexene diamine (C6), dodecanic diacid (C12)</b>         | <b>215°C</b>                  |
| <b>PA 6</b>            | <b>caprolactam (C6)</b>                                    | <b>220°C</b>                  |
| <b>PA 11</b>           | <b>aminoundecanic acid (C11)</b>                           | <b>185°C</b>                  |
| <b>PA 12</b>           | <b>aminododecanic acid (C12)</b>                           | <b>178°C</b>                  |
| <b>PA 6/66 (85/15)</b> | <b>caprolactam (85%), hexene diamine+adipic acid (15%)</b> | <b>195°C</b>                  |
| <b>PA 6/66 (80/20)</b> | <b>caprolactam (80%), hexene diamine+adipic acid 20%</b>   | <b>190°C</b>                  |
| <b>PA 6I/6T</b>        | <b>hexene diamine (C6), terephthalic+isophthalic acid</b>  | <b>Tg = 132°C *)</b>          |

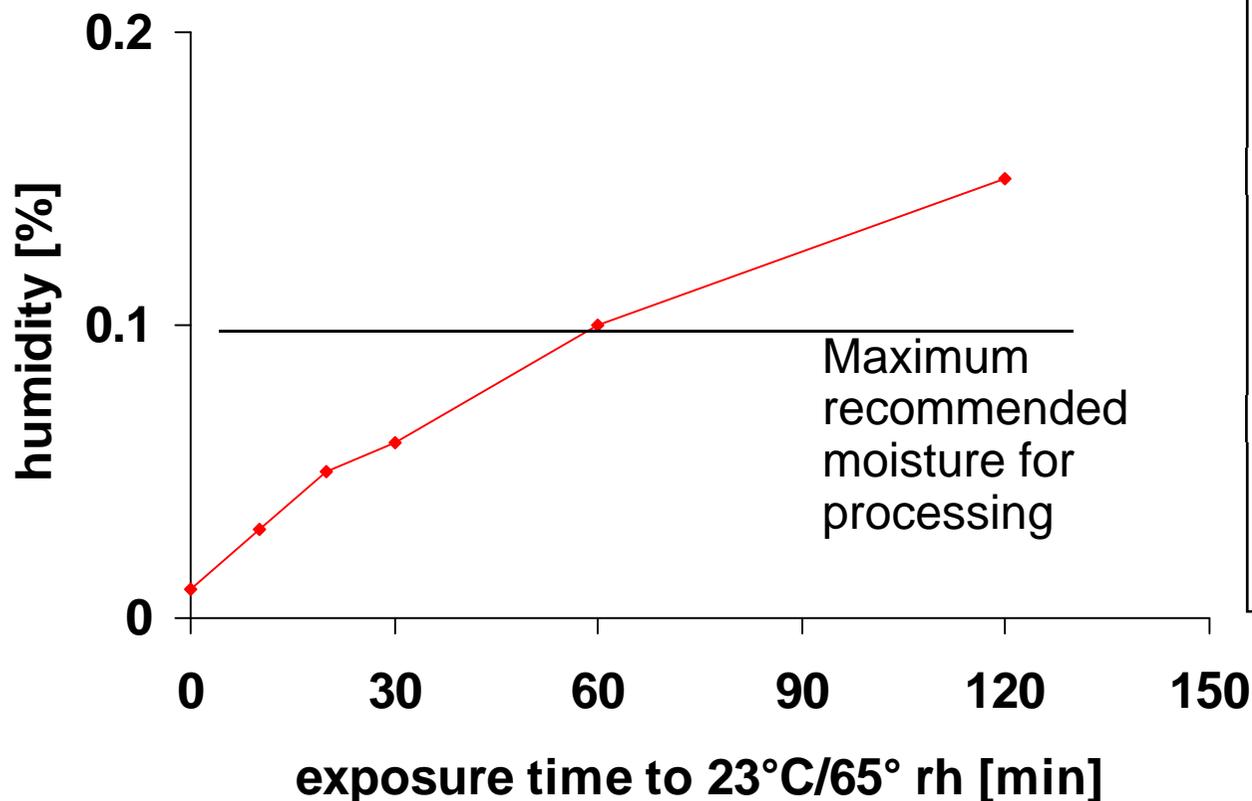
# Pre-Processing: Humidity

## Polyamides absorb water

- water decomposes PA at high temperatures
- PA must be processed dry



# Processing: Drying



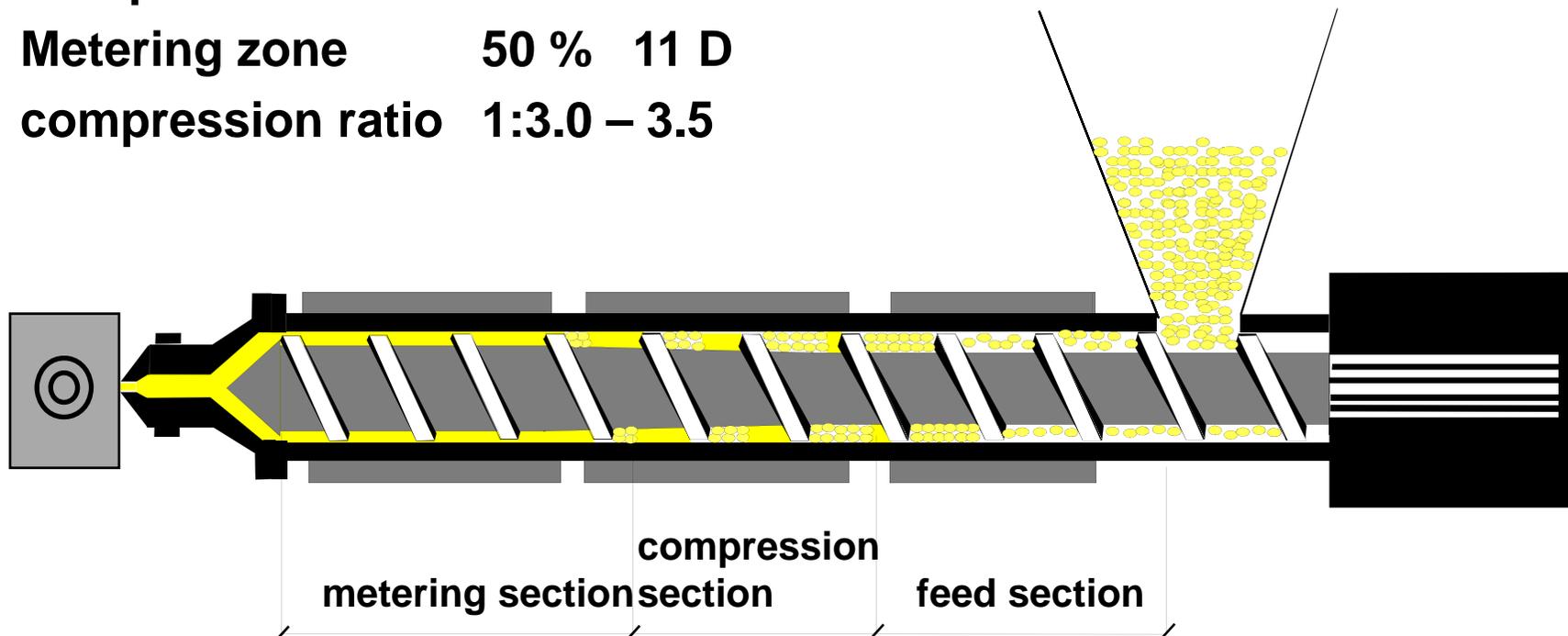
- PA pre-dried for processing
- minimize contact with humidity
- if drying then only dry-air dryer

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

# Processing: Extruder

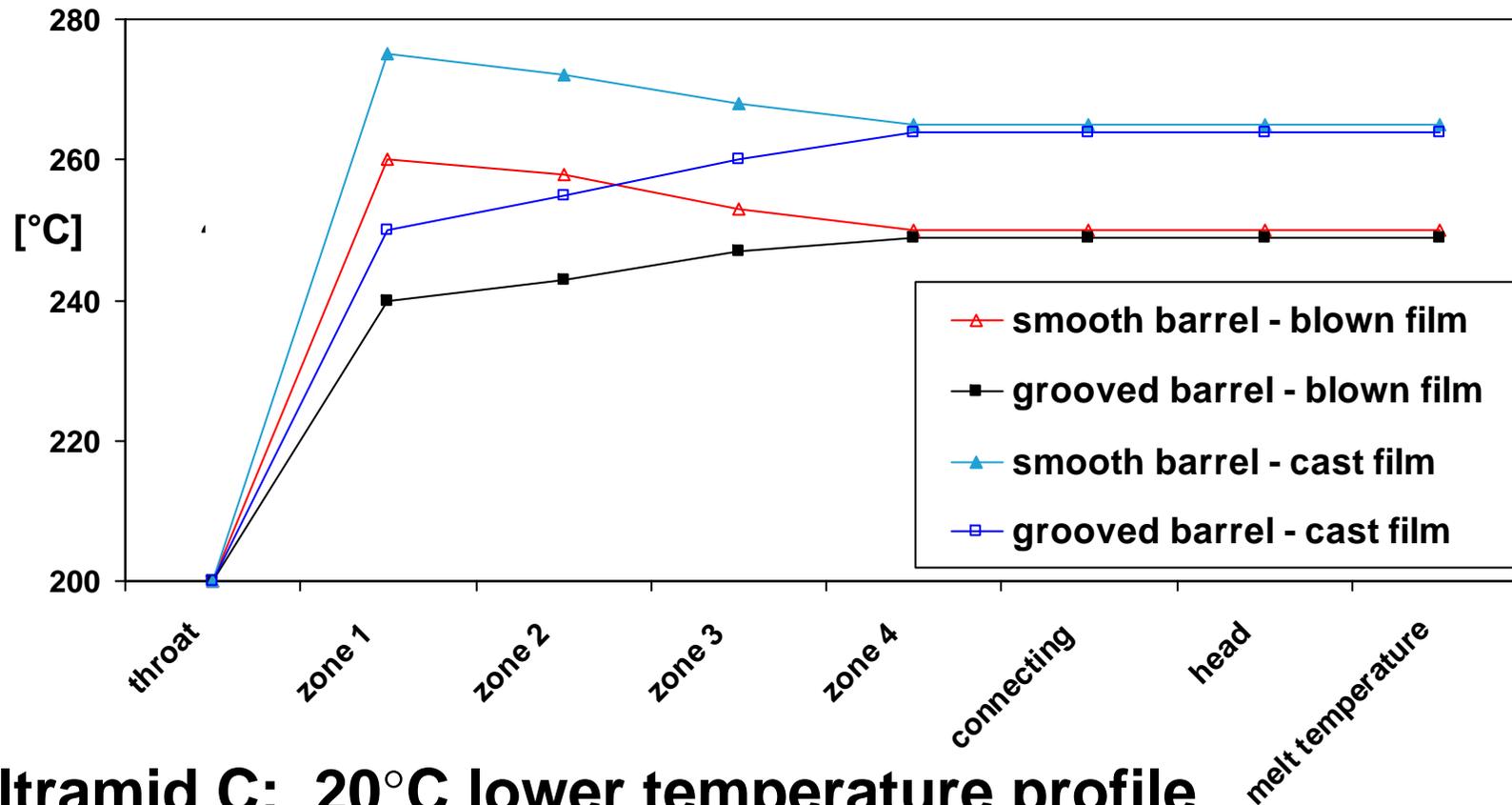
- barrier or 3-zone screw
- L/D) min 24:1
- Feed zone 35 % 9 D
- Compression zone 15 % 4 D
- Metering zone 50 % 11 D
- compression ratio 1:3.0 – 3.5

|                     |      |       |      |
|---------------------|------|-------|------|
| screw $\varnothing$ | 45mm | 60mm  | 90mm |
| feed                | 6mm  | 8mm   | 12mm |
| metering            | 2mm  | 2.5mm | 4mm  |



# Processing: Temperature Settings

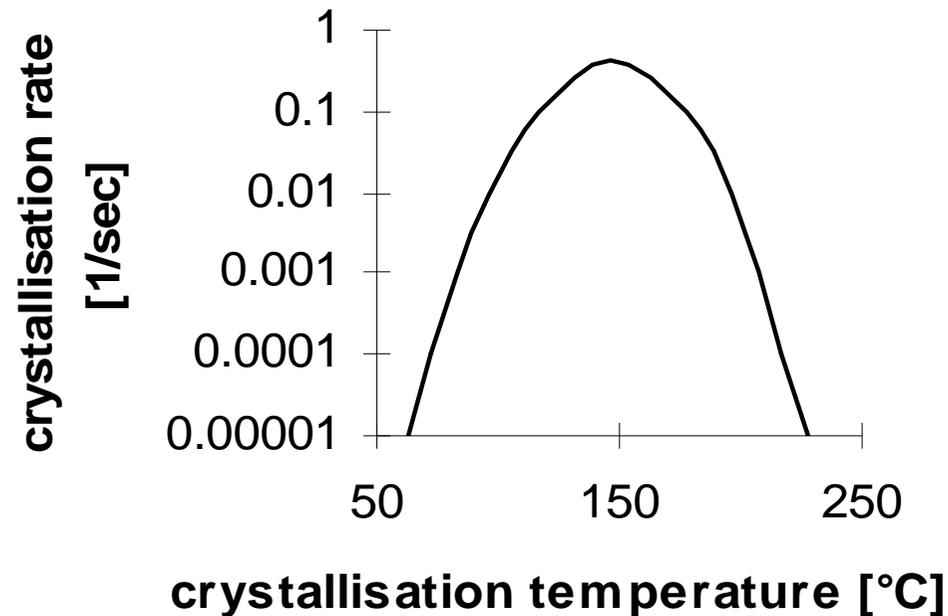
## Examples for Ultramid B grades temperature profile



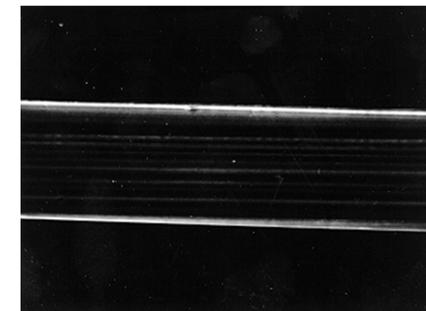
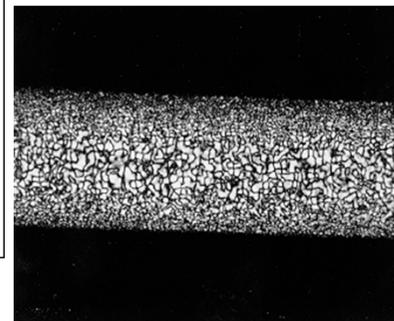
## Ultramid C: 20°C lower temperature profile

# Processing: Crystallisation

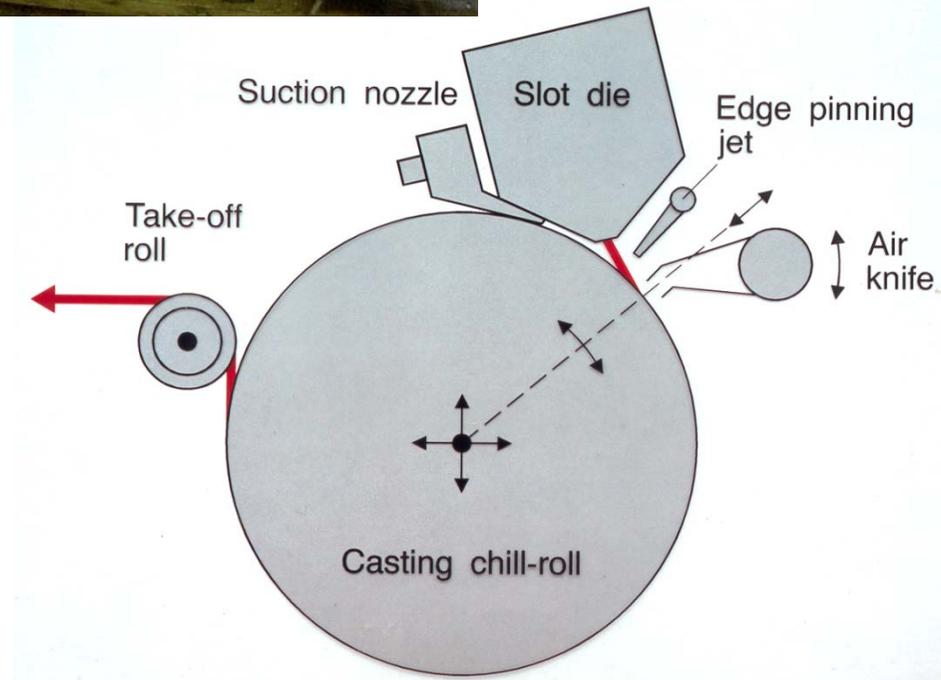
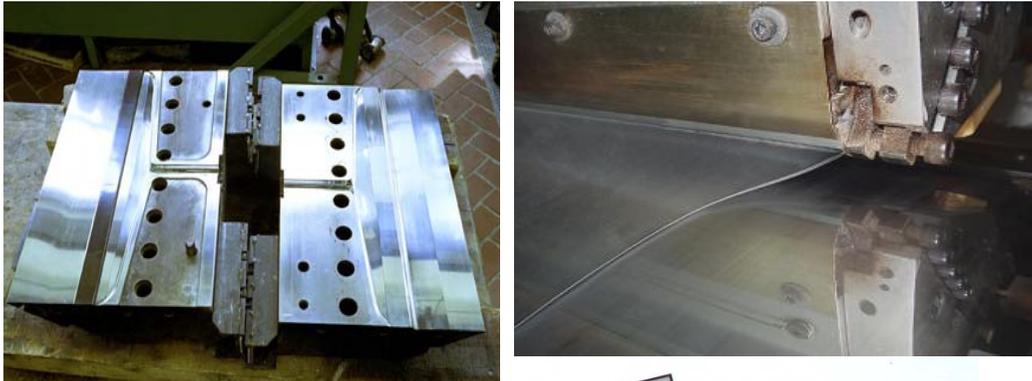
## crystallisation rate of PA6



- **180 – 100°C: moderate crystallisation rate**
- **< 80°C: crystallisation frozen**
- **rapid cooling: amorphous**
- **slow cooling: crystalline**



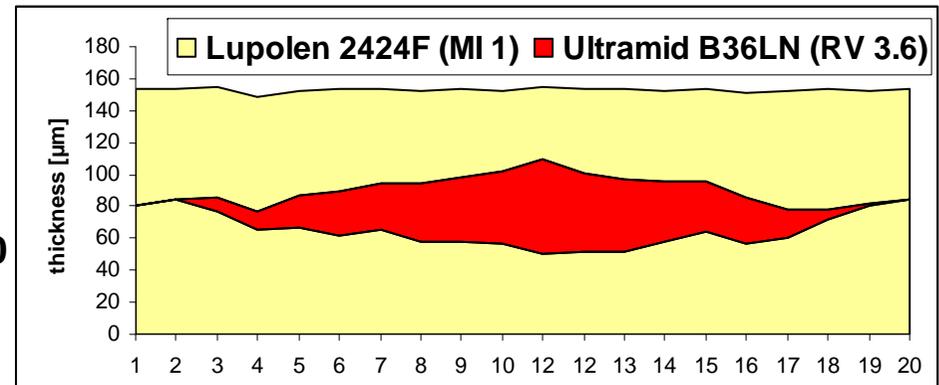
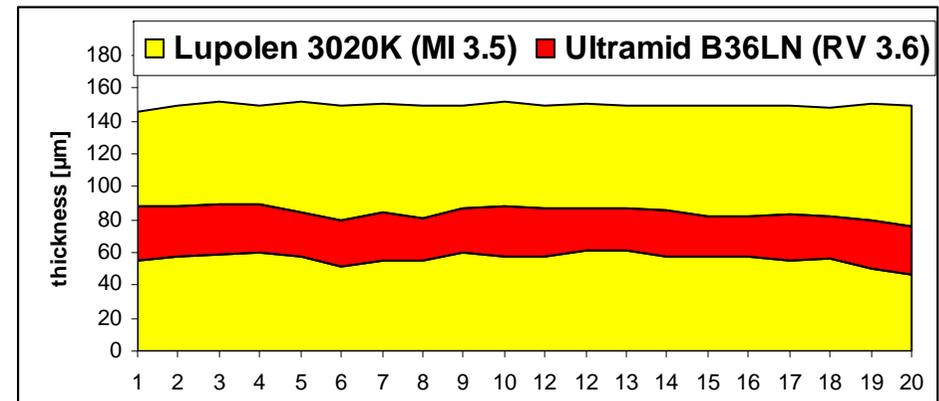
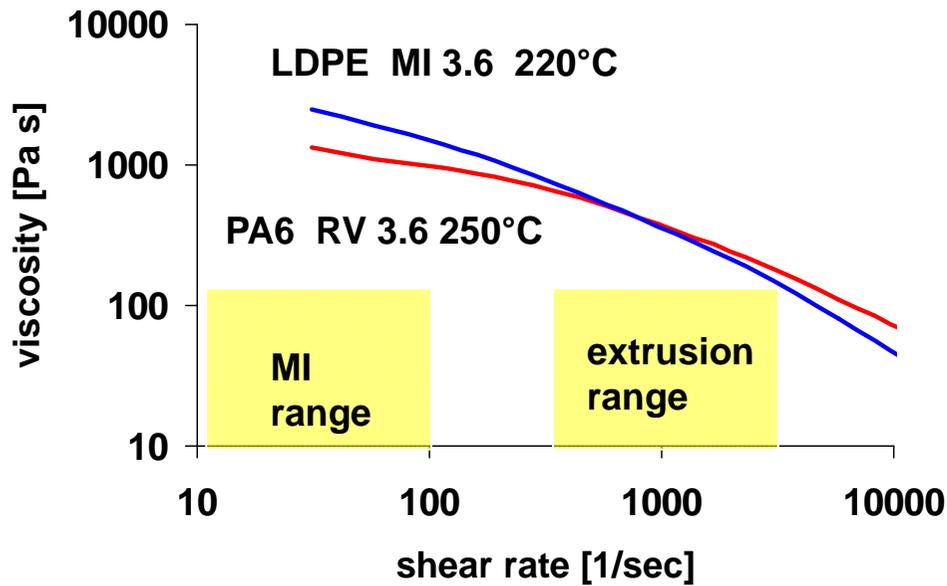
# Processing: Cast Film



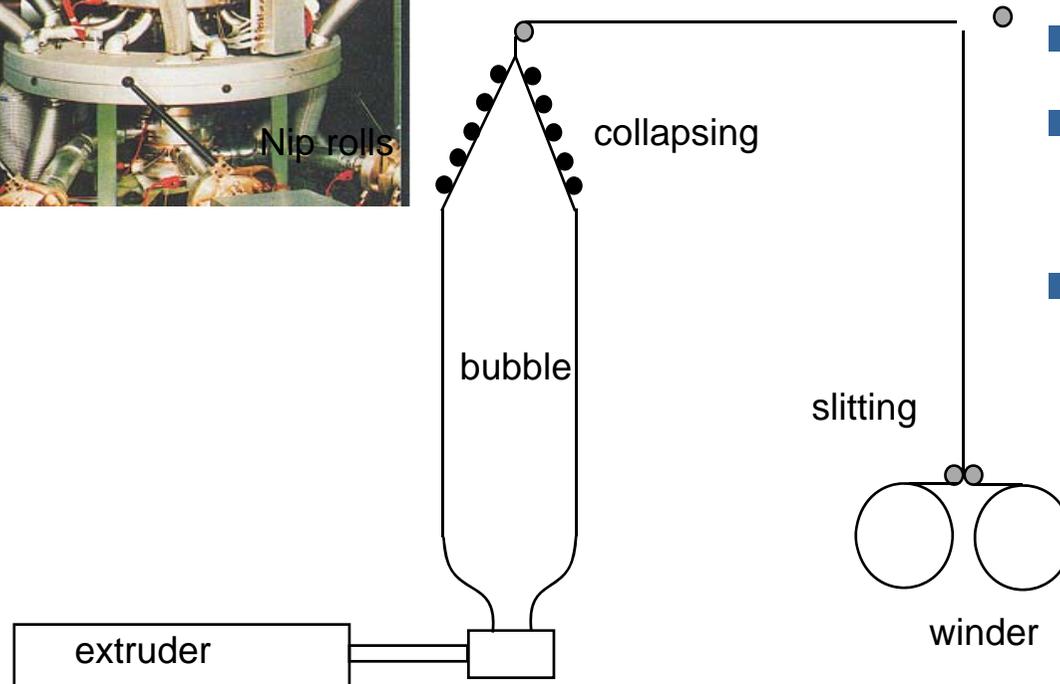
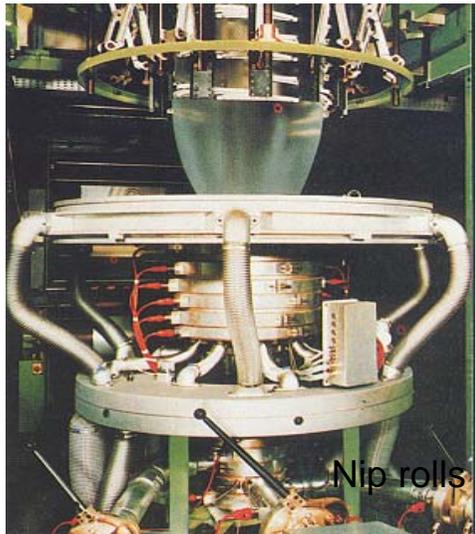
- standard cast film equipment
- chill roll 70-85°C : dimensional stability
- chill roll 20-35°C: high thermoformability
- PE (MI = 3-4)
- PA6 (RV3,2-3,6)
- **Ultramid® B36LN**

# Processing: Cast Film

## viscosity match PE-PA for uniform layer distribution



# Processing: Blown Film



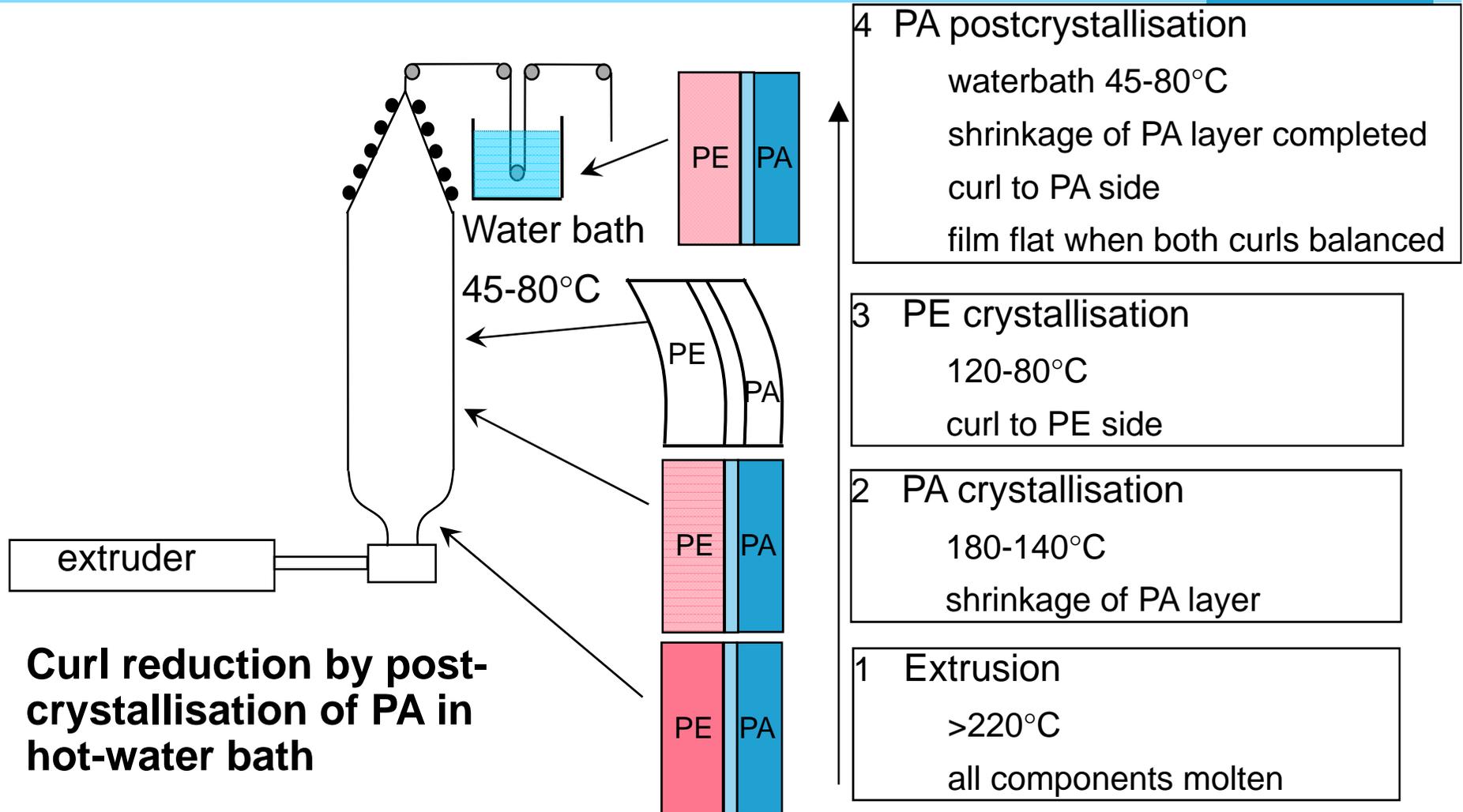
- standard blown film equipment
- air cooling / IBC
- PE (MI=0.7–1 cm<sup>3</sup>/10min)
- PA 6/66 (RV 3.2- 4.0)  
**Ultramid® C40L**
- PA6 (RV 3.8 - 4.0)  
**Ultramid® B40L, B33SL**

# Processing: Curl in multilayer PA/PE film

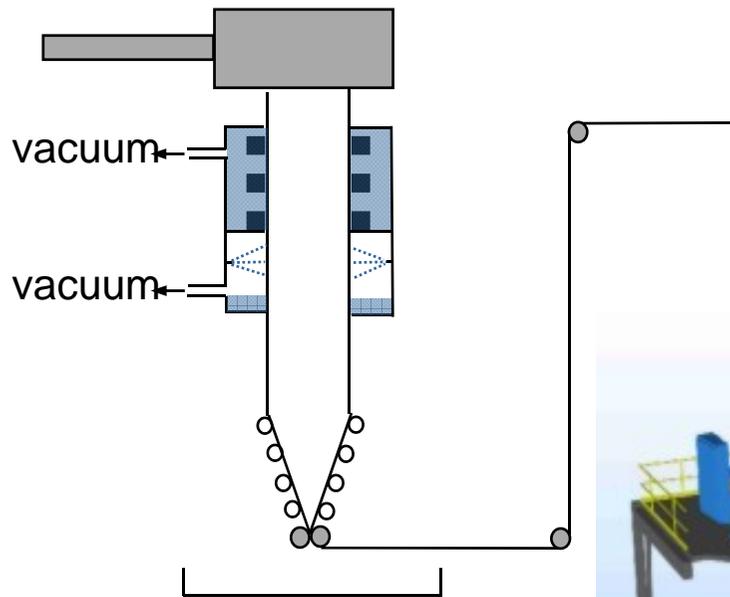
**CURL = rolling of non-symmetric multilayer film**  
**→ processing problem**



# Processing: Curl reduction by hot-water bath



# Processing: Water-Cooled Blown Film



## ■ very high cooling rate

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

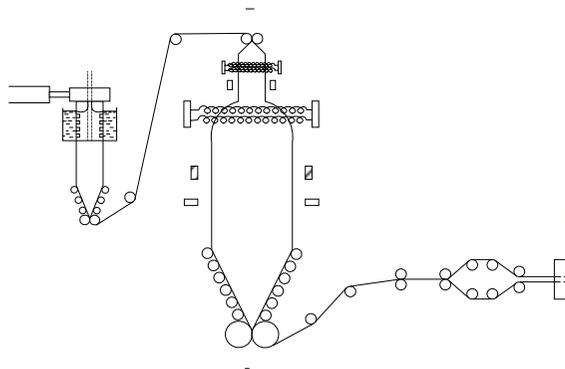


**Ultramid® B40L**

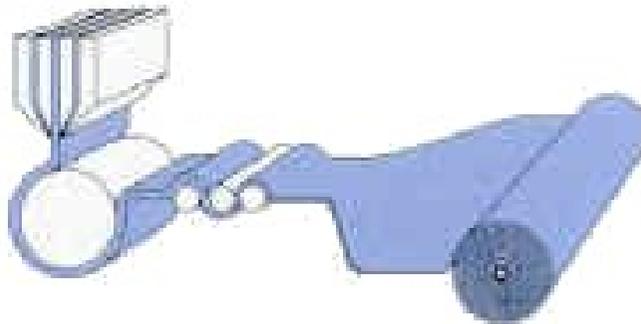
# Processing: Biaxially Oriented PA Film

**BOPA Biaxially Oriented PA Film: Ultramid® B33L**

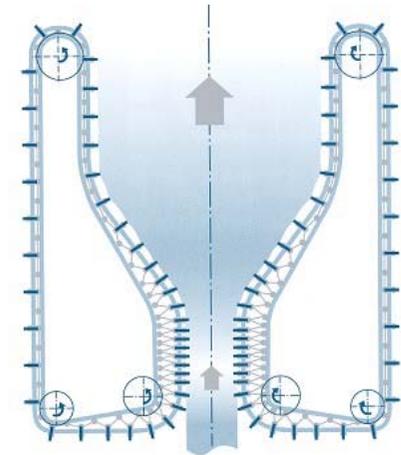
- high stiffness
- high strength and puncture resistance



**double bubble  
process**



**2-step tenter  
frame process**



**1-step tenter  
frame process**

# Processing: Sausage Casing Film

**double bubble stretching process**

- ⇒ **defined shrinkability**
- ⇒ **oxygen barrier**
- ⇒ **meat (protein) adhesion**
- ⇒ **good printability**



Polyamide for Flexible Packaging Film



**Ultramid® B40L**

**B33SL**

# Multilayer Film

## Ultramid nylon provides

- + oxygen and aroma barrier
- + heat resistance
- + good mechanical properties
- + thermoformability

## Polyethylene provides

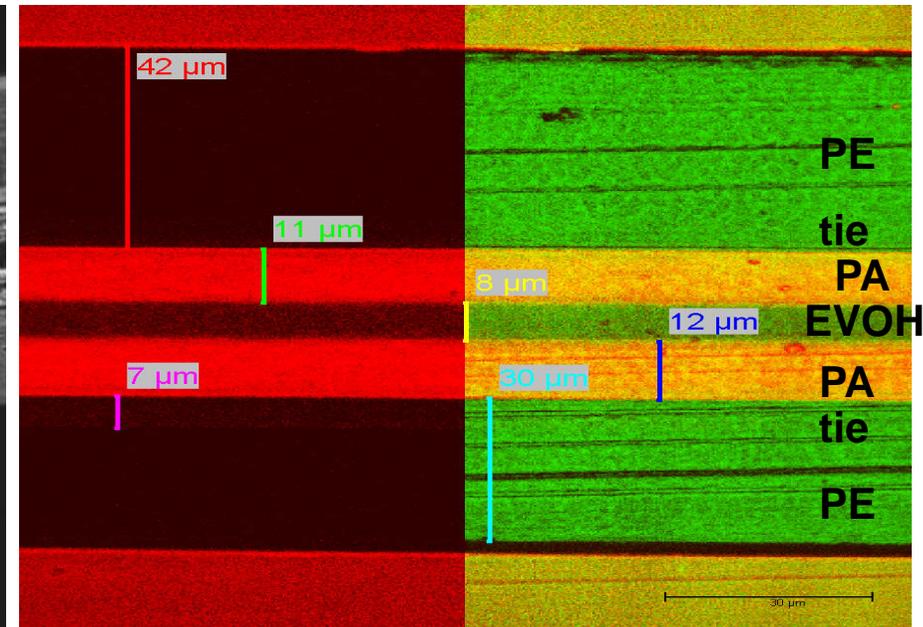
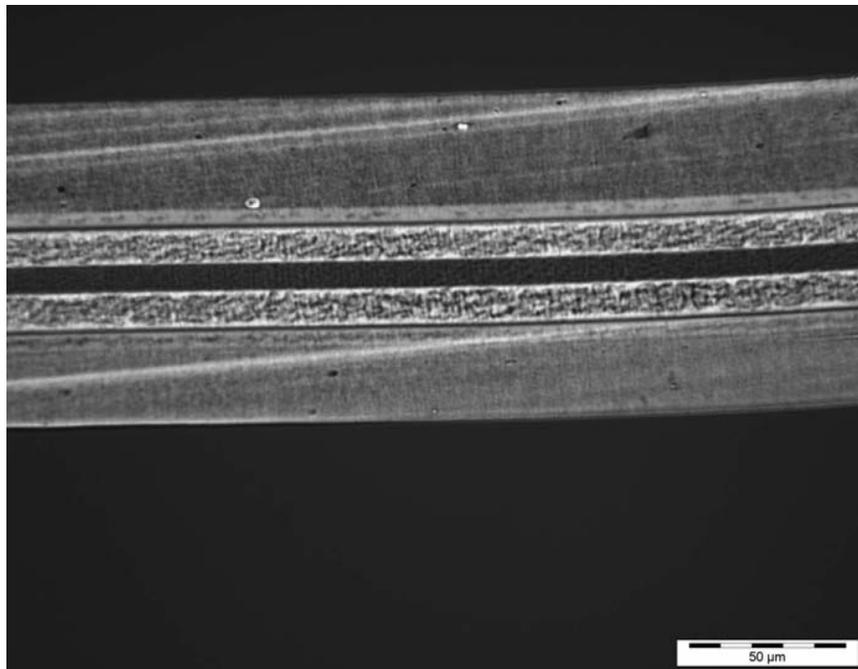
- + high water barrier
- + sealability

**multilayer film**

**combines properties of multiple components**

# Multilayer Film: Coextrusion

typical 7-layer film PE/adh/PA/EVOH/PA/adh/PE



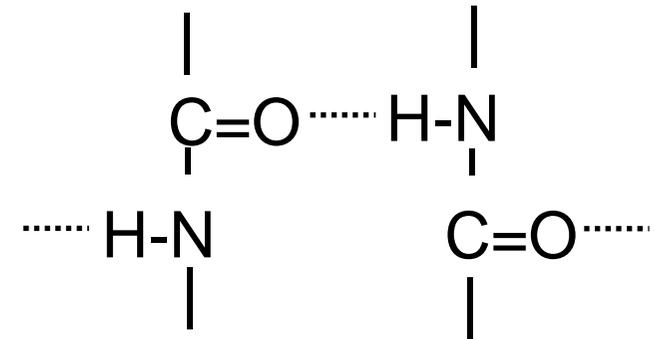
microtome / polarized light

PA stained with Neocarmine

# Properties

amide-amide interactions provide

- high melting point
- high strength + stiffness
- good abrasion resistance
- high barrier/resistance to gases + chemicals
- good printability



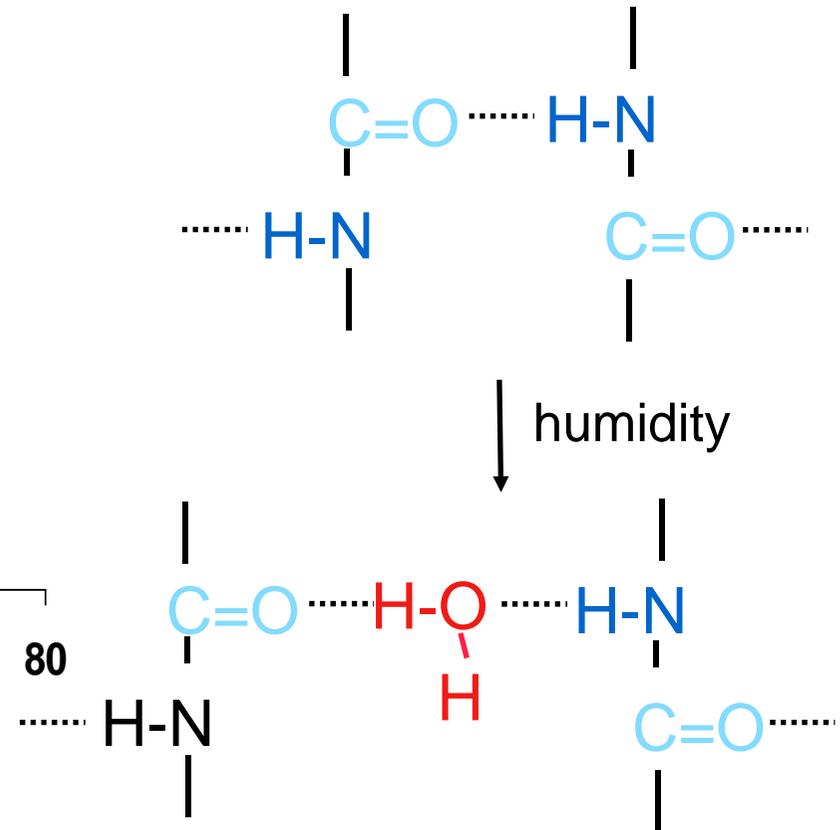
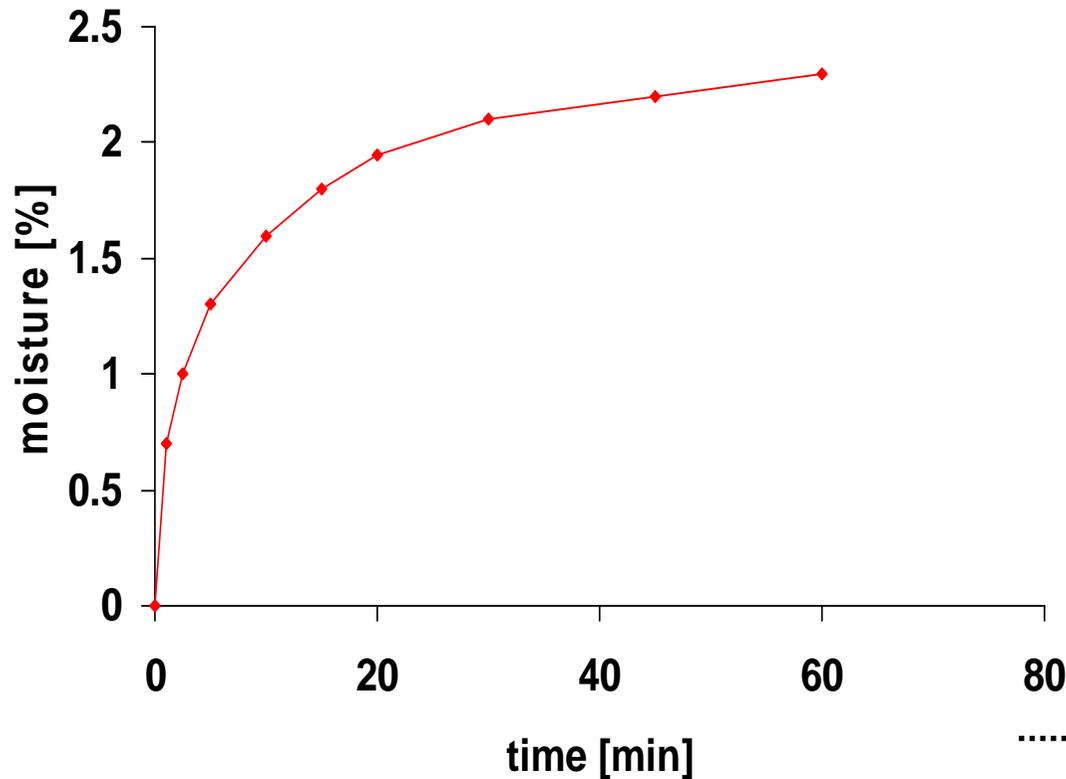
amide-water interactions provide

- toughness and flexibility
- good thermoformability

→ PA achieves many of its advantageous properties

**only after water absorption**

# Properties: Moisture Absorption

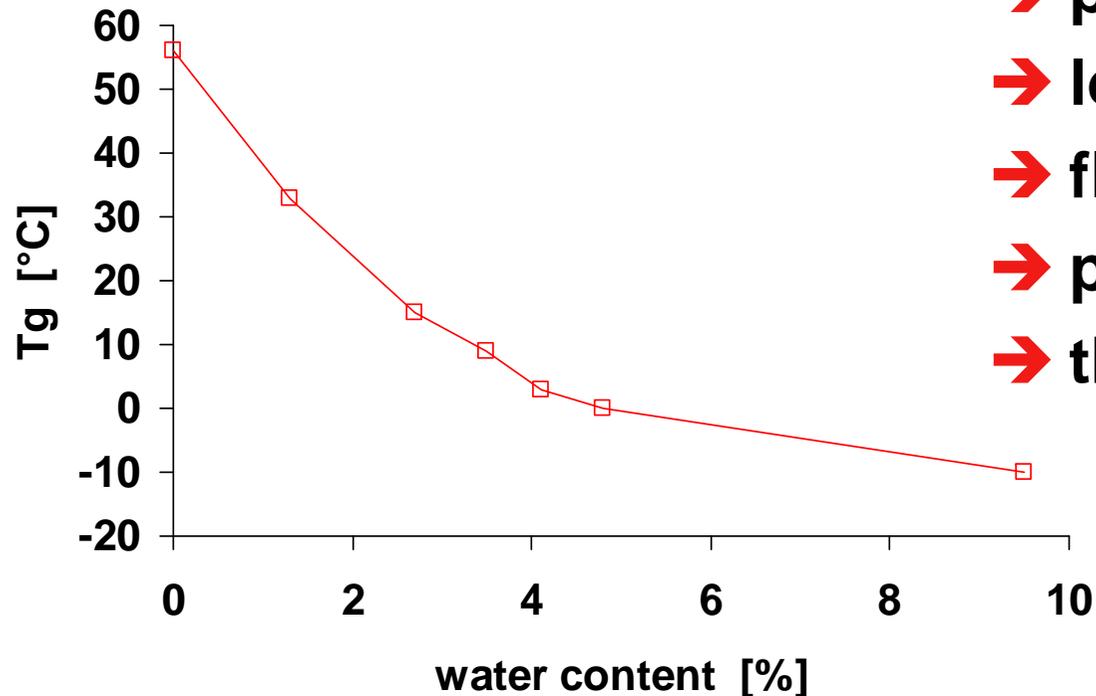


moisture absorption of a 50µm PA6 mopnolayer film; 23°C / 65% r.h.

# Properties: Moisture Absorption

water inserted into H-bond

- plasticizer
- lowers Tg
- flexibility
- puncture resistance
- thermoformability

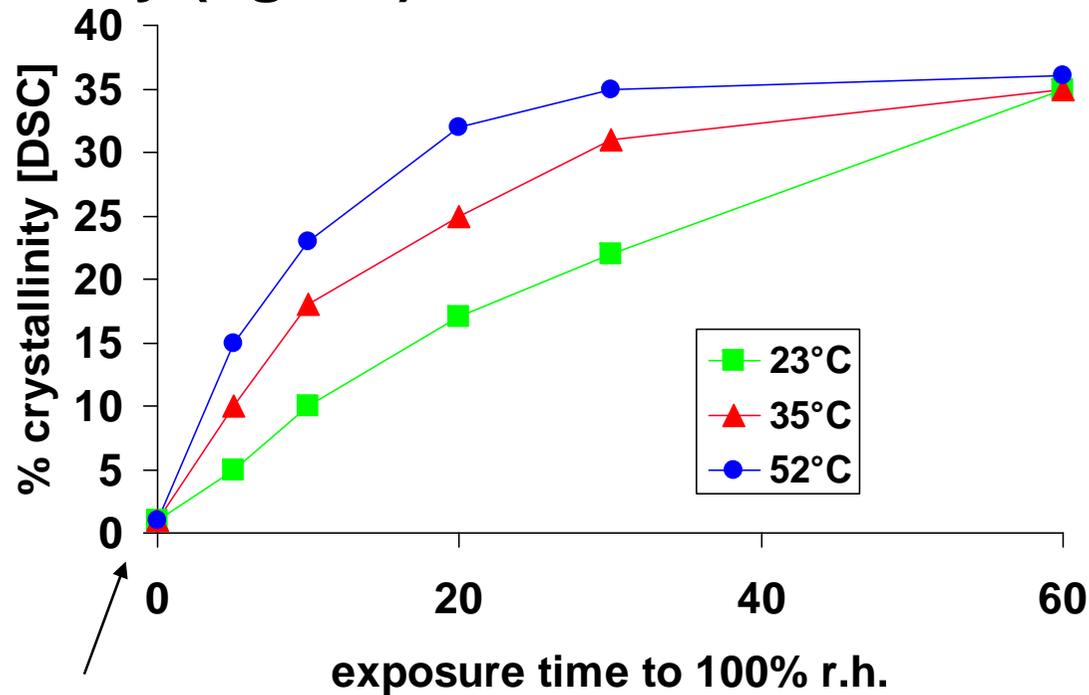


glass transition temperature of 1mm PA6 plates, torsion pendulum

# Postcrystallisation

solid state postcrystallisation by

- temperature ( $T > T_g$  ( $56^\circ\text{C}$ ))
- humidity ( $T_g < T$ )



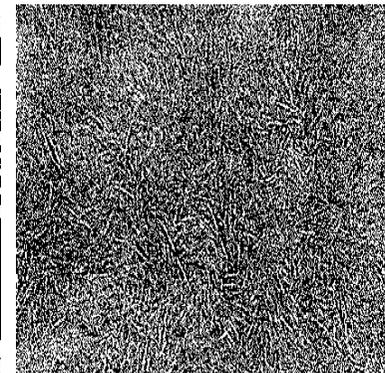
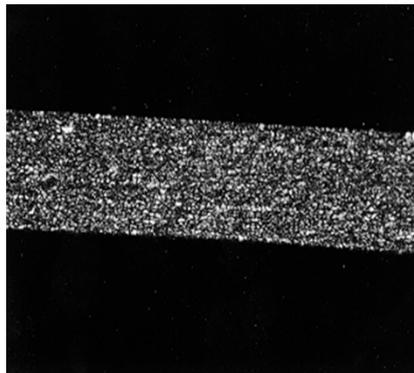
X-ray: <1%

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

# Postcrystallisation

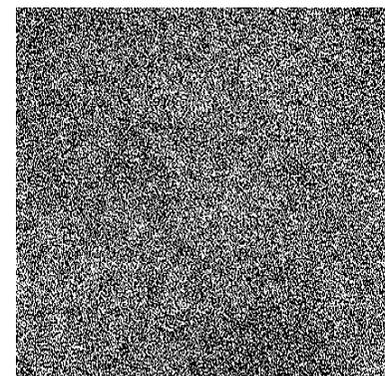
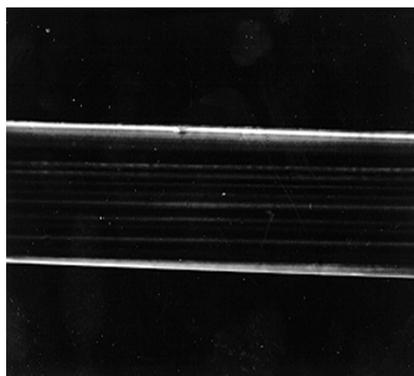
**crystalline film: spherulites**

**„amorphous“ film: microcrystallinity by post-crystallisation**



slowly  
cooled

X-ray:  
34% cryst.



rapidly  
cooled

X-ray:  
25% cryst

1:640x / light

1:10 000x / TEM

1:212 500x / TEM

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

# Properties and Applications: Barrier

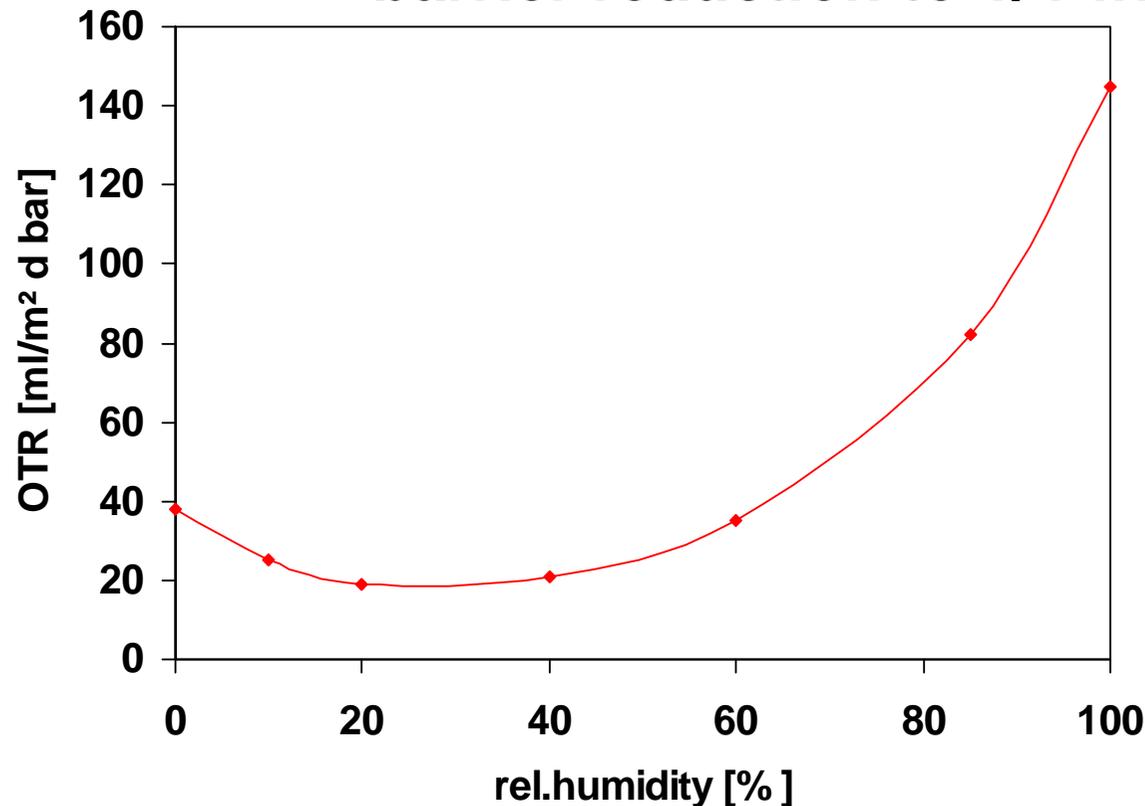
Polyamide is used in packaging films for its....

- **barrier properties**
- smoked fish
- meat
- processed meat, bacon, sausage
- “TV dinner“



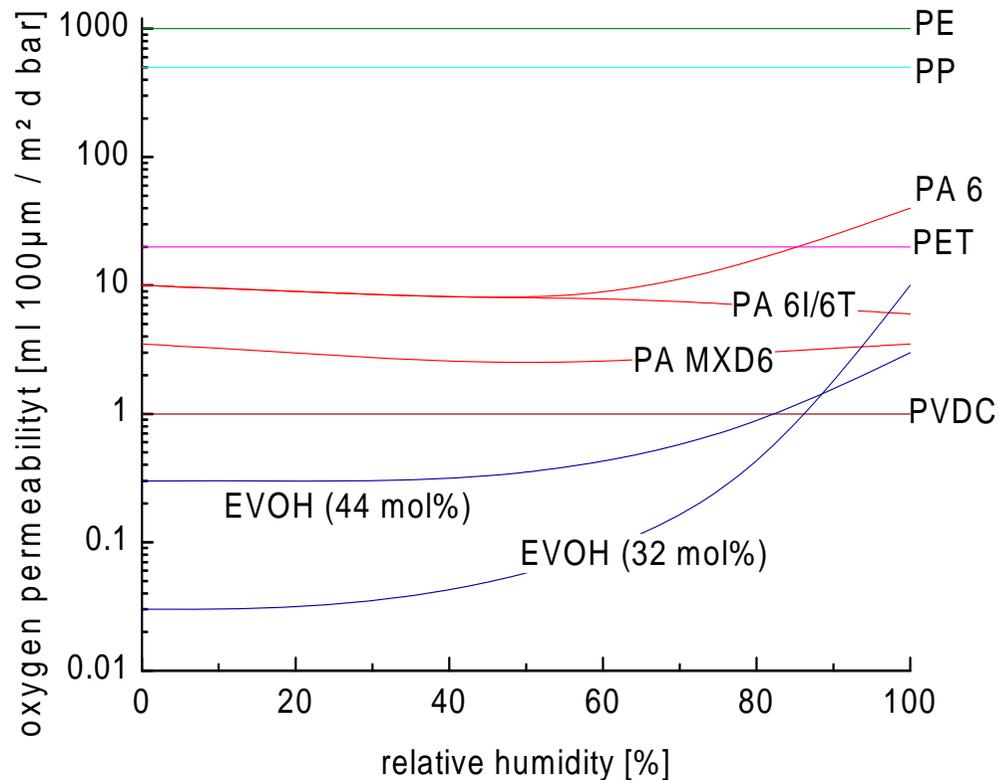
# Properties and Applications: Barrier

- high oxygen barrier for 0-70% humidity
- barrier reduction to 1/4 when humidity = 100%



**\*Oxygen barrier of 25µm PA6 (Ultramid B50 L 01) cast monolayer film, 23°C**

# Properties and Applications: Barrier

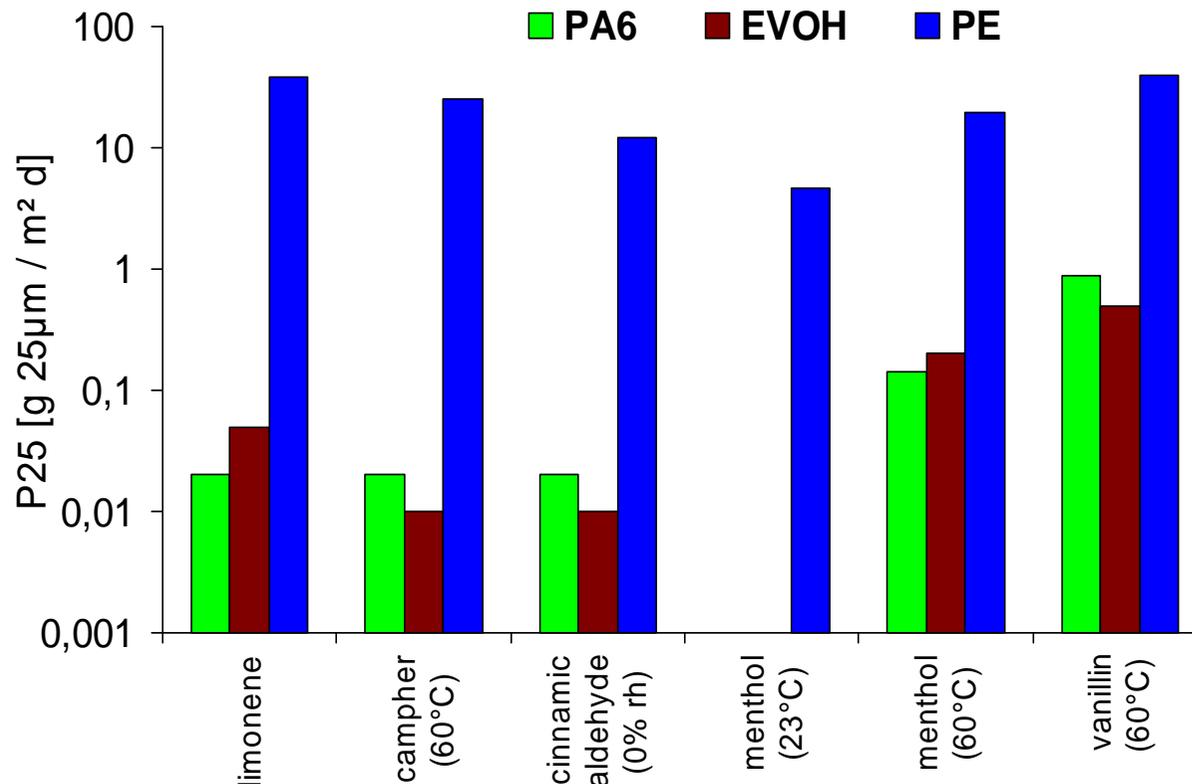


- high oxygen barrier of PA6
- some aromatic polymers with even higher barrier
- EVOH very high barrier, but strong reduction at high humidity

\* Oxygen barrier for 100 µm of various packaging polymers

# Properties and Applications: Barrier

**Aroma Barrier: very high barrier to bulky aroma molecules of low to intermediate polarity**



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

# Properties and Applications: Thermoforming

Ultramid is used in Packaging Films for its....

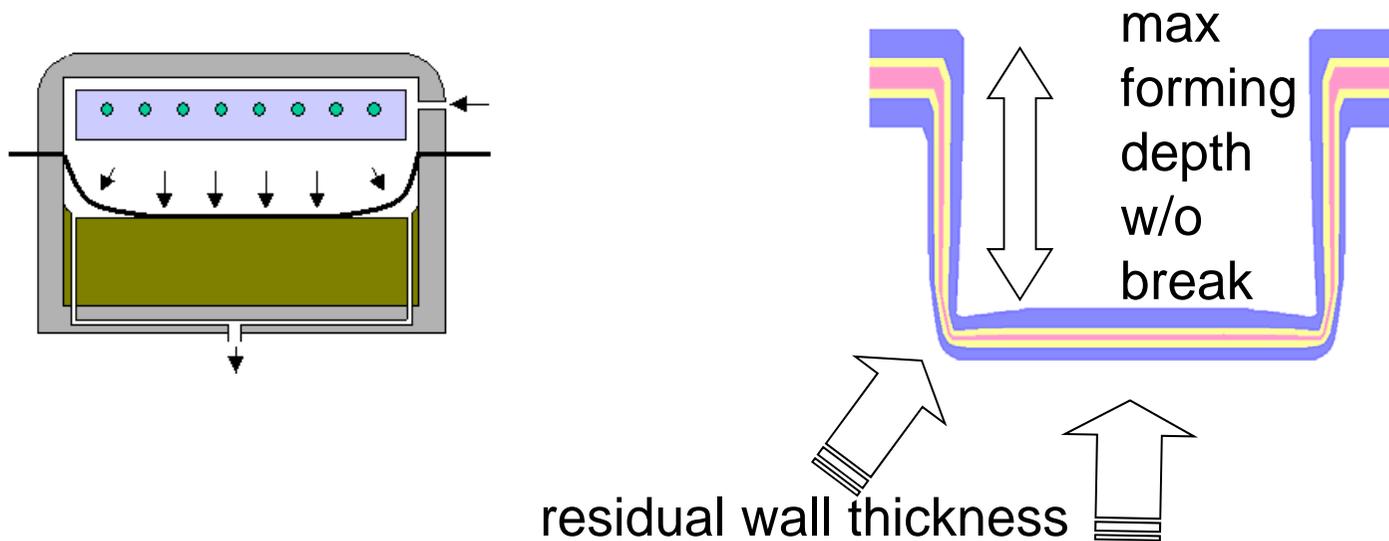
- **thermoformability**

for applications as

- cheese
- ham
- processed meat



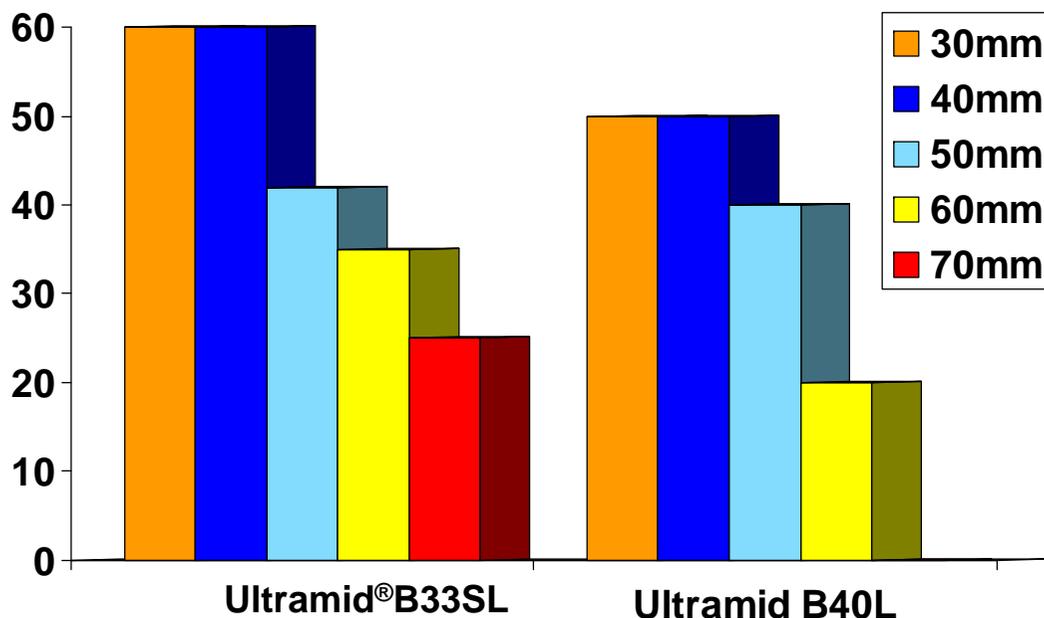
# Properties and Applications: Thermoforming



„thermoformability“ =

- maximum forming depth before film breaks
- residual wall thickness in corners (% of original thickness)
- optical quality after forming (avoid haze by stretching)

# Properties and Applications: Thermoforming



**Residual wall thickness [%]  
blown film PE/tie/PA/tie/PA/tie/PE 150µm**

# Thermoforming: Typical Structures coextruded cast film structures

**185 µm cast film (chill roll 25°C)**

|              |  |
|--------------|--|
| <b>15 µm</b> | <b>LDPE 3.5/0.924 + LLDPE 4/0.915+mLLDPE 4/0.906</b> |
| <b>20 µm</b> | <b>LDPE 3.5/0.924 + LLDPE 4/0.915</b>                |
| <b>10 µm</b> | <b>adh (MA-grafted LLDPE 4-6)</b>                    |
| <b>25 µm</b> | <b>Ultramid B36 LN</b>                               |
| <b>15 µm</b> | <b>EVOH 44mol%</b>                                   |
| <b>25 µm</b> | <b>Ultramid B36 LN</b>                               |
| <b>10 µm</b> | <b>adh (MA-grafted LLDPE 4-6)</b>                    |
| <b>40 µm</b> | <b>LDPE 3.5/0.924 + LLDPE 4/0.915</b>                |
| <b>10 µm</b> | <b>adh (MA-grafted LLDPE 4-6)</b>                    |
| <b>15 µm</b> | <b>Ultramid B36 LN</b>                               |



# Properties and Applications: Mechanical Properties

Ultramid<sup>®</sup> is used in Packaging Films

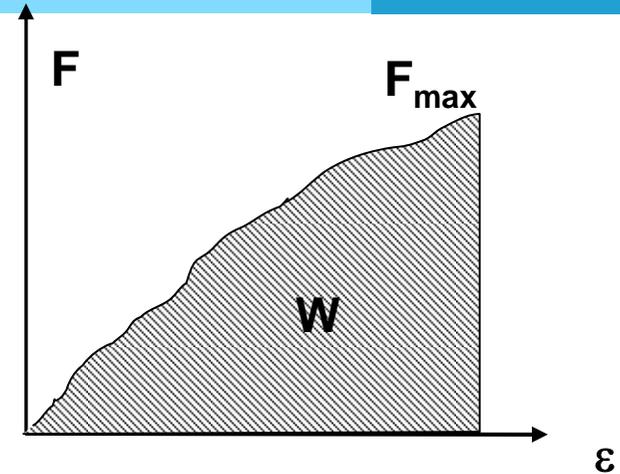
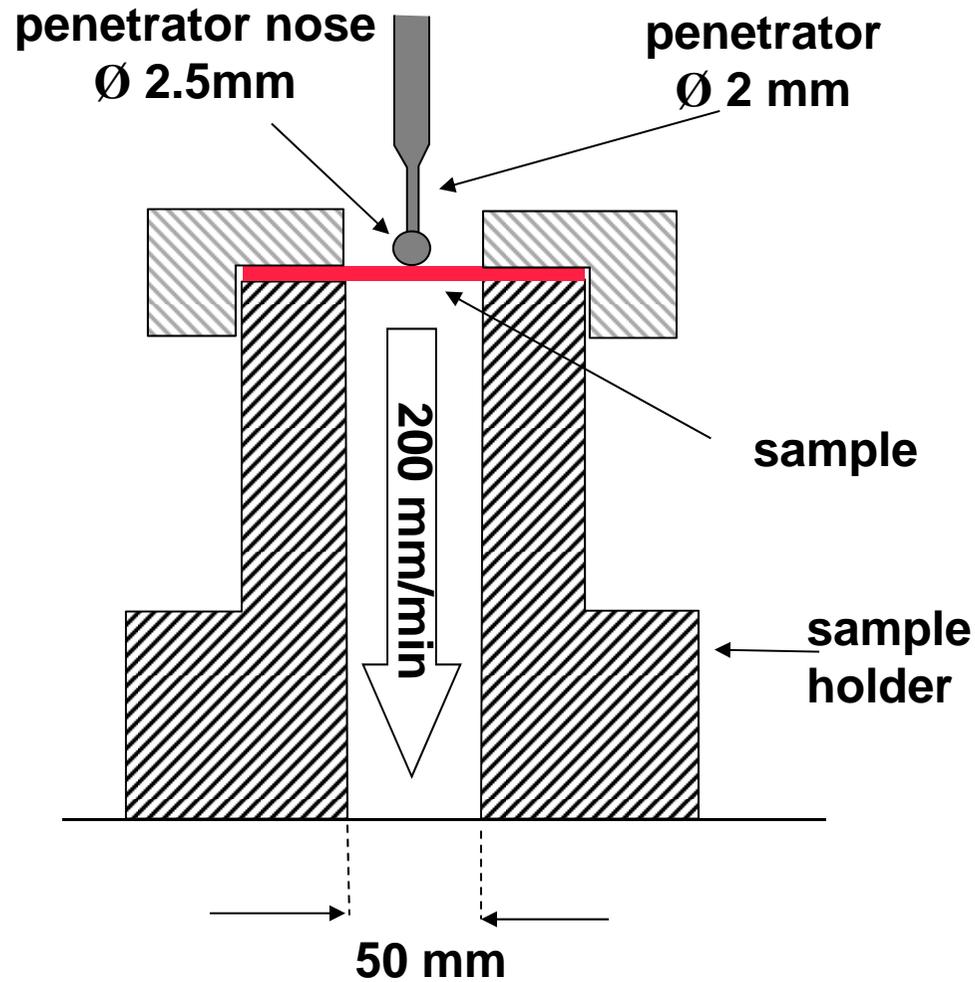
for its....

## Mechanical properties

- high strength
- high toughness and puncture resistance
- high tear propagation resistance



# Puncture Resistance Test



|   | W [N mm] | Fmax [N] |
|---|----------|----------|
| Ultramid <sup>®</sup> B40L water-cooled | 155      | 25       |
| Ultramid <sup>®</sup> B36LN cast        | 135      | 23       |
| Ultramid <sup>®</sup> B40L blown        | 120      | 20       |

# Properties and Applications: Lidding Film

Polyamide is used in Packaging Films for its....  
**heat resistance and sealability**

for

- lidding film
- pouches



# Bag/Pouch : Typical Structures coextruded barrier structure

**80 μm blown film**

|              |   |
|--------------|---|
| <b>20 μm</b> | <b>40% LDPE .7/.924+40%LLDPE 2/.916 + 20%uLLDPE 2/0.902</b> |
| <b>10 μm</b> | <b>adh (MA-grafted LLDPE MI=1.5-2</b>                       |
| <b>18 μm</b> | <b>Ultramid B33 SL</b>                                      |
| <b>10 μm</b> | <b>adh (MA-grafted LLDPE MI=1.5-2</b>                       |
| <b>22 μm</b> | <b>70% LLDPE 2/.922 + 30% LDPE 0.7/.928</b>                 |



**80 μm blown film (with hot-water anti-curl bath)**

|              |   |
|--------------|---|
| <b>12 μm</b> | <b>40% LDPE .7/.924+40%LLDPE 2/.916 + 20%uLLDPE 2/0.902</b> |
| <b>20 μm</b> | <b>70% LLDPE 2/.918 + 30%LDPE .7/.924</b>                   |
| <b>20 μm</b> | <b>70% LLDPE 2/.918 + 30%LDPE .7/.924</b>                   |
| <b>10 μm</b> | <b>adh (MA-grafted LLDPE MI=1.5-2</b>                       |
| <b>18 μm</b> | <b>Ultramid C40 LN 07</b>                                   |



# Typical Structures laminated high-barrier structure

**BOPET // PE/tie/PA/EVOH/PA/tie/PE  
barrier/seal film for lamination  
for lidding film (top web)**

**12µm BOPET (printed)  
laminated (solvent or solvent-less) to  
45µm blown film**

**20µm LDPE 0.7/0.924 + LLDPE 1-2/0.918  
or EVA 4-5mol%**

**2µm adh (MA-grafted LLDPE 1-2)**

**2µm Ultramid B40 L (or Ultramid B36SL)**

**2µm EVOH-32mol%**

**2µm Ultramid B40 L (or Ultramid B36SL)**

**2µm adh (MA-grafted LLDPE 1-2)**

**15µm EVA-4.5% or**

**LDPE 0.7/0.924 + LLDPE 1-2/0.915+mLLDPE 2/0.906**

**properties (of blown lamination film)**

|                  |                                       |     |
|------------------|---------------------------------------|-----|
| tensile strength | MPa                                   | 35  |
| elongation break | %                                     | 500 |
| OTR (23°C/0%rh)  | cm <sup>3</sup> /m <sup>2</sup> d bar | 2.5 |
| OTR /23°/65%rh)  | cm <sup>3</sup> /m <sup>2</sup> d bar | 6   |
| WVTR (23°/85-0%) | g/ m <sup>2</sup> d                   | 3   |
| haze             | %                                     | 7   |



# Summary

**Ultramid® Polyamide resin is widely used as raw material for coextruded packaging film due to its unique combination of**

- **high mechanical properties**
- **good transparency**
- **heat resistance**
- **high barrier to oxygen and chemicals**
- **good thermoformability**



# Ultramid<sup>®</sup> Product line for extrusion

| <b>Ultramid<sup>®</sup> B (homopolyamide PA6) grades</b>   |            |            |                                    |  |
|--|------------|------------|------------------------------------|--|
| <b>Ultramid<sup>®</sup></b>                                | <b>VN</b>  | <b>RV</b>  | <b>additives</b>                   | <b>applications</b>                                    |
| <b>Ultramid<sup>®</sup> B33 L</b>                          | <b>195</b> | <b>3.3</b> | <b>lubricant</b>                   | <b>BOPA, monofilaments, paper coating</b>              |
| <b>Ultramid<sup>®</sup> B36 LN</b>                         | <b>218</b> | <b>3.6</b> | <b>lubricant, nucleating agent</b> | <b>cast film</b>                                       |
| <b>Ultramid<sup>®</sup> B40 L</b>                          | <b>250</b> | <b>4.0</b> | <b>lubricant</b>                   | <b>blown film, monofilaments, casing</b>               |
| <b>Ultramid<sup>®</sup> B40 LN</b>                         | <b>250</b> | <b>4.0</b> | <b>lubricant, nucleating agent</b> | <b>cast film (blown film)</b>                          |
| <b>Ultramid<sup>®</sup> SL slow crystallisation grades</b> |            |            |                                    |  |
| <b>Ultramid<sup>®</sup> B33 SL</b>                         | <b>195</b> | <b>3.3</b> | <b>lubricant</b>                   | <b>BOPA, casing, blown film</b>                        |
| <b>Ultramid<sup>®</sup> B36 SL</b>                         | <b>218</b> | <b>3.6</b> | <b>lubricant</b>                   | <b>casing, blown film</b>                              |
| <b>Ultramid<sup>®</sup> B36 SLN</b>                        | <b>218</b> | <b>3.6</b> | <b>lubricant, nucleating agent</b> | <b>cast film,</b>                                      |
| <b>Ultramid<sup>®</sup> C (copolyamide PA6/66) grades</b>  |            |            |                                    |  |
| <b>Ultramid<sup>®</sup> C33 L 01</b>                       | <b>195</b> | <b>3.3</b> | <b>lubricant</b>                   | <b>blown film</b>                                      |
| <b>Ultramid<sup>®</sup> C33 LN 01</b>                      | <b>195</b> | <b>3.3</b> | <b>lubricant, nucleating agent</b> | <b>blown film</b>                                      |
| <b>Ultramid<sup>®</sup> C40 L 07</b>                       | <b>250</b> | <b>4.0</b> | <b>lubricant,</b>                  | <b>blown film</b>                                      |
| <b>Ultramid<sup>®</sup> C40 LN 07</b>                      | <b>250</b> | <b>4.0</b> | <b>lubricant nucleating agent</b>  | <b>blown film (symmetric, nonsymm. with waterbath)</b> |

# Thank you very much for your attention!



## further information

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