



Latest Developments in Polyester Films for Flexible Electronics and Photovoltaics

Bill MacDonald, Keith Rollins

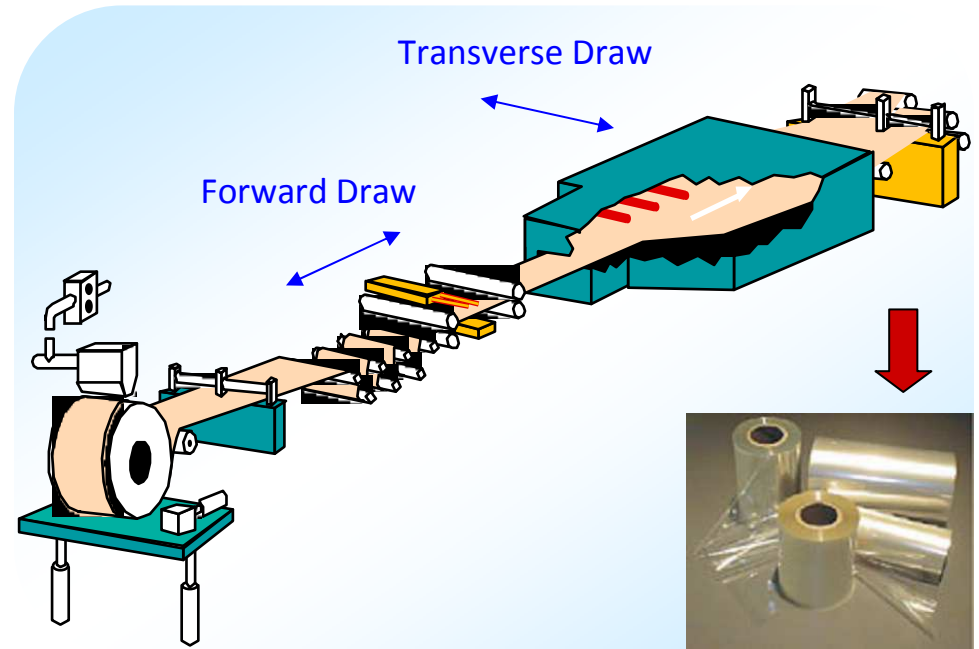


Opening Comments

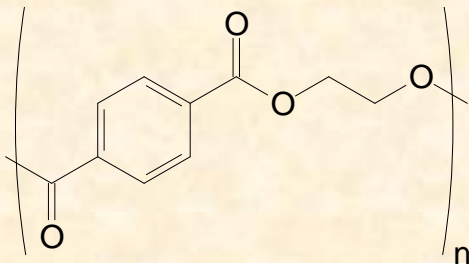
- DTF have been active in flexible electronics for ca 12 years
- In that time we have seen device fabrication move from demonstrator to prototype to production scale...and then pull back again (Plastic Logic , Polymer Vision)
- Having focussed on achieving basic properties of film required for flex electronics, focus has moved to achieving consistency and reproducibility as first manufacturing scale plants emerge
- This can only really be achieved by manufacture of films on commercial scale assets-so less cutting edge material science pushing boundaries of film performance and more focus on “hygiene” issues and manufacturing
- Cost effective barrier remains a major the rate limiting step for commercialisation of both flexible displays and PV devices

Polyester Film Technology (1)

- PET and PEN polyester films
- Biaxially oriented, semi-crystalline
 - High stiffness
 - Dimensional stability
 - Optical transparency
 - Solvent resistance
 - Thickness = 0.6-500 μm

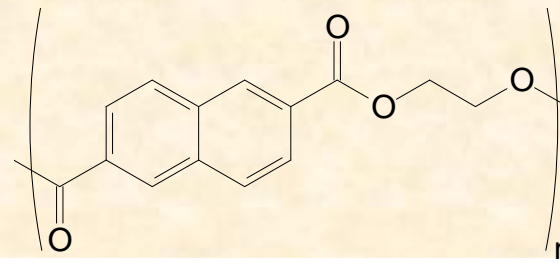


Melinex[®], Mylar[®] and Teijin[®] Tetoron[®]
Polyethylene terephthalate (PET)



$T_m = 255\text{ }^\circ\text{C}$
 $T_g = 78\text{ }^\circ\text{C}$

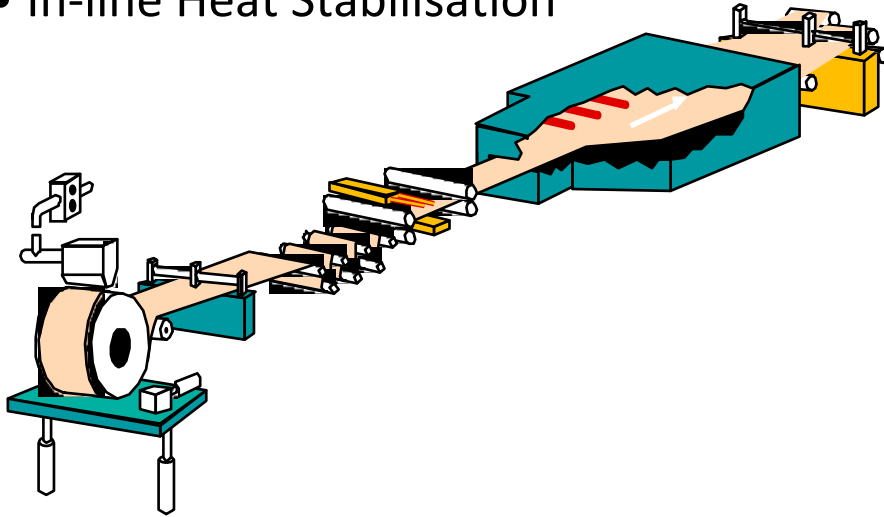
Teonex[®]
Polyethylene naphthalate (PEN)



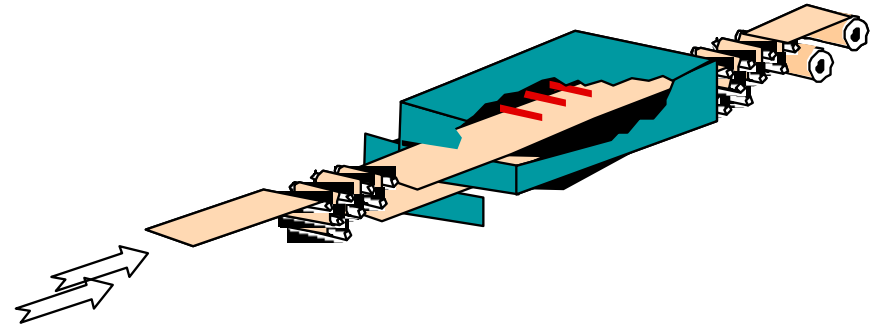
$T_m = 263\text{ }^\circ\text{C}$
 $T_g = 120\text{ }^\circ\text{C}$

Polyester Film Technology (2)

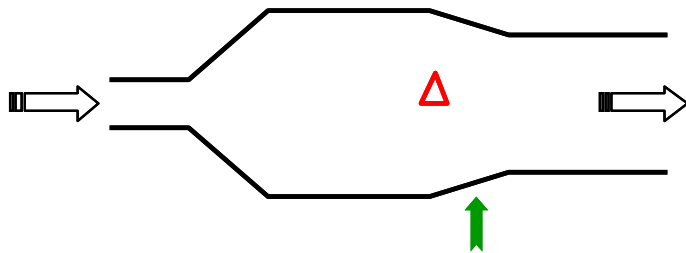
- In-line Heat Stabilisation



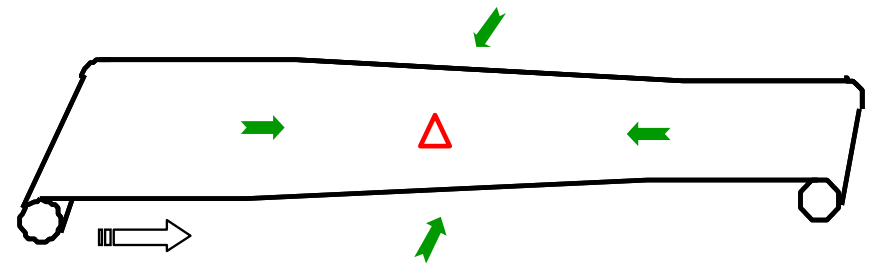
- Off-line Heat Stabilisation



- Oven



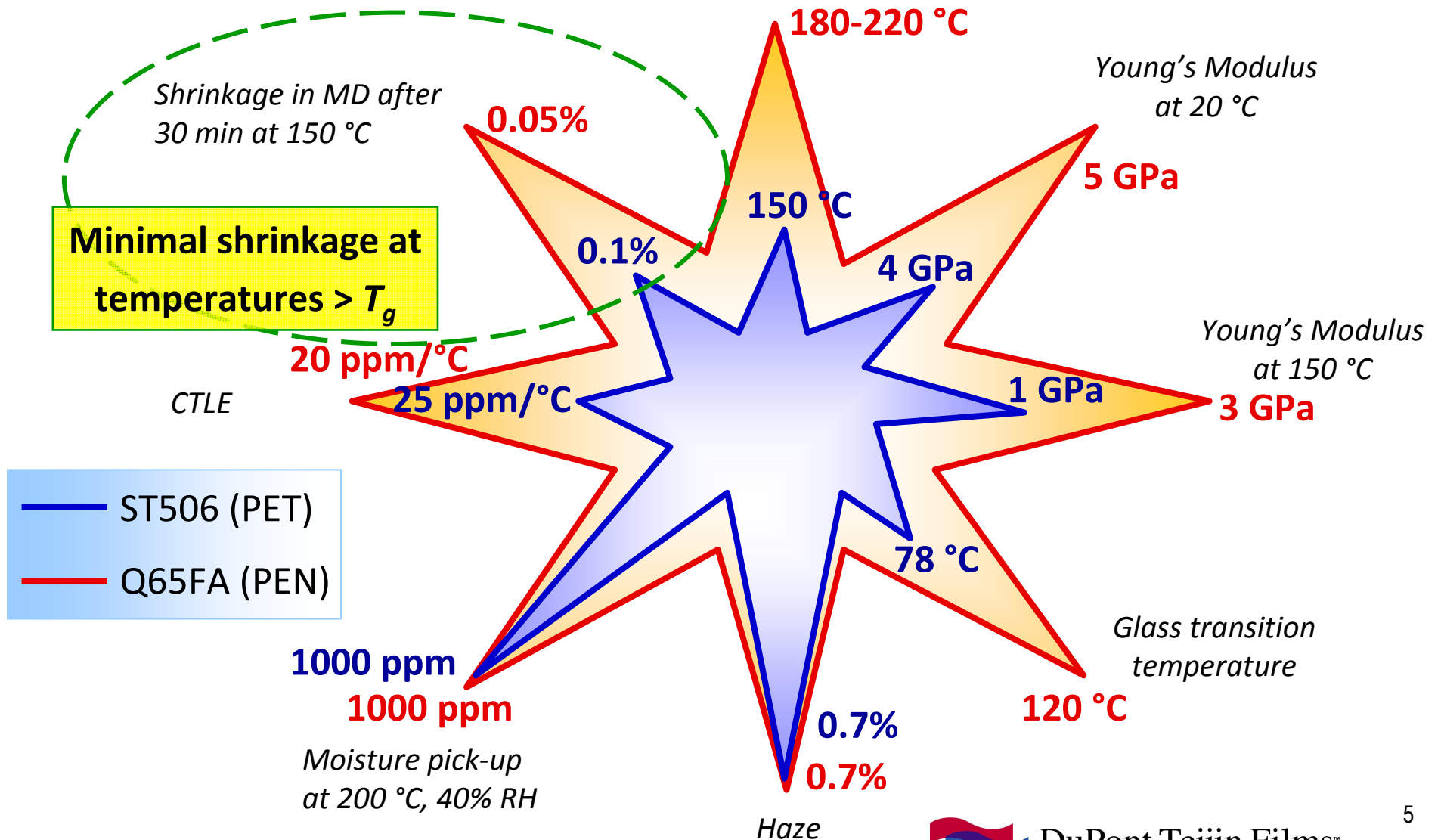
- Film can relax in TD but not in MD
- Leads to shrinkage on subsequent processing



- Allows relaxation in MD
- Minimum shrinkage on both directions

Heat-Stabilised PEN and PET Films

Upper temperature for processing

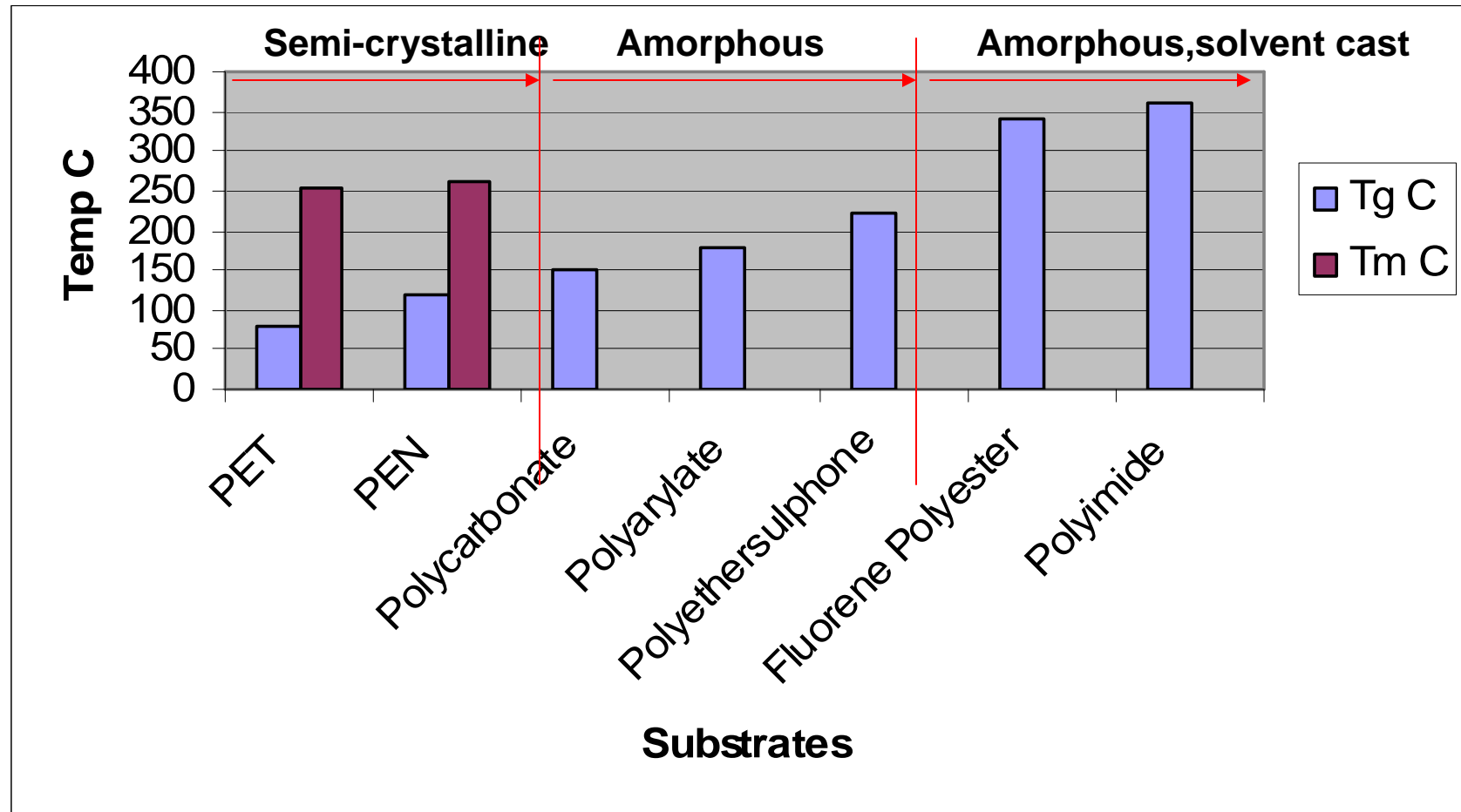


DTF Film range for Flexible Electronics

- Red denotes new
- Melinex® -A diverse range of heat stabilised PET films
 - Dimensionally stable up to 150C
 - Thickness 50 micron to 250 micron
 - UV stabilised
 - Range of pretreats for enhanced adhesion to functional coatings
- Teton®-Low shrink, planarised PET films
 - Ultrasmooth defect free surface for improved device performance
- Teonex® -Leading range of high performance PEN films
 - Dimensionally stable up to 180-200C
 - Thickness 25-200micron
 - Pretreated for enhanced adhesion to functional coatings
 - White film at 75 micron
- Teonex®- Low shrink, planarised PEN films
 - High temperature performance with ultrasmooth defect free surface
 - 50 and 125 micron film
 - Protect film (one or two side) available

Factors Influencing Film Choice-Substrate Properties

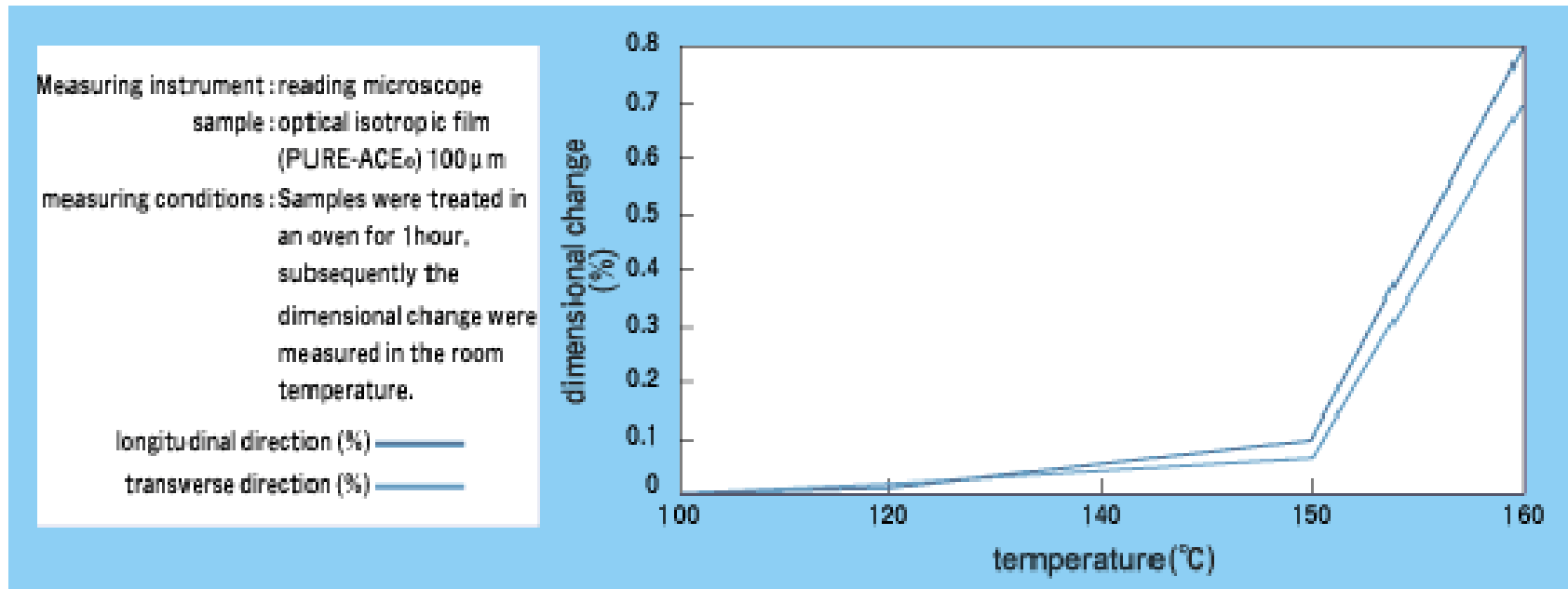
Films grouped by thermal properties



Requirements and technology hurdles

| | Voice of Customer | Film Requirements |
|----------------------------------------------------------|--------------------------------------|--------------------------------------------|
| E-paper and OLED frontplanes | Barrier against oxygen and moisture | Smooth surface |
| | | Clean surface |
| | | Low outgassing properties |
| | | Robustness |
| | | Low defects |
| | Maximum light extraction | Low haze |
| | | Low optical defects |
| | | High transparency |
| Display Backplanes for Inorganic (aSi) and Organic TFT's | Alignment of TFT's during processing | Dimensional stability at high temperatures |
| | | Low moisture absorption |
| | | Low shrinkage |
| | | Low CTLE |
| | Correct functioning of TFT's | Clean, smooth surface |
| | | Clean surface maintained on processing |
| | | Chemical resistance |
| All | Bonding to rigid carrier | Surface energy - contact angle |
| | | Adhesion properties |
| | Easy handling | Rigidity |

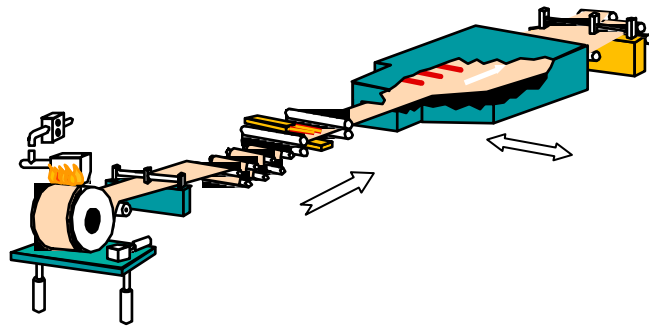
Polycarbonate-Dimensional Stability



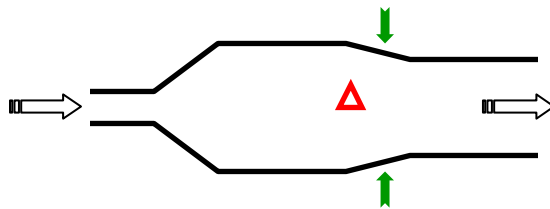
From Teijin web site
Considerable change in CTE at T_g

Dimensional Stability

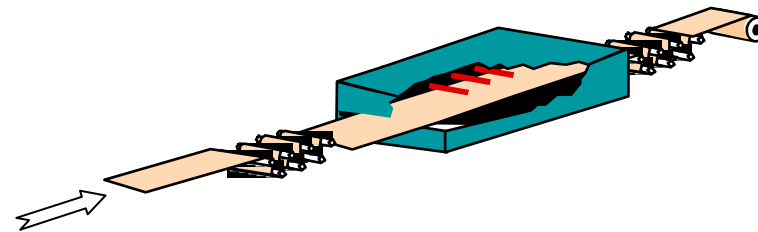
Polyester Film Off-line Stabilisation/Relaxation Process



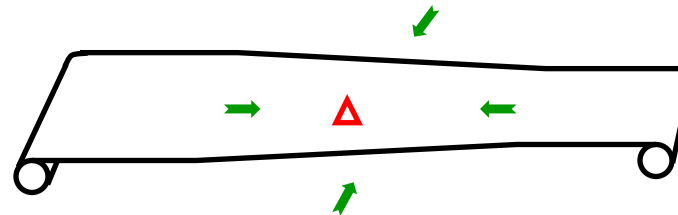
Stenter Heat Set (X1-3)



Film can relax in TD but not in MD
-this leads to shrinkage on
Subsequent processing

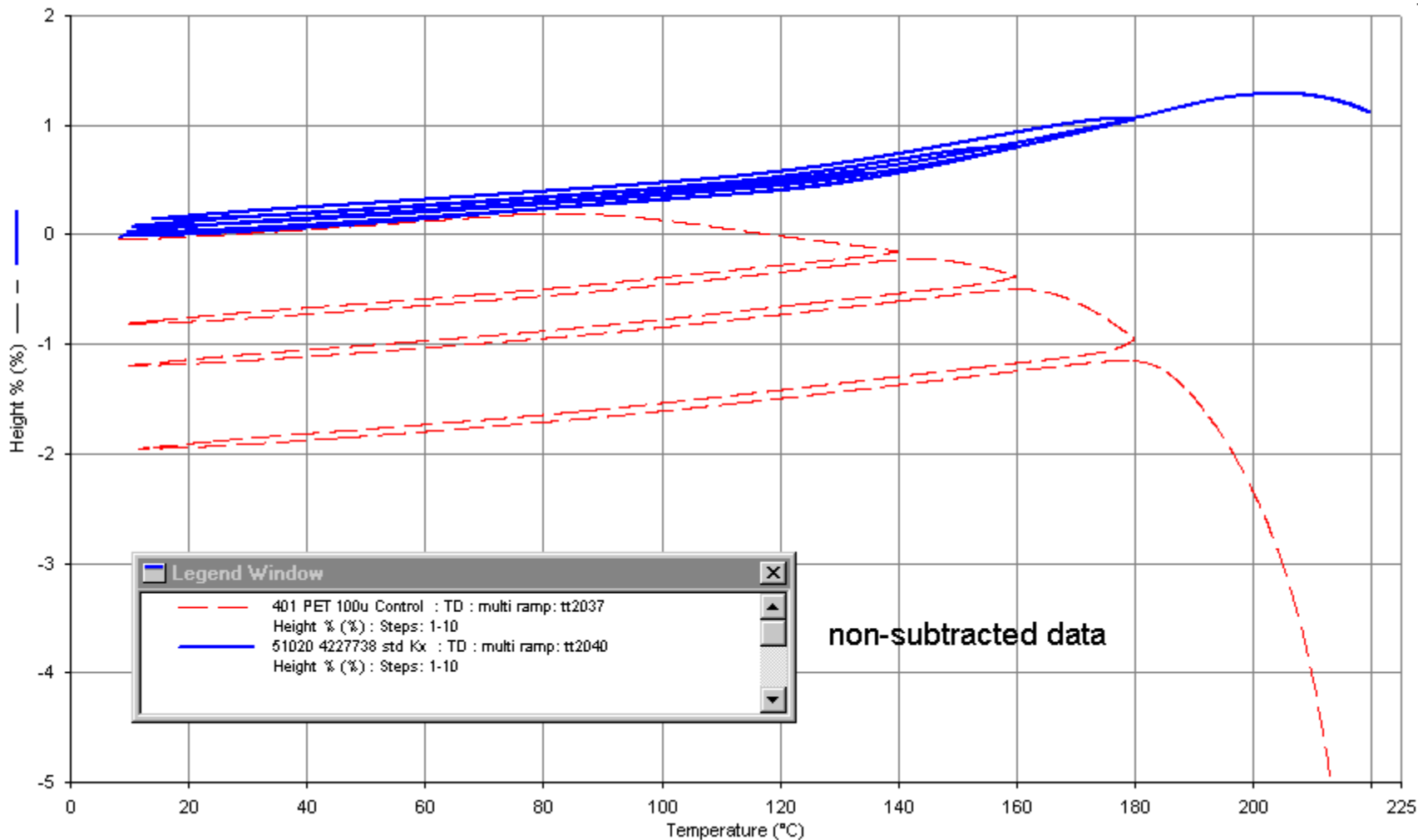


Off-line Stabilisation

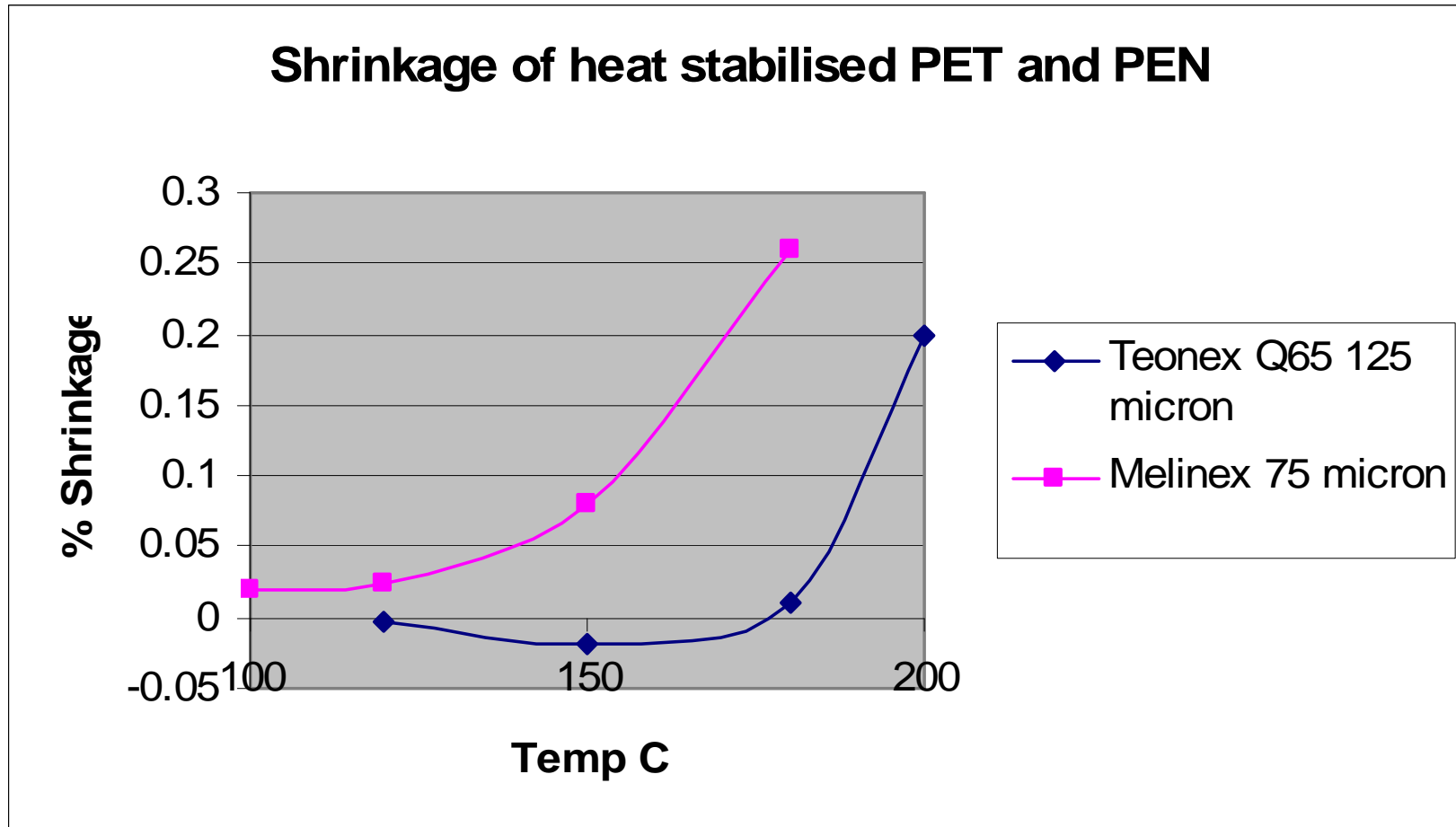


Film put through further process
Allows relaxation in MD

Unstabilised PET vs. Heat Stabilised PEN : TD



Shrinkage of heat stabilised PET and PEN



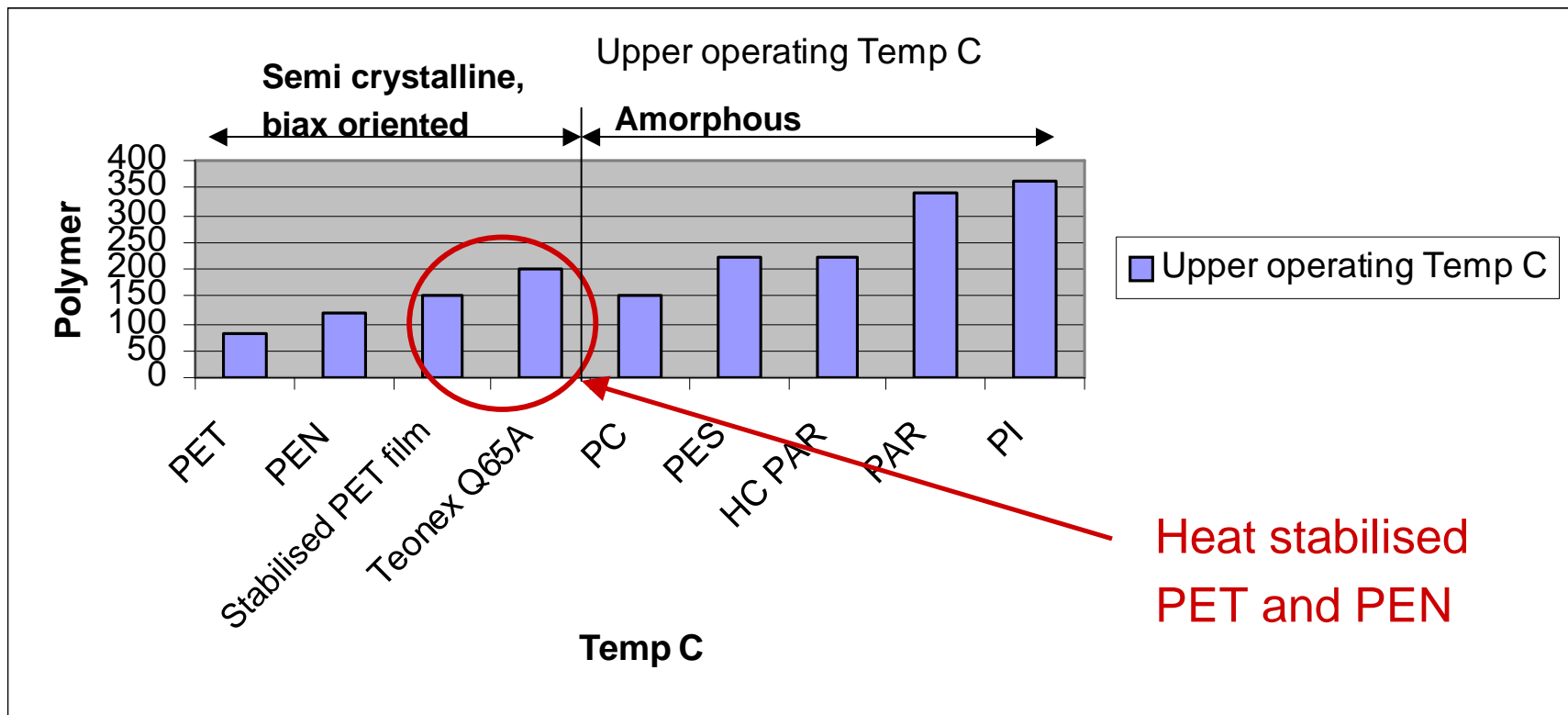
Shrinkage

Film with dimensional stability good enough for TFT backplanes is achievable

- Backed up by evidence from end users

Upper Temperature for Processing

- The temperature at which films can be processed on without dimensional reproducibility or degradation issues
- Tg does not define upper temperature for processing for biaxially oriented films-defined by temperature of heat stabilisation process



CLTE

- Melinex®/TeonexQ65®- CLTE is ca <18ppm/C in range room temp to 100 C
- CLTE of glass/metal ca 10-20ppm/C
- Compare
 - CLTE of isotropic PEN ca 35ppm/C
 - CLTE of amorphous polymers ca 50ppm/C
- Low CLTE from biaxially orientation coupled with crystallinity
- Good match with glass/metal

Control of Dimensional Stability

1. Offline stabilisation

Stiffness

- Easier handling with a stiffer film
- Tooling geared up for glass-stiffer is better!
- **Biaxially oriented crystalline films are ca 3 times stiffer than amorphous films**

| Properties | Unit | Kapton HN/VN | AryLite™ A 100HC | Appear™ 3000 | Sumilite® FST-X014 | PureAce | Teonex® Q65 | Melinex® ST504 |
|------------------|------|-----------------|---------------------|-----------------|-----------------------|---------|----------------|-------------------|
| Young's modulus | GPa | 2.5 | 2.9 | 1.9 | 2.2 | 1.7 | 6.1 | 5.3 |
| Tensile strength | MPa | 231 | 100 | 50 | 83 | | 275 | 225 |

Rigidity

- Youngs Modulus is independent of thickness
- Rigidity defined below

$$D = \frac{E t^3}{12(1-\nu)}$$

E is the tensile or Youngs Modulus.
t is the thickness, ν is Poissons ratio (0.3-0.4).

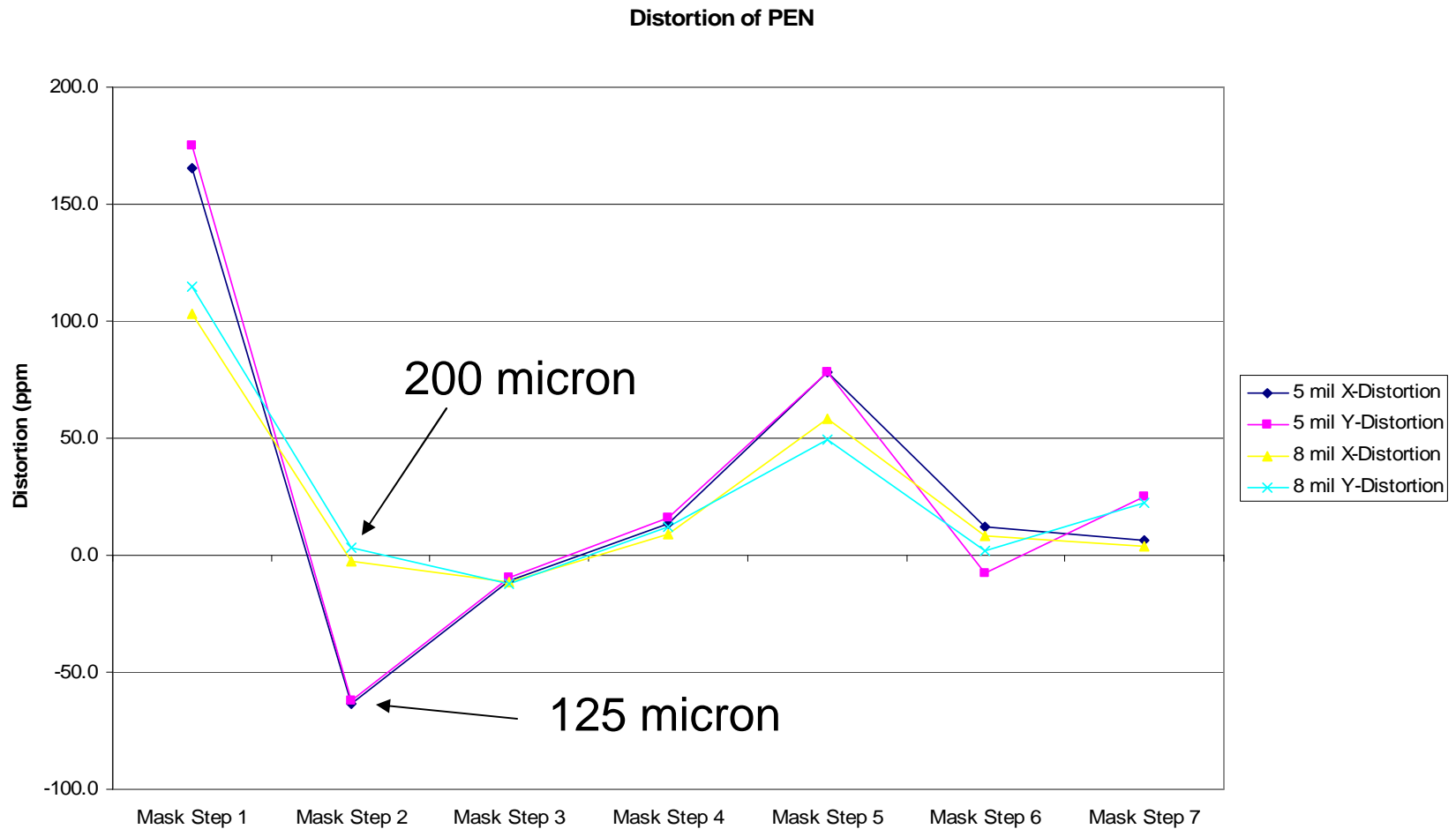
| Material | Thickness Micron | Modulus Gpa | Rigidity Nm x 10 ⁻⁴ |
|------------|---------------------|----------------|-----------------------------------|
| Amorphous | 125 | 2 | 5 |
| Amorphous | 200 | 2 | 20 |
| Teonex®Q65 | 125 | 6 | 15 |
| Teonex®Q65 | 200 | 6 | 61 |

- 200 micron Teonex®Q65 is 4 times more rigid than 125 micron, 12 times more rigid than 125 micron amorphous film

Why is this important?

- a-Si TFT preparation
- 200 micron Teonex is able to withstand the mismatch in CTE between inorganic dielectric coatings and organic based polymeric substrates.
- This leads to less distortion on processing

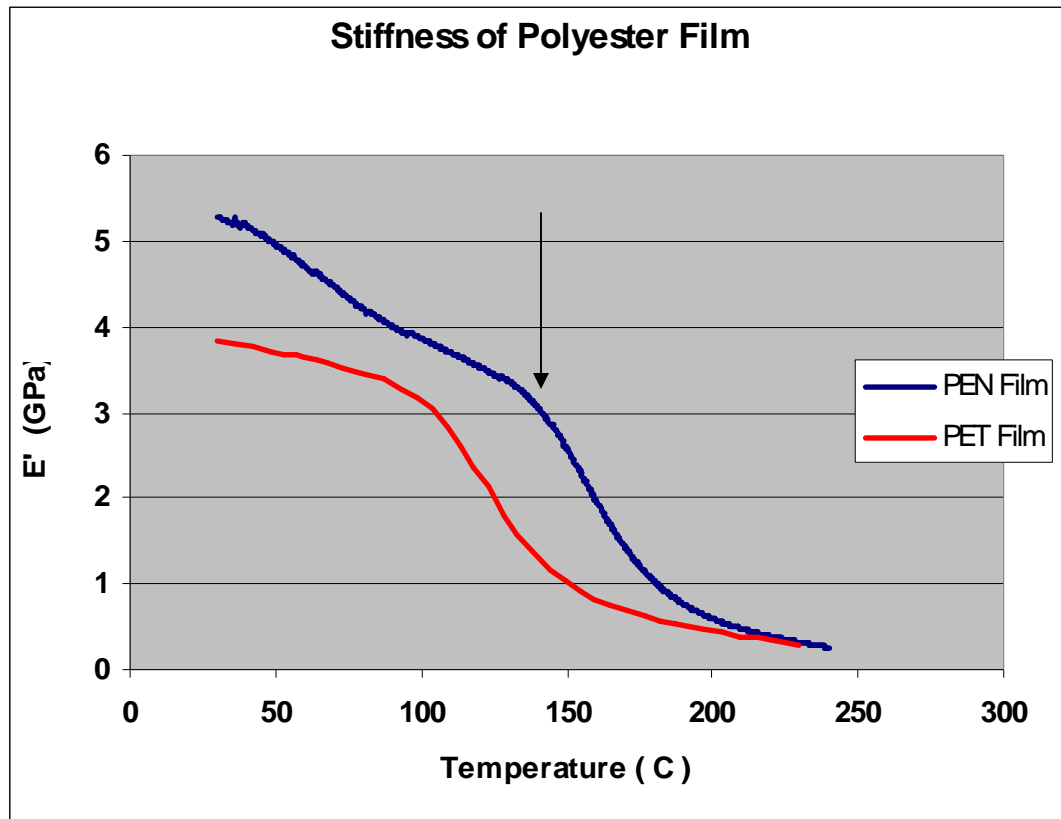
Distortion of Teonex Q65 125 vs 200 micron through a-Si TFT Process



Information courtesy of Flexible Display Centre, ASU



Change in Stiffness with Temperature



- At 120-160C PEN is significantly stiffer than PET
- Implications for processing
 - under a winding tension or
 - if films constrained on processing,films with low moduli will be susceptible to internal deformation
- This will manifest itself as shrinkage upon reheating

Control of Dimensional Stability

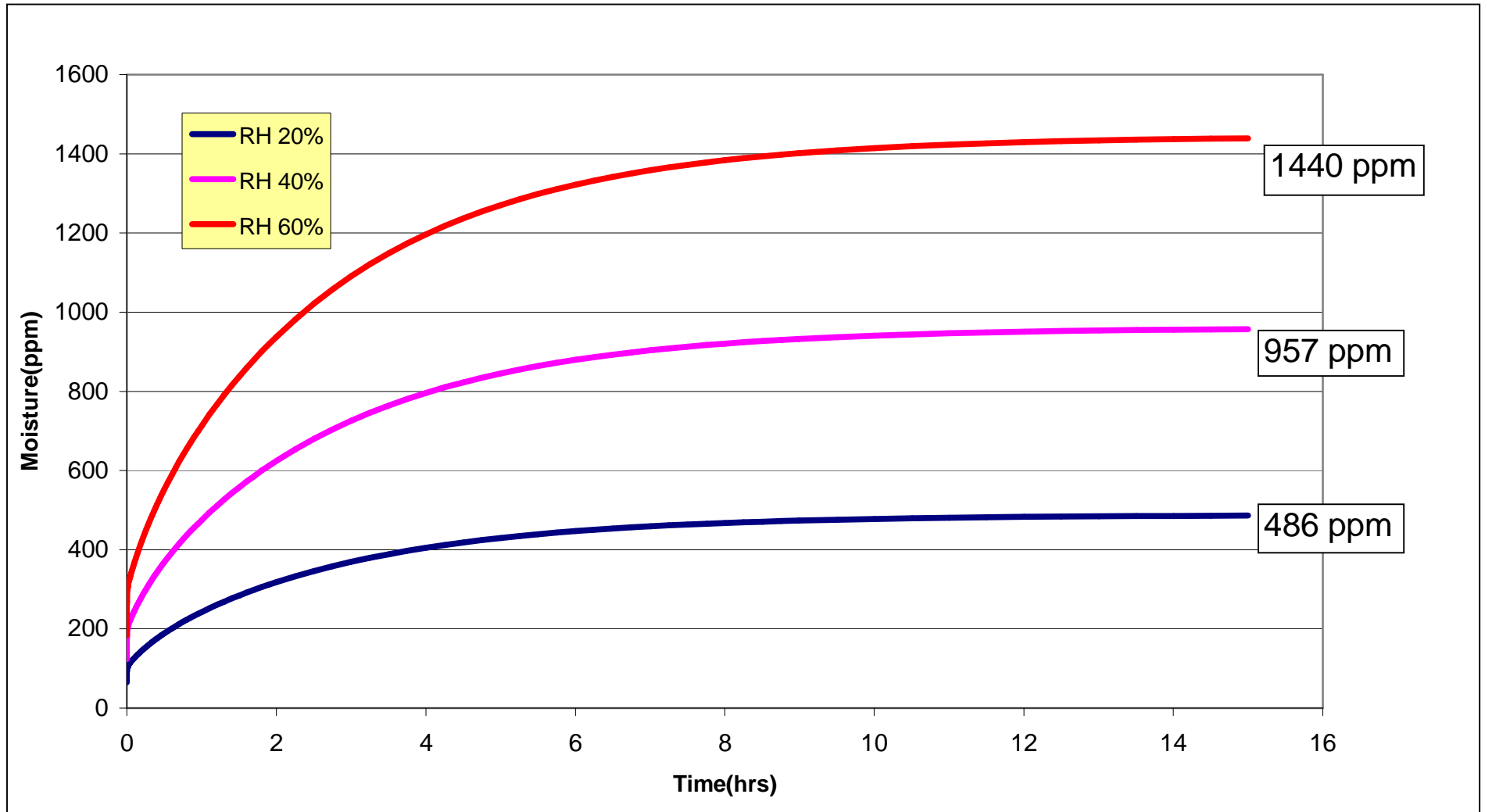
1. Offline stabilisation
2. Control of mechanical stress
 - i. Film thickness
 - ii. Control of tension through processing

Dimensional Stability-Effect of Environment

- Biax crystalline films have generally superior moisture resistance compared to amorphous films
- Polyimide/ PES ca >1.4% moisture pickup
- Experimental studies on controlled moisture pickup show ca 45ppm dimensional change in a given direction per 100ppm moisture
- With the knowledge of the solubility level of moisture in PEN film and its rate of diffusion as a function of temperature, it is possible to model the impact of various environmental conditions on moisture content changes and hence volumetric changes in the different thicknesses of film

Dimensional reproducibility

Effect of RH on Moisture Pickup at 20C



Conclusions

- Crystalline Melinex®/Teonex® films picks up ca 1500ppm
- Can take several hours to reach equilibrium level depending upon film thickness, temp and RH
- Moisture pickup will have a significant effect on dimensional change-ca 45ppm in a given direction per 100ppm moisture
- Critical to understand how equilibrium level of moisture will change through device manufacturing process to obtain registration and to maximise dimensional reproducibility
 - this will vary depending upon a given set of processing conditions and film type

Control of Dimensional Stability

1. Offline stabilisation
2. Control of mechanical stress
 - i. Film thickness
 - ii. Control of tension through processing
3. Control of processing environment
 - i. Moisture

Teonex®Q65A Versus Other Substrates

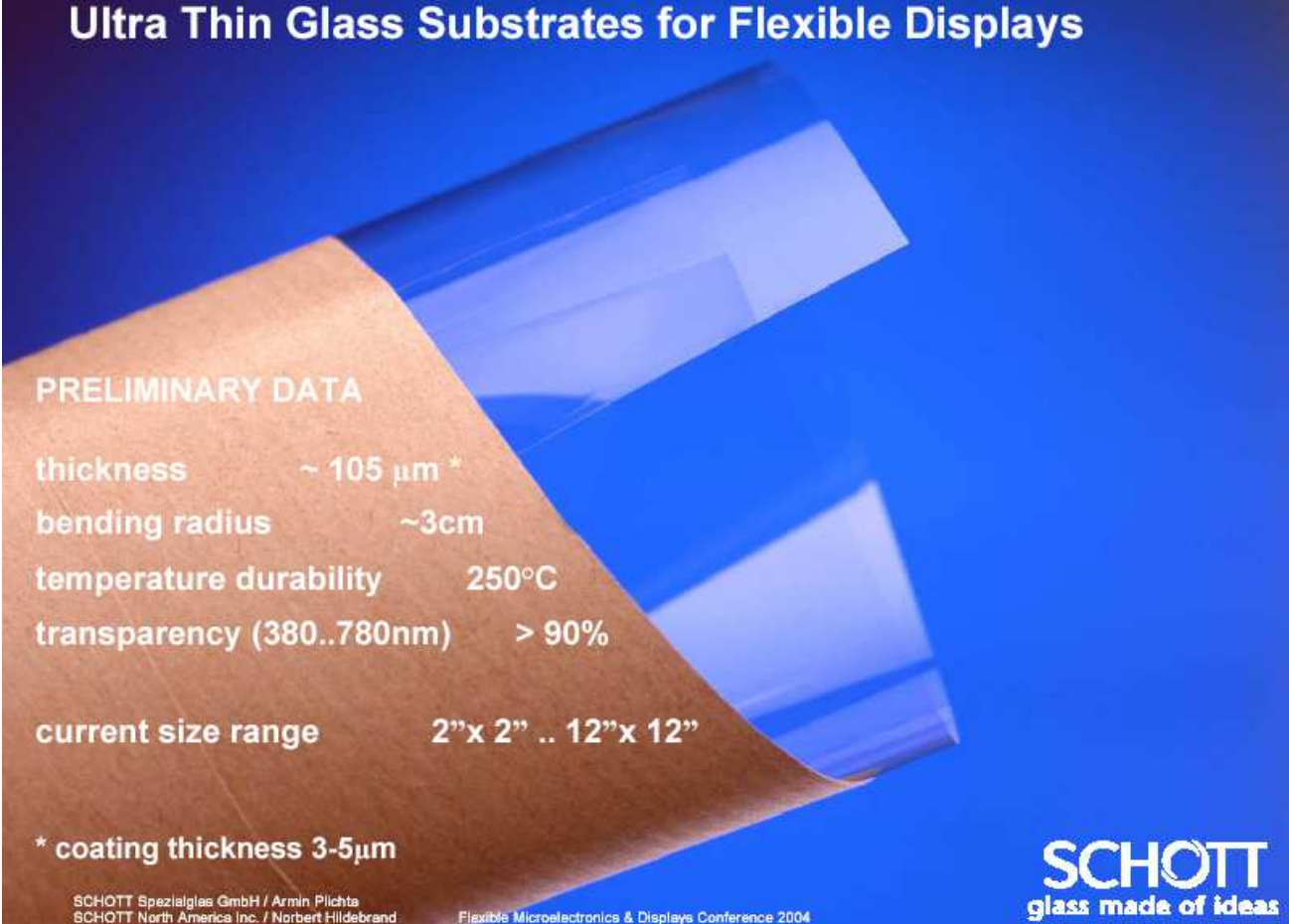
- Based on properties gleaned from data sheets
- Properties for Teonex® Q65A and Melinex® ST504 are for biaxially oriented film
- Teonex® Q65 has the best overall balance of properties of relevance to displays

| Property | Substrate | | | | | |
|--------------------------------------|-------------|---------------|---------------|-------------------|-------------|-----------|
| | Teonex Q65A | Melinex ST504 | Polycarbonate | Polyethersulphone | Polyarylate | Polyimide |
| CTE (-55 to 85 °C) ppm/°C | √√ | √√ | √ | √ | √ | √√ |
| %Transmission (400-700 nm) | √√ | √√ | √√√ | √√ | √√ | X |
| Water absorption % | √√ | √√ | √ | X | √ | X |
| Young's modulus Gpa | √√ | √√ | √ | √ | √ | √ |
| Tensile strength Mpa | √√ | √√ | √ | √ | √ | √ |
| Solvent resistance | √√ | √√ | X | X | X | √√ |
| Commercial availability for displays | √√ | √√ | √√ | √√ | √ | √ |
| Birefringence | X | X | √√ | √√ | √√ | √√ |
| Upper Operating Temp | √√ | √ | √ | √√ | √√√ | √√√ |

| | |
|-----|-----------|
| √√√ | Excellent |
| √√ | Good |
| √ | Moderate |
| X | Poor |

..But the Competition is not just other plastic films

Ultra Thin Glass Substrates for Flexible Displays



PRELIMINARY DATA

| | |
|---------------------------|-----------------------|
| thickness | ~ 105 μm * |
| bending radius | ~3cm |
| temperature durability | 250°C |
| transparency (380..780nm) | > 90% |
| current size range | 2"x 2" .. 12"x 12" |

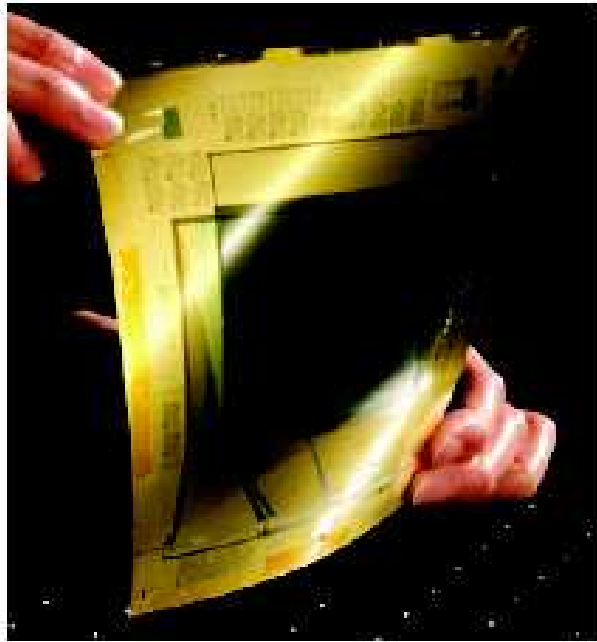
* coating thickness 3-5 μm

SCHOTT
glass made of ideas

SCHOTT Spezialglas GmbH / Armin Plichte
SCHOTT North America Inc. / Norbert Hildebrand
Flexible Microelectronics & Displays Conference 2004

- Flexible glass
 - 50 micron glass with a polymeric coating to give mechanical integrity

Stainless Steel



Picture courtesy of UDC

- Stainless steel
 - Requires planarising coating and insulating coating

Teonex versus Stainless Steel and Glass

| Property | Teonex Q65A | Glass | SS |
|----------------------------|-------------|-------|-----|
| CTE (-55 to 85 °C) ppm/°C | √√ | √√√ | √√√ |
| %Transmission (400-700 nm) | √√ | √√ | X |
| Water absorption % | √√ | √√√ | √√√ |
| Young's modulus Gpa | √√ | √√ | √√ |
| Tensile strength Mpa | √√ | √√ | √√ |
| Plastic deformation | √√√ | X | X |
| Solvent resistance | √√ | √√√ | √√√ |
| Upper Operating Temp | √ | √√ | √√√ |
| Barrier | X | √√√ | √√√ |
| Parasitic capacitance | √√√ | √√√ | X |
| Surface smoothness | √√ | √√√ | X |
| R2R | √√√ | X | √ |
| Cut | √√ | X | √ |
| Commercial availability | √√√ | X | √ |

NB The authors view!!

Requirements and technology hurdles

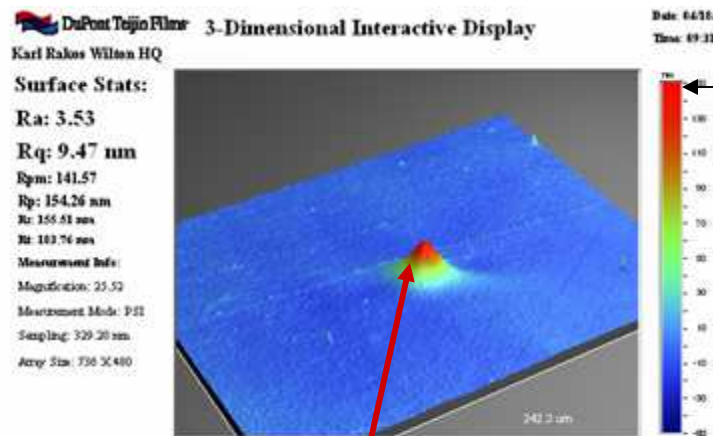
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| | Correct functioning of TFT's | Clean, smooth surface |
| | | Clean surface maintained on processing |
| | | Chemical resistance |
| All | Bonding to rigid carrier | Surface energy - contact angle |
| | | Adhesion properties |
| | Easy handling | Rigidity |

Surface quality of polyester films

- Surface “Quality” is described by 1) Surface smoothness and 2) Surface cleanliness
- 1) Surface Smoothness
 - Determined by the internal cleanliness of the film or surface pretreatment. Depends on ;
 - Polymer recipe (e.g level of inorganic particles within polymer)
 - Process conditions (film and polymer manufacture)
 - Captured quantitatively by the parameters Ra, Rq, Rp etc
- 2) Surface Cleanliness
 - Comprised of external, foreign contamination and scratches

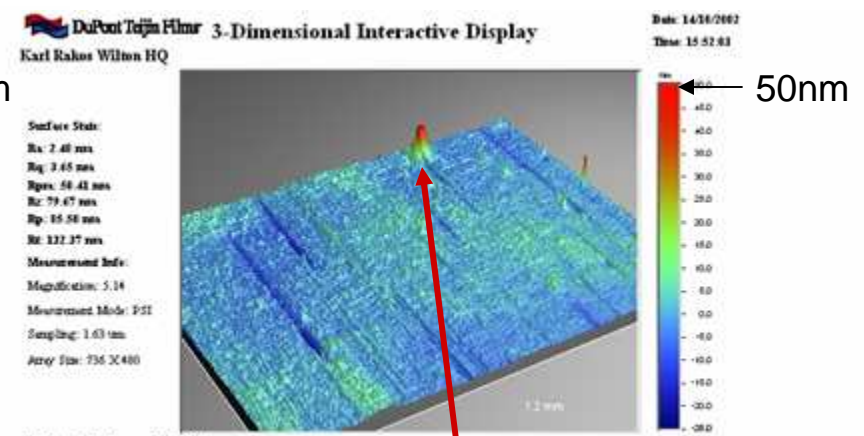
Surface Quality of base film - Intrinsic contamination

- Films have sporadic surface peaks up to 10's microns lateral dimensions, 100's nm height
- Due to internal particulate burden (both organic and inorganic)
- Largely controlled via polymer recipe, plant hygiene



Title: Surface Peak (Rp)
Note: (internal polymeric contaminant)

Internal contaminant

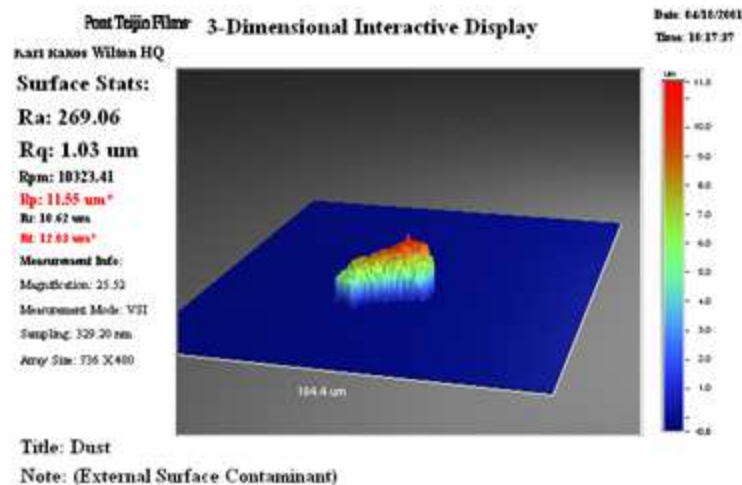


Title: Melnex ST504
Note:

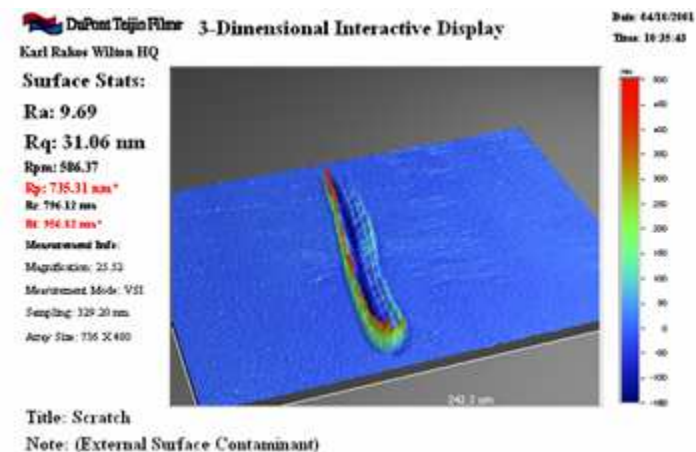
Catalyst residue

Surface Quality of base film - Surface cleanliness

- Films also have sporadic 'external' contaminants such as air-borne debris, scratches etc. Up to 10 micron high, 10's of microns long
- Air borne debris can be removed through surface web cleaning techniques (e.g tacky adhesive roller)
- Film “hygiene” –area of active research



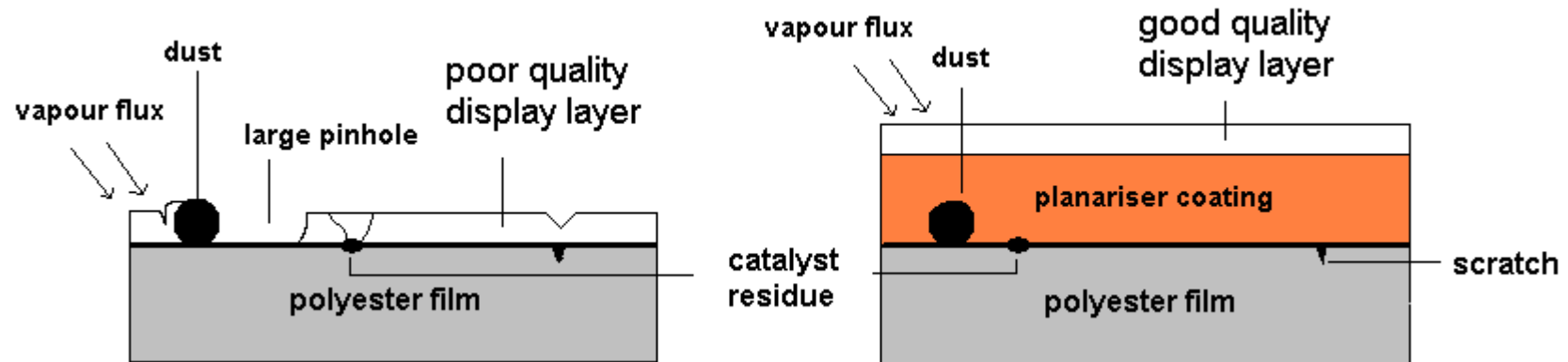
Dust : 40 microns long
10 microns high



Scratch : 150 microns long
0.5 microns high at ridge

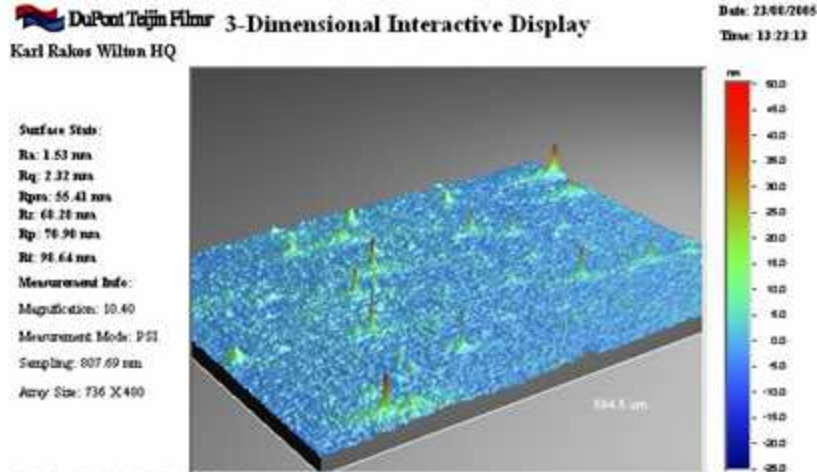
General function of planariser coating

- DTF is developing a family of planarised coated films to give performance improvements
- General principle behind planariser coating process



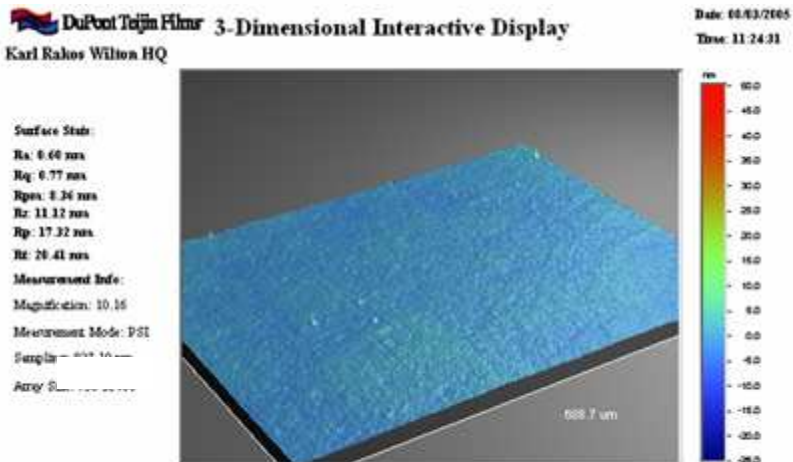
- Planariser coating acts to cover surface projections on the polyester film
 - Intrinsic contamination (e.g catalyst residues)
 - Extrinsic contamination (e.g dust)

Surface smoothness (micron scale)



Title: MELINEX ST506
Note: 'Pre treated surface'

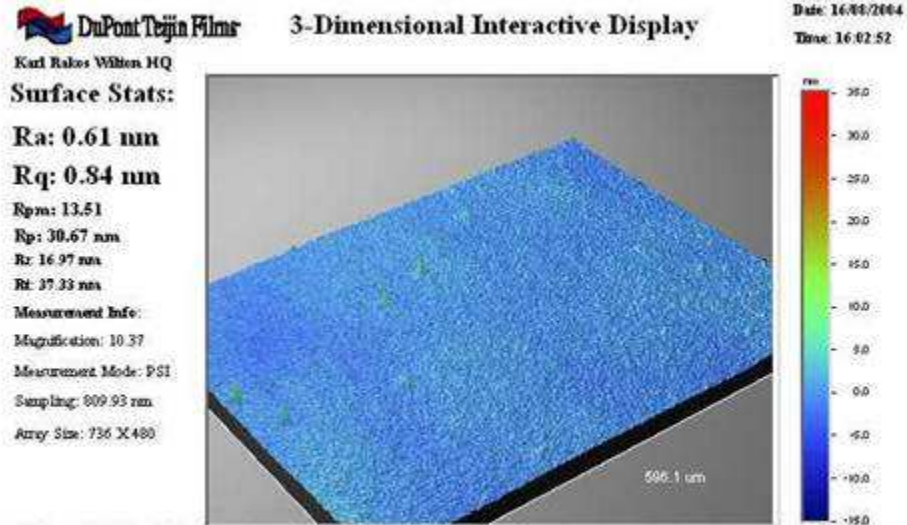
Pretreat on ST506 gives good
adhesion to subsequent coatings
But at expense of surface roughness
Ra 1.53nm



Title: MELINEX ST506
Note: C - Hardcoat

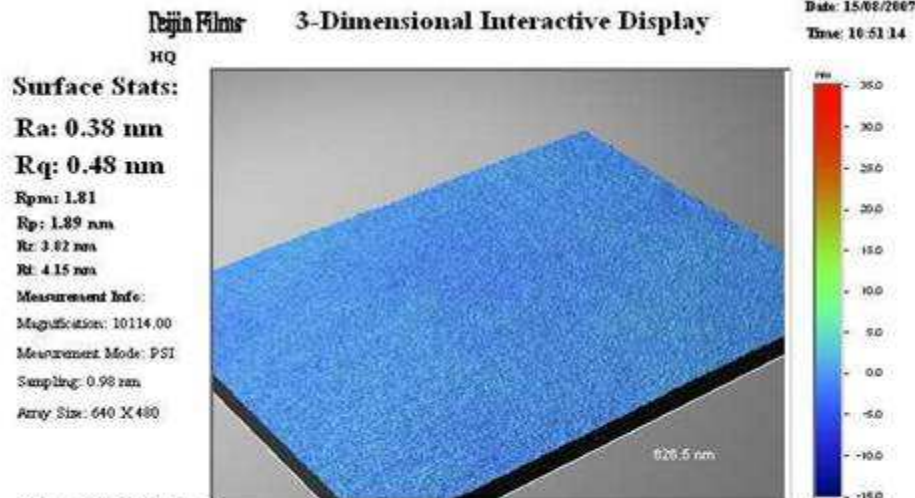
Planarised ST506
Very smooth surface - on a par with a
polished mirror
Ra 0.6nm

Surface smoothness



Title: TEONEX Q65 'raw'

Note:



Title: HCQ6Z1 5_Sum

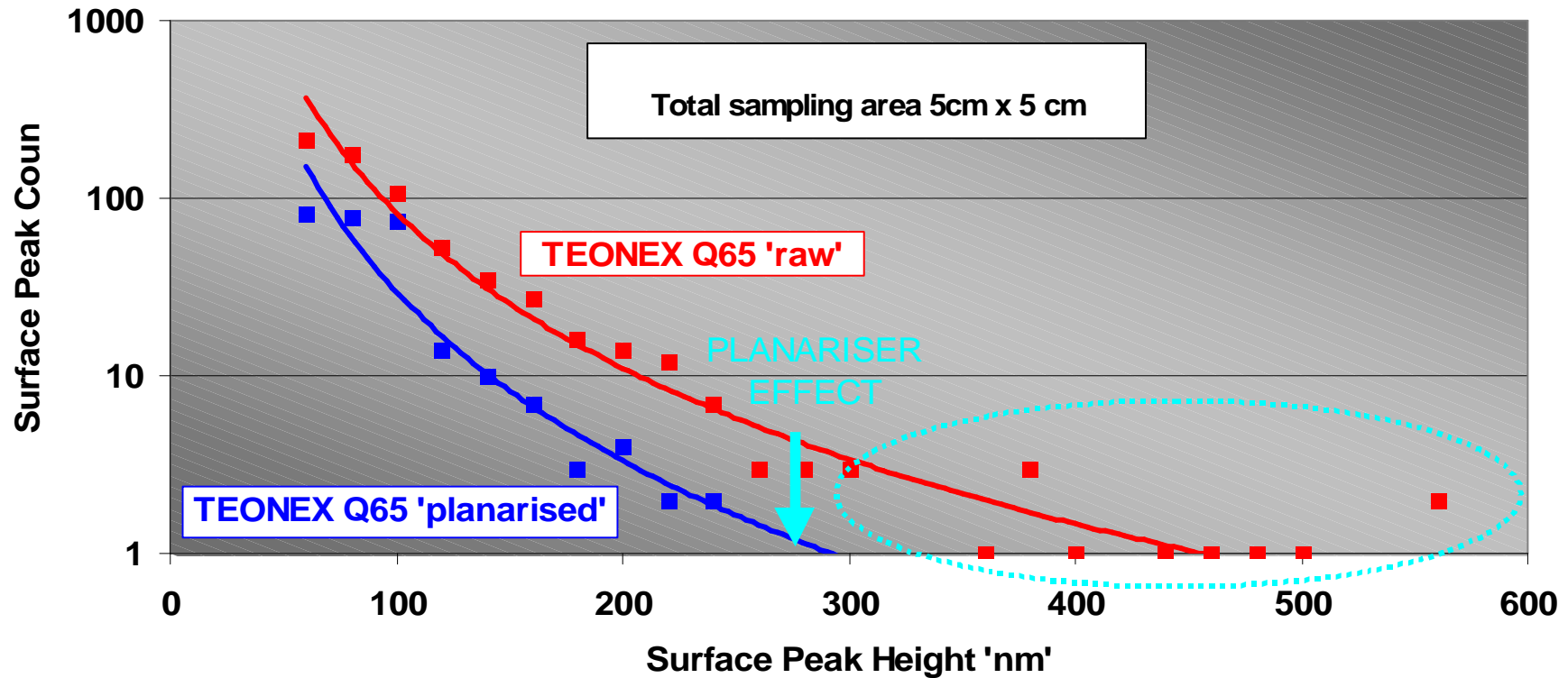
Note:

Surface of Teonex[®]
Q65FA
plain side

Surface of
planarised Teonex[®]
Q65FA

Effectiveness of planariser

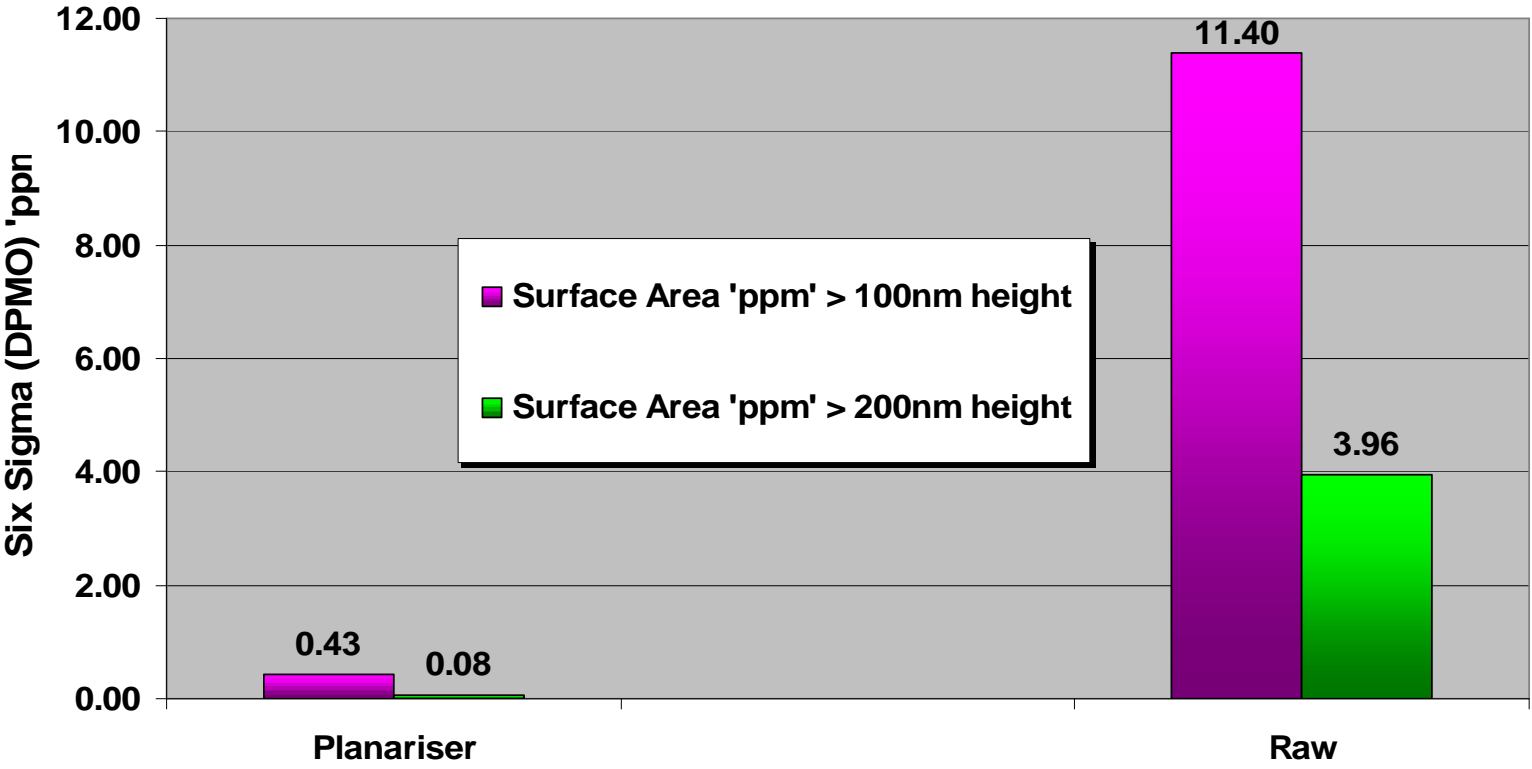
EFFECTIVENESS OF PLANARISER ON INTRINSIC SURFACE ROUGHNESS .



Effectiveness of Planariser

A factor of 50 reduction in occupied surface area of peaks greater than 200nm in height for planarised PEN film compared to standard PEN film

Intrinsic Surface Defect rate Six Sigma DPMO 'ppm' for both 'raw' and 'planarised' Teonex® Q65



Film type

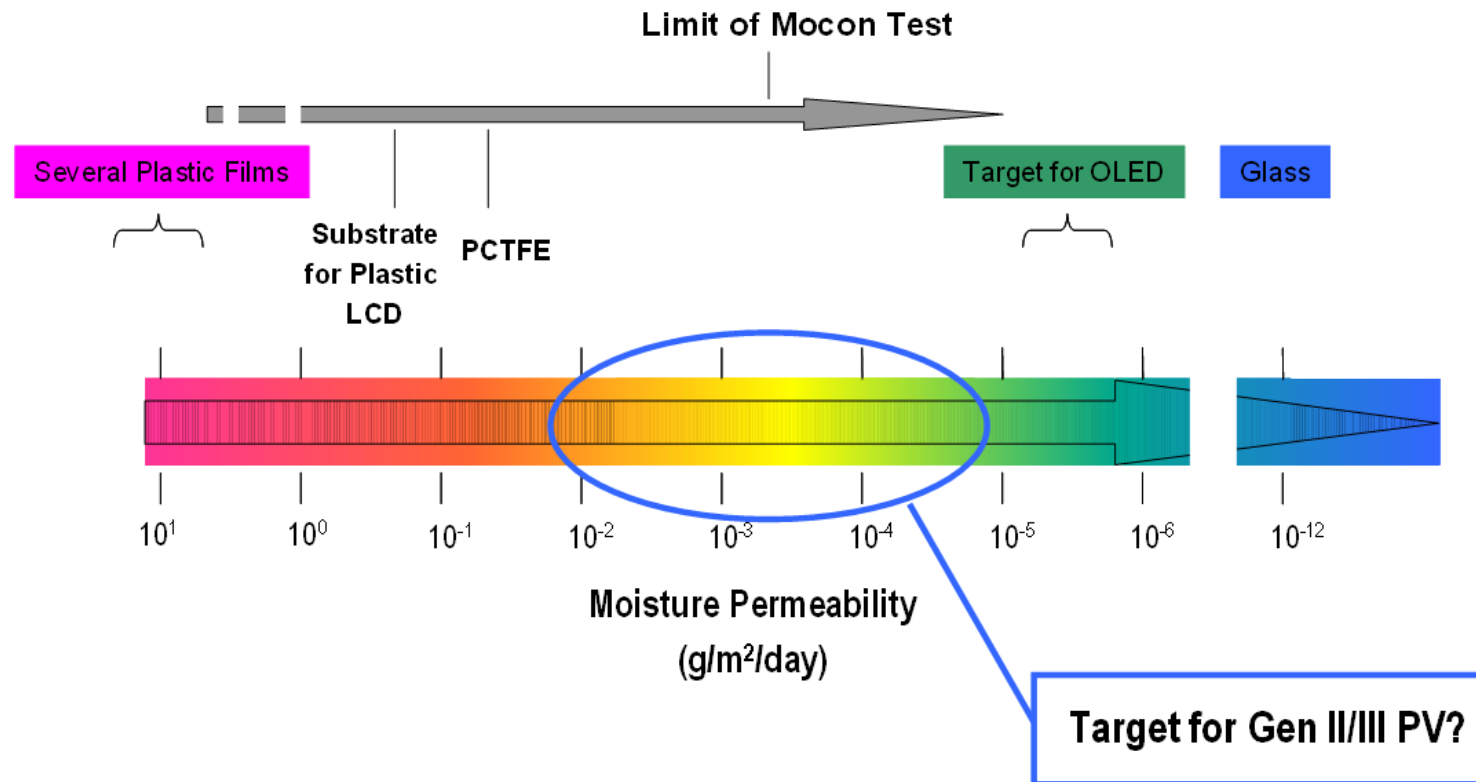


Current Situation

- Planarised coated films are now prepared on our commercial scale coater-widths ca 1.4m
- Situated in clean room
- Step change in defect count observed moving from research coater to commercial scale coater
 - Benefit of long runs with same formulation

Barrier Performance

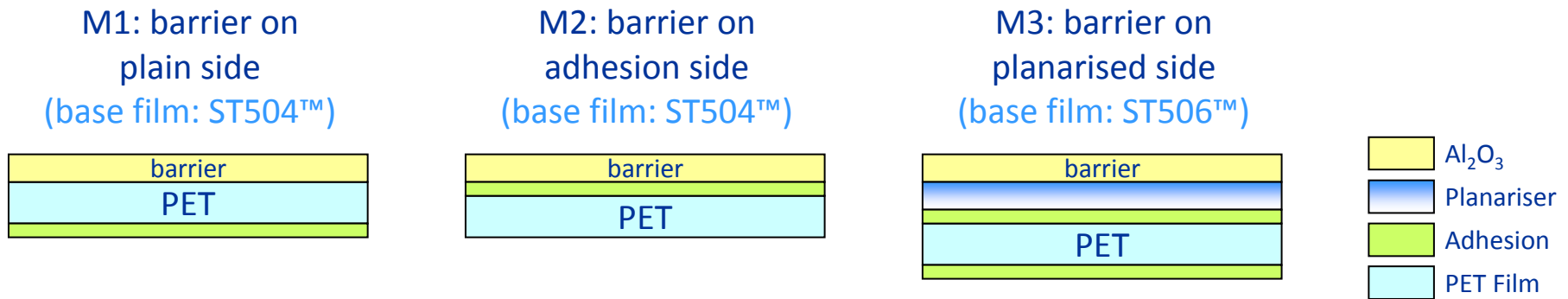
- Range of PV technologies have a requirement for enhanced barrier against O₂ and H₂O ingress



- No unmodified plastic material can deliver against these targets, even at the 10⁻² g/m²/day level

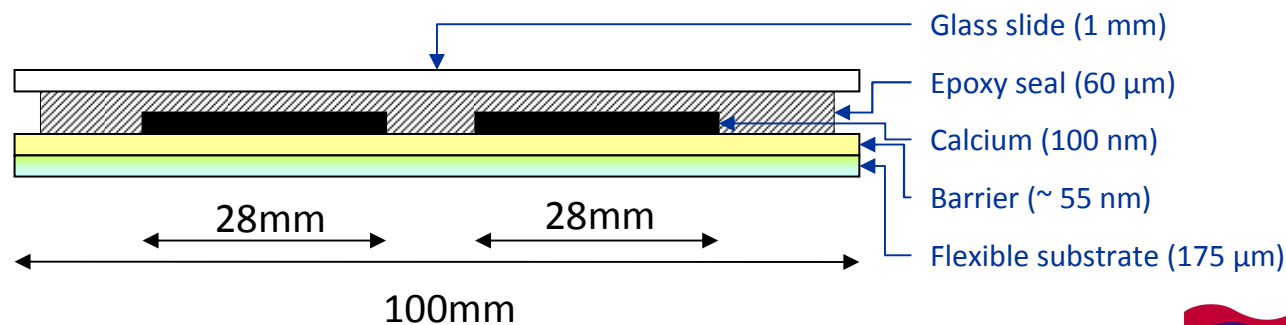
Use of Planariser Coatings to Improve Barrier Performance

- Al₂O₃ barrier layer deposited on three different surfaces



• Calcium Test

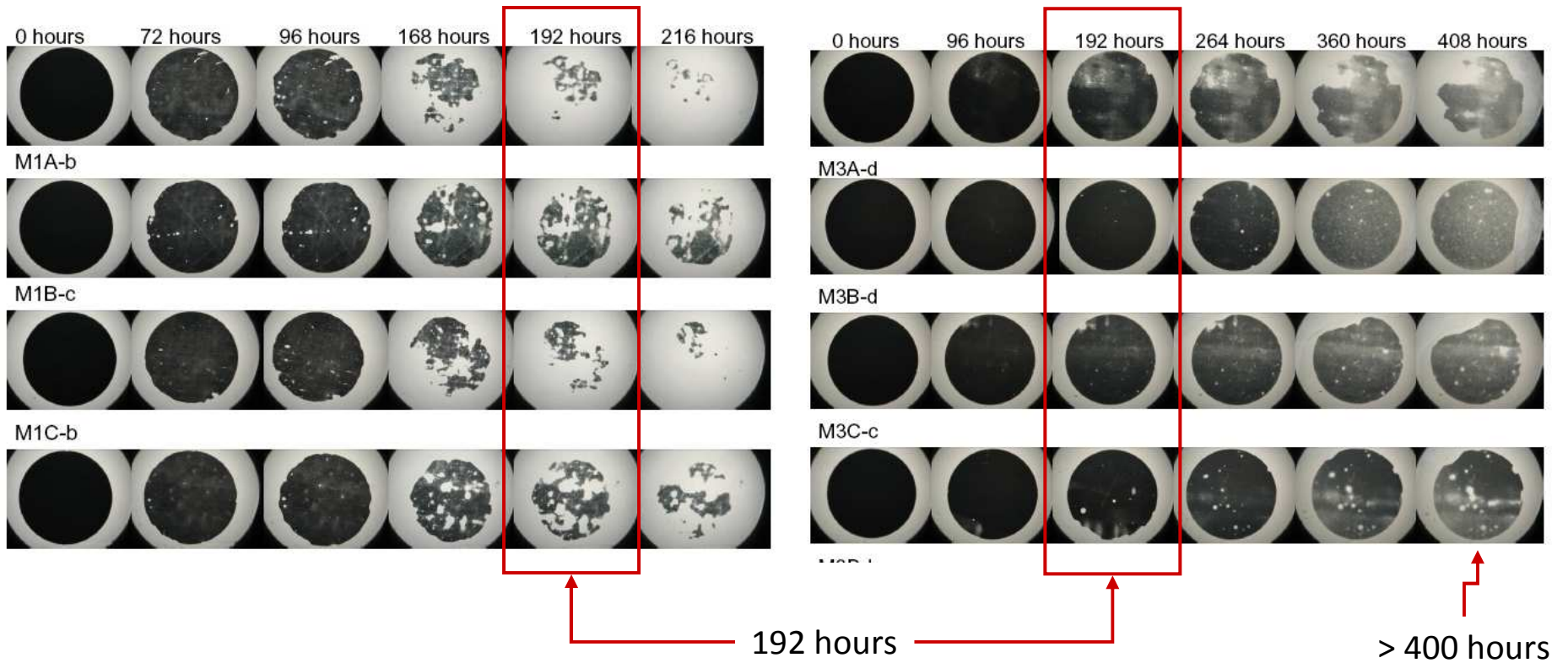
- Four 10 × 10 cm² samples of each, 4 Ca spots each
- Monitoring of Ca degradation with accelerated ageing (60 °C, 90% RH) gives indication of film barrier properties



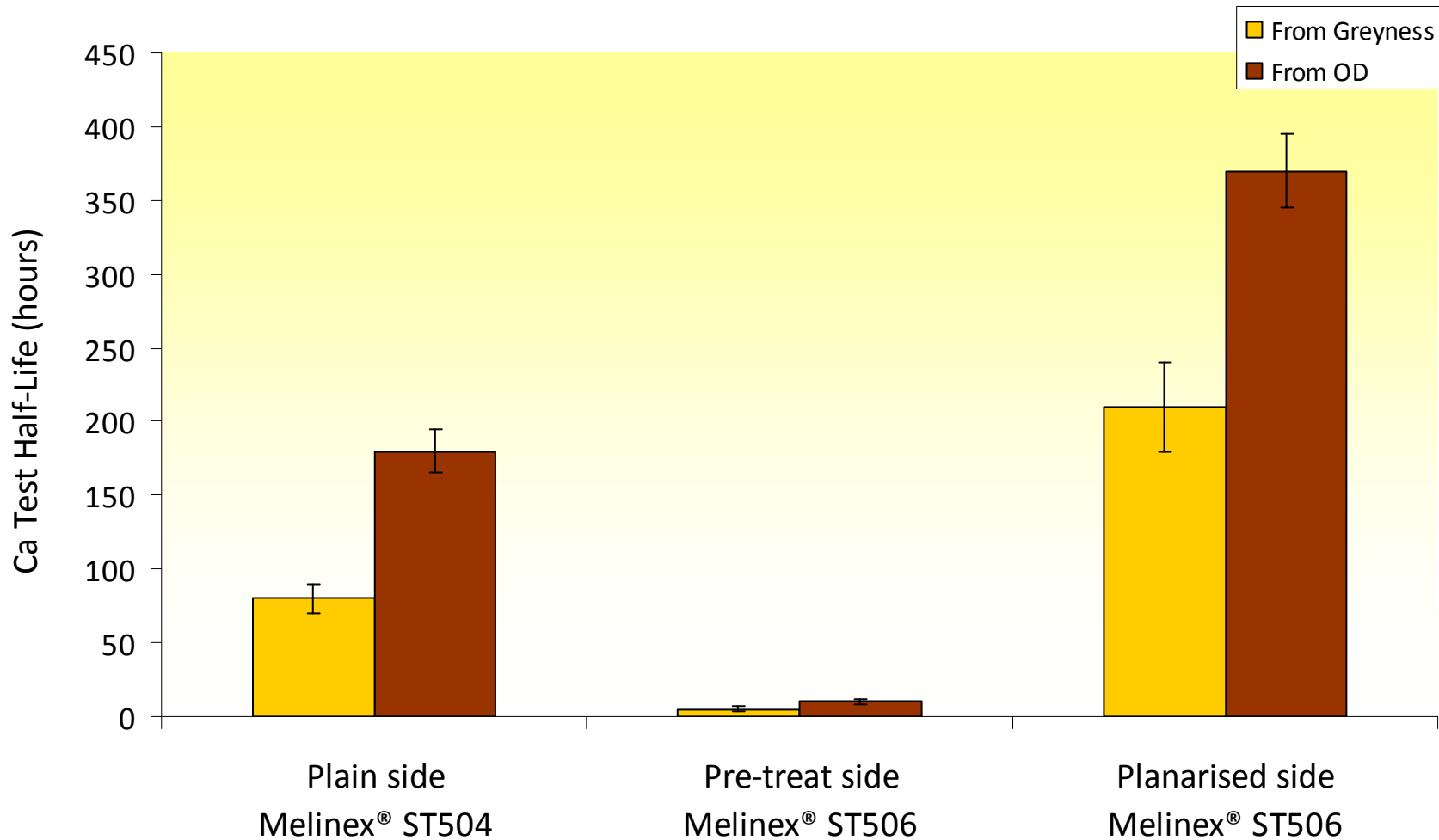
Calcium Test Results

- Non planarised (“raw”) – M1

- Planarised – M3



Calcium Test Half Life



- Half life = Time for calcium thickness to reduce to $\frac{1}{2}$ its original value
- OD measures 3mm diameter spot between pinholes / Greyness full 28mm diameter area

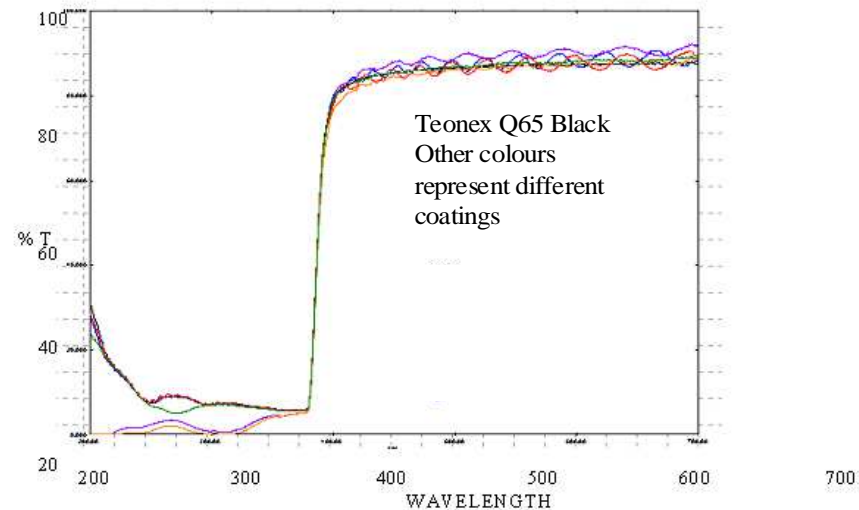
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| | | Adhesion properties |
| | Easy handling | Rigidity |

Optical properties

Planarised coated films offer high transparency

| Property | Test Method | Units | ST506 - 175 micron | Planarised ST506 - 175 micron | Q65FA - 125 micron | Planarised Q65FWA - 125 micron |
|--------------------------|---------------------------------------------------------------------------|-------|--------------------|-------------------------------|--------------------|--------------------------------|
| Total Light Transmission | M57D Hazemeter, BS5750/ISO 9002, standards calibrated to BS2782/ASTM 1003 | % | 90.7 | 91.3 | 89.8 | 90.5 |
| Haze | M57D Hazemeter, BS5750/ISO 9002 | % | 0.8 | 0.7 | 0.6 | 0.9 |

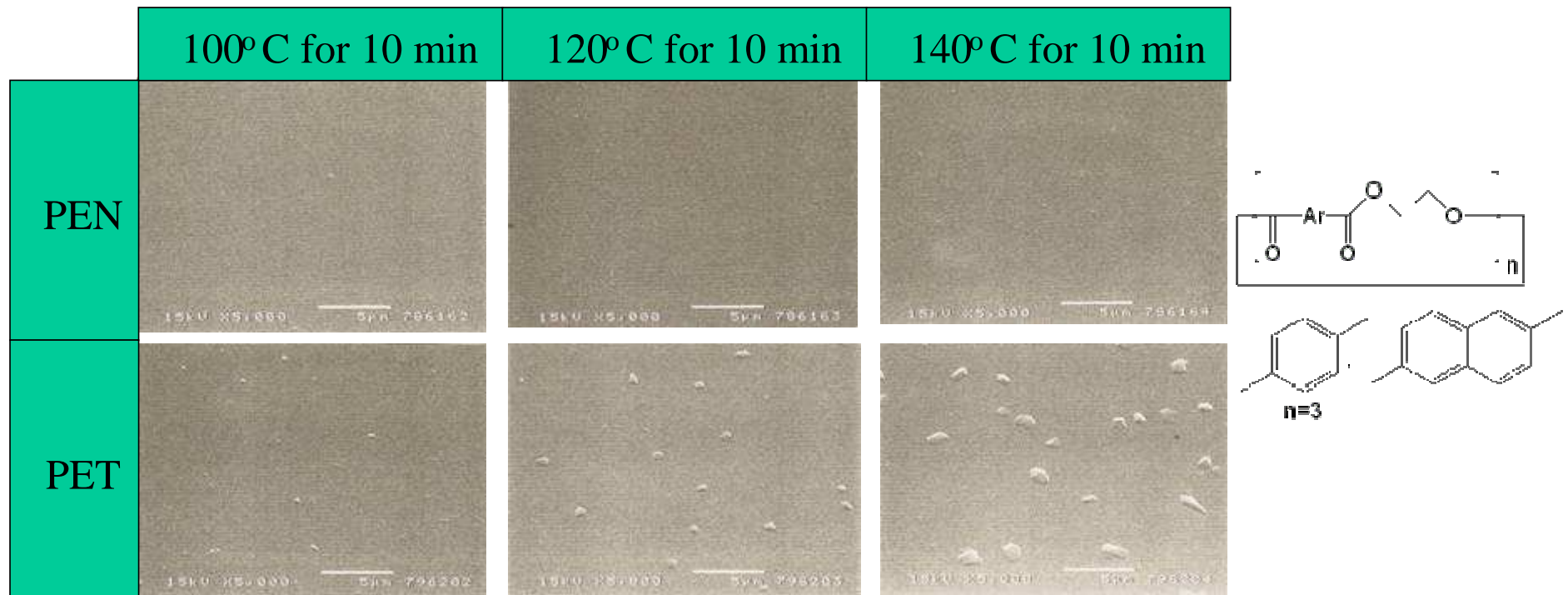


Requirements and technology hurdles

| | Voice of Customer | Film Requirements |
|----------------------------------------------------------|--------------------------------------|--------------------------------------------|
| E-paper and OLED frontplanes | Barrier against oxygen and moisture | Smooth surface |
| | | Clean surface |
| | | Low outgassing properties |
| | | Robustness |
| | | Low defects |
| | Maximum light extraction | Low haze |
| | | Low optical defects |
| | | High transparency |
| Display Backplanes for Inorganic (aSi) and Organic TFT's | Alignment of TFT's during processing | Dimensional stability at high temperatures |
| | | Low moisture absorption |
| | | Low shrinkage |
| | | Low CTLE |
| | Correct functioning of TFT's | Clean, smooth surface |
| | | Clean surface maintained on processing |
| | | Chemical resistance |
| All | Bonding to rigid carrier | Surface energy - contact angle |
| | | Adhesion properties |
| | Easy handling | Rigidity |

Clean surface maintained on processing

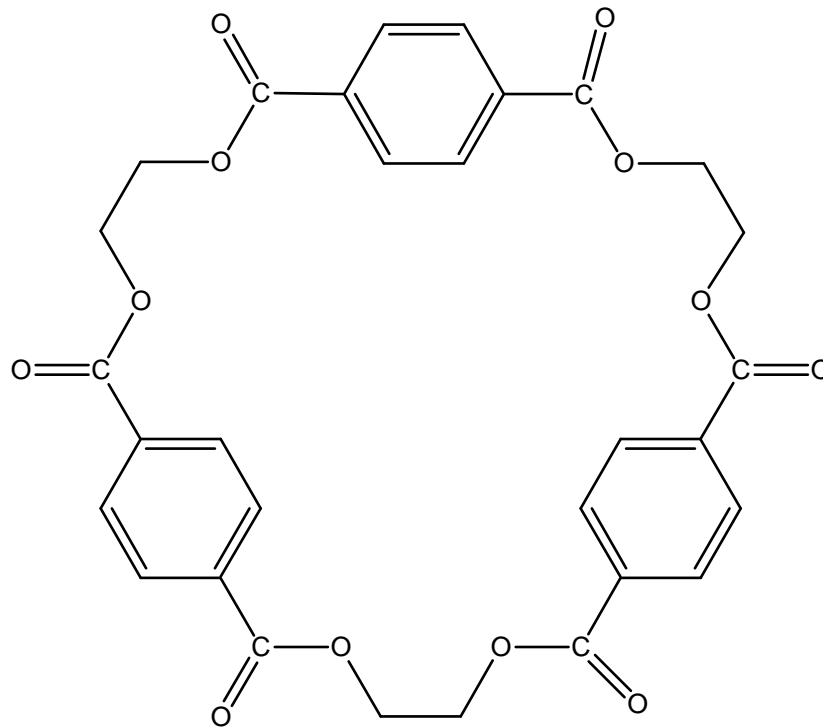
Cyclic oligomer is a by-product of the PET polycondensation reaction
PET film has 1.1 wt% cyclic oligomer (after 200 days in R134/ester oil at 150C)
PEN film has 0.3 wt %



Polyhedral or hexagonal platelike oligomer crystals form, a few microns in size
Soluble in solvents (e.g. MEK)

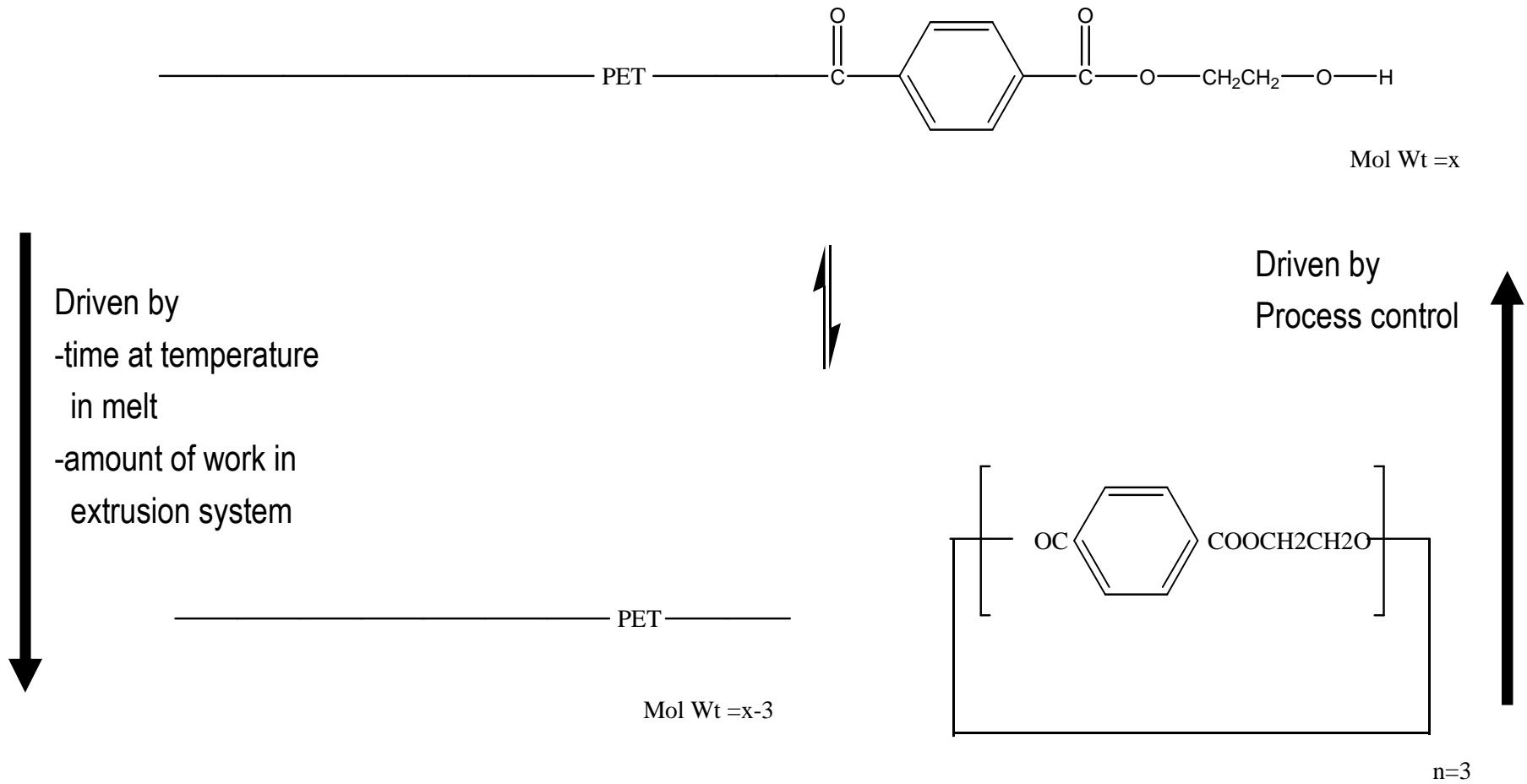
Cyclic Trimer

Cyclic trimer Tm 318C present at ca 1.1 to 1.4wt%



Other cyclics present but in lower amounts. Trimer is low strain relative to other cyclics.

The Cyclic Oligomer Equilibrium



Traditional Strategy

- Traditional strategy used is to coat the surface with a coating that acts as a barrier to oligomers migrating to surface
- ITO blocks to an extent but blooming becomes more of an issue with other approaches to conductive films eg printed silver grids etc

Strategies for Control -Block

- Presence of planarising coatings significantly reduces bloom
- Coatings acting as a barrier



Non planarised PET : 30mins / 120 C

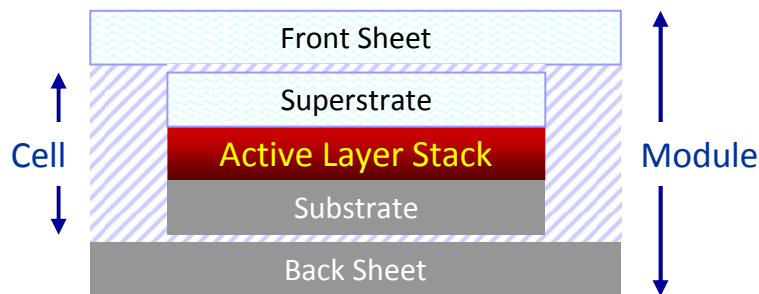
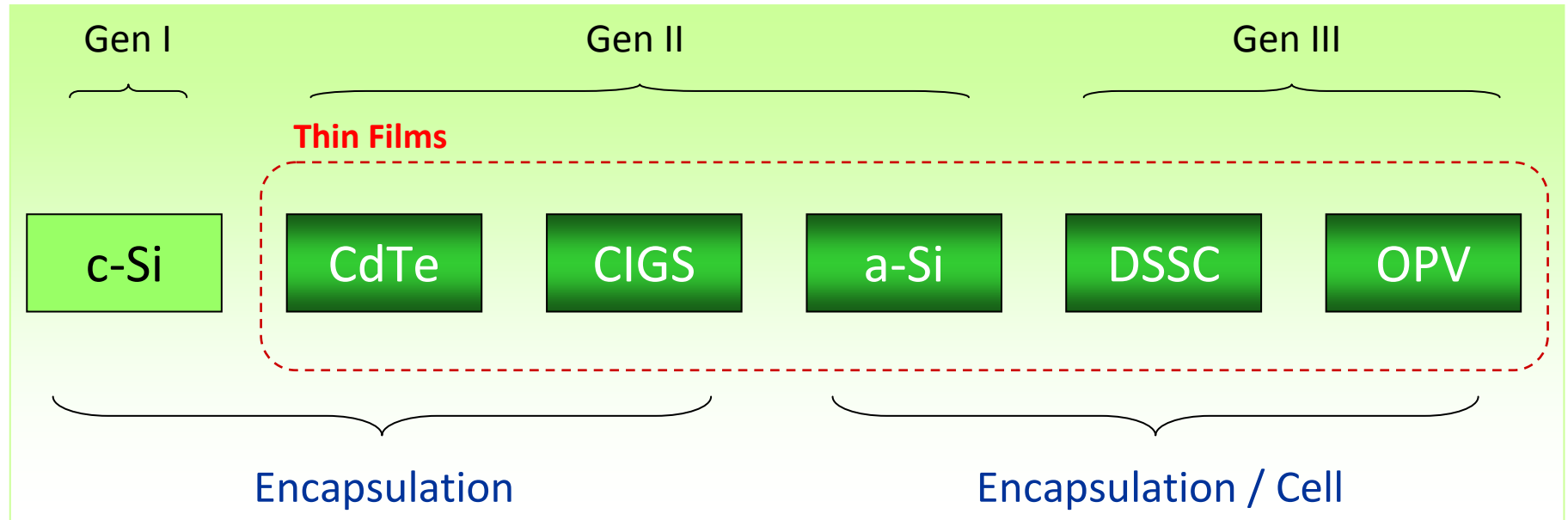


Planarised PET : 30mins / 120 C

New Strategy for Control -Process Control

- Through process control at PET polymerisation stage and during film processing it is possible to
 - Significantly reduce the cyclic content in the PET polymer
 - Minimise the reformation of the cyclic oligomers during subsequent filming process
- New development grade, 1% haze on ageing at 150°C /30 mins
- Now in qualification with customers
- Able to tailor with respect to surface treatments for specific applications
- DTF is investigating further strategies to minimise the impact of blooming on subsequent processing

Substrates for PV Cells – Gen. 2 & 3



→ A complex film development agenda!!

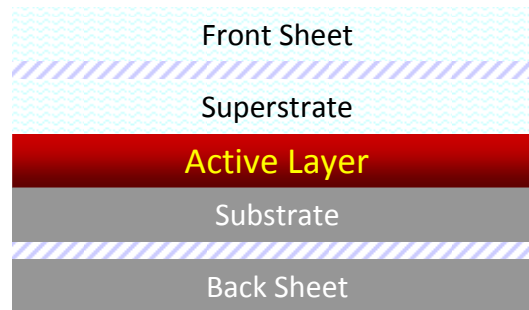
Functionalities

Dimensional Stability

Surface Quality

Barrier

Heat Stability



Weatherability

Conductivity

Light Management

Adhesion

Dimensional Stability

Surface Quality

Barrier

Heat Stability

Front Sheet

Superstrate

Active Layer

Substrate

Back Sheet

Weatherability

Conductivity

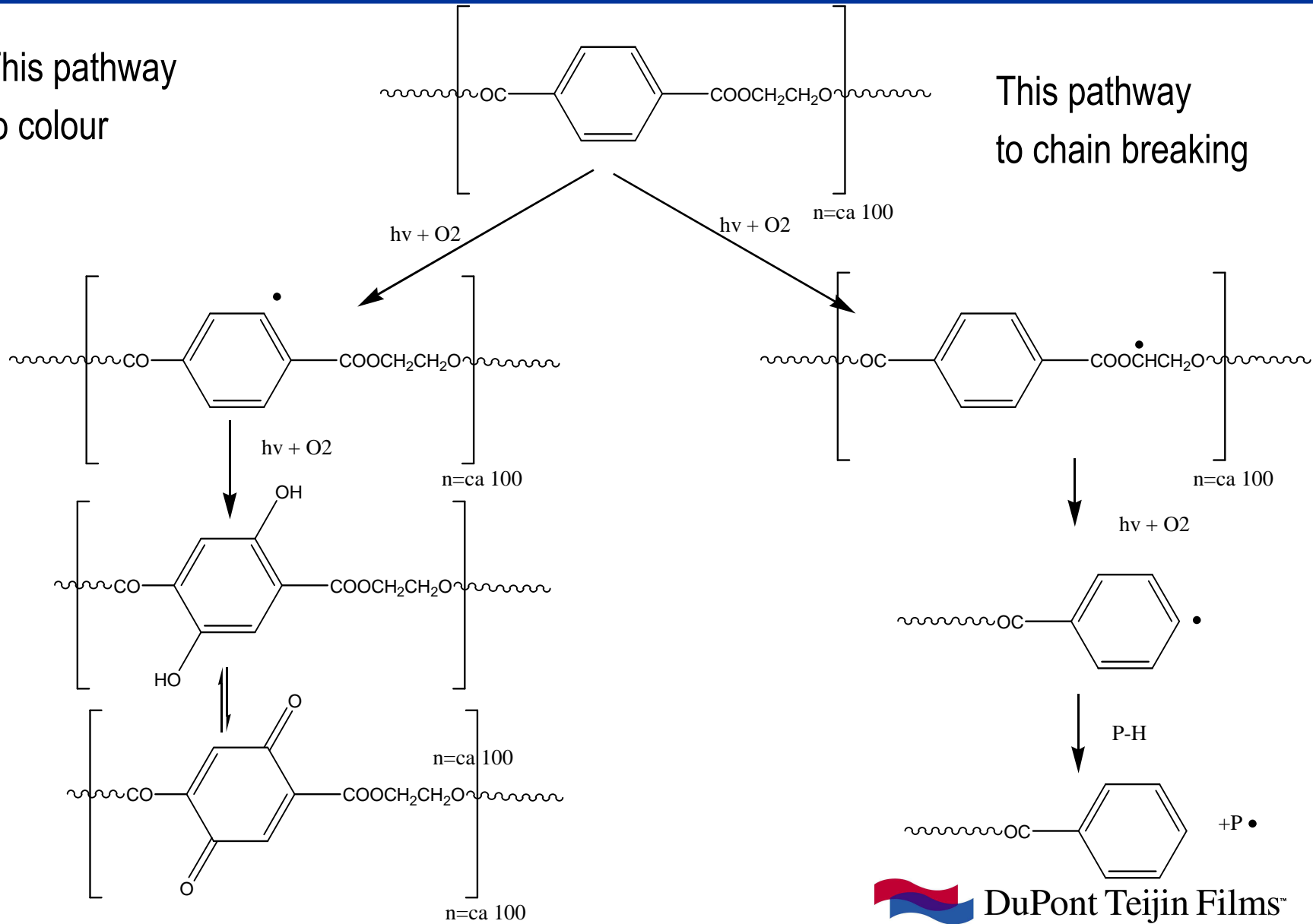
Light Management

Adhesion

Photo-oxidative Degradation

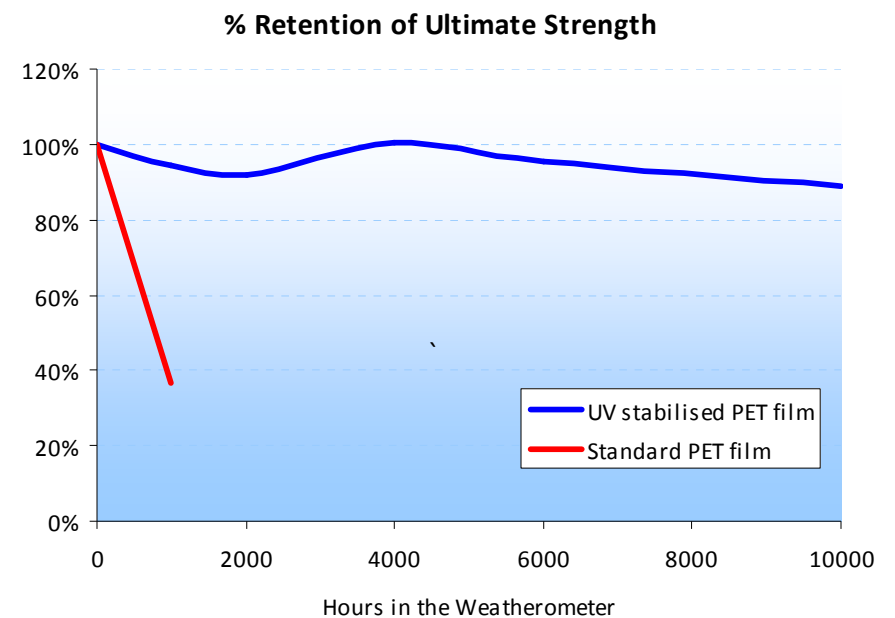
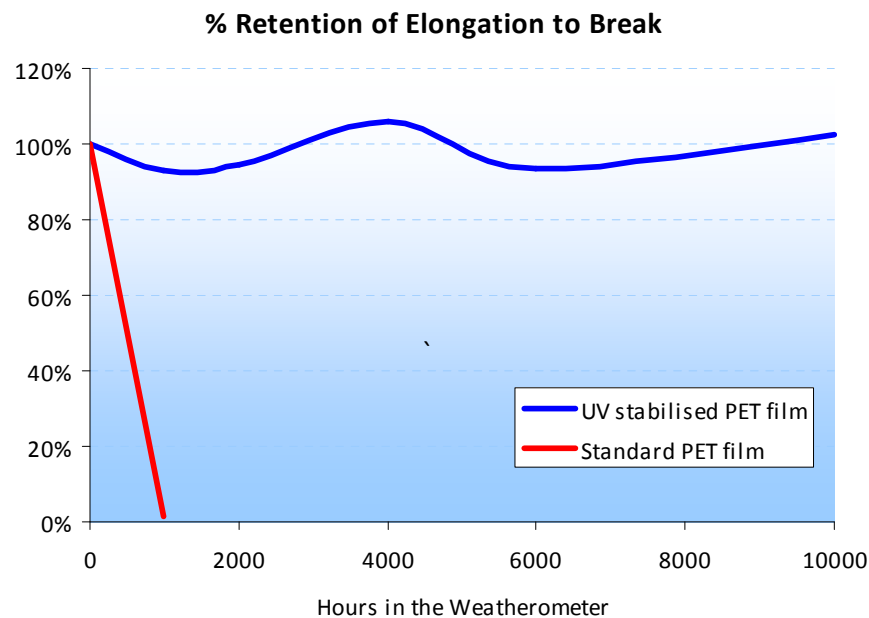
This pathway
to colour

This pathway
to chain breaking



Weatherability – UV Resistance

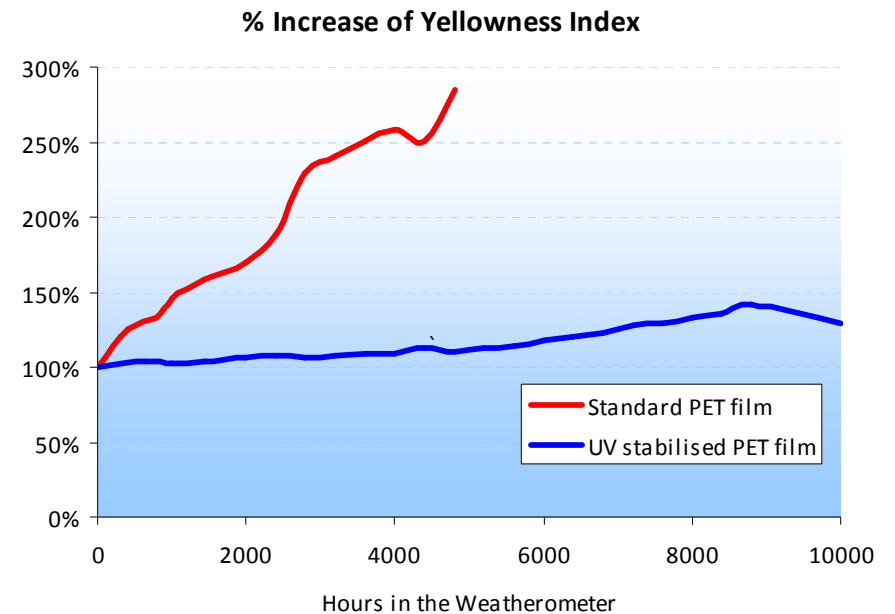
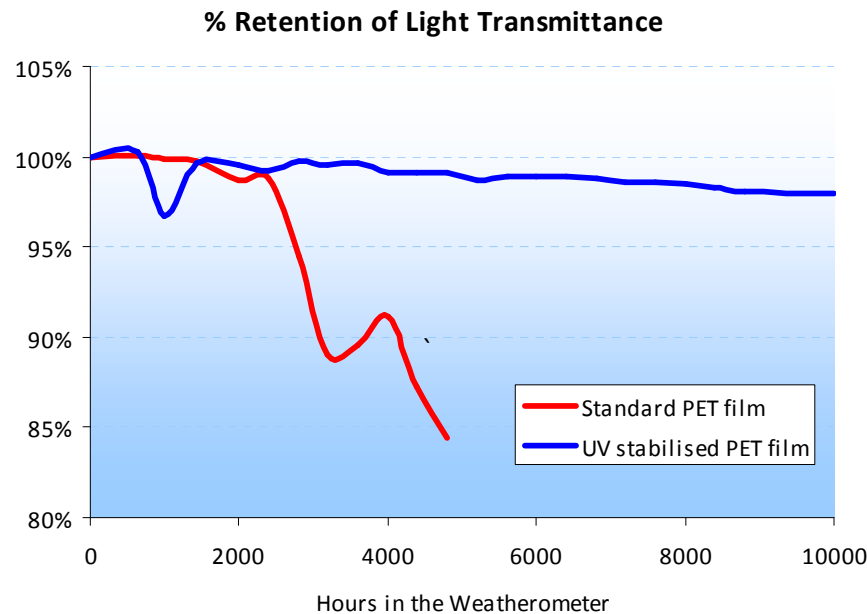
- Lifetime perception: “Polyester films degrade rapidly under UV light exposure”
→ In reality, only non-UV stabilised films will!
- Polyester films can be modified to have improved resistance to UV light
- Typical results from Weather-O-meter® ageing of a DTF UV stabilised film
1) Mechanical properties:



Method: ASTM 4892-2

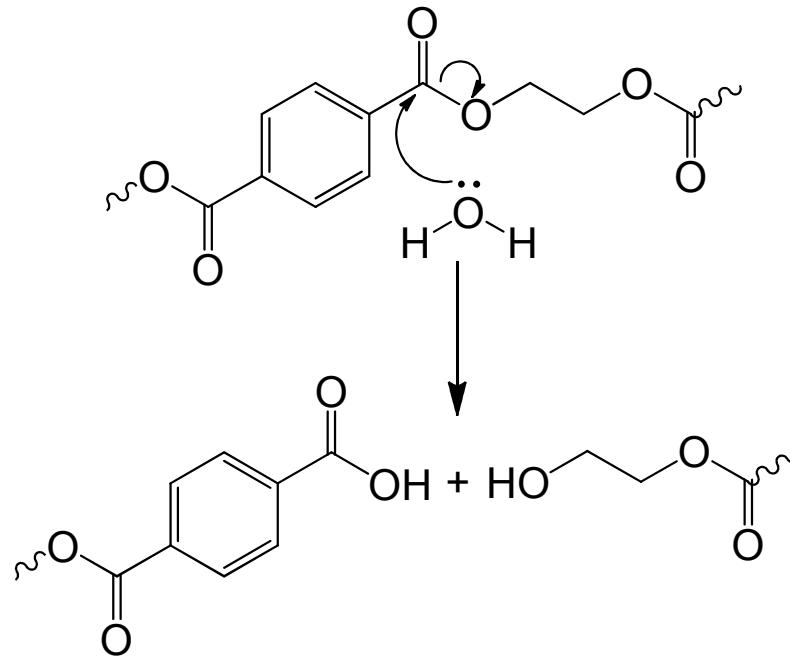
Weatherability – UV Resistance

- Typical results from Weather-O-meter® ageing of a DTF UV stabilised film
 - 2) Optical properties:



- 10,000 hours in Weather-O-meter® – Equivalent irradiation to 5 years (Florida) to 11 years (Northern Europe)
 - This is not a lifetime guarantee

Hydrolysis of PET



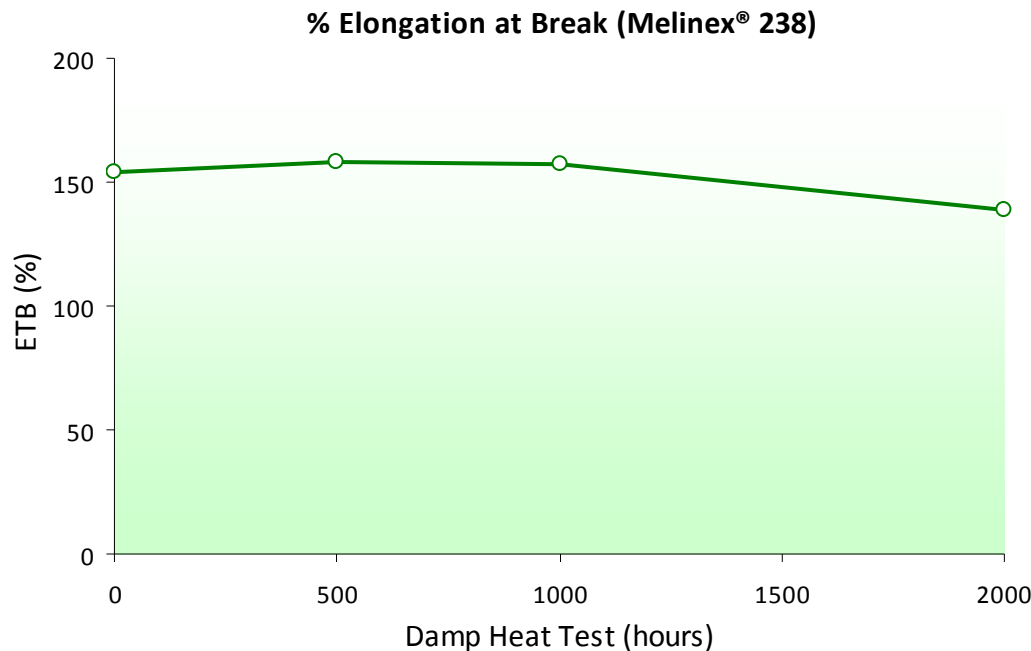
- Catalysed by $-\text{COOH}$ end groups in PET

Strategies for Improving Hydrolysis Resistance (1)

- Increasing the molecular weight of the film
- Control of crystallinity through film process control

Weatherability – Hydrolysis Resistance

- Lifetime perception: “Polyester films hydrolyse rapidly”
→ This is very slow under normal atmospheric (T,P) conditions
- Polyester films can be designed to pass the standard “Damp Heat Test” – Retention of 10% ETB after 1000 h at 85°C / 85% RH
- Significant industry interest in higher performance PET films for extended testing times (2000 or even 3000 hours in Damp Heat Test)

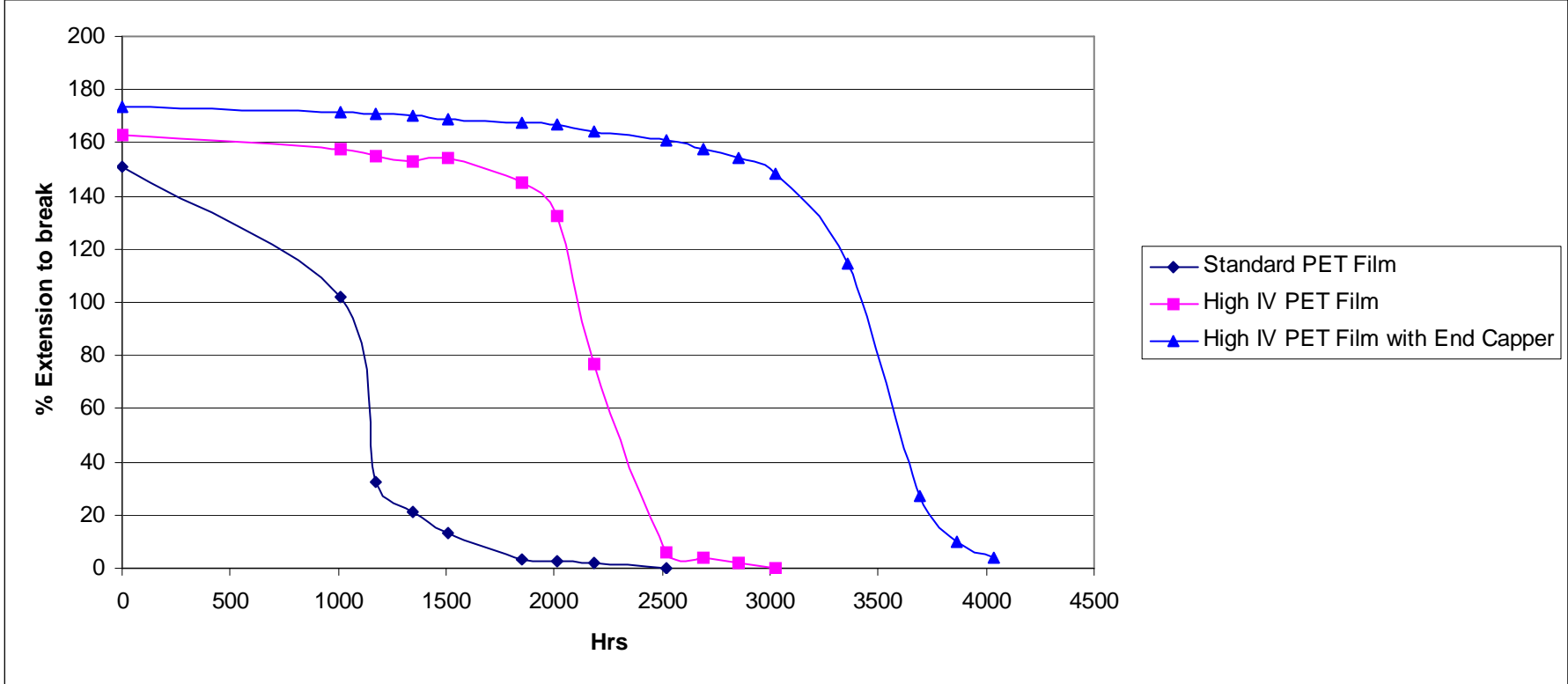


➔ DTF's Melinex® 238 can reach 2000h at 85°C/85% RH
➔ DTF can also apply this technology to optically clear films

Strategies for Improving Hydrolysis Resistance (2)

- Chemically modifying end groups

Damp Heat Test - End Capped PET



Dimensional Stability

Surface Quality

Barrier

Heat Stability

Front Sheet

Sun-facing Substrate

Weatherability

Conductivity

Light Management

Adhesion

PV Cell

Non Sun-facing Substrate

Back Sheet

Conclusion

- DTF remains committed to supporting flex display and PV applications
- Quality of film surface has direct impact on barrier quality
 - But how best to achieve high quality surface in cost effective manner?
- DTF continues to investigate the underlying science issues that affect processing on polyester films
- DTF happy to provide knowhow on how to get the most out of handling and processing on polyester film
- Please contact us to discuss above