Thermal characterization of sustainable polymers

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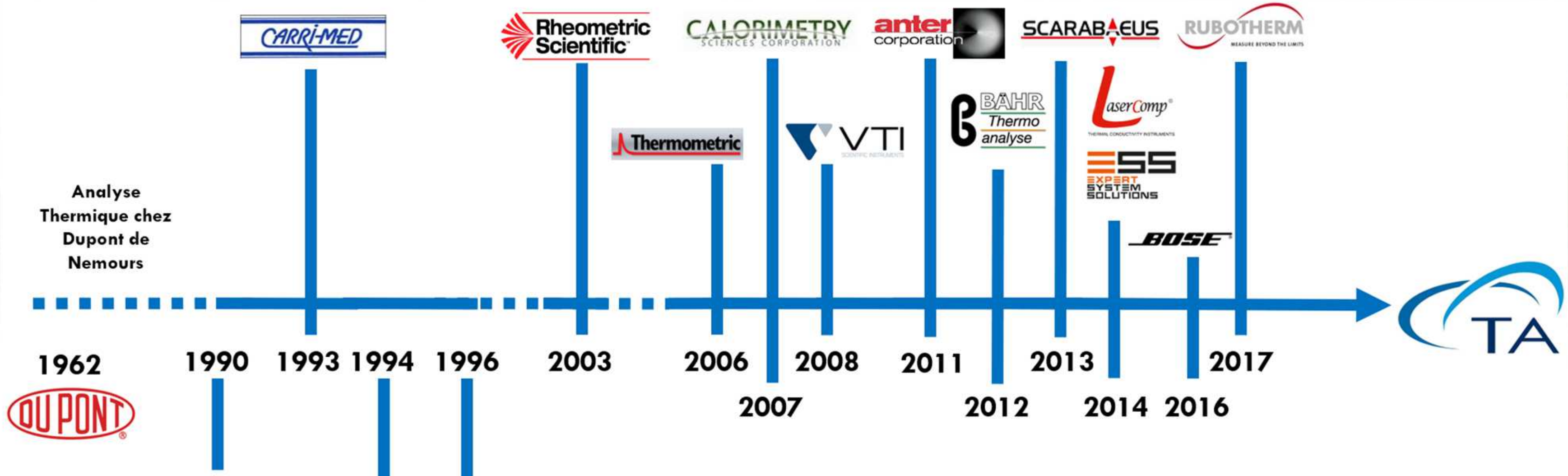
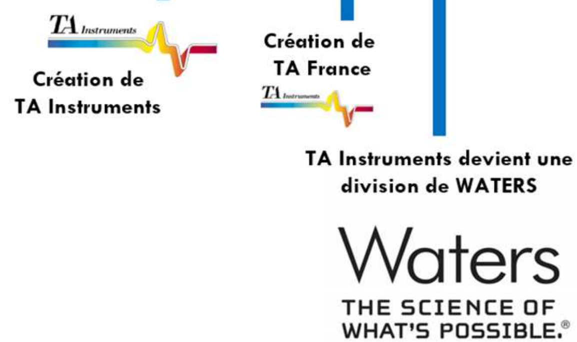
TA Instruments history





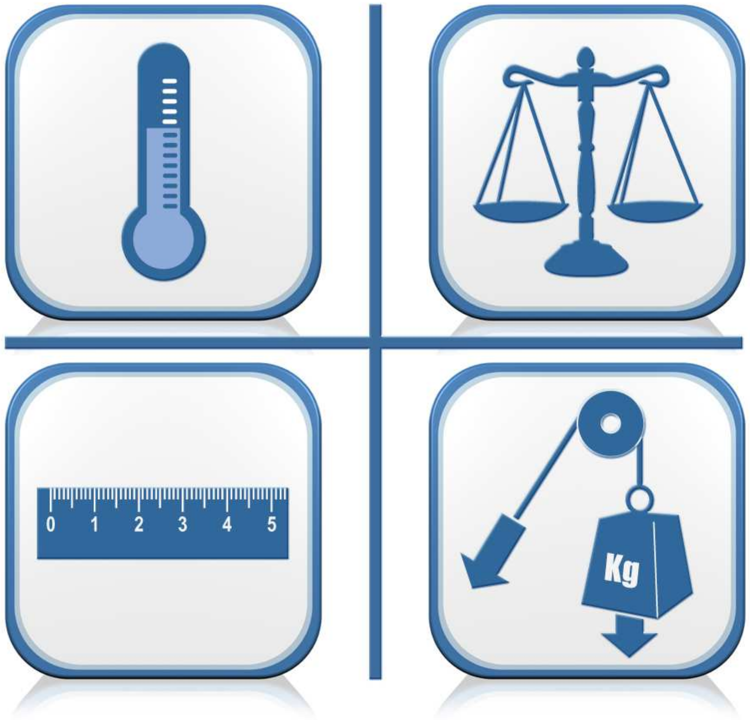
- Division de WATERS Corporation
- TA Instruments basé à proximité de Philadelphie
- Filiales directes dans 28 pays,
- 60 ans d'expérience en Analyse Thermique

What do we measure ?

TA Instruments is involved in 4 types of technologies

Thermal Analysis

Rheology /DMA



Microcalorimetry

Thermophysical Properties


THERMAL ANALYSIS
DILATOMETRY
THERMO PHYSICAL PROPERTIES
DVS & HIGH PRESSURE TGA
CALORIMETRY
DMA & RHEOLOGY
MECHANICAL TESTING
Modulated® DSC
High-Res® TGA
SDT
TMA
Energy Pulse
Front Face
Rear Face
Initial Temperature, T_0
Thickness, L
Final Temperature = $T_0 + \Delta T(t)$
HEAT FLOW
Heater/Temperature Sensor
Specimen
Heat Flow Transducer
Heat Sink
DVS
HP TGA
ITC
Nano DSC
Waters™
TA Instruments

Sustainable polymers

Plastics are diverse –
but a few types and applications dominate the market

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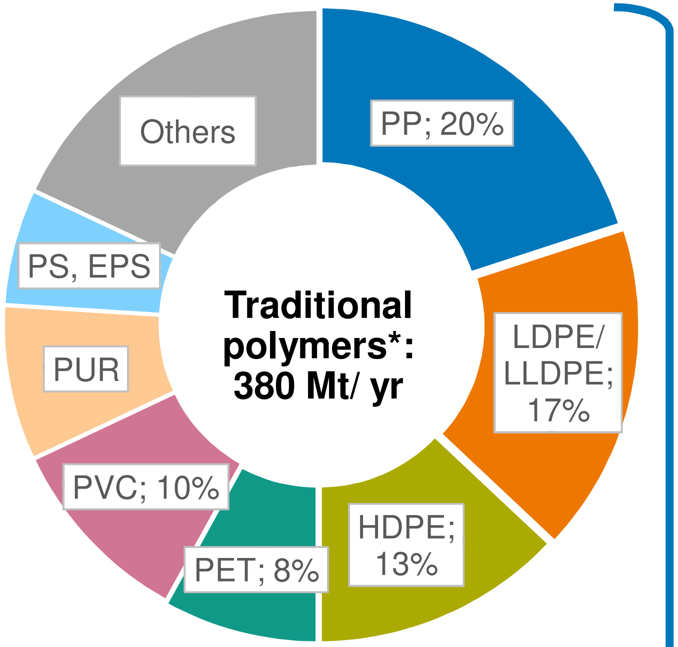
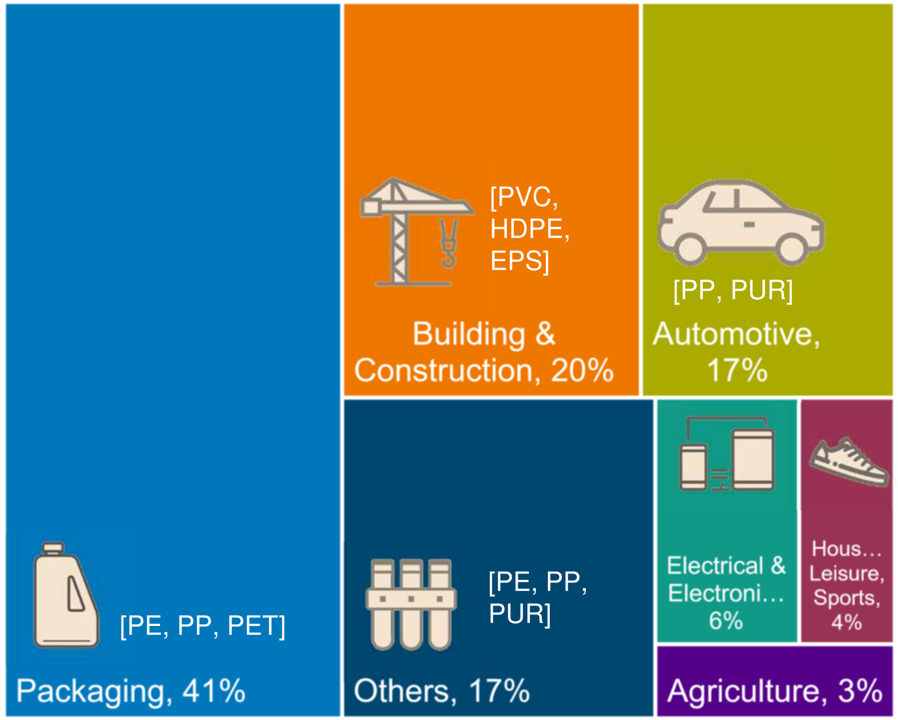
Global Plastics Market (2020)



60% Polyolefins (PE/PP/PET)

Packaging is #1 application

Applications by End-use Market



* Biopolymers: 2 Mt/yr, < 1% of total market

Source: Plastics Europe 2021

Plastics packaging is helpful, but *plastics waste* is a problem

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- Packaging: #1 application for plastics
- Why use plastics?
  - Lightweight and durable
  - Safe and hygienic for food, medicine and personal care
  - Cost-effective
  - Low food spoilage
- But…
  - Recycling remains low
  - Plastics waste is a worldwide problem

How is Recycled Resin converted into new products?

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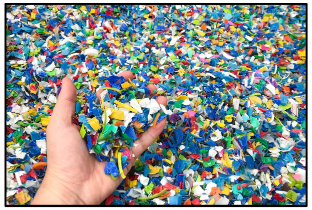
Waste Plastic Feedstock

Post-industrial resin
(PIR/ regrind/ scrap)

Post-consumer resin (**PCR**) –
Collected in recycling bins

Mechanical Recycling



PCR flakes

PCR pellets

Breaks waste plastics into flakes for reprocessing

- Dominant technology today
- Sensitive to contamination
- Quality reduces in every recycle loop

Chemical Recycling*

Pyrolysis Oil

Polymer pellets

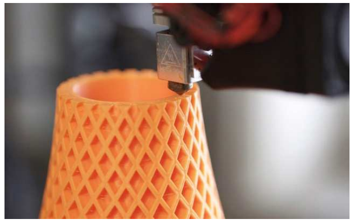
* Also known as Advanced Recycling, Depolymerization

Techniques include Pyrolysis, Solvolysis, Gasification

Converts waste plastics into raw material

- Accommodates mixed polymer waste
- Can handle inks, additives in waste
- Produces pellets with properties identical to virgin material
- Higher energy cost, more expensive

Plan of the presentation



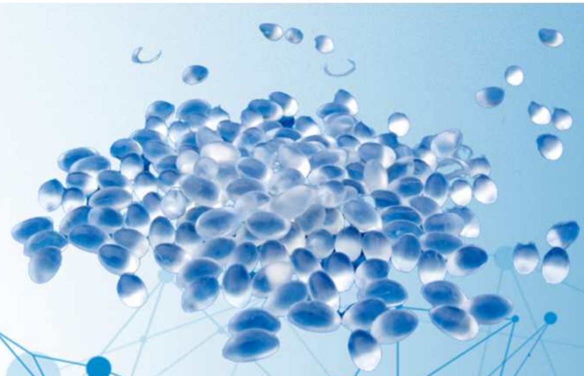
1 **Fingerprinting the raw material**

2 **Optimizing process**

3 **Characterize final product**

Visit https://www.tainstruments.com/applications/polymers/

Application notes referred too as TAxx or RHxx in the presentation



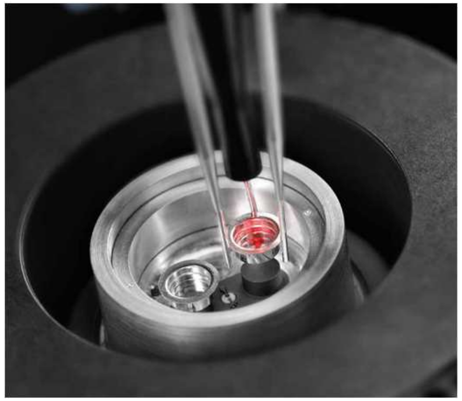
Part 1 : Fingerprinting raw material

PET study by DSC : What is DSC ?

Step 1: Fingerprinting of Raw Material

- Differential Scanning Calorimetry (DSC)
  - Patented Tzero Technology to enhance sensitivity and resolution TA271
  - Modulated DSC to separate overlapping heat flow effects TP006
  - X3 DSC to measure 3 samples simultaneously TA448
    - Increased productivity, statistical datasets, etc

- DSC to fingerprint the raw material
  - A couple of mg of sample is sufficient (5 à 10mg)
  - Granules, powders, films, liquids, etc
  - Test time typically 20-60 min

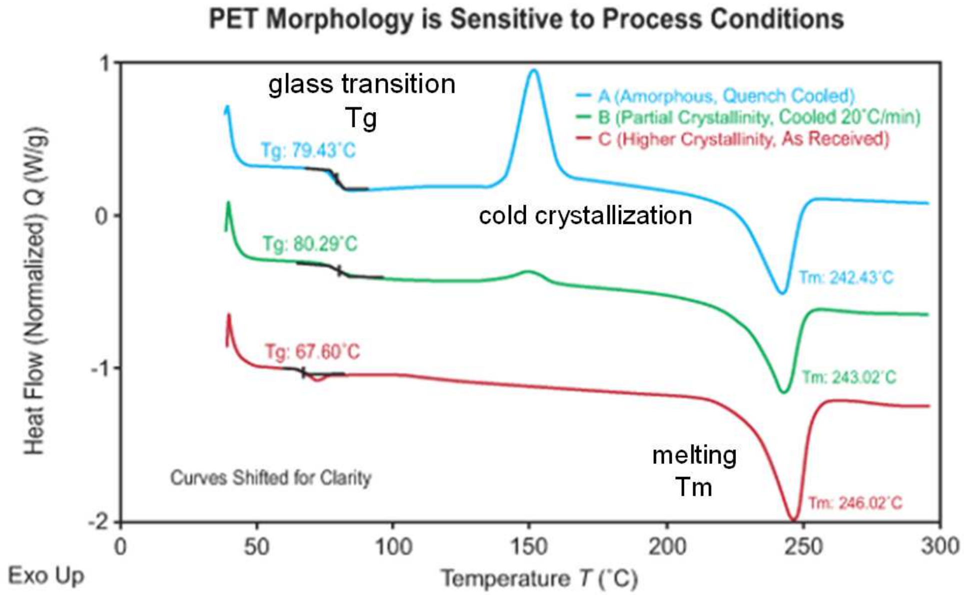


- Difference measurement of heat flow rate as a function of time and temperature (canceling out pan contribution)
  - Heat absorbed by the sample gives endothermic response
  - Heat released by the sample gives an exothermic response

PET study by DSC-25 TA instruments

Step 1: Fingerprinting of Raw Material

- PET from different sources can largely differ with respect to e.g.
  - Molecular weight
  - Impurities
- PET granules from three different sources
  - Viscosity decreases from a sample to another (lower viscosity related to lower MW)
- Conclusions from DSC heating runs:
  - Crystallinity can be calculated from heating run (by ratioing enthalpy to 140 J/g reference value for 100% crystalline PET) TN048 TA448



DSC heating run of several PET

Part 2 : Optimizing process conditions

Thermoplastics processing has common themes

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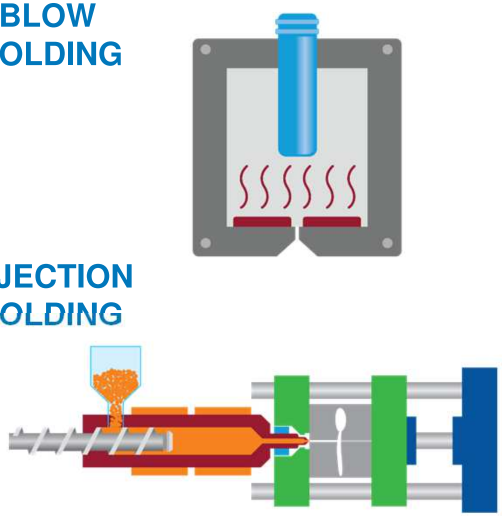
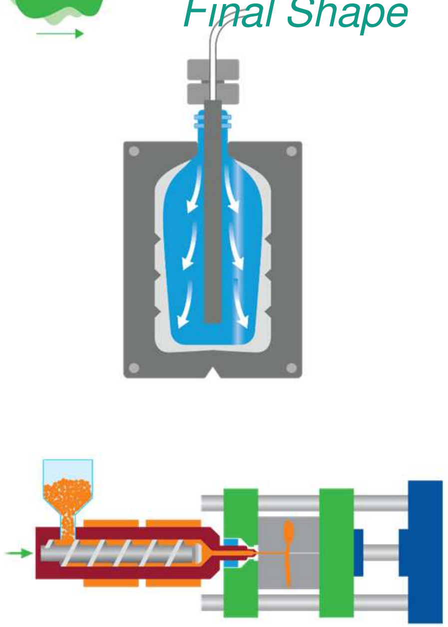
BLOW MOLDING

INJECTION MOLDING

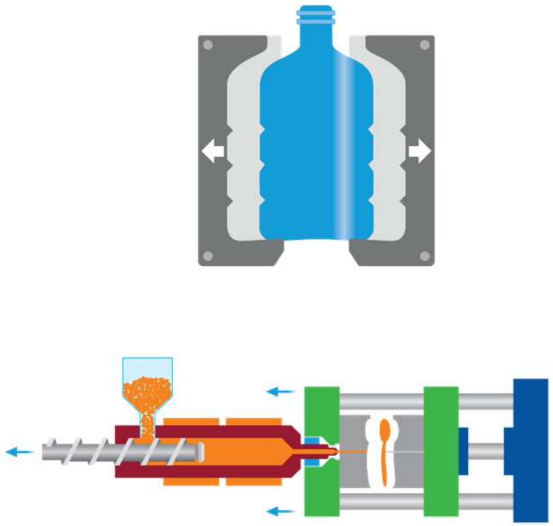
Heat *to Melt/ Soften the Resin*



Deform *into Final Shape*



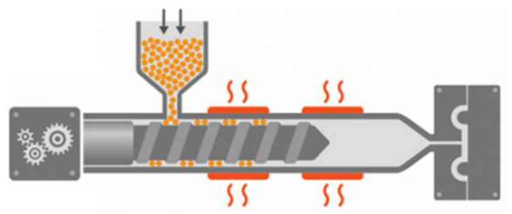
Cool *the Product & Release*



Complex interplay between these 3 steps determines cycle time/ throughput and product quality

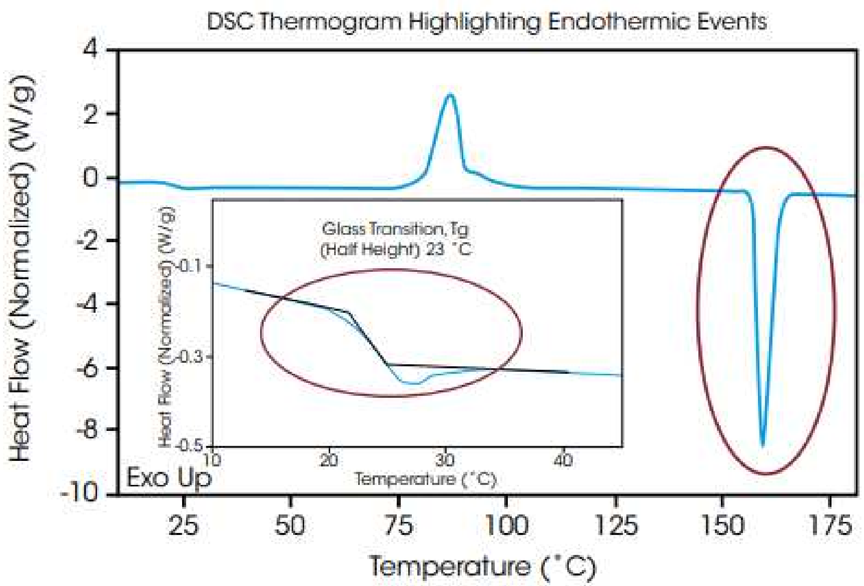
What is the processing temperature for this resin?

Heat to Melt/ Soften the Resin



- Measure fundamental material properties relevant to processing conditions
- **DSC X3** → Melting peak, Glass transition, Heat of fusion (measure of crystallinity)
- Feedstock evaluation: Is this a neat polymer, or is it a blend? Are vendors A/B/C the same?
- After processing: Is there a thermal history after processing vs. as-received? (1st vs. 2nd heat)

End-of-life: Does this bale have significant contamination from other polymers? (semi-quantitative test)



What is the processing temperature for this resin?

Heat to Melt/ Soften the Resin

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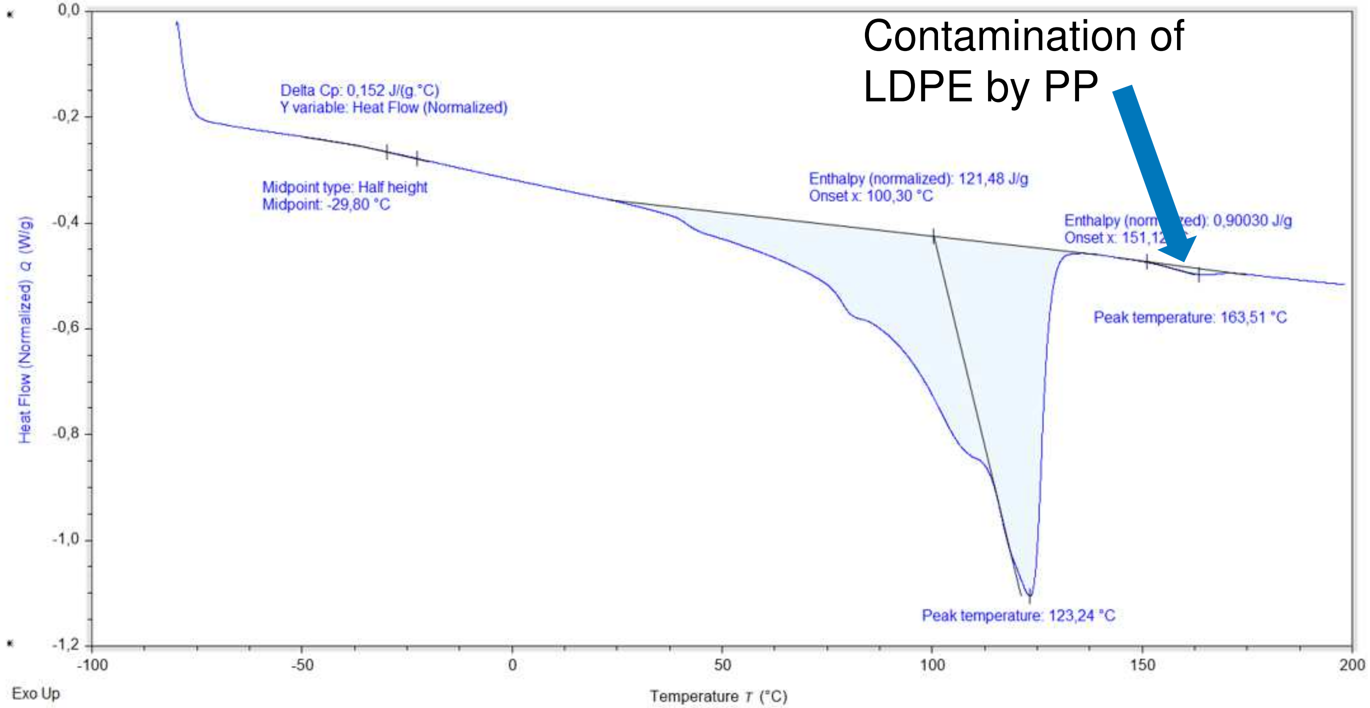


Contamination in Recycled Polymers

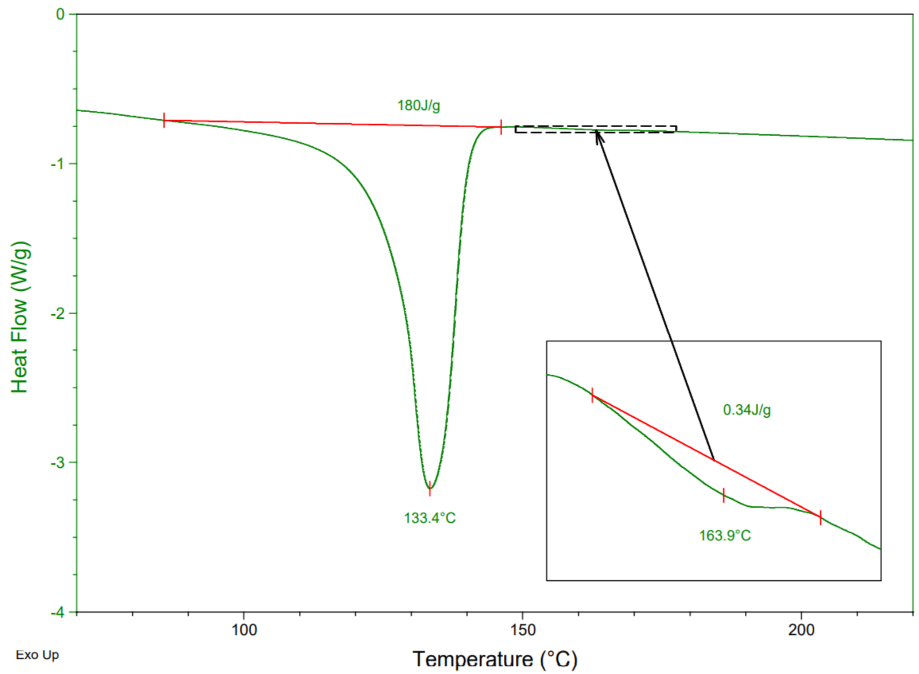
DSC to Qualify and Quantify the Contamination

Heat to Melt/ Soften the Resin

- DSC to measure Tg and/or Tm

Acronym	Polymer	T_g(°C)	T_m(°C)
PET	Polyethylene Terephthalate	73 – 80	245 – 265
LDPE	Low Density Polyethylene	-133 – -100	98 – 115
HDPE	High Density Polyethylene	-133 – -123	130 – 137
PP	Polypropylene	-15	160 – 175
Nylon 6	Nylon 6	40 – 87*	210 – 220
Nylon 6,6	Nylon 6,6	50*	255 – 265

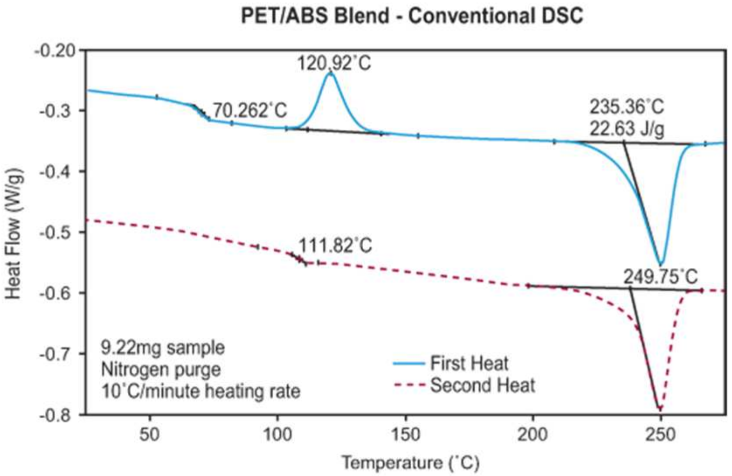
- HDPE with small amount of PP contamination



DSC heating run

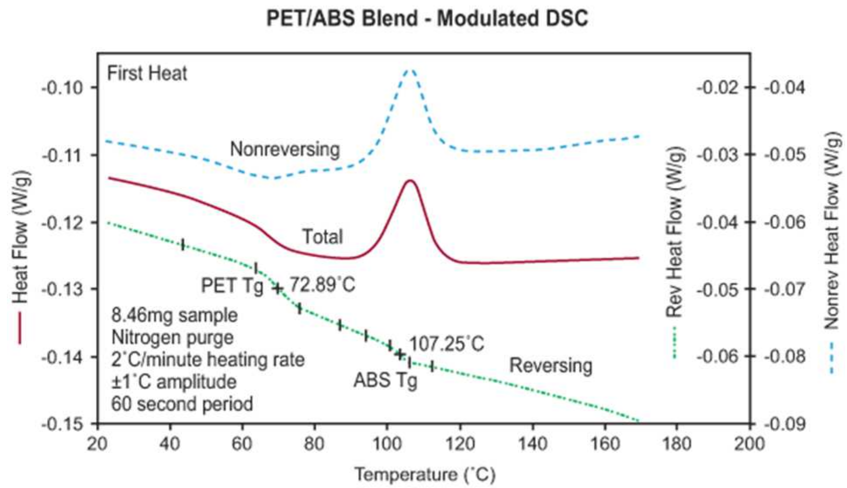
Analyze Complex Transitions using Modulated DSC

Heat to Melt/ Soften the Resin



DSC provides information about phase transitions

- Conventional DSC only picks up one polymer at a time
  - 1st Heat: PET transitions only → Tg (70.2°C), cold crystallization (121°C), Tm (235.4°C); no ABS Tg
  - 2nd Heat: ABS Tg (111.82°C) and PET melting only



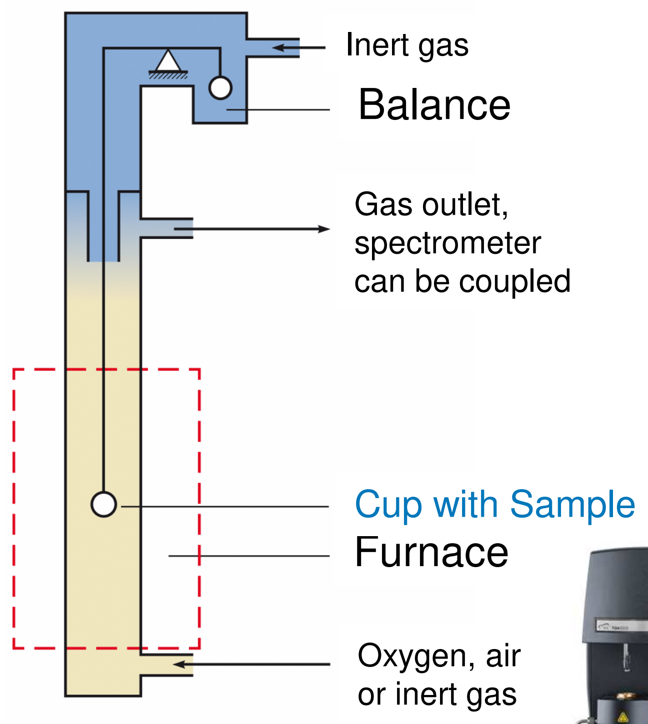
MDSC splits heat flow into non-reversing and reversing components

- MDSC reveals transitions in the 1st heat itself
  - Reversing: Tg of PET (72.3°C) & ABS (107.2°C)
  - Non-reversing: PET cold crystallization exotherm → Overwhelms ABS Tg in conventional DSC

What is the Processing Temperature for the Resin ?

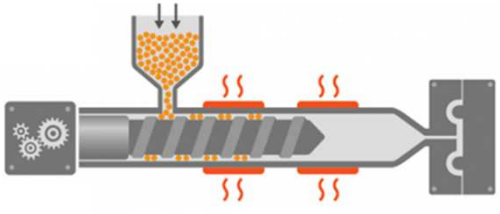
Heat to Melt/ Soften the Resin

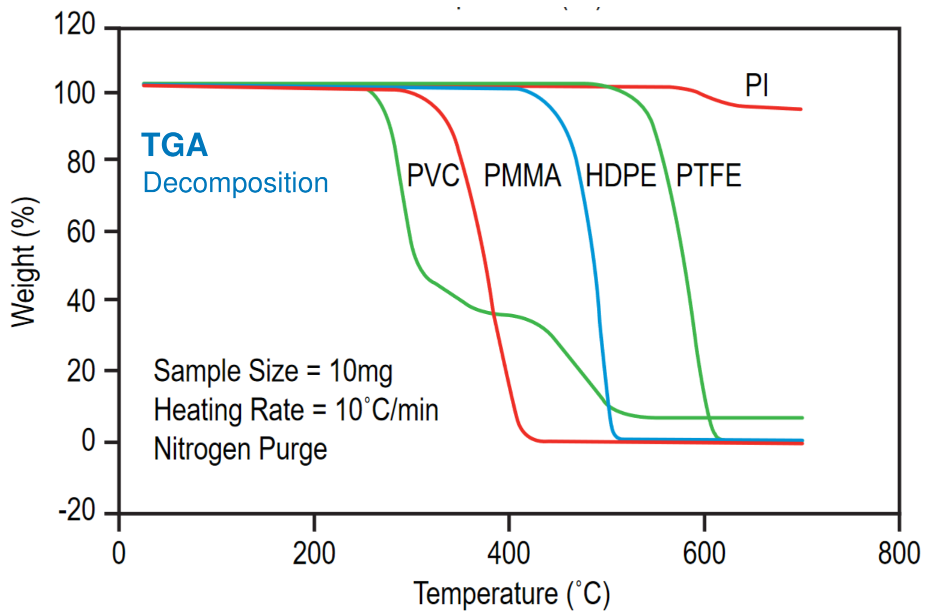
- **ThermoGravimetric Analysis (TGA)** to measure weight changes as a function of temperature or time
  - Identify the start of decomposition
  - Quantify the amount of volatiles
  - Quantify the filler content
- Hi-resolution TGA for better separation of overlapping decompositions TA127
- Modulated TGA (MTGA) to obtain kinetic information TA251
- TGA-EGA (Evolved Gas Analysis) to qualify decomposition products, volatiles, contaminants TA434



How does this resin decompose?

Heat to Melt/ Soften the Resin





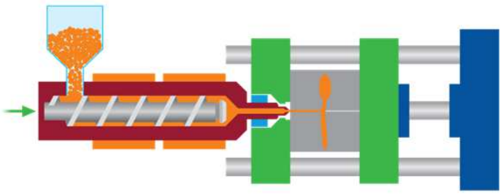
- TGA → Quantitative evaluation of major ingredients in resin (base polymer/ plasticizer/ filler)
- Feedstock evaluation: At what T does this resin decompose? What is the decomposition profile?
- Processing: Are there volatile materials in this batch of resin? Will there be off-gassing after processing?
- Failure Analysis: Is there a difference in the filler content or the decomposition profile?

End-of-life: At what temperature does the maximum weight loss occur? (for pyrolysis)

- What contaminants are present? (EGA)

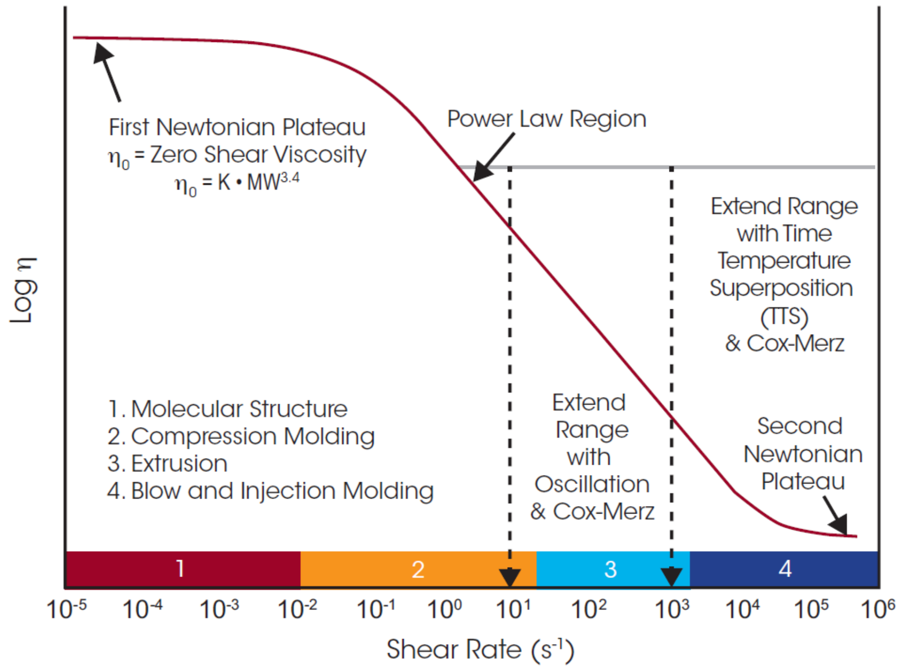
Is this resin's viscosity suitable for processing?

Deform into the Final Shape



- Measure flow properties critical to injection molding, extrusion processes
- Viscosity → quantifies resistance to deformation
- Feedstock evaluation: How is the viscoelastic profile affected by batch-to-batch changes in the resin's MW/ MWD?
- Processability: Does the resin have the right viscosity at all shear rates relevant to the manufacturing process?

End-of-life: How do contamination and MW variation in the recycled resin impact processing?



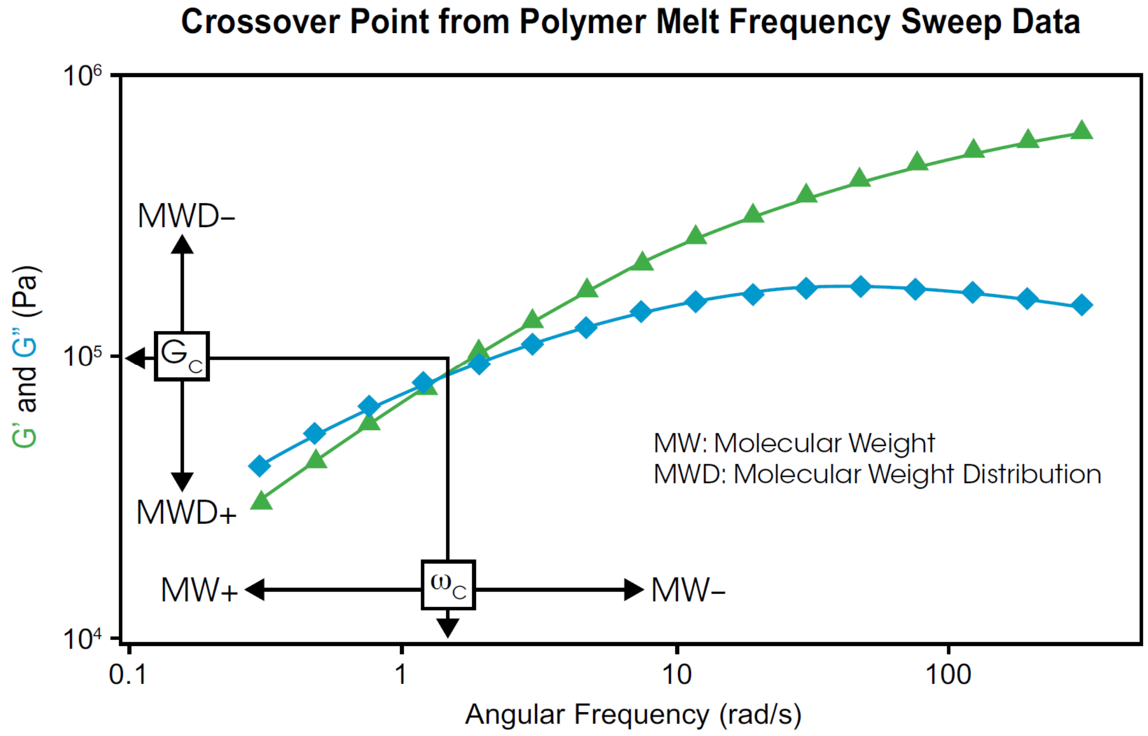
Study polymer viscoelastic behavior with oscillatory tests

Deform into the Final Shape

- Obtain information beyond viscosity and flow properties
- Probe polymer structure at different times scales of deformation (frequencies)
- Higher frequencies → Elastic response (G' > G")
- Lower frequencies → Viscous response (G' < G")

Cross-over point location is sensitive to MW/MWD

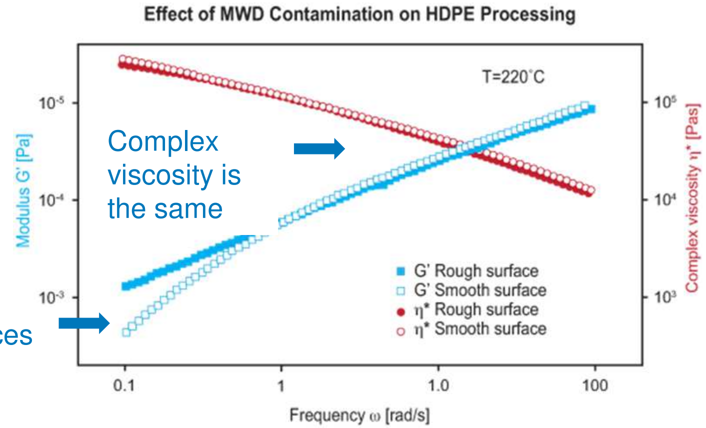
Quickly screen polymer melts with oscillatory tests



Case Study: Troubleshooting processing problems

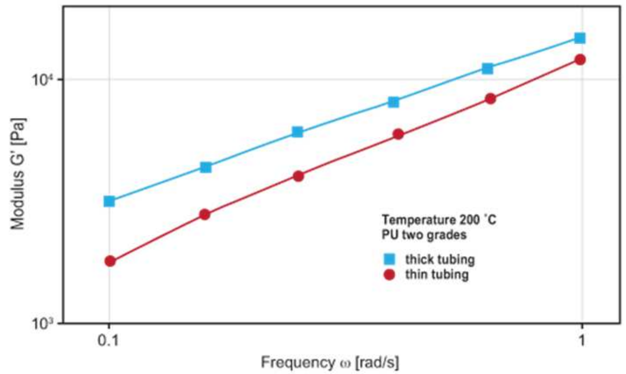
Deform into the Final Shape

Material: HDPE Pipes



Differences in G'

Material: PU Tubing



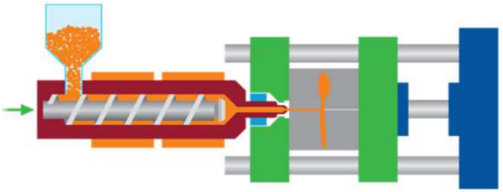
Viscoelastic data from rheometers provides insights to solve production problems

- Large batch-to-batch variations in pipe smoothness (HDPE)/ tube thickness (PU)
- Resin lots showed no differences in capillary, MFI tests
- Frequency sweep data showed differences at low frequencies → Presence of high MW chains

Related Collateral: AN013:Understanding Rheology of Thermoplastic Polymers

What is the compatibility of this blend? (End-product)

Deform into the Final Shape



D.M.A.

- Polymer blends offer superior properties compared to individual resins but need to be mixed for uniformity
    - Improper mixing affects product performance

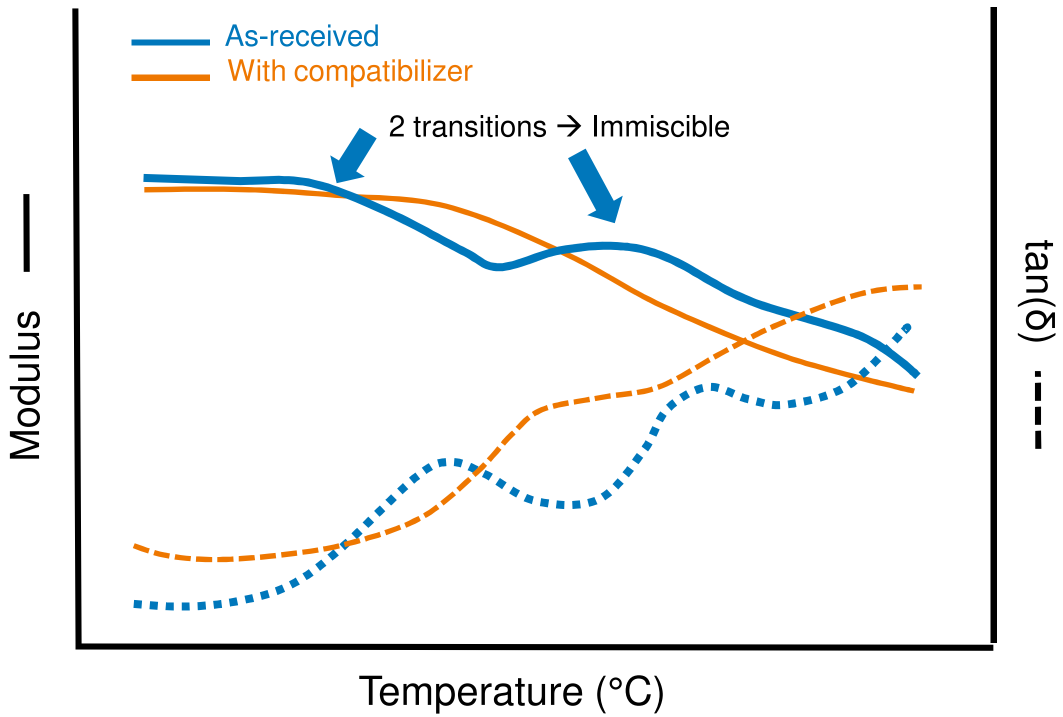
- Processability: How much mixing is needed to get uniform blend morphology?

End-of-life: Are incompatible contaminants in recycled resin affecting product performance? (eg, mix of PE and PP)

- How much compatibilizer is needed to process this batch with incompatible polymers?

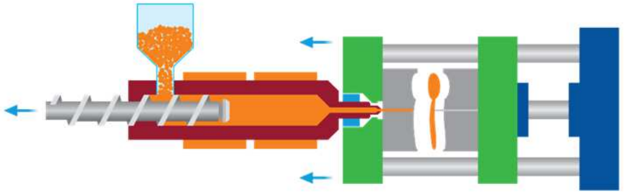
What is the compatibility of this blend? (End-product)

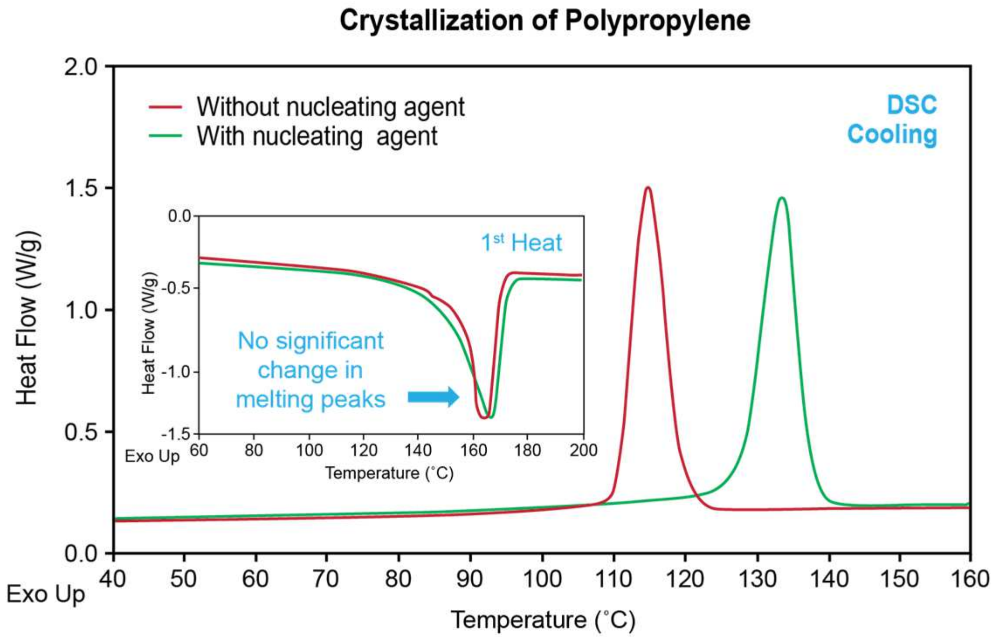
Deform into the Final Shape



What is the crystallinity of the product?

Cool the Molded Product and Release





- For semi-crystalline polymers, process conditions affect crystallinity
  - Impacts end-use properties: mechanical stiffness/ strength, optical clarity
- Processing: What cooling rates are needed to achieve the required crystallinity?
  - Are nucleating agents needed?

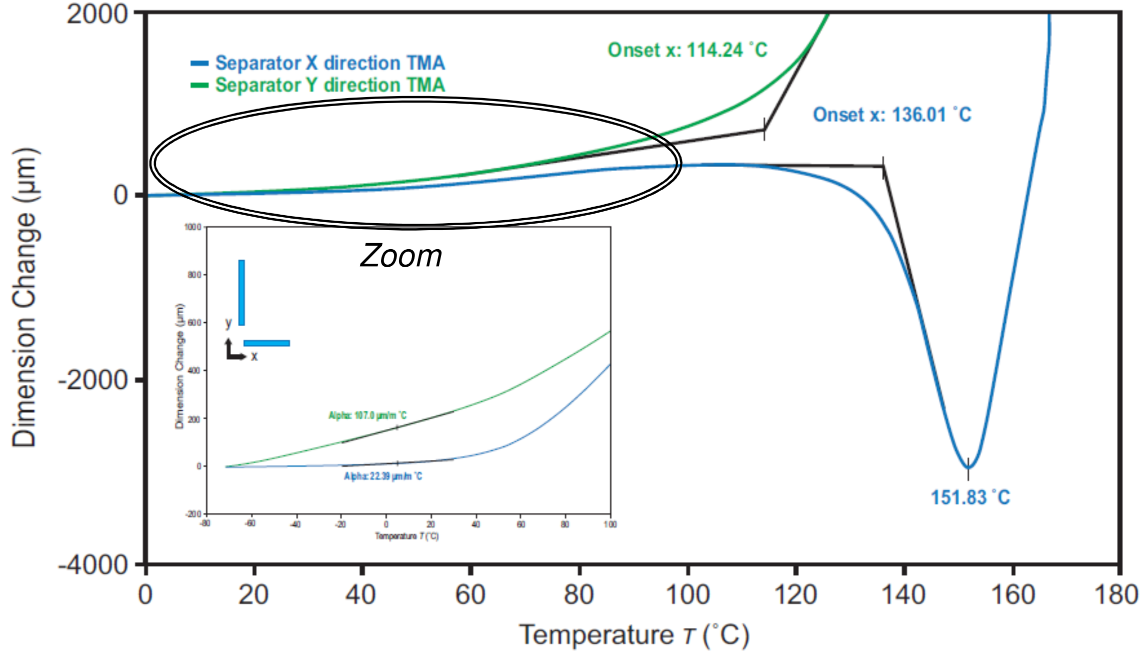
End-of-life: How can the crystallinity of products made with PCR be matched with those from virgin materials?

Part 3 : Characterization of final product

Thermal Expansion of Packaging Films

TMA-450 - TA Instruments

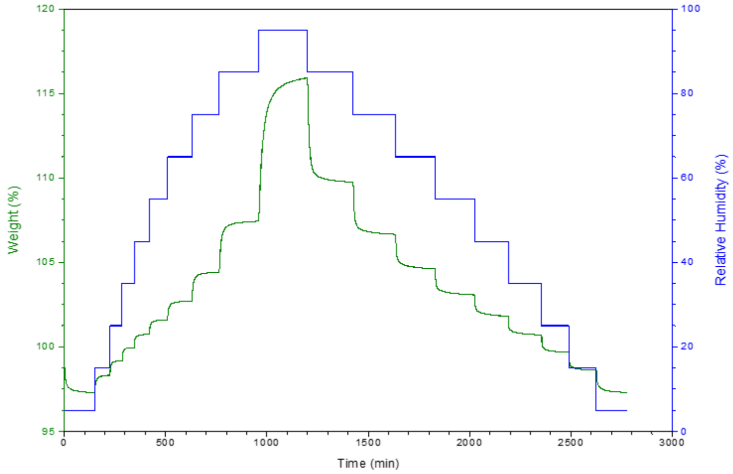
- Example: anisotropic polyolefin film
- TMA highlights that in the x-direction the sample starts shrinking at 136°C
- In the y-direction the sample begins to expand at 114°C

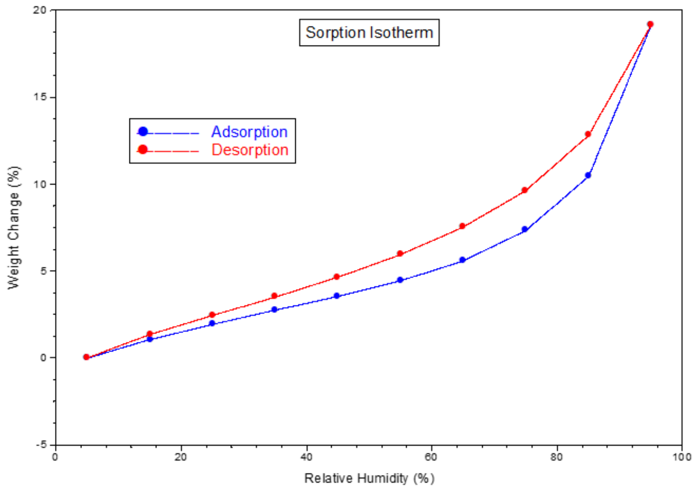


Influence of Relative Humidity on Material Properties

Dynamic Vapor Sorption Analysis - DVS

- In a DVS the water adsorption or desorption is measured as a function of relative humidity (RH) and temperature.
- A DVS instrument consists of a high performance microbalance and a temperature controlled humidity chamber.





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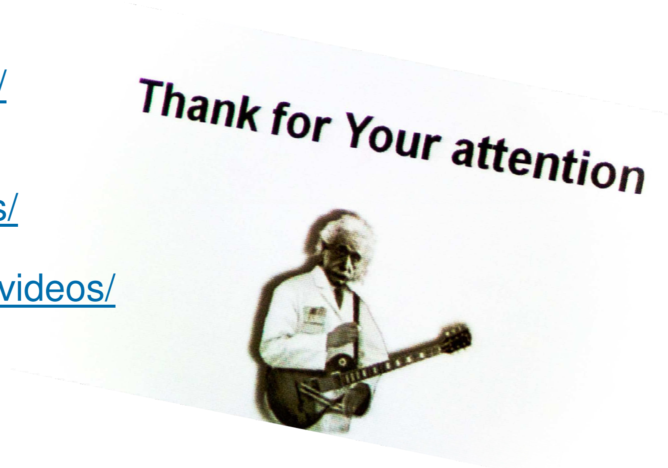

Thanks for your attention