

Processing and Characterization of Bio-Plastics

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Introduction

- Bio-Plastics are **not a single class of polymers** but rather a family of products which can vary considerably
- A generally recognized **definition** of the concept **does not exist**
- Bio-Plastics consist of
 - **Biobased** plastics, based on renewable resources
 - **Biodegradable** polymers, which meet all criteria of scientifically recognized norms for biodegradability and compostability

Bio-Plastics' Properties

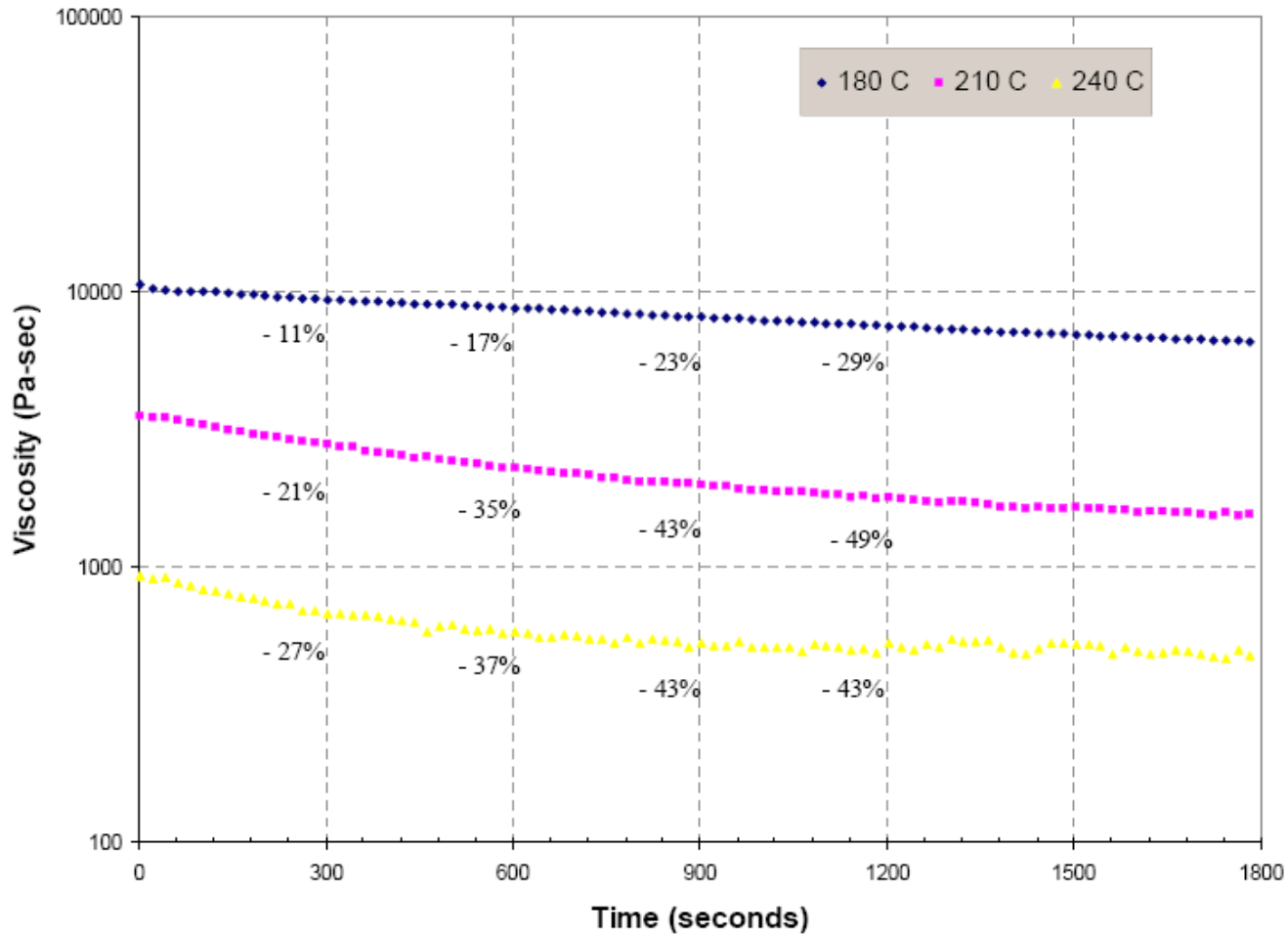
- Slow Recrystallization
- Moisture absorption
 - Hydrolytical degradation, mainly PLA above T_g
 - Bulk imperfections for PHA
- Thermal degradation
 - Mw reduction affecting Melt strength, Mechanical properties
- Viscosity
 - Melt elasticity of linear polyesters
 - Foaming, Thermoforming, Blown Film, Blow Molding
 - Shear thinning effects, coupled with Mw reduction

Processing Considerations

- Implications
 - Drying
 - Increased cycle time, lower line speeds (compare to polyolefines)
 - Low processing temperatures, many times at relatively high viscosity
 - High Pressure, and Torque requirements
 - Tools' design for reduced viscous heating and residence time

Processing of Bio-Plastics

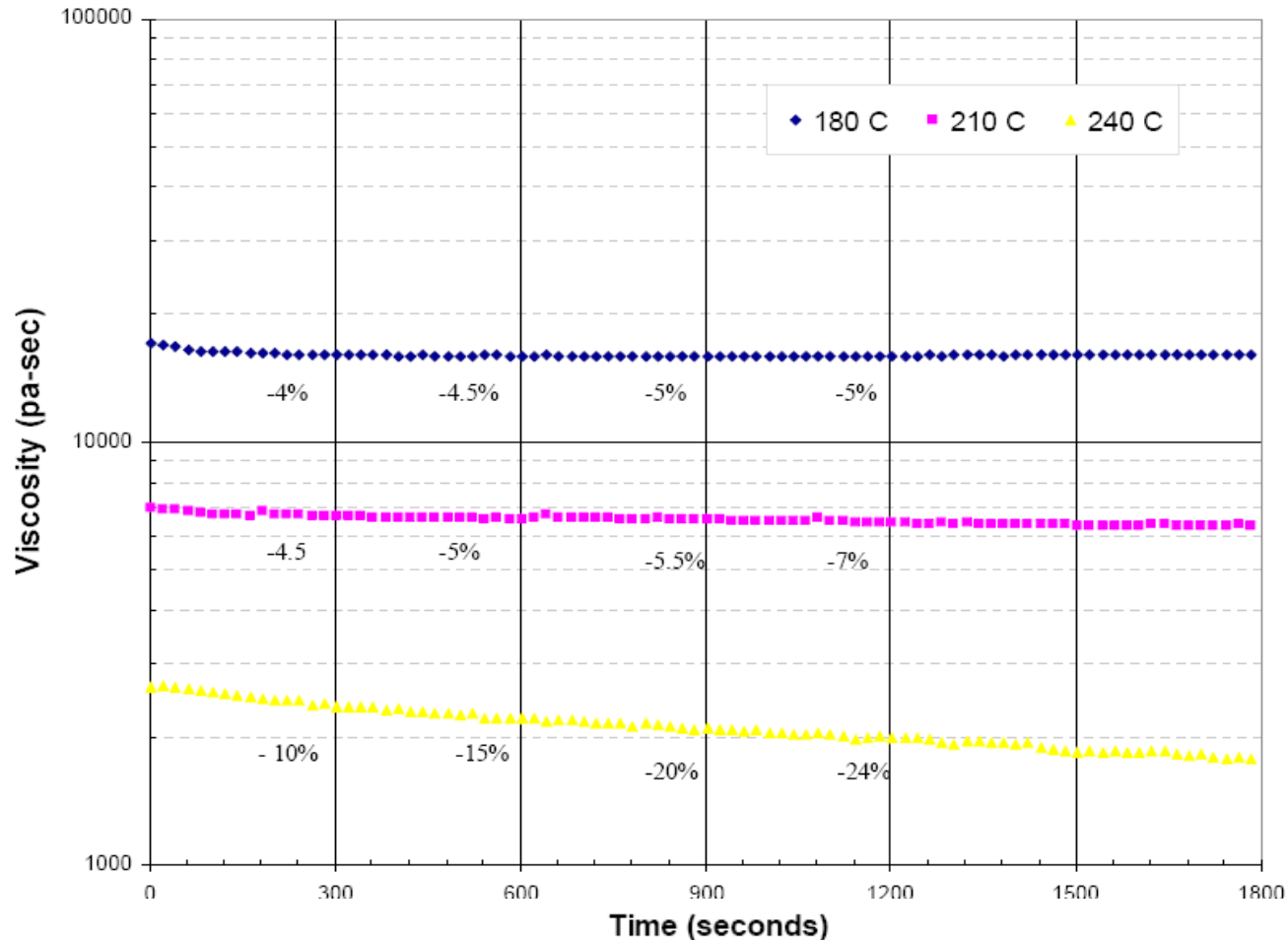
Viscosity Stability of PLA with 850 ppm of Water
(constant shear rate of 10 sec⁻¹)



Nature Works, Jim Nangeroni 2007

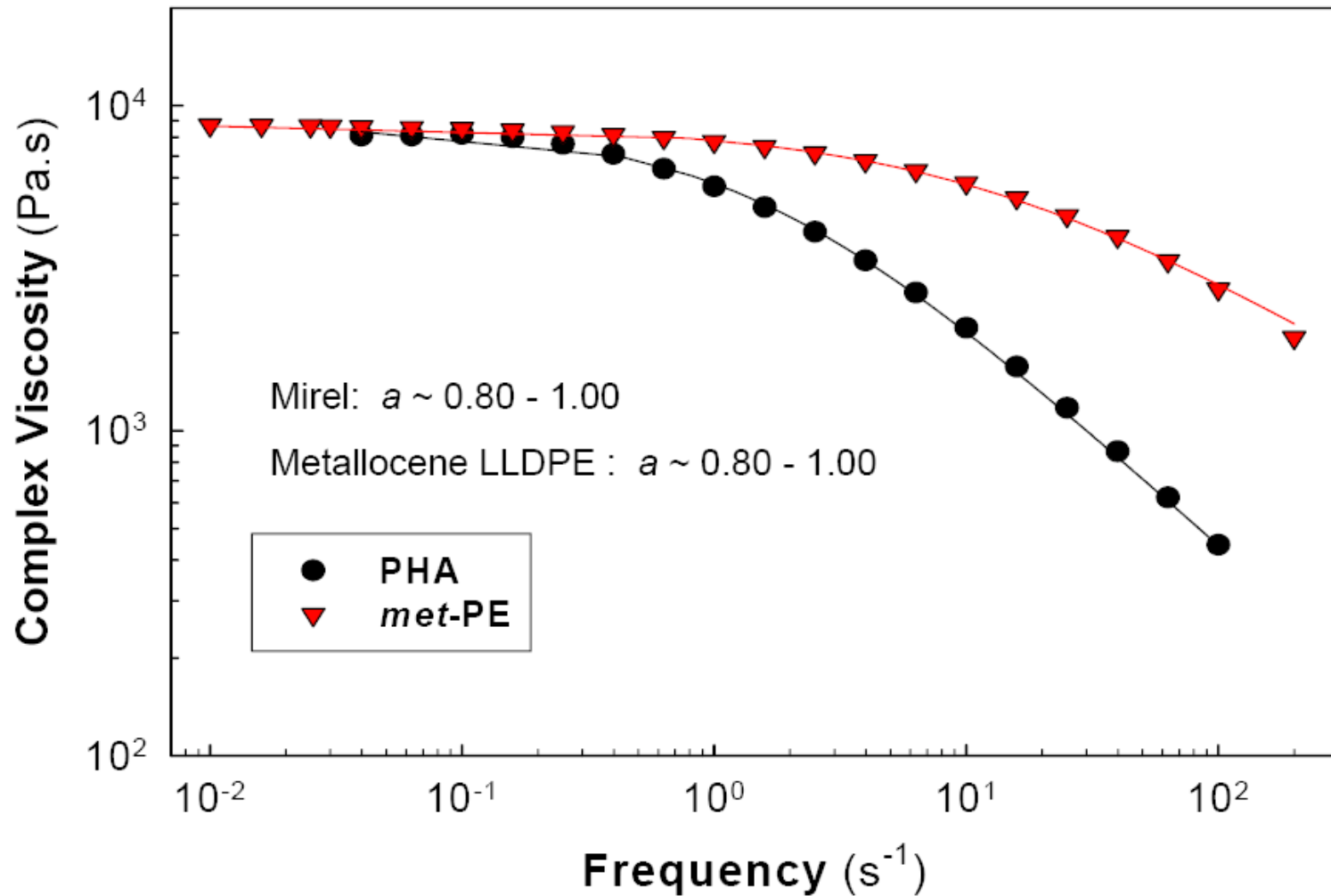
Processing of Bio-Plastics

Viscosity Stability of PLA with < 100 ppm Water
(constant shear rate of 10 sec⁻¹)



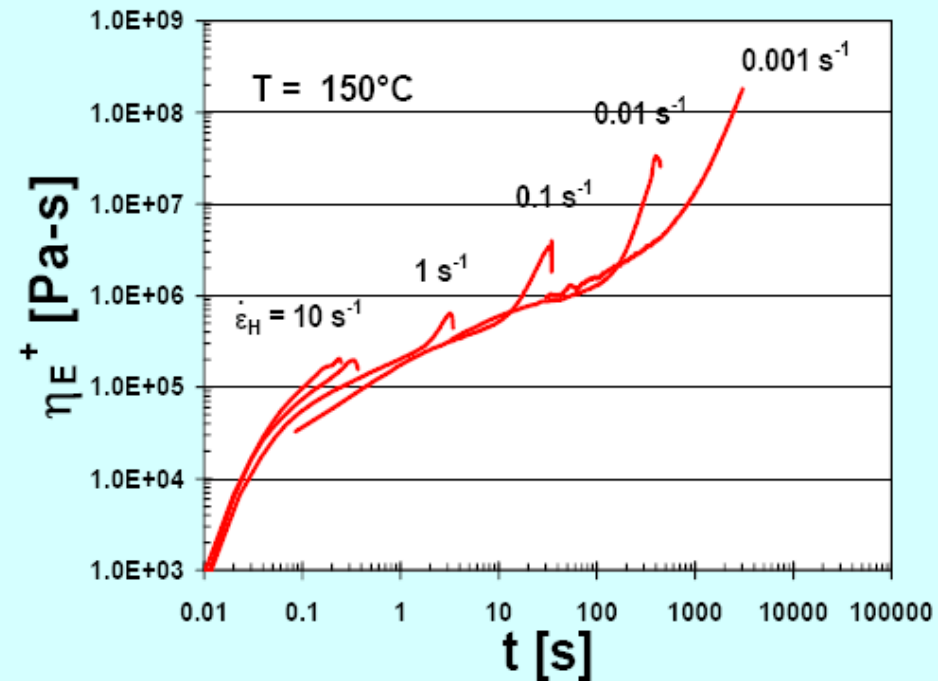
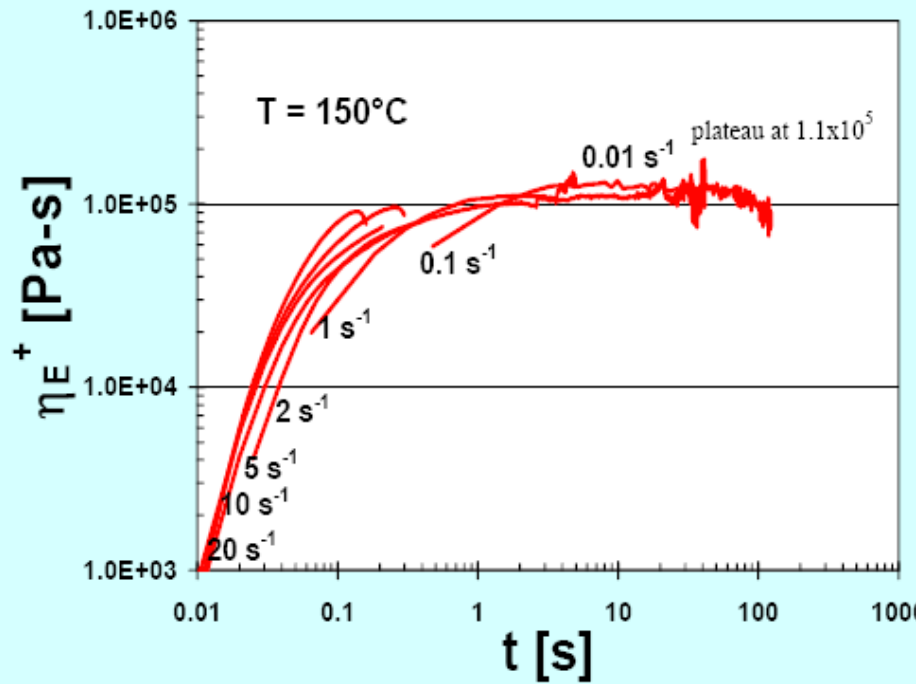
Nature Works, Jim Nangeroni, 2007

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Telles, Robert S Whitehouse, 2007

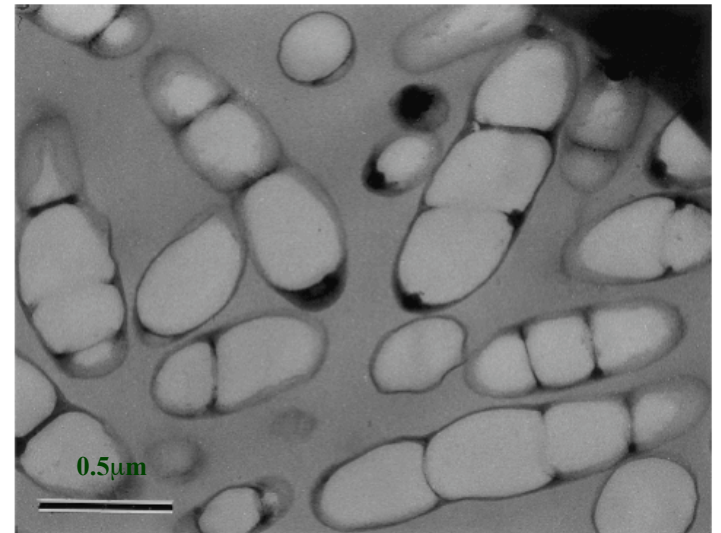
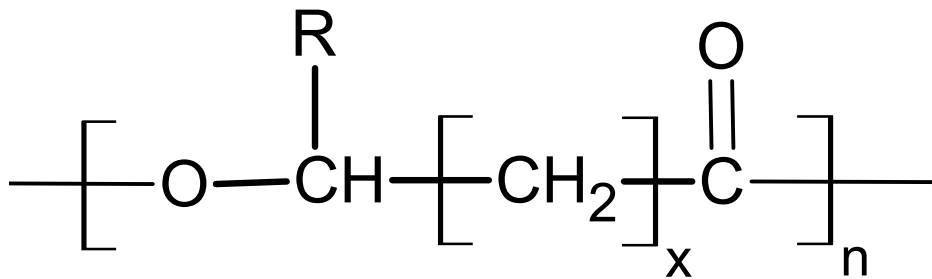
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Nature Works, Jim Nangeroni, 2007

Poly Hydroxybutyrate

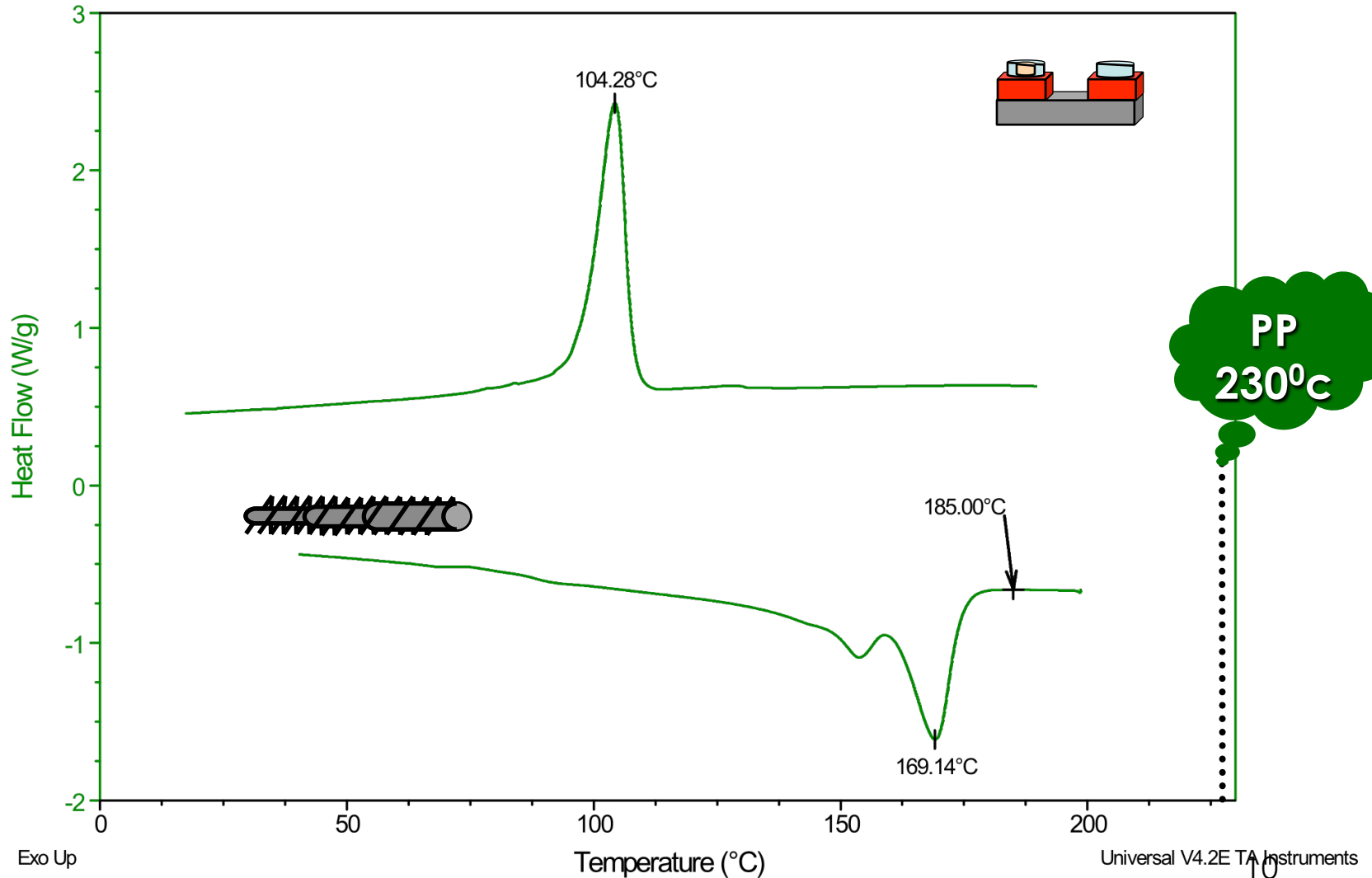
- Poly Hydroxybutyrate, **PHB**, is the most common of PHA
- **Bio-Based** and **Bio-Degradable** Polymer
- Aliphatic, thermoplastic, linear, semi-crystalline polyester
- When copolymerized can cover a wide range of mechanical properties



K. Sudesh et al, 2009

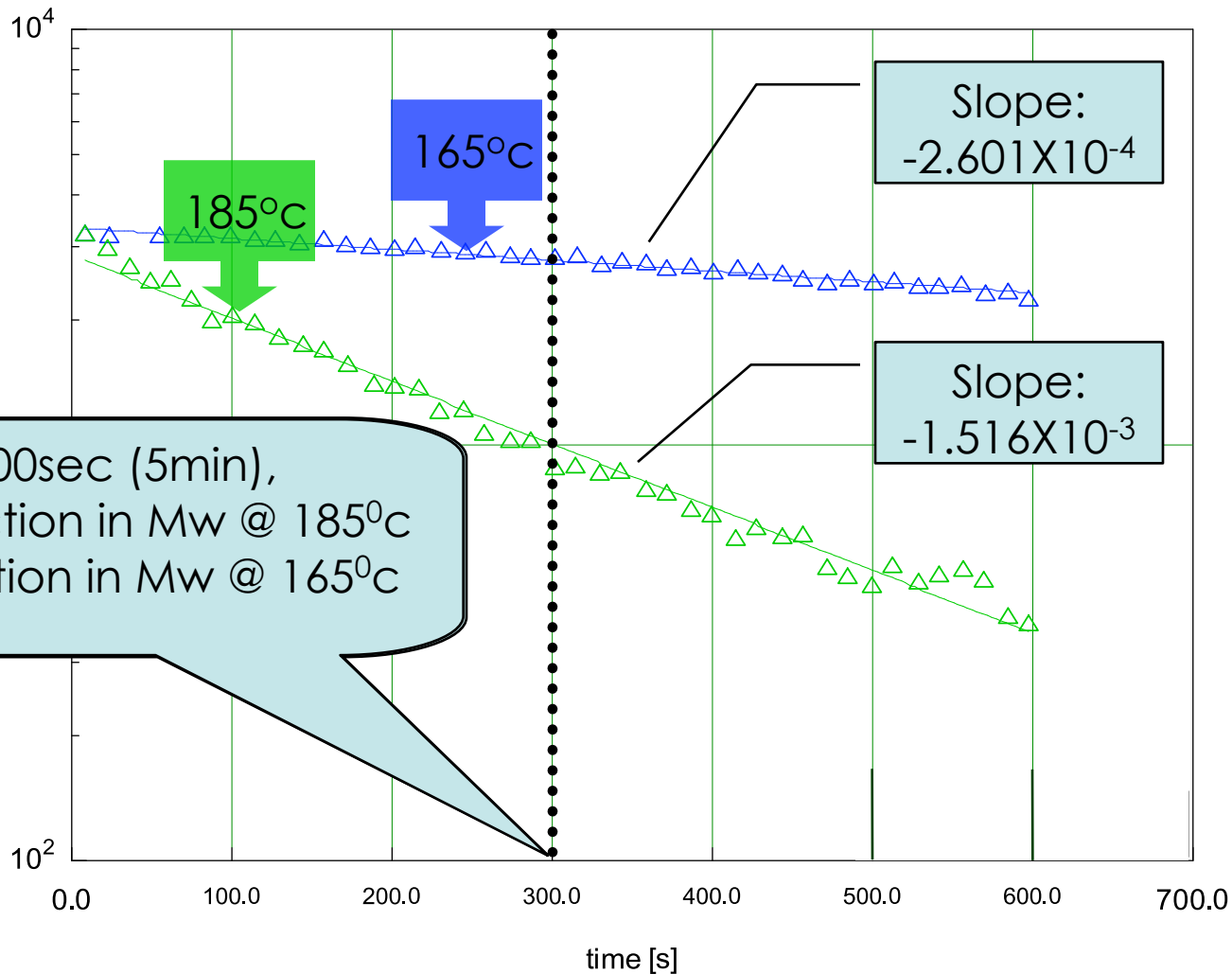
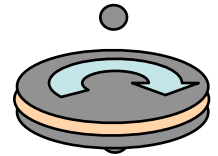
PHB, Melt Characteristics

DSC



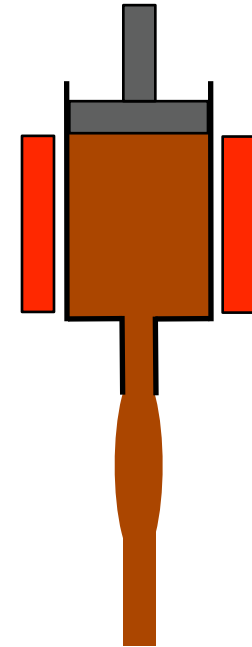
PHB, Melt Characteristics

Parallel Plate Rheology



Rheological Characterization

- $T_m - 170^{\circ}\text{C}$
- Capillary Rheometer @ 180°C
 - 27% MW loss



The Molecular Weight of Biopol™ XB 407 Versus Processing Temperature^a

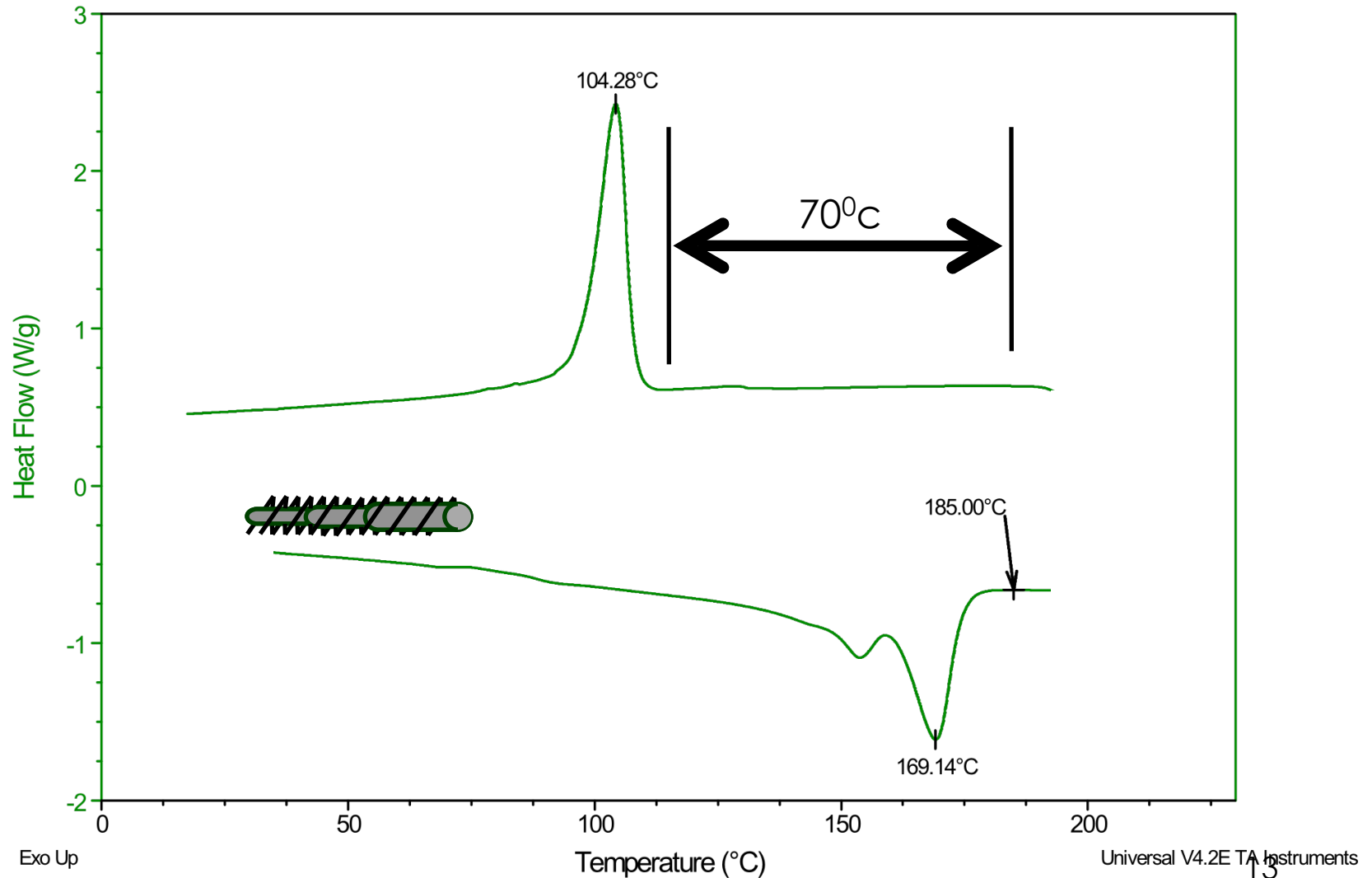
	M_w	M_n	PDI
Control (resin)	574,558	339,807	1.69
170°C	480,573	275,311	1.75
180°C	421,321	242,506	1.74
190°C	396,549	220,585	1.80
200°C	323,347	182,365	1.77
205°C	298,615	169,797	1.76
220°C	81,030	24,508	3.31

^a Experiment was conducted in a capillary rheometer. After melting for 4 min at the specific temperature, the viscosity at shear rate of $1,000 \text{ s}^{-1}$ was measured, and the molecular weight of the extruded material was analyzed.

J. Zhang, et al, 2004

PHB, Melt Characteristics

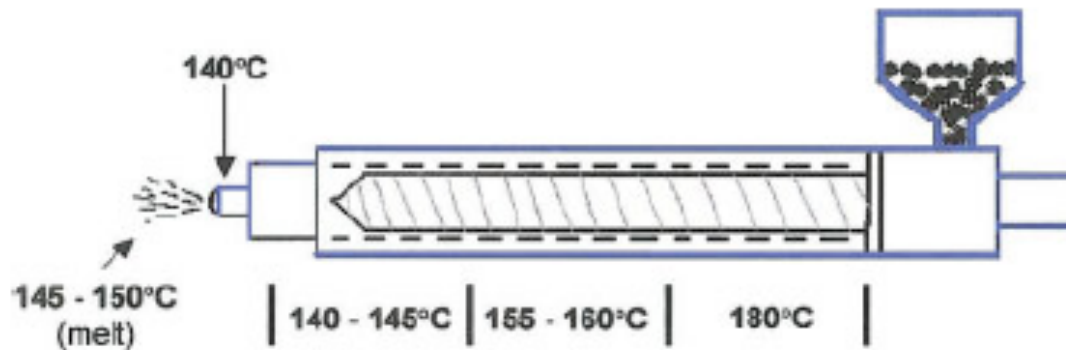
DSC



Universal V4.2E TA Instruments

PHB, Processing

- Super cooling
 - Processing below T_m
 - Reverse Temperature Profile

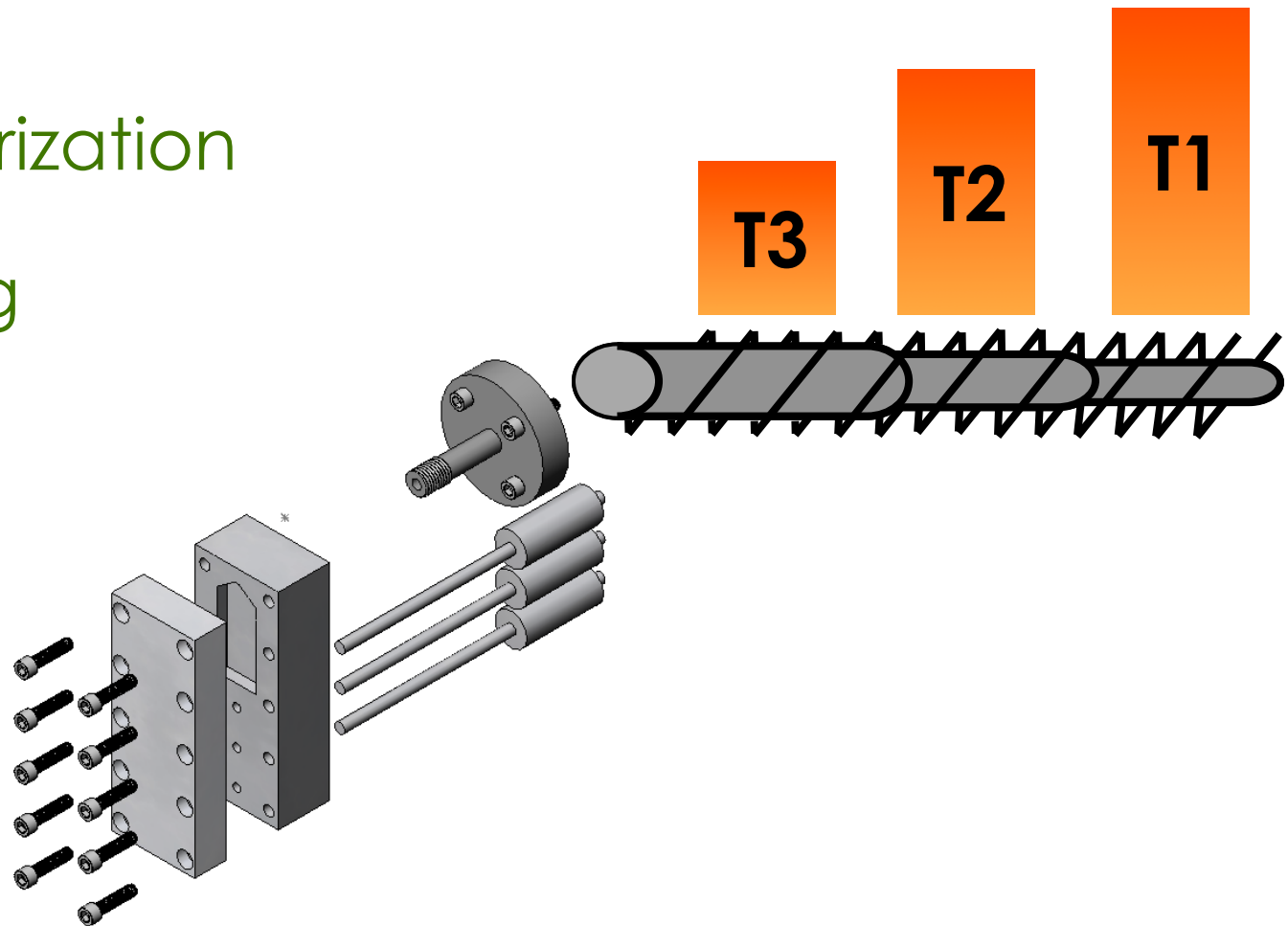


J. Zhang, et al, 2004

PHB, Processing

- Implement

- Characterization
- Processing



PHB, Extrusion Rheology

- Extrusion Rheology
 - True steady state
 - Separate variables
 - Viscous heating – Screw RPM and Design
 - Residence time – Screw RPM and Design
 - Temperature – Extruder and Die temperature profiles
 - Extensive super-cooling

PHB, Extrusion Rheology

- Apparent shear rate from flow rate

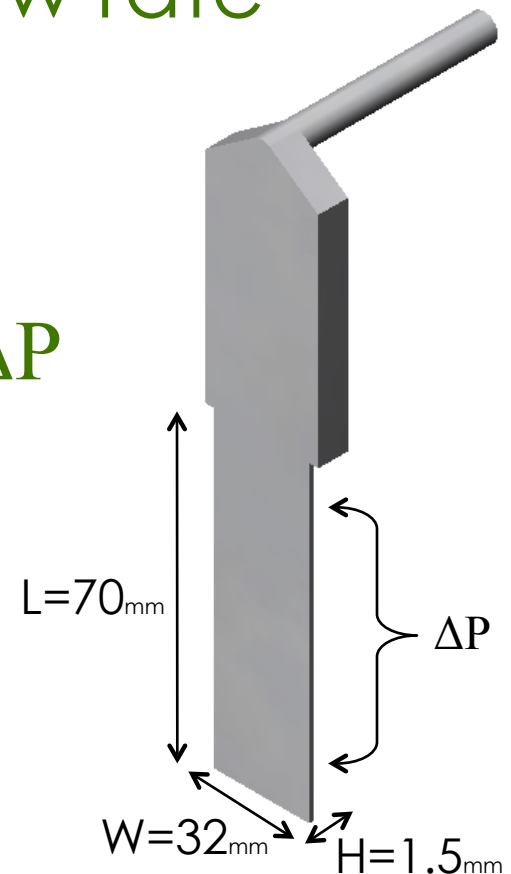
$$\dot{\gamma}_w = \frac{6Q}{WH^2}$$

- Apparent shear stress from ΔP

$$\tau_w = \frac{H(\Delta P)}{2L}$$

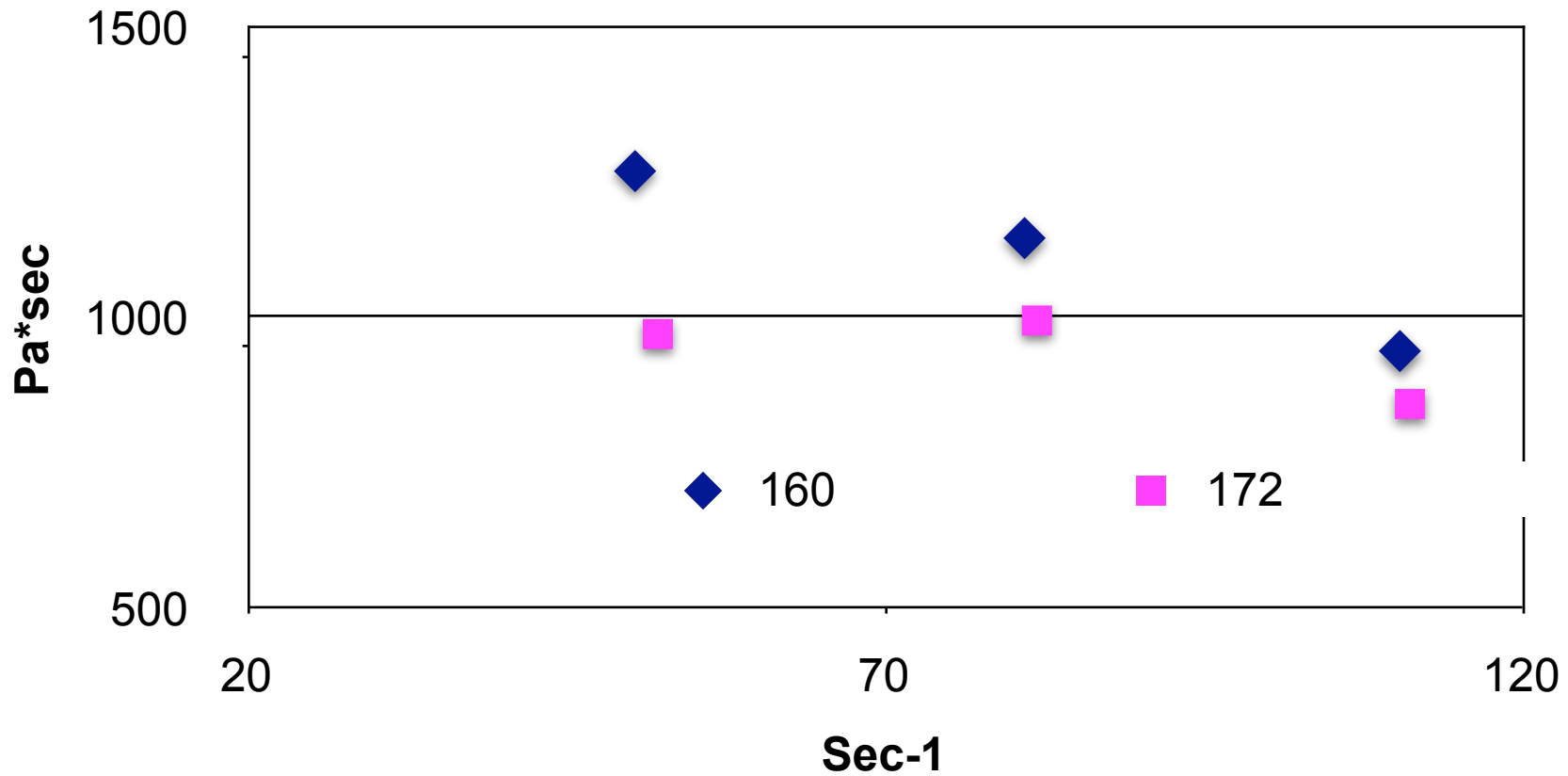
- Apparent viscosity

$$\eta_a = \frac{\tau_w}{\dot{\gamma}_w}$$



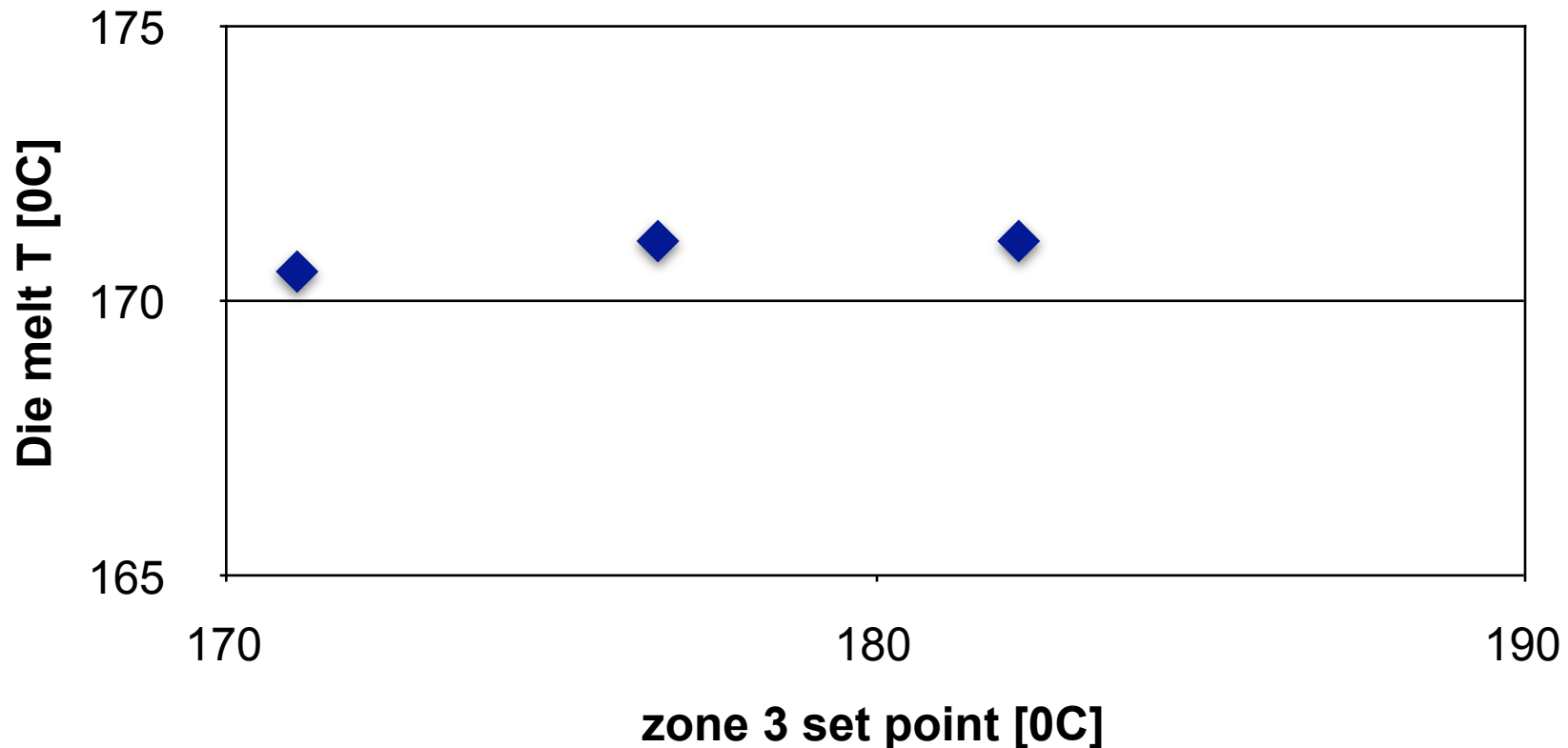
PHB, Extrusion Rheology

Flow Curve



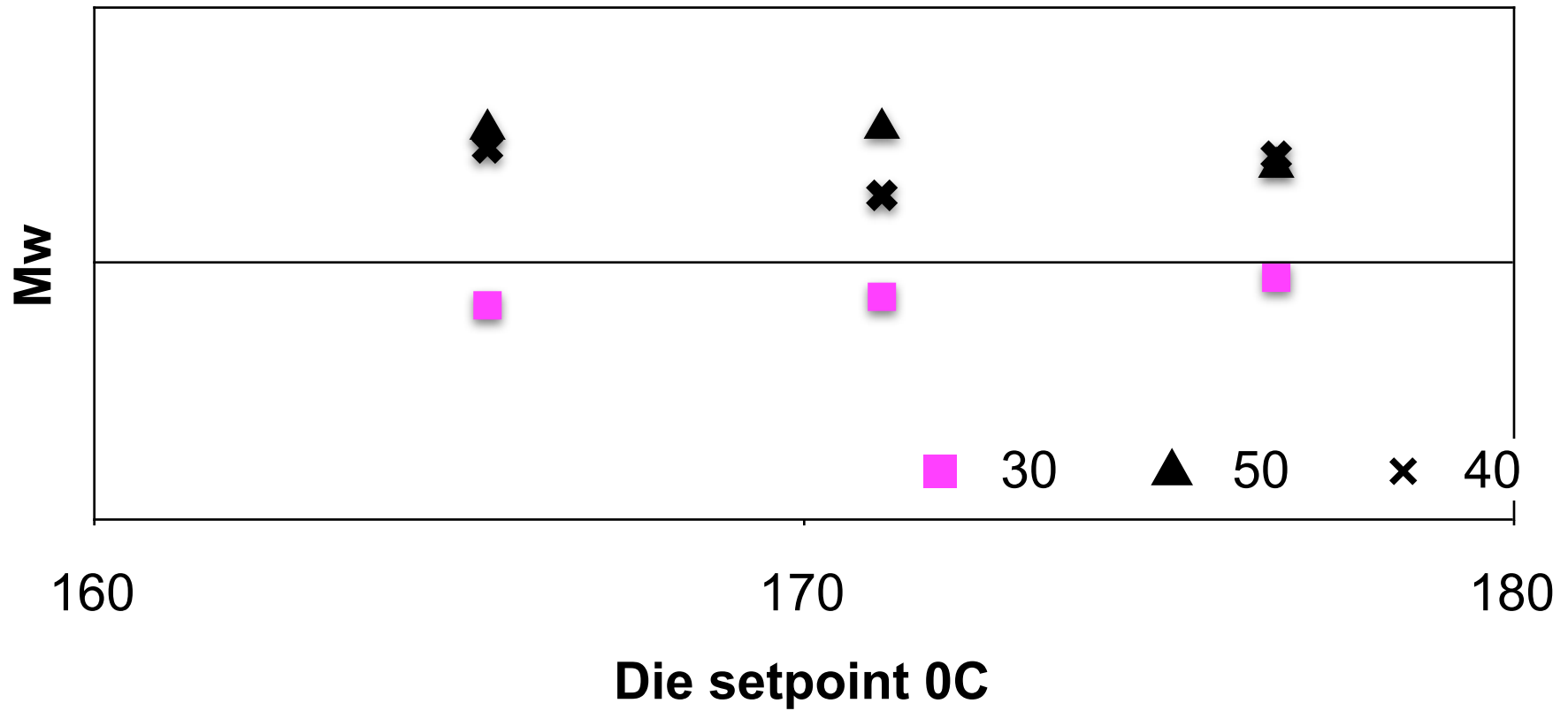
PHB, Extrusion Rheology

Die melt temperature, different extruder temperatures



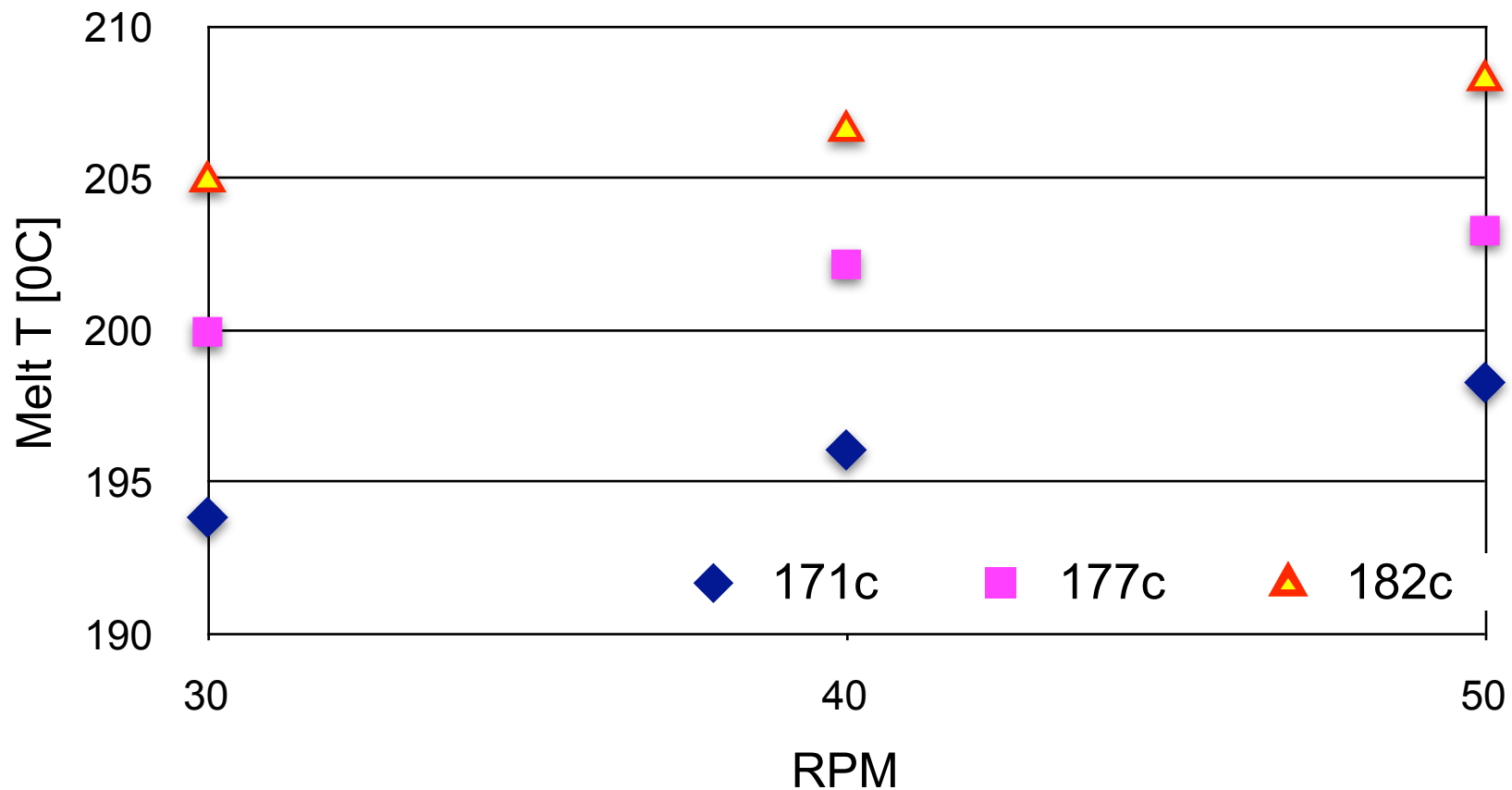
PHB, Extrusion Rheology

Mw as a function of die set point, different RPM



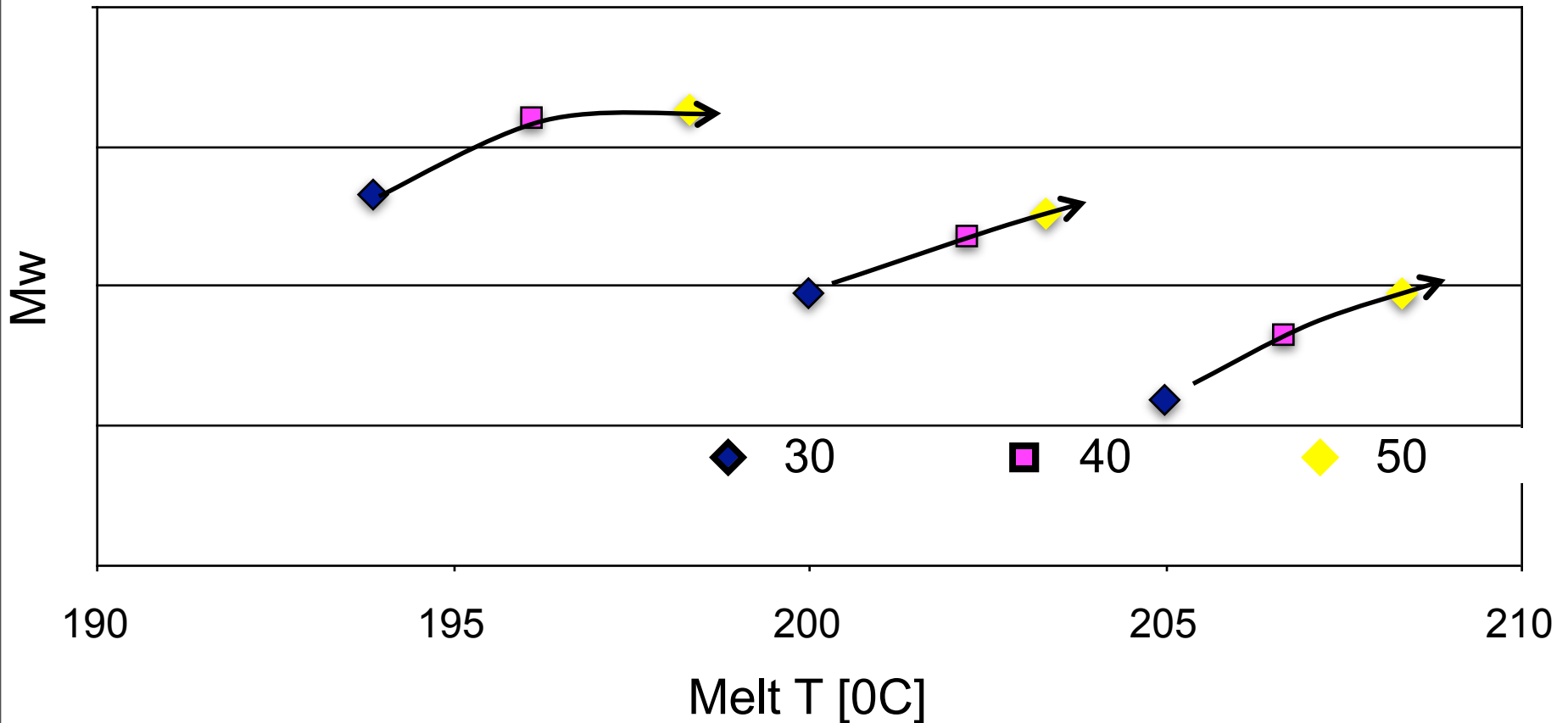
PHB, Extrusion Rheology

Extruder Melt temperature as a Function of RPM, different Temp. Set Point



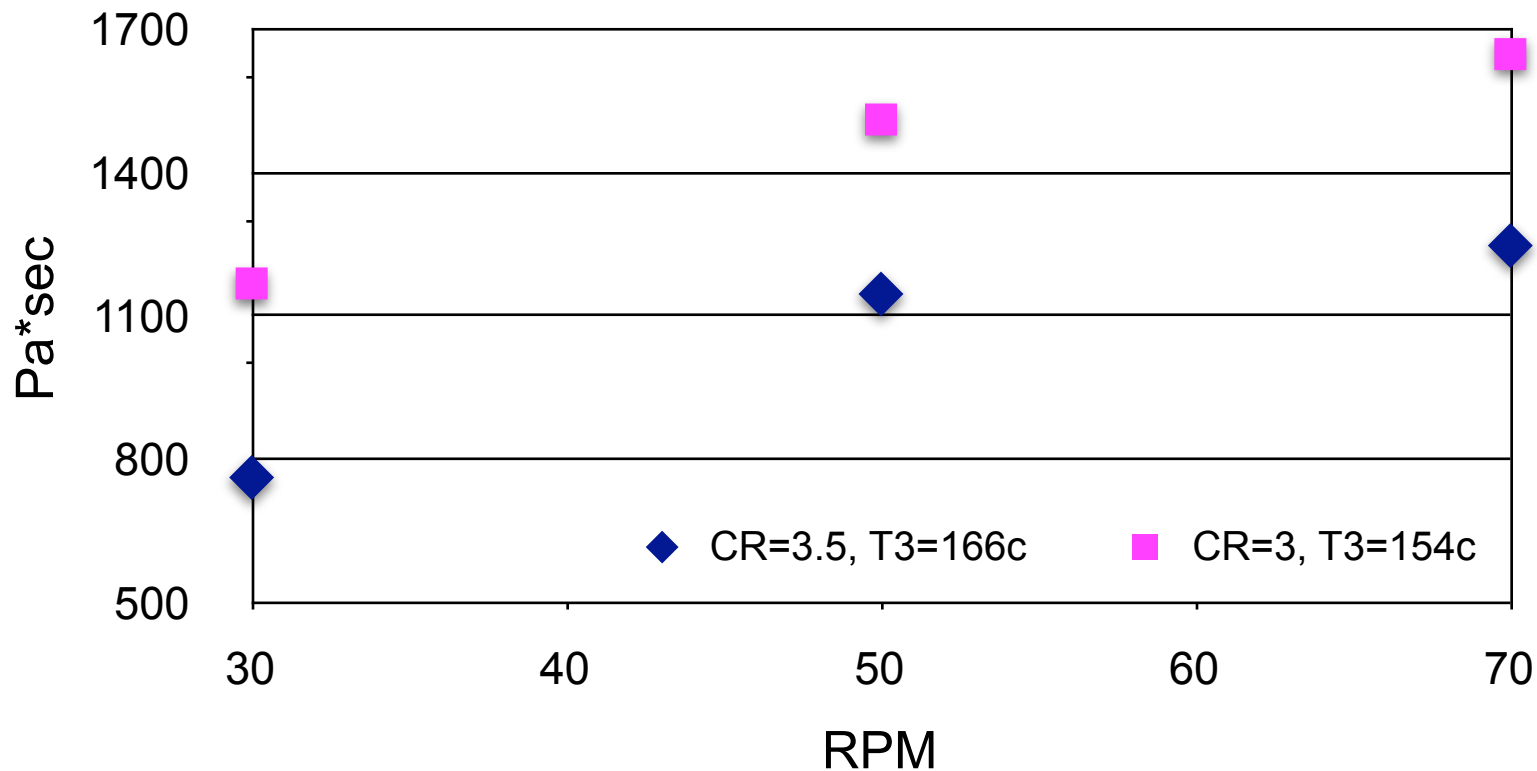
PHB, Extrusion Rheology

Mw as a function of Melt temperature,



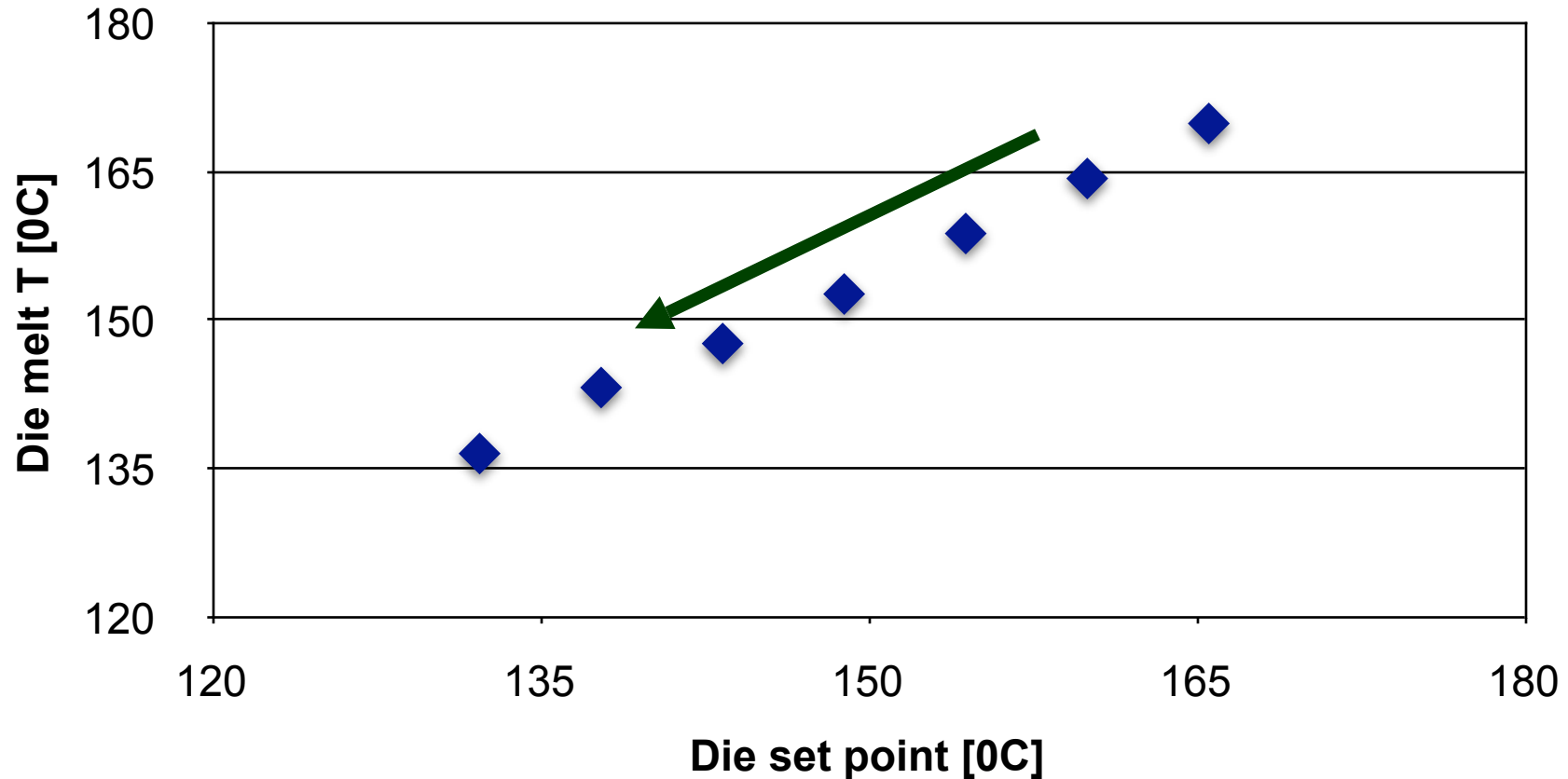
PHB, Extrusion Rheology

Parallel plate Rheology, η_0 as a function of



PHB, Extrusion Rheology

Extrusion well below T_m

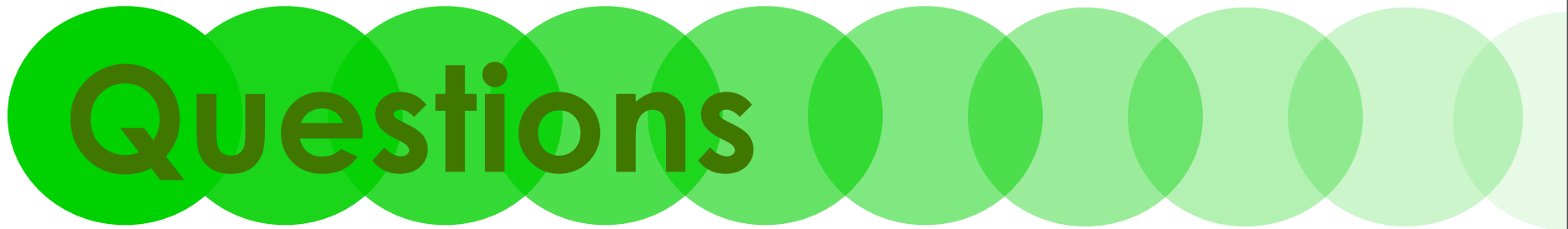


Conclusions

- **Extrusion Rheology** is a very powerful tool for the determination of PHB flow characteristics, and possibly other **thermally unstable Bio-Plastics**
- Residence time effects overwhelm temperature effect, for the evaluated range
- **Super cooling** of the melt is possible up to 135°C , $\sim 35^{\circ}\text{C}$ below T_m
- Best MW retention achieved at **low temperatures, short residence times, and low shear**

Conclusions

- While as **solid PHB resembles** the behavior of other **known polymers**, its melt state differs substantially
- **Loss in molecular weight** during processing should be taken into account
- There will always be **some reduction in MW** down the process stream
- **Knowing the polymer's limitations** will ease its implementation into existing processes
- **The use of Bio-Plastics in large scale manufacturing is doable**



Questions