EVERSPRING CHEMICAL COMPANY

Results-based Processing Stabilization

Why polymer stability is more than the sum of the antioxidants

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Overview

1. Degradation and Stabilization

2. Evaluating Processing Stabilization

3. The importance of conditions on antioxidant performance

Degradation & Stabilization

- **Degradation** is a loss of properties
  - *mechanical properties*
  - *chemical properties*
  - *physical properties*
  - *aesthetic properties*
  - *organoleptic properties*
  - *processability…*

caused by changes to the polymer molecules (or polymer morphology)

- Chain scission
- Cross-linking
- Chemical functionalization (oxidation)
- Secondary crystallization

Degradation & Stabilization

- **Stabilization** is maintaining those properties
  - or at least slowing down the rate of deterioration

Basic Oxidation Scheme

Initiation

$$\text{Polymer} \xrightarrow{\text{Initiator}} R^{\bullet}$$

$$R^{\bullet} \xrightarrow[\text{rearrangement}]{\text{fragmentation}} R^{\bullet}_{X}$$

Propagation

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}$$

$$RO_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}$$

Chain Branching

$$ROOH \longrightarrow RO^{\bullet} + HO^{\bullet}$$

$$2\,ROOH \longrightarrow RO_2^{\bullet} + RO^{\bullet} + H_2O$$

$$RO^{\bullet} + RH \longrightarrow ROH + R^{\bullet}$$

$$HO^{\bullet} + RH \longrightarrow R^{\bullet} + H_2O$$

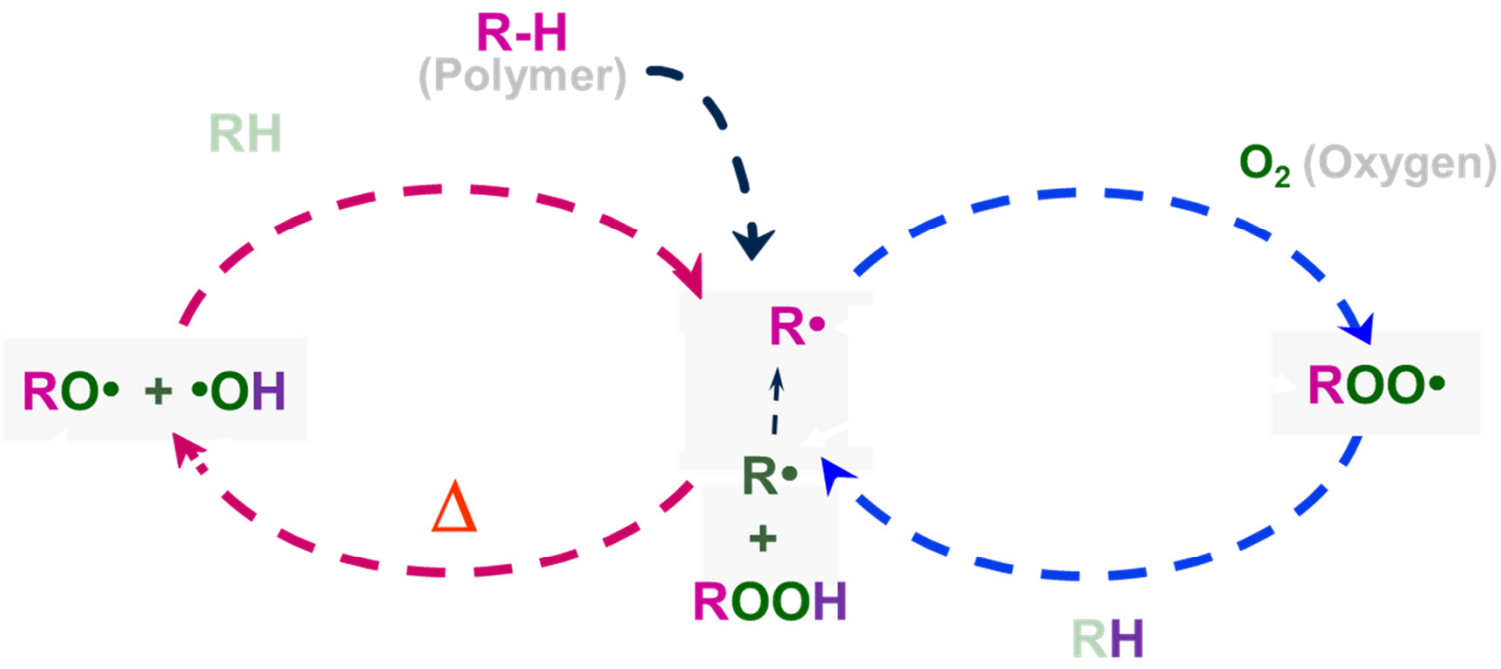
Termination

$$2\,RO_2^{\bullet} \longrightarrow \text{Inert Products}$$

$$RO_2^{\bullet} + R^{\bullet} \longrightarrow ROOR$$

$$2\,R^{\bullet} \longrightarrow R\text{-}R$$

Oxidation Cycle



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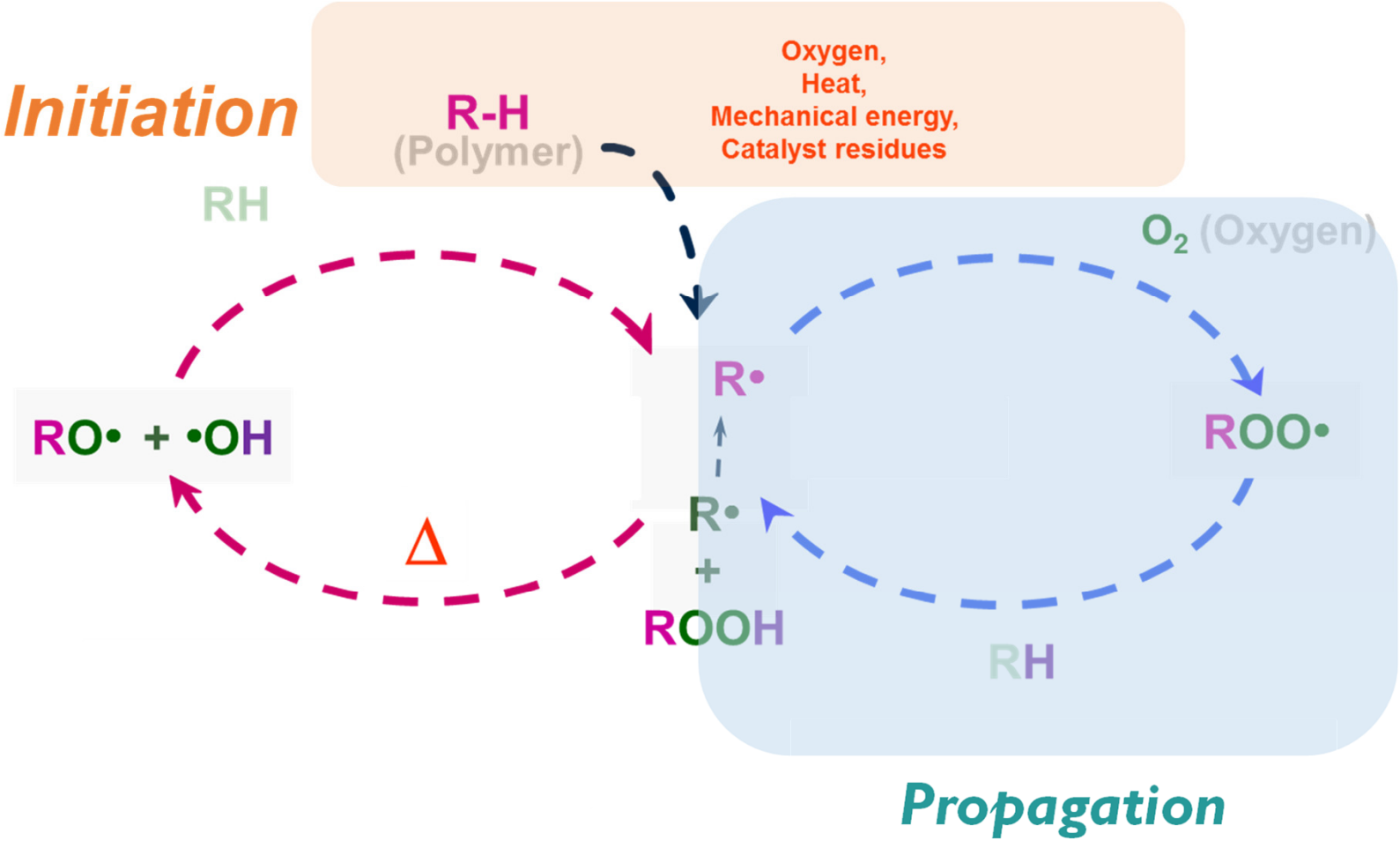

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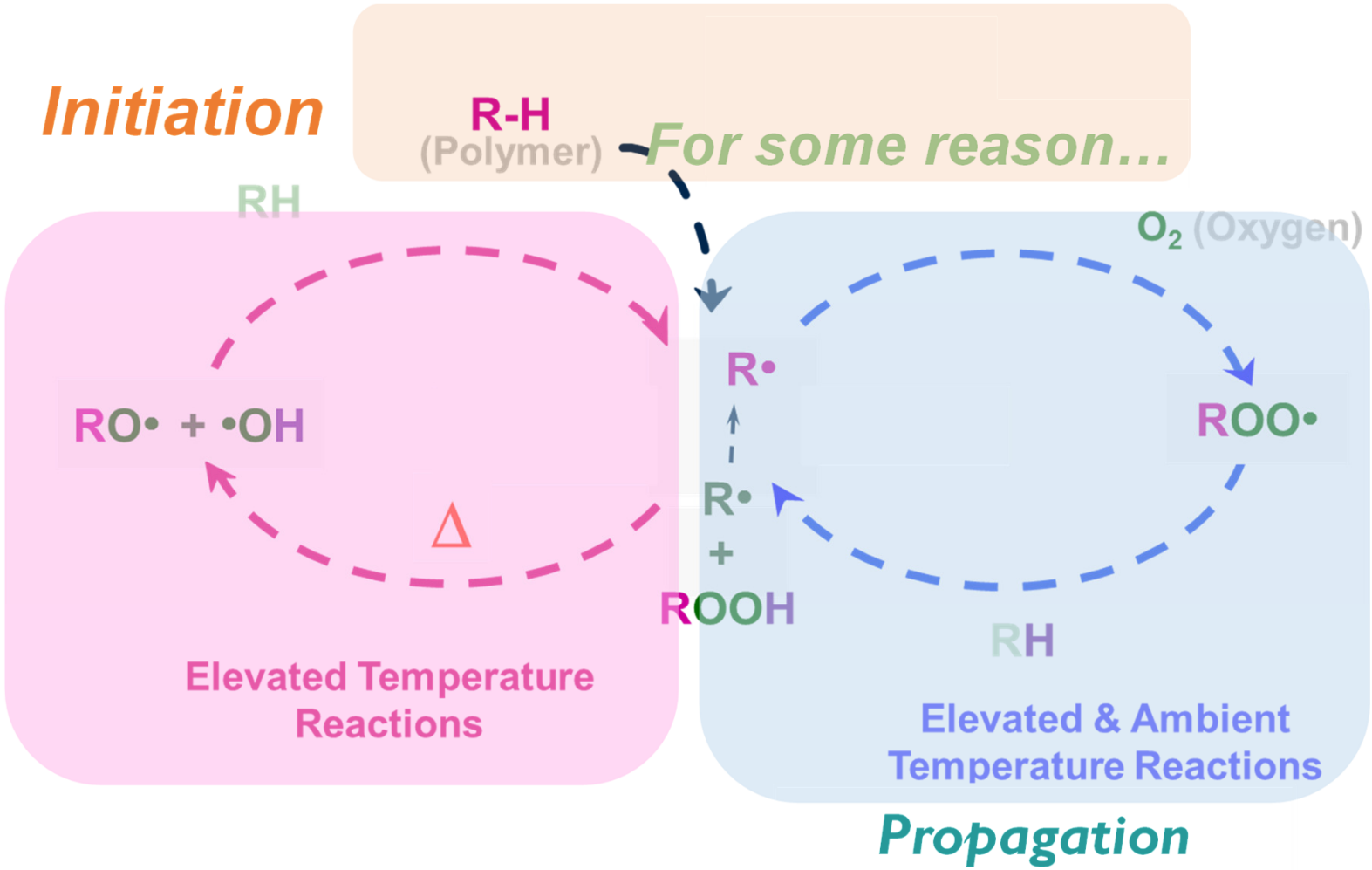

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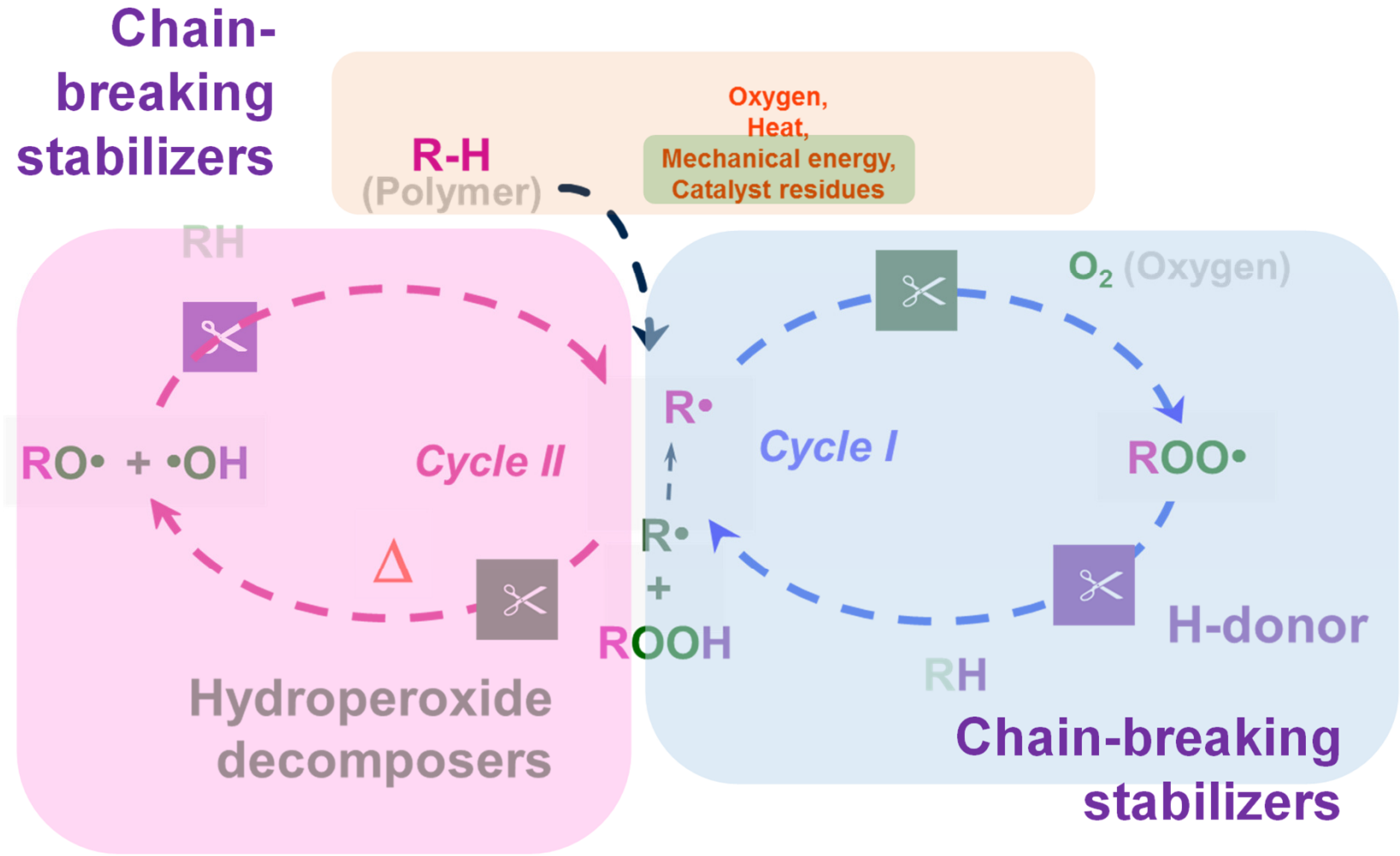
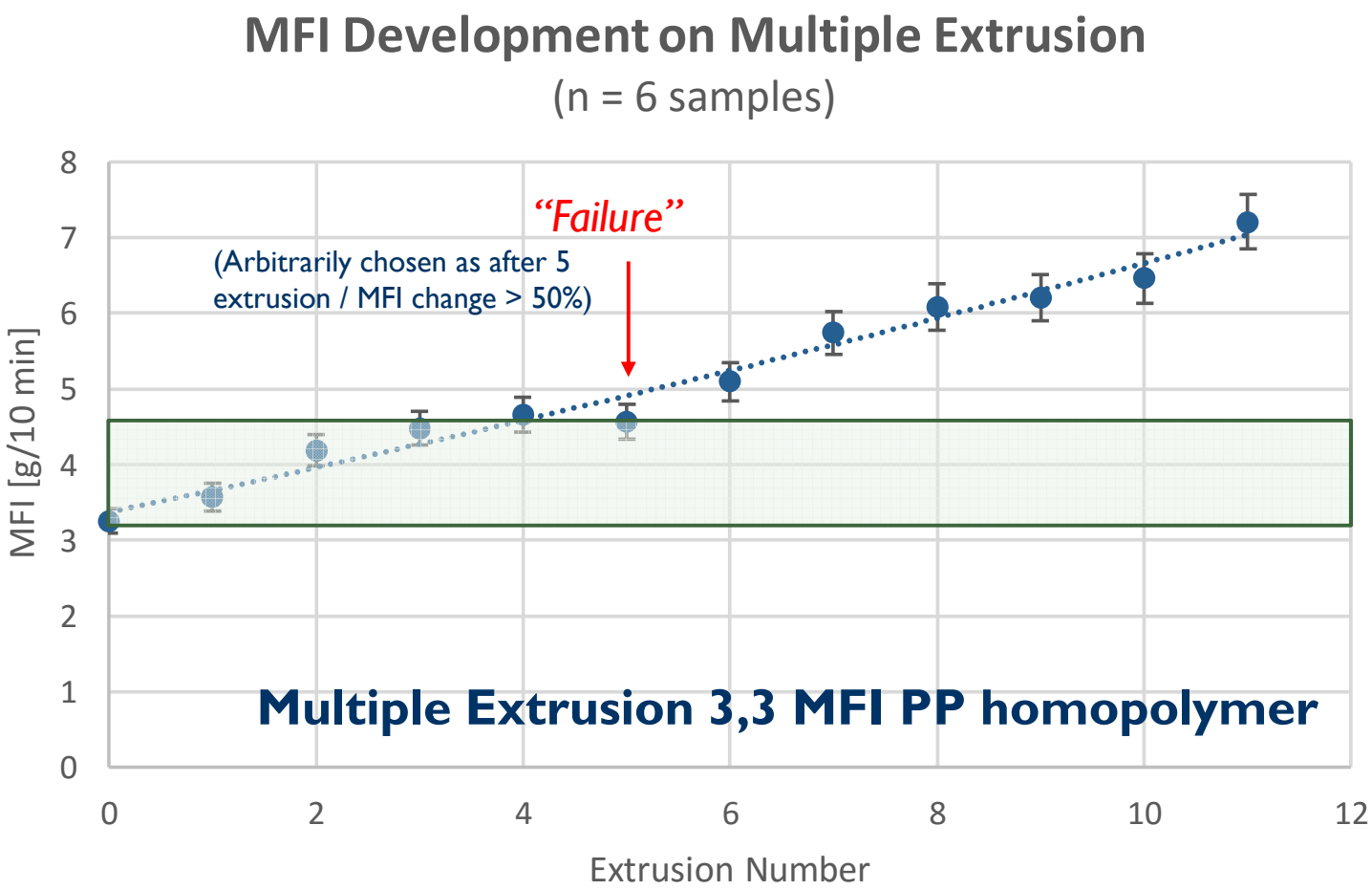
Break the oxidation cycle



Evaluating processing stability

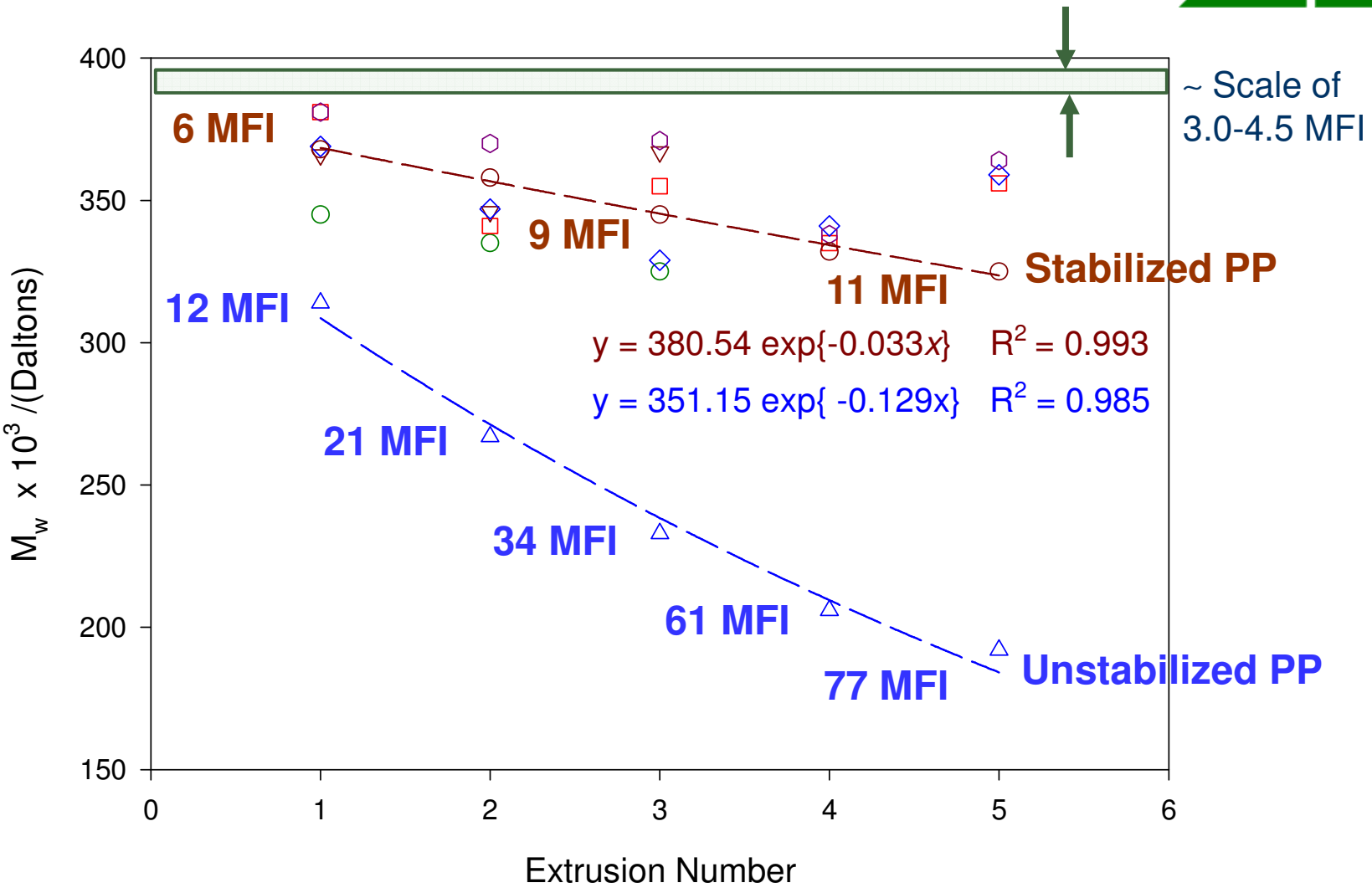
- Usually evaluated using multiple extrusion
  - polymer extruded a number of times (typically five times)
  - samples retained after each extrusion for analysis
  - monitor changes to MW, YI, mechanical properties, residual stability etc.

Multiple Extusion of hPP

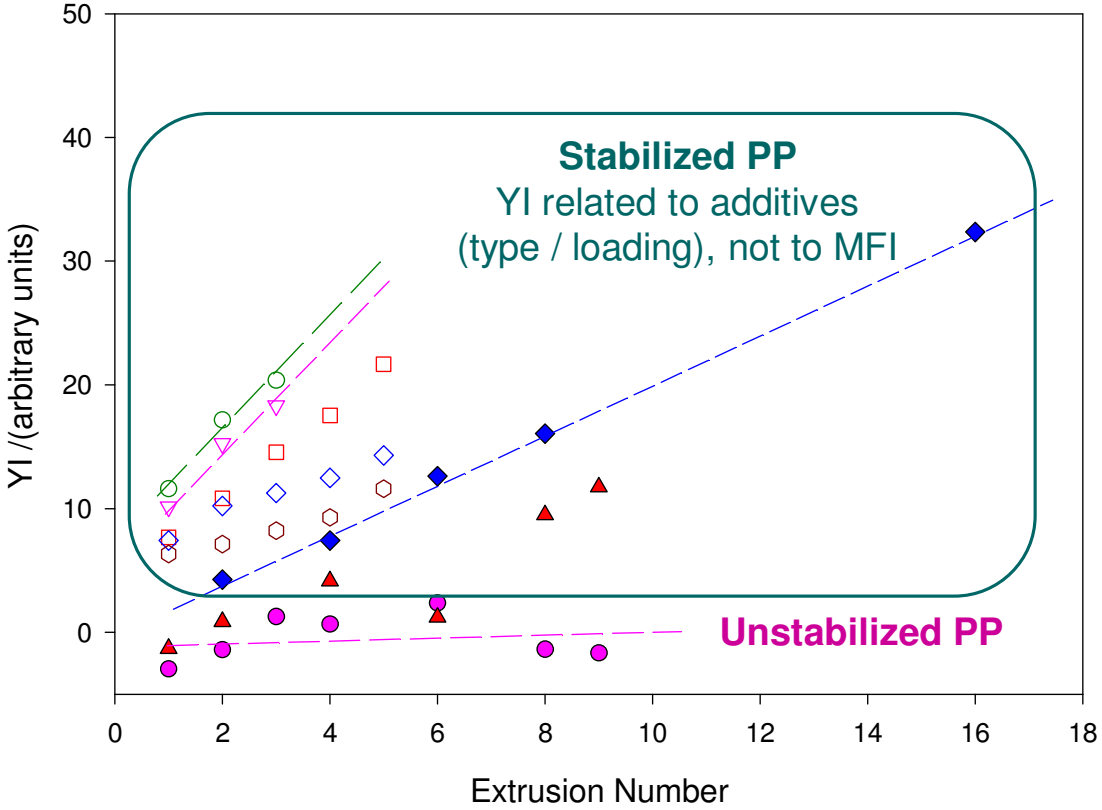


Extruded at 230°C
Brabender PL2000-6 single screw extruder (19 mm, 25D)

GPC of multiple extruded PP

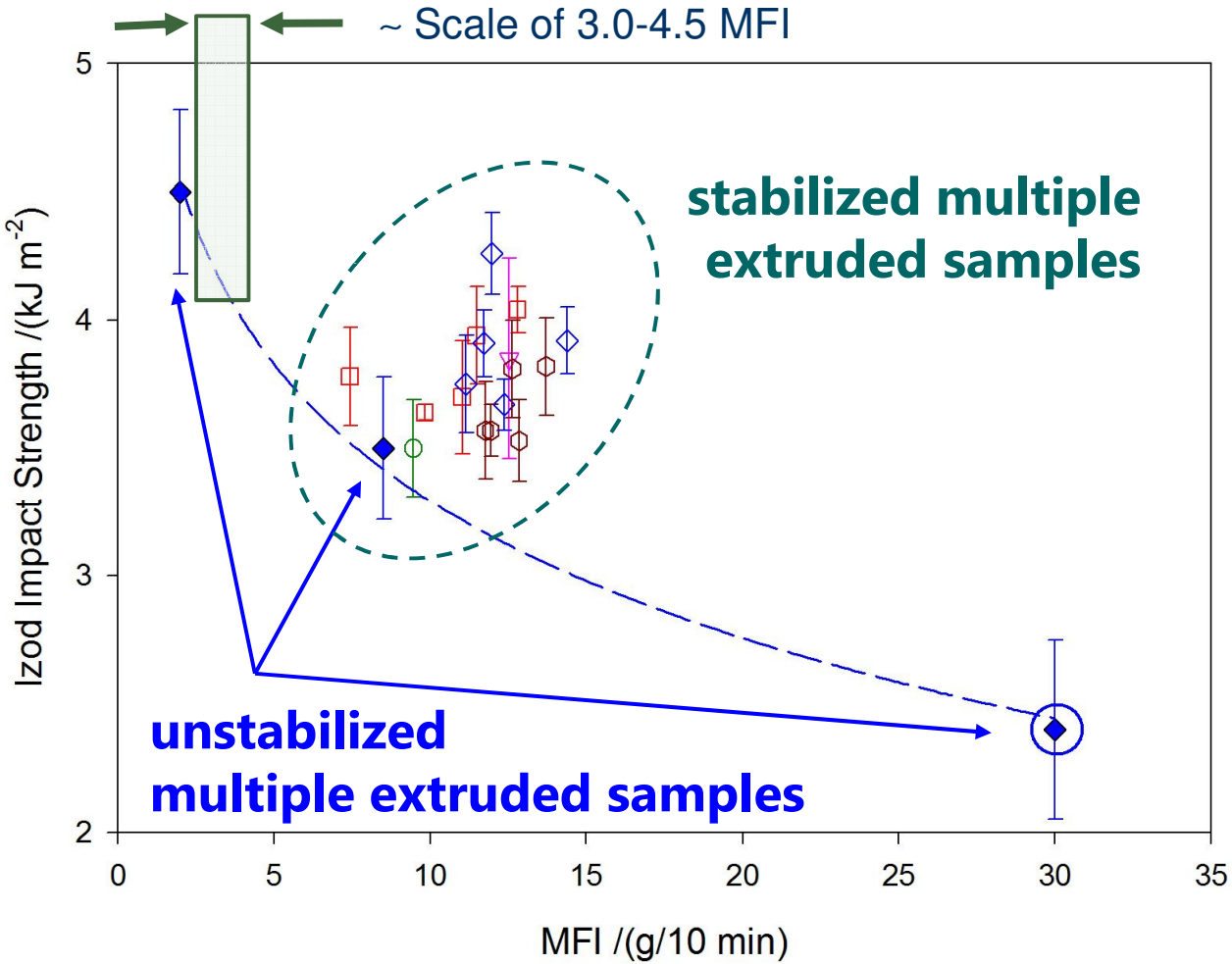


Yellowness Index of Multiple extruded PP

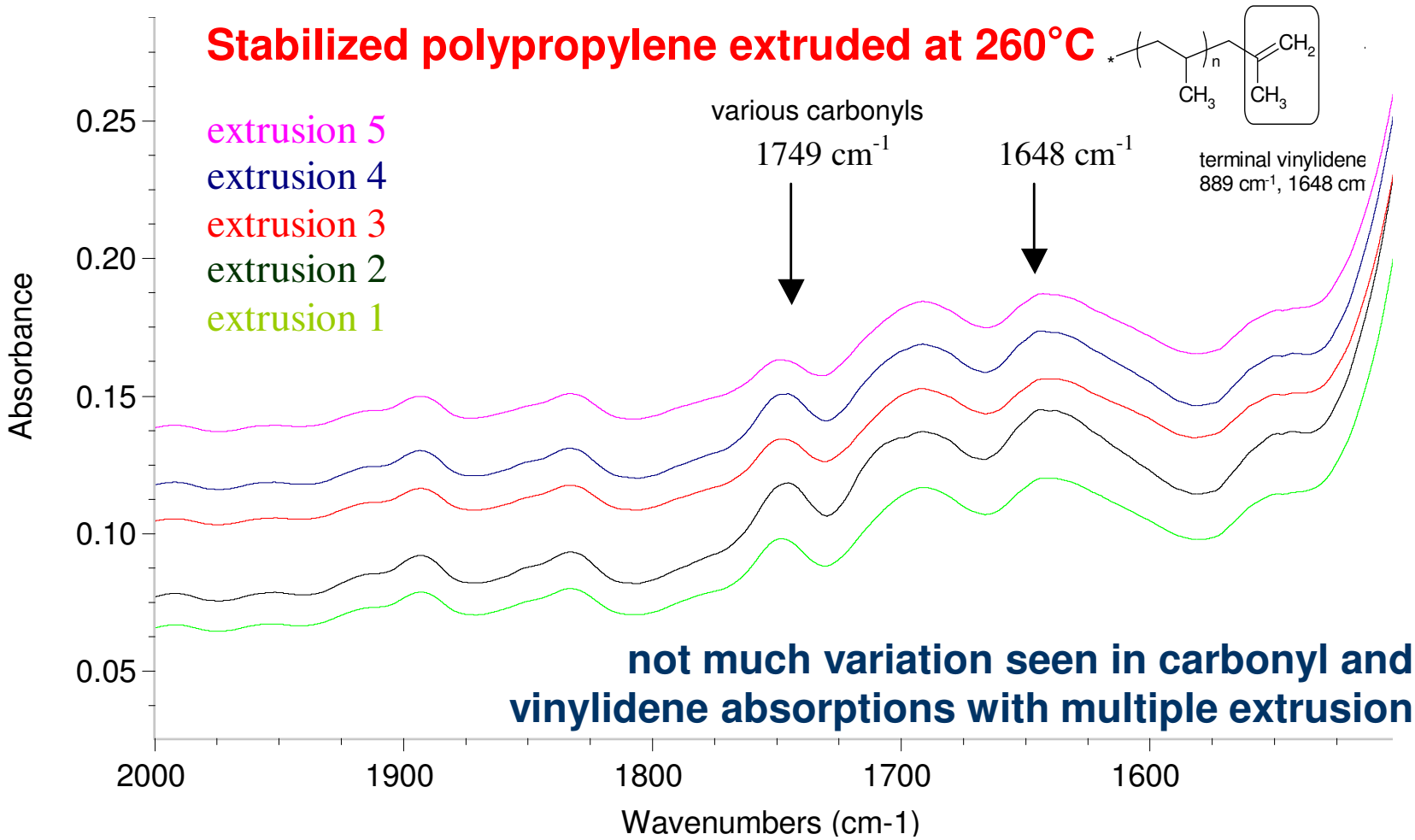


Color is an important property in itself, but it does not correlate to degradation (especially when different stabilizers are used)

Impact resistance vs. MFI

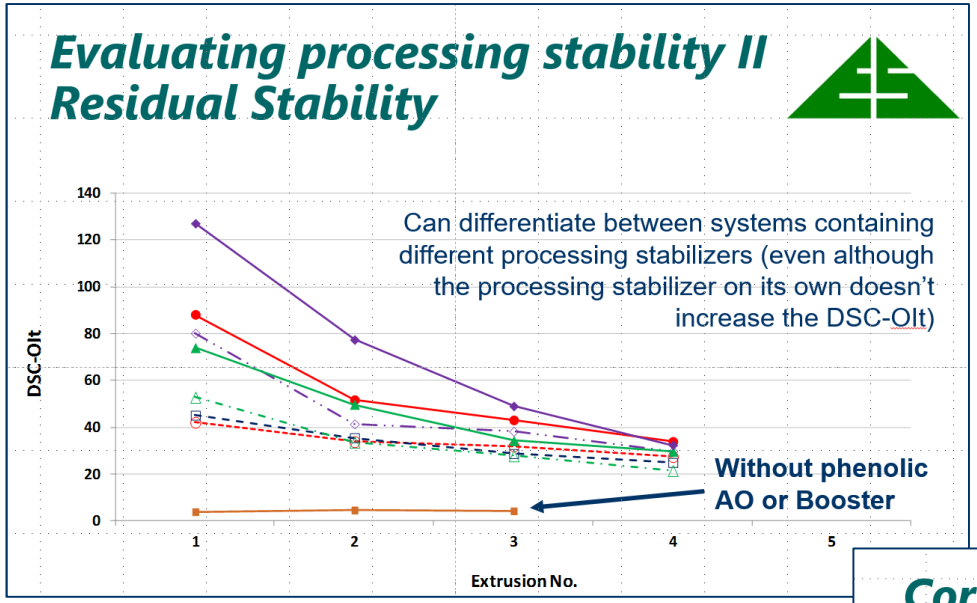


FTIR (multiple extruded)

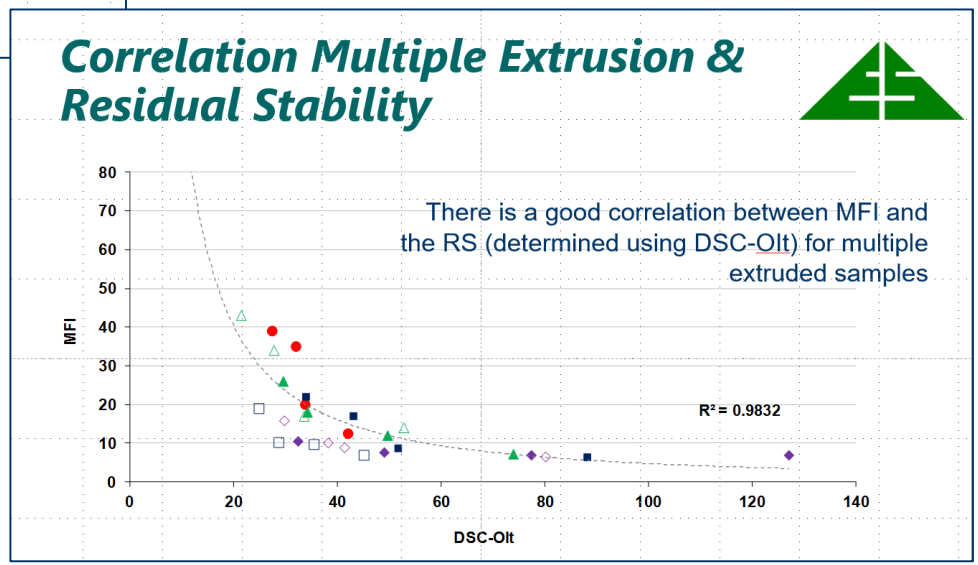


not much variation seen in carbonyl and vinylidene absorptions with multiple extrusion

Residual Stability



- Determine the residual active antioxidant(s) using DSC-OIt or CL-Oit
- Get good correlation between Residual Stability and MFI even when different stabilizer systems are evaluated



From:

N. Marshall, "**Reconstructing Stabilization**", AMI Polyolefin Additives Conference 2015 (Cologne, Germany)

The effect of test conditions on stabilizer performance

Consider:

1. Extrusion temperature
2. Extrusion time (number of extrusions)
3. The nature of the antioxidants
4. The contribution from different phenolic antioxidants

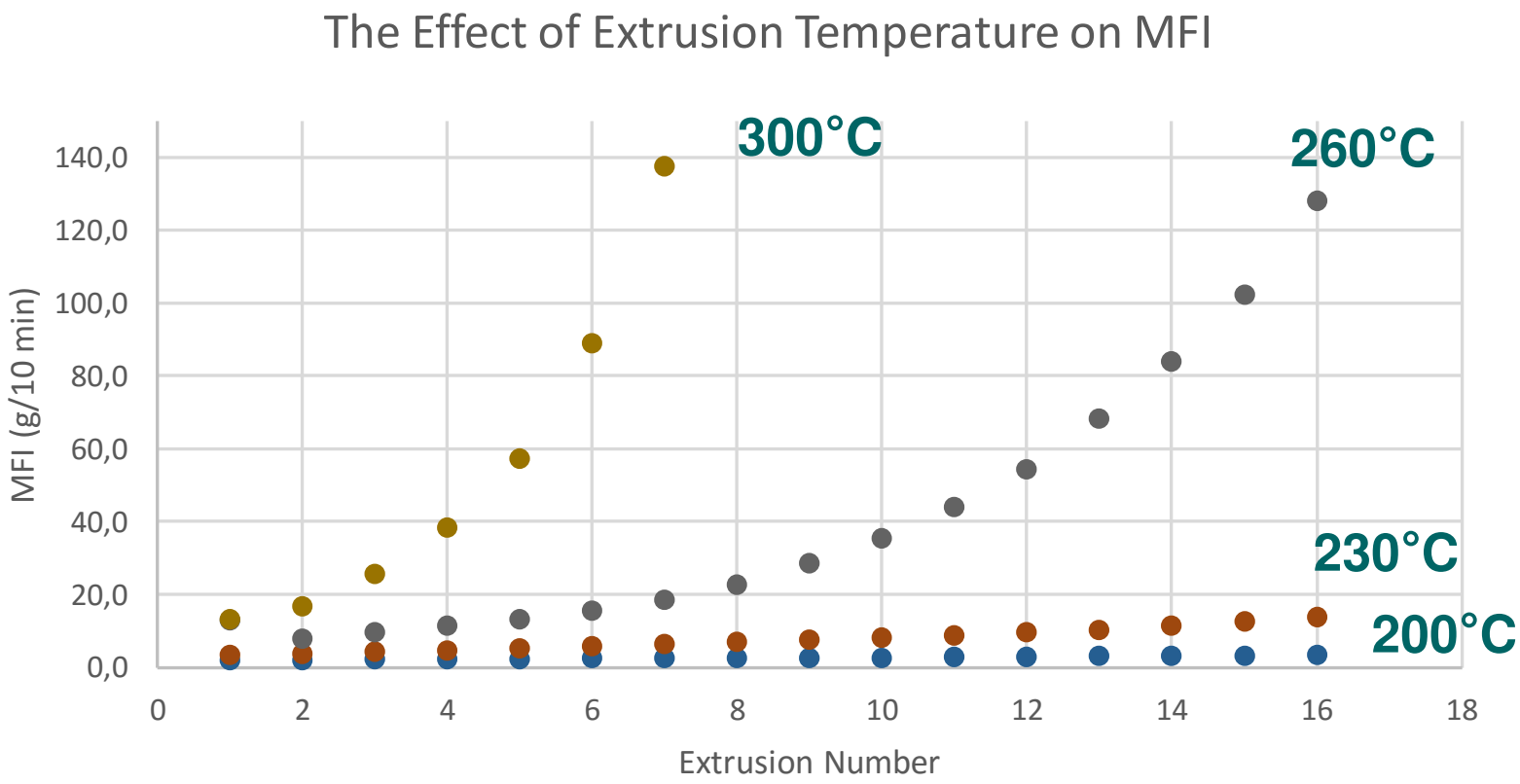
Test conditions & performance

- Polymer:
  - Polypropylene homopolymer stabilized with:
    - 0.05% Phenolic Antioxidant
      - EVERNOX10 EVERNOX 76, EVERNOX 3114, EVERNOX 1330
    - 0.05% EVERFOS 168
    - 0.10% Calcium Stearate

- Multiple extruded at 230°C (446°F)
  - Each formulation repeated at least three times, each time for 15 extrusions
  - Samples retained for **MFI, YI**, FTIR (carbonyl & vinylidene) and CL-OIt

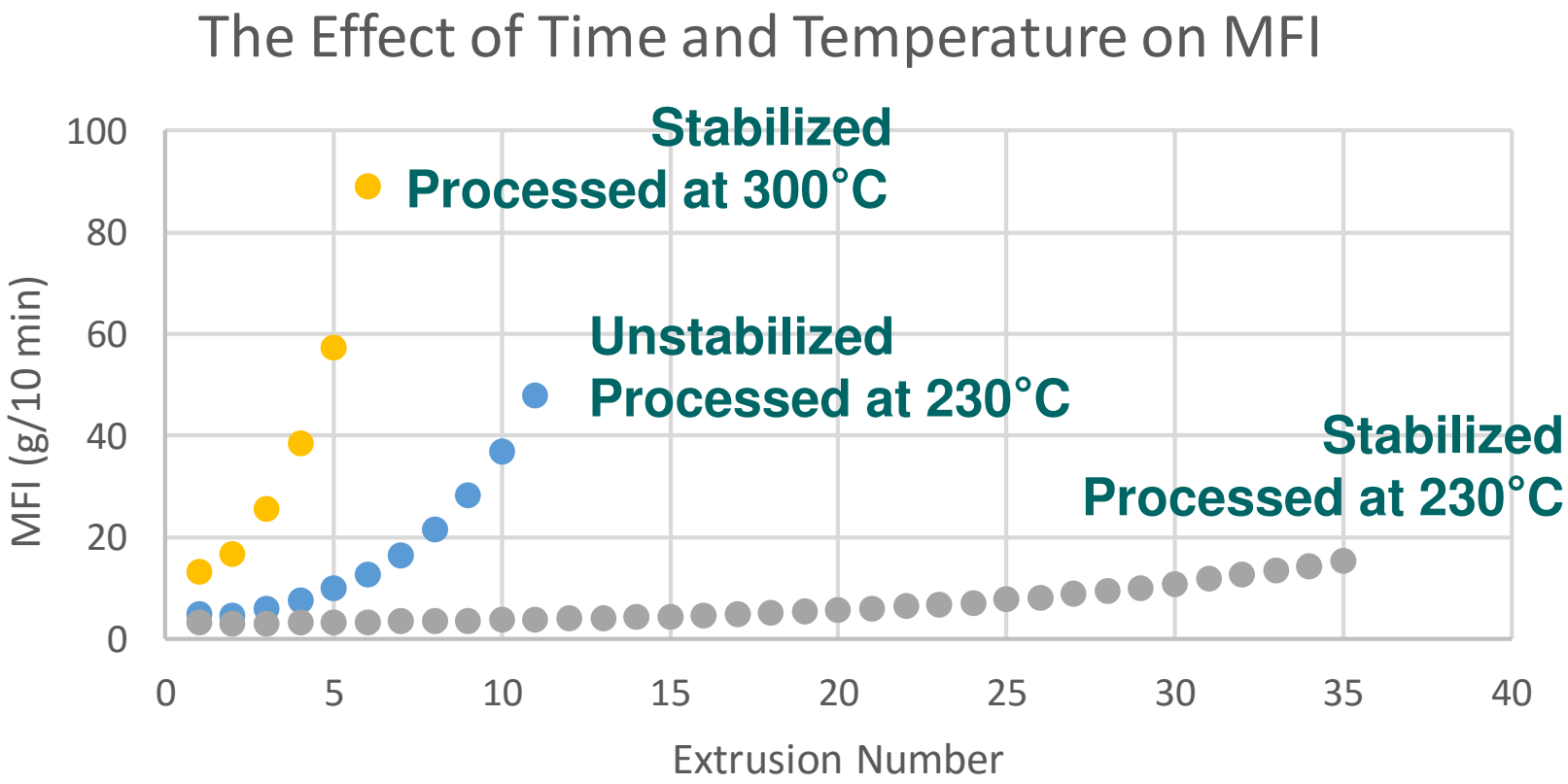
200°C / 392°F
230°C / 446°F
260°C / 500°F
300°C / 572°F

Extrusion Temperature on MFI



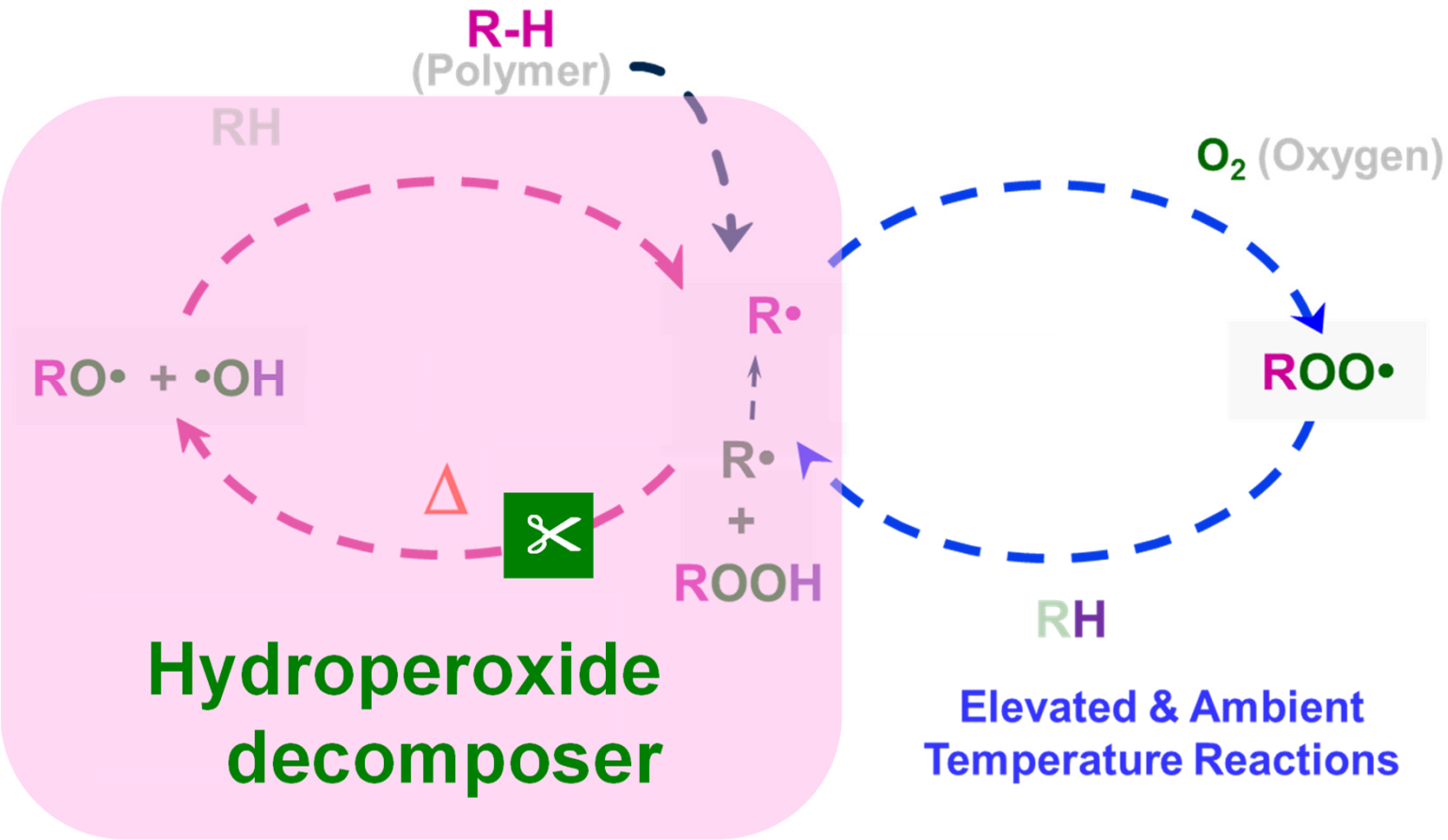
As expected degradation happens (much) faster at higher temperatures (and effect more noticeable with more extrusions)

Extrusion Time on MFI



Temperature has more of an effect on stabilization than extrusion time (at constant screw speed)

Hydroperoxide decomposers



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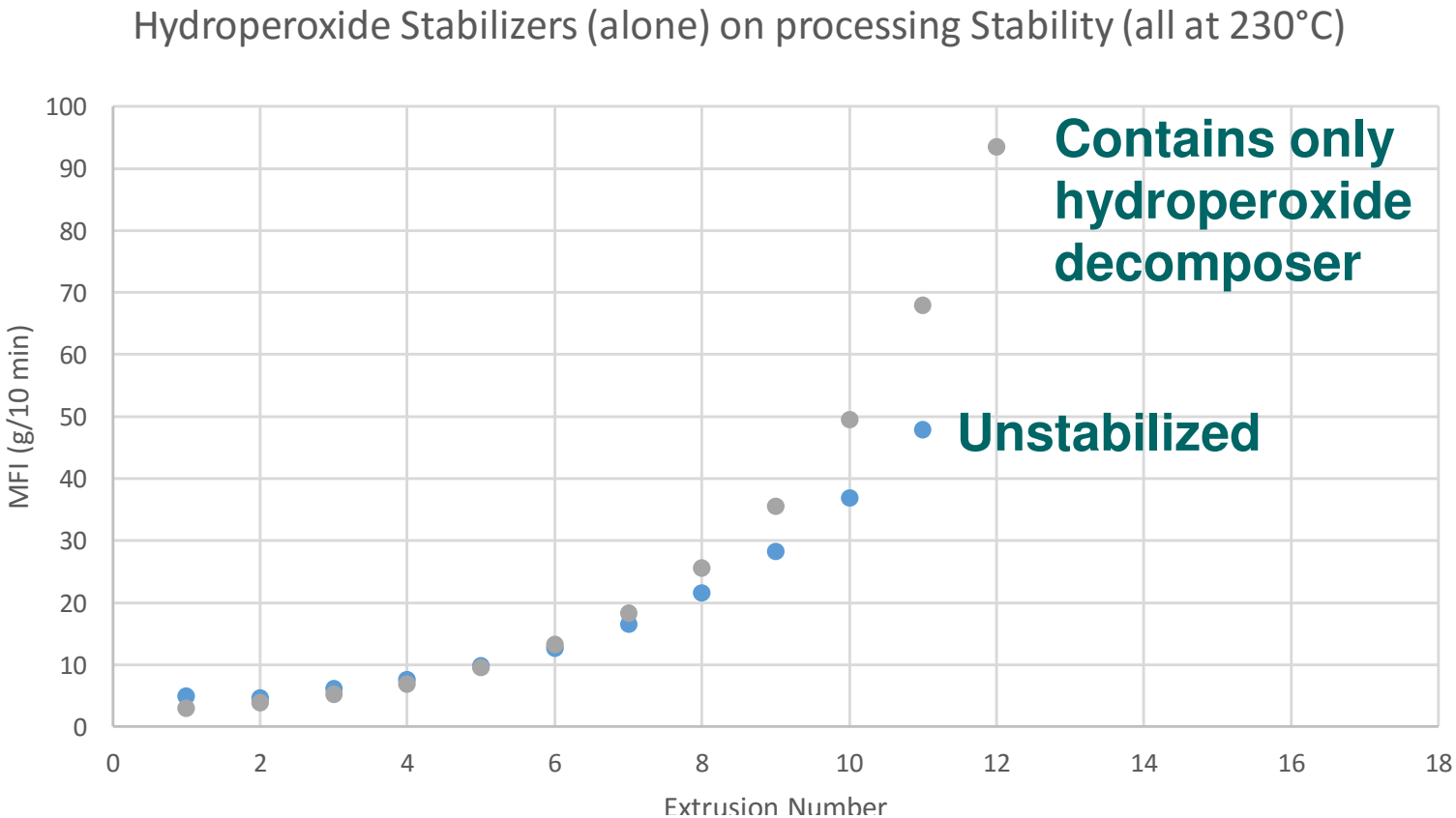

Systems containing only a hydroperoxide decomposer (and no chain-breaking antioxidant) have a similar stability to unstabilized PP

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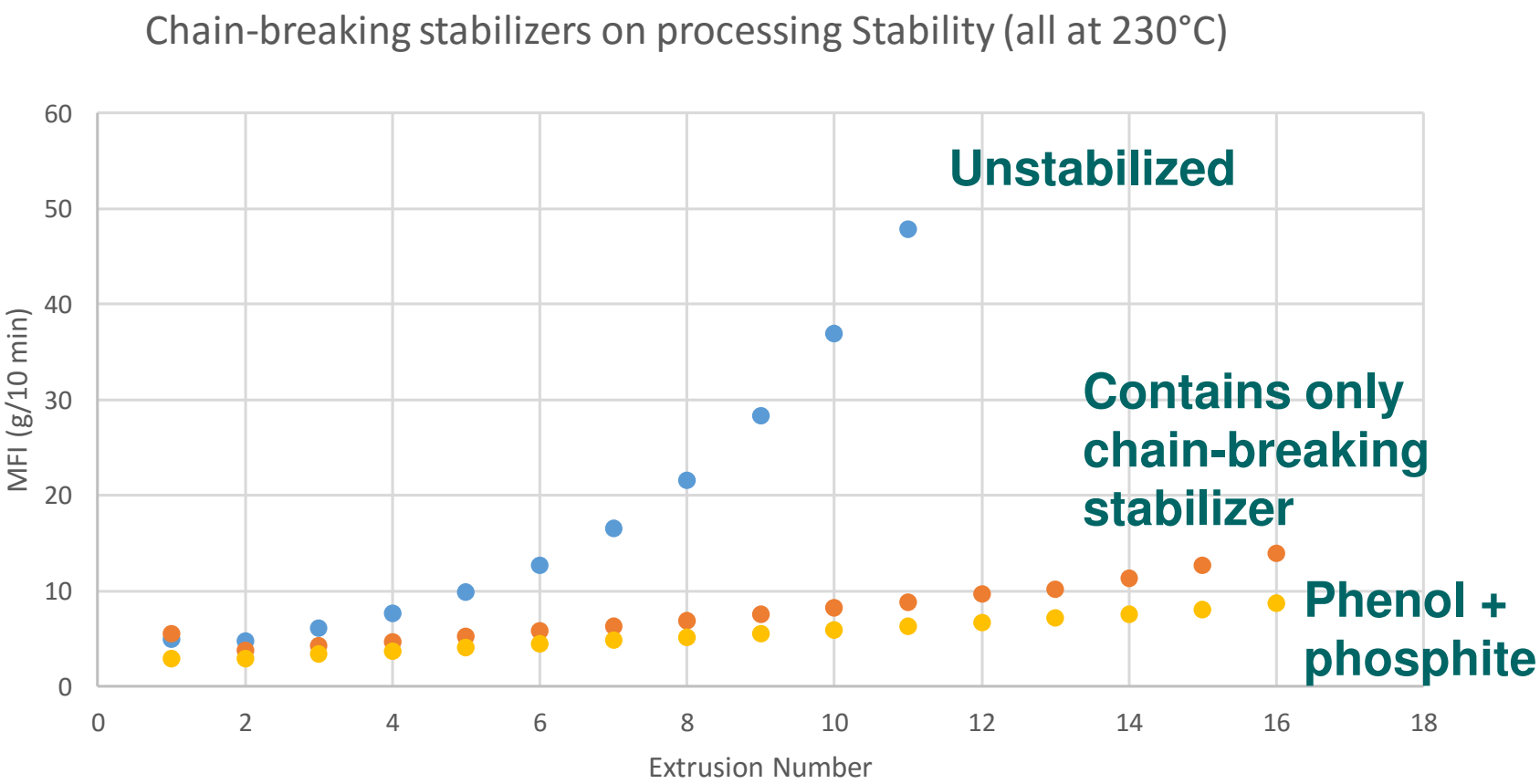
Chain-breaking stabilizers



Systems containing only a chain-breaking antioxidant have a similar processing stability to PP containing a phenol + phosphite system

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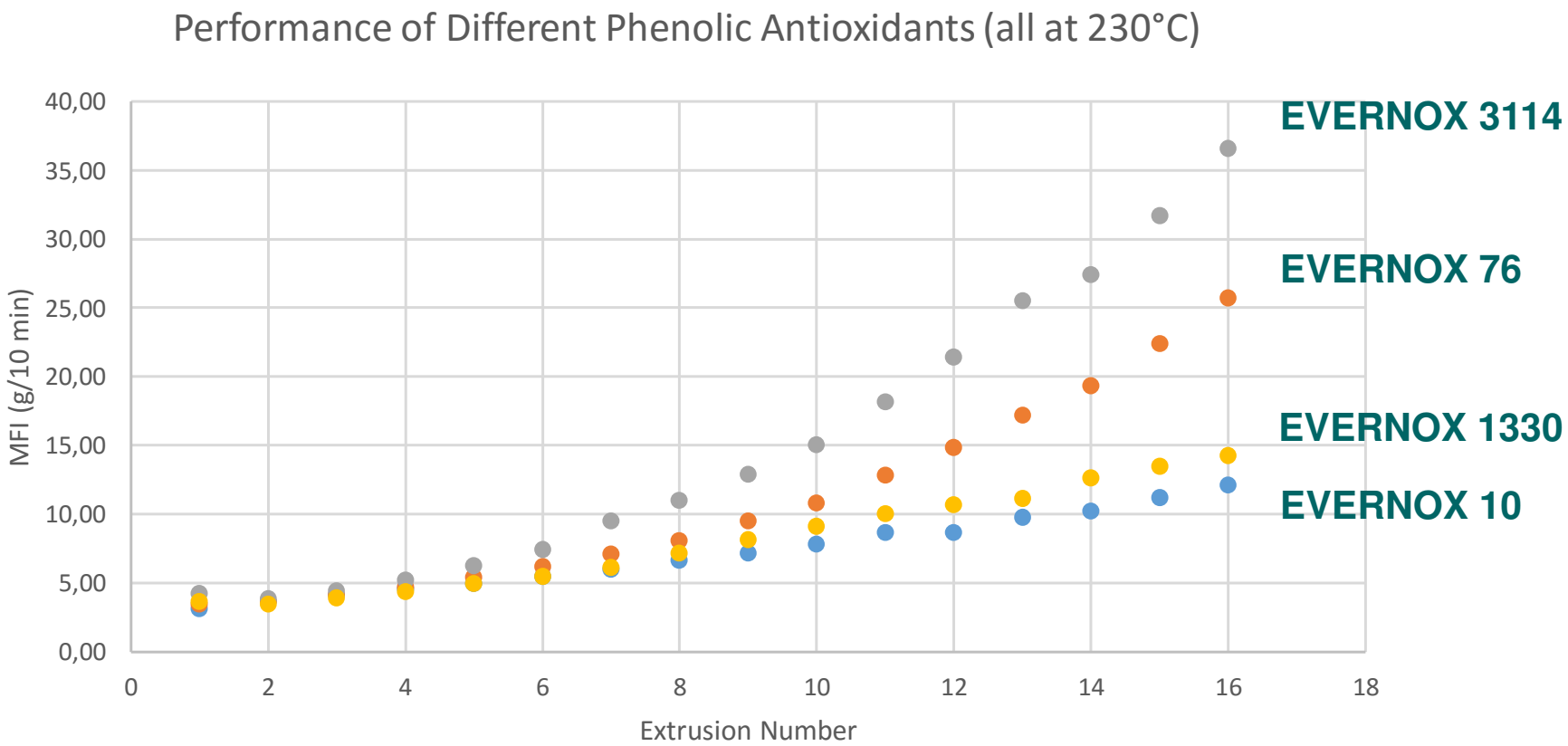
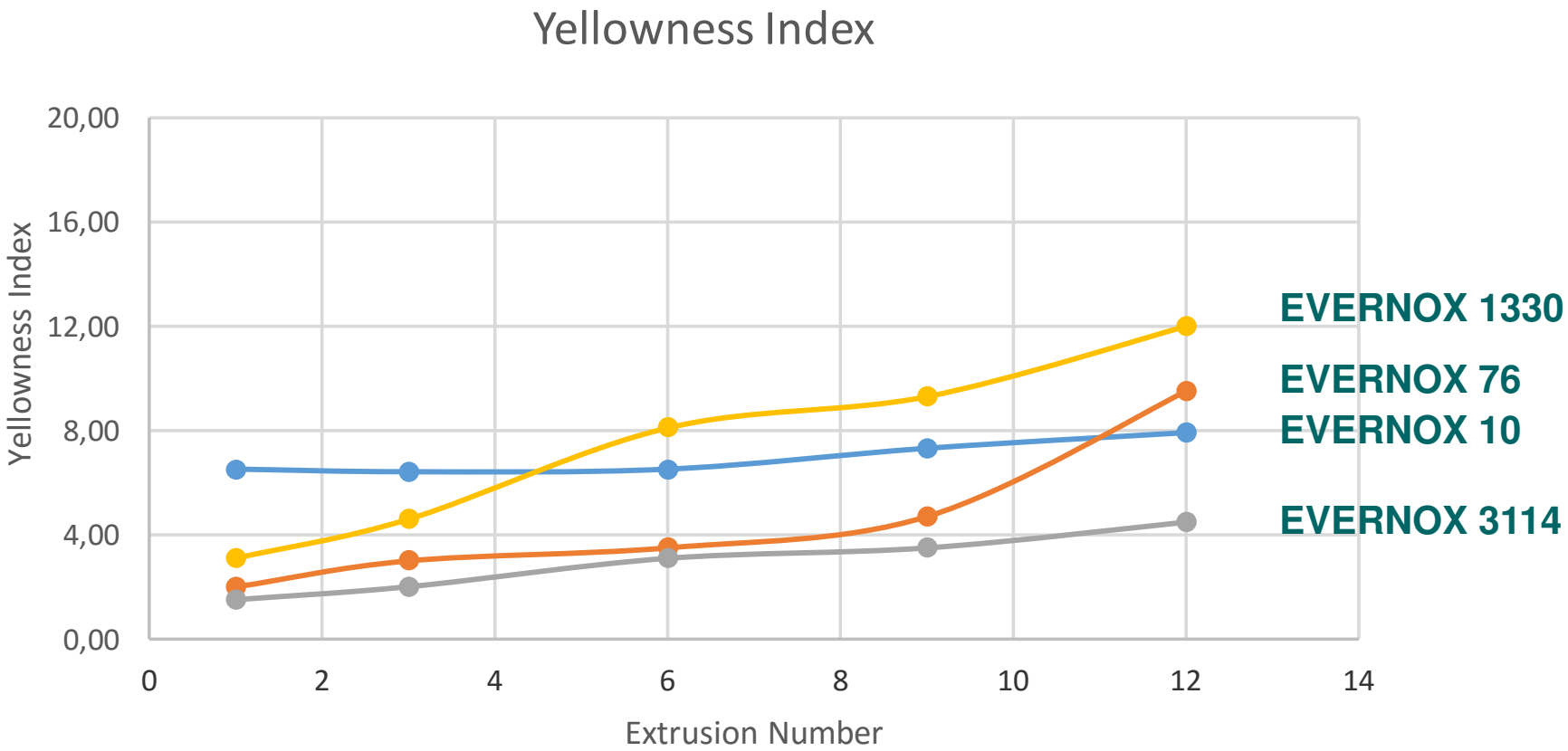
Different phenolic AO



Different phenolic antioxidants have different efficiencies as processing stabilizers (more apparent with longer processing times)

YI of different phenolic antioxidants



Color (YI) is often as important as stabilization efficiency and sometimes antioxidant selection must be based on this criterion

Conclusion

- Evaluating processing stability needs to take into account the expected ***processing temperature*** (and time)
- For processing stabilization it is important to have ***chain-breaking antioxidants*** (active at high temperatures)
- Processing stability is not always the main criterion for selecting a stabilizer (also color, migration, regulatory, etc.)

Thank you