EVERSPRING CHEMICAL COMPANY

Evaluating Processing Stability using MicroCompounding

...and how this helps us develop better extrusion grades!

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Overview

1. The importance of polymer stabilization during extrusion

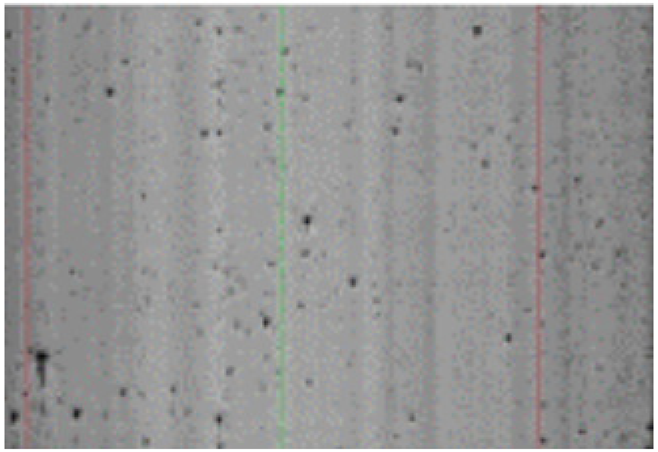
2. Evaluating Processing Stabilization

3. Batch re-circulating MicroCompounding

Without stabilization

Observe:

- Gels
- Black specks
- Breakages
- Die build-up
- Discoloration



This is caused by Degradation

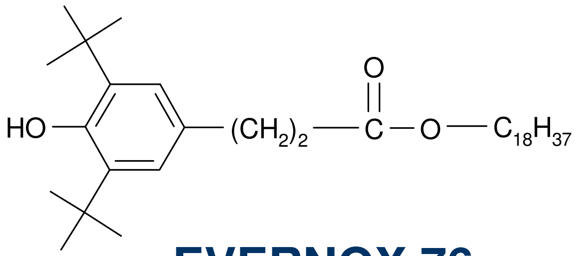
caused by changes to the polymer molecules (or polymer morphology)

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

Reducing Degradation

- **Stabilization** is maintaining those properties
  - or at least slowing down the rate of deterioration
- This is done by adding **Antioxidants** to the polymer
  - Either polymer producer or using a masterbatch

Many different Antioxidants commonly used in Polyolefins



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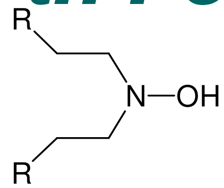

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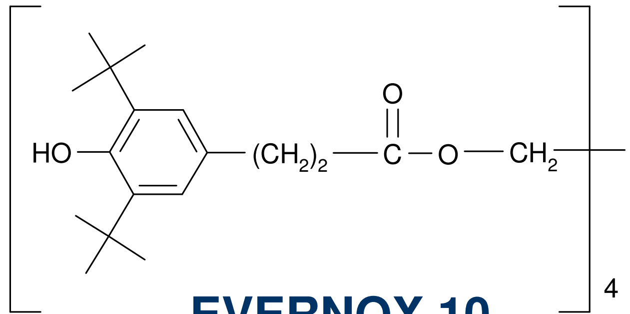

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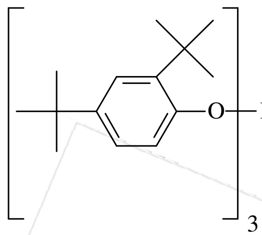
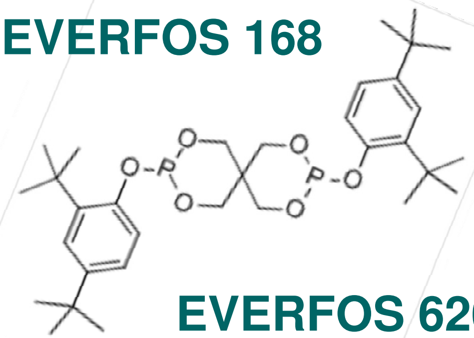


EVERFOS 168



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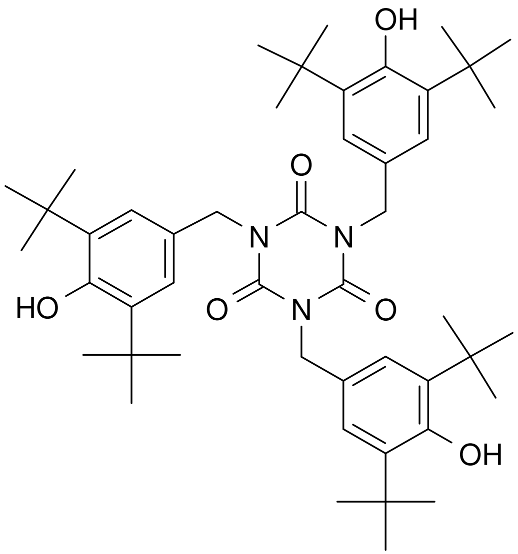

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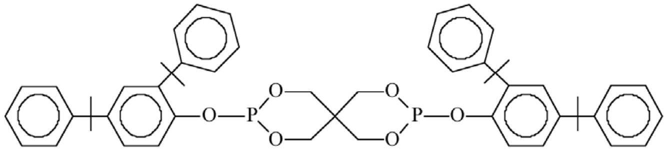
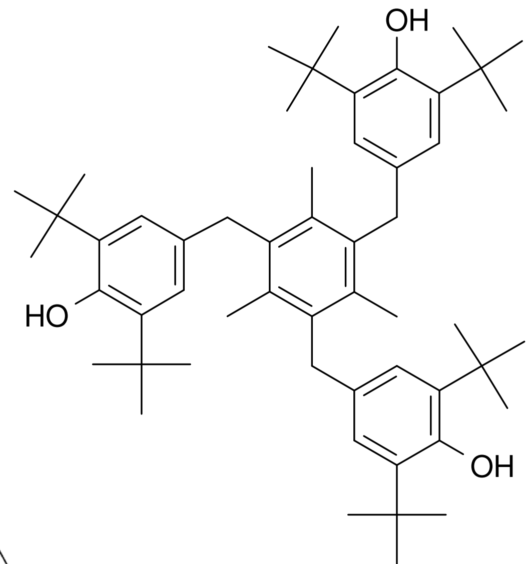


EVERFOS 9228



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Stabilizer Formulations

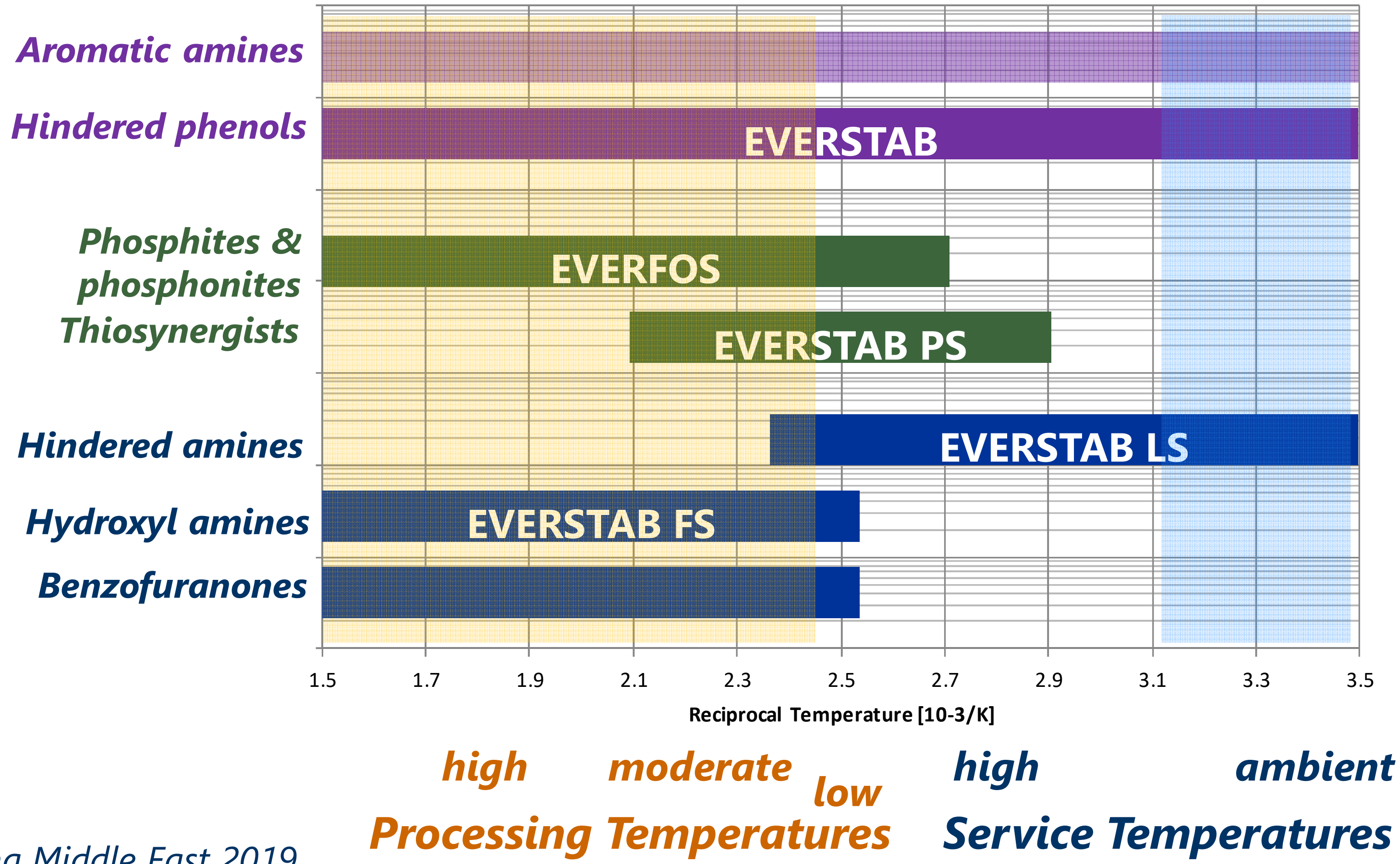
- Select antioxidants based on
  - compatibility with the polymer
  - stabilization conditions
    - **Processing at high temperatures (polymer melt)**
    - Service conditions (room / high temperature)
    - Outdoors (exposed to sun – UV light)
    - Exposure (including water, chemicals, acidic / basic)
  - required service life
  - regulatory requirements
  - cost

Classifying Antioxidants

- Primary (1°) antioxidants
  - Radical scavengers
    - e.g., phenolic antioxidants, hindered amines, lactones, hydroxylamines
- Secondary (2°) antioxidants
  - Hydroperoxide decomposers
    - e.g., phosphites, phosphates, thioesters / thioethers
- Synergistic combinations of 1° and 2° antioxidants are commonly used in PO

EVERSPRING Antioxidants

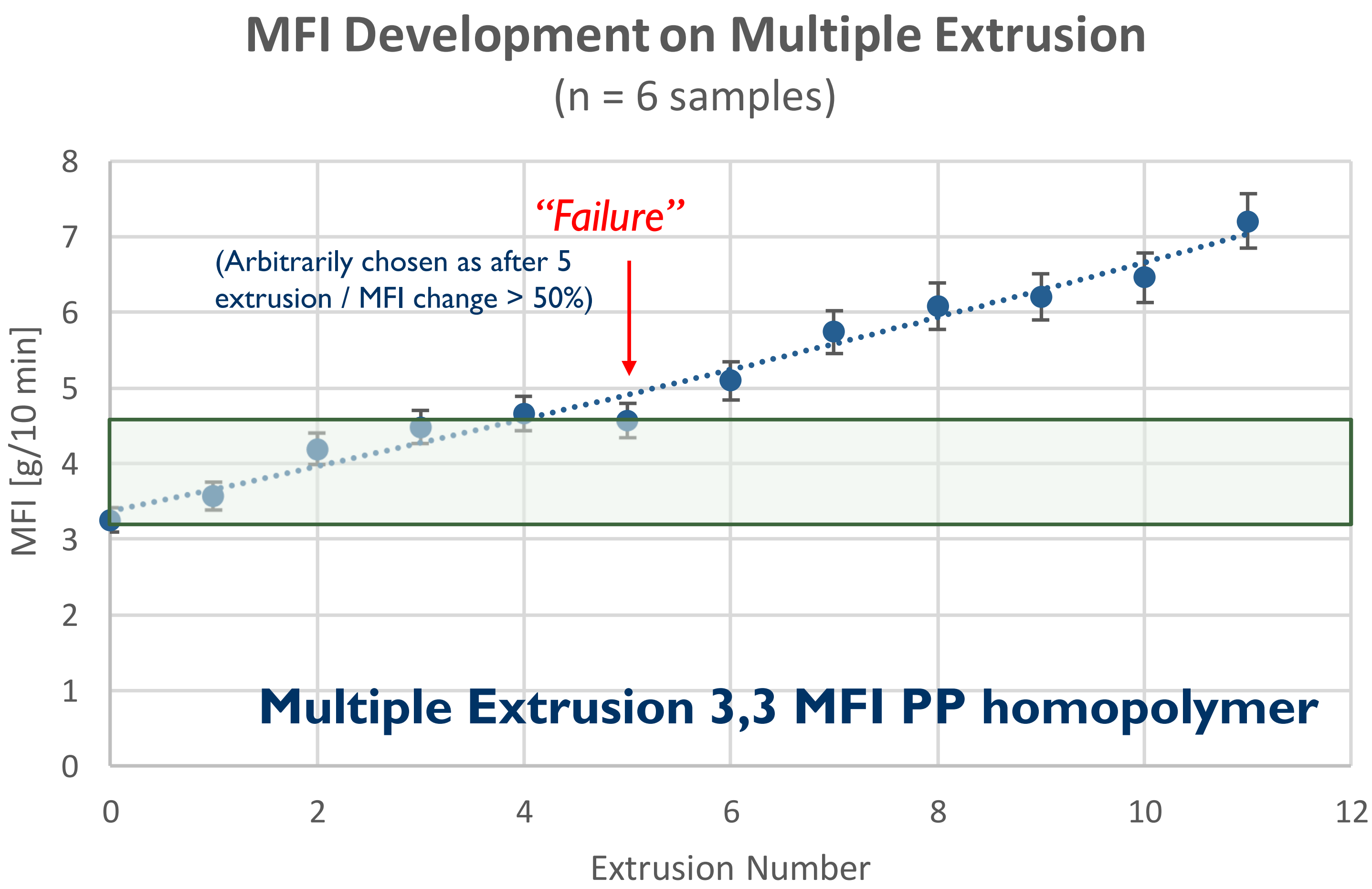
Main Stabilizer Chemistries



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



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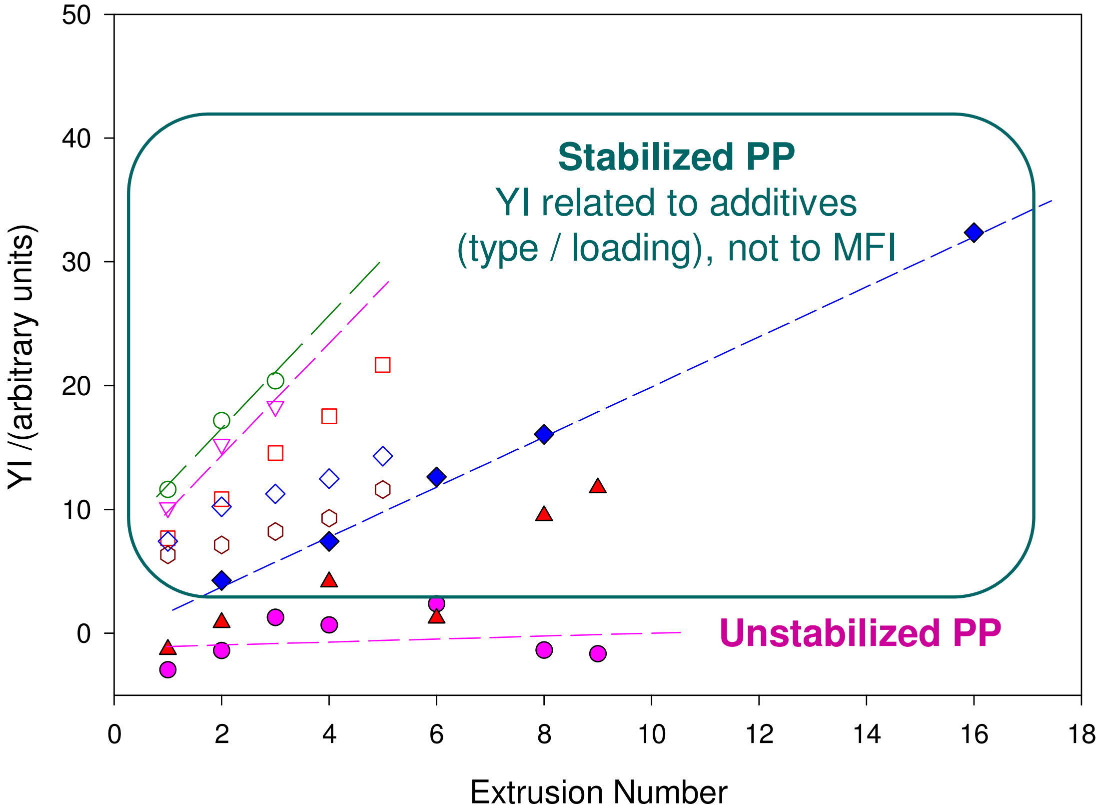
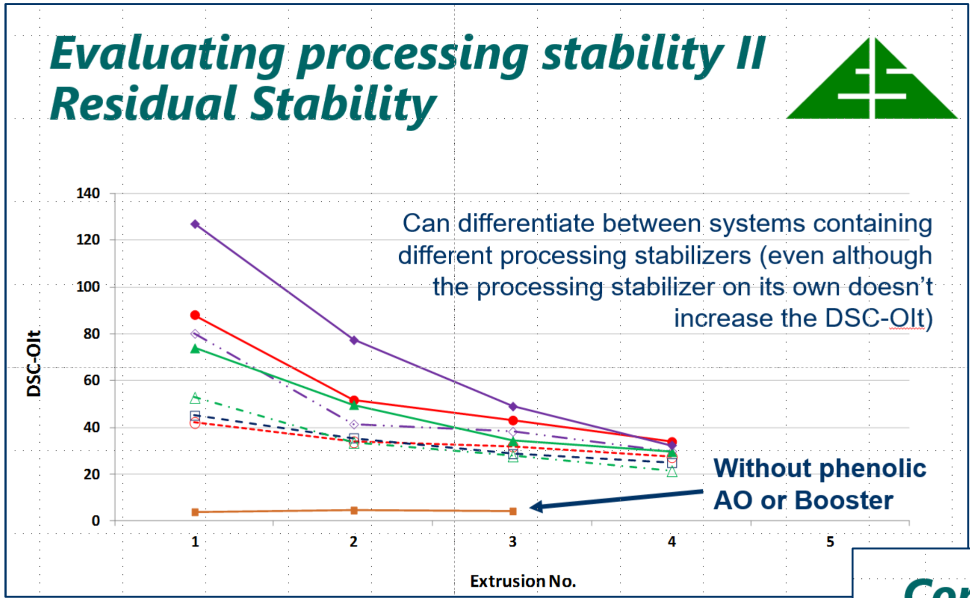
Extruded at 230°C
Brabender PL2000-6 single screw extruder (19 mm, 25D)

Yellowness Index of Multiple extruded PP

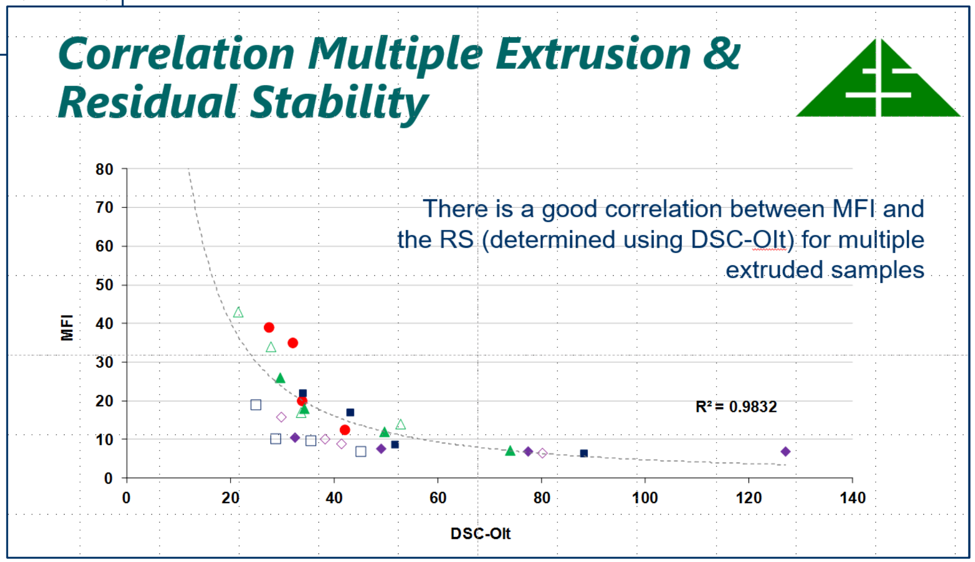


Color is an important property in itself, but it does not correlate to degradation (especially when different stabilizers are used)

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)

MicroCompounding

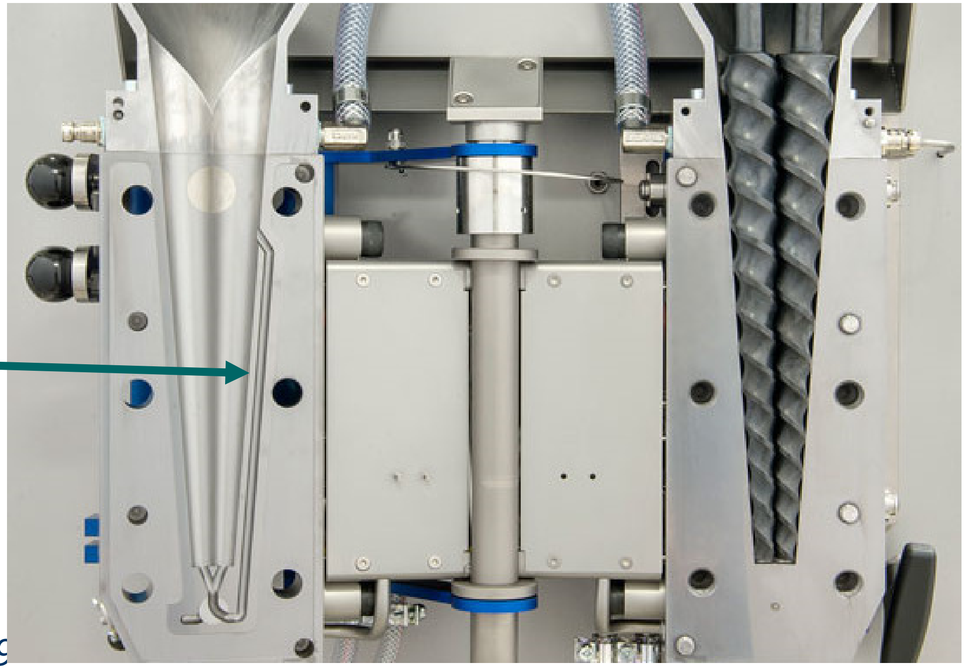
- Novel alternative approach to multiple extrusion

- Processing evaluated using a **DSM-Xplore MicroCompounder**
  - 15 cm^3 volume = 13,5 g polymer
  - can be operated in continuous extrusion mode or in a batch-recycling mode
  - Continuous extrusion = small extruder

MicroCompounding

- DSM-Xplore MicroCompounder
  - conical co-rotating vertical extruder with recycling of melt stream

Melt stream recycled



MicroCompounding Approach

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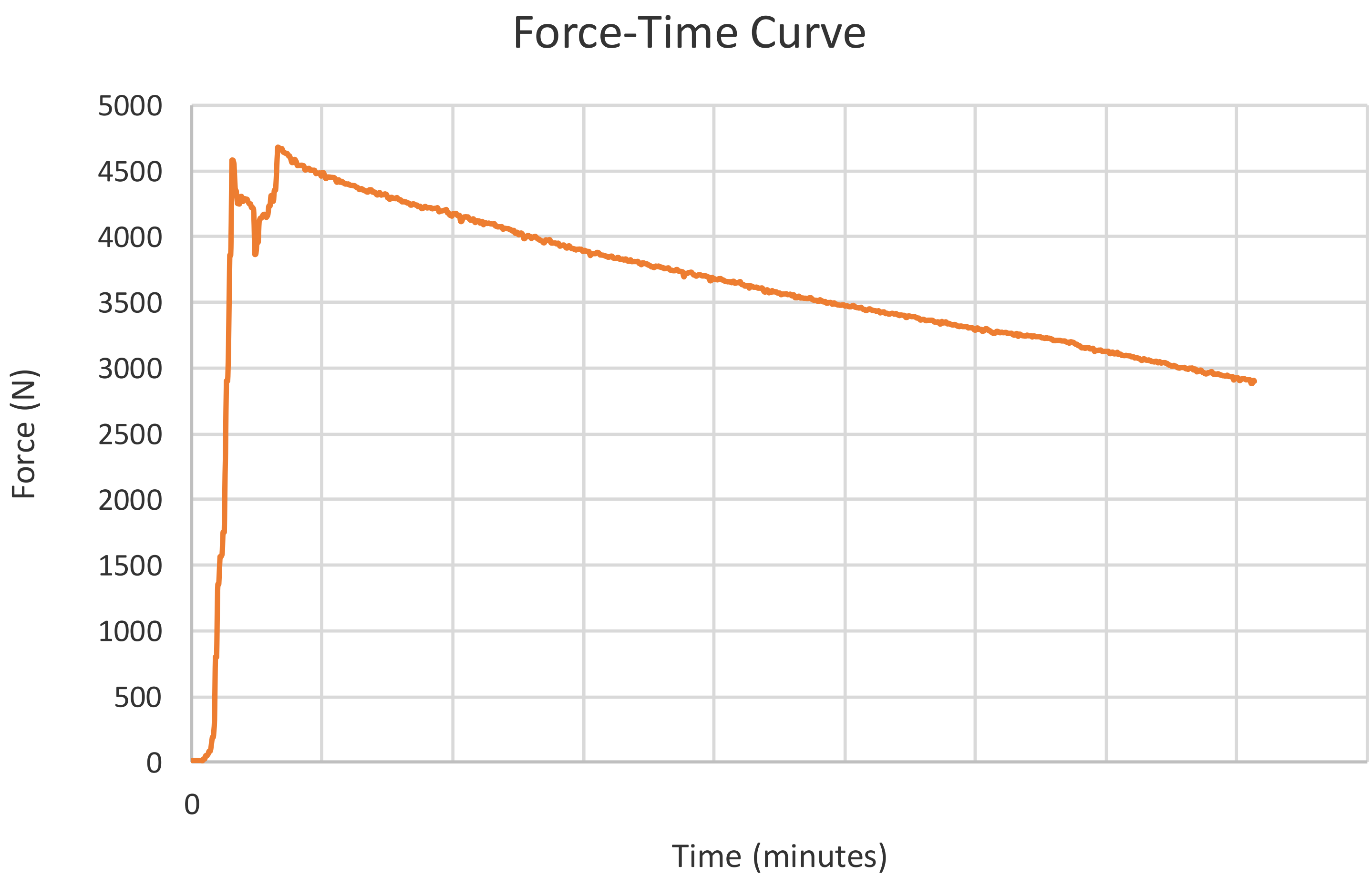
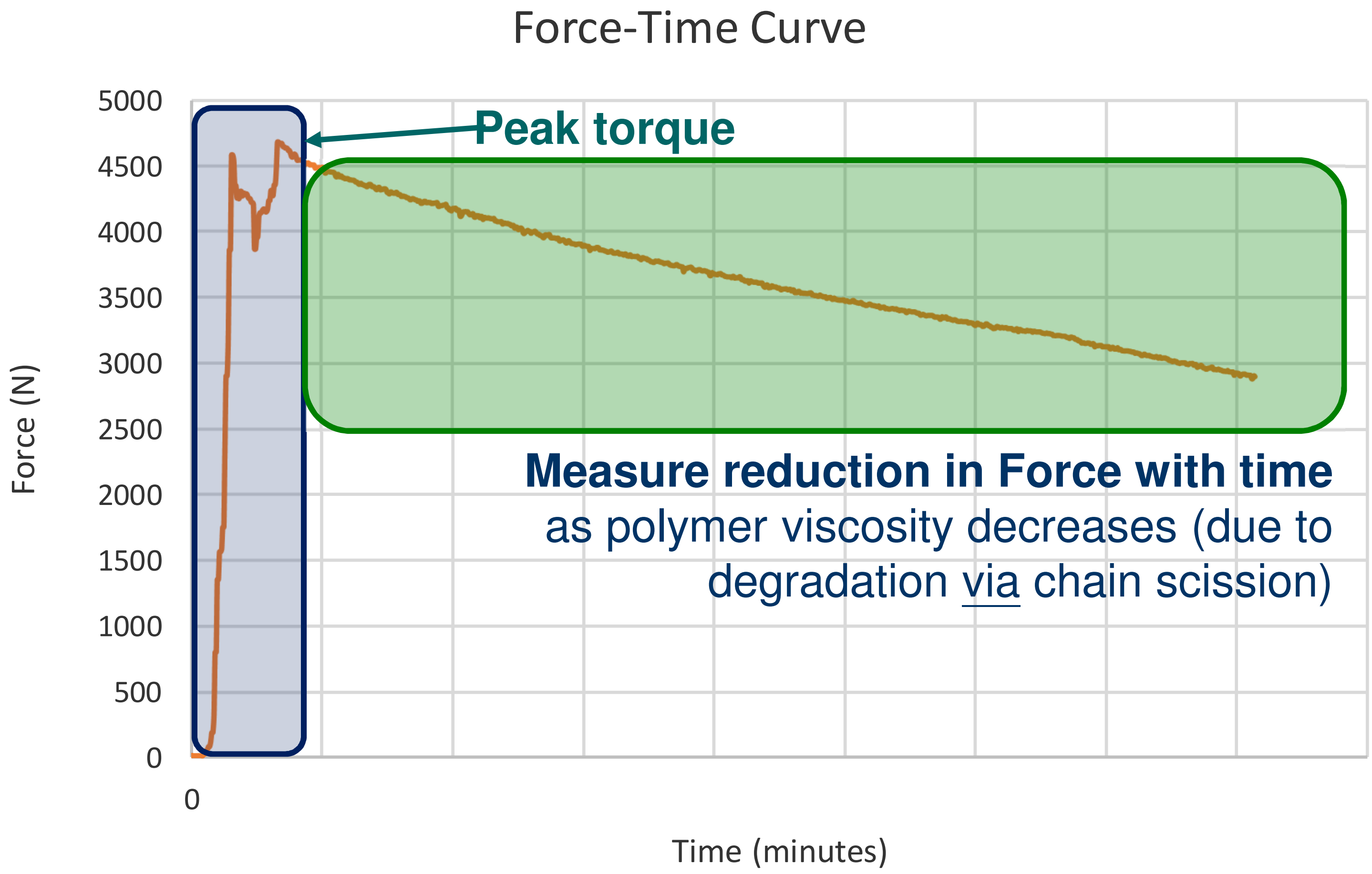
- polymer re-circulated for a certain time (typically ten minutes)
- samples retained after each extrusion for analysis
- monitor changes to ***Force*** to maintain screw speed (i.e., melt viscosity), FTIR, YI, ***residual stability***, etc.

MicroCompounder Data

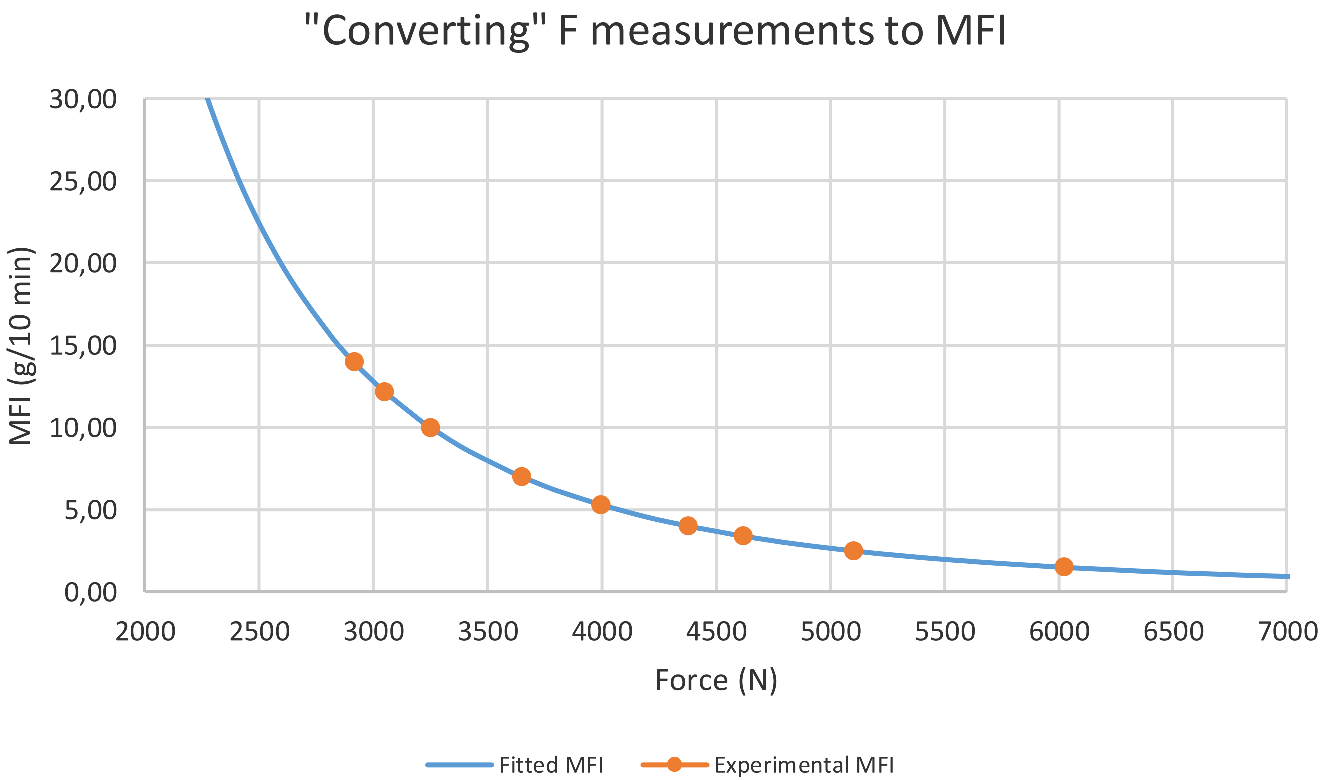


MicroCompounder Data

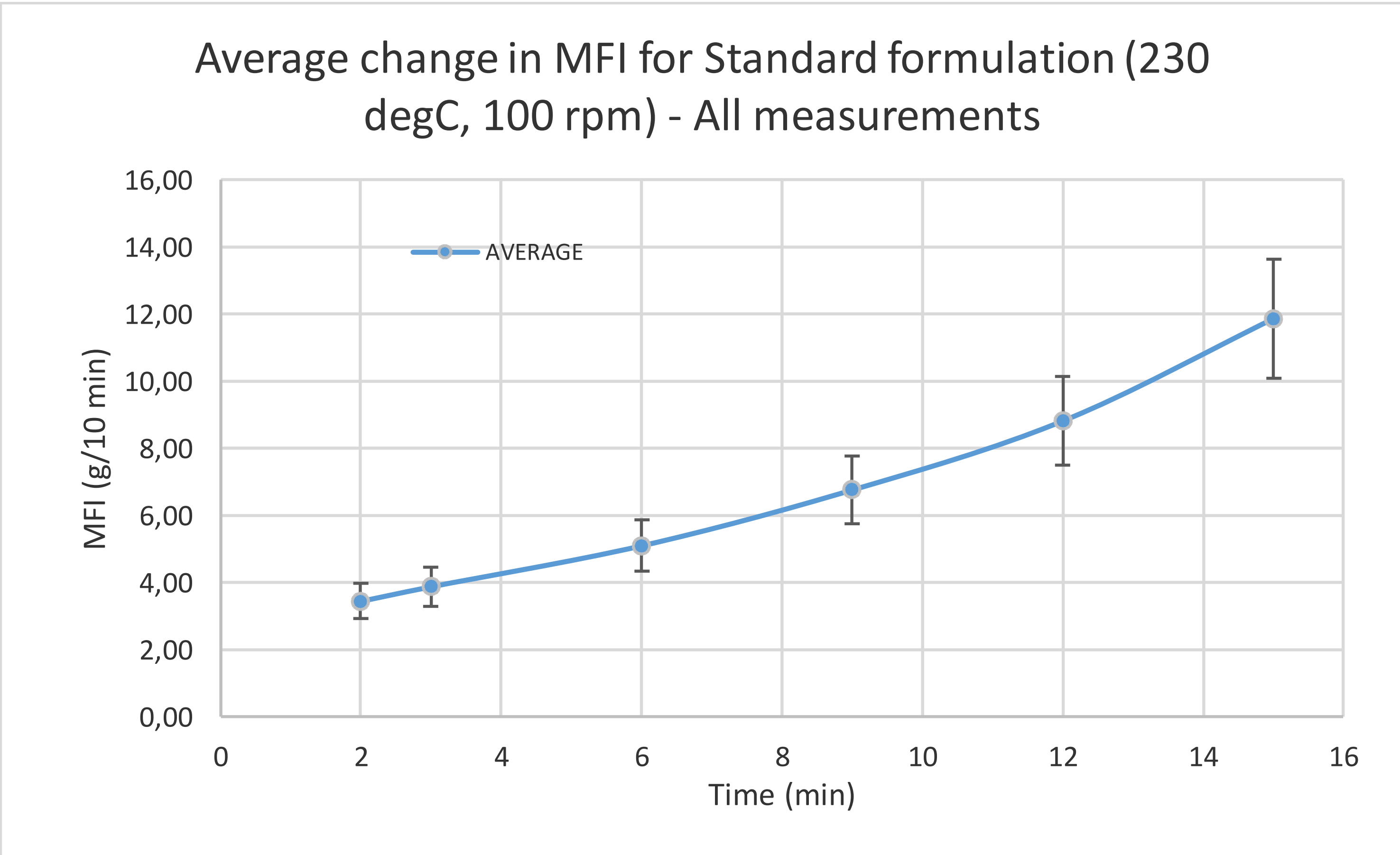


Converting Force to MFI

- Measure Force using samples of known (measured) MFI



Converting Force to MFI



"Extrusion (residence) Time"

- In multiple extrusion you extrude a certain number of times (pelletizing after each extrusion)
  - from the literature residence time can be anything from 20 seconds to 5 minutes!

- The residence time on a 19 mm single screw extruder running at 100 rpm has previously been determined to be approximately 1 minute

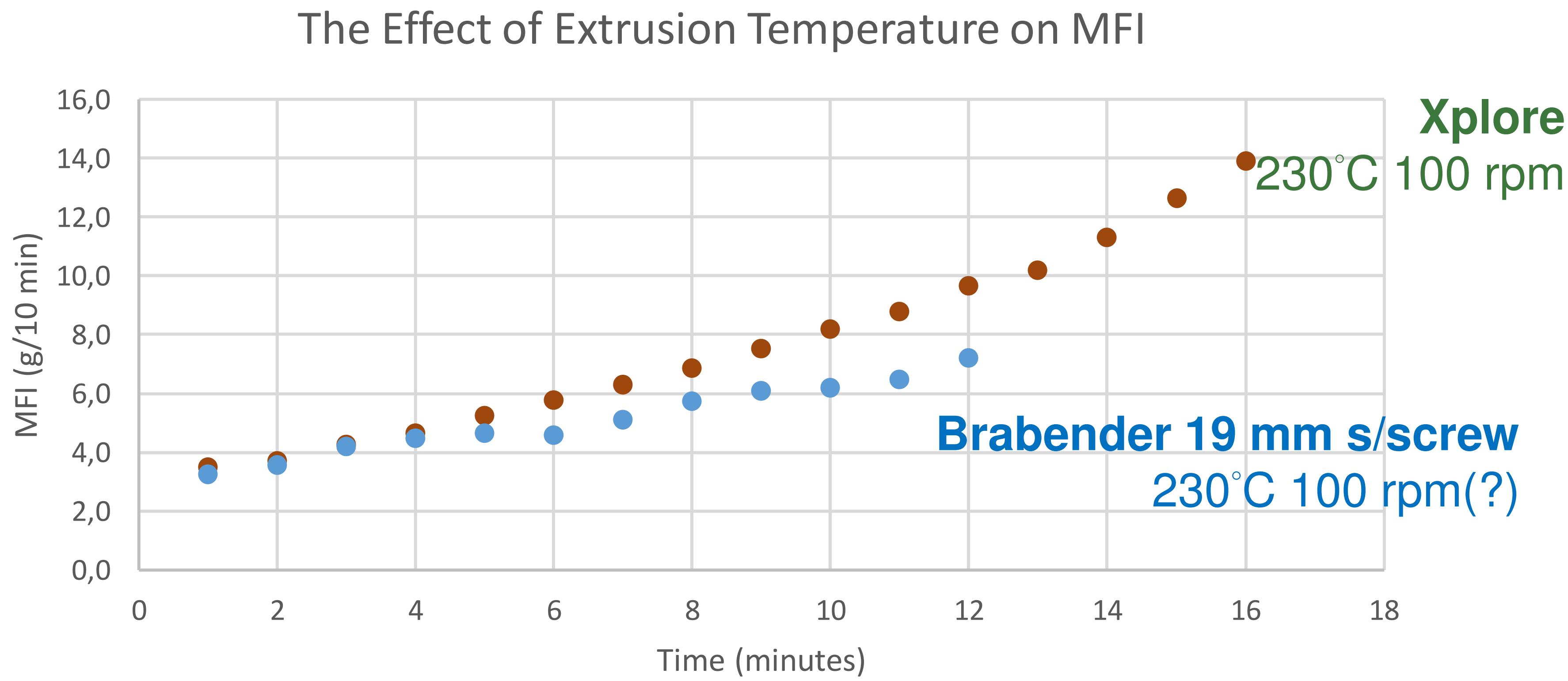
"Extrusion (residence) Time"

- The MicroCompounder circulates the melt for a certain time before extruding the material
  - This extrudate was then further tested

- We chose to circulate the material for up to 15 minutes, and considered this to be the equivalent of 15 extrusions.

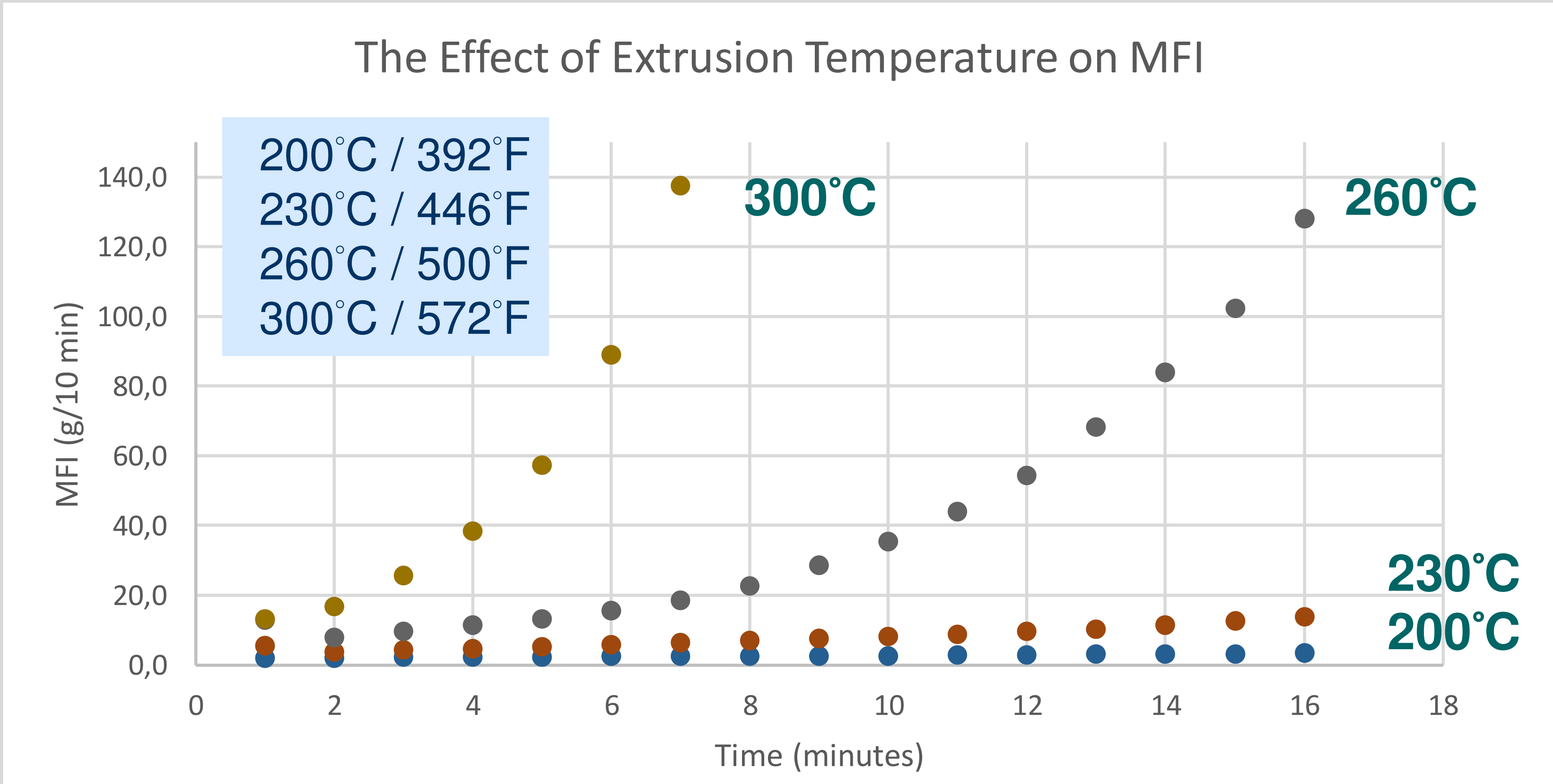
- We also ran the material for shorter times to approximate 3-, 6-, 9- and 12-one-minute extrusions
  - each "extrusion" was taken to be 3 minutes

Multiple Extrusion (single screw) vs. MicroCompounder



So our 15 minutes is approximately equivalent to 15 1-minute extrusions

Influence of Conditions - Temperature

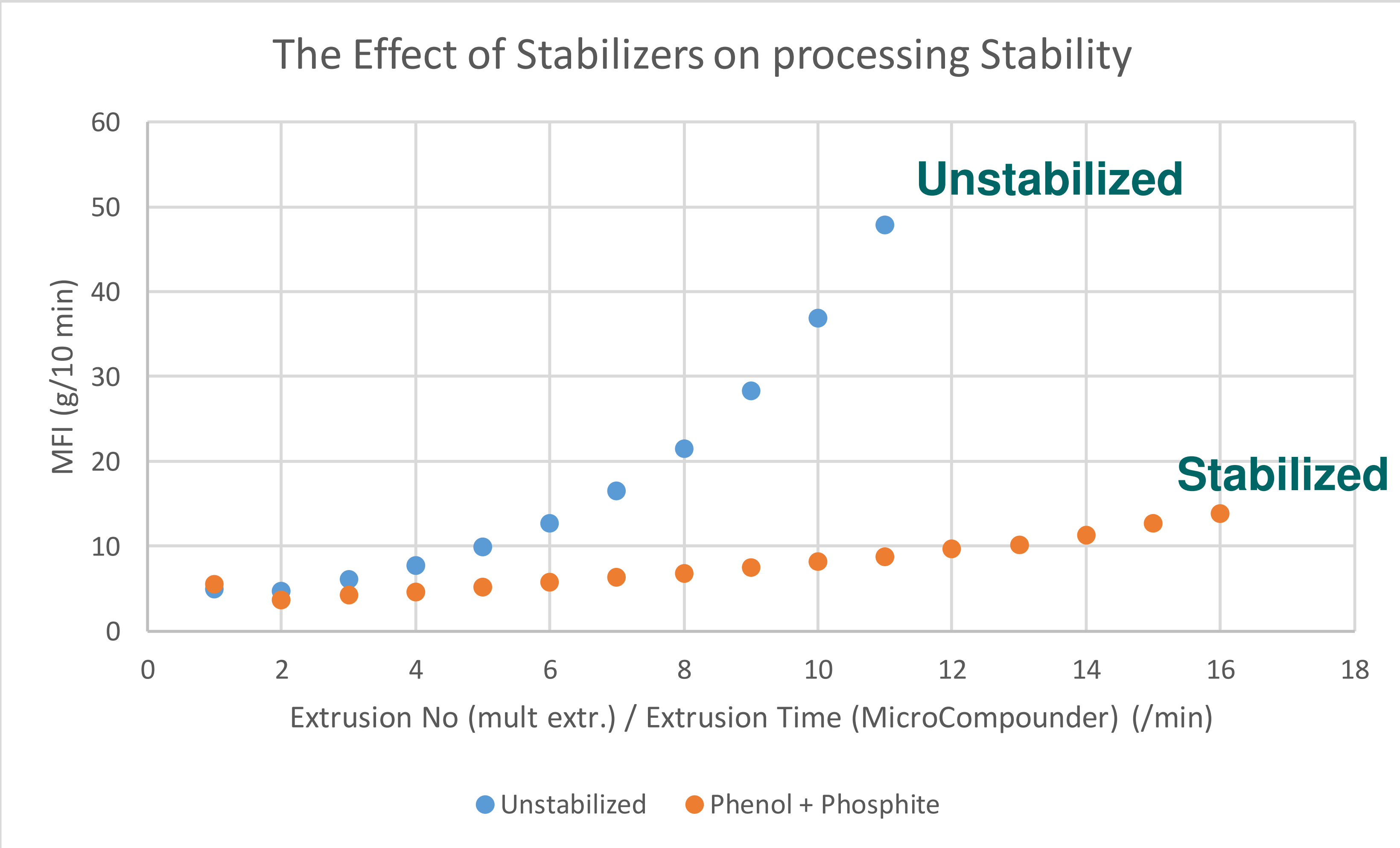


As expected degradation happens (much) faster at higher temperatures (and effect more noticeable with more extrusions)

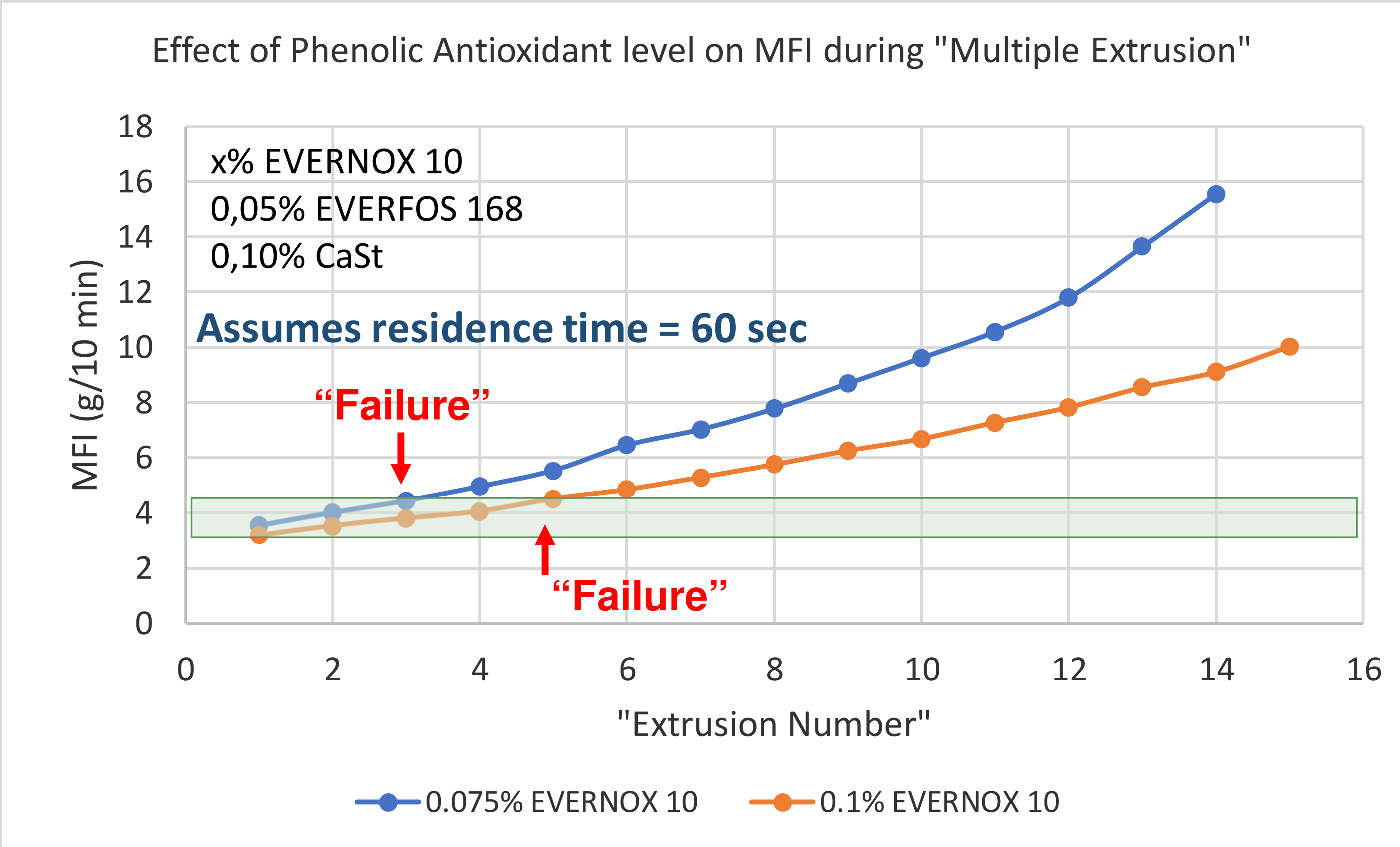
Test conditions & performance

- Polymer:
  - Polypropylene homopolymer stabilized with:
    - Phenolic Antioxidant
      - EVERNOX10 EVERNOX 76, EVERNOX 3114, EVERNOX 1330
    - EVERFOS 168
    - Calcium Stearate
- Multiple extruded at 230°C (446°F) at 100 rpm for 15 minutes (ca. 15 x 1 min extrusion passes)
  - Each formulation repeated at least three times

Importance of Stabilizers



Antioxidant loading



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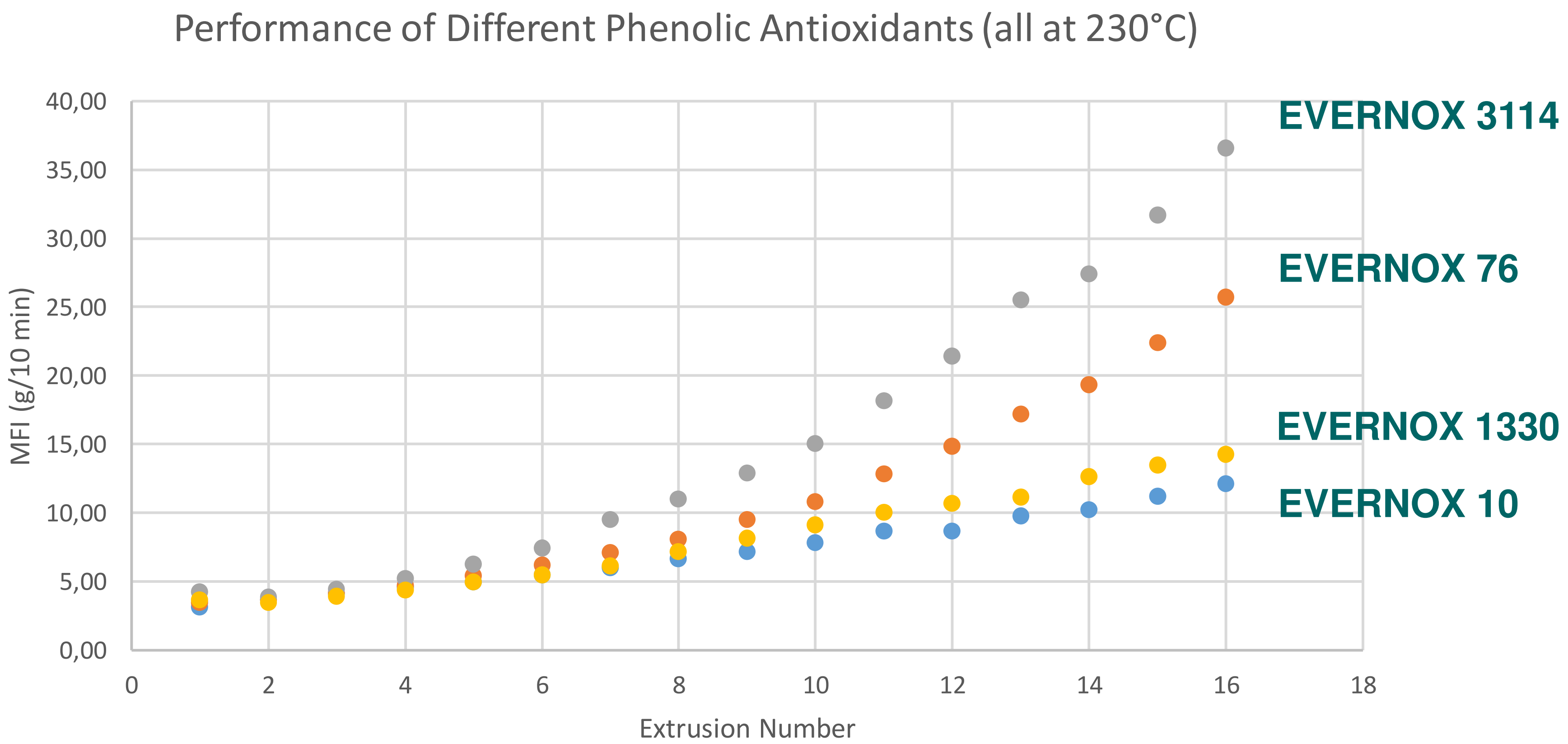
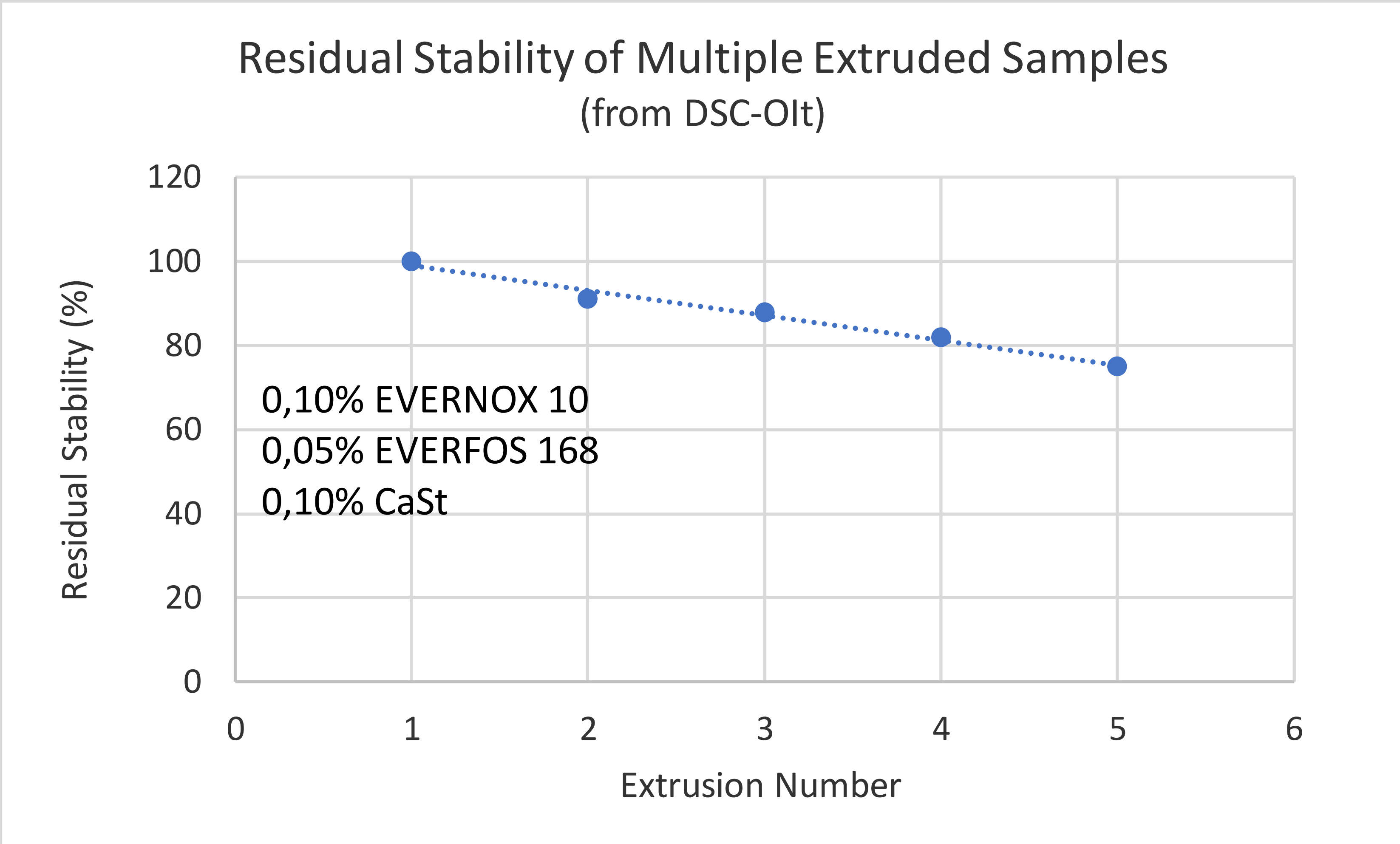
Failure arbitrarily chosen as MFI change > 50%

Different phenolic AO



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

Residual Stability



Comparison of Approaches

Traditional-scale Multiple Extrusion

- Large samples required
  - 1-3 kg depending on extruder and intended testing
- Time consuming
  - typically > 1hr /extrusion pass
- Off-line testing MFI
- Samples suitable to test residual stability, YI, FTIR
- Can test mechanical properties (large samples)

Batch re-circulating MicroCompounding

- Small samples
  - Less than 50 g, down to 15 g
- Fast
  - typically < 30 min /formulation
- On-line measurement “MFI”
- Samples suitable to test residual stability, YI, FTIR
- No reliable determination of mechanical properties

High Throughput Screening

- Rapid testing allows for larger sets of samples to be evaluated
  - different antioxidants (two or more in a formulation)
  - different total antioxidant level loadings
  - different ratios of 1°: 2° antioxidants
  - the effect of different acid scavengers / slip additives / antistatics / etc.
  - different processing conditions (melt temperature / residence times)

Scaling-Up for BOPP

- Made use of a factorial experimental design to evaluate:
  - 3 phenolic antioxidants
  - 3 phosphite antioxidants
  - 1 booster
- Processing based on temperature and residence times of commercial BOPP line
- Most promising formulations scaled up for pilot-plant trials

Conclusion

- The use of MicroCompounding using batch re-circulating gives reproducible results for evaluating processing stability and results are comparable with multiple extrusion
    - allows for both statistical confidence in results and, because of small samples and speed of evaluation, the use of statistically designed experiments

Thank you

Products*: Primary Antioxidants

- Primary antioxidants react with peroxy ($ROO^{\bullet}$) radicals to terminate the oxidation process, providing long term stability to polymers as well as protection during processing. Most primary antioxidants are sterically hindered phenols.

Phenolic Antioxidants		CAS Number
Evernox 10	General purpose providing excellent long term thermal stability in all polyolefins	6683-19-8
Evernox 76	General purpose with good compatibility in PE	2082-79-3
Evernox MD1024	High performance with metal (Cu) deactivator	32687-78-8
Evernox 1330	High performance with low extractability (pipes)	1709-70-2
Evernox 3114	High performance with low discoloration (fibres)	27676-62-6
Evernox 1520	High performance suitable for use in XLDPE (wire and cable) without affecting cross-linking	110553-27-0

** For a complete list contact Everspring Middle East*

Products*: Secondary Antioxidants

- Secondary antioxidants react with hydroperoxides (ROOH) , preventing the hydroperoxides from decomposing to form peroxy radicals. Secondary peroxides provide processing stability to polymers and are also called "processing stabilizers". Most secondary antioxidants are phosphites or phosphonites although thioesters or thioethers are also used in certain applications.

Phosphite Antioxidants		**CAS Number**
Everfos 168	General purpose, hydrolytically stable, providing good processing stability	31570-04-4
Everfos 626	High performance processing stabilizer	26741-53-7
Thioester Antioxidants		**CAS Number**
Everstab PS800	Improved long term thermal stability when used with phenolic antioxidants in high temperature applications	123-28-4
Everstab PS802	Improved long term thermal stability when used with phenolic antioxidants in high temperature applications	693-36-7

** For a complete list contact Everspring Middle East*

Products: Antioxidant Blends*

- It is well known that blends of high performance hindered phenolic antioxidants used together with phosphites act synergistically to provide improved polymer stability.

Phenol-Phosphite Antioxidant Blends			
Evernox B110	1:1	Evernox 10: Everfos 168	"B225"
Evernox B210	1:2	Evernox 10: Everfos 168	"B215"
Evernox B310	1:3	Evernox 10: Everfos 168	"B220"
Evernox B410	1:4	Evernox 10: Everfos 168	"B561"
Evernox B201	1:2	Evernox 76: Everfos 168	"B921"
Evernox B401	1:4	Evernox 76: Everfos 168	"B900"

** For a complete list contact Everspring Middle East*

Products: Light Stabilizers*

- Hindered amine light stabilizers (HALS) react with the radicals formed by high energy ultraviolet (UV) light and terminate the oxidation process. In addition to providing light stability HALS also improve the long term thermal stability of polymers.

Hindered Amine Light Stabilizers		**CAS Number**
Everstab LS 622	General purpose low molecular weight tertiary-amine HALS for low color applications	70198-29-7
Everstab LS 944	General purpose high molecular weight secondary-amine HALS	71878-19-8
Everstab LS 770	High performance monomeric secondary-amine HALS	52829-07-9
Everstab LS 119	High performance high molecular weight tertiary-amine HALS providing good long term stability	106990-43-6
Hindered Amine Light Stabilizer Blends		
Everstab LS 783	1:1 Everstab LS 622: Everstab LS 944	

** For a complete list contact Everspring Middle East*

Products*: Light Stabilizers

- Ultraviolet (UV) absorbers stabilize polymers by absorbing the harmful UV light preventing the formation of radicals.

Ultraviolet Absorbers (UVA)		CAS Number
Everstab 326	General purpose benzotriazole UVA with broad food contact approvals	3896-11-5
Everstab 327	General purpose benzotriazole UVA	3864-99-1
~~Everstab 328~~	~~General purpose benzotriazole UVA with good color~~	~~25973-55-1~~
Everstab 234/900	High performance benzotriazole UVA for high temperature applications (low volatility)	70321-86-7
Everstab 360	High performance benzotriazole UVA for high temperature applications	103597-45-1
Everstab 5411	High performance benzotriazole UVA	3147-75-9
Everstab P	High performance benzotriazole UVA	2440-22-4
Everstab 531	General purpose benzophenone UVA with excellent compatability in PE	1843-05-6

** For a complete list contact Everspring Middle East*