Fluoropolymer Polymer Processing Additive - Antiblock Interactions

Madhusudan Chari, January 2014 for SPE Polyolefins 2014

Fluoropolymer Processing Additives (PPAs) in Melt Processing

LLDPE w/o PPA

LLDPE with PPA

- Elimination of Melt Fracture
- Reduction in Operating Pressure
- Reduction of Die Build-Up
- Reduction in Gel Formation
- Faster Color Transitions

No detrimental effects on Mechanical, Optical and Surface properties

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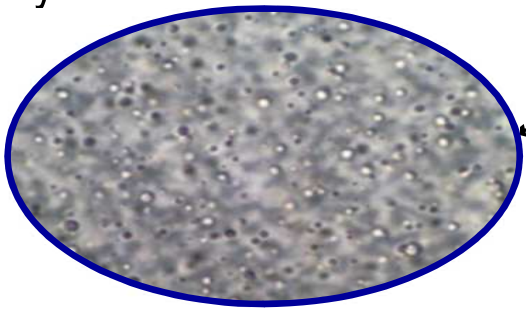
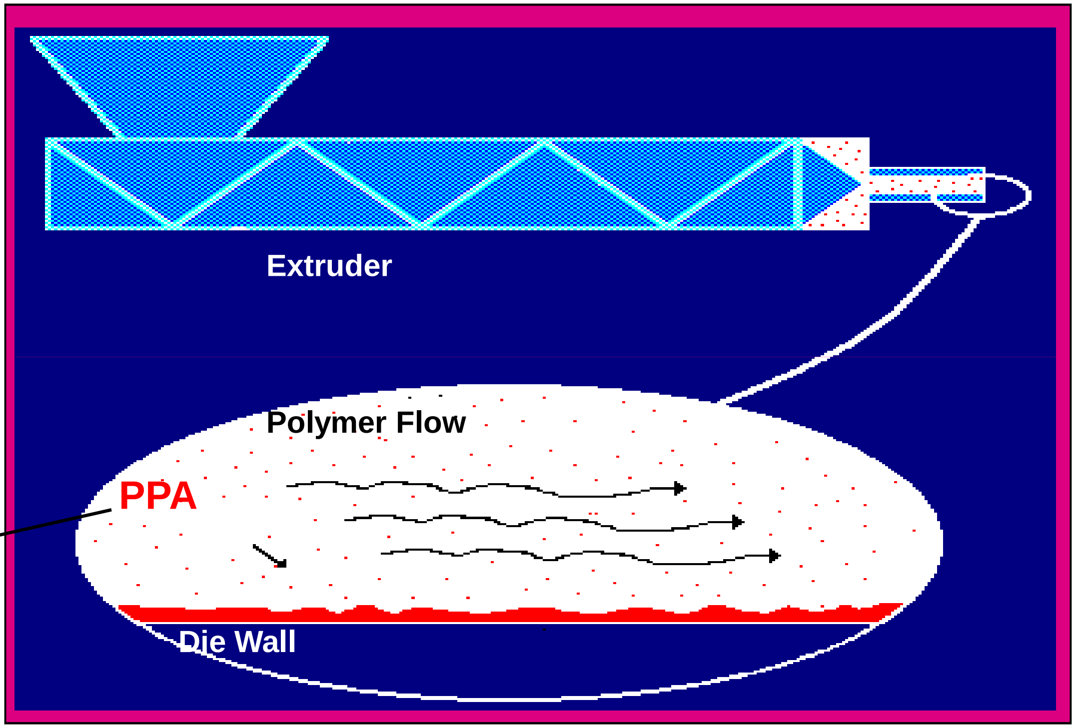
PPA Mode of Action

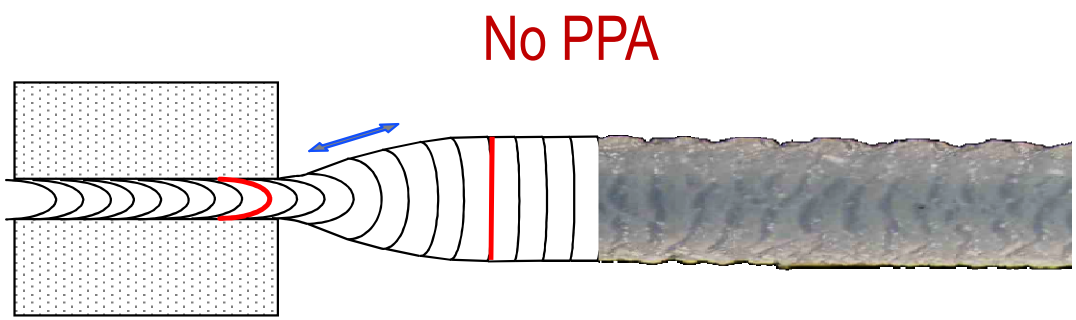
- Immiscible droplets in (e.g. polyolefin) polymer matrix
- High affinity for metal die wall
- Dynamic, low surface energy coating
- Allows melt to flow through the die more easily



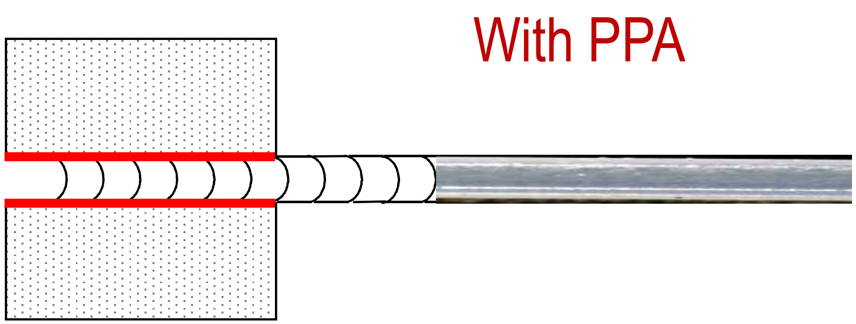
Photomicrograph: PPA in LLDPE



PPA Mechanism: Strand extrusion

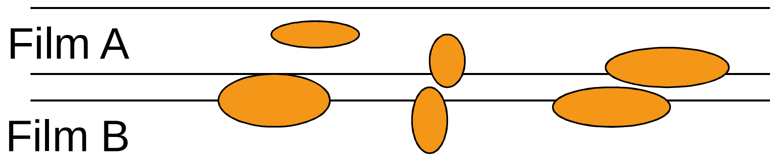


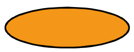
Upon die exit, the outer layer of the melt is stretched by the elastic recovery of the flow profile.



When the die is coated, there is slip at the die wall, reducing stresses that create melt fracture.

Antiblock (AB) mechanism





- Plastic films stick, form "block" together
- AB→ Small bumps on film surface
- Film to film contact reduced, "blocking" reduced
- Factors to consider:
  - → Blocking effectiveness
  - → Optics
  - → Concentration
  - → Cost

AB & Polymer Processing Additives (PPA)

Found together in:

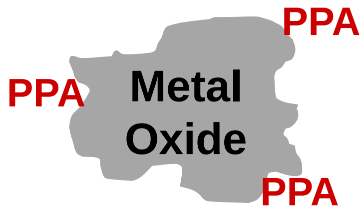
- Fully formulated resins
- Powder blends and "Master mixes"
- Combined masterbatches (CMB)

PPAs do not interfere with Antiblocking

AB can reduce effectiveness of PPA performance

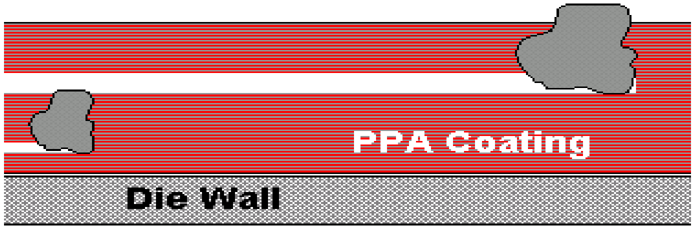
- Adsorbing PPA so it is unavailable for processing improvement
- Abrading PPA layer (dynamic coating)

PPA - AB interactions



Adsorption of PPA on to AB influenced by:

- Surface Area
- Coating Technology of AB
- Synergist Technology of PPA
- PPA/AB Addition Methods



Abrasion of PPA coating by AB influenced by:

- AB Type and Concentration
- PPA Type and Concentration

PPA-AB Interaction Evaluations *(PPA Performance in presence of AB)*

- *With newer ABs & newer PPA*
- *With different PPAs*
- *At different AB concentrations*

Take-away points:

1. ***Ranking levels of different PPAs required, when using specific ABs***
2. ***Basis for comparing PPA-AB interactions at different AB concentration***
3. ***Examples of Separate vs. Combined masterbatches of PPA & AB***

Not in scope:

Antiblocking performance

Study Outline

Masterbatch (MB) Preparation

Carrier 2MI LLDPE
Antioxidant 0.10%
Acid neutralizer 0.07%
One PPA

→ Twin Screw Compounding → 3 % PPA MBs

PPA = One of PPA -1 through PPA-3

Carrier 2MI LLDPE
Antioxidant 0.10%
Acid neutralizer 0.07%
One Antiblock

→ Twin Screw Compounding → 50 % AB MBs (all except)

Optibloc 8 MB @ 60 %
Sipernat 310 @ 25%

Antiblock = One of AB-1 through AB-10

Performance Evaluation

c6 LLDPE 0.9 MI (0.918 g/cc)
50% AB MB
Slip MB
\+
3% PPA MB

Constant PPA level trials

Data: Melt Fracture elimination

→ Blown film (test line) →

@ 410°F, 220 s^{-1}
7500 ppm AB
Or
2000 ppm AB

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ABs used for Lab Masterbatches (MBs)

Label	*Antiblock*	*Type*	*Manufacturer*	*Particle size (microns) (method)*
AB-1	ABT® 2500	Uncoated talc	(® and ™ of) Specialty Minerals	2.3 (average)
AB-2	Optibloc® 8	Talc, “clarity antiblock”; “low interactions with stabilizers, slip agents and processing aids”		2.5 (median), 8.0 (top size
AB-3	Optibloc® 10			2.5 (average), 12.0 (max. PSD 90%)
AB-4	Polybloc™	Coated talc		2.3 (average)
AB-5	Microbloc®	Talc, “to minimize stabilizer and slip adsorption”		2.3 (average)
AB-6	Clear-Bloc® 80	Talc	(® of) CIMBAR Performance Minerals	4.2 (PSD 50%)
AB-7	Minbloc® HC1400	Nepheline syenite	(® of) Unimin Specialty Minerals, Inc.	4.3 (d50)
AB-8	Minex® 7			3.5 (Median particle size)
AB-9	Sipernat® 44 MS	Synthetic alumino-silicate	(® of) Evonik Degussa	3.5 (d50)
AB-10	Sipernat® 310			8.5 (d50)

Commercial AB MBs

Commercial AB MB	Type	AB Concentration in MB (wt. %)
MB w/ Nat. Silica	Natural silica	15 %
MB w/ Talc	Talc	60 %

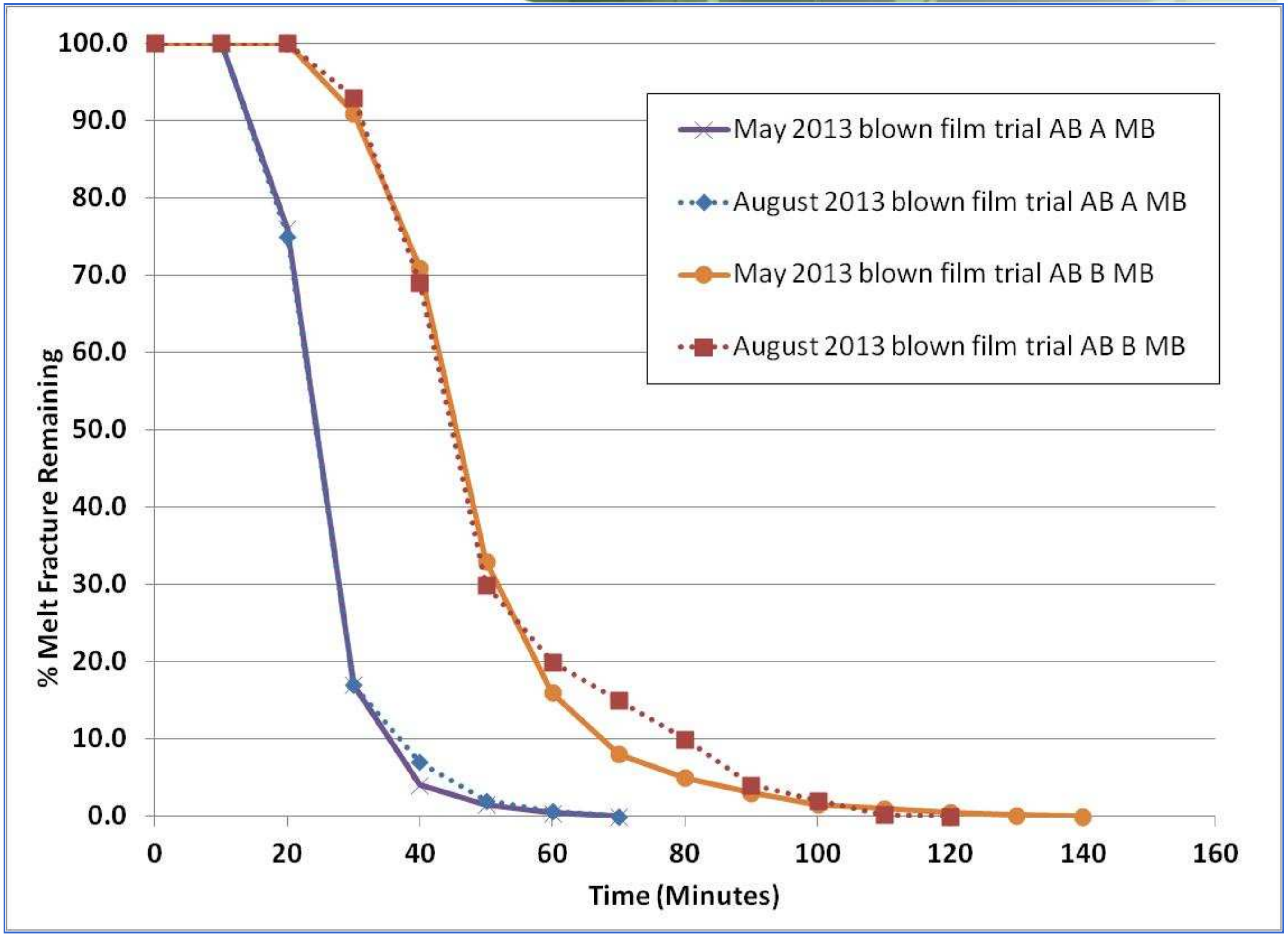
Reference points for
- *commercial MBs used in blown film applications*
- *relating lab-made and commercial MBs*
- *PPA performance in presence of natural silica*

PPAs

Label	PPA (3M™ Dynamar™)
PPA-1	FX 5927
PPA-2	FX 5920A
PPA-3	FX 9613

Registered trademarks:
1) 3M™ Dynamar™: 3M

Test Reproducibility



Blown film conditions

400 ppm PPA-1

C6 LLDPE 0.9 MI (0.918 g/cc)

1500 ppm erucamide

7500 ppm antiblock

220s^{-1}

210°C (410°F) melt

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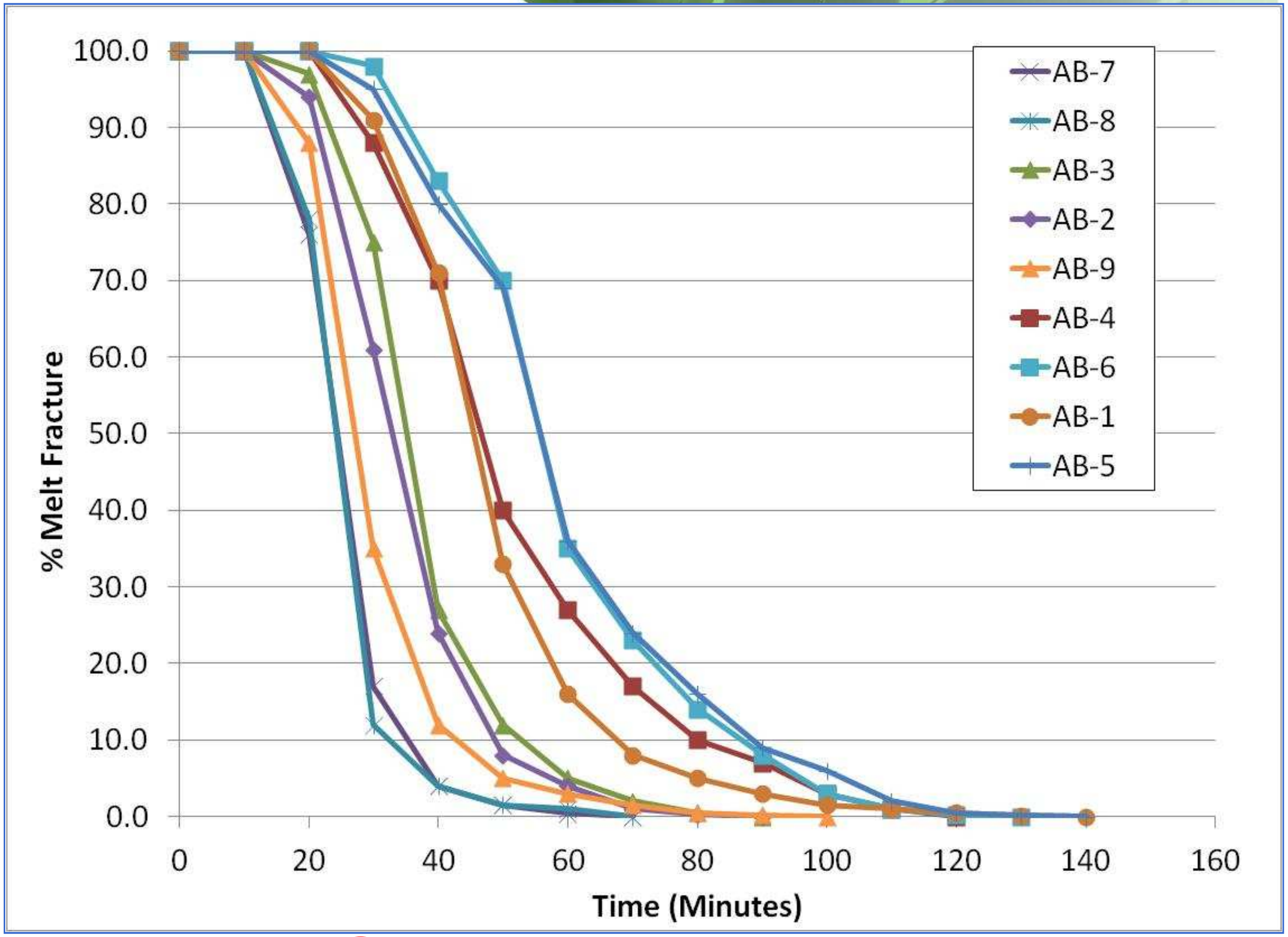
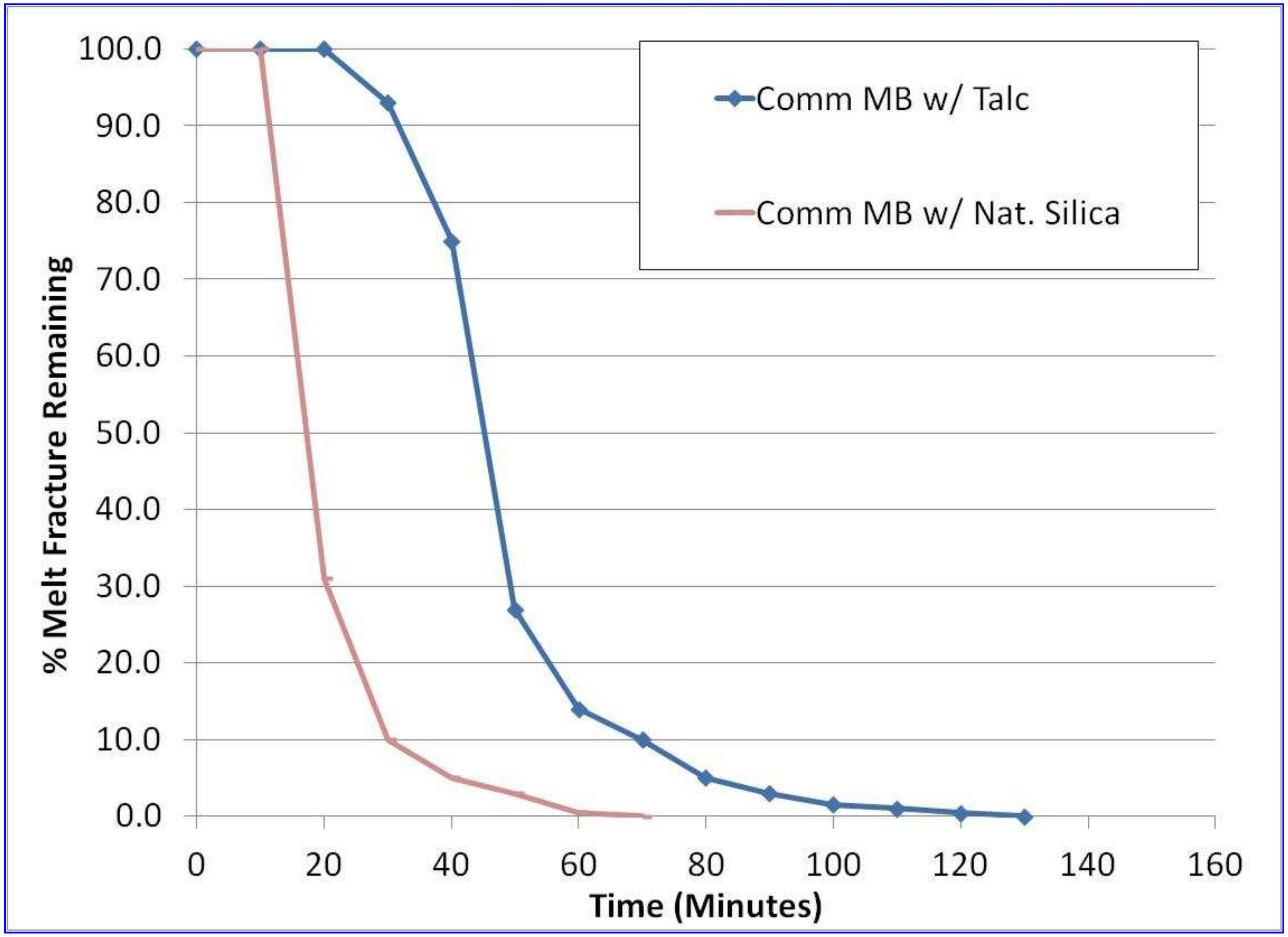
Impact of ABs on PPA Performance (Lab MBs)



Blown film conditions
400 ppm PPA-1
C6 LLDPE 0.9 MI (0.918 g/cc)
1500 ppm erucamide
7500 ppm antiblock
220s^{-1}
210°C (410°F) melt

Impact of ABs on PPA Performance (Commercial MBs)



Blown film conditions

400 ppm PPA-1

C6 LLDPE 0.9 MI (0.918 g/cc)

1500 ppm erucamide

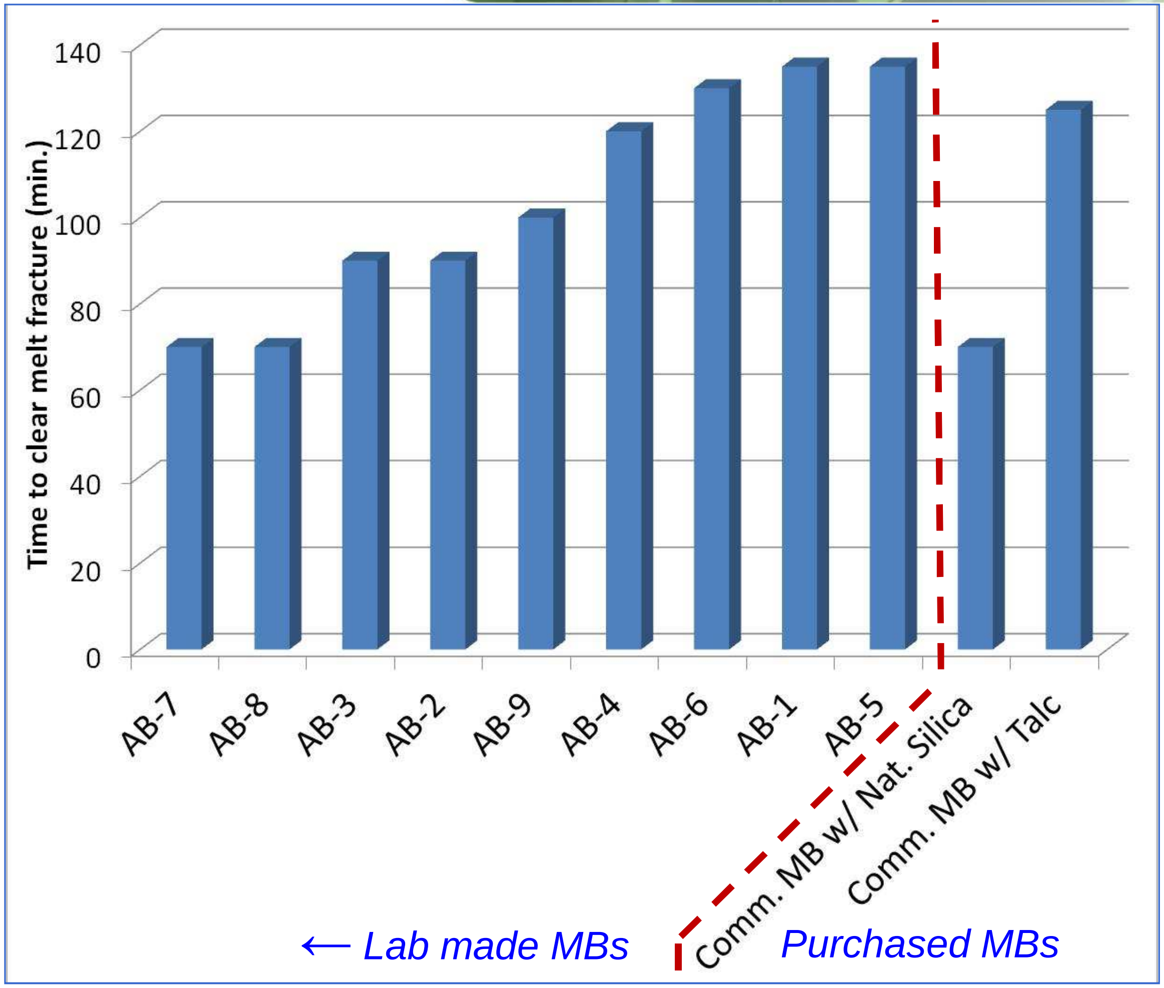
7500 ppm antiblock

220s^{-1}

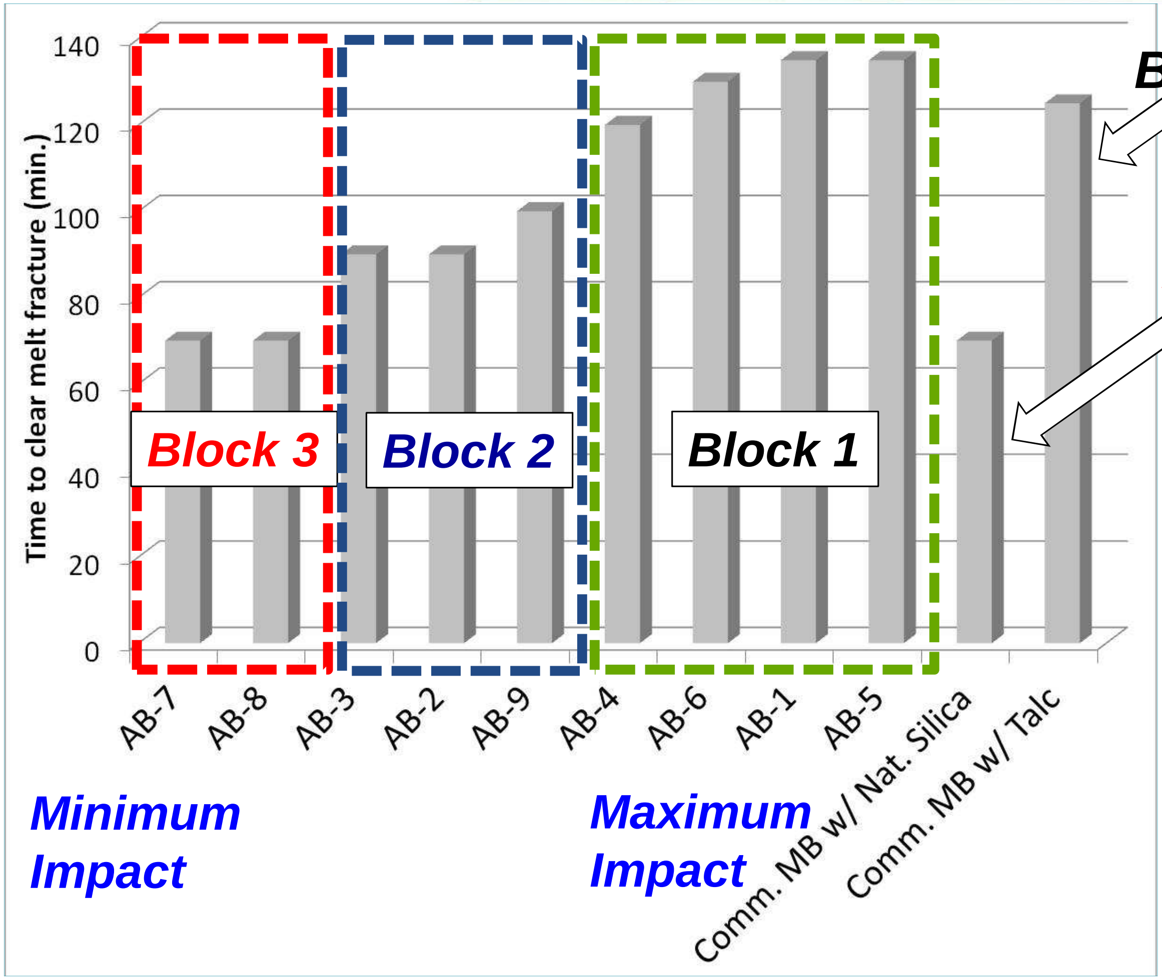
210°C (410°F) melt

Impact of ABs on PPA Performance Time to Clear Melt Fracture (TTCMF) (All ABs)

Blown film conditions
400 ppm PPA-1
C6 LLDPE 0.9 MI (0.918 g/cc)
1500 ppm erucamide
7500 ppm antiblock
220s^{-1}
210°C (410°F) melt



Impact of ABs on PPA Performance Time to Clear Melt Fracture (TTCMF) (All ABs)



Blown film conditions

400 ppm PPA-1

C6 LLDPE 0.9 MI (0.918 g/cc)

1500 ppm erucamide

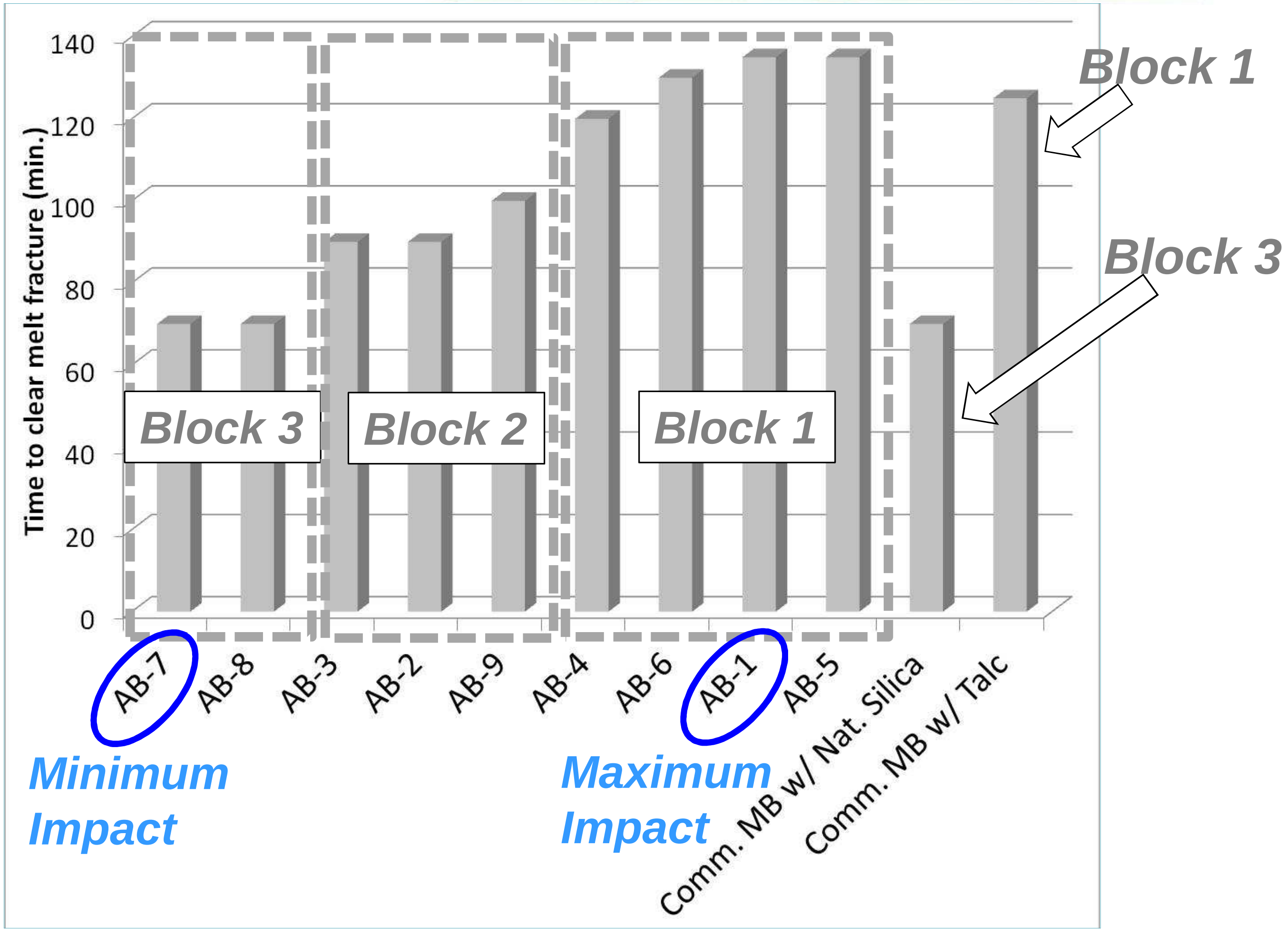
7500 ppm antiblock

220s^{-1}

210°C (410°F) melt

Impact of ABs on PPA Performance Time to Clear Melt Fracture (TTCMF) (All ABs)

Blown film conditions
400 ppm PPA-1
C6 LLDPE 0.9 MI (0.918 g/cc)
1500 ppm erucamide
7500 ppm antiblock
$220 s^{-1}$
210°C (410°F) melt



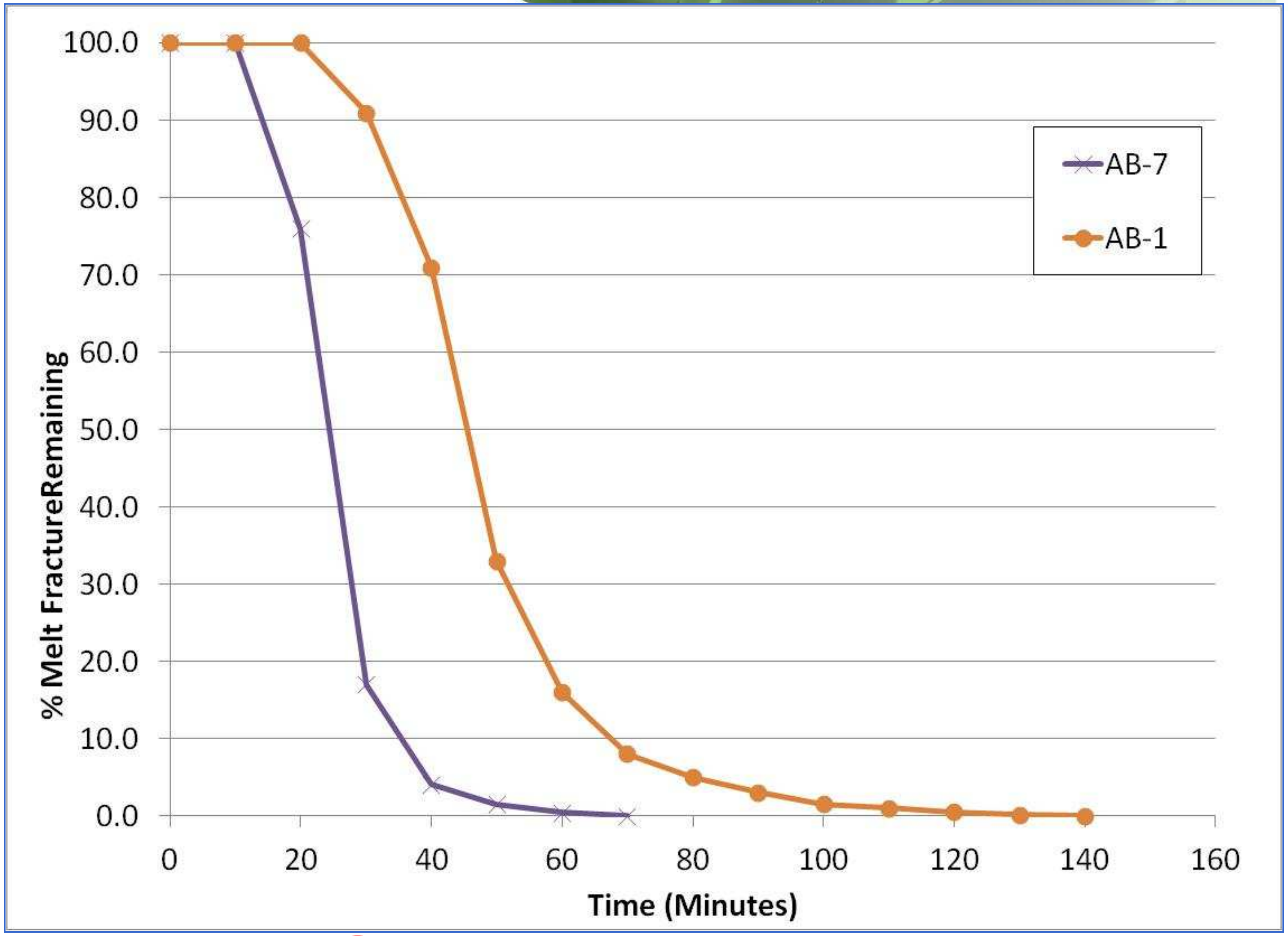
Impact of AB-1 & AB-7 on Performance of PPAs: PPA concentration

ppm PPA required for ~120 minute time to clear MFat 7500ppm AB-1 (lab MB), under study conditions

PPA-2 concentration: too high? cleared MF in ~100 minutes

Label	PPA	Concentration used
PPA-1	FX 5927	400 ppm
PPA-2	FX 5920A	1400 ppm
PPA-3	FX 9613	700 ppm

Impact of AB-1 & 7 on PPA-1 Performance (Lab AB MBs)



Blown film conditions

400 ppm PPA-1

C6 LLDPE 0.9 MI (0.918 g/cc)

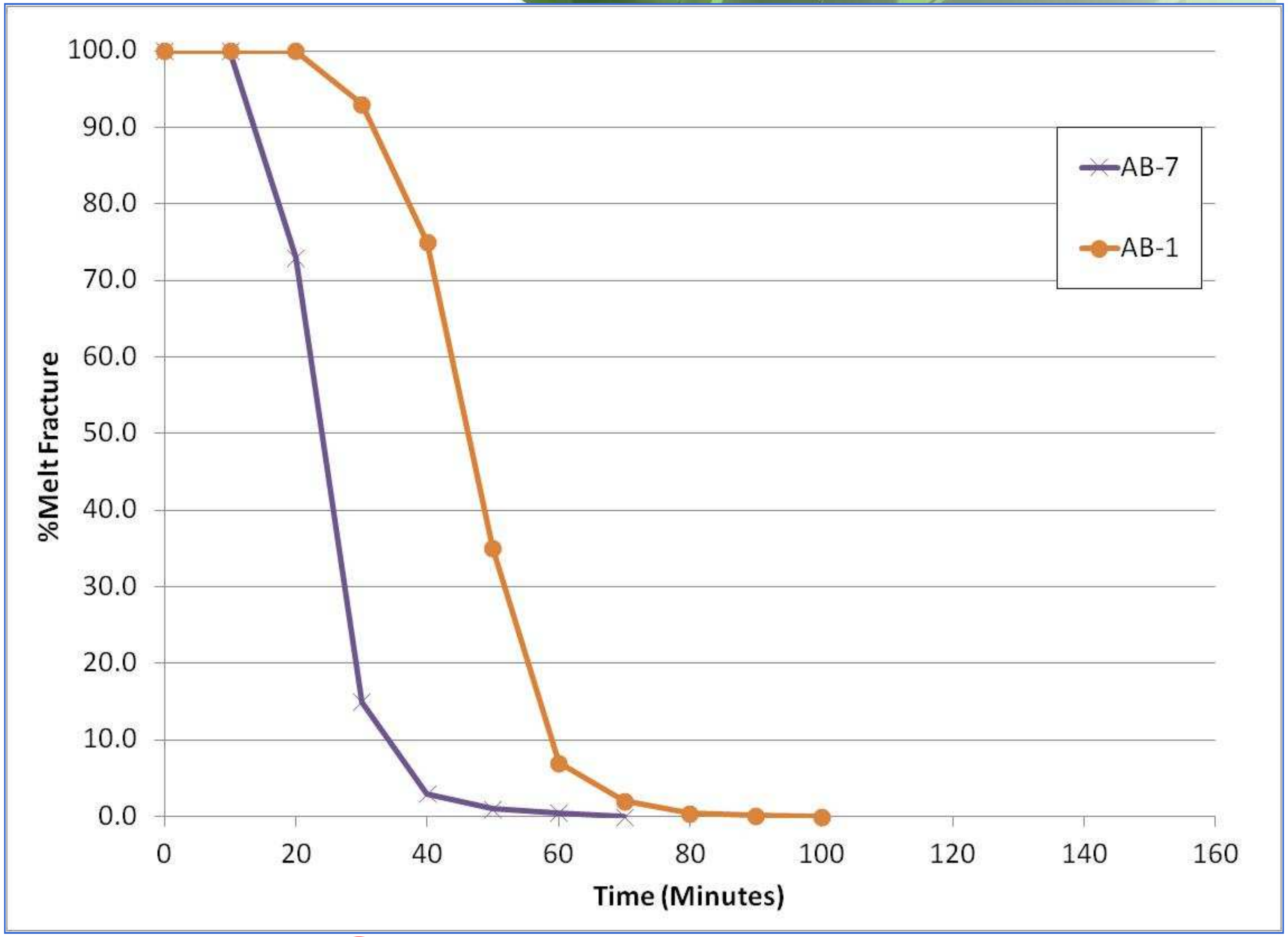
1500 ppm erucamide

7500 ppm antiblock

220s^{-1}

210°C (410°F) melt

Impact of AB-1 & 7 on PPA-2 Performance (Lab AB MBs)



Blown film conditions

1400 ppm PPA-2

C6 LLDPE 0.9 MI (0.918 g/cc)

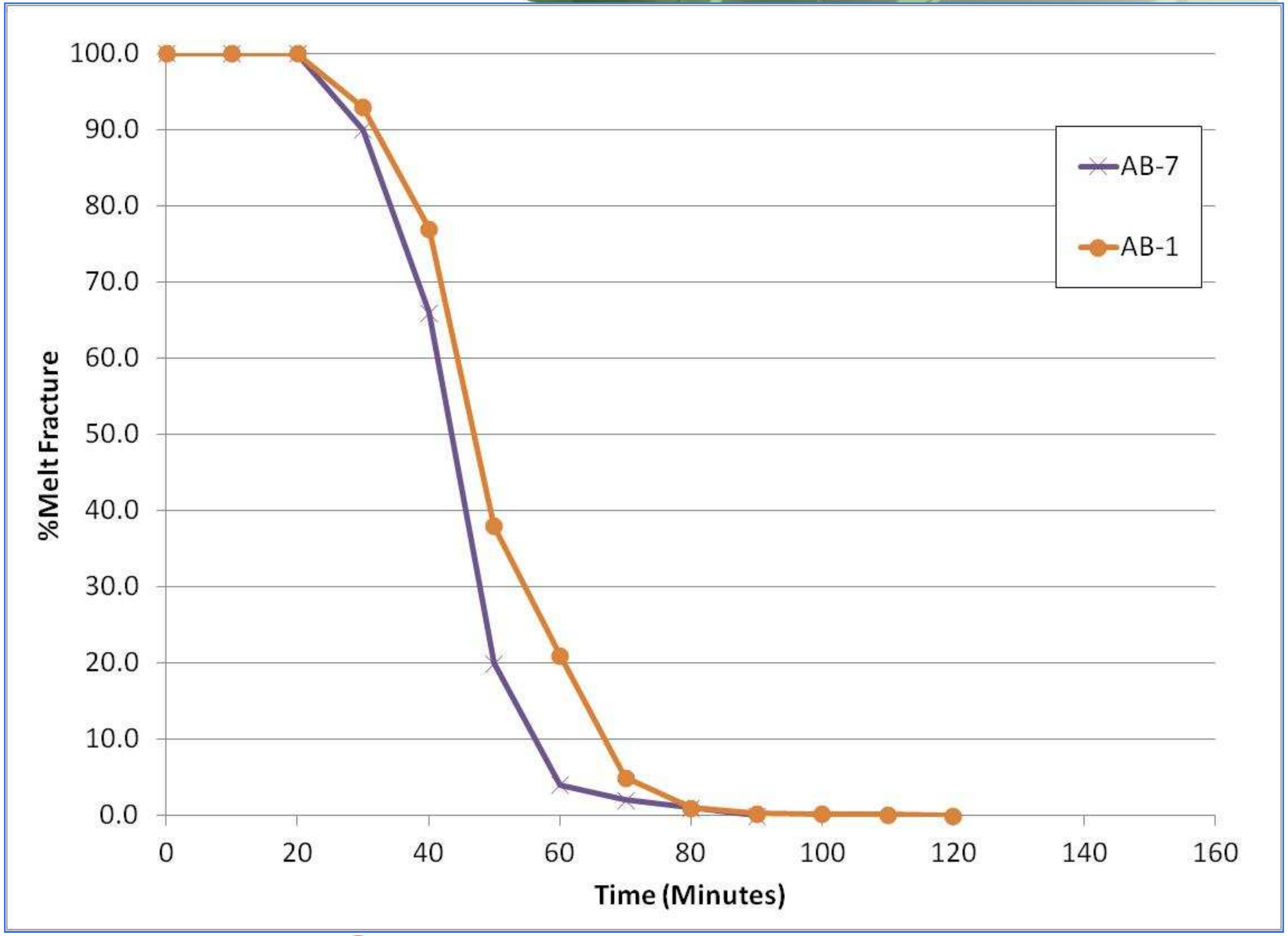
1500 ppm erucamide

7500 ppm antiblock

220s^{-1}

210°C (410°F) melt

Impact of AB-1 & 7 on PPA-3 Performance (Lab AB MBs)



Blown film conditions

700 ppm PPA-3

C6 LLDPE 0.9 MI (0.918 g/cc)

1500 ppm erucamide

7500 ppm antiblock

220s^{-1}

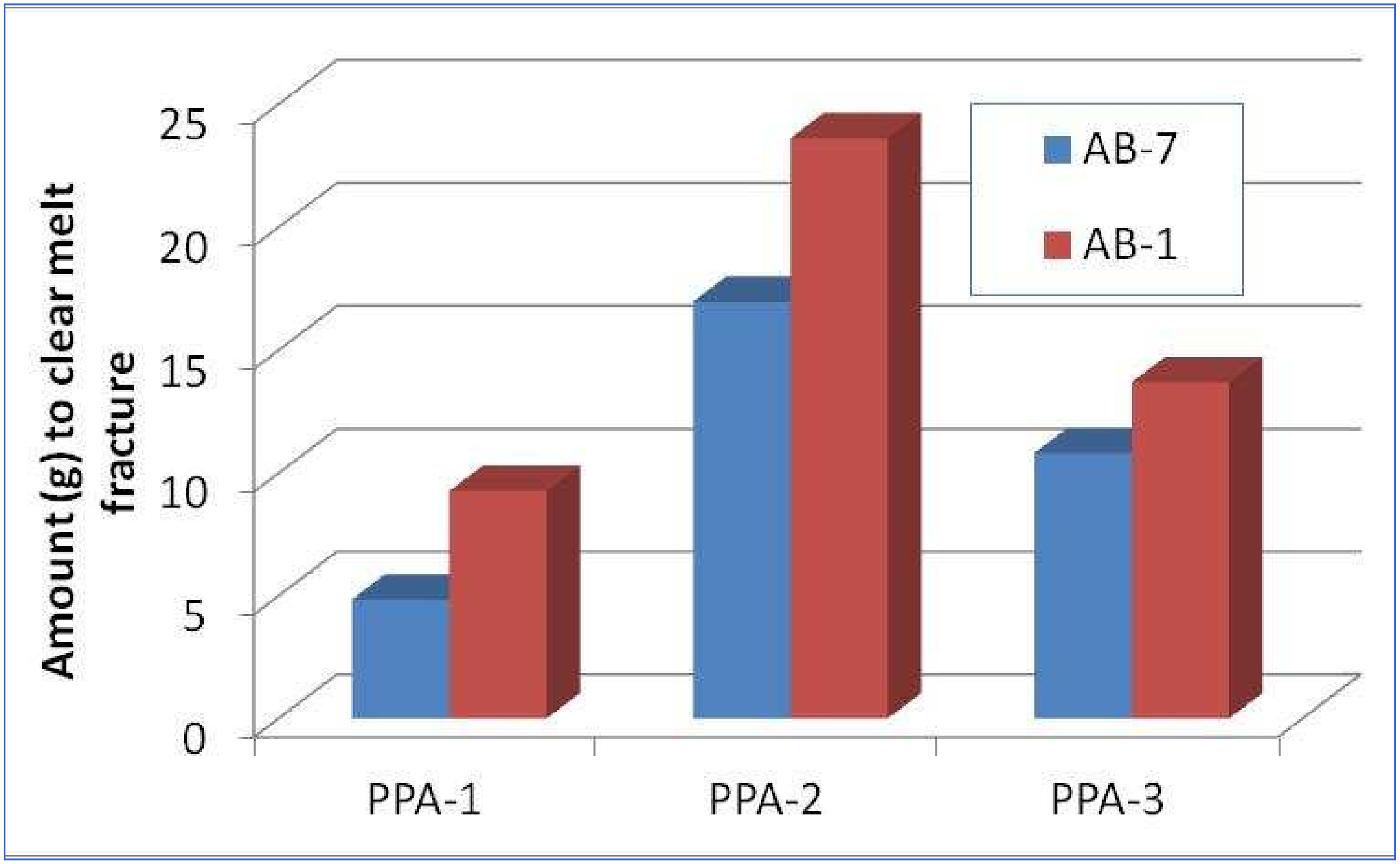
210°C (410°F) melt

Summary Impact of ABs on PPA-1, PPA-2 & PPA-3 Performance
(Lab AB MBs)

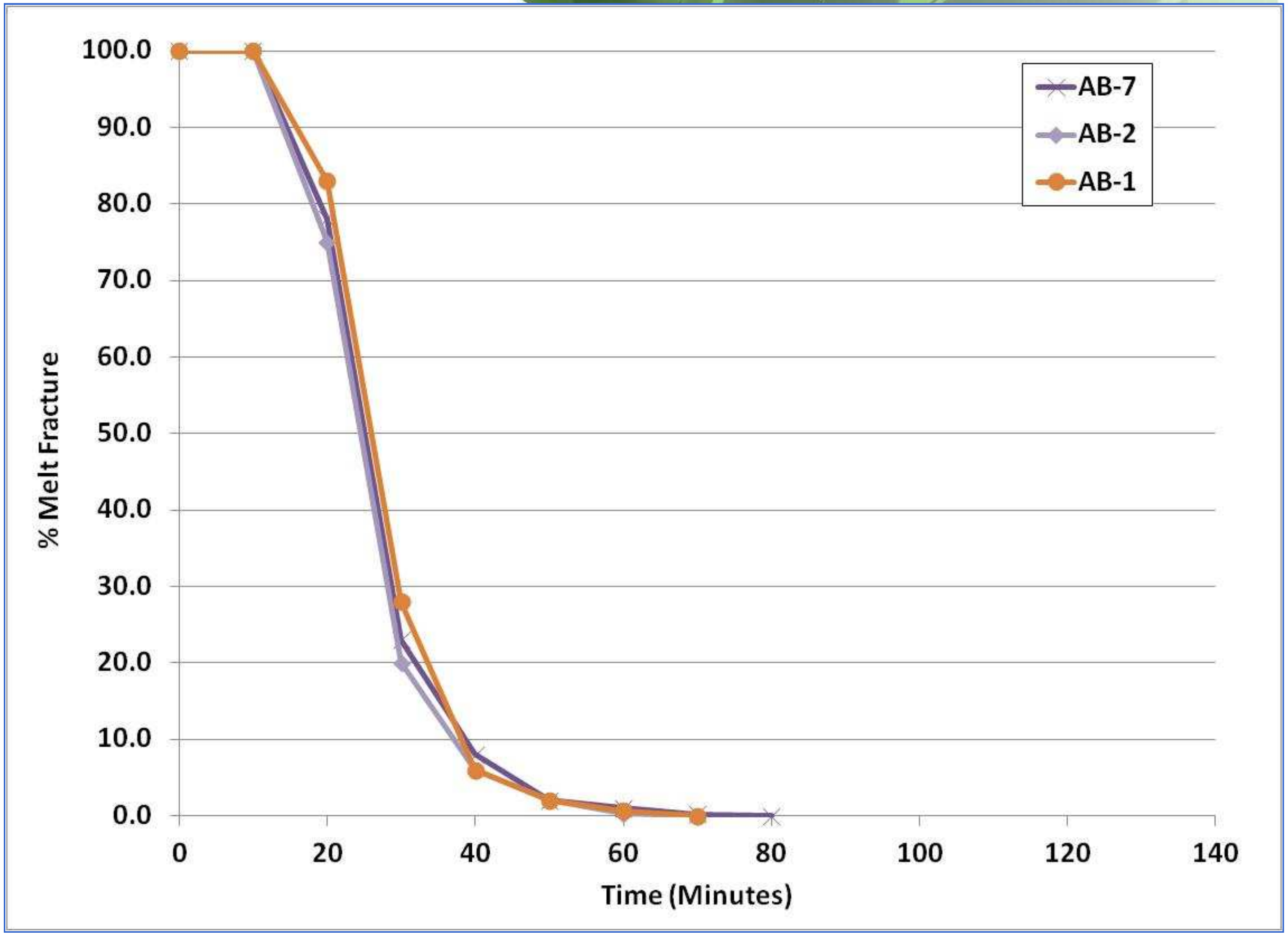
Amount to clear melt fracture (g) =
= PPA level (ppm) x 10^{-6} x film line throughput (kg/h) x TTCMF (h) x 1000 (g/kg)

Blown film conditions
C6 LLDPE 0.9 MI (0.918 g/cc)
1500 ppm erucamide
7500 ppm antiblock
$220 s^{-1}$
210°C (410°F) melt

PPA levels used (one of):
400 ppm PPA-1
1400 ppm PPA-2
700 ppm PPA-3

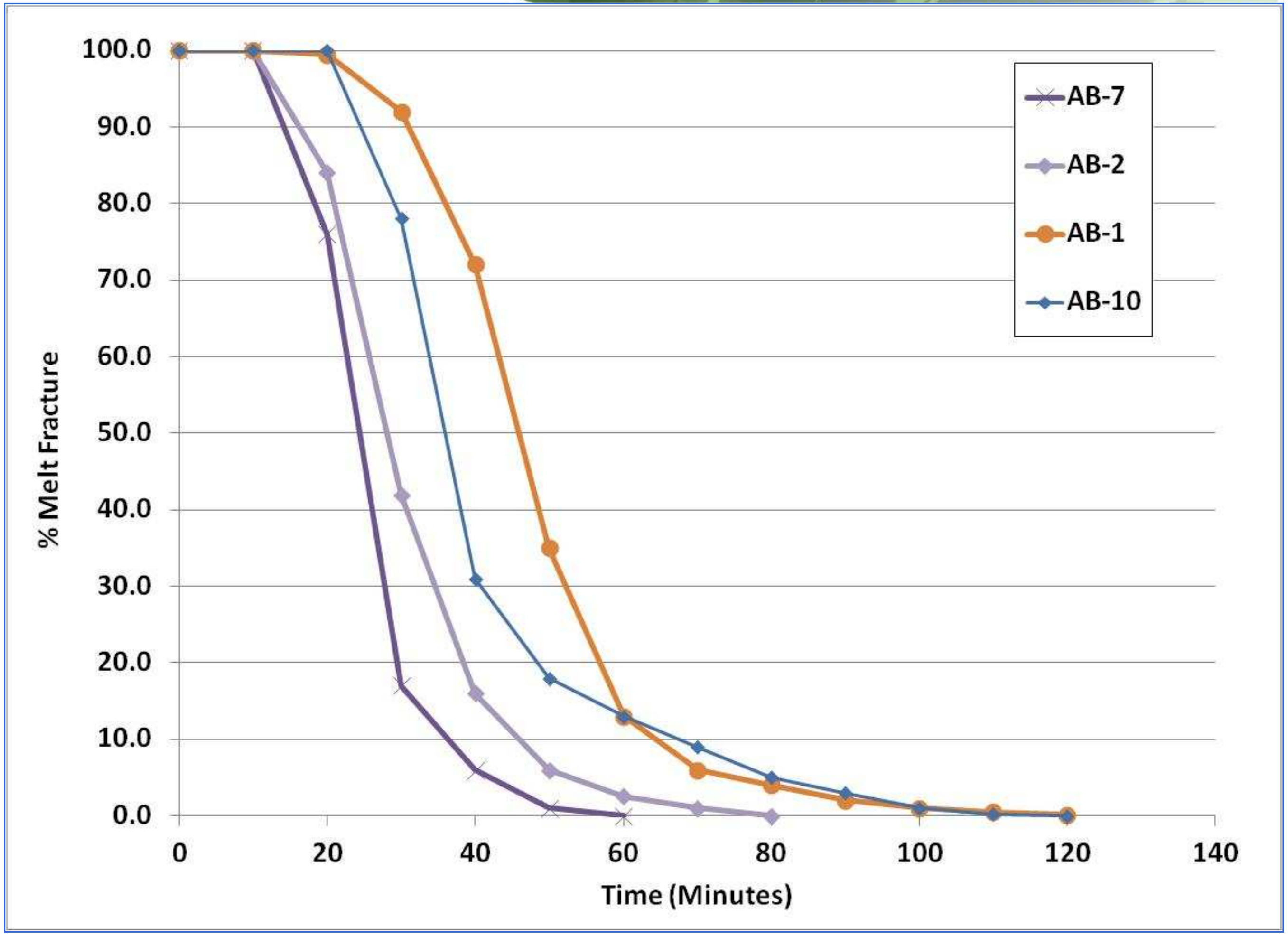


Impact of 2000ppm ABs on PPA-1 Performance; (Lab MBs)



Blown film conditions
350 ppm PPA-1
C6 LLDPE 0.9 MI (0.918 g/cc)
750 ppm erucamide
2000 ppm antiblock
220s^{-1}
210°C (410°F) melt

Impact of 7500 ppm ABs on PPA-1 Performance; (Lab MBs)



Blown film conditions

350 ppm PPA-1

C6 LLDPE 0.9 MI (0.918 g/cc)

750 ppm erucamide

7500 ppm antiblock

220s^{-1}

210°C (410°F) melt

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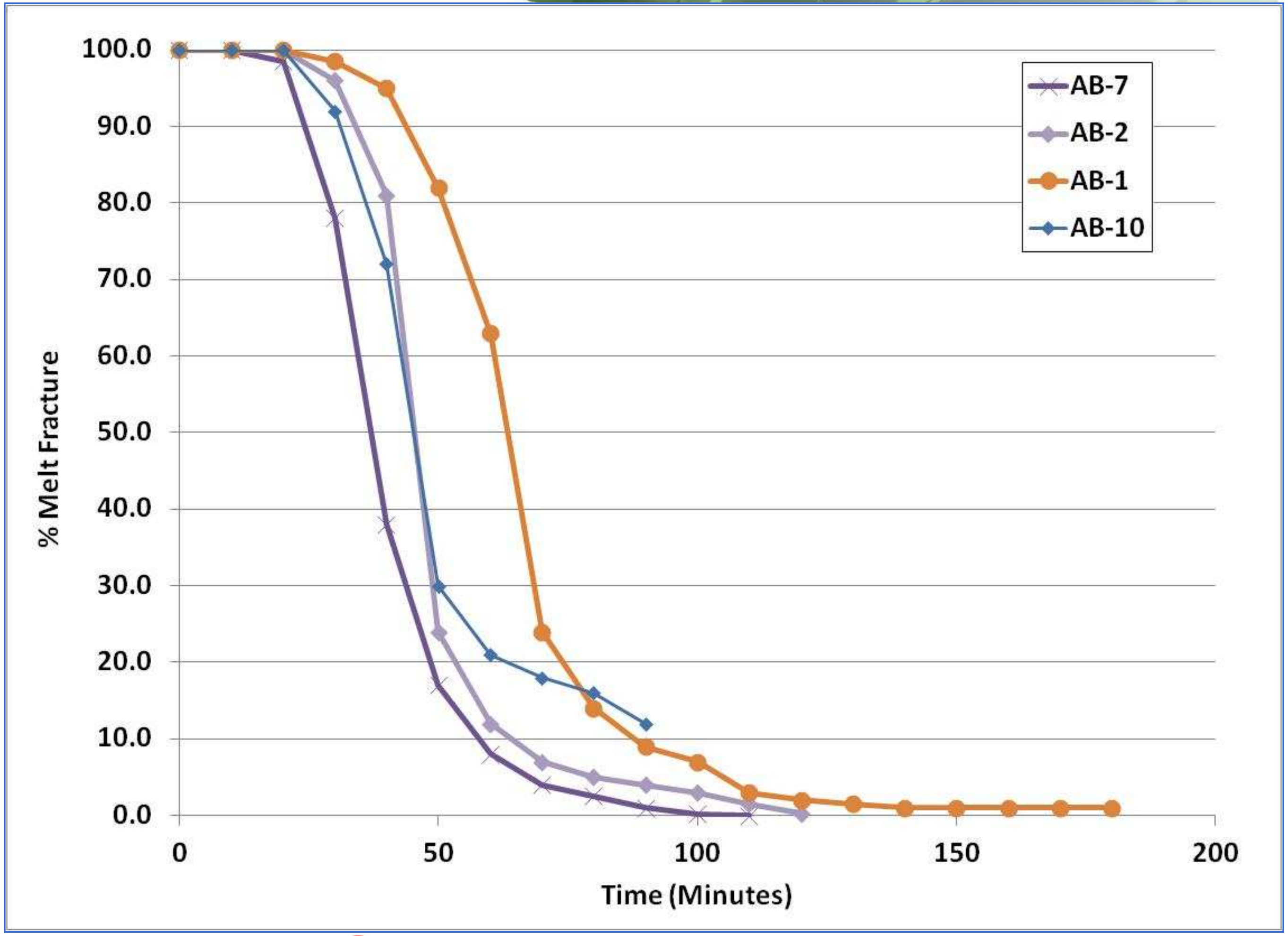
Impact of 2000 ppm ABs on PPA-1 Performance @ *Lower PPA Level* (Lab MBs)



Blown film conditions

***125** ppm PPA-1*

C6 LLDPE 0.9 MI (0.918 g/cc)

750 ppm erucamide

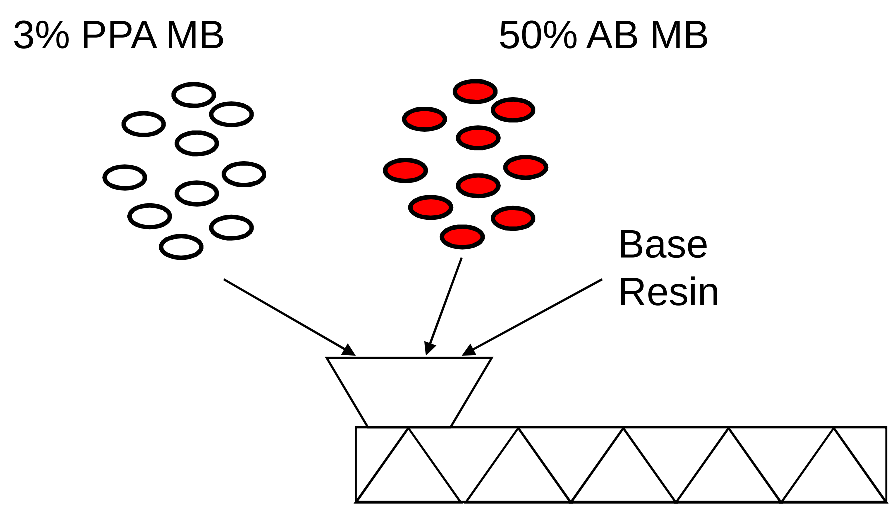
7500 ppm antiblock

220s^{-1}

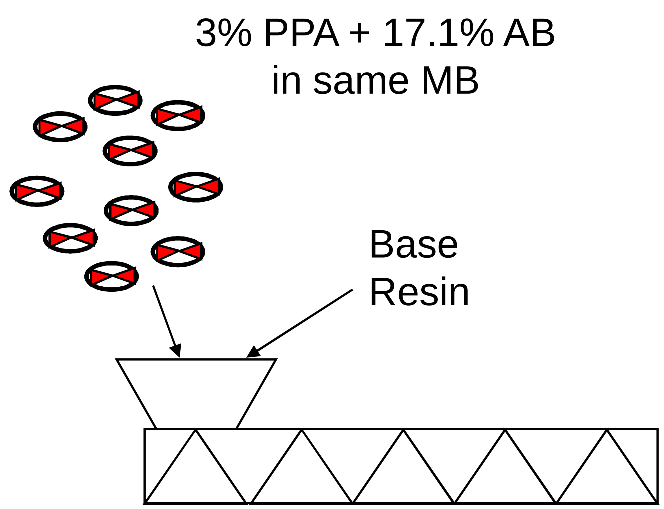
210°C (410°F) melt

Impact of compounding method on PPA performance

Separate Masterbatch SMB



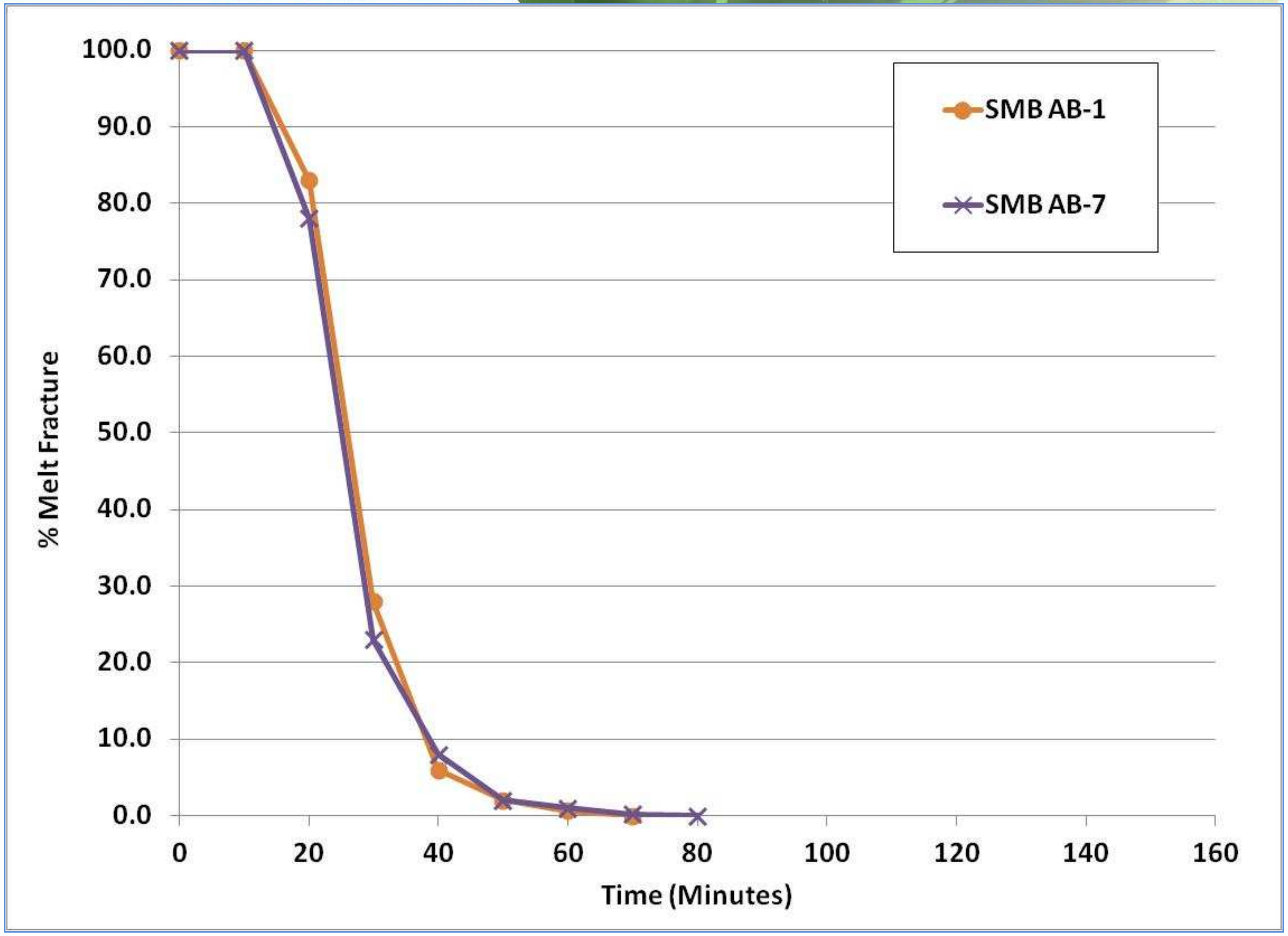
Combined Masterbatch CMB



Blown film with 350 ppm PPA, 2000 ppm AB

Impact of compounding on PPA-1 Performance; (SMB vs CMB)

Blown film conditions
***350** ppm PPA-1*
C6 LLDPE 0.9 MI (0.918 g/cc)
750 ppm erucamide
2000 ppm antiblock
220s^{-1}
210°C (410°F) melt



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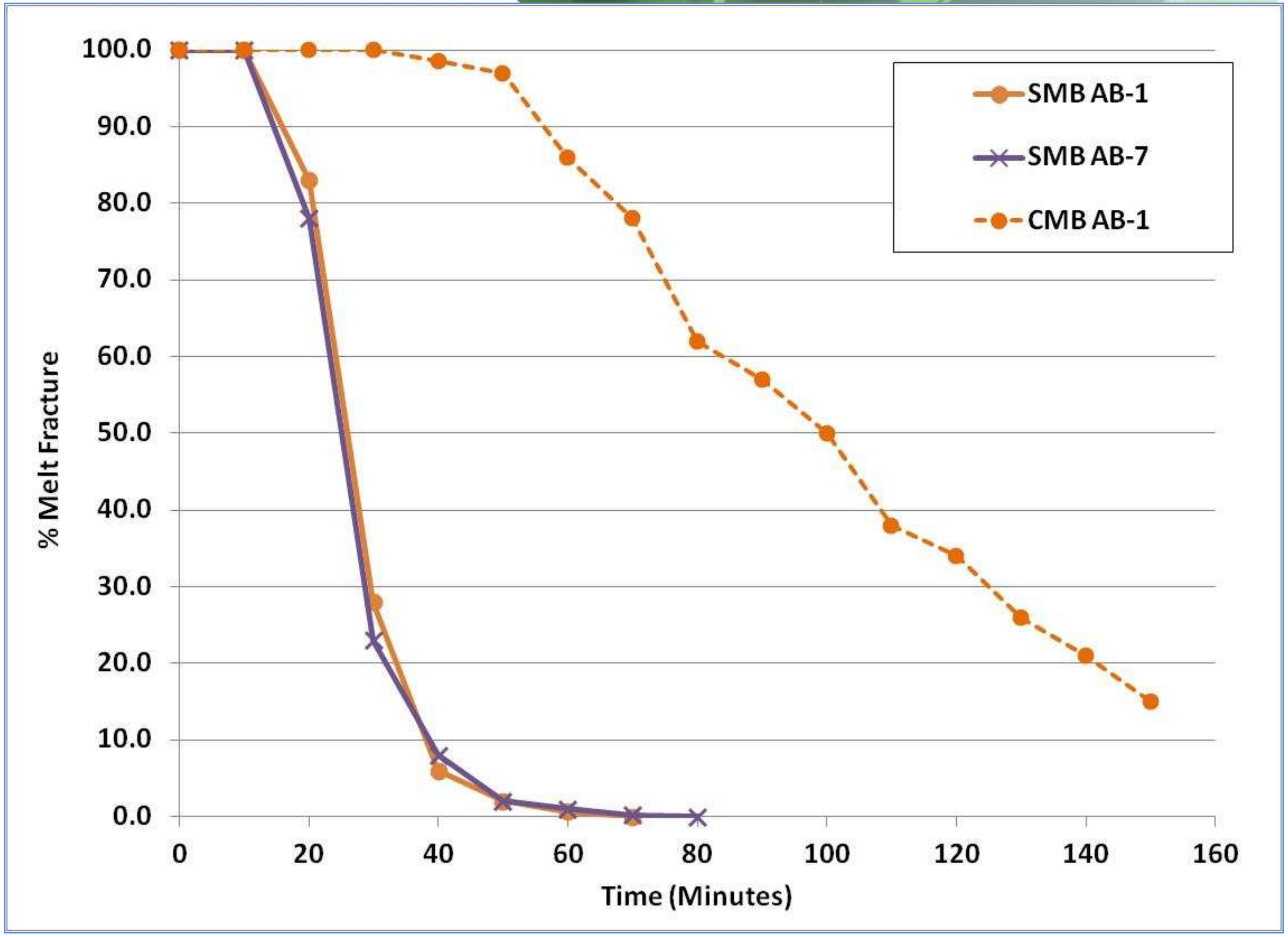
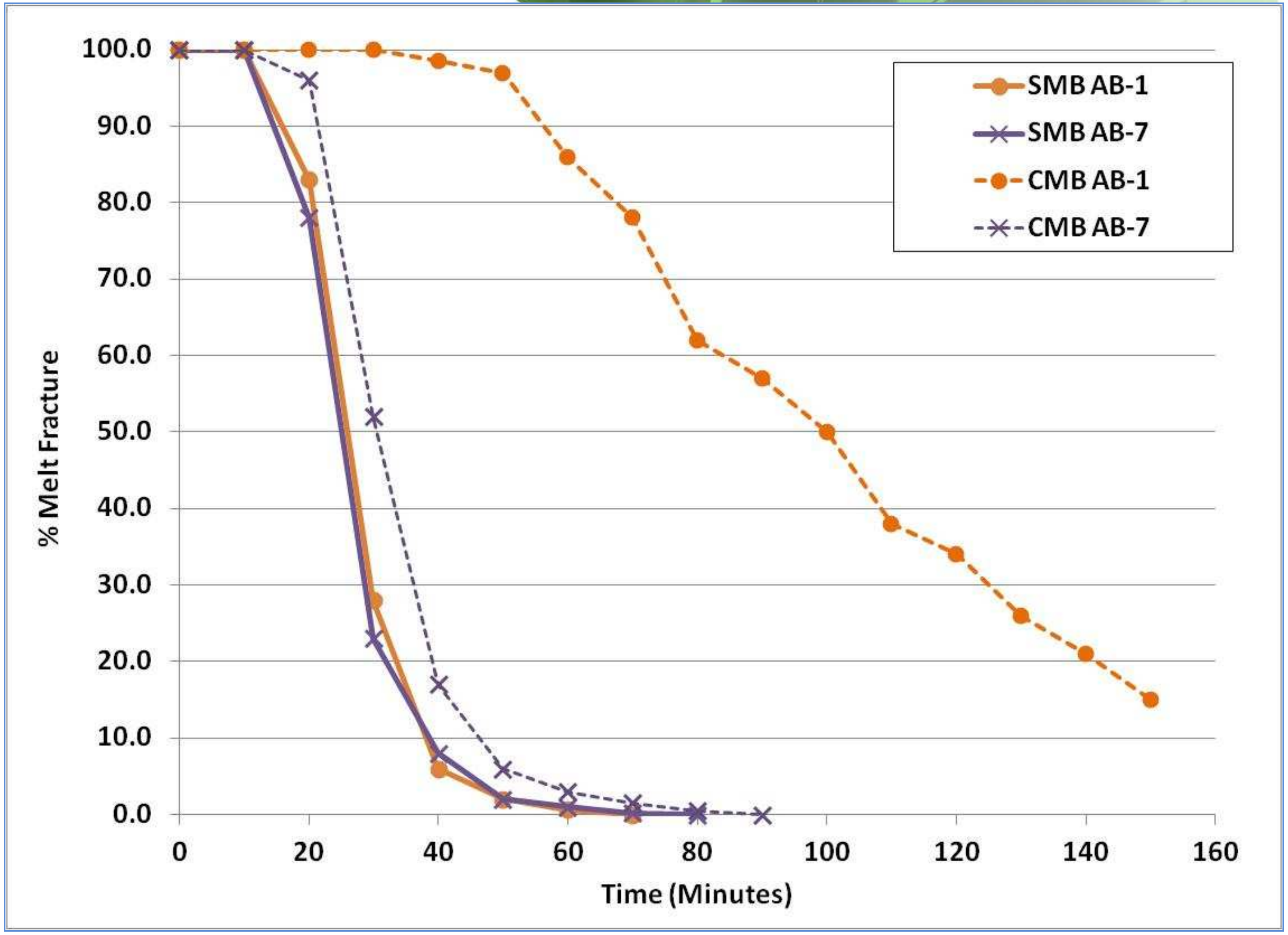
Impact of compounding on PPA-1 Performance; (SMB vs CMB)

Blown film conditions
350 *ppm PPA-1*
C6 LLDPE 0.9 MI (0.918 g/cc)
750 ppm erucamide
2000 ppm antiblock
220s^{-1}
210°C (410°F) melt

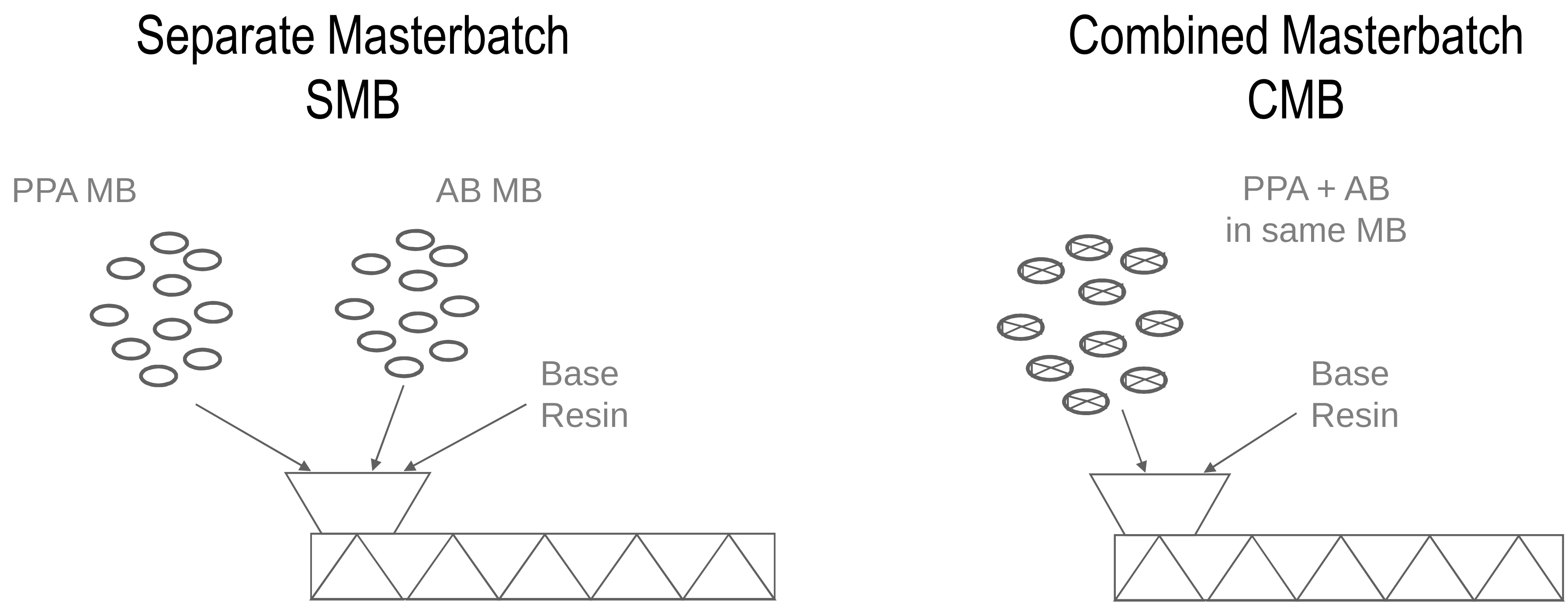


Impact of compounding on PPA-1 Performance; (SMB vs CMB)



Blown film conditions
***350** ppm PPA-1*
C6 LLDPE 0.9 MI (0.918 g/cc)
750 ppm erucamide
2000 ppm antiblock
$220s^{-1}$
210°C (410°F) melt

Summary: Impact of compounding method on PPA performance



SMBs require less PPA,
Some ABs, CMB similar to SMB

Impact of ABs on PPA Performance Time to Clear Melt Fracture (TTCMF) (All ABs)

Blown film conditions

400 ppm PPA-1

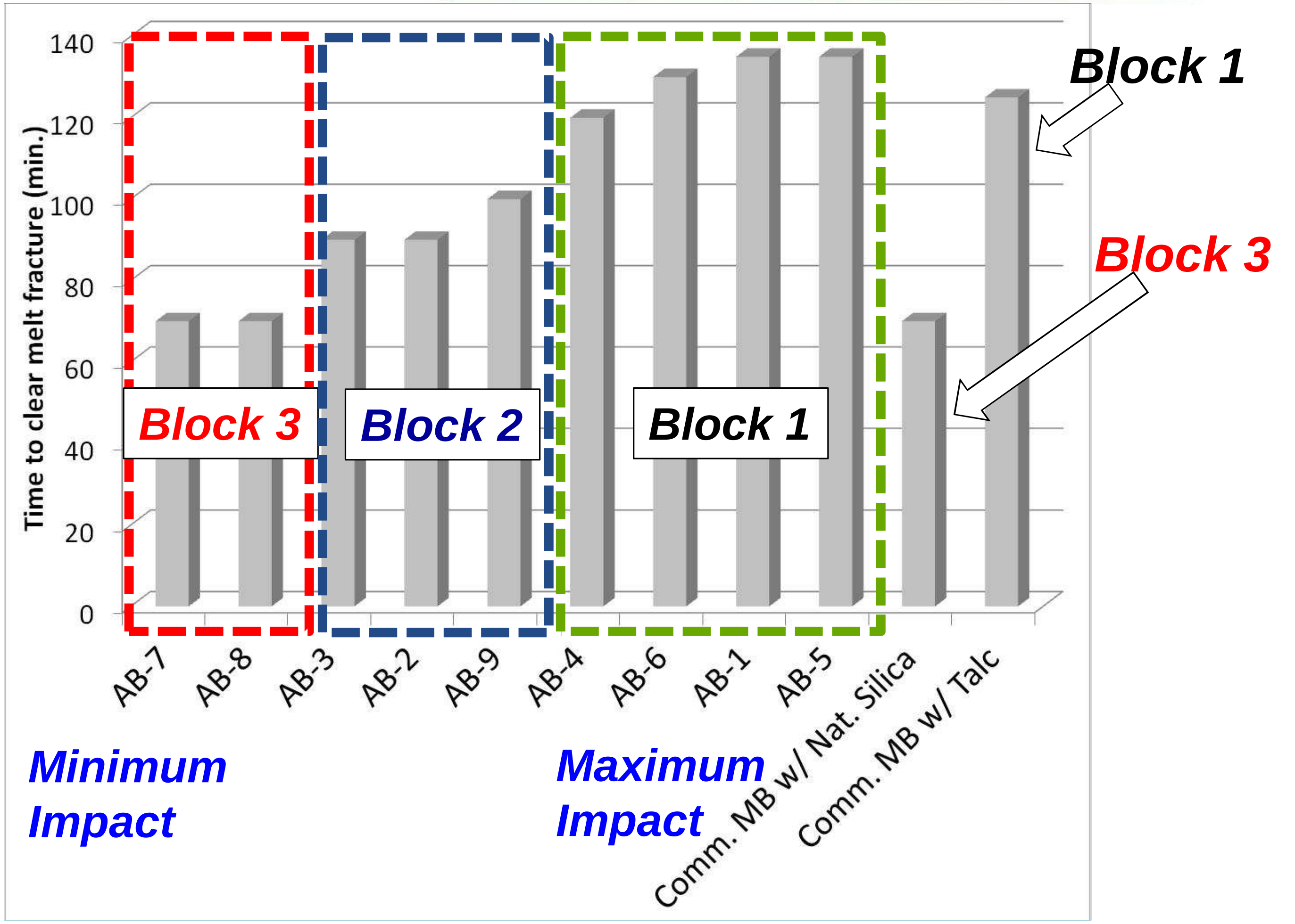
C6 LLDPE 0.9 MI (0.918 g/cc)

1500 ppm erucamide

7500 ppm antiblock

220s^{-1}

210°C (410°F) melt



Summary: Ranking of PPA needed for equivalent AB use levels

PPA level required to eliminate MF

Most

- Uncoated Talc
- Specialty Synthetic Silicas
- Coated Talc
- Nepheline syenite

Least

Impact of ABs on PPA Performance Time to Clear Melt Fracture (TTCMF) (All ABs)

Blown film conditions

400 ppm PPA-1

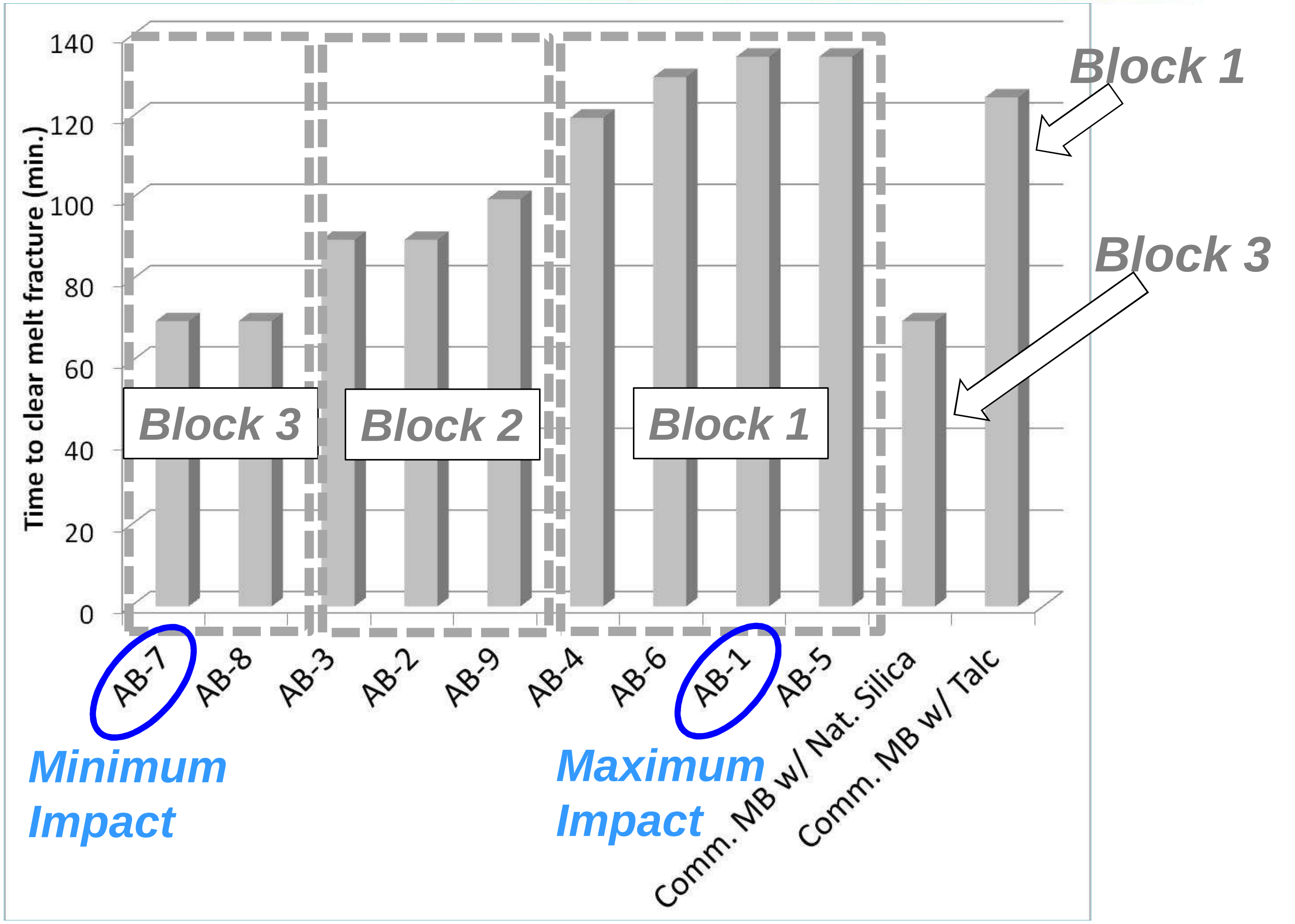
C6 LLDPE 0.9 MI (0.918 g/cc)

1500 ppm erucamide

7500 ppm antiblock

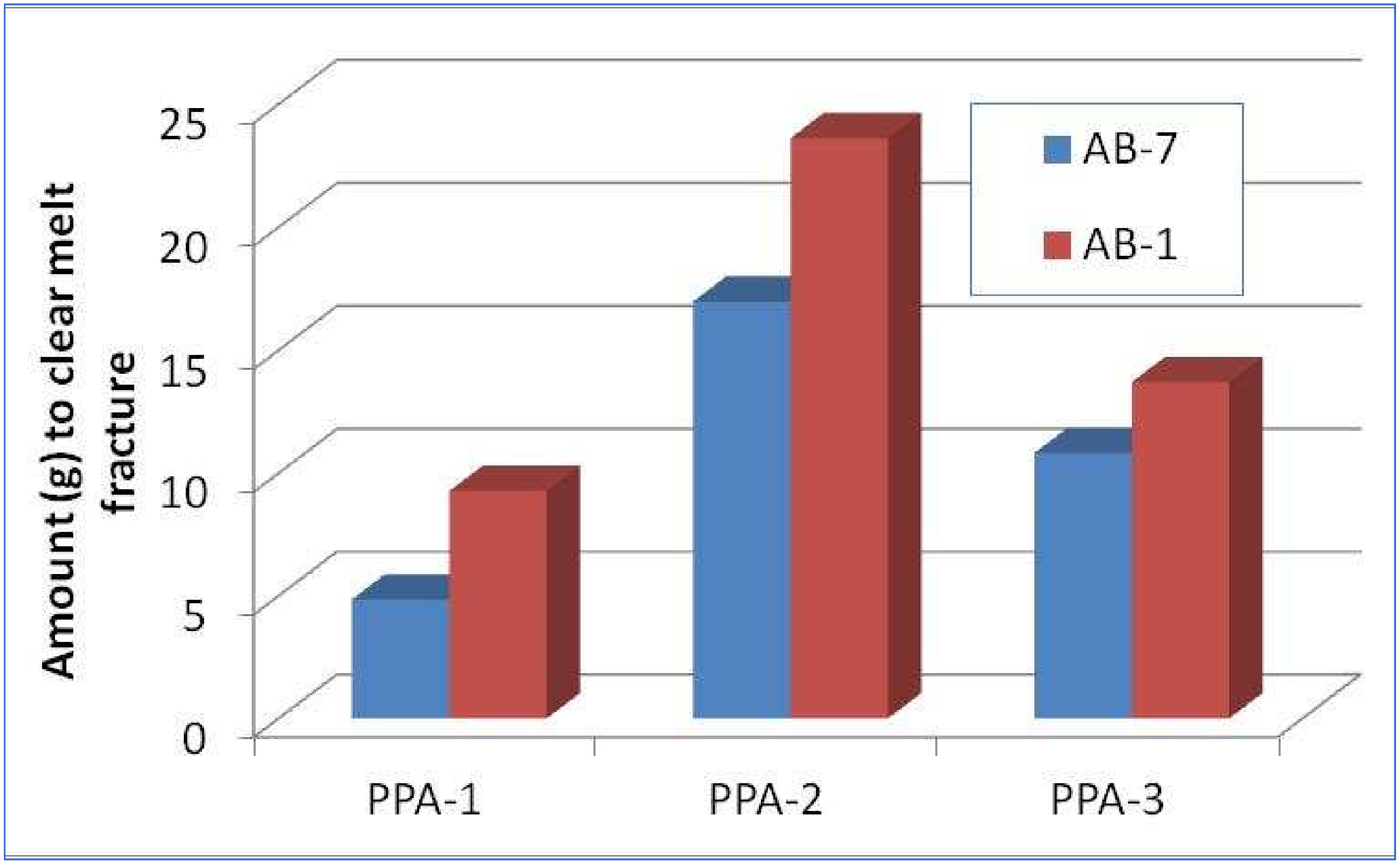
220s^{-1}

210°C (410°F) melt



Summary Impact of ABs on PPA-1, PPA-2 & PPA-3 Performance
(Lab AB MBs)

Amount to clear melt fracture (g) =
= PPA level (ppm) x 10^{-6} x film line throughput (kg/h) x TTCMF (h) x 1000 (g/kg)



Blown film conditions
C6 LLDPE 0.9 MI (0.918 g/cc)
1500 ppm erucamide
7500 ppm antiblock
220s^{-1}
210°C (410°F) melt

PPA levels used (one of):
400 ppm PPA-1
1400 ppm PPA-2
700 ppm PPA-3

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Overall Summary: PPA/AB Interactions

- PPA-1, 2 & 3 used successfully with all 12 different ABs evaluated in this study
- When optimizing additive package, considering both AB and PPA type is important
- Choosing optimal PPA → significant impact on reducing needed PPA level when ABs present
- AB impact on PPA performance consistent at high and low AB levels
- AB to PPA ratio important, AB effect masked by higher PPA levels
- SMB require less PPA, Some ABs, CMB similar to SMB

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