PVC101 WORKSHOP #1: INTRO TO PVC, GELATION THEORY, AND PVC FORMULATION

ARKEMA PLASTIC ADDITIVES

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INTRO TO PVC, GELATION THEORY AND PVC FORMULATION

Intro to PVC and PVC Gelation Theory

- PVC powder particle and properties
- PVC Gelation Theory
- Torque rheometers and PVC rheology

PVC Formulating Basics

- PVC Lubrication Theory
- Modifying PVC gelation and properties: process aids and impact modifiers
- PVC formulation components and blend order

PVC Formulations, examples

- Formulation examples by market / type

ARKEMA PLASTIC ADDITIVES

CLEARSTRENGTH BY ARKEMA

MBS IMPACT MODIFIERS

- Core shell based on METHYL METHACRYLATE / BUTADIENE / STYRENE
- Excellent cold impact performance
- Best balance of transparency / impact performance
- Main applications: PVC film & sheet, CPVC pipes & fittings, and engineering resins

DURASTRENGTH BY ARKEMA

ACRYLIC IMPACT MODIFIERS

- Core-shell based only on ACRYLIC monomers
- Best balance of impact performance / weathering properties
- Main applications: PVC window profiles, pipe and fittings, fencing, siding, roofing membranes

PLASTISTRENGTH BY ARKEMA

ACRYLIC PROCESSING AID

- High molecular weight ACRYLIC copolymers
- PVC fusion promotion and rheology modifier
- Tailored molecular weight and composition allows additive selection by application
- Main applications: PVC Flooring, Foam, Film & Sheet, Pipe and Profiles, Vinyl cladding, and Fence and Rail

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DURASTRENGTH® BY ARKEMA
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INTRO TO PVC AND PVC GELATION THEORY

WHAT DEFINES ADEQUATE PVC PROCESSING AND HOW TO ACHIEVE IT

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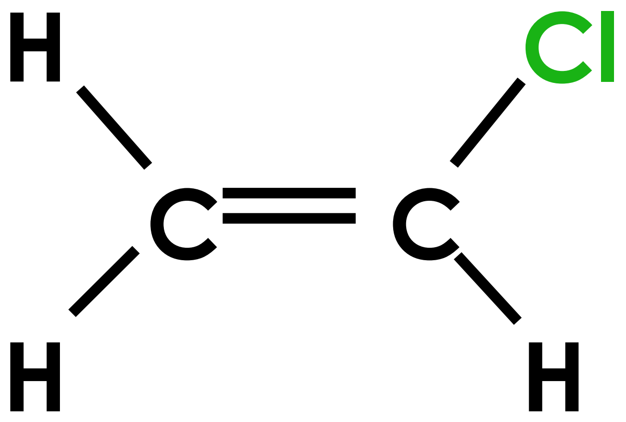
INNOVATIVE CHEMISTRY

VINYL CHLORIDE MONOMER



Odorless, Colorless, Gas (Liquid under Pressure)

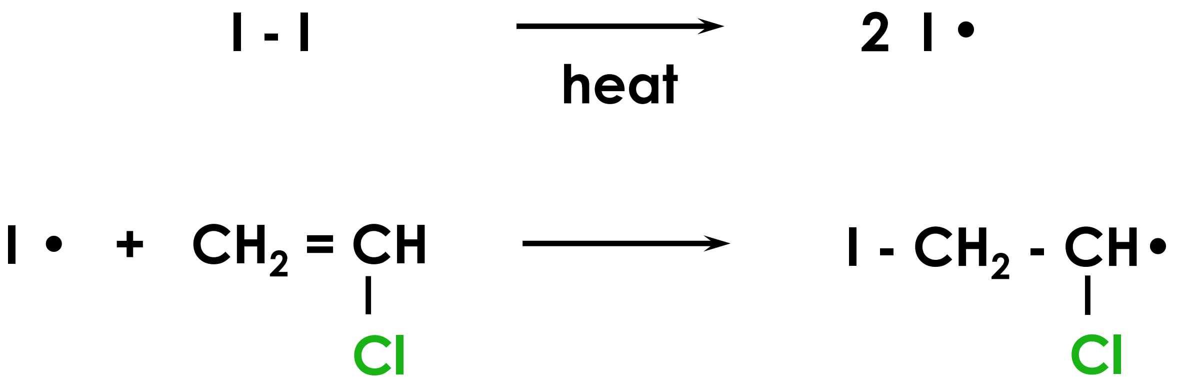
Boiling Point -14° C

MW = 62.5

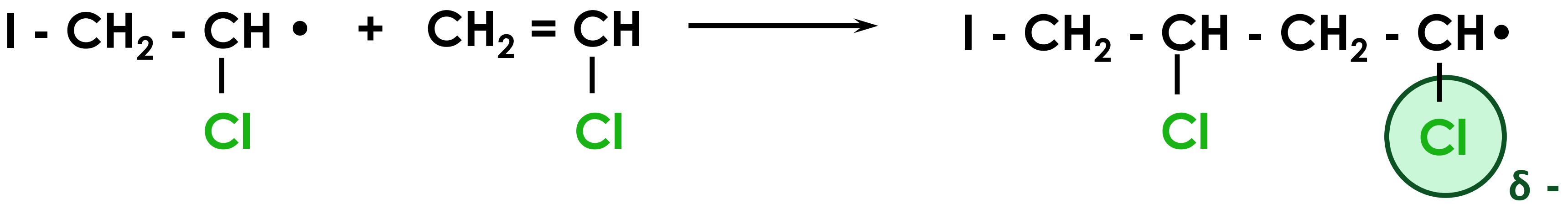
Very Low Solubility in Water

FREE RADICAL MECHANISM

Initiation



Propagation



PVC RESINS FOR RIGID (AND FLEXIBLE) APPLICATIONS

3 main PVC resin product processes:

- Suspension: Majority
- Mass: PVC synthesized in its own monomer
- Emulsion: plastisols, dispersion resin, some flexibles

Suspension PVC process: (K-value or IV (Intrinsic viscosity) characterizes MW)

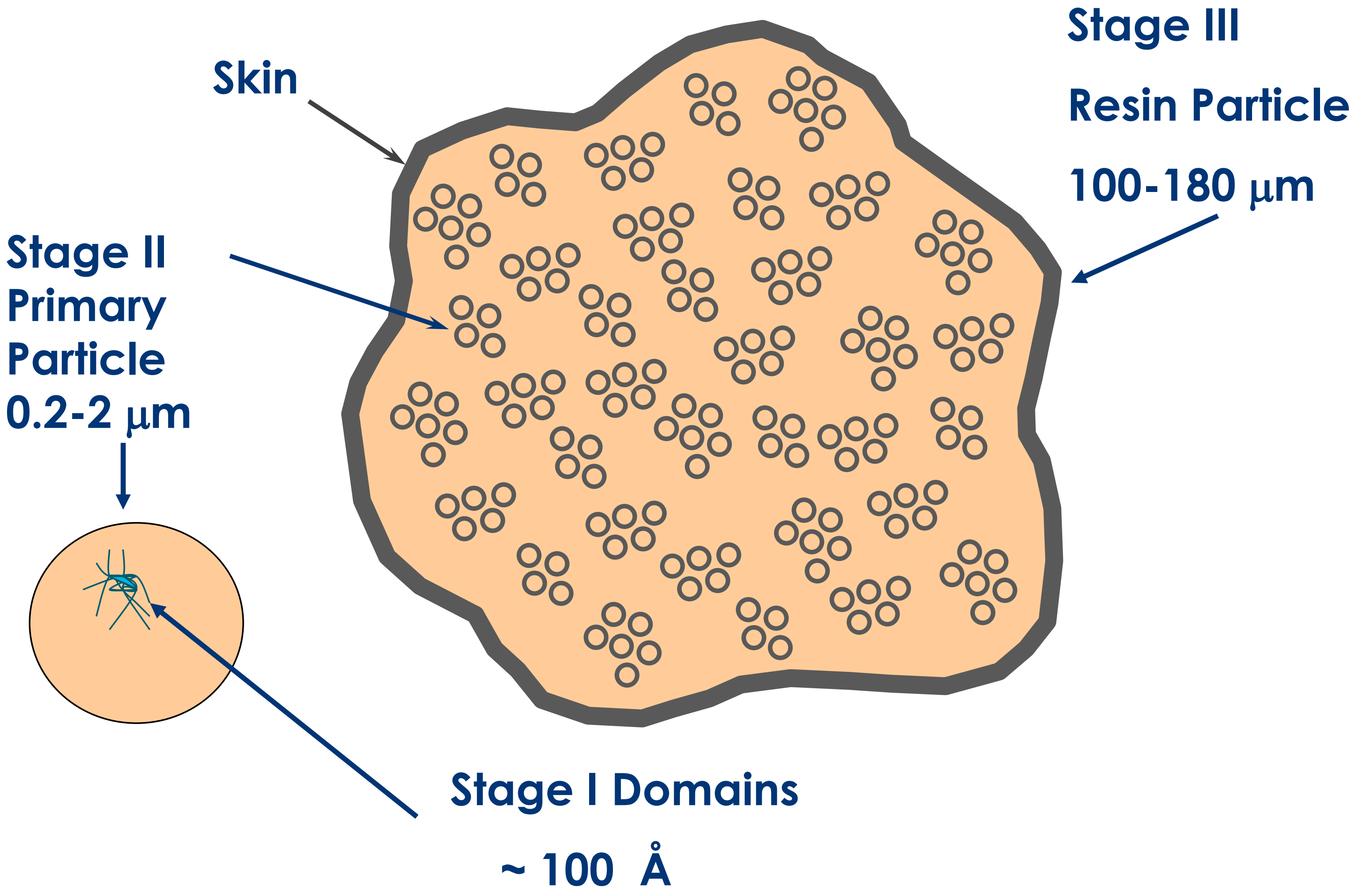
- VCM polymerized in water where PVC grains are maintained in suspension with dispersion agents (PVC, surfactants, emulsifiers, etc.)
- Initiator in monomer phase
- PVA and suspending additives remain in the final product
- Skin around PVC grains
- Remaining (residual) additives have some influences on the applicative performance:
  - Heat stability (+)
  - Color (+)
  - Haze (-)
  - Water blush (-)

WHY A PVC PARTICLE?

PVC is the only polymer that is processed into end products in the same physical form that it was produced in the reactors. All other major polymers are compounded and sold as pellets. The formation and morphology of the PVC particles in the reactor is the key to processing and its many uses.

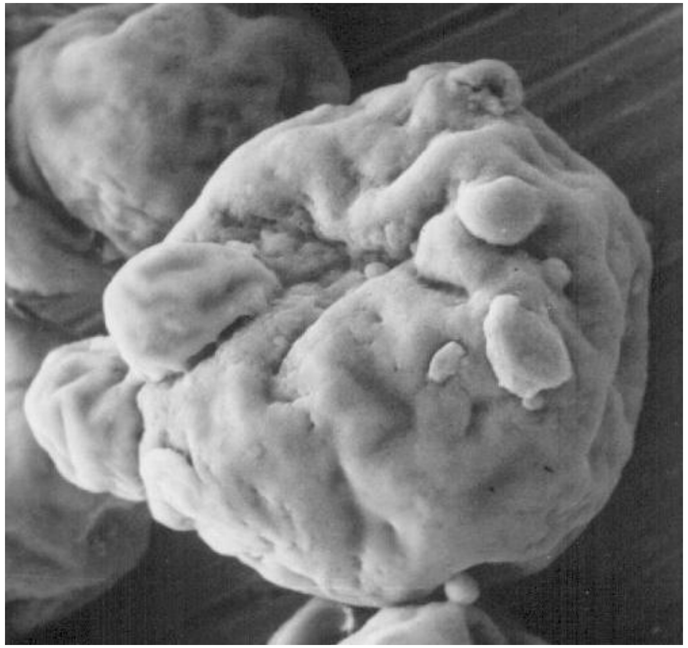
- Bob Paradis (Formosa)

SUSPENSION PVC PARTICLE



Zooming out to look at a PVC particle:

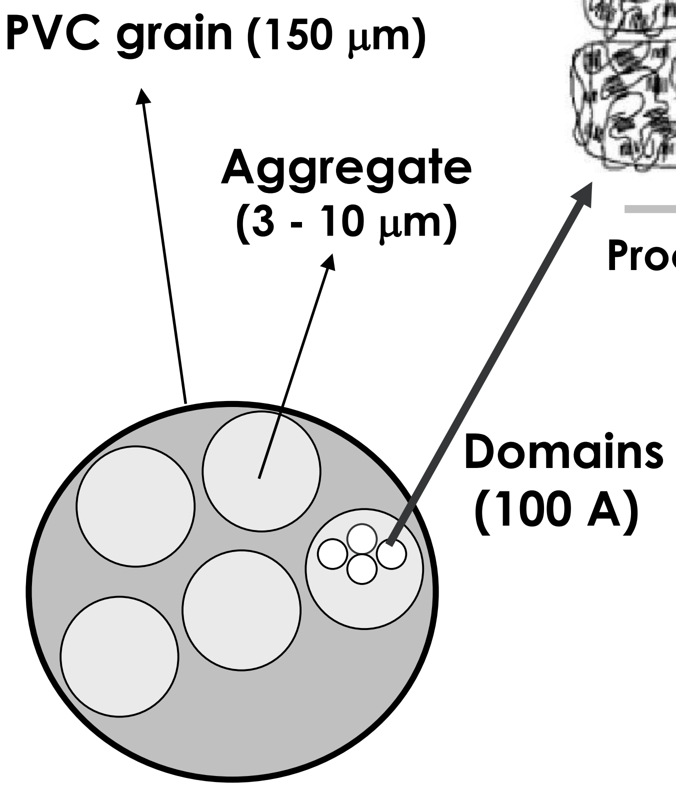
- Wrinkled surface (popcorn structure) due to change in density from monomer to polymer (> 1 g/cc → 1.4 g/cc)
- Resin particle size 100 - 180µm

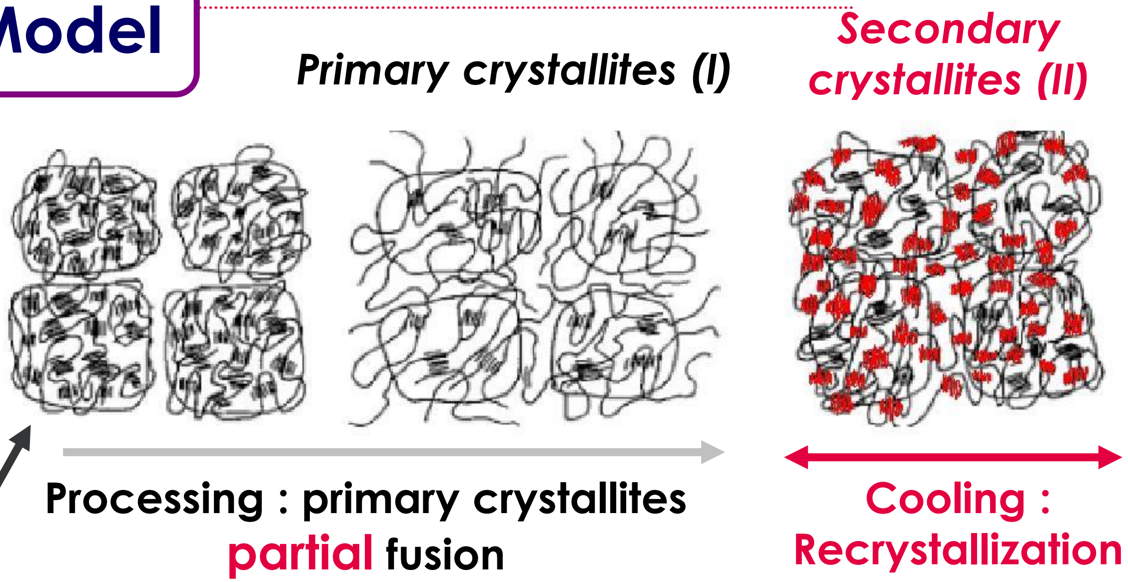


PVC GELATION

Summers Model

- **Gelation:**
  - The act of breaking down all the Stage III particles (grains)
  - Melting the Stage II particles (primary particles) and forcing them together
  - The degree that one melts the Stage I particles is the key to the final physical properties of the PVC compound
- **Gelation of 70 – 90% is considered optimum for opaque formulations:**
  - Considerable molecular interdiffusion between the Stage II particles
  - Interface in part still exist resulting in better impact





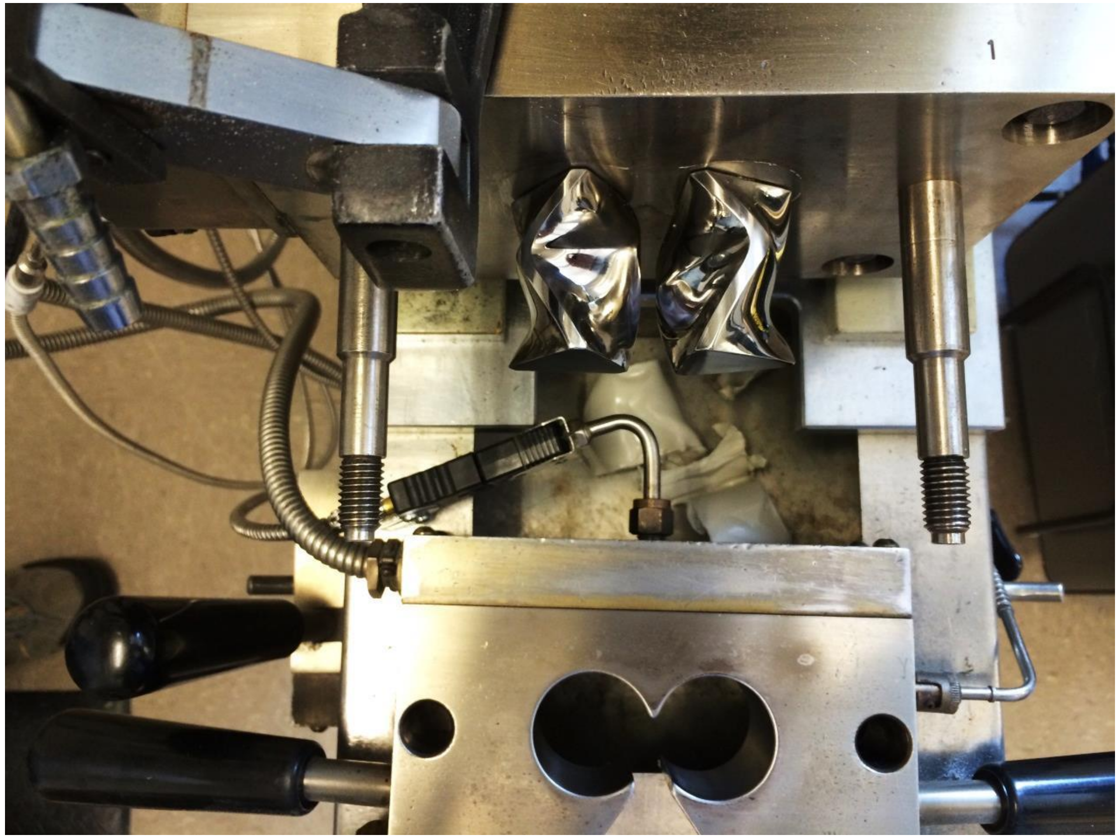
Crystallites → **3D network** → **Mechanical Properties**

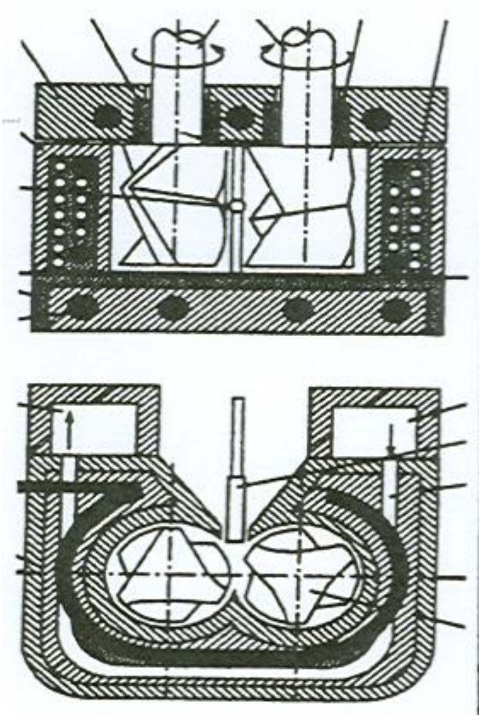
Summers, J.W., Rabinovitch, E.B., Booth, P.C. Measurement of PVC fusion (gelation). Journal of Vinyl Technology, March 1986, pp 2-6.

TORQUE RHEOMETER (PLASTICORDER) TESTING INSTRUMENT

Torque rheometry (ASTM D2547)

- Fusion Time
  - Appearance at vent
  - Temperature specific
- Fusion Torque
  - Related to extrusion amperage
- Equilibrium Torque
  - Melt viscosity in die
- Stability Time
  - Time to degradation
- Color chip analysis
  - Important for stabilization
  - Tool for tech service trouble shooting

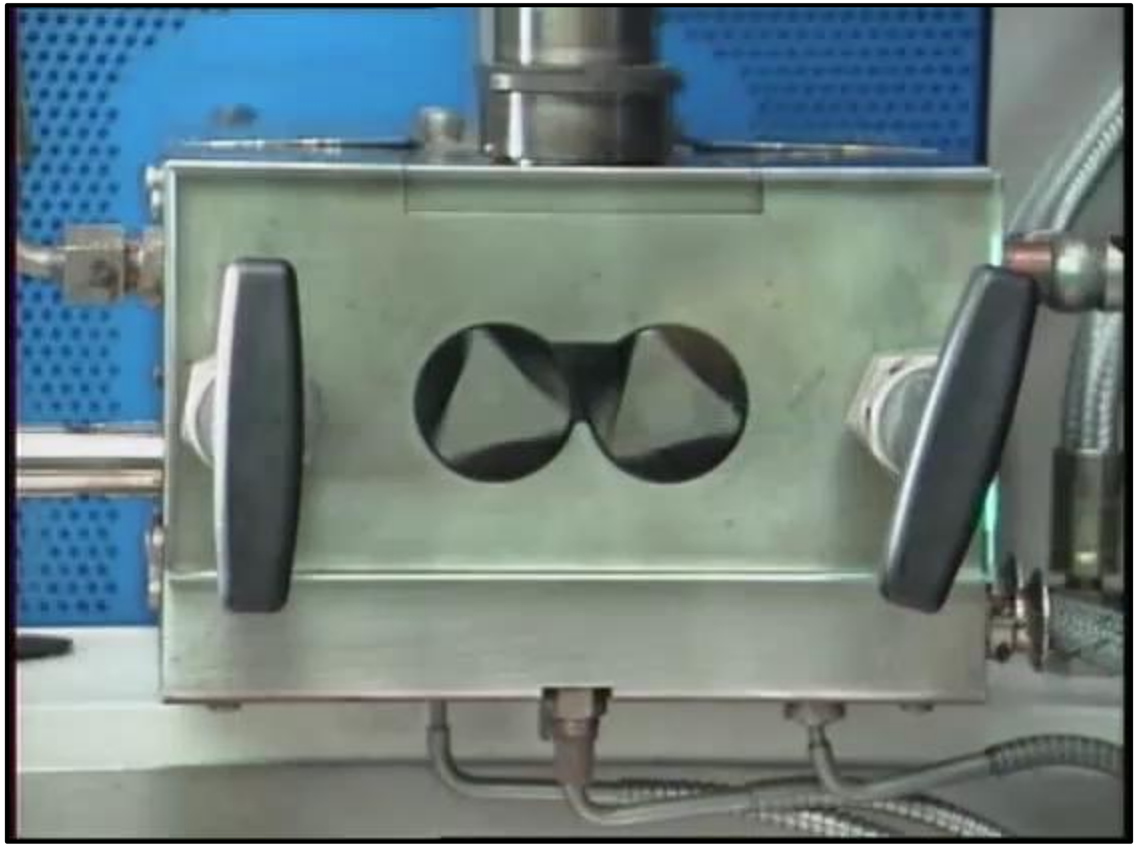




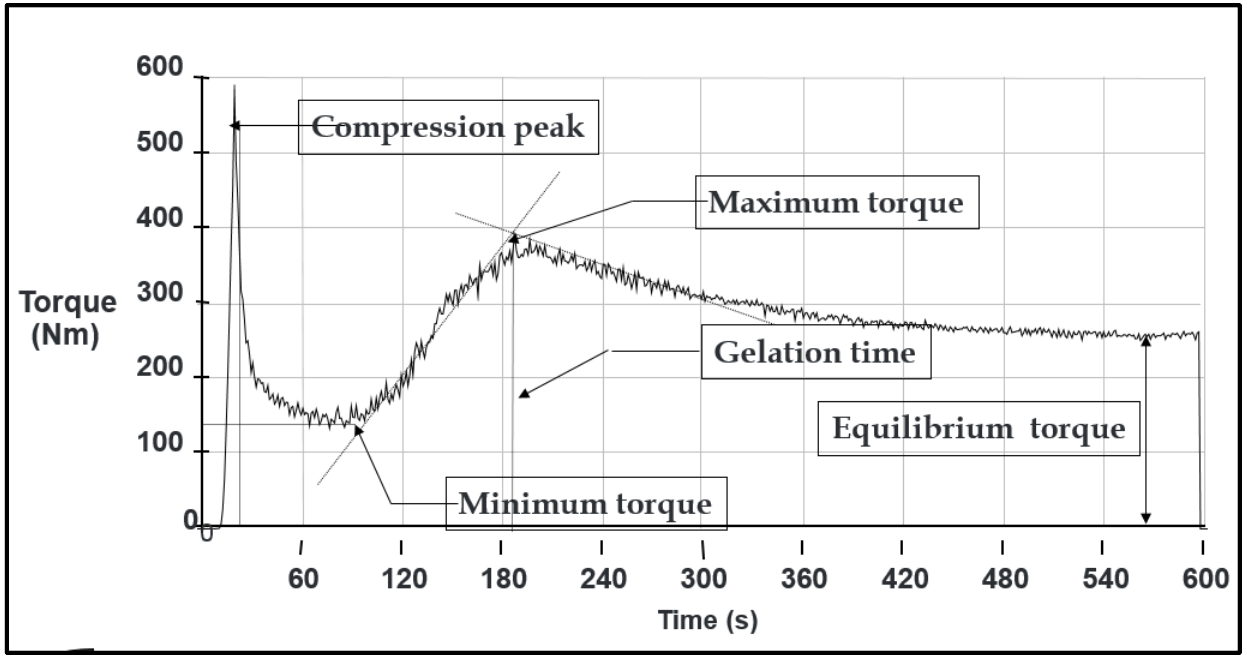
"The Brabender Bowl"

TORQUE RHEOMETER: A.K.A. THE "BRABENDER CURVE"

Promotion of the Gelation of PVC



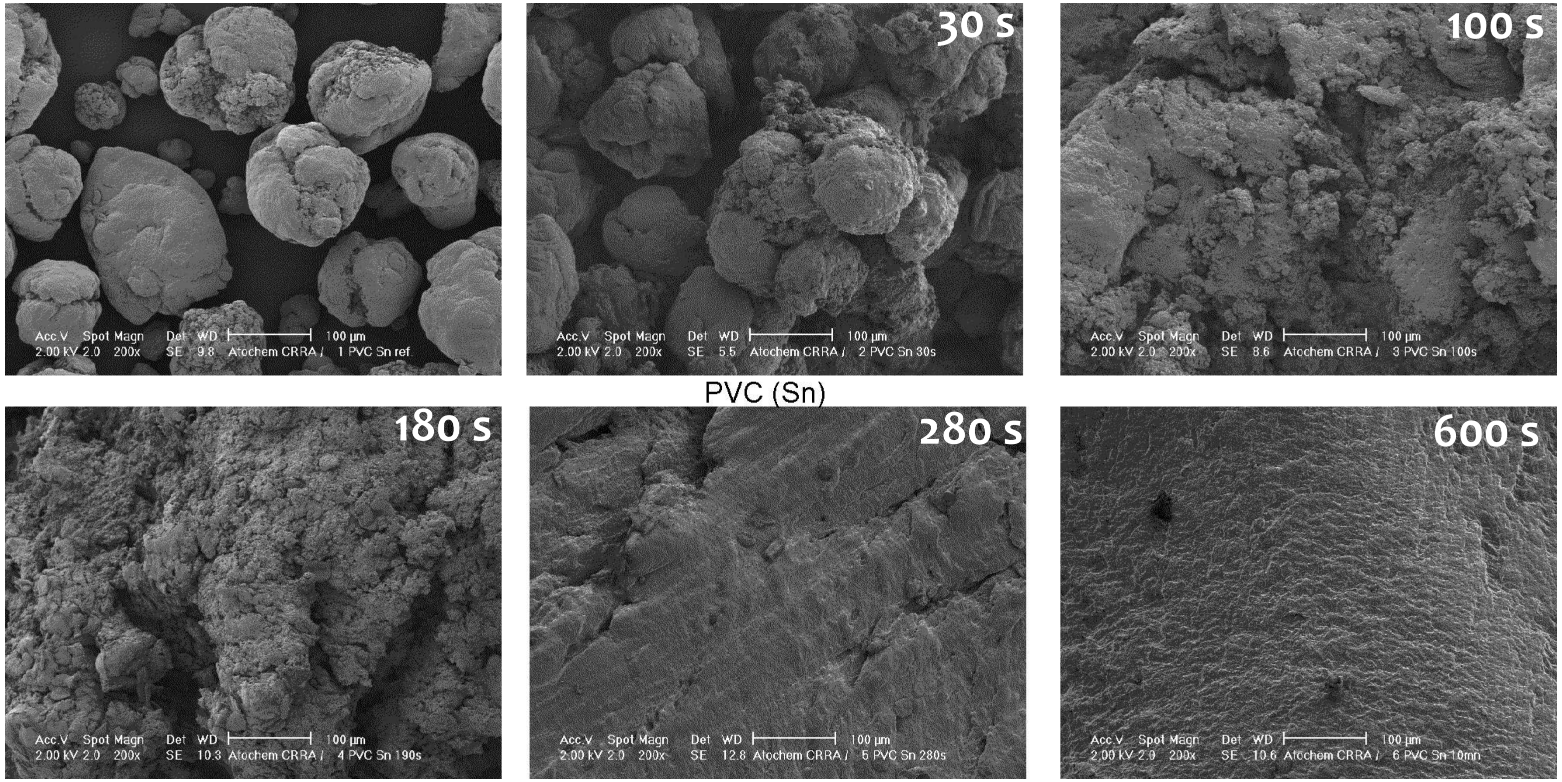
Torque Rheometer Test with Haake Internal Mixer
(https://www.youtube.com/watch?v=zICP3D3tnD8)



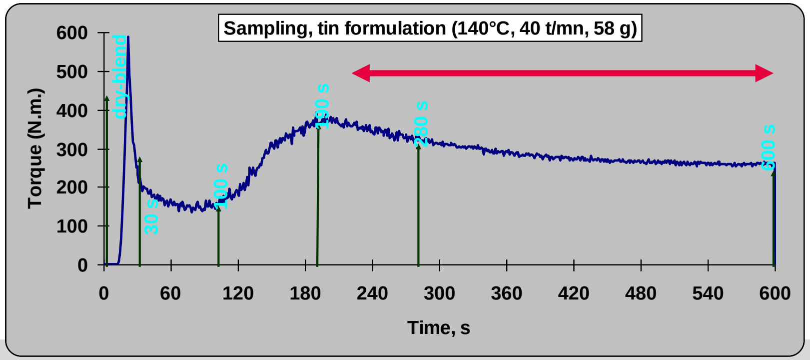
PVC GELATION: MICROSCOPIC STRUCTURE EVOLUTION

Gelation via torque rheometer:

- Breakdown of PVC grains to a continuous melt easier to imagine as it relates to a Brabender test
- Skin of PVC powder grain opens up releasing primary particles (PVC flow units)
- Eventually a continuous melt is developed with the desired rheology based on formulation



Bar = 100 µm
Time = 100 s



Creation of a macromolecular network is key. Low levels of gelation will lead to poor mechanical properties.

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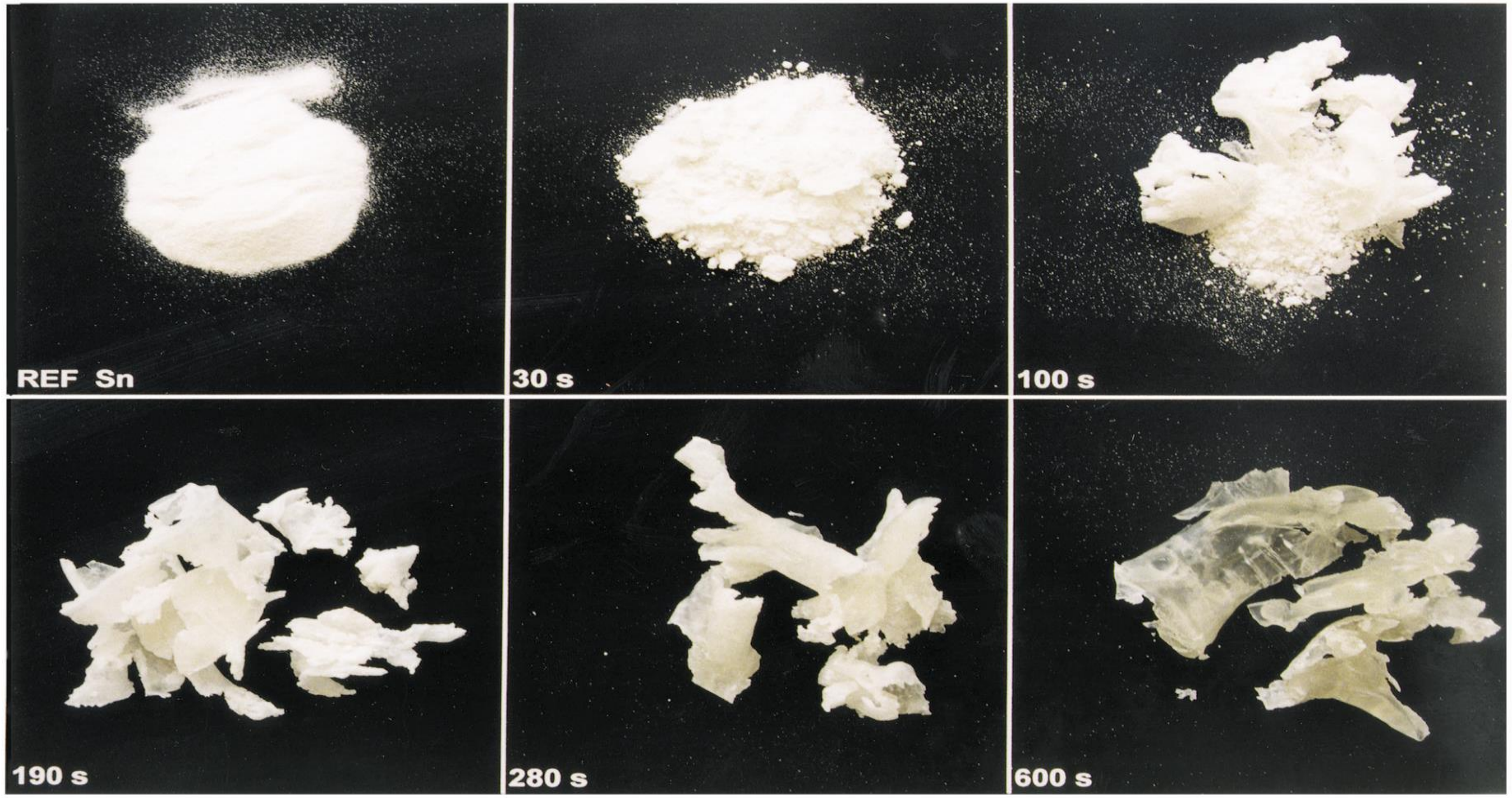
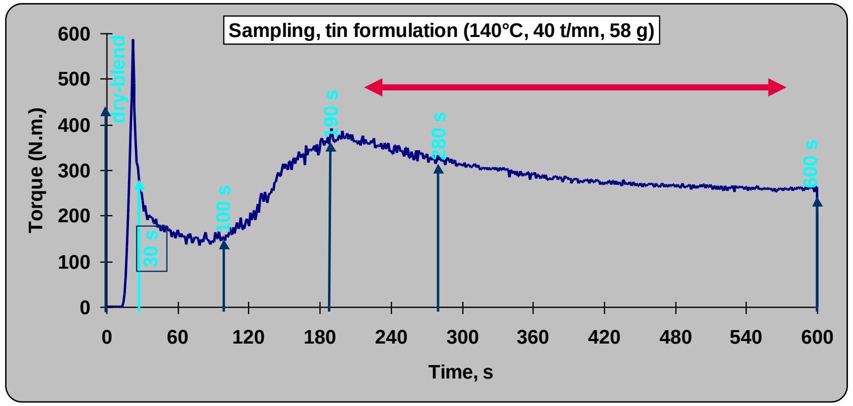
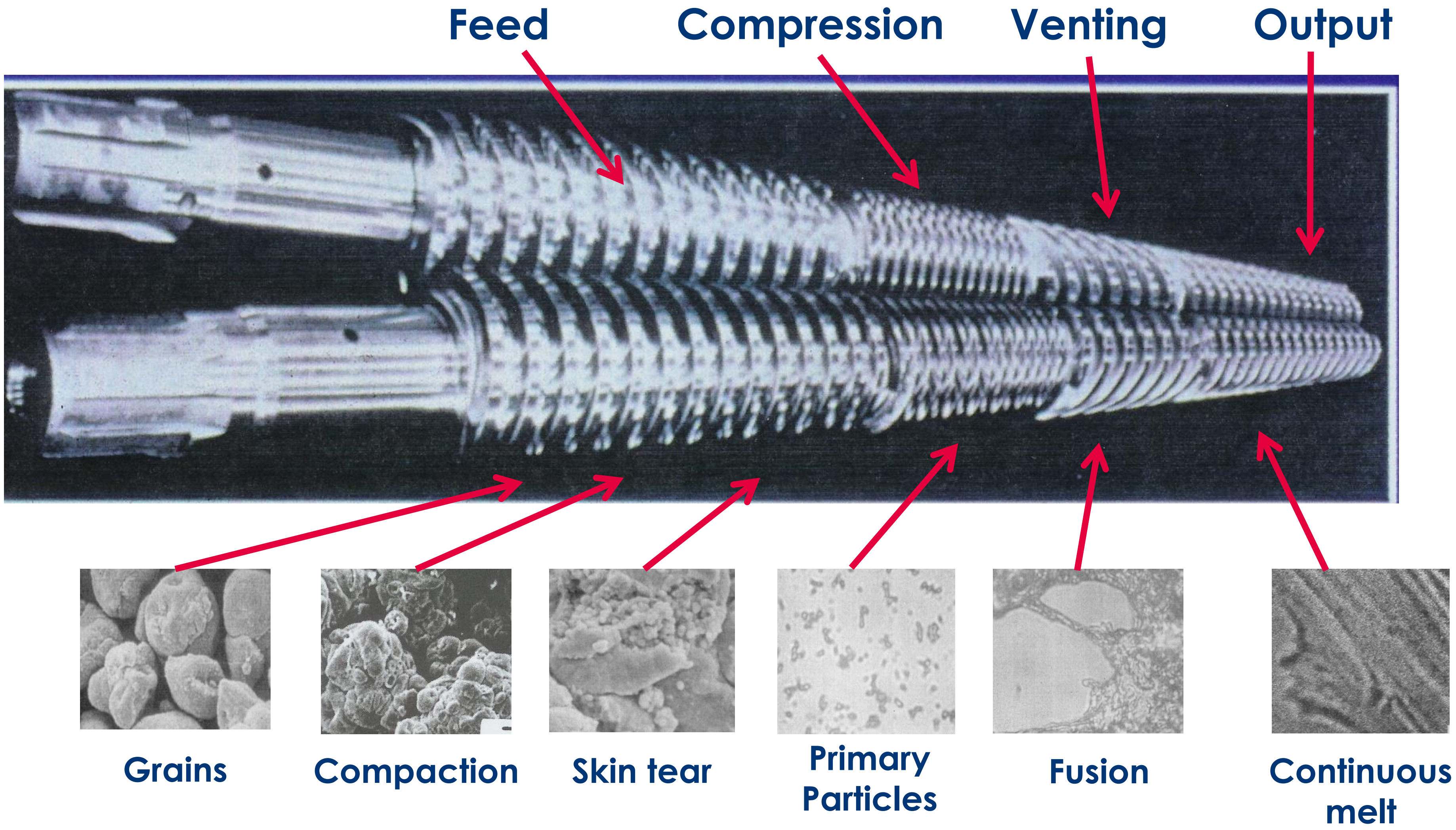
MACROSCOPIC STRUCTURE EVOLUTION

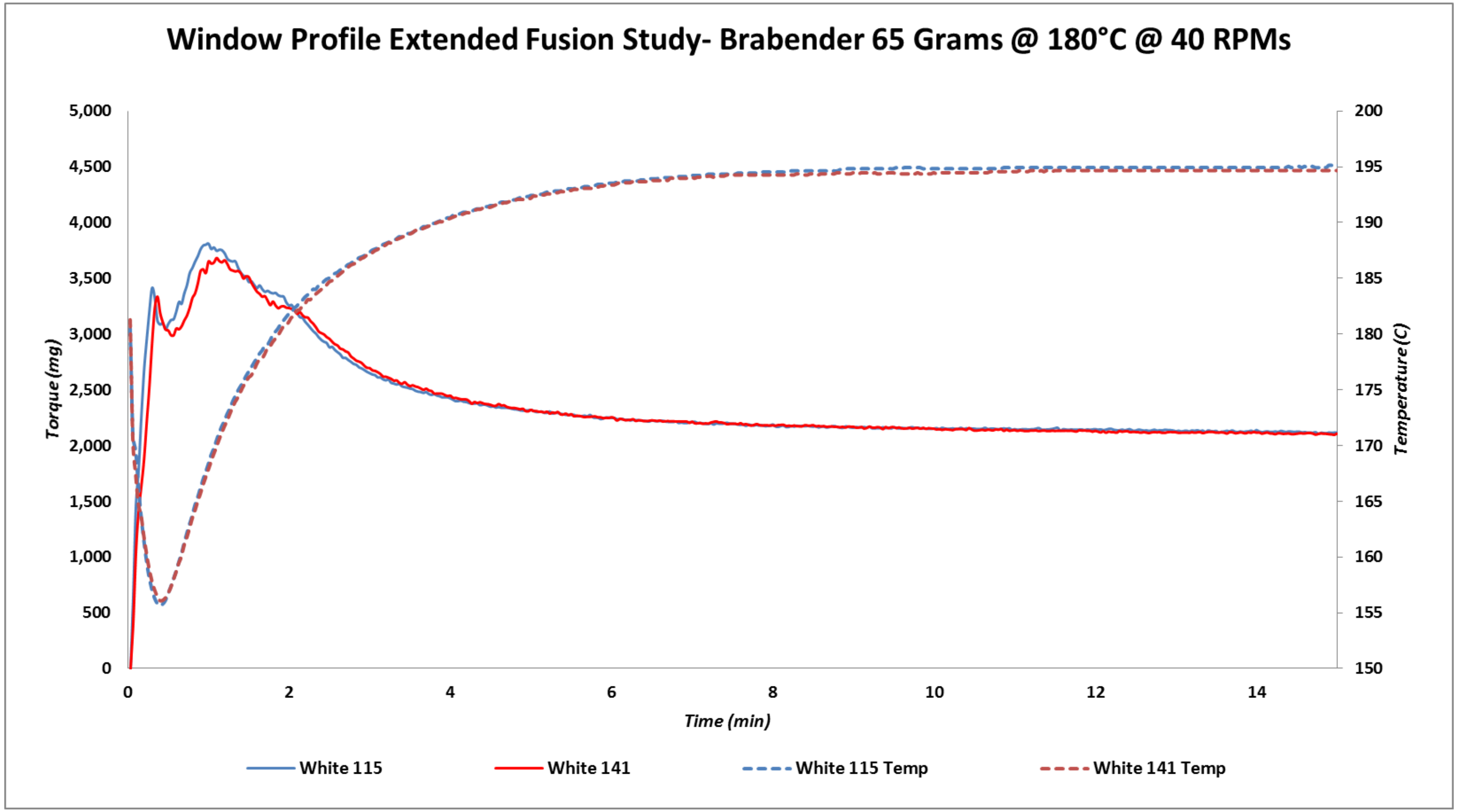




GELATION: PROCESSING BY CONICAL TWIN SCREW

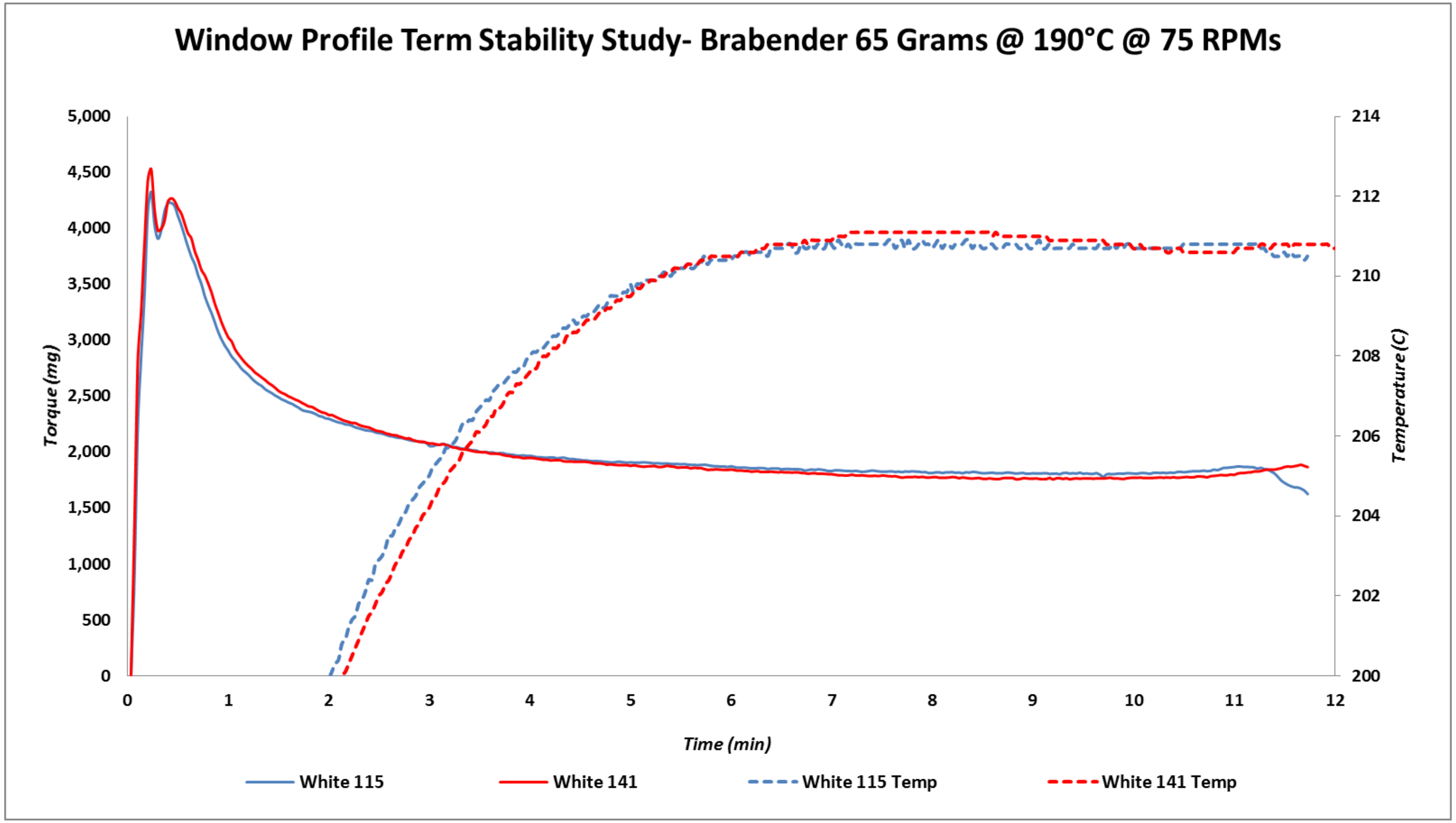


PVC RHEOLOGY – EXPANDED FUSION TESTING

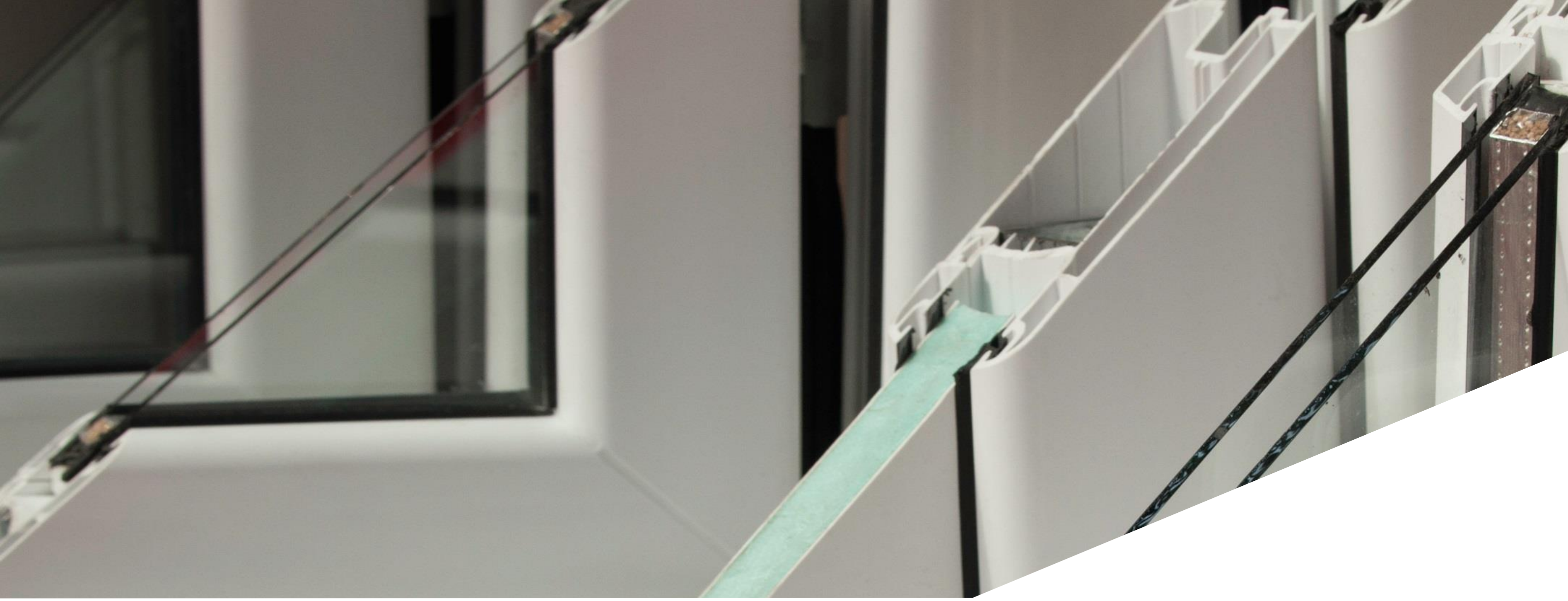


Brabender Extended Fusion - 65 Grams @ 180°C @ 40 RPM's	White 115	White 141
Load Peak (mg)	3,413	3,336
Fusion Time (min)	***0:42***	***0:44***
Fusion Temp (°C)	168	170
Fusion Torque (mg)	3,811	3,682
7½-Minute Torque	2,194	2,197
7½-Minute Temp	194	194
15-Minute Torque (mg)	2,116	2,096
Final Temp (°C)	195	195

PVC RHEOLOGY – THERMAL STABILITY TESTING



Brabender Term Stability - 65 Grams @ 190°C @ 75 RPM's		
	White 115	White 141
Load Peak (mg)	4,327	4,530
Fusion Time (min)	*0:12*	*0:12*
Fusion Temp (°C)	170	169
Fusion Torque (mg)	4,226	4,268
7½-Minute Torque	1,824	1,798
7½-Minute Temp	211	211
Final Torque (mg)	1,624	1,852
Final Temp (°C)	211	210
Term Stability (min)	11:16	11:34

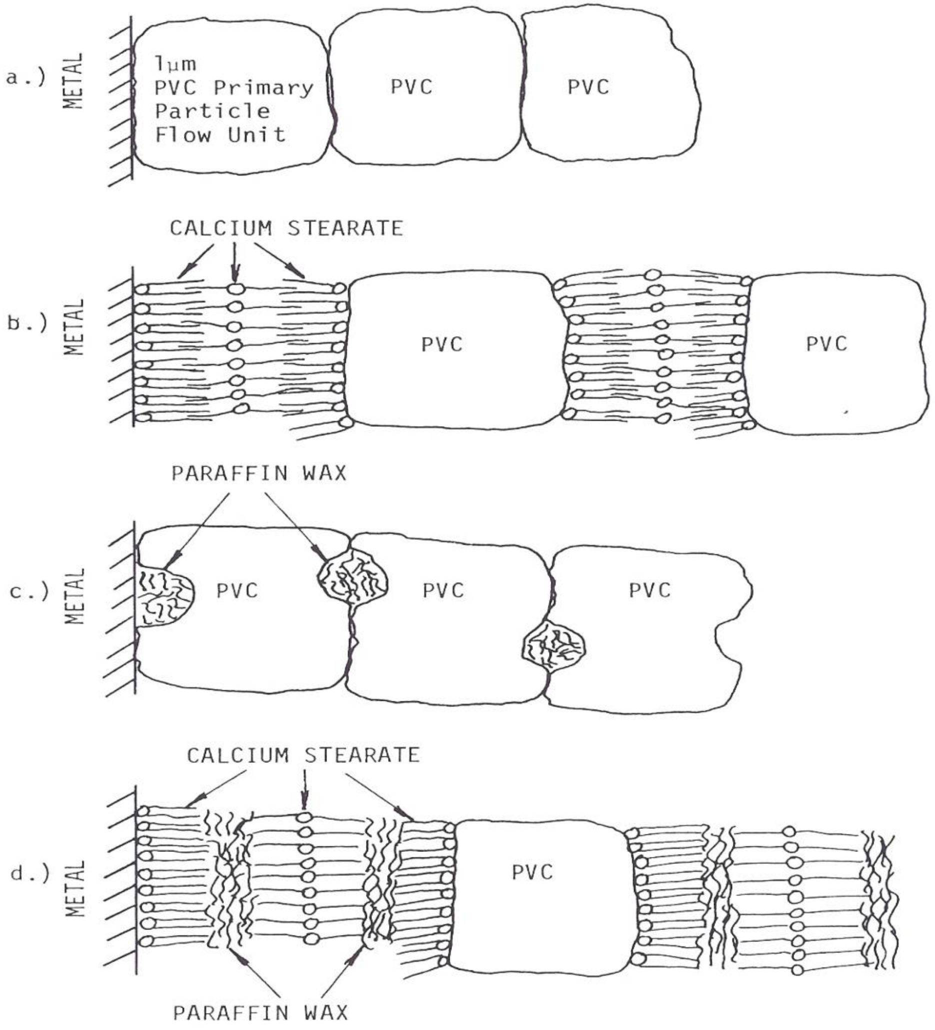


PVC FORMULATING

ESSENTIALS OF WHAT AND WHY IN THE PVC DRY BLEND

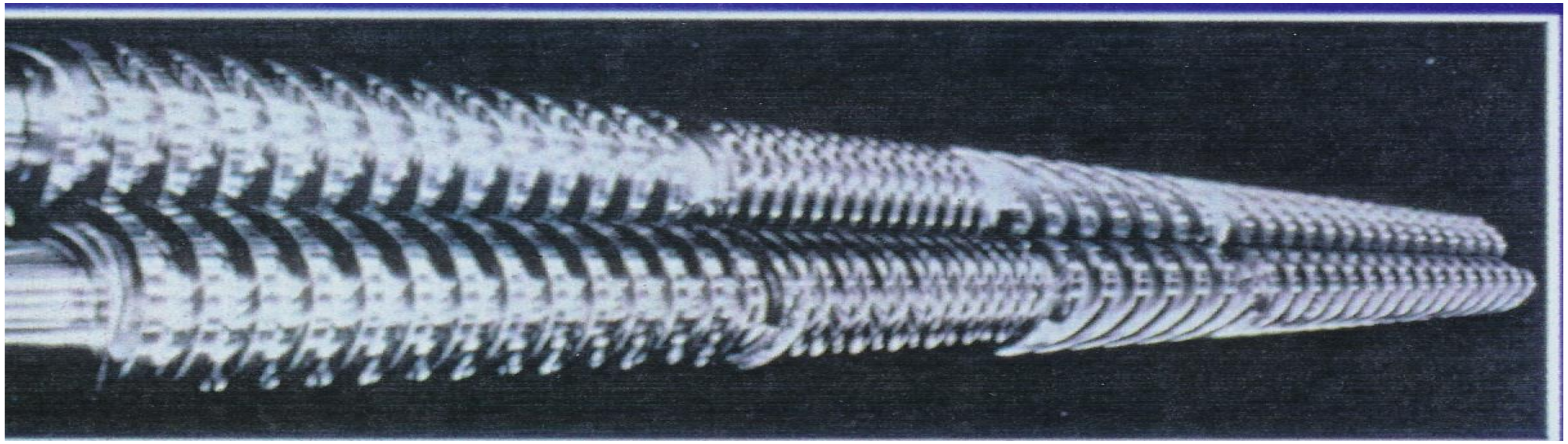
FUNDAMENTAL LUBRICATION THEORY

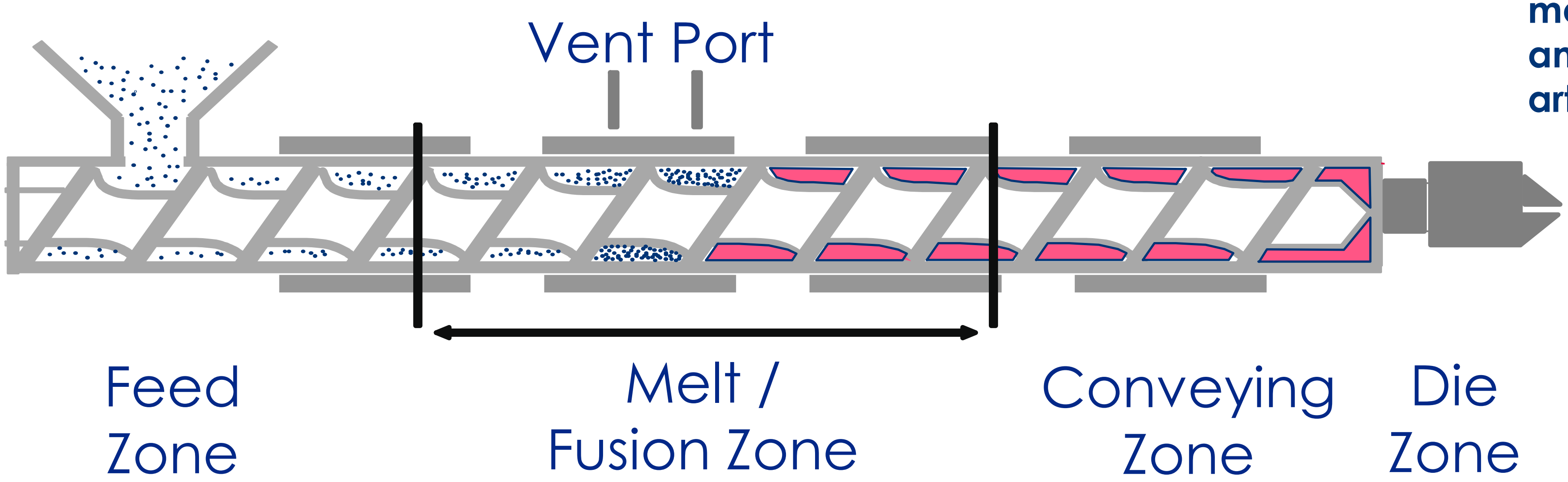
- Combination of Calcium Stearate (CaSt) and Paraffin Wax are the most common throughout the industry
- Fundamental building blocks of most rigid PVC formulations to control gelation
- The Summers model for lubrication explains how these work together during processing



Summers, J.W., Proceedings SPE ANTEC 2006, p2882

WHAT IS THE ULTIMATE GOAL FOR THE FORMULATION?

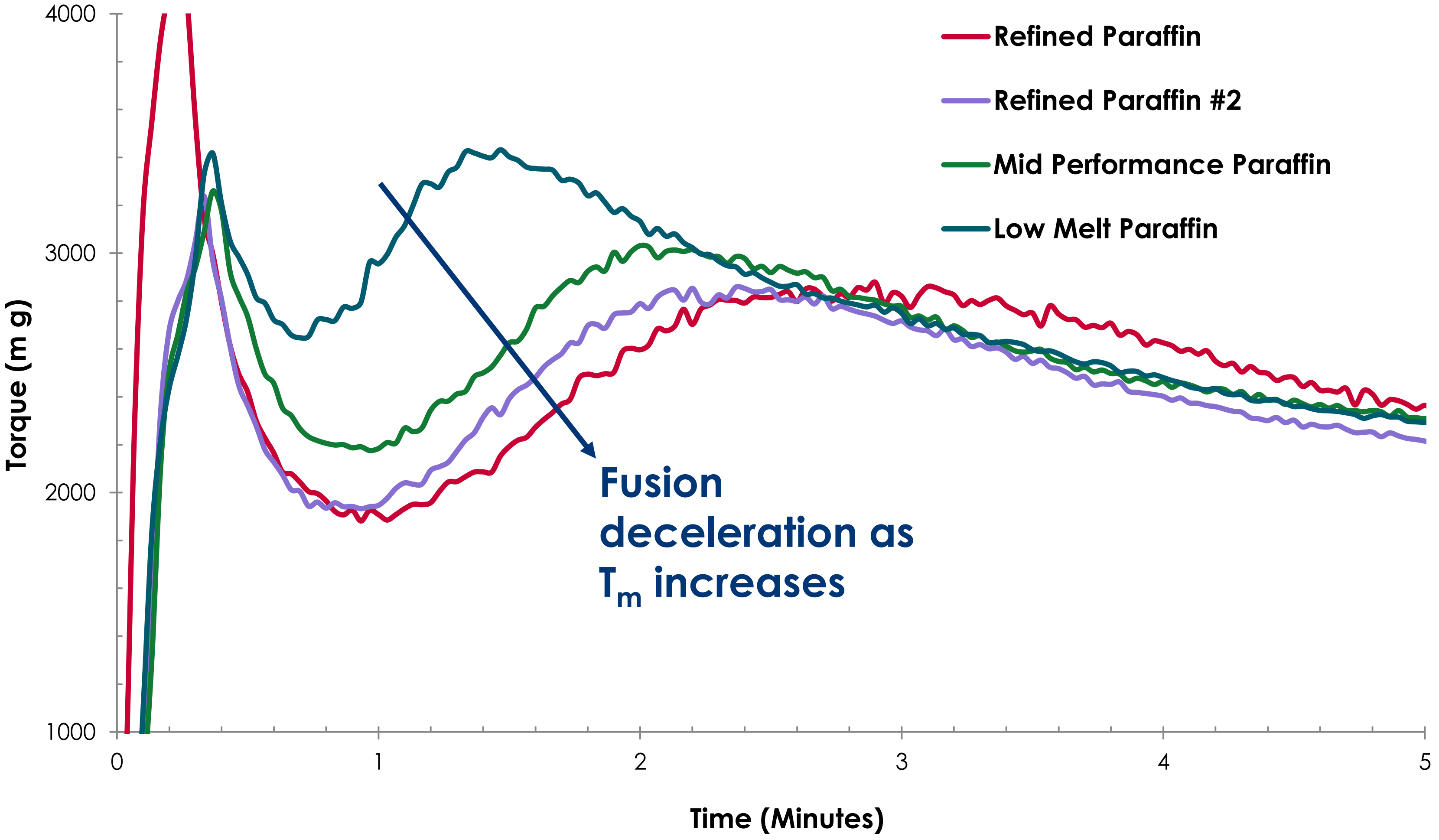




- Formulate for the equipment where the PVC blend will be processed
- Choose components necessary for mechanical property and aesthetic requirements
- Think about the output speed, manufacturing requirements and tooling for the final PVC article

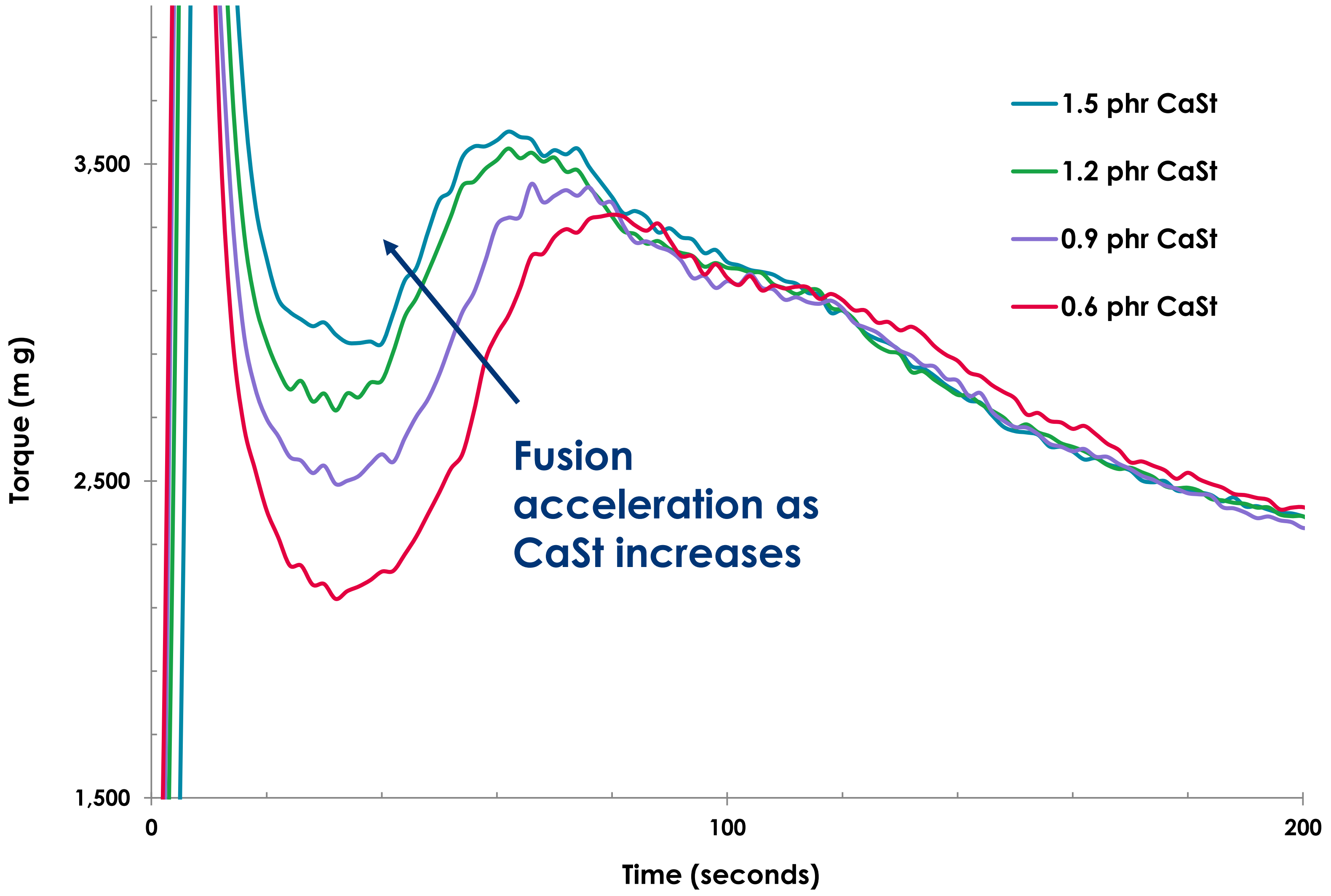
EFFECT OF PARAFFIN WAX MELTING POINT ON FUSION

Component	phr
PVC Resin (0.91 IV)	100
8% Sn reverse ester stab.	0.5
Calcium stearate	0.8
Paraffin wax (varied by T_m)	1.0
Oxidized PE	0.1
$CaCO_3$ (0.7 µm, treated)	5.0
Titanium dioxide	0.5



EFFECT OF CALCIUM STEARATE LOADING LEVEL ON FUSION

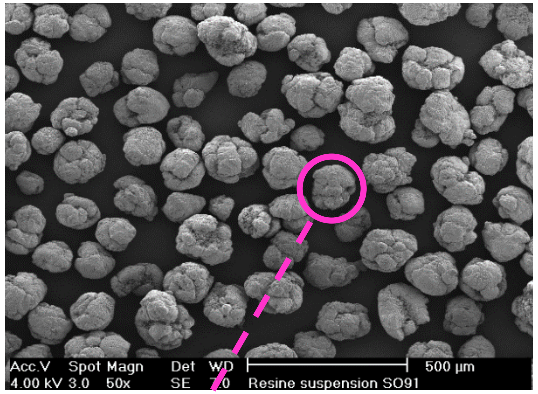
Component	phr
PVC Resin (0.91 IV)	100
8% Sn reverse ester stab.	1.0
Calcium stearate	-
Paraffin wax	0.7
Durastrength® 200H	2.5
Plastistrength® 530	0.5
$CaCO_3$ (0.7 µm, treated)	18
Titanium dioxide	1.0

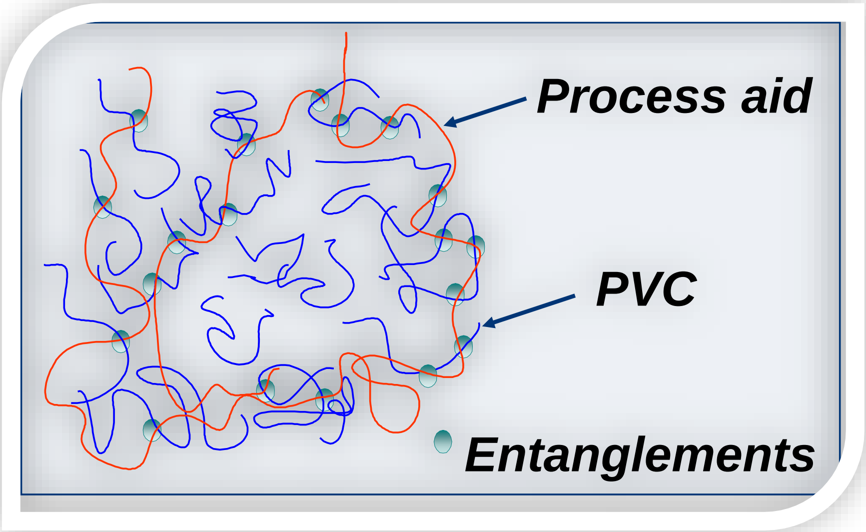


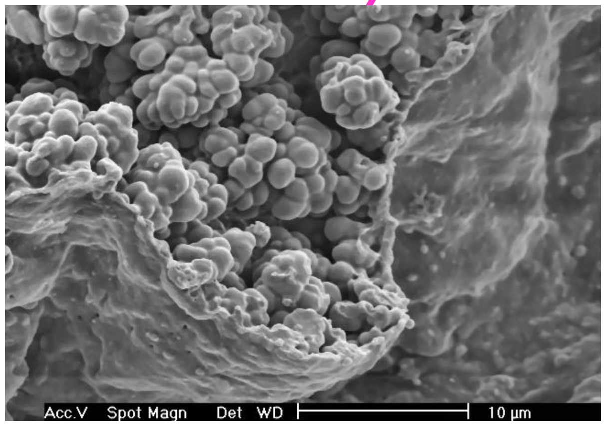
MODIFYING GELATION AND RHEOLOGY: ACRYLIC PROCESS AIDS

- Copolymers synthesized by Emulsion Polymerization
- Based on MMA, BA, and other acrylics or specialty monomers
- Excellent compatibility with polar polymer matrices, especially PVC
- Molecular weights *100k to >10 MM g/mol* vs. PVC resin (~ 60k g/mol)
- Functionality: fusion promotion, lubrication, cellular structure, melt strength

- Process aids started with one goal:
  - Force and shear transfer between primary PVC particles







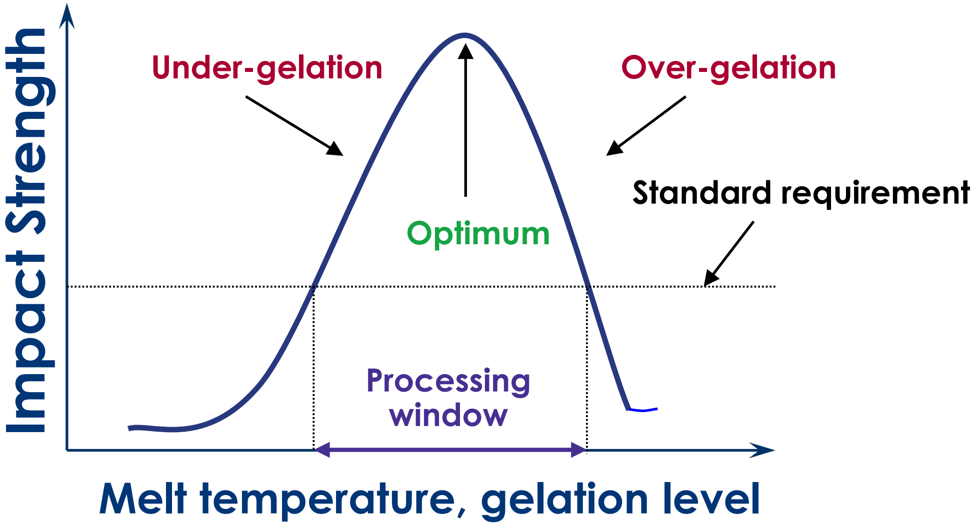
GELATION AND MECHANICAL PROPERTIES: ACRYLIC MODIFIERS / PROCESSING

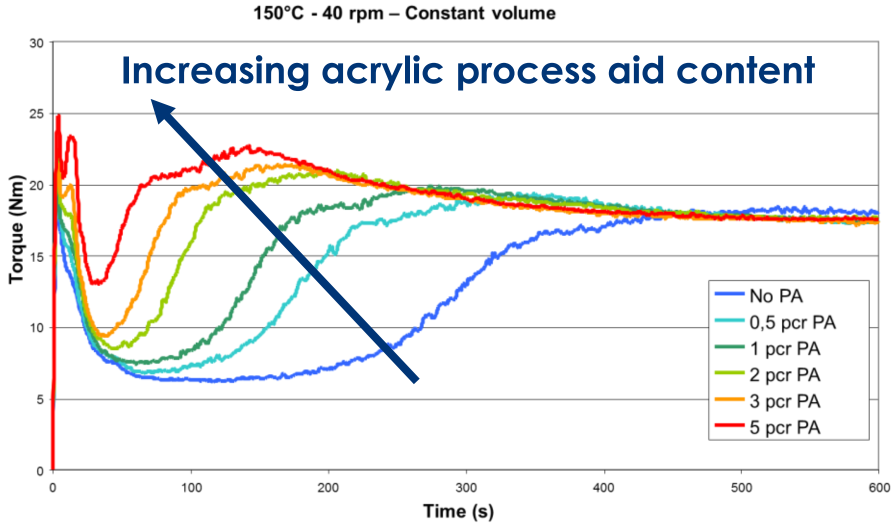
Gelation vs Fusion

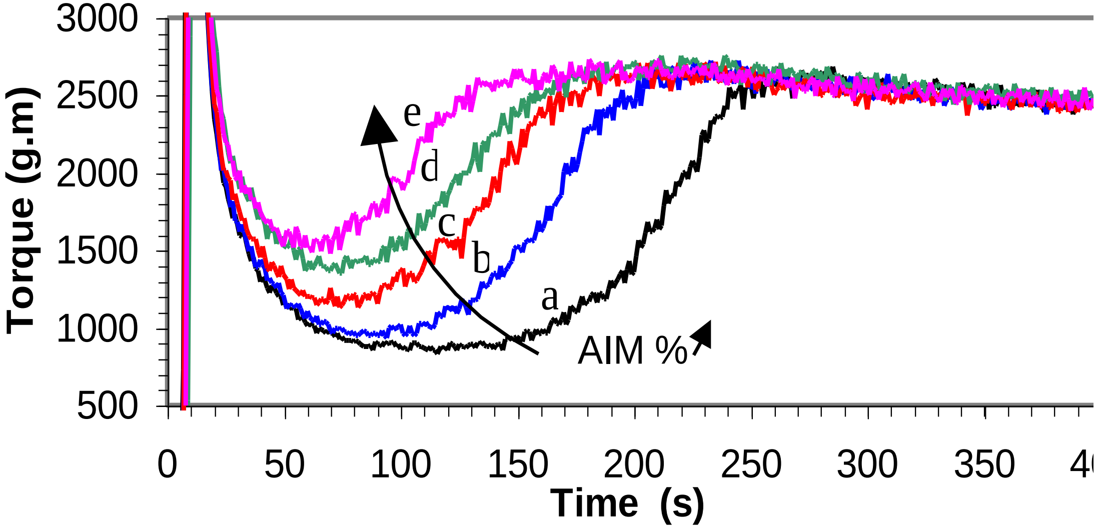
- Any PVC material will become ductile above a certain level of impact modifier ***OR*** gelation level
- At the transition, it will randomly break brittle or ductile: ***high standard deviation***
- The position of the transition depends on several factors: Gelation, MW of PVC, impact test, modifier type, °C / °F

Rheology can make it even more complicated

- Increasing modifier levels generally expedite fusion
- Increased fusion can lead to increased gelation
- Better gelation does not necessarily mean better impact properties







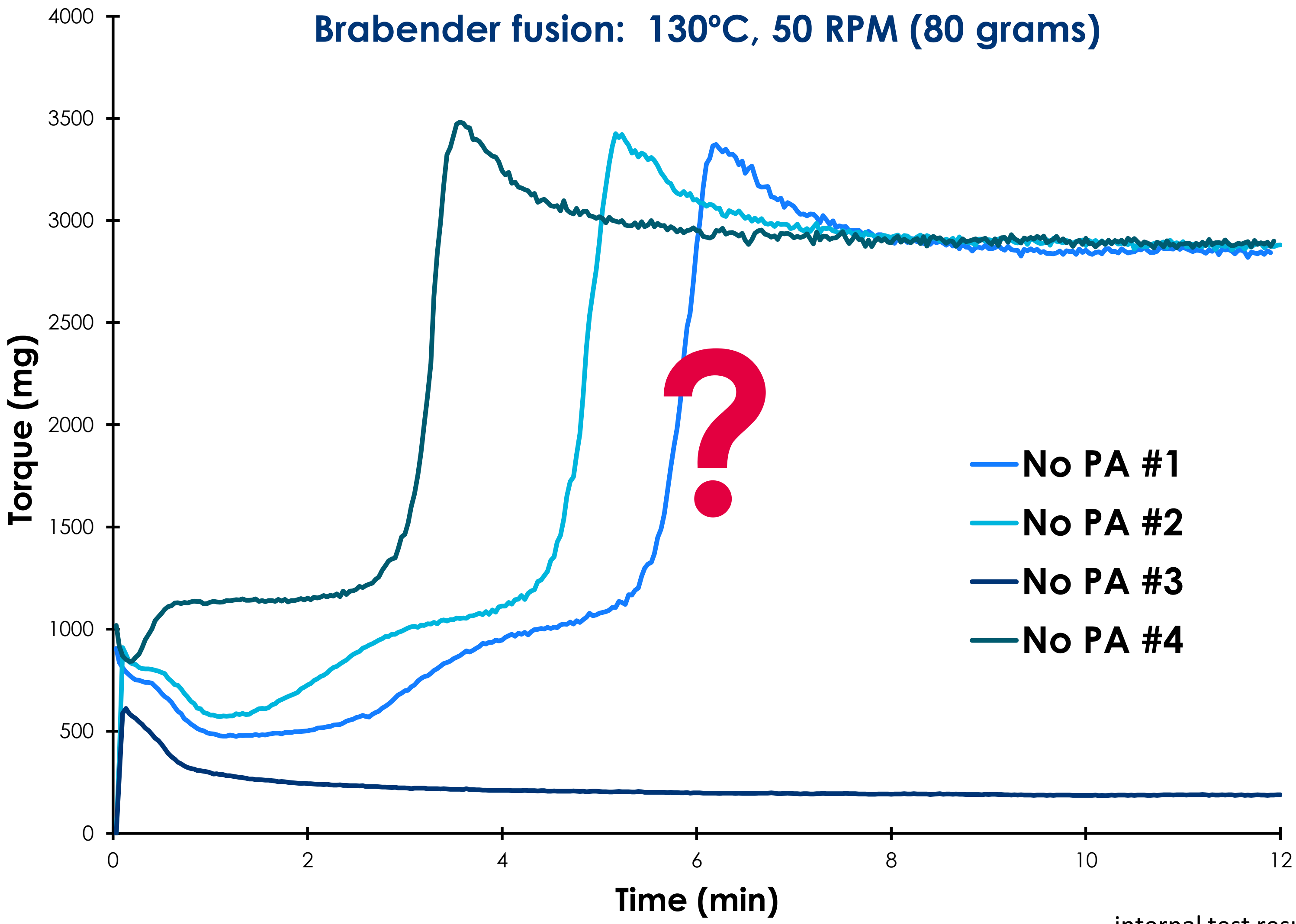
(a)=4.5 phr; (b) = 5.5 phr; (c)=6.5 phr; (d)=7.5 phr; (e)=8.5 phr

CONSISTENT PROCESSING PARAMOUNT WITH ELEVATED FILLER CONTENT

Challenging production with higher filler incorporation continues:

- **At ultra-high filler loading levels,** Luxury vinyl tile backlayer is ~ 65% $CaCO_3$
- **Filler necessary** for product performance with consumers, but difficult to incorporate into a continuous melt

Component	phr
PVC resin (0.82 IV)	100
Plasticizer (DOTP)	20
Plasticizer (ESBO)	10
CaZn stabilizer	2.5
Stearic acid	0.2
Process aid	***0***
Calcium carbonate (3 µm)	250
Titanium dioxide	2.5

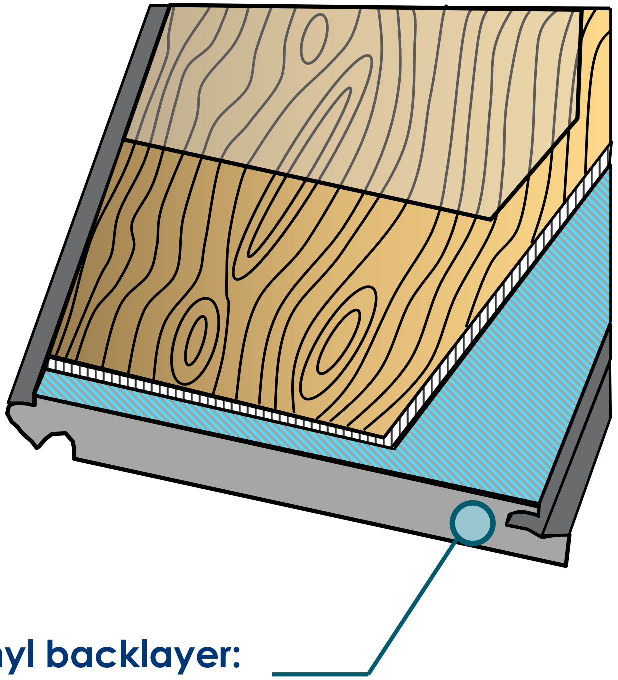


internal test results

ACRYLIC PROCESS AID IN HIGHLY FILLED FORMULATIONS

Excels in highly filled PVC formulations:

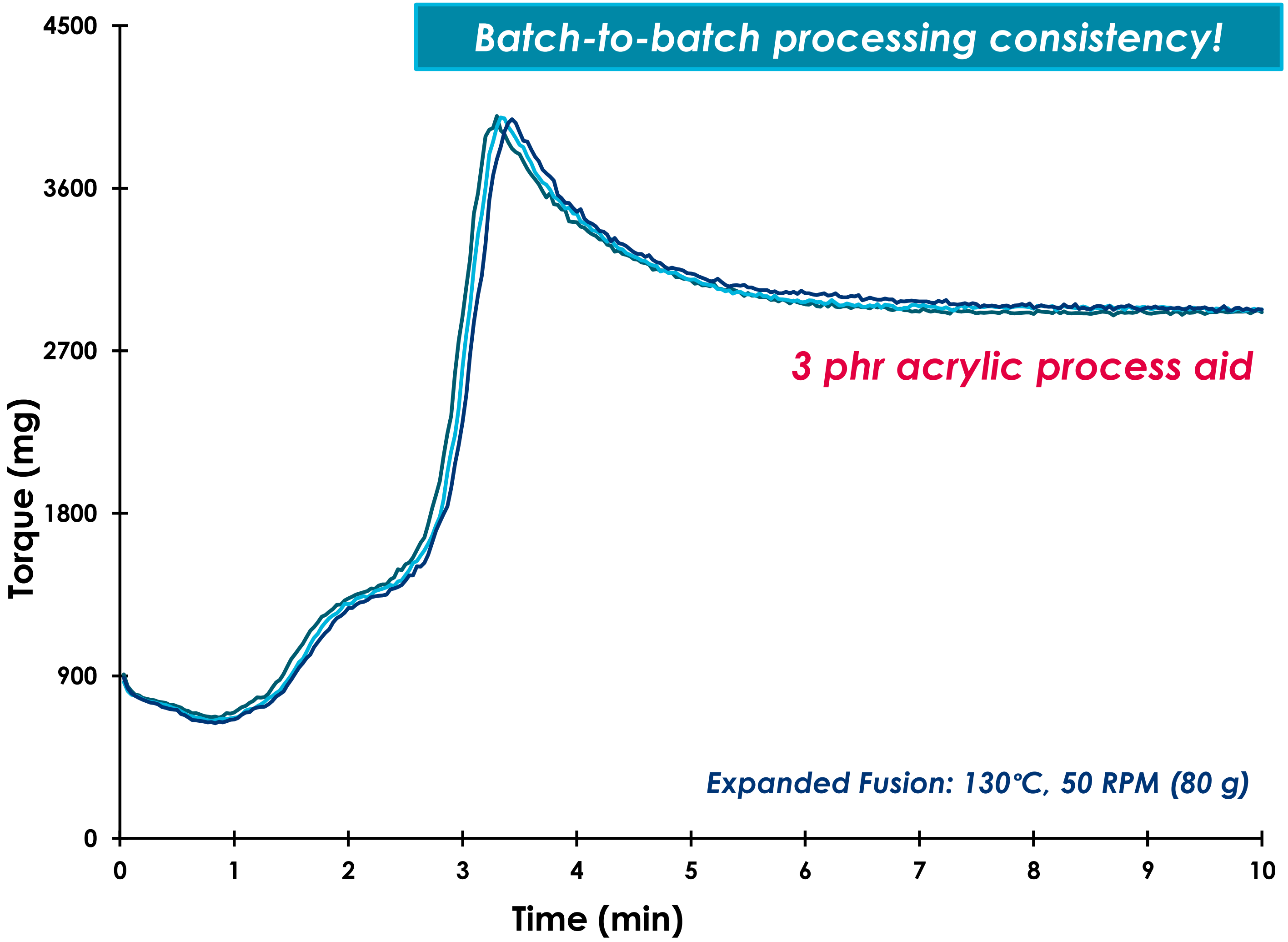
- *Process aid* provides processing consistency and promotes fusion



Reinforced vinyl backlayer:

- Extreme filler content levels
- Wide D50 range of calcium carbonate and filler used (20+ µm)
- Wide range of blending and processing equipment

Batch-to-batch processing consistency!



internal test results

PVC FORMULATION – RIGID PVC BASICS

Function	Ingredient	Role Within Formulation
Base Resin	PVC Resin	Basic properties
Heat Stability	Organotin Heat Stabilizer	Thermal stability, PVC resin can be easily degraded by exposure to high temperatures
Internal Lubricant	Calcium Stearate	Helps to process PVC by promoting PVC particle breakdown
External Lubricant	Paraffin Wax	Helps regulate extrusion process
External Lubricant	PE / OPE Wax	Helps regulate extrusion process / metal release
Fusion Promotion Melt Strength	Process Aid (PLASTISTRENGTH®)	Helps molten PVC compound maintain integrity during processing / promote fusion as needed
Impact Resistance	Impact Modifier (DURASTRENGTH®)	Provides PVC articles with improved toughness
Filler	Calcium Carbonate (0.7 µm)	Used for cost reduction in PVC processes. May help, or hurt certain physical properties
Pigment / UV Protection	Titanium Dioxide	Provides protection from UV light
Color	Pigments / Colorants	As Needed

BLENDING ORDER – IT MATTERS!

- Blended in order listed at defined temperatures.
  - Deviations May Have Consequences
- Suggested Blending Procedure
  - Start: PVC Resin
  - Start: Stabilizers
  - At 151 F / 66 C: Lubricants, Plasticizers
  - At 162 F / 72 C: Impact Modifiers, Process Aids
  - At 191 F / 88 C: Fillers (CaCO3)
  - At 208 F / 98 C: Titanium Dioxide, Blowing Agent
  - Blend to 212 F / 100 C or higher
  - Discharge to cooler
- Procedure should be tailored to equipment
- 60-85% of mixer capacity

PROCESSING EFFECTS TO DUE TO BLEND ORDER CHANGES

Ingredients	Too early? Impact on the compound? Effect at the extrusion?	Too late? Impact on the compound? Effect at the extrusion?
Stabilizer	n/a	Degradation of PVC resin may occur (>120°C) resulting in lower stability time. Poor dispersion.
Solid Paraffin Wax	Could interfere with stabilizer migration into PVC particles	Could preferentially coat fillers and additives rather than resin. Poor dispersion.
Calcium Stearate	Could interfere with stabilizer migration into PVC particles. If CaSt added before stabilizer, it can lead to agglomeration of stearate leading to conveying issues.	Could preferentially coat fillers and additives rather than resin. Poor dispersion.
Paraffin / PE Wax	Could interfere with stabilizer migration into PVC particles	Could preferentially coat fillers and additives rather than resin. Poor dispersion.
Titanium dioxide	Premature equipment wear. Waxes could preferentially coat the TiO_2 lessening their effect on the PVC resin.	Poor dispersion.
Calcium carbonate / filler	Waxes could preferentially coat the $CaCO_3$ lessening their effect on the PVC resin / could lead to conveying issues to extrusion lines	Poor compound homogeneity at higher filler levels.
Pigment	Agglomeration of pigment particles	Poor mixing.
Process Aid	Could be preferentially coated by lubricants	Poor dispersion.
Impact Modifier	Could be preferentially coated by lubricants. Rubber agglomeration resulting in loss of impact properties and of conveying issues.	Poor dispersion.

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PVC FORMULATIONS

SOME EXAMPLES OF NORTH AMERICA-BASED PVC FORMULATIONS

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INNOVATIVE CHEMISTRY

RIGID WEATHERABLE PVC: WINDOW LINEALS AND CAPSTOCK

Rigid Weatherable PVC:

- **Window profile and capstock**
- **Titanium dioxide critical**
- **High L-based colors > 85 (White, off-white, beige, sandstone, yellow, light green, etc.)**
- **Acrylic "heavy" applications with 3 – 7 phr acrylic**
  - One-packs are common like Durastrength® 510, 535, 527
- **For every 1 phr of $CaCO_3$ added, b-value after weathering shifts > 0.5**
- **Window profile utilizes more metal release / ester-based waxes**
- **Izod and drop dart impact critical**

Component	PHR
PVC Resin (0.91 IV or K-65)	100.0
Sn Stabilizer (> 18% Sn, 2-ME/DDM, TGA, or RE)	0.6 – 1.2
Calcium stearate	0.8 – 1.2
Internal lubricant (ester-based)	0.3 – 0.6
Paraffin wax (165°F MP)	0.8 – 1.0
Durastrength® 200, 320, 350	***3.0 – 5.0***
Plastistrength® 550, 530	***0.6 – 1.2***
Metal release: oxidized PE (AC629A) ***Plastistrength® 770*** ***Plastistrength® L-1000***	***0 – 0.2*** ***0 – 0.7*** ***0 – 0.5***
Calcium Carbonate (0.7 µm) – treated common	0 – 8.0
Titanium dioxide (chalk / non-chalk)	8.0 – 12.0
Color / pigments	< 0.5 as needed
total	***~ 123.0***

PVC SUBSTRATE: SIDING AND FENCE

- **PVC substrates:**
  - **Base layers for siding and fence**
  - **Calcium carbonate loading is king**
  - **Titanium dioxide only used for hiding**
  - **Need enough impact modifier to meet drop-dart standards**
    - Vinyl siding has minimum requirements
    - Fence has cell class requirements
  - **One-pack lubricants very common**

Component	PHR
PVC Resin (0.91 IV or K-65)	100.0
Sn Stabilizer (< 12% Sn, reverse ester pipe stab.)	0.6 – 1.2
Calcium stearate	0.8 – 1.2
Paraffin wax (145 - 165°F MP)	0.8 – 1.0
Metal release (oxidized PE – E10 or E14 waxes)	0 – 0.2
Durastrength® 350, 4000	***2.0 – 3.5***
Plastistrength® 530, 576	***0.6 – 1.2***
Calcium Carbonate (0.7 μm) – can be treated	16.0 – 24.0
Titanium dioxide (chalk / non-chalk)	0.5 – 1.5
Color / pigments – regrind from capstock color	< 0.5 as needed
total	***~ 128.0***

PVC PIPE: LOW SHEAR, NON-WEATHERABLE PVC

- **PVC Pipe:**
  - **Accounts for largest PVC resin consumption (by far!)**
  - **Formulating largely governed by HSB TR-2 listing (range formulation)**
  - **Pipe extrusion can be lower shear vs. window profile processing**
  - **Tensile and burst physical properties most critical (less impact needed)**
  - *** impact modifier used in foam core pipe (FCP) skin**
  - **** process aid used in FCP core for cellular PVC (> 0.90 g/cc density)**

Component	PHR
PVC Resin (0.91 IV or K-65)	100.0
Sn Stabilizer (< 12% Sn reverse ester stab.)	0.3 – 1.0
Calcium stearate	0.4 – 1.5
Paraffin wax (165°F MP)	0.6 – 1.5
Oxidized PE (low MW common)	0 – 0.5
Durastrength® 200, 320, 350	***0 – 3.0***
*****Plastistrength® 379, 580***	***0 – 3.0***
*****Plastistrength® 770***	***0 – 2.0***
Calcium Carbonate (3.0 µm) – can vary	0 – 5.0
Titanium dioxide (chalk / non-chalk)	0.5 – 3.0
Color / pigments	0 – 1.0, as needed
total	***~ 108***

CELLULAR PVC: FOAM! A.K.A LIGHTWEIGHTING B&C MATERIALS

Cellular PVC:

- **Can be densities as low as 0.45 g/cc – 0.75 g/cc (shutters vs. deck boards)**
- **Thickest foam sheet ~ 0.50 g/cc**
- **Generally: highest MW leads to lowest loading level**
- **Most formulations use lubricating process aid**
- **Chemical blowing agent can be powder, pellet, liquid form**
- **Need to identify Celuka vs. free foam processes for product selection**
- ***Old and new technologies flourish in the market due to equipment and formulation types!***

Component	PHR
PVC Resin (0.65 – 0.70 IV or K-56, 57)	100.0
Sn Stabilizer (> 18% Sn, TGA)	1.5 – 2.5
Calcium stearate	0.8 – 1.2
Internal lubricant (ester-based, e.g. EGDS)	0.3 – 0.8
Paraffin wax (165°F MP)	0.3 – 0.6
Oxidized PE (high MW, fusion promoting)	0 – 0.3
Plastistrength® 580	***3.0 – 9.0***
Plastistrength® 770	***1.5 – 2.5***
Calcium Carbonate (0.7 µm)	5.0 – 15.0
Titanium dioxide (chalk / non-chalk)	2.0 – 8.0
Chemical blowing agent (active content)	0.5 – 1.0
total	***~ 128***

SEMI-RIGID / FLEXIBLE PVC SHEET: INTRODUCING PLASTICIZER

Semi-rigid / Flexible PVC:

- **Products generally calendered versus extruded for processing**
- **Clear formulations for wear layers and packaging (* opaque, weatherable also made)**
- **MBS products needed for clear impact modification**
- **Plasticizer introduction leads to flexible performance vs. rigid**
- **Non-Sn based stabilizer system for low volatile / odor, low shear processing**
- **Metal release important to prevent sticking on rolls / tackiness and smooth surface quality**

Component	PHR
PVC Resin (0.77 – 0.82 IV or K-61 - 63)	100.0
Plasticizer (DOP, DOTP, or Vikoplast® products)	18 - 25
Calcium / Zinc stabilizer (or other based on clarity)	2.0 – 3.0
Stearic acid	0 – 1.0
Clearstrength® W300 or other (*Durastrength)	***3.0 – 10.0***
Plastistrength® 550 or 551	***1.0 – 2.0***
Plastistrength® 770 or L-1000	***0 – 1.0***
*Calcium Carbonate (0.7 µm) – e.g. Omyacarb UFT	0 - 20
*Titanium dioxide (chalk / non-chalk)	0.5 – 1.5
total	***~ 131***

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*Please join us for our second PVC Workshop with SPE on July 21st 2021, **Acrylic impact modifiers for PVC: core-shell modifier chemistry and performance.***

We look forward to seeing you there!

- **Please visit our website for more information about Arkema and our newest technology:**
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Thank you!