PVC101 WORKSHOP #2: ACRYLIC IMPACT MODIFIERS FOR PVC: CORE-SHELL MODIFIER CHEMISTRY AND PERFORMANCE

ARKEMA PLASTIC ADDITIVES

RABER INOUBLI

JULY 21, 2021

SPE PREFERRED PARTNER

COATING RESINS ARKEMA GROUP

ACRYLIC IMPACT MODIFIERS FOR PVC

Impact Modifiers: acrylic core-shell chemistry

- Core-shell design and chemistry
- Emulsion chemistry to core-shell powder isolation
- Key core-shell component elements

Core-shell modification of PVC: how do they work?

- Impact modification mechanisms
- Importance of core-shell modifier dispersion
- Core-shell acrylic impact modifier property influence
- Acrylic impact modifier formulation synergies

PVC Formulations, examples

- Highlighted acrylic impact modifier use

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

PVC APPLICATIONS FOR B&C MARKETS OPTIMIZING PERFORMANCE

PVC formulating continues to innovate around synergies between impact modifiers and filler incorporation:

- **Applications in B&C pushing limits of inorganic filler incorporation via extrusion**
  - Thresholds for addition vs. mechanical property integrity in constant balance
- **PVC application growth domestically in NA around highly filled applications or adding weatherable capstocks to a vinyl substrate**
- **Vinyl B&C industry overall trending to high rubber impact modifier products – BUT – effects of rheology modification and processing can be a hurdle (legacy formulations)**




VINYL B&C FORMULATIONS REQUIRING IMPACT STRENGTH VARY WIDELY

What does the vinyl application require?

- Weatherable vs. non-weatherable
- Filler content: mono-extruded vs. substrate
- ASTM / industry standard specifications
- Drop dart impact vs. Izod impact requirements
- Cost-efficient formulation

The balancing act …

- Meeting market specifications
- Maintaining impact strength
- Incorporating incrementally higher filler content
- Reducing material costs further
- Matching rheology for a wide range of extrusion equipment in manufacturing sites

Component	PHR
PVC Resin (0.91 IV or K-65)	100.0
Sn Stabilizer (< 12% Sn to > 18% Sn products), [calcium zinc packages in some applications]	0.6 – 1.8 [2.0 – 4.0]
Calcium stearate	0.6 – 1.5
Paraffin wax (145 - 165°F MP)	0.6 – 1.0
Metal release (oxidized PE typical)	0 – 0.2
Impact Modifier	***?***
Process Aid	***?***
Calcium Carbonate (0.7 - 50 µm), Talc, others	5 – 25, 100 – 300
Titanium dioxide (chalk / non-chalk)	0.5 – 1.5; 8 - 12
Color / pigments – regrind from capstock color	< 0.5 as needed
total	***~ 110 – 400 (!)***

PLASTISTRENGTH® BY ARKEMA
DURASTRENGTH® BY ARKEMA
CLEARSTRENGTH® BY ARKEMA

IMPACT MODIFIERS

ACRYLIC IMPACT MODIFIERS: CORE-SHELL TECHNOLOGY

ARKEMA
INNOVATIVE CHEMISTRY

THE GOAL OF IMPACT MODIFIERS

To lower the DBTT (ductile-brittle transition temperature) of the material

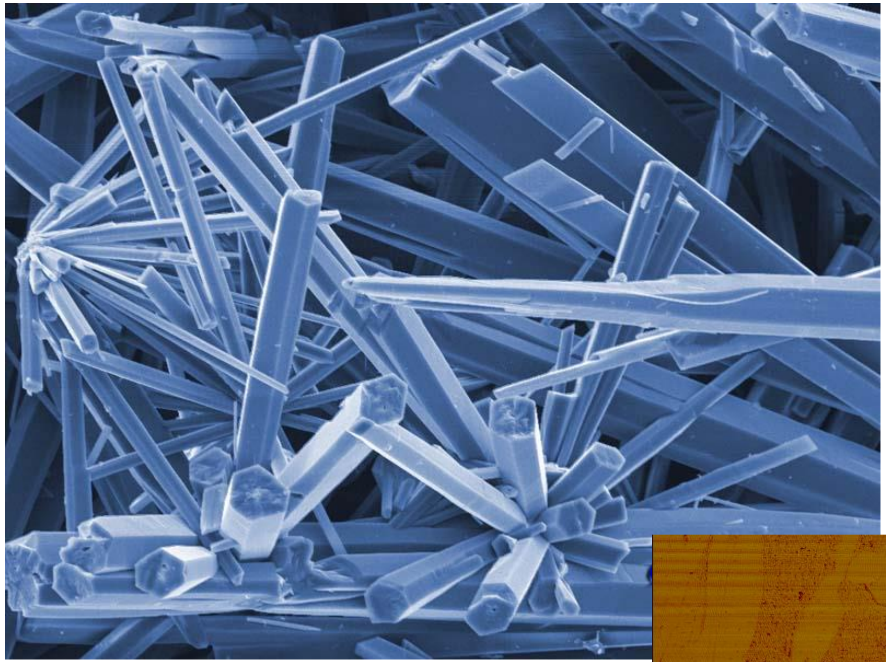
- As temperature decreases, a material's ability to absorb a specific amount of energy without fracturing decreases
- Make your matrix tougher!

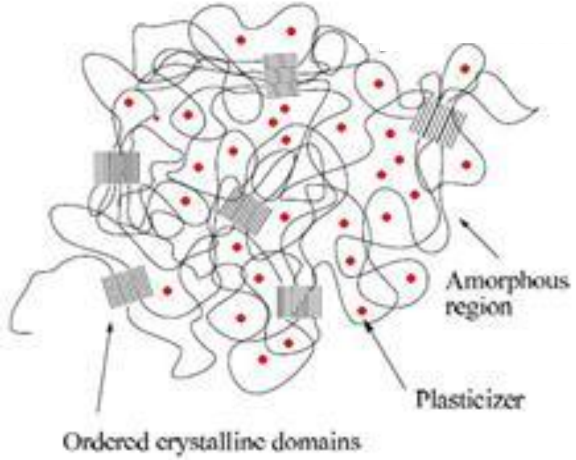
To assist in the absorption of energy

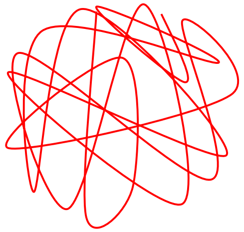
- Act as stress concentrators
- Initiate crazing
- Act as sites for shear-banding
- Cavitate to create new surfaces
- De-bond to facilitate crazing and/or shear banding

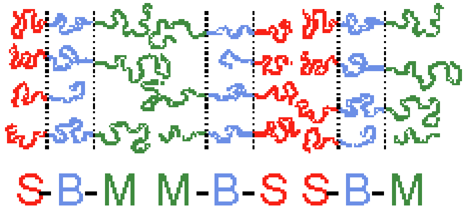
METHODS OF IMPACT MODIFICATION

- Blends
- Plasticizers
- Fibrous materials
- Minerals
- Rubbery materials
  - Linear Molecules
  - Core-shells
  - Network polymers

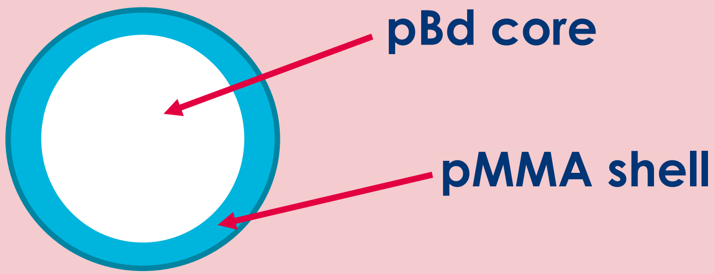
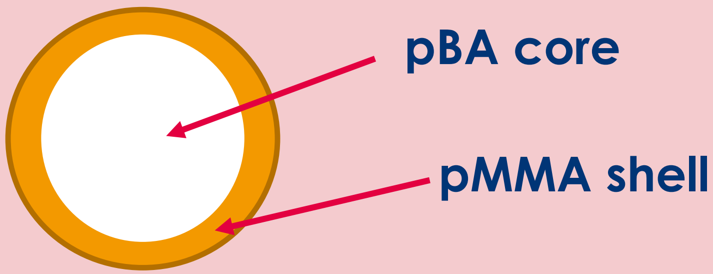
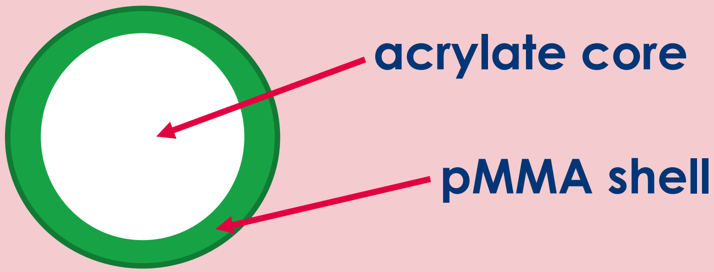






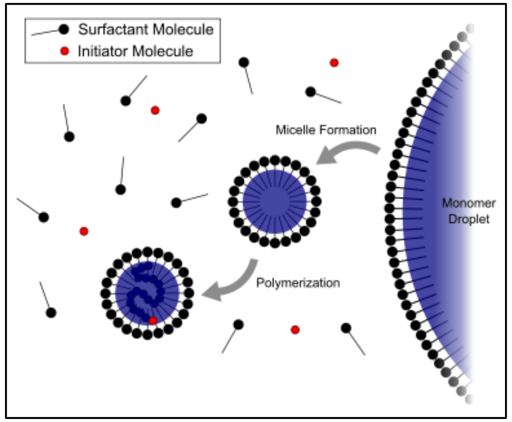


CORE / SHELL IMPACT MODIFIER TECHNOLOGIES

Methacrylate – Butadiene – Styrene (MBS)	Acrylic Impact Modifiers (AIM)	
	Traditional	Specialty
		
• Excellent low temperature impact • Acceptable thermal stability • **Refractive index similar to PVC** **→ Good transparency** • **Non-weatherable**	• Very good low temperature impact • Excellent thermal stability • **Lower refractive index than PVC** **→ Higher haze** • **Excellent weatherability**	• Good low temperature impact • Excellent thermal stability • **Refractive index similar to PVC** **→ Good transparency** • **Good weatherability**

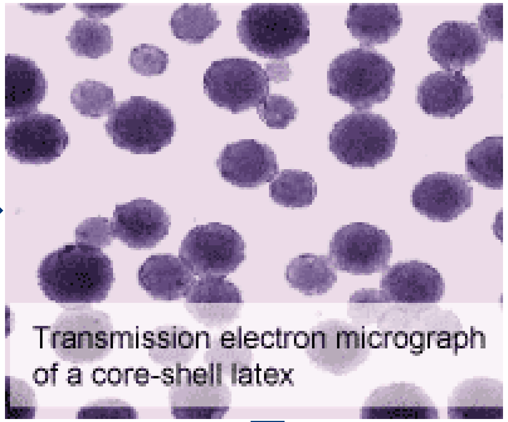
CORE/SHELL AIM SYNTHESIS, STRUCTURE, AND KEY PARAMETERS

Monomers



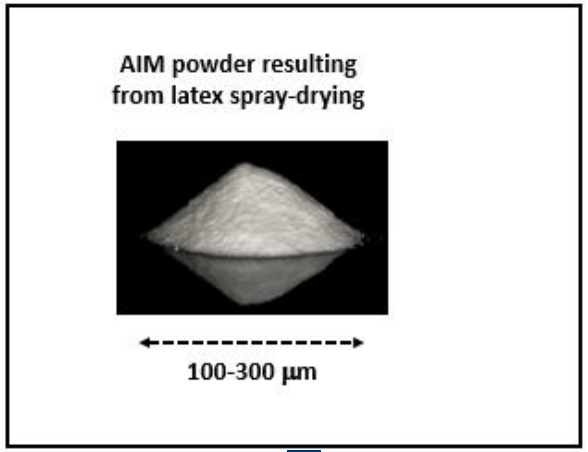
Emulsion Polymerization

AIM Latex



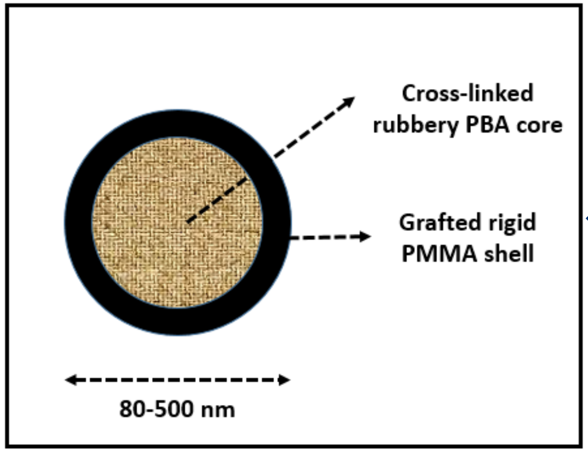
Isolation and drying

AIM Powder

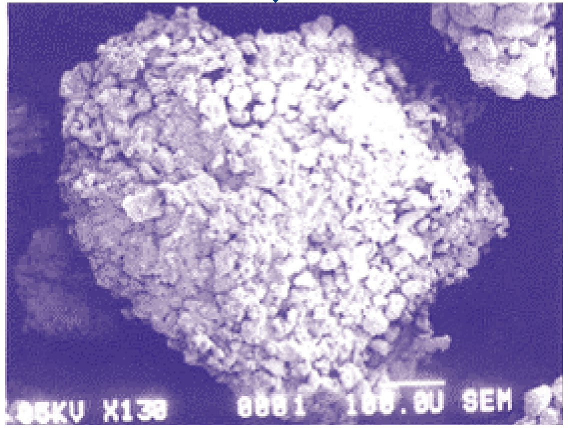


Key performance parameters

- Rubber content
- CS particle size (80-500 nm)
- Core modulus design
- Core rubber type
- Chemistry improving PVC compatibility



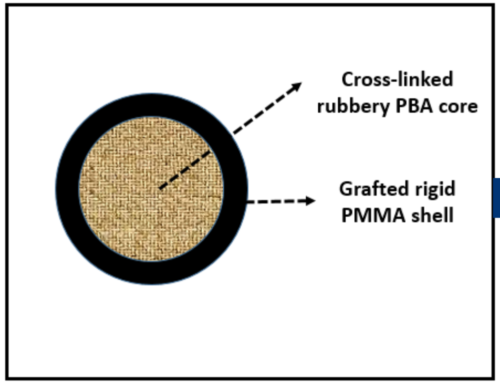
AIM CS primary particle



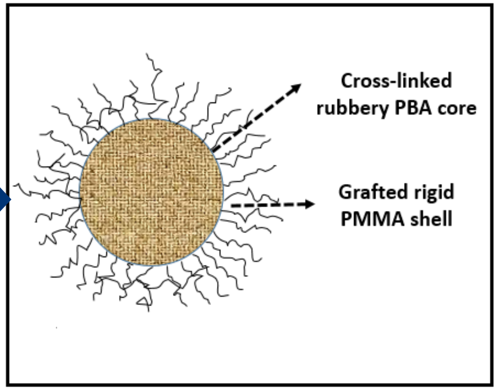
AIM Powder grain

CORE/SHELL VS POWDER GRAIN PARTICLES

AIM CS primary particle

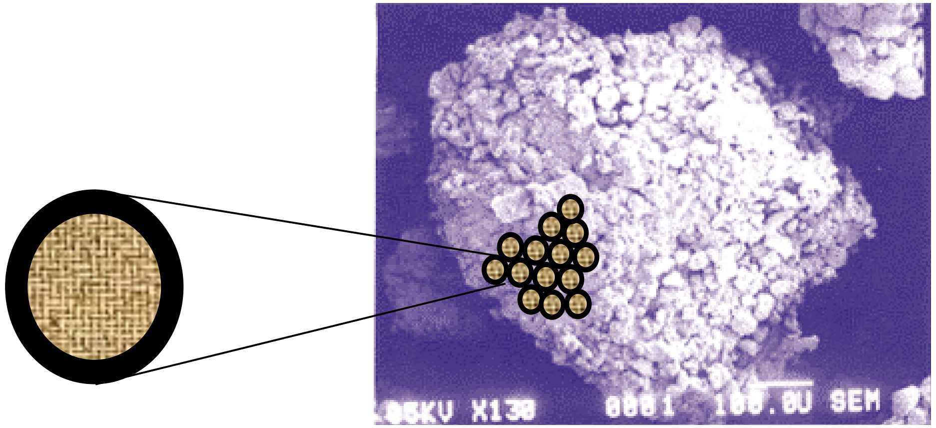


Ideal schematisation



More realistic view

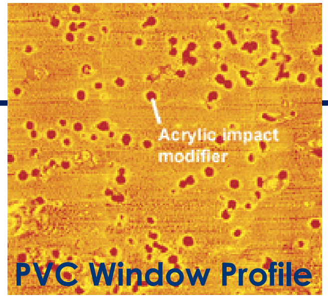
Rubber content can vary from 50 to > 90% and remain a free-flowing powder → improved shell chemistry improves anti-blocking properties



AIM CS primary particle
D50≈ 200 nm

AIM Powder grain
D50≈ 200 µm

There are about 1 billion of active CS AIM particles into a single AIM powder grain!
→ Easily released and dispersed into the PVC matrix during the extrusion step



CORE-SHELL PARAMETERS - BROADLY

Core

- Low Tg materials provide impact modification by allowing stress concentration
- General rule of thumb is impact modifiers work to about 50°C above the core Tg
- Mechanisms differ from matrix to matrix so particle size and crosslink density become critical for success
- Required particle size of the core differs by resin matrix, for example:
  - PVC: 100 – 300 nm
  - Polycarbonate: 150 – 500 nm
  - HIPS: 700 nm +

Shell

- Because of the high Tg, it provides excellent powder properties (i.e. flowabilitiy)
- Allows for improved dispersion of the primary particles into the polymer matrix
- The shell facilitates energy transfer between the matrix and the rubbery core – can promote gelation!
- pMMA exhibits good compatibility with many polymers (PVC, PC, and others), which can be further improved by the incorporation of functional monomers (i.e. tailor selectivity)

CORE-SHELL MODIFICATION OF PVC

OPTIMIZING THE IMPACT MODIFIER PERFORMANCE

PRINCIPLE OF IMPACT MODIFICATION

Nano / Micro-structure Approach

- Particle size
- Mechanical properties
- Polymerization techniques

Microscopic Scale

- Theory of micro-mechanical damage and fracture
- Modifier / resin interactions
- Observations of microscopic deformation via AFM / TEM / SEM

Macroscopic Scale

- Fracture behavior
- Ductile to brittle transition temperature

Inclusions are the key to toughening polymers. They play the role of inducing crazing, initiating shear yielding of the matrix as well as ending the propagation of cracks.

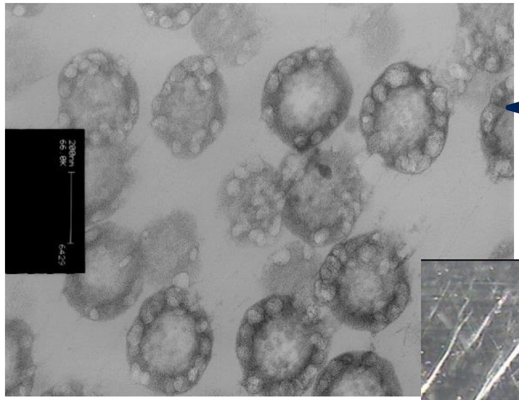
MODES OF ENERGY ABSORPTION: MECHANICAL FAILURE

3 criteria for micromechanisms of damage

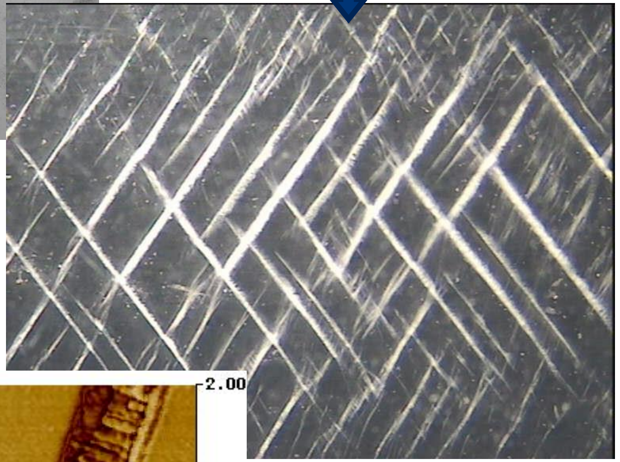
Cavitation
- Particle / matrix debonding
- Voids in rubbery domains
- Stress-whitening zone

Shear Banding
- Sliding of molecules due to shear stress
- Favored by plane stress
- Distortion of material, constant volume process
- Best for high fracture toughness

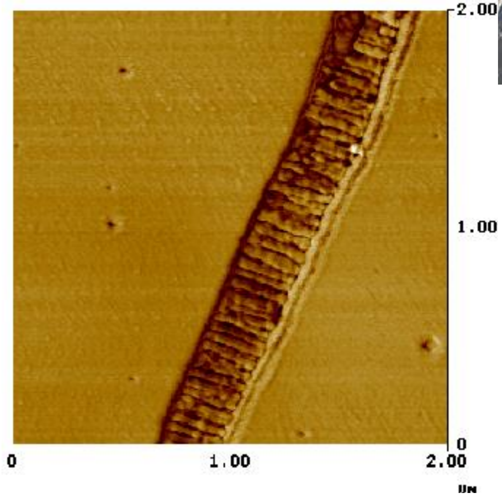
Crazing
- Localized high alignment of polymer
- Voids and fibrils
- Favored by plane strain
- Mostly for brittle polymers



RT-PMMA (TEM analysis)

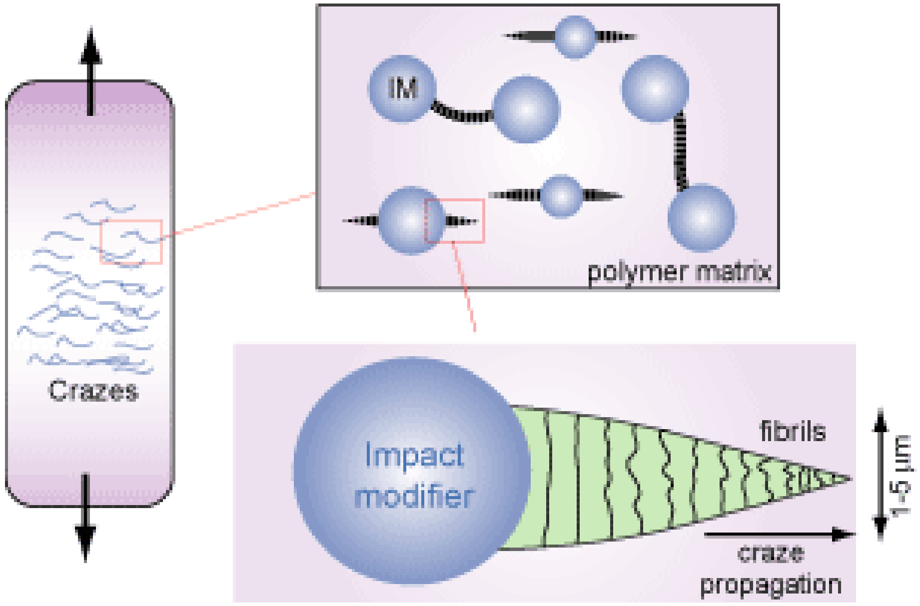


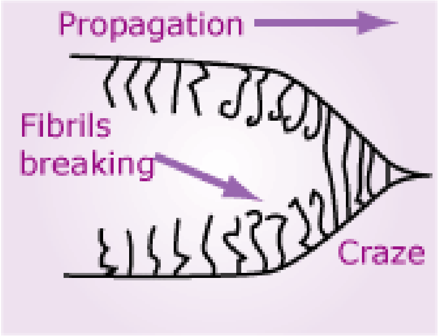
SBS (Optical microscopy)

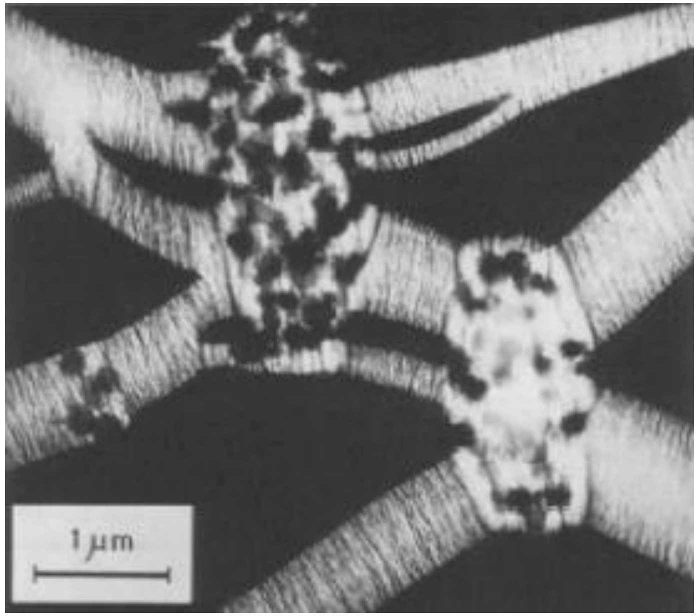


HIPS (Traction under AFM)

CRAZING IN BRITTLE POLYMERS

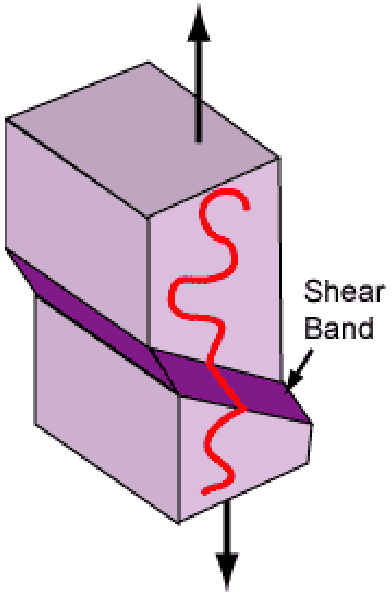


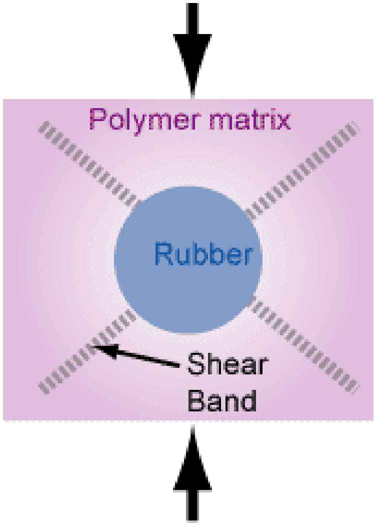


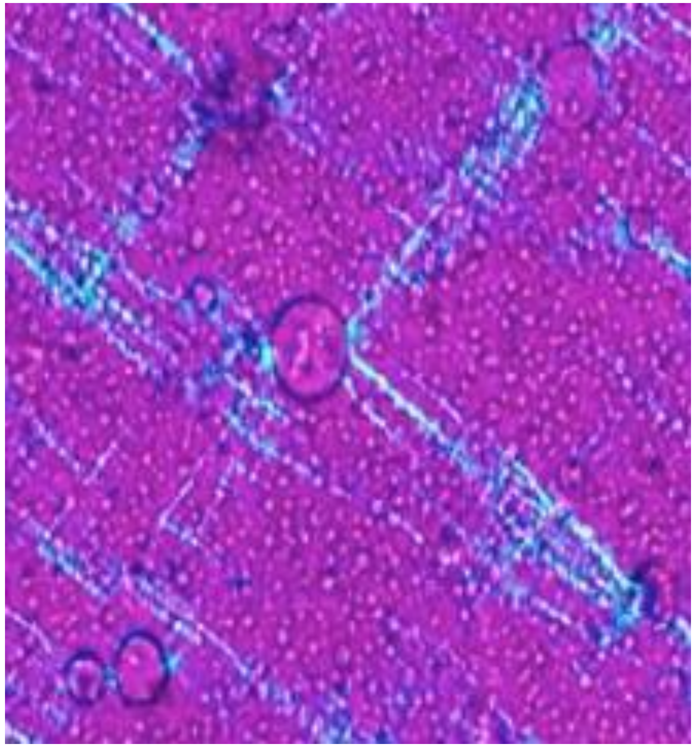


- Cracks bridged by polymer fibrils
- Perpendicular to loading direction
- Voids substantially increase free volume (can create whitening!)
- Chain slippage and molecular disentanglement
- Rupture of primary bonds

SHEAR-BANDING IN DUCTILE POLYMERS



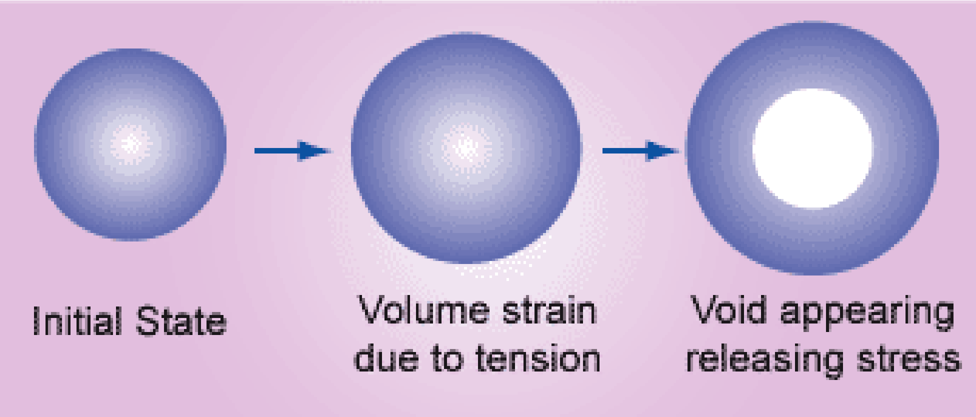


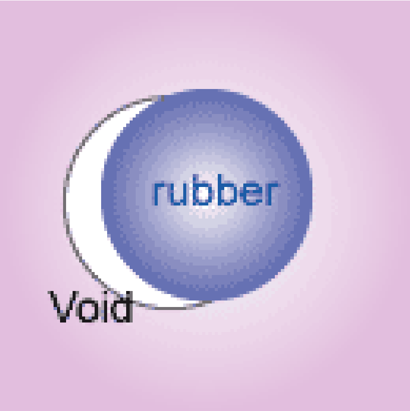


- Localized plastic deformation
- Commonly form at 45° from loading (maximal shear)
- No significant change in volume

CAVITATION AND VOID FORMATION

- Cavitation is a mechanism that allows a reduction in crack propagation
  - In MBS-modified systems this creates voids that scatter light
  - “stress-whitening”
- A stress whitening resistant MBS will have limited impact performance (and likely a smaller particle size!)





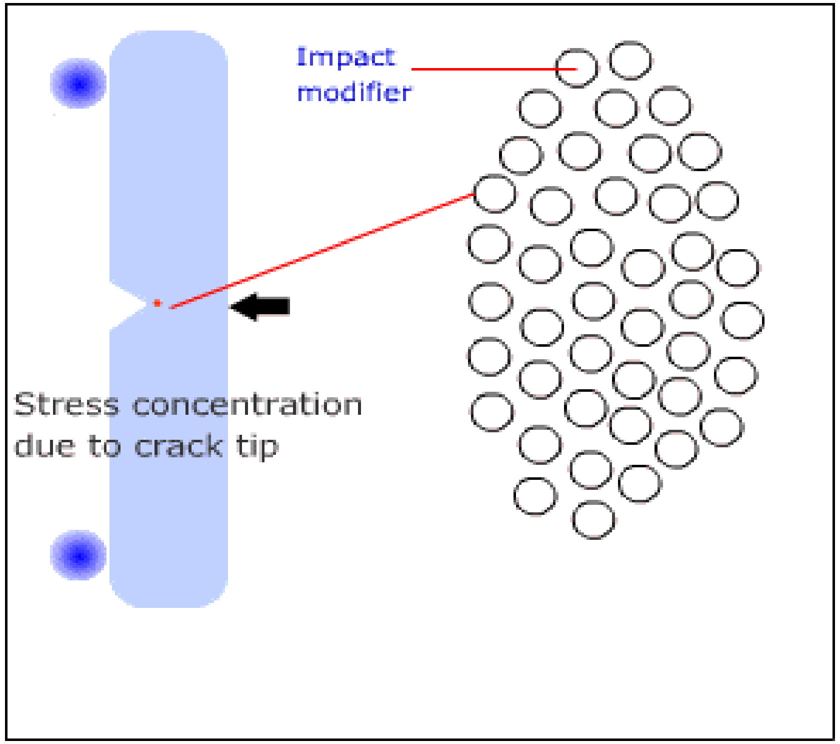
HOW DO CORE-SHELL AIM WORK IN RIGID PVC?

- **Rubber core must exist as a separate phase**
  - Large modulus differences versus PVC matrix

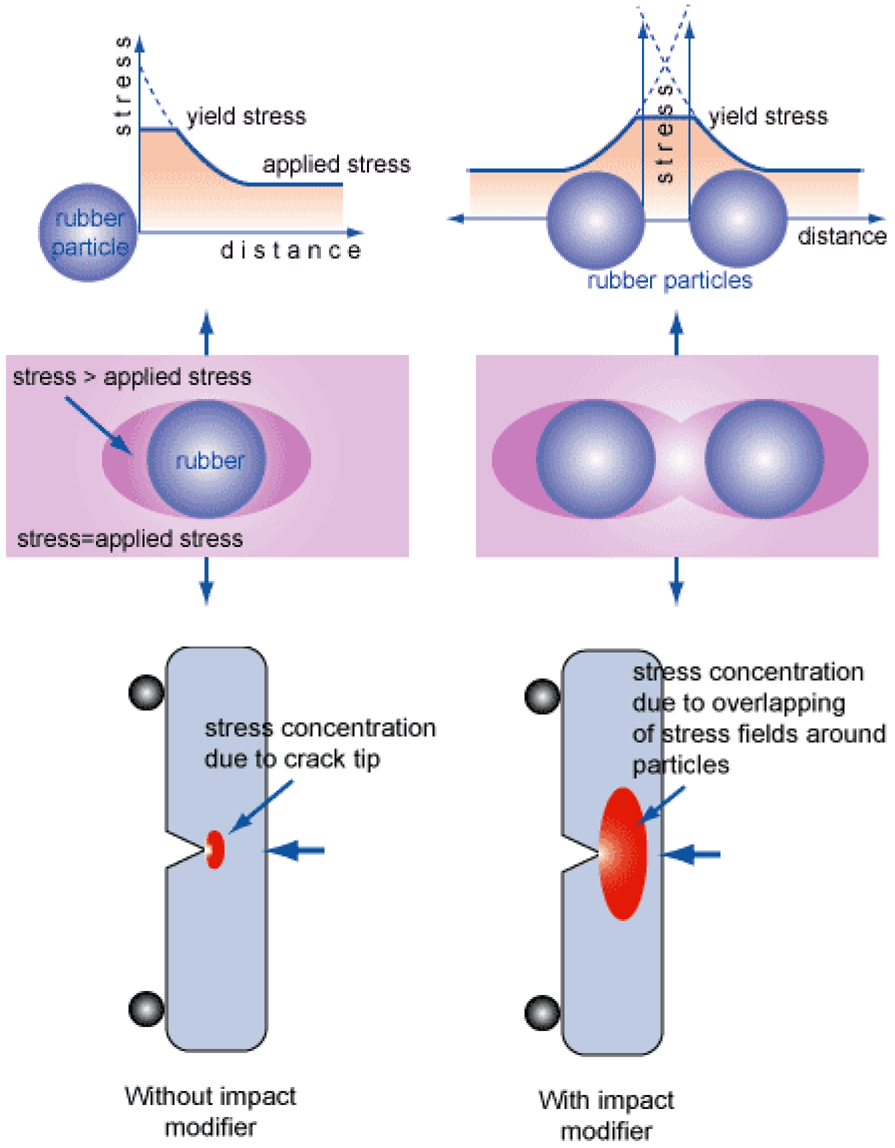
- **Large numbers of particles well dispersed in the PVC matrix actually induce a stress field in the PVC article**
  - Stress field actually lowers the bulk stress required to initiate response from the glassy matrix
  - When deformation load is applied, shear flow and bulk yielding of the matrix occur due to energy absorbtion by the impact modifier particles

- **Stress field depends primarily on the concentration and separation of impact modifier particles (volume fraction) and not their absolute size**

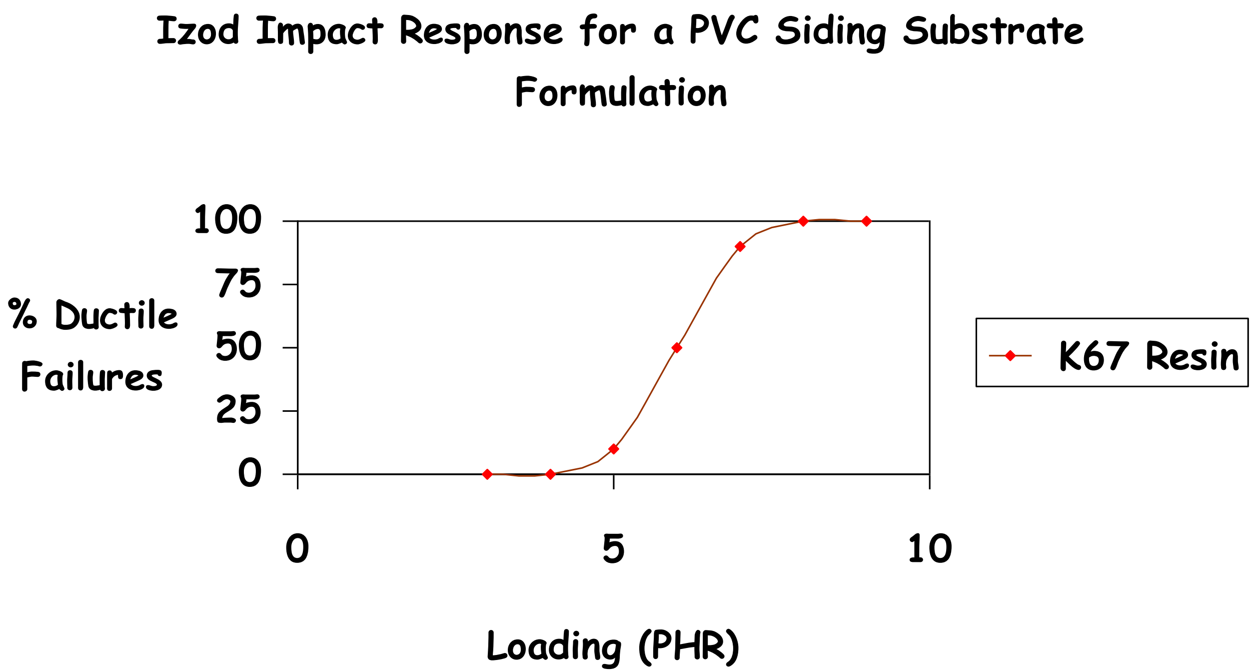
Stress concentration



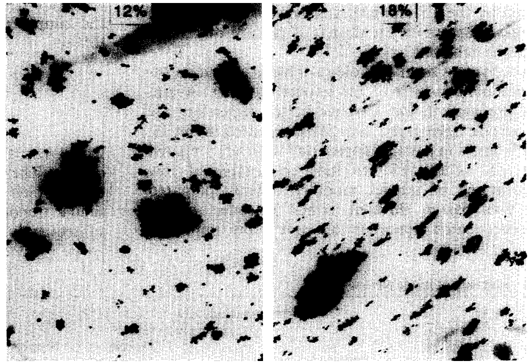
OPTIMAL DISPERSION OF MODIFIERS

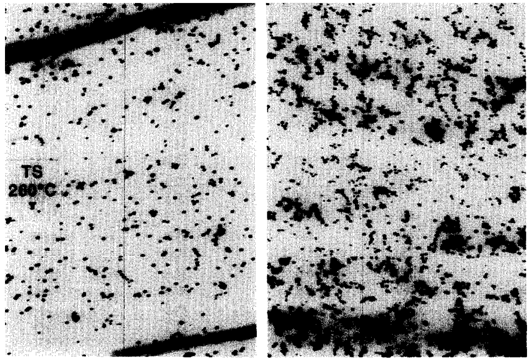


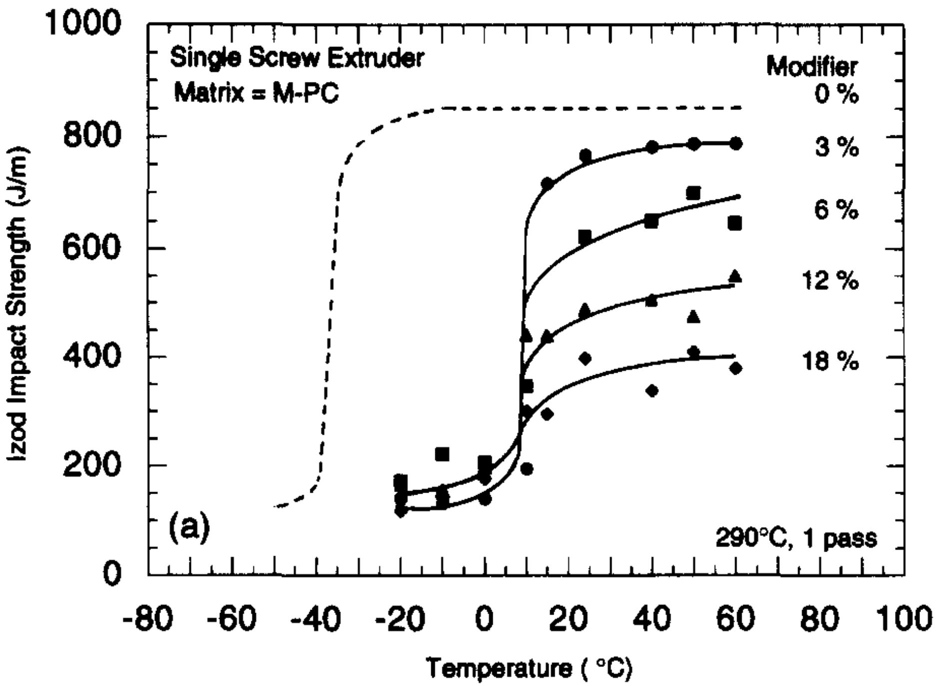
- Overlapping stress zones is optimal
- Dispersion becomes crucial
- Size, volume fraction (interparticle distance), testing conditions

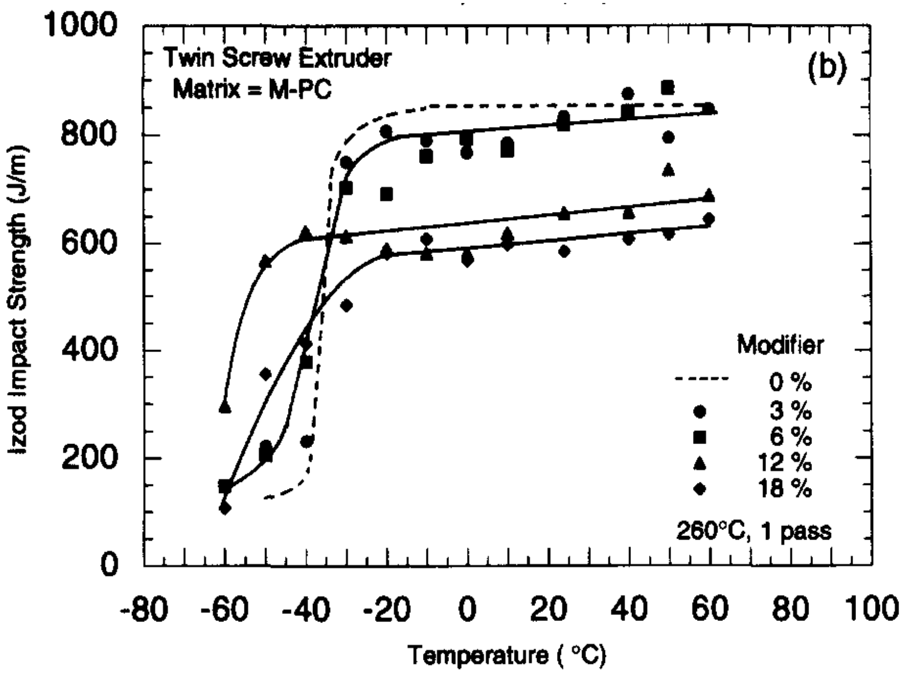


PROCESSING: DISPERSION OF CORE-SHELL PARTICLES





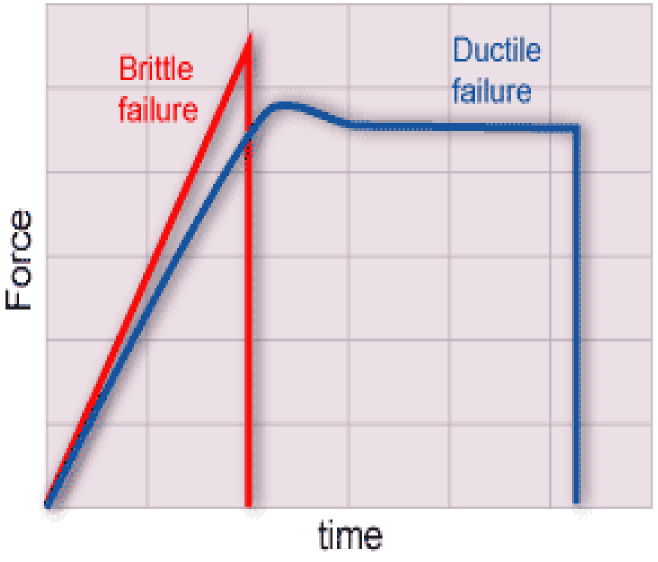


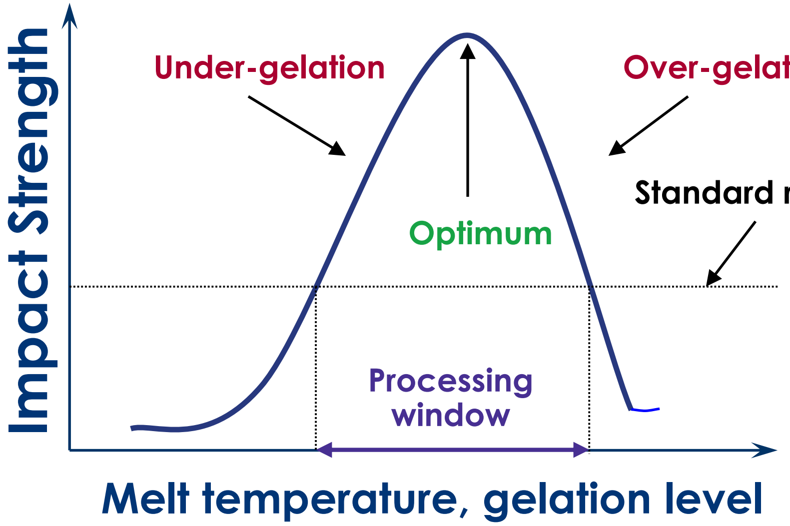


- Processing plays a key role in achieving success with impact modifiers
- An impact modifier is only as good as the process that disperses it

Y. Kayano et al., Polymer 37 (1996) 4505-4515.

APPLICATIONS PERSPECTIVE: PROCESSING AND RHEOLOGY



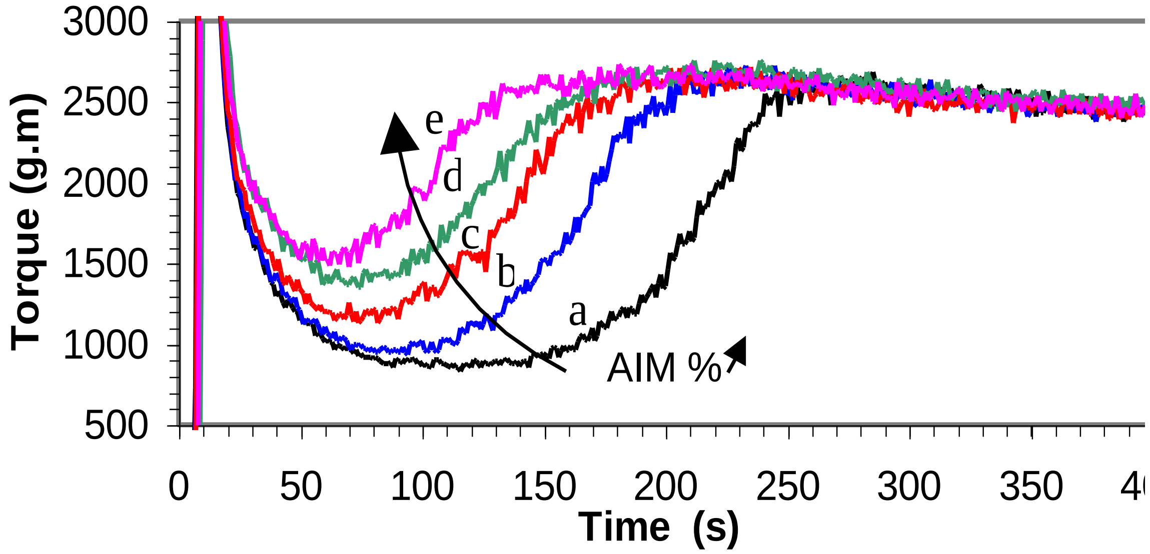


Gelation vs Fusion

- 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

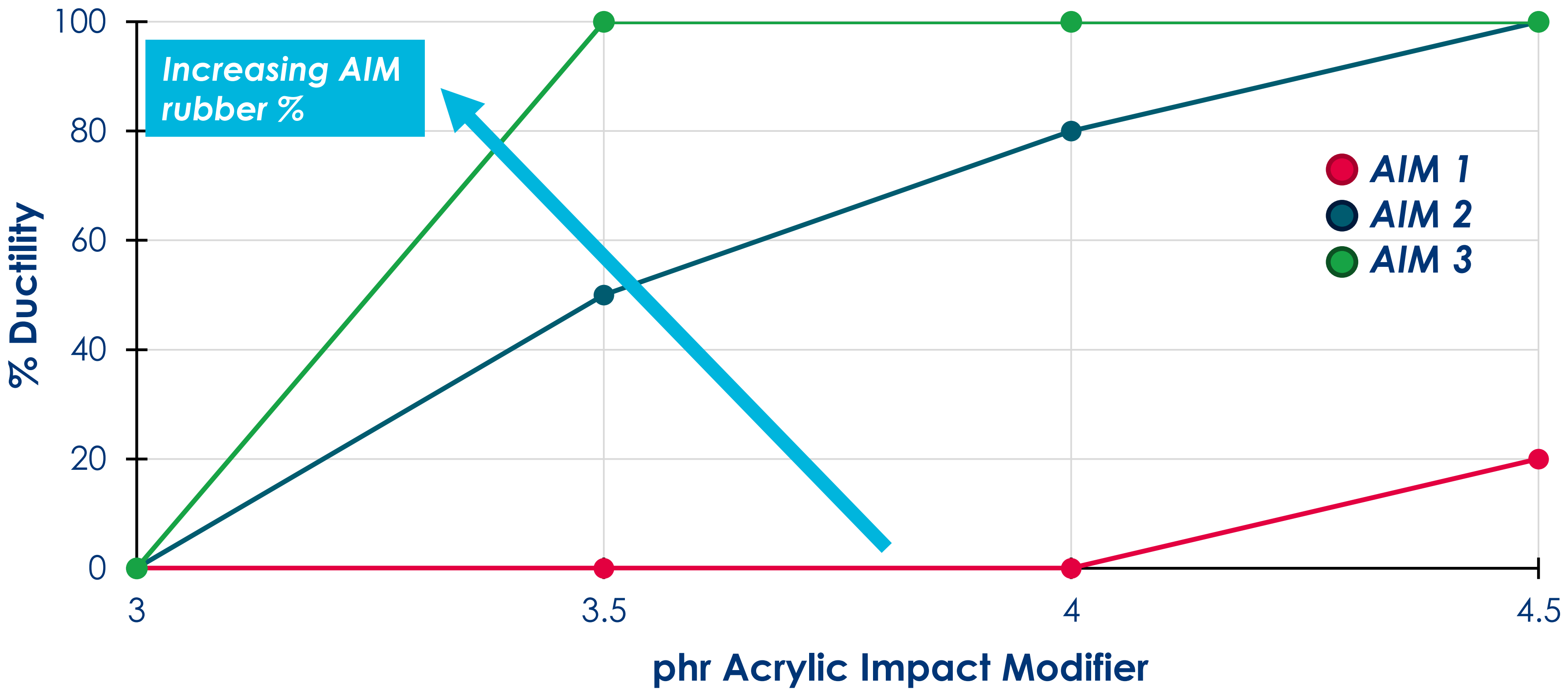
- Increasing modifier levels generally expedite fusion
- Increased fusion can lead to increased gelation
- Better gelation does not necessarily mean better impact properties



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

IMPACT MODIFIER RUBBER CONTENT AND PERFORMANCE

- More rubber content generally leads to better impact performance
- Using core rubber's low Tg is the easiest way to shift DBTT
- Observing PVC formulations by % rubber content for performance comparisons can be useful
- Loading more impact modifier will not always lead to improved performance



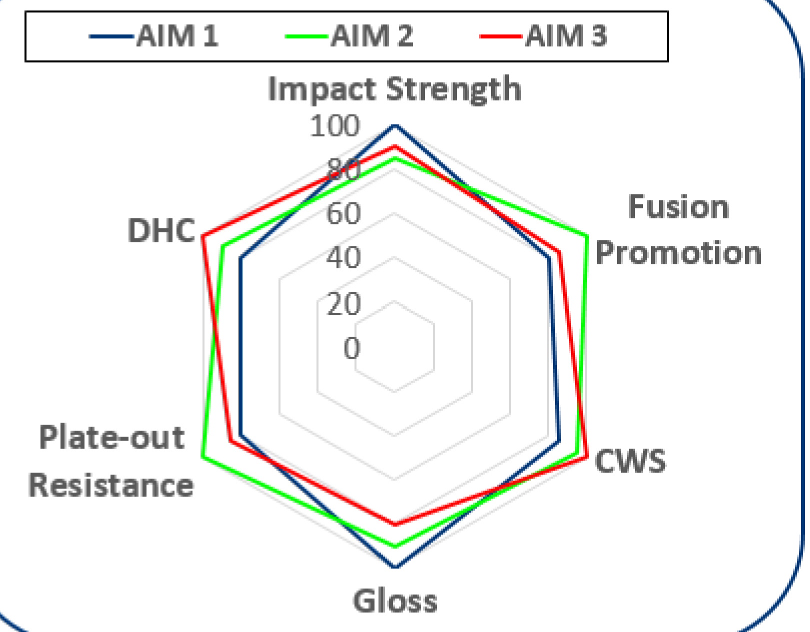
CORE/SHELL AIM SYNERGIES: OTHER KEY APPLICATION PROPERTIES

- Gelation promotion
- Corner Weld Strength (CWS)
- Plate-out
- Surface gloss

AIM acts as rheology modifier (particulate system + shell processing aid effect)

- Dehydrochlorination (DHC)
  - Small amounts of acidic species can be released without any effect on real thermo-stability of PVC profiles

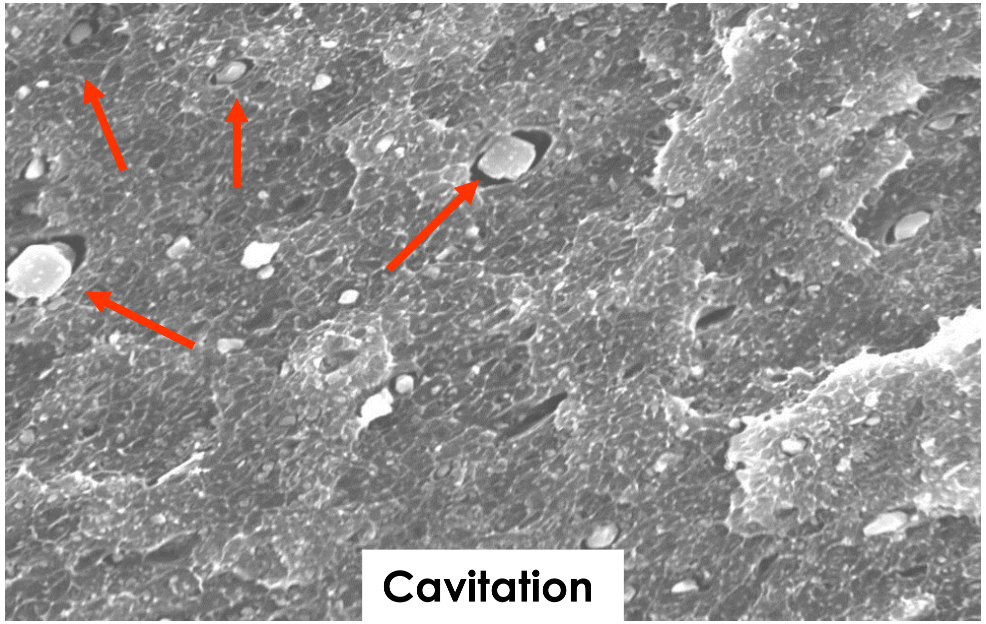
These differences between AIM grades generally remain within the technical specifications…

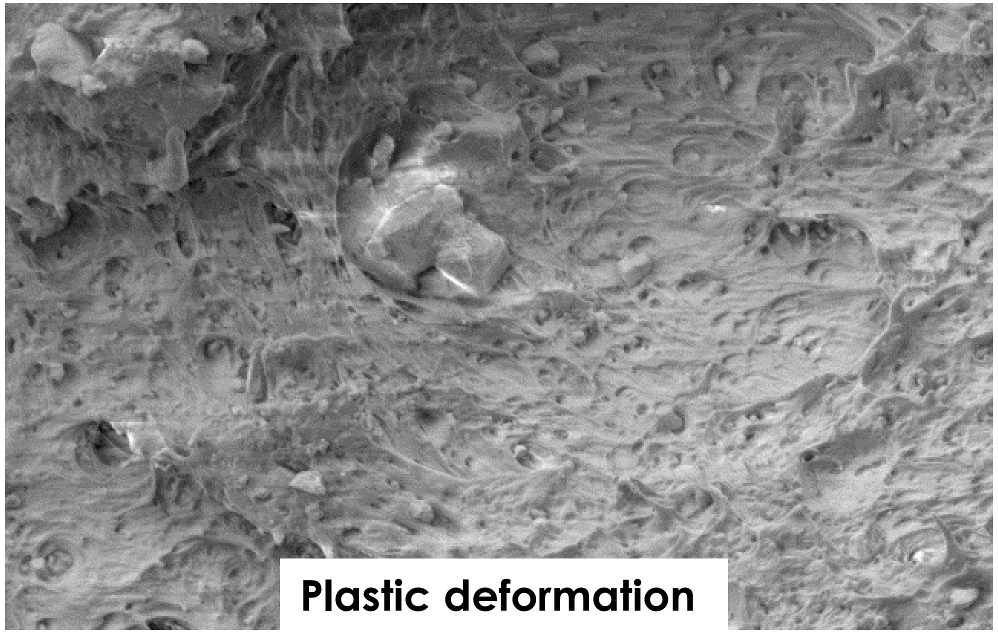


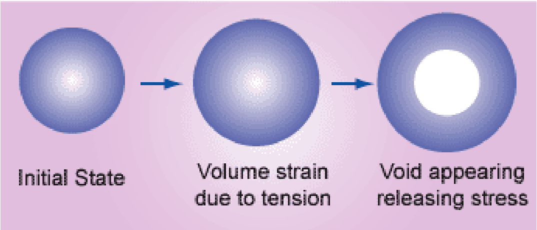
IMPACT MODIFIER – INORGANIC FILLER SYNERGIES

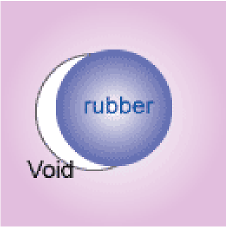
Example of mineral / AIM synergy via stress concentrators

SEM Morphology investigations after impact testing (ductile break)









- *Dewetting of inorganic/PVC interfaces leads to cavitation promoting shear yielding*
- *Larger energy dissipation*
- *Impact modifiers AND filler particles can participate to aid the matrix*

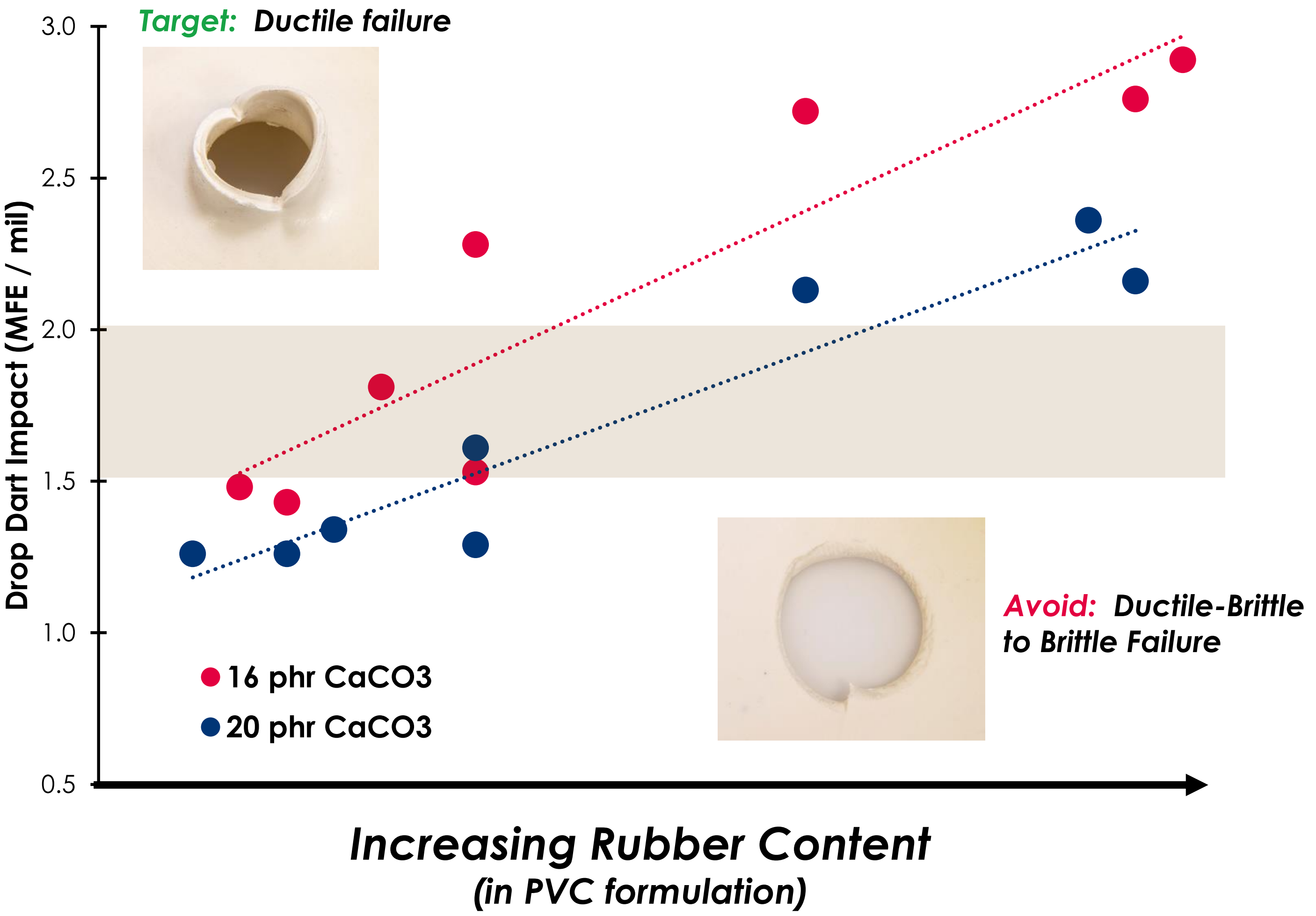
CATASTROPHIC IMPACT / FALLING WEIGHT EVALUATIONS

Core-shell impact modifiers protect against catastrophic failure

- Engineer formulations for ductile failure
- Prevent brittle "blow-outs" and cracking
- Withstand building material shipping, handling and installation
- Enhance extreme temperature performance

Formulation perspective:

- Increasing filler content typically reduces overall impact strength
- Monitoring overall rubber content in formulations can balance failure mode
- Acrylic content can compensate for processing differences leading to gelation optimization

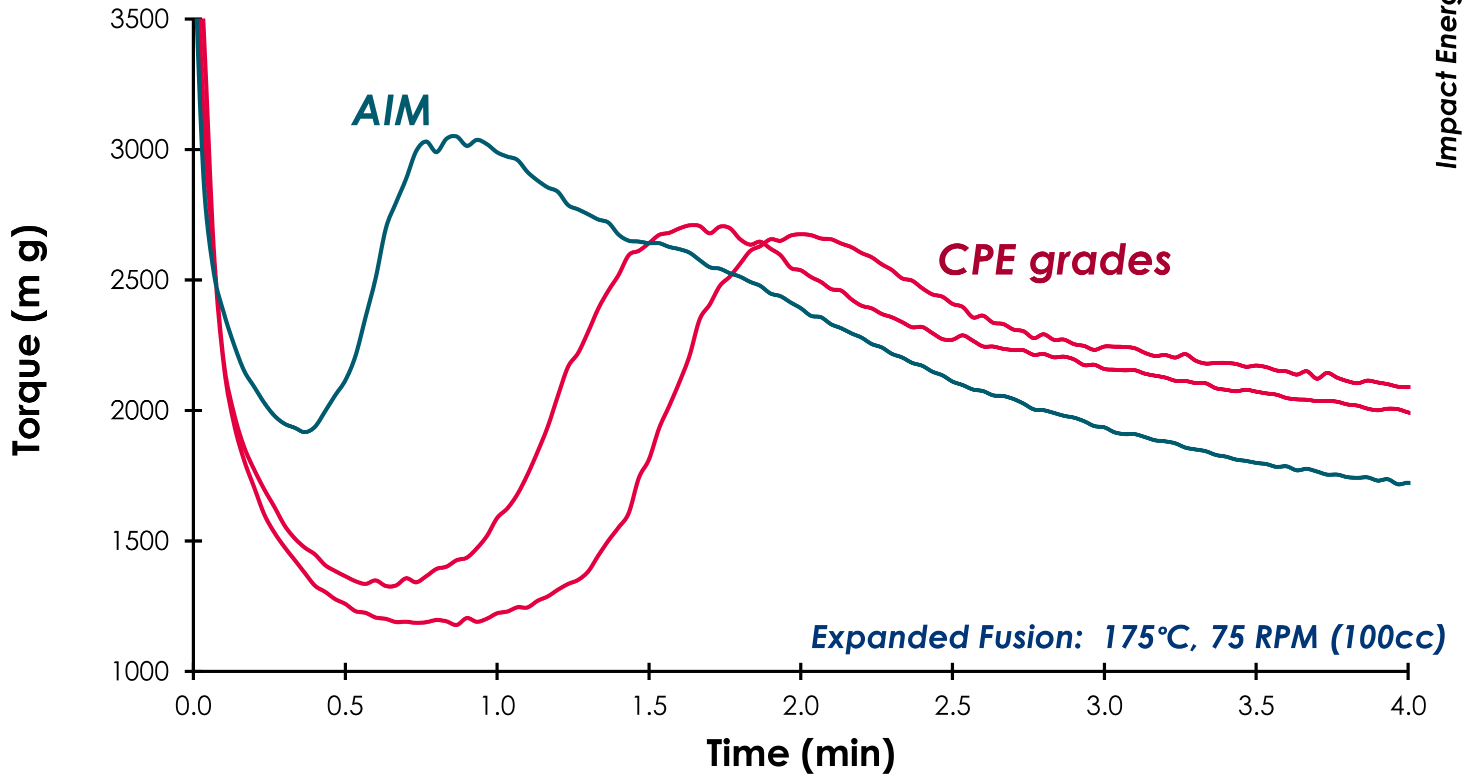


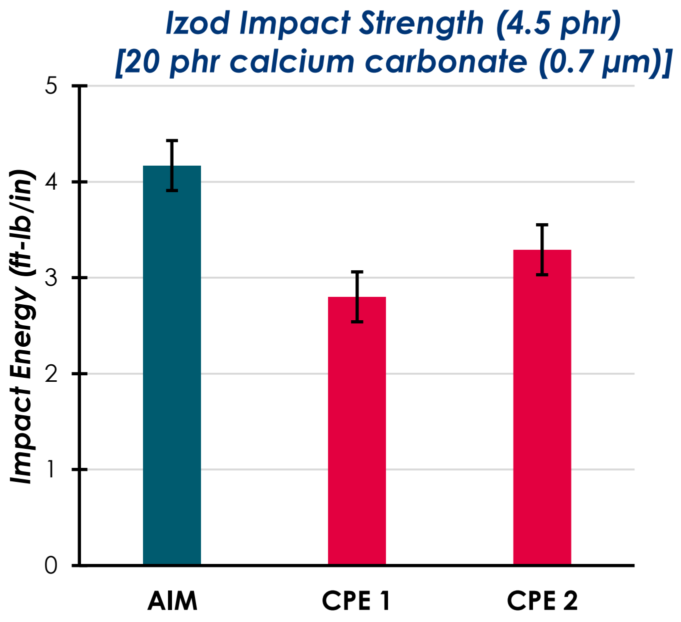
internal test results

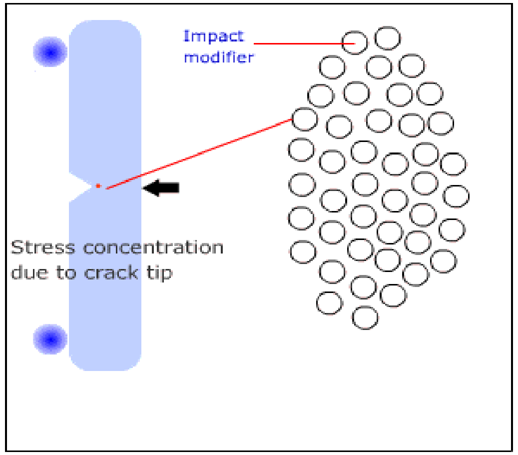
NOTCH SENSITIVITY AND IMPACT STRENGTH

Gelation AND mechanical performance balance:

- Acrylic impact modifiers provide impact performance and enhanced fusion promotion
- Added mechanical integrity to tongue and groove assemblies, profiles, and notch sensitive / exposed building material parts







internal test results

PLASTISTRENGTH® BY ARKEMA
DURASTRENGTH® BY ARKEMA
CLEARSTRENGTH® BY ARKEMA

PVC FORMULATIONS WITH IMPACT MODIFIER

SOME EXAMPLES OF NORTH AMERICA-BASED PVC FORMULATIONS

ARKEMA
INNOVATIVE CHEMISTRY

RIGID WEATHERABLE PVC: WINDOW LINEALS AND CAPSTOCK

Rigid Weatherable PVC:

- **Window profile and capstock**
- **Acrylic impact modifier key:**
  - One-packs (offer multi-functional product with acrylic impact modifier and process aid pre-formulated)
  - Standalone impact modifiers – formulators can select rubber content, efficiency, gloss performance
- **Gloss performance:**
  - Switch from low to high rubber AIM often leads to shift in surface gloss (can be a critical hurdle)
- **Weatherability: acrylic impact modifiers offer excellent option**
  - Many years of field tested formulations
- **Izod and drop-dart testing can be required**

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**
- **Finding synergy with filler and impact modifier technology is important**
- **Need enough impact modifier to meet drop-dart standards**
  - Vinyl siding has minimum requirements
  - Fence has cell class requirements
  - Other substrate applications may vary
- **Impact modifier often accompanied by process aid to boost incorporation of filler content**
- **Improving cost-efficiency often involves multiple factors:**
  - Substrate / panel thickness
  - Filler content level
  - Bulk density of the overall PVC compound
  - Impact modifier rubber content

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!)**
- **Impact modifiers important for some segments:**
  - Electrical conduit (higher filler / falling weight testing – UL)
  - Pipe fittings (injection molded, high shear)
  - Dual wall corrugated (sewer pipe)
  - others
- **Impact modifier use levels typically lower vs. weatherable rigid PVC**
  - Tensile and burst physical properties most critical (less impact needed)
  - Balance of properties for applications requiring cell class
- *** high or low rubber AIM can be used**
- **** process aid functionality based on processing needs**

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 or 350	***0 – 3.0***
*****Plastistrength® 550 or 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***

DISCLAIMER

The statements, technical information and recommendations contained herein are believed to be accurate as of the date hereof. Since the conditions and methods of use of the product and of the information referred to herein are beyond our control, ARKEMA expressly disclaims any and all liability as to any results obtained or arising from any use of the product or reliance on such information; NO WARRANTY OF FITNESS FOR ANY PARTICULAR PURPOSE, WARRANTY OF MERCHANTABILITY OR ANY OTHER WARRANTY, EXPRESSED OR IMPLIED, IS MADE CONCERNING THE GOODS DESCRIBED OR THE INFORMATION PROVIDED HEREIN.

The information provided herein relates only to the specific product designated and may not be applicable when such product is used in combination with other materials or in any process. The user should thoroughly test any application before commercialization. Nothing contained herein constitutes a license to practice under any patent and it should not be construed as an inducement to infringe any patent and the user is advised to take appropriate steps to be sure that any proposed use of the product will not result in patent infringement. See SDS for Health & Safety Considerations. Arkema has implemented a Medical Policy regarding the use of Arkema products in Medical Devices applications that are in contact with the body or circulating bodily fluids: http://www.arkema.com/en/social-responsibility/responsible-product-management/medical-device-policy/index.html

Arkema has designated Medical grades to be used for such Medical Device applications. Products that have not been designated as Medical grades are not authorized by Arkema for use in Medical Device applications that are in contact with the body or circulating bodily fluids. In addition, Arkema strictly prohibits the use of any Arkema products in Medical Device applications that are implanted in the body or in contact with bodily fluids or tissues for greater than 30 days. The Arkema trademarks and the Arkema name shall not be used in conjunction with customers' medical devices, including without limitation, permanent or temporary implantable devices, and customers shall not represent to anyone else, that Arkema allows, endorses or permits the use of Arkema products in such medical devices.

It is the sole responsibility of the manufacturer of the medical device to determine the suitability (including biocompatibility) of all raw materials, products and components, including any medical grade Arkema products, in order to ensure that the final end-use product is safe for its end use; performs or functions as intended; and complies with all applicable legal and regulatory requirements (FDA or other national drug agencies) It is the sole responsibility of the manufacturer of the medical device to conduct all necessary tests and inspections and to evaluate the medical device under actual end-use requirements and to adequately advise and warn purchasers, users, and/or learned intermediaries (such as physicians) of pertinent risks and fulfilll any postmarket surveillance obligations. Any decision regarding the appropriateness of a particular Arkema material in a particular medical device should be based on the judgment of the manufacturer, seller, the competent authority, and the treating physician.

Contact us!

Plastic Additives Global B&C Team

- **Kevin Yocca**
  Plastic Additives Global Market Manager, B&C
  kevin.yocca@arkema.com

- **Raber Inoubli**
  Plastic Additives R&D – Sr. Polymer Scientist
  raber.inoubli@arkema.com

- **Eric Peterson**
  Plastic Additives R&D – Sr. Technical Service Engineer
  eric.peterson@arkema.com

Please look for the recorded versions of the PVC workshops on the SPE YouTube channel – we appreciate your engagement, do not hesitate to reach out with any additional questions.

- **Please visit our website for more information about Arkema and our newest technology:**
  - *ARKEMA Plastic Additives:* www.arkemacoatingresins.com/en/products/spotlights/luxury-vinyl-tile/

Thank you!

ARKEMA INNOVATIVE CHEMISTRY