Rubber and Plastics Formulations for Food Contact

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Outline

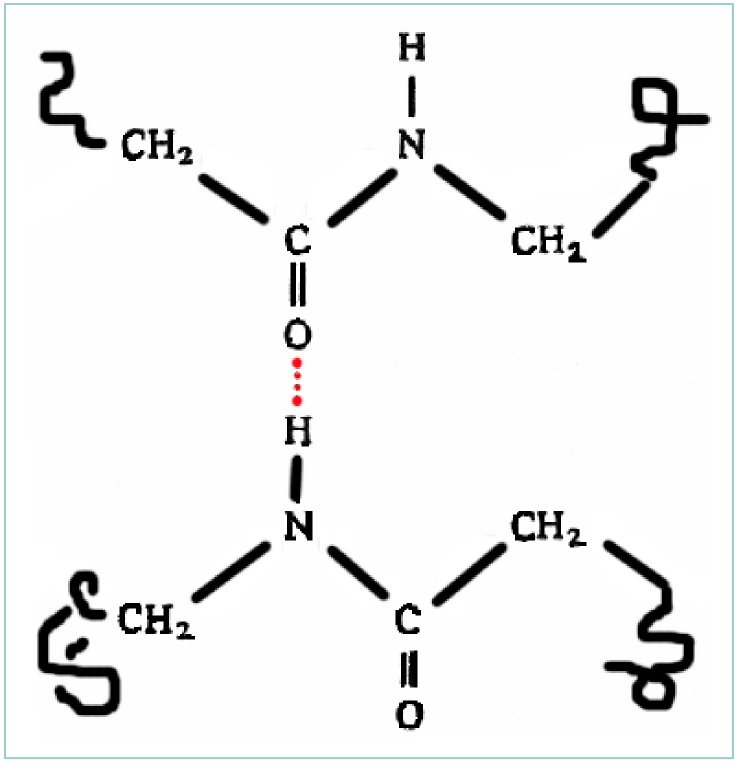
- Introduction: Polymer Parameters
- Example Formulations
- Impact of Additives
- Optimizing Formulations
- Applications
- Conclusions
- Acknowledgements

Polymer Parameters

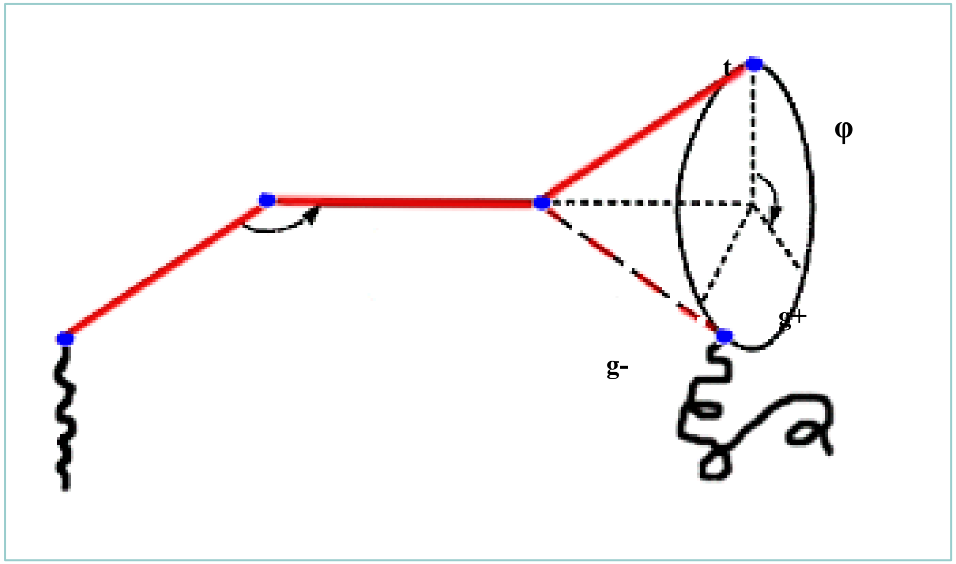
- Chemical Composition
- Molecular Weight & Distribution
- Stereochemistry
- Topology
- Morphology
- Additives

Important Energies to Consider

Intermolecular | Intramolecular



Hydrogen Bonding in Polyamides



Chain Stiffness and Bond Rotation

Microstructures of Chemical Composition

Homopolymer ~~AAAAAAAAAAAAAAAAAAAAAAAAAAA~~

Random Copolymer ~~AABABBBABBABABBBABAABBBBB~~

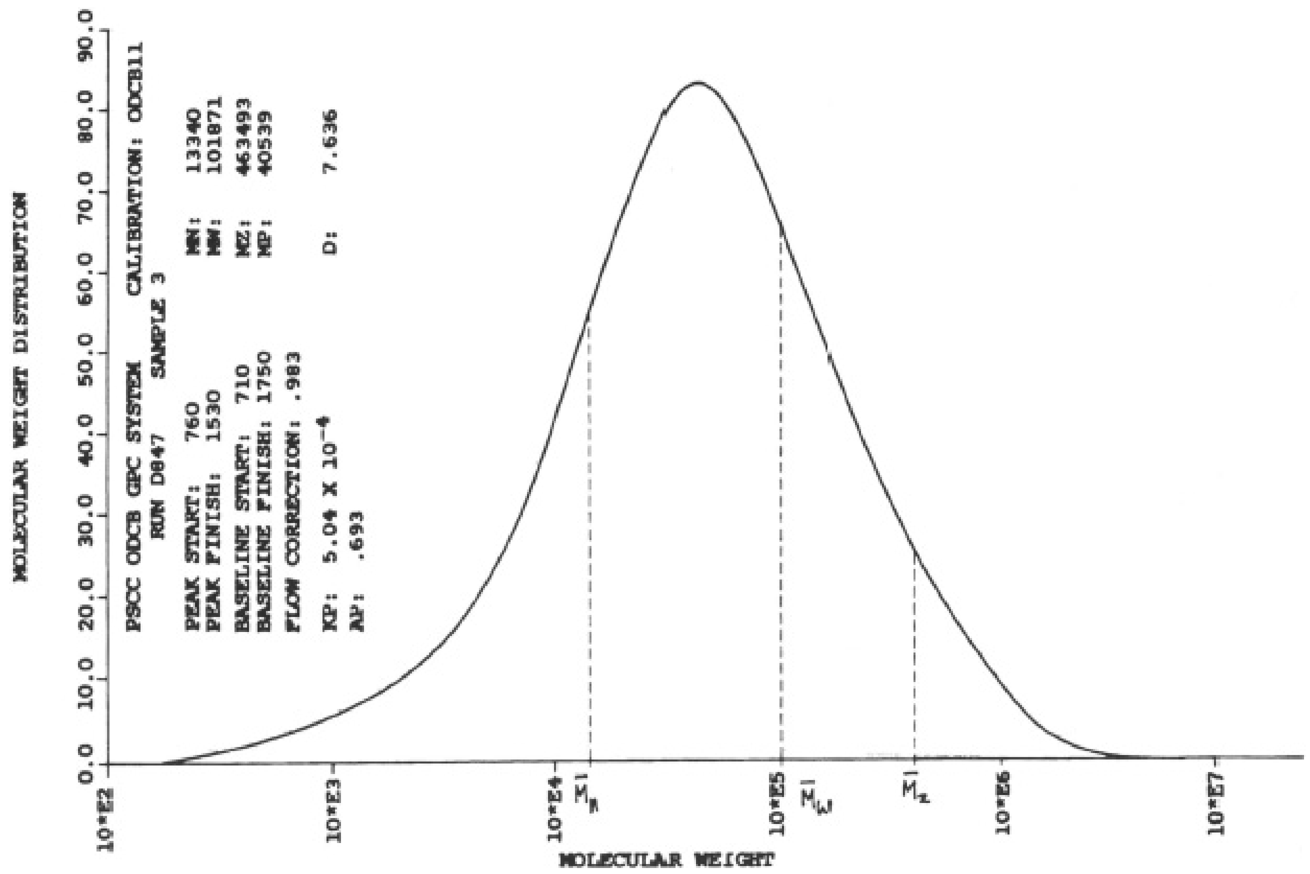
Block Copolymer ~~AAAAAAAA~~AAAAABBBBBB~~~BBBBBBBBB

Graft Copolymer ~~AAAAAAAAAAAAAAAAAAAAAAAA~~

BBBBBB~~	BBBBBBBBB~~

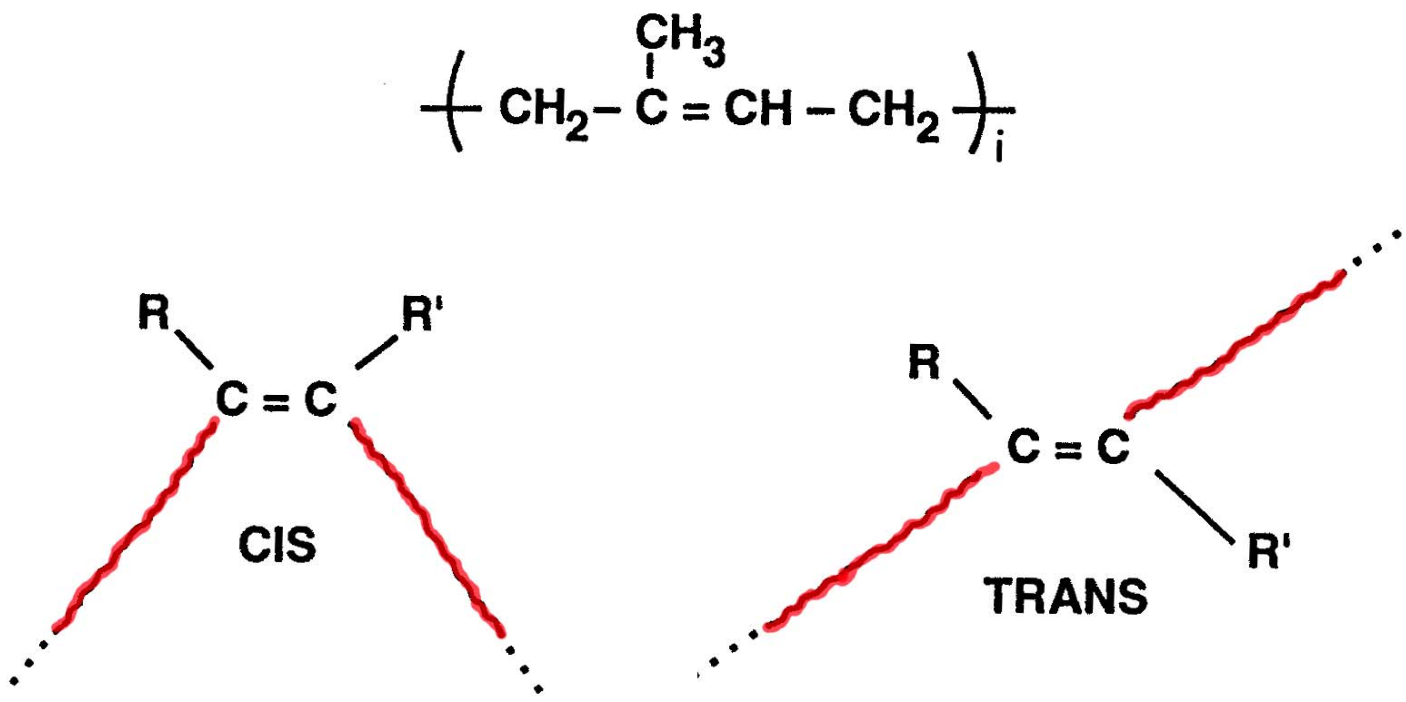
Terpolymer **Example ABS plastic**

Molecular Weight Distribution

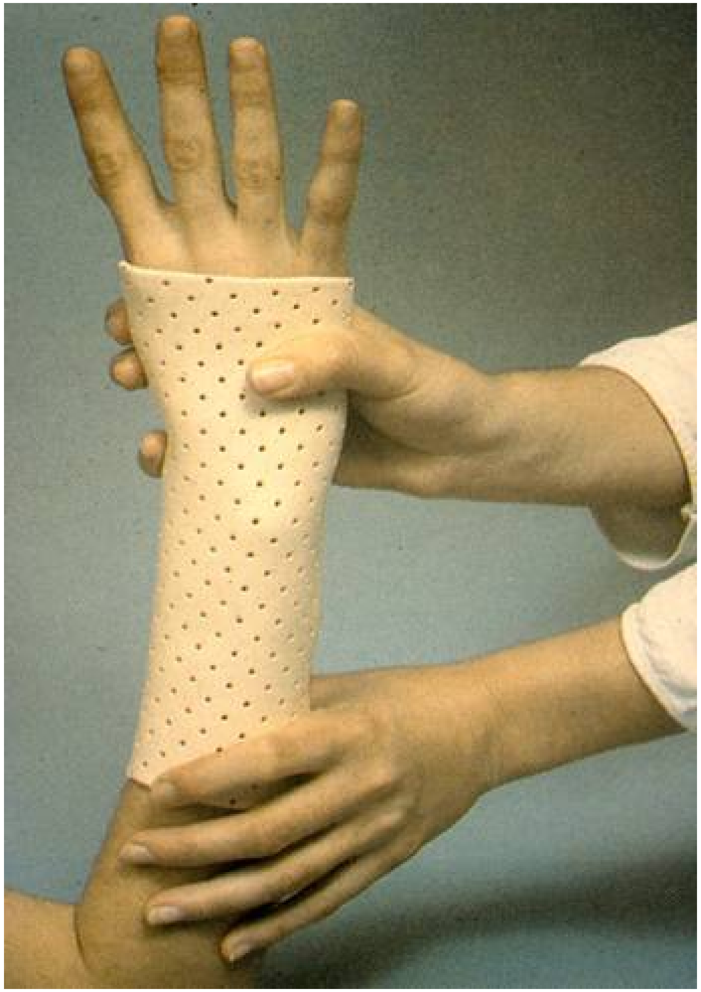


http://openlearn.open.ac.uk/mod/resource/view.php?id=196637

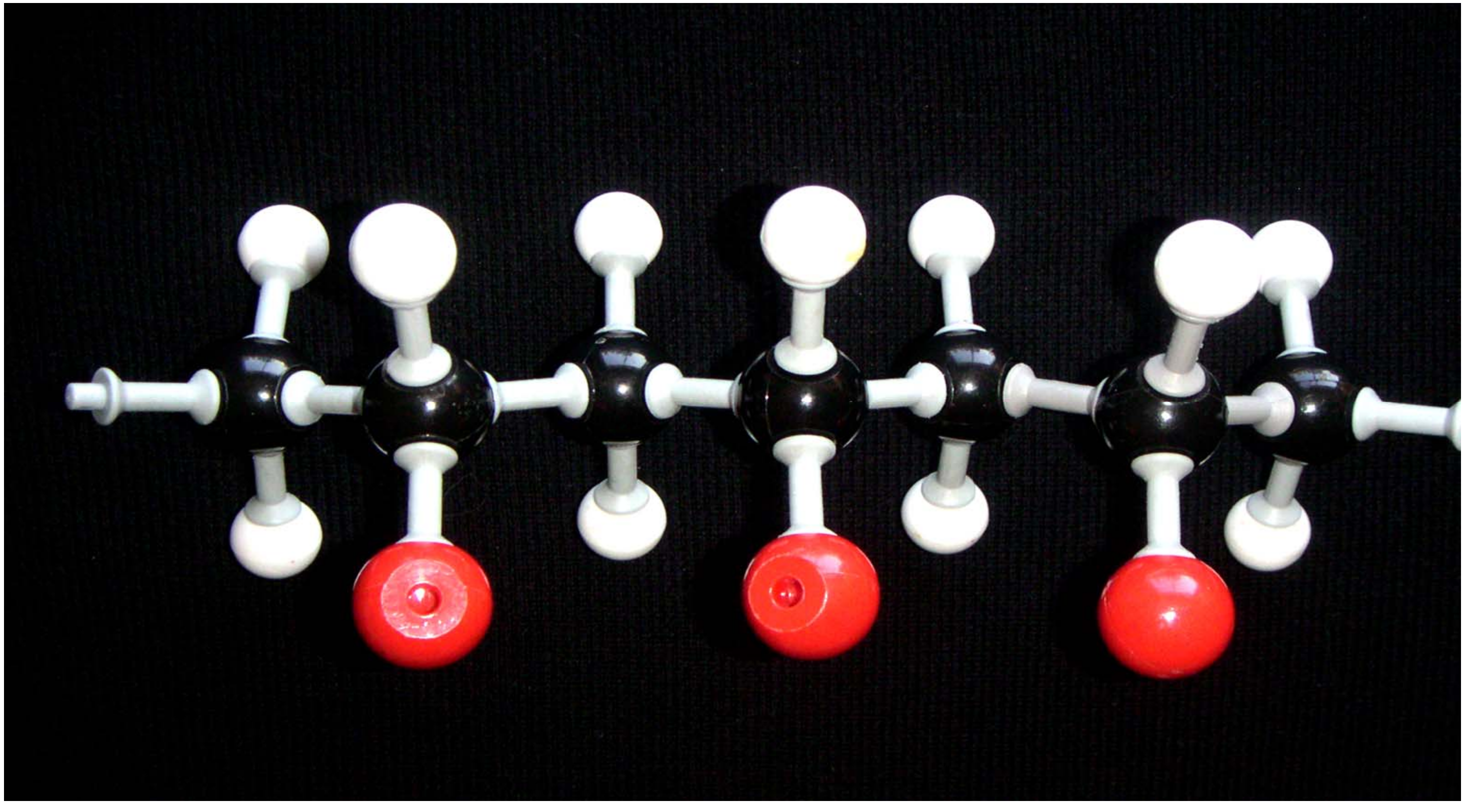
Effects of Stereochemistry:
Geometric Isomers of Polyisoprene



Trans-Polyisoprene



Additional Stereochemistry:
Tacticity of Polymers

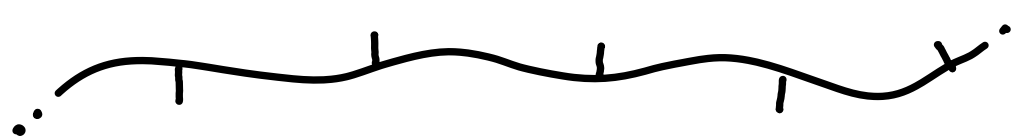


Effect of Tacticity on Glass Transition Temperature (T_g) of Polyacrylates

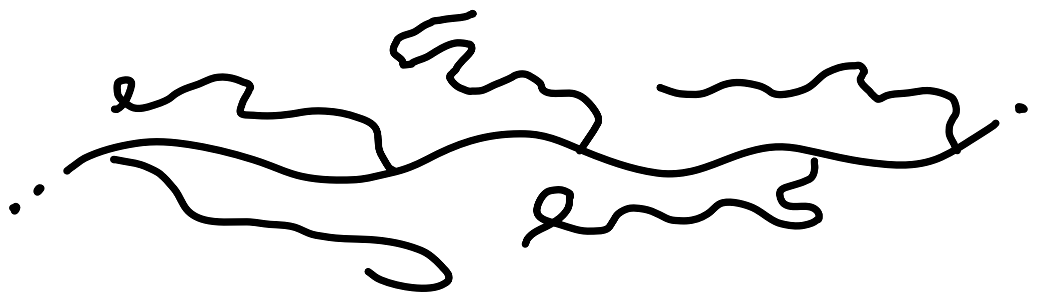
	T_gs (°C)	
Polymer	Syndiotactic	Isotactic
Methyl	160	43
Ethyl	120	8
Isopropyl	139	27
Butyl	88	–24
Isobutyl	120	8
Cyclohexyl	163	51

Topology of Polyethylene

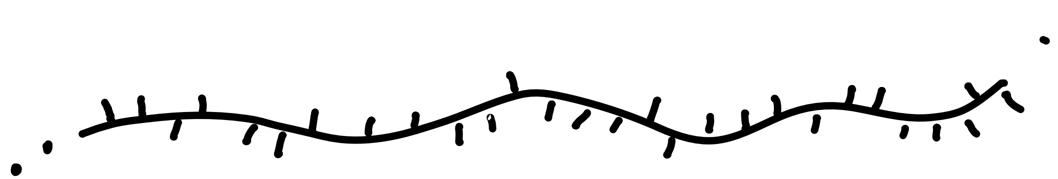
HDPE



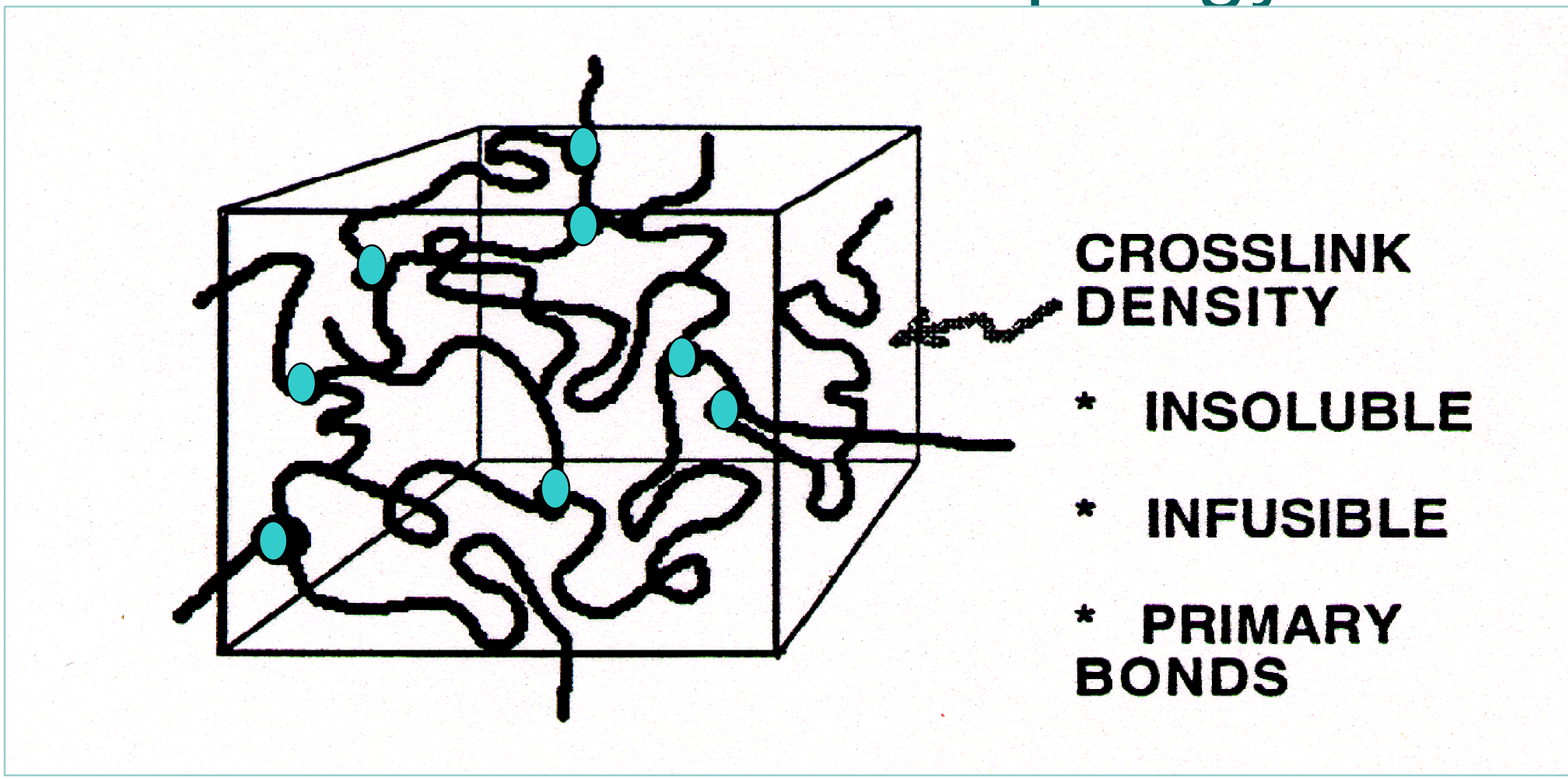
LDPE



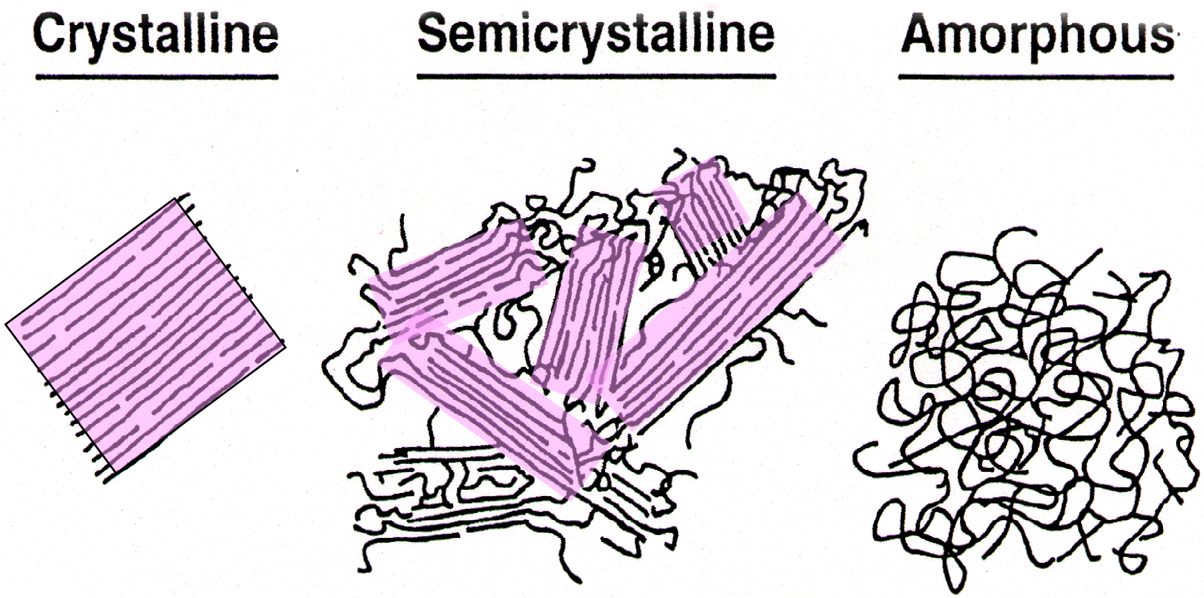
LLDPE



Thermoset Network Topology

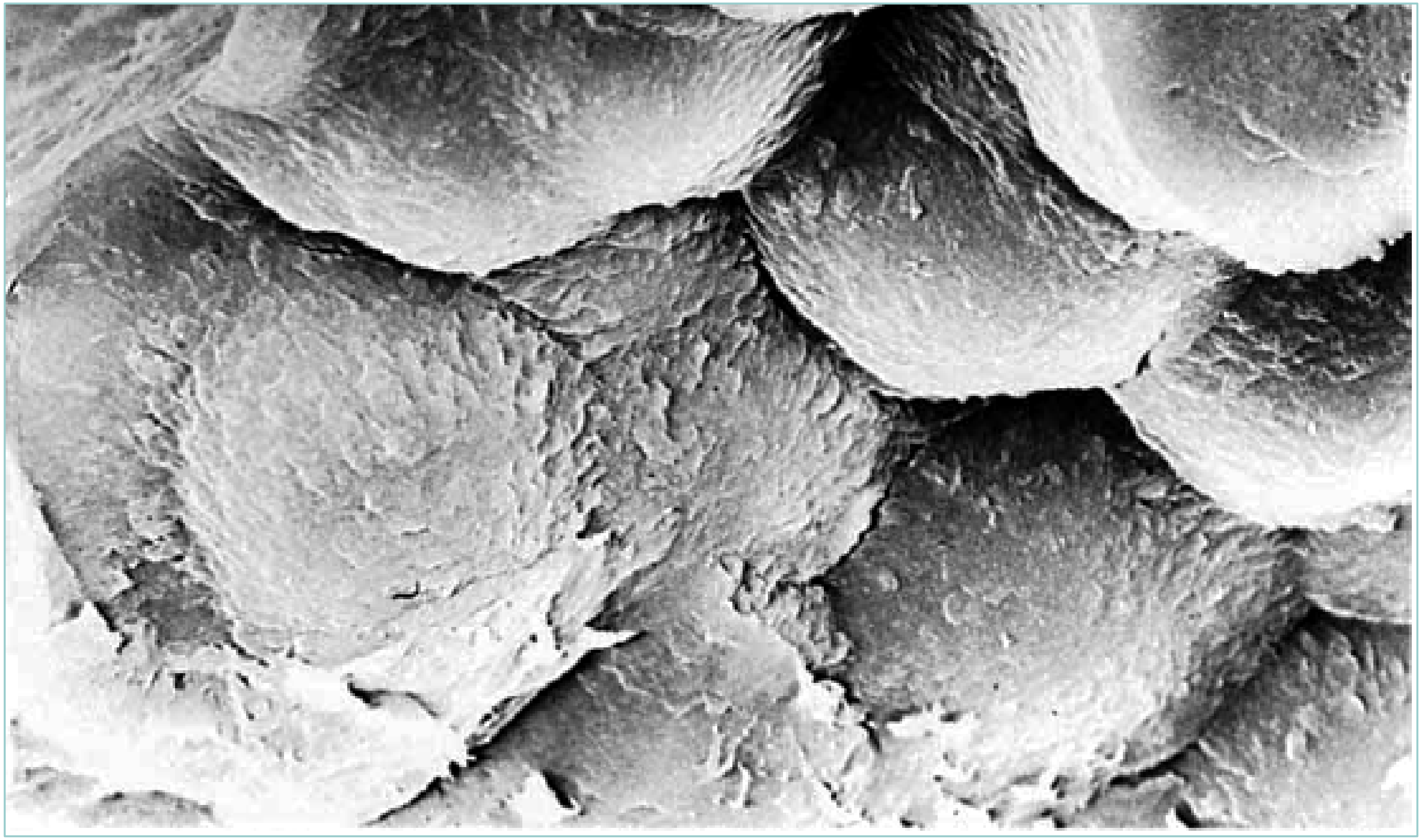


Morphology of Polymers



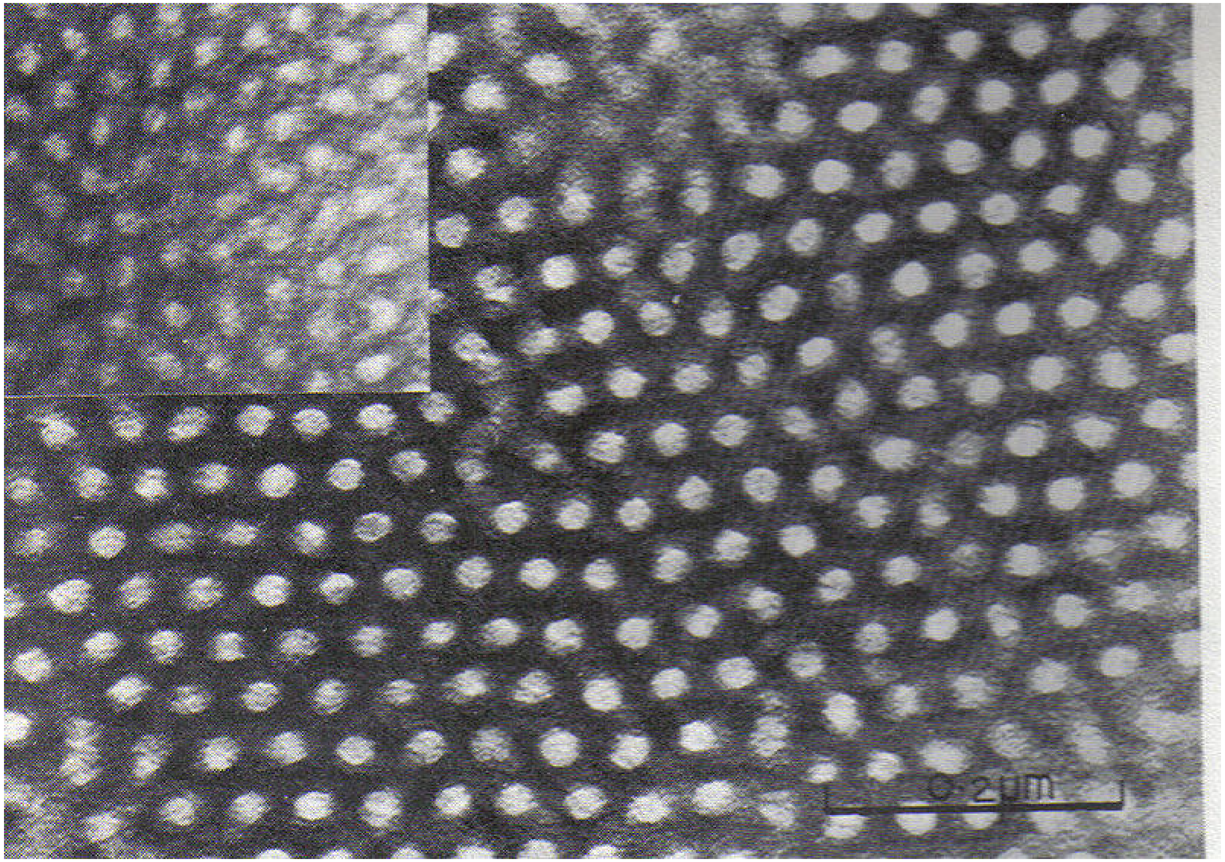
T_m T_g

Spherulitic Morphology of PET



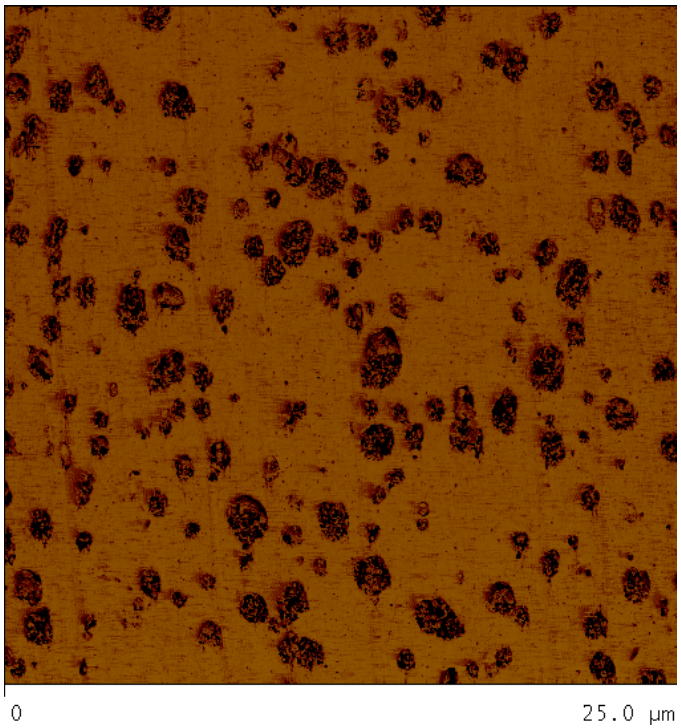
20 μ

Microphase Separated Morphology of Styrene Butadiene Block Copolymer

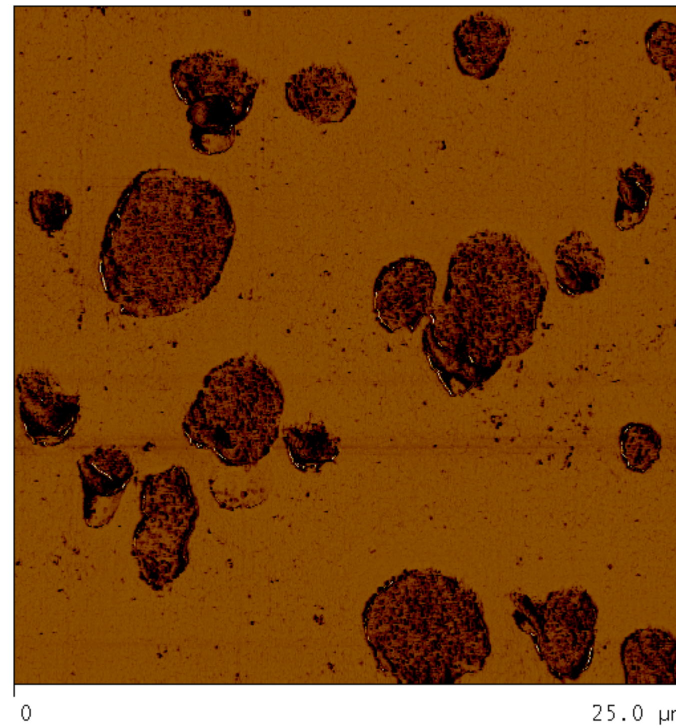


PR Lewis and C Price, *Polymer*, 13, 22 (1972)

Morphology of Impact Modified Nylon



IM1/Compatibilizer



Only IM1

Smaller Impact Modifier Size
Gives Better Impact in this System

Polymer Parameters

- Chemical Composition
- Molecular Weight & Distribution
- Stereochemistry
- Topology
- Morphology
- Additives

21CFR177.2600

i. Elastomers—EPDM, Silicone, NR
ii. Vulcanization Materials
    i. Vulcanizing Agents—Sulfur
    ii. Accelerators/Retarders—TMTM, DiCUP
    iii. Activators—Stearic Acid
iii. Antioxidants—BHT, TNPP (21CFR178.2010)
iv. Plasticizers—Dioctyl phthalate
v. Fillers—ATH, TiO2, SiO2, carbon black
vi. Colorants
vii. Lubricants
viii. Emulsifiers
ix. Miscellaneous—blowing agents

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Example Formulations

Thermosets:

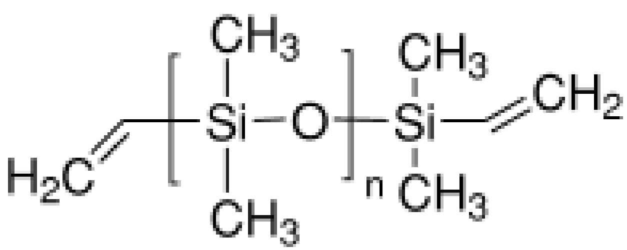
- Platinum silicone
- EPDM

Thermoplastics:

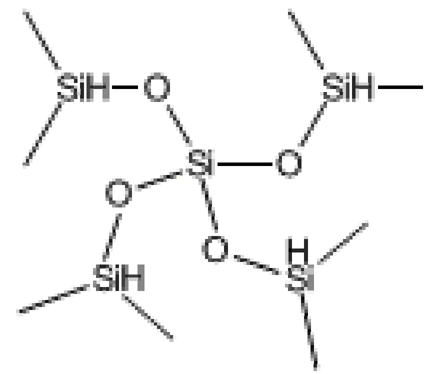
- Styrenic block copolymer (TPE)
- Polypropylene
- PET

Platinum Silicone Formulation

Vinyl Siloxane	70 %	Base Polymer
Fumed Silica	25 %	Reinforcement
Hydride Siloxane	5 %	Crosslinking
Ethynyl Cyclohexanol	0.1 %	Inhibitor
Platinum Catalyst	15 ppm	Hydrosilylation



Vinyl Siloxane



Hydride Siloxane

EPDM Formulation

EPDM	63 %	Base Polymer
Carbon Black	31 %	Reinforcement
Oil	(15 %)	Extender
Stearic Acid	0.6 %	Co-activator
Zinc Oxide	3 %	Activator
Sulfur	0.9 %	Curative
TMTM	0.9 %	Accelerator
Mercapto BZ	0.3 %	Co-accelerator
Antioxidant	0.5 %	Heat Stabilizer

Could have 20 different ingredients

Thermoplastic Elastomer (TPE) Styrenic Block Copolymer

S-EB-S	58 %	Base Polymer
Polystyrene	22 %	Reinforcement
Polypropylene	Optional	Toughness
Mineral Oil	16 %	Softness
BHT	0.3 %	Stabilizer
Alphamethyl styrene	3.4 %	Processing

Broad range of properties available depending upon composition

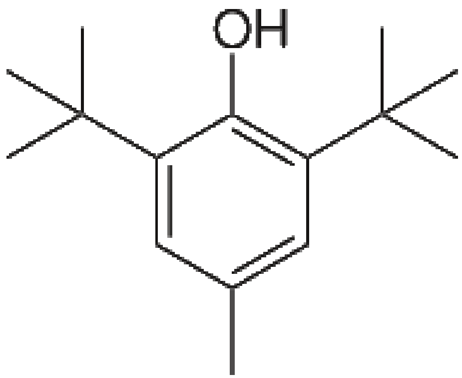
Composition called out in FCN from Kraton

Polypropylene Formulation

Polypropylene	99 %	Base Polymer
Phosphite	500 ppm	Processing stabilizer
BHT	1000 ppm	Co-stabilizer
Nucleant	0.5 %	Crystallization

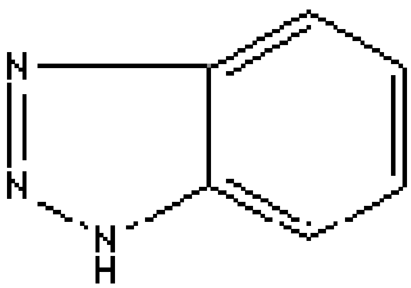
Thermoplastic formulations have fewer ingredients.

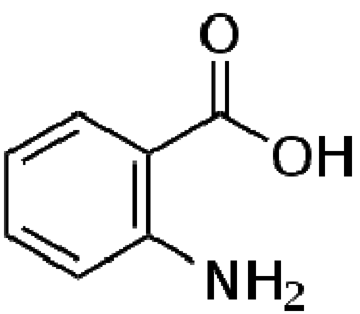
Materials sold as produced from resin manufacturer.



PET Formulation

Polyethylene Terephthalate	99 %	Base Polymer
Phosphite	100 ppm	Stabilizer
Anthranilic Acid derivative	200 ppm	Scavenger
(Amorphous Nylon & cobalt catalyst) in masterbatchs	(3 %)	Oxygen scavenger
Anthraquinone dye	50 ppm	Colorant
Benzotriazole	1000 ppm	UV Absorber





Very low levels of additives today
Depends upon application (ie. bottles)

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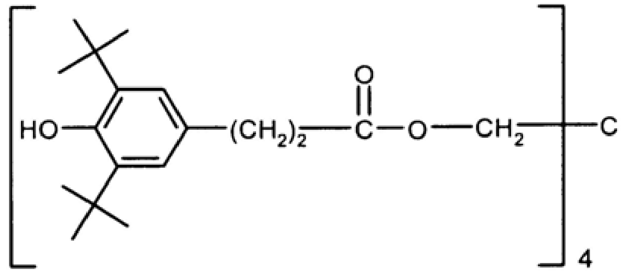
Types of Additives

- Stabilizers/Antioxidants (21CFR178.2010)
- Modifiers (plasticizers)
- Colorants
  - Organic (phthalocyanine, anthraquinone)
  - Inorganic (TiO_2, carbon black)
- Mold Releases & Slip Agents
  - Euracamides, waxes, silicones
- Flow Aids
  - Low MW olefins
  - Glycerol monostearate
  - Vulcanized vegetable oil
- Conductive materials
- Others

Why Use Stabilizers/Antioxidants?

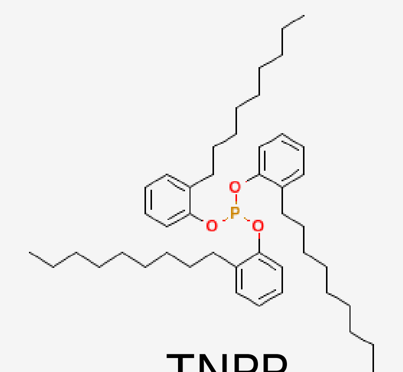
- Protect Polymer During:
  - Drying
  - Processing—Extruding; molding
  - In Use Exposure
  - Long Term Exposure



BNX 1010

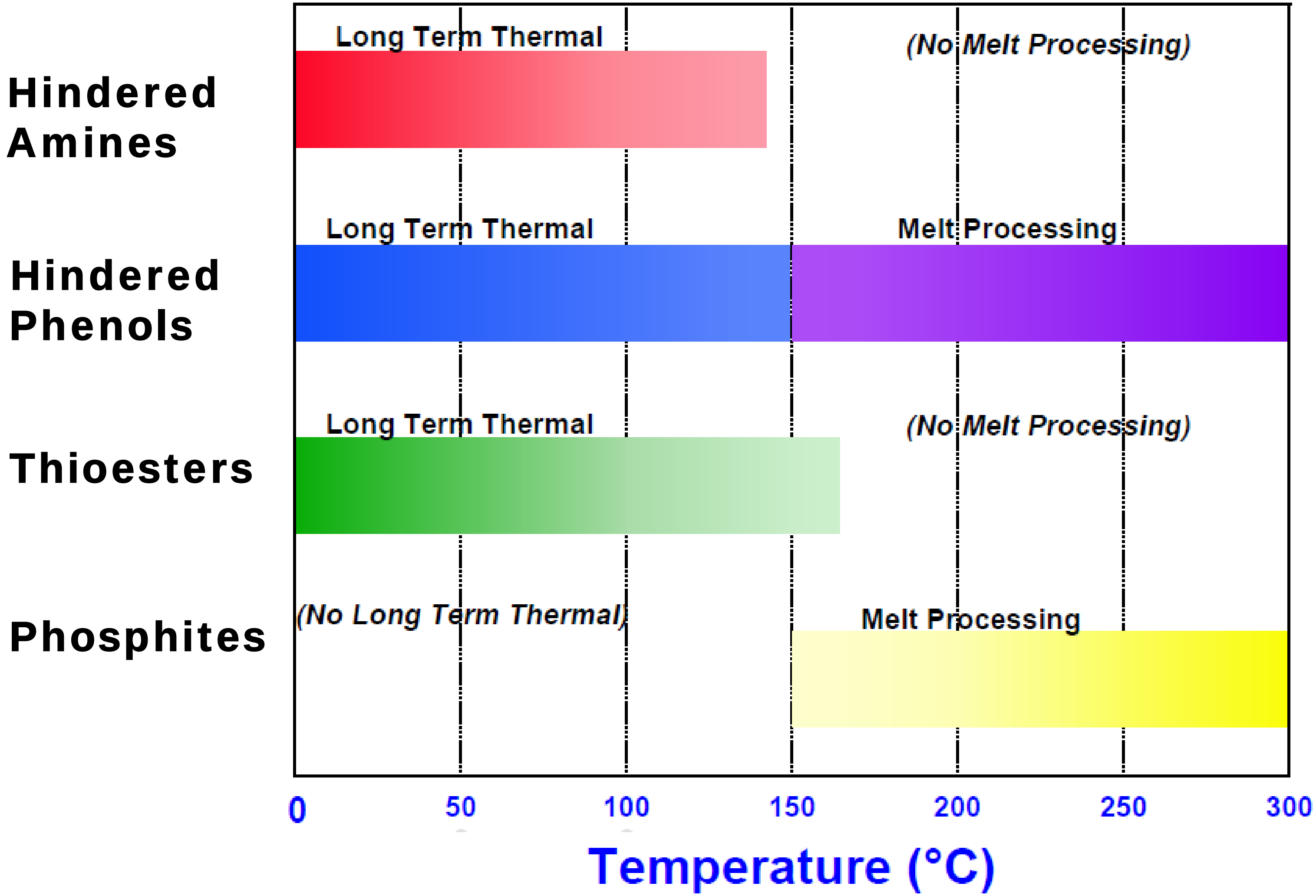
- Protect Against:
  - Thermo-oxidative Degradation
  - Long Term Heat/UV Radiation
  - Harmful Effects of Gamma Radiation Sterilization
  - Gas Fading – reactions with NO_x

- Common Stabilizers
  - Hindered phenols
  - Phosphites—TNPP
  - Thio-esters
  - Aluminum Trihydrate (ATH) $Al_2O_3 \cdot 3H_2O$



TNPP

Temperature Range for Stabilizers



http://www.ampacet.com/usersimage/File/tutorials/Antioxidants.pdf

Modifiers

(Typically Used at Levels >1 wt.% to ~40 wt. %)

- Plasticizers
  - Dioctyl phthalate
  - Mineral oil
- Impact Modifiers
  - rubbery material
  - core shell
  - functionalized EPDM
  - HIPS—polybutadiene

Testing to Identify Extractables & Leachables

- Test Conditions: Some Standard…Many Custom
  - Usually 24 hrs at fixed temperature using:
    - Distilled Water
    - 5% Acetic Acid
    - 95% Ethanol or hexane to simulate Fatty Foods
      - Sometimes a "Synthetic Olive Oil" is Used

- Analytical Methods
  - Gravimetric
  - Organic analysis: Chromatography—GC & LC
  - Elemental analysis: ICP & Ion Chromatography

Concerns about Leachables

- Residual Monomers
  - Styrene (Suspect Carcinogen)
  - Bis-phenol A (Suspect Endocrine Disrupter)
  - VCM (Vinyl Chloride Monomer) Carcinogen
- Modifiers
  - Plasticizers
    - Phthalates (Suspect Endocrine Disrupters)
  - Mercaptothiazole (Suspect Carcinogen)
- Stabilizers
  - TNPP tris(nonyl phenyl) phosphite (Endocrine Disrupter)

Nanotechnology

- Extractability of Inorganic Particulates
- Carbon Nanotubes
  - Fibrous Irritant like asbestos?
- Do Nanomaterials penetrate cell walls?
- Can they be inhaled, or consumed internally from packaging
- End of Life
- Where do they go upon combustion, land burial, disposal at sea?

New Approaches

- Naturally Occuring Stabilizers
  - Vitamin E
  - Glycerol Monostearates
- Bound Stabilizers
- Inorganic Stabilizers
  - Non-migrating, e.g. nano Zn Oxide
- Nanoplatelets
  - Synthetics: α-zirconium phosphate

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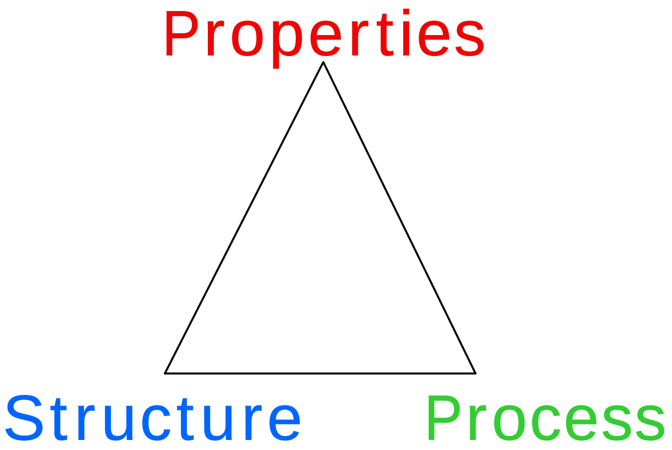
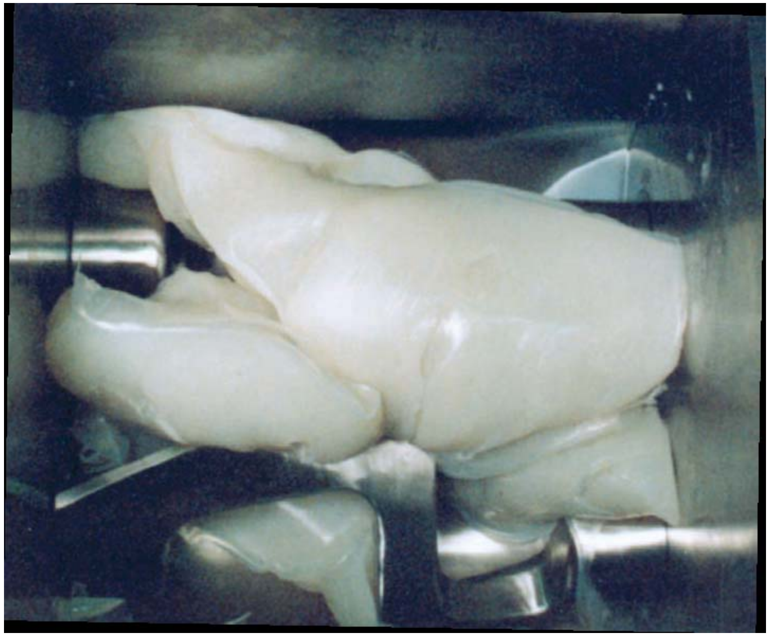
Optimizing Formulations

- Structure
  - Chemical Composition, MW, stereochemistry
  - Fillers
  - Crosslinkers
  - Additives
- Process
  - Shear/Dispersion
  - Coupling Agents
  - Temperature/time
- Properties
  - Modulus, strength, fatigue life, compatibility



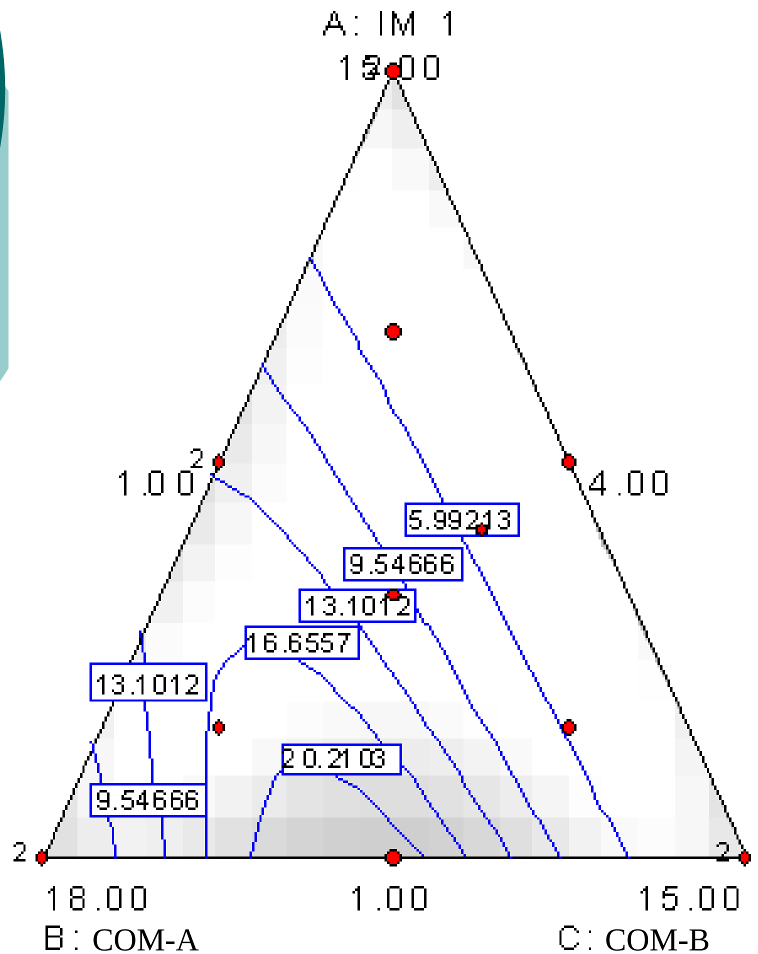
Extrusion and Compounding

16 mm Twin Screw Extruder

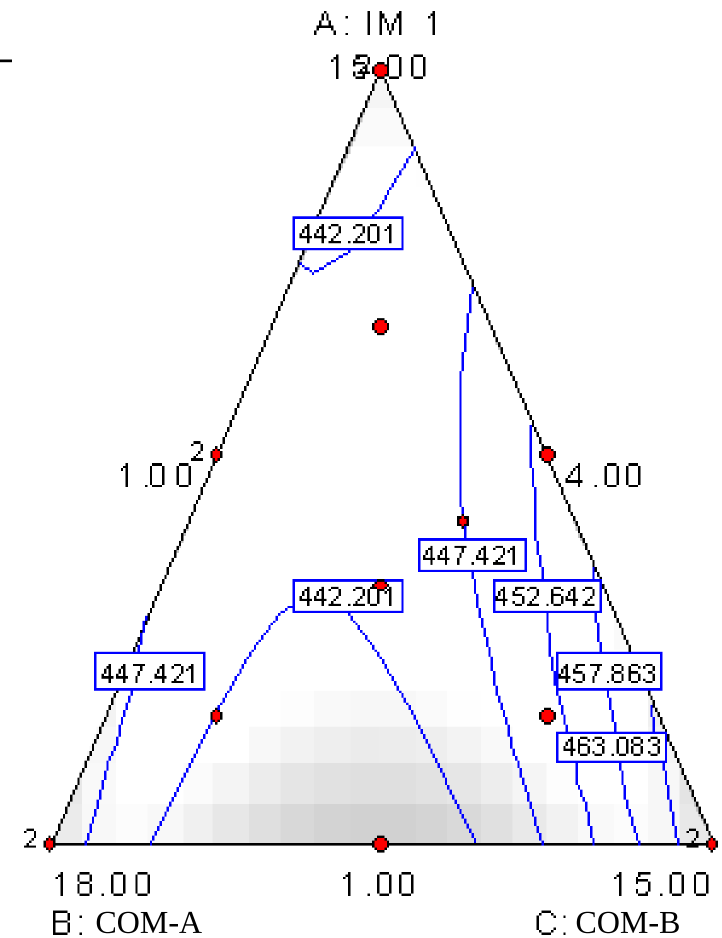


Sigma Blade Dough Mixer

Example of a Optimized Mixture Design



Impact

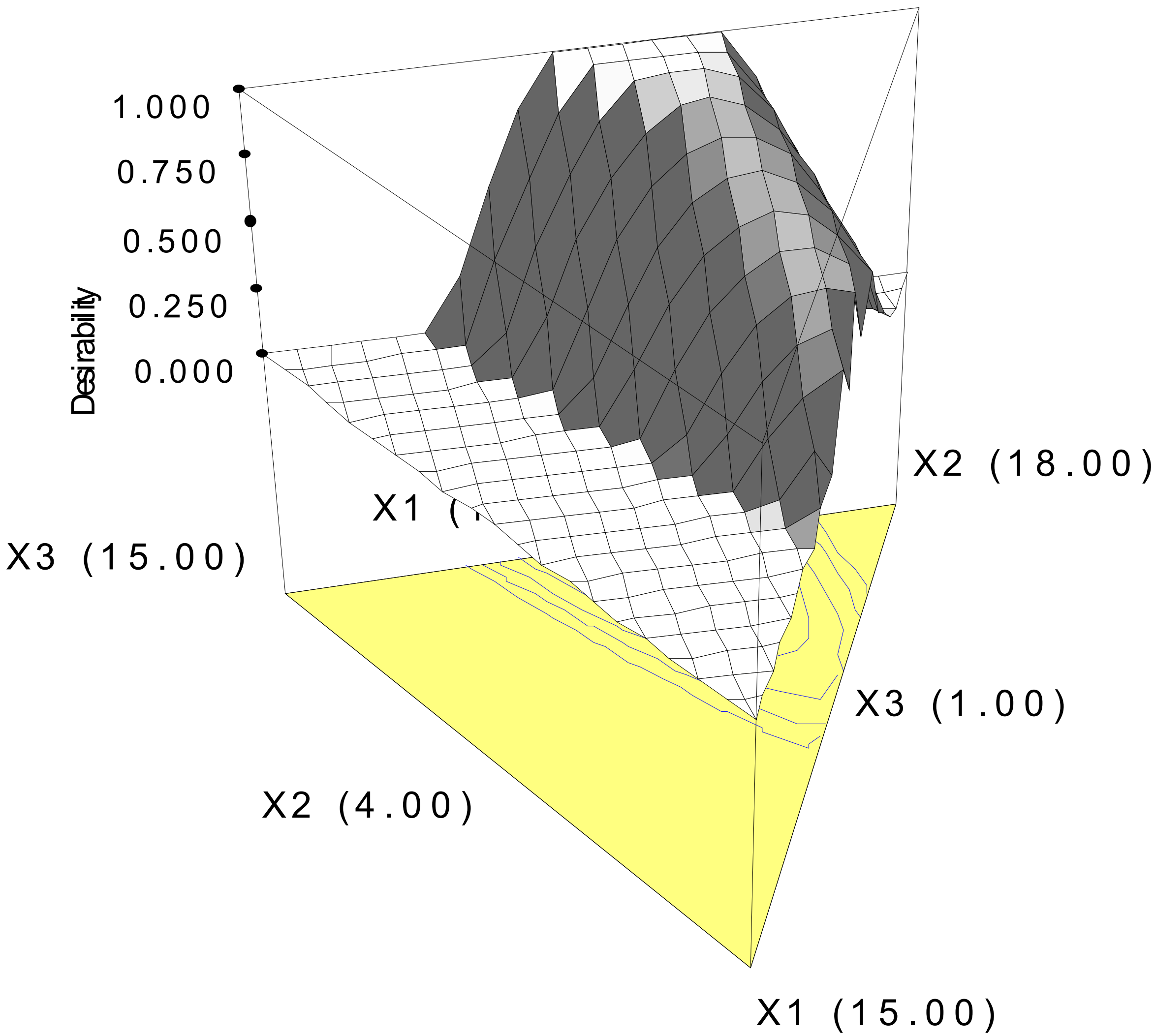


Flex Modulus

Impact=a*ComA+b*ComB+c*IM1

F.M.=a'ComA+b'ComB+c'*IM1

Typical Response Surface Plot



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Hygienic Envelope Gaskets

Hygienic EPDM Gaskets

BPE Standard Test Conditions

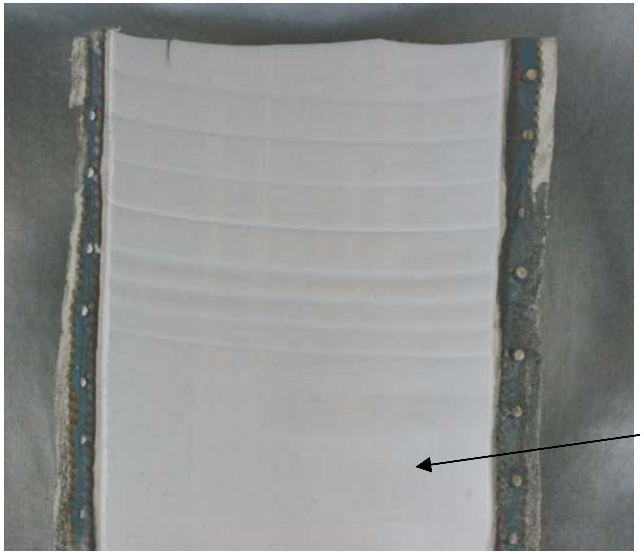
- Install Gaskets
  - Pre-SIP Pressure Hold Test
    - SIP at 125° C and cool
    - Post-SIP Pressure Hold Test
    - Repeat 10-15X (nightly)
  - CIP
  - Repeat to a total of 100 steam cycles
- Record gasket properties

Dynamic Application: Effects of Fatigue on EPDM Diaphragm

New

Failed

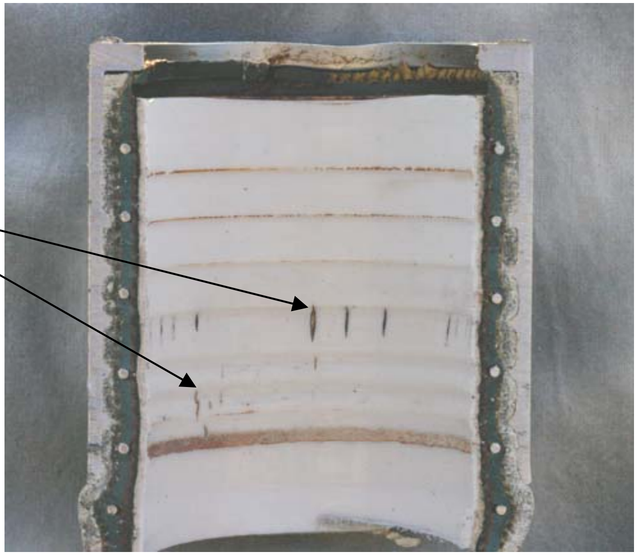
Effects of Thermal & Chemical Cycling on Fluoropoymer Lined Hose



Smooth,
Straight,
New Liner

New Hose

Severe Cracks



Failed Hose

Conclusions

- Start with the polymer parameters
- Additives are often necessary—watch for leachables
- Optimize by understanding structure-property-process interrelationships
- Understand the application requirements

Acknowledgements

- Tim Rugh – 3-A Standard
- Roger Avakian – PolyOne Corp.
- Tom Ward – VA Tech
- Bob Elbich – Exigo Manufacturing