Rubber and Plastics Formulations for Food Contact

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Dr. Roger Avakian, PolyOne Corp.
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

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Microstructures of Chemical Composition

Homopolymer

Random Copolymer

Block Copolymer

Graft Copolymer

Terpolymer

Example ABS plastic

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Molecular Weight Distribution

Effects of Stereochemistry:
Geometric Isomers of Polyisoprene

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Trans-Polyisoprene
Additional Stereochemistry:
Tacticity of Polymers

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

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Syndiotactic</th>
<th>Isotactic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>160</td>
<td>43</td>
</tr>
<tr>
<td>Ethyl</td>
<td>120</td>
<td>8</td>
</tr>
<tr>
<td>Isopropyl</td>
<td>139</td>
<td>27</td>
</tr>
<tr>
<td>Butyl</td>
<td>88</td>
<td>-24</td>
</tr>
<tr>
<td>Isobutyl</td>
<td>120</td>
<td>8</td>
</tr>
<tr>
<td>Cyclohexyl</td>
<td>163</td>
<td>51</td>
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Topology of Polyethylene

HDPE

LDPE

LLDPE

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Thermoset Network Topology

CROSSLINK DENSITY
* INSOLUBLE
* INFUSIBLE
* PRIMARY BONDS

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Morphology of Polymers

- **Crystalline**
  - $T_m$

- **Semicrystalline**

- **Amorphous**
  - $T_g$

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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

Smaller Impact Modifier Size
Gives Better Impact in this System

Only IM1
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%
- Fumed Silica: 25%
- Hydride Siloxane: 5%
- Ethynyl Cyclohexanol: 0.1%
- Platinum Catalyst: 15 ppm

- Base Polymer
- Reinforcement
- Crosslinking
- Inhibitor
- Hydrosilylation

Vinyl Siloxane

Hydride Siloxane
## EPDM Formulation

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percentage</th>
</tr>
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<tbody>
<tr>
<td>EPDM</td>
<td>63 %</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>31 %</td>
</tr>
<tr>
<td>Oil</td>
<td>(15 %)</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>0.6 %</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>3 %</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.9 %</td>
</tr>
<tr>
<td>TMTM</td>
<td>0.9 %</td>
</tr>
<tr>
<td>Mercapto BZ</td>
<td>0.3 %</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>0.5 %</td>
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</tbody>
</table>

- Base Polymer
- Reinforcement
- Extender
- Co-activator
- Activator
- Curative
- Accelerator
- Co-accelerator
- Heat Stabilizer

Could have 20 different ingredients
**Thermoplastic Elastomer (TPE) Styrenic Block Copolymer**

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-EB-S</td>
<td>58 %</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>22 %</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>Optional</td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>16 %</td>
</tr>
<tr>
<td>BHT</td>
<td>0.3 %</td>
</tr>
<tr>
<td>Alphamethyl styrene</td>
<td>3.4 %</td>
</tr>
</tbody>
</table>

- **Base Polymer**
- **Reinforcement**
- **Toughness**
- **Softness**
- **Stabilizer**
- **Processing**

**Broad** range of properties available depending upon composition

**Composition called out in FCN from Kraton**
Polypropylene Formulation

- Polypropylene 99 %
- Phosphite 500 ppm
- BHT 1000 ppm
- Nucleant 0.5 %

- Base Polymer
- Processing stabilizer
- Co-stabilizer
- Crystallization

Thermoplastic formulations have fewer ingredients.

Materials sold as produced from resin manufacturer.
PET Formulation

- Polyethylene Terephthalate 99 %
- Phosphite 100 ppm
- Anthranilic Acid derivative 200 ppm
- (Amorphous Nylon & cobalt catalyst) in masterbatchs (3 %)
- Anthraquinone dye 50 ppm
- Benzotriazole 1000 ppm

- Base Polymer
- Stabilizer
- Scavenger
- Oxygen scavenger
- Colorant
- 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 (TiO2, 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

- **Protect Against:**
  - Thermo-oxidative Degradation
  - Long Term Heat/UV Radiation
  - Harmful Effects of Gamma Radiation Sterilization
  - Gas Fading – reactions with NO\textsubscript{x}

- **Common Stabilizers**
  - Hindered phenols
  - Phosphites—TNPP
  - Thio-esters
  - Aluminum Trihydrate (ATH) \( \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \)
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: $\alpha$-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=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 Fluoropolymer Lined Hose

New Hose

Failed Hose

Severe Cracks

Smooth, Straight, New Liner
Conclusions

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