Synthetic Rubber

For HIPS, MBS and Mass-ABS

Mitsubishi International Corporation
Classification of Diene Rubber

- Butadiene Rubber
  - Polybutadiene (BR)
    - High Cis BR
    - Low Cis BR
    - High Trans BR
    - High Vinyl BR
    - Emulsion-SBR
    - Solution-SBR
  - Styrene-Butadiene Copolymer (SBR)
    - Styrene-Butadiene-Styrene block Copolymer (SBS: Thermoplastic Elastomer)
    - Hydrogenated SBS-SEBS
  - Natural Rubber (NR)
  - Polyisoprene (IR)

- Isoprene Rubber
  - Polyisoprene (IR)
Characteristics of Solution Polymerization Technique

**Butadiene**  
**Styrene**  

<table>
<thead>
<tr>
<th>Control of Macro-structure</th>
<th>Molecular Weight</th>
<th>Controllable by ratio between Feed Monomer/Catalyst because of living anionic polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWD (Mw/Mn)</td>
<td>MWD (Mw/Mn)</td>
<td>Narrow due to living anionic polymerization. Changeable according to polymerization conditions and reactions</td>
</tr>
<tr>
<td>Branch</td>
<td>Branch</td>
<td>Little during polymerization. Easily controlled by adding coupling agent</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Microstructure</th>
<th>1,4-Cis; 1,4-Trans; 1,2-Vinyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>(polybutadiene parts)</td>
<td>Vinyl content easily controlled by adding modifier (polar compounds)</td>
</tr>
<tr>
<td>Bound Styrene Content</td>
<td>Easily controlled by butadiene/styrene feed ratio</td>
</tr>
<tr>
<td>Block Styrene Content</td>
<td>Random, block, tapered</td>
</tr>
<tr>
<td>Hydrogenated (Bd)</td>
<td>Controlled by polymerizations conditions</td>
</tr>
</tbody>
</table>

**Stabilizer**

**Catalyst**

**Terminator**

**Polybutadiene (BR)**

**Styrene-butadiene copolymer (SBR)**
## Relationship between Low Cis, High Cis Rubber

<table>
<thead>
<tr>
<th>Low Cis Rubber</th>
<th>Polymerization</th>
<th>Polymer Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Anionic polymerization</strong>&lt;br&gt;(Solution)&lt;br&gt;Rli catalyst</td>
<td>- MWD narrow, Little branching&lt;br&gt;- Microstructure: Cis 35%, Trans 52%, Vinyl 13%&lt;br&gt;- Tg: -98 degree C  Tm: nil&lt;br&gt;- Control of polymer structure  Large variation&lt;br&gt;  -- Vinyl content&lt;br&gt;  -- Block SBR, Random SBR&lt;br&gt;  -- Coupling reaction, Terminal modification, etc.</td>
</tr>
<tr>
<td></td>
<td><strong>Radical polymerization</strong>&lt;br&gt;(Emulsion)&lt;br&gt;Potassium peroxodisulfate</td>
<td>- Broad MWD, Much branching&lt;br&gt;- Microstructure: Cis 12%, Trans 70%, Vinyl 18%&lt;br&gt;- Control of polymer structure  Little variation&lt;br&gt;  -- Styrene content&lt;br&gt;  -- Molecular weight</td>
</tr>
<tr>
<td>High Cis Rubber</td>
<td><strong>Coordinate polymerization</strong>&lt;br&gt;(Solution)&lt;br&gt;Ni catalyst&lt;br&gt;Co-Al catalyst</td>
<td>- Broad MWD (Mw/Mn 3), Much branching&lt;br&gt;- Microstructure: Cis 96%, Vinyl 4%&lt;br&gt;- Tg: -105 degrees C  Tm: 10 degrees C&lt;br&gt;- No copolymerization of styrene</td>
</tr>
</tbody>
</table>
## Microstructure of Polybutadiene

<table>
<thead>
<tr>
<th>Polymer structure</th>
<th>Homopolymer Tg, Tm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tg (Elasticity)</strong></td>
<td><strong>Tm (Crystallization)</strong></td>
</tr>
<tr>
<td><strong>Cis Bond</strong></td>
<td>-110 °C</td>
</tr>
<tr>
<td><strong>Trans Bond</strong></td>
<td>-100 °C</td>
</tr>
<tr>
<td><strong>Vinyl Bond</strong></td>
<td>-7 °C</td>
</tr>
<tr>
<td><strong>Styrene</strong></td>
<td>100 °C</td>
</tr>
</tbody>
</table>
# Microstructure of Polybutadiene (2)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Microstructure (%)</th>
<th>Styrene Copolymerizable</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cis</td>
<td>Trans</td>
</tr>
<tr>
<td><strong>RLi</strong></td>
<td>35</td>
<td>52</td>
</tr>
<tr>
<td><strong>RLi / Polar solvent</strong></td>
<td>~30</td>
<td>~50</td>
</tr>
<tr>
<td><strong>Ni</strong></td>
<td>96 ~ 98</td>
<td>1 ~ 2</td>
</tr>
<tr>
<td>- Ni(Naphtanate)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- AIR₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- BF₃·(C₂H₅)₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Co</strong></td>
<td>96 ~ 98</td>
<td>1 ~ 2</td>
</tr>
<tr>
<td>- Co(Octanate)₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- AIR₂Cl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- H₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Radical</strong></td>
<td>10 ~ 20</td>
<td>60 ~ 80</td>
</tr>
<tr>
<td>- K₂S₂O₄</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

○ = Copolymerizable with styrene
× = Not copolymerizable with styrene
Comparison of Batch Polymerized Rubber with Continuous Polymerized Rubber: Molecular weight Distribution

- **Continuous Polymerization**
  - Asadene 55 A E
  - Mw/Mn=2.2

- **Batch polymerization**
  - Asaprene 730AX
  - Mw/Mn=1.2

- **High Cis Rubber**
  - Mw/Mn=3.5
Synthetic Rubber for HIPS Use

- Acquired Characteristics
  - Ability to crosslink/Graft during HIPS polymerization
  - Styrene insolubles (gel) - Extremely low
  - Impurity - Extremely low
  - Colorless
  - Handling flow - Improved cold
Synthetic Rubber for HIPS Use

- Commercial Rubber for HIPS Use
  - Polybutadiene rubber: Low Cis BR, High Cis BR
    - Comparison of Low Cis BR with High Cis BR as rubber for HIPS:

<table>
<thead>
<tr>
<th></th>
<th>Graft</th>
<th>Crosslinking</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Cis BR</td>
<td>High reactivity</td>
<td>High reactivity</td>
</tr>
<tr>
<td>High Cis Br</td>
<td>Low reactivity</td>
<td>Low reactivity</td>
</tr>
</tbody>
</table>

- Styrene-butadiene copolymer
  - Random SBR
  - Block SBR
    - Special grade: Super high gloss HIPS, Transparent HIPS, etc.
## Synthetic Rubber for HIPS (Mass-ABS)

<table>
<thead>
<tr>
<th>Grade</th>
<th>Styrene (%)</th>
<th>ML</th>
<th>SV (CPS)</th>
<th>Microstructure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>General</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Asadene 55AE</td>
<td>0</td>
<td>50</td>
<td>170</td>
<td>35 52 13</td>
</tr>
<tr>
<td>Asadene 35AE</td>
<td>0</td>
<td>33</td>
<td>85</td>
<td>35 52 13</td>
</tr>
<tr>
<td><strong>Low SV</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Asaprene 720AX</td>
<td>0</td>
<td>40</td>
<td>25</td>
<td>33 49 18</td>
</tr>
<tr>
<td>Asaprene 730AX</td>
<td>0</td>
<td>47</td>
<td>35</td>
<td>33 49 18</td>
</tr>
<tr>
<td><strong>Low Modulus</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Asaprene 760AX</td>
<td>0</td>
<td>55</td>
<td>77</td>
<td>33 49 18</td>
</tr>
<tr>
<td><strong>PH-BR</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H300A</td>
<td>0</td>
<td>75</td>
<td>Partially hydrogenated BR</td>
<td>Thermal Stability</td>
</tr>
<tr>
<td><strong>SBR</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Asaprene 610A</td>
<td>15</td>
<td>–</td>
<td>10</td>
<td>35 51 14</td>
</tr>
<tr>
<td>Asaprene 625A</td>
<td>35</td>
<td>–</td>
<td>20</td>
<td>35 51 14</td>
</tr>
<tr>
<td>Asaprene 670A</td>
<td>39</td>
<td>–</td>
<td>34</td>
<td>35 51 14</td>
</tr>
</tbody>
</table>

- **General purpose**
- **High Gloss**
- **High Impact**
- **High Gloss Mass-ABS**
- **Transparent**
- **Super High Gloss**
Relationship between Mooney and Solution Viscosities

Mooney Viscosity [ML1+4, 100°C] vs Solution Viscosity [5wt% in Styrene]

- High Cls
- 55AE
- 730AX
- 35AE
- 760AX
- 720AX
Cold Flow of Asaprene, Asadene, Other Rubbers

Cold flow % = \( \frac{H_O - H_t}{H_O} \times 100 \)

- \( H_O \): Initial height of sample
- \( H_t \): Height of sample after t min.

Sample size (mm): LXWXH=40X40X50
Relationship between Solution Viscosity and Rubber Particle Size (Using Polybutadiene rubber)

- 1.5L Glass bottle
- Rubber/SM = 595 (wt%)

**Agitation speed: 25 rpm**

**Agitation speed: 75 rpm**

- 730AX
- 35AE
- 55AE

Solution viscosity (cps)

R.P.S. (µm)
Molecular Distribution of Weight for Asadene 55AE/35AE

![Retention time (min.)](chart)

- **Asadene 55AE**
- **Asadene 35AE**

**Fraction (%)**

- High molecular weight
- Low molecular weight
Distribution of Molecular Weight in Asaprene Series

Asaprene 730AX
Asaprene 760AX

Retention time (min.)

Fraction (%)

High molecular weight
Low molecular weight
Relationship between Rubber Particle Size and Izod, Gloss (Using polybutadiene rubber)

![Graph showing the relationship between rubber particle size and Izod impact, as well as gloss percentage.](image-url)
Asaprene 760AX

- Rubber for super high-impact PS
- Molecular structure
  - Polybutadiene rubber
  - Branched structure
  - Vinyl/cis/trans: 18/33/49
  - Solution viscosity: 77cps
Asaprene 760AX

- Characteristics
  - By using low-modulus Asaprene rubber, impact energy can be absorbed easily

![Graph showing the relationship between modulus and Izod impact strength](image-url)
Asaprene 670A  (1)

- Rubber for
  - Super high-gloss HIPS
  - Transparent HIPS
- Molecular structure
  - Styrene-butadiene rubber (39% styrene)
  - Vinyl/cis/trans: 14/36/50
  - Solution viscosity: 34 cps
Asaprene 670A (2)

- Characteristics
- Allows for easy formation of core-shell rubber particles
- Makes it easy to obtain transparent HIPS
- Corresponds to refractive Index of Styrene/Methacrylic copolymer and rubber phase

<table>
<thead>
<tr>
<th></th>
<th>SBR</th>
<th>PMMA</th>
<th>PBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive Index</td>
<td>1.59</td>
<td>1.49</td>
<td>1.46</td>
</tr>
</tbody>
</table>

Core-shell particles (thermal polymerization)
Asaprene 625A

- Rubber for transparent HIPS
- Molecular structure
  - Styrene-butadiene rubber (35% styrene)
  - Vinyl/cis/trans: 14/36/50
  - Solution viscosity: 20 cps

Matrix Resin

Styrene unit

Methacrylic ester unit

Acrylic ester unit
Asaprene 625A

- **Characteristics**
  - Transparency HIPS are easily obtained compared with other styrene-butadiene block copolymers
  - Easier to handle:
    - Bale is
      - Easier to cut
      - Less likely to crack
      - Bites into cutter more easily

<table>
<thead>
<tr>
<th></th>
<th>PS</th>
<th>SBR</th>
<th>PMMA</th>
<th>PBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive Index</td>
<td>1.59</td>
<td>1.54</td>
<td>1.49</td>
<td>1.46</td>
</tr>
</tbody>
</table>
Asaprene 720AX

- Rubber for high-gloss mass ABS
- Characteristics:
  - Easier to obtain small rubber particles
- Molecular structure:
  - Polybutadiene rubber
  - Vinyl/cis/trans: 18/33/49
  - Solution Viscosity: 25 cps

Relationship between Solution viscosity and R.P.S.
Asaprene 610A

- Rubber for high-gloss mass ABS
- Characteristics:
  - Easier to obtain small rubber particles
- Molecular structure
  - Styrene-butadiene rubber (15% styrene)
  - Vinyl/cis/trans: 14/36/50
  - Solution viscosity: 10 cps

Relationship between Solution viscosity and R.P.S.
H300A  (1)

- Rubber for HIPS with excellent thermal stability
- Molecular structure:
  - 1,4-cis/trans: 63%
  - 1,2-vinyl: 1%
  - Tetramethylene: 26%
  - Butylene: 10%
- Solution viscosity: 75 cps
H300A (2)

- Characteristics
  - HIPS and styrenic copolymer (e.g. mass-polymerized ABS) with PHBR have excellent thermal stability.
  - As a result, the decline in impact strength is very small when molding at high temperatures
  - Outstanding capabilities for recycling applications
Asaprene 630A  (1)

- Rubber for translucent (high-gloss) HIPS
- Molecular structure
  - Styrene-butadiene rubber (22% styrene)
  - Vinyl/cis/trans: 14/36/50
  - Solution viscosity: 33cps
Asaprene 630A (2)

- Characteristics
  - Core-shell rubber particles can be obtained easily
- Comparison with other styrene-butadiene block copolymers:
  - Less rubber content
  - Easier to handle: Bale is
    - Easier to cut
    - Less likely to crack
    - Bites into cutter more easily
  - Dissolving time is shorter

Core-shell particles
Asaprene 610A, 720AX  (1)

- Rubber used for mass ABS
- Molecular structure
  - 610A
    - Styrene-butadiene rubber (15% styrene)
    - Vinyl/cis/trans: 14/36/50
    - Solution viscosity: 10cps
  - 720AX
    - Polybutadiene rubber
    - Vinyl/cis/trans: 18/33/49
    - Solution viscosity: 25cps
Asaprene 610A, 720AX (2)

- Characteristics
  - Small rubber particles the size of ABS are easily obtained, making it possible to obtain a high-gloss ABS

Polymerization Condition
- Apparatus: 1.5L glass bottle
- Composition: SM/AN/Rub.=65/25/10 (wt%)
- Initiator: 150ppm
- Chain Transfer: 1200ppm
Next Steps

- Mitsubishi International offers a variety of outstanding synthetic rubbers for HIPS and Mass-ABS applications
- To learn more about how MIC can meet your product needs, please contact us at (212) 605-2440, or email rafi.khan@mitsubishicorp.com

Thank you.