Styrenic Block Copolymers in Medical Applications

Presented by Julie Li
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Outline

- Introduction to Kraton Polymers, Inc.
- What are Kraton™ Polymers?
- Kraton Enhanced Rubber Segment (ERS) Grades and Applications
- Kraton Adhesive Compounds for Protective Film Applications
- Cariflex™ Polyisoprene Rubber and Applications
- Summary
Kraton Polymers, Inc. at a Glance

- Specialty polymer company with 2012 revenues of $1.4B (KRA);
- Inventor and a leading producer of styrenic block copolymers (SBCs);
- Manufacturer of highly engineered polymer solutions with product breadth, service, and technical support second to none;
- Designer of customized solutions on a molecular level to meet specific performance needs;
- Serves a highly diverse set of end-use applications in addition to dedicated emerging businesses;
- Seller of over 800 products to approximately 800 customers in 60 countries;
- Holder of approximately 1,400 patents; issued or pending;
- Employer of approximately 940 people in 9 locations in all major regions of the world.
Kraton Polymers Can Support Your Global Demand
50 Years of Innovation and Growth

1960
Footwear

1970
Viscosity Modifiers

1980
Adhesives

1990
Roof felts

1990
Diapers

1990
Overmolding

1960

New growth

2009
HiMA Technology

2009
Nexar™ Polymers

2010
Automotive Soft Skin Technology

2011
Cariflex™ Polyisoprene Products

2011
What are Kraton™ Polymers?
What are Kraton™ Polymers?

Styrenic Block Copolymer (SBC)
SEBS, SEPS, SBS, SIS, SIBS, ...

Features of Anionic Polymerization

1. Precise control of block size and formation;
2. Precise control of molecular weight;
3. Narrow molecular weight distribution;
4. Precise control of midblock structure;
5. High hydrogenation ratio.

PS Rubber PS
USBC → Kraton D polymers

SBS

+ H₂

HSBC → Kraton G polymers

SEBS
What are Kraton™ Polymers?

Styrenic Block Copolymer (SBC) is a thermoplastic elastomer

**Domain Size**

TEM micrograph (S/B=20/80%)

- **Polystyrene End Block**
  - Hard
  - \( T_g = 100^\circ C \)
  - Incompatible with soft block
  - Strength enhancer
  - Physical crosslinks at room temperature

- **Rubber Mid Block**
  - Soft & Flexible
  - Low \( T_g \)
  - \( SBS = -90^\circ C, SIS = -60^\circ C, SEBS = -55^\circ C \)
  - Oil-able, Strength
  - Hydrophobic
  - Stable

**Two incompatible phase structures:** vulcanization NOT Required

- **Morphology of Kraton Polymer**
  - Domain Size ~200 Å

Incompatible with soft block
Strength enhancer
Physical crosslinks at room temperature

Strength enhancer

Hydrophobic

Stable

- **SBS = -90^\circ C, SIS = -60^\circ C, SEBS = -55^\circ C**
- Oil-able, Strength
- Hydrophobic
- Stable
Product Families

Kraton™ D
(Unhydrogenated SBC)

- SIS
- SBS
- Neat polymers
- Oil extended polymers
- SIBS
- D Compounds

HSBC Compounds

- G2705
- G2832
- G7705
- G7720
- G7723
- G7820
- ...

SEBS

Kraton G
(Hydrogenated SBC)

- G1650
- G1651
- G1652
- G1654
- G1657
- G1660
- G1663
- G1726
- ...

ERS polymers

- G1641
- G1642
- G1643
- G1645

A1535 (RP6935)
A1536 (RP6936)
A1537 (MD6937)

Kraton A

Functionalized HSBC

- FG1901
- FG1924
- MD6684
- MD6670

Oil Extended SEBS polymers

Solid IR

- IR0307 (IR 307)
- IR 310
- ...

Cariflex™ IR
(Unique anionic polymerized isoprene rubber)

- G1701
- G1702
- G1730
- ...

SEPS

IR0401 Latex (IR401)
Enhanced Rubber Segment ERS and Applications
Kraton™ ERS grade - Enhanced Rubber Segment

Key Benefits:

- FDA and USP VI approved for food / medical applications;
- Add materials at the machine, no need to pre-compound;
- High stiffness and impact allows for reduced wall thickness;
- Use in injection molding, sheet extrusion and blow molding.

   PVC alternative for e.g. medical bags & tubing

Transparent PP impact modifications for packaging

Clarity and flexibility for films and food wrap
ERS for Transparent PP Modification

Features/Benefits
- Kraton™ G polymers show good weather and aging performance;
- ERS grades show better compatibility with PP than conventional SEBS grades;
- Clear blends with clarified PP;
- G1643 shows lowest viscosity for easy dispersion: Injection molding;
- G1645 is the softest SEBS grade available, higher viscosity: Injection molding possible, but more suited for film extrusion (Cast/Blown);
- G1643 and G1645 pass ISO 10993 testing (USP Class VI);
- G1643 and G1645 are available in dense pellets for easy extruder handling and blending with PP pellets: no need for separate compounding step;
- Articles of PP and G1643 (or G1645) can be steam, EO, EB, or gamma sterilized.

Typical Properties

<table>
<thead>
<tr>
<th></th>
<th>G1643</th>
<th>G1645</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>SEBS</td>
<td>SEBS</td>
</tr>
<tr>
<td>Rel. MW</td>
<td>1.1</td>
<td>1.4</td>
</tr>
<tr>
<td>PSC %</td>
<td>20</td>
<td>13</td>
</tr>
<tr>
<td>Shore A</td>
<td>52</td>
<td>34</td>
</tr>
<tr>
<td>Rubber Tg, °C</td>
<td>-35</td>
<td>-35</td>
</tr>
<tr>
<td>MFR (200°C, 5kg)</td>
<td>18</td>
<td>3.5</td>
</tr>
<tr>
<td>MFR (230/5kg)</td>
<td>&gt;70</td>
<td>7</td>
</tr>
<tr>
<td>Physical Form</td>
<td>Pellet</td>
<td>Pellet</td>
</tr>
</tbody>
</table>

Enhanced Rubber Segment
ERS: Finer Dispersion in PP Matrix

Transmission Electron Microscopy Pictures

Standard SEBS: Coarse network

ERS → Improved compatibility → Finer network
In PP homopolymer the haze reduces and the impact properties improve with increasing amount of G1643;

Note! Increasing amount of G1643 reduces the flexural modulus and heat deflection temperature.
Improved clarity of PP/G1643 Blends

Haze = 69%  
(100% PP)  

(20% G1643)  

Haze = 8.0%  
(60% G1643)  

(40% G1643)
### Kraton™ ERS modified PP vs. PVC

<table>
<thead>
<tr>
<th></th>
<th>ERS modified PP</th>
<th>Soft PVC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Gravity</td>
<td>~0.9</td>
<td>&gt;1.2</td>
</tr>
<tr>
<td>Low MW Plasticizer</td>
<td>Not Necessary</td>
<td>&gt;30%</td>
</tr>
<tr>
<td>Plasticizer Migration</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>Service Temp. Range</td>
<td>-20–70°C, less hardness change in work temperature range</td>
<td>Hardness highly affected by temperature</td>
</tr>
<tr>
<td>Thermal Stability</td>
<td>Minimal degradation below 250°C</td>
<td>Start degrading at 130°C</td>
</tr>
<tr>
<td>Durability</td>
<td>Excellent UV, Ozone &amp; chemical resistance</td>
<td>Poor heat &amp; UV resistance</td>
</tr>
<tr>
<td>Environmental Impact</td>
<td>Minimal hazardous chemicals generated during thermo processing or combustion</td>
<td>Hazardous chemicals e.g. HCL, Dioxins etc. generated at high temperature</td>
</tr>
<tr>
<td>Recyclability</td>
<td>Easy recyclable due to excellent compatibility with polyolefin</td>
<td>Hard to recycle when blend with other polymers</td>
</tr>
</tbody>
</table>

Kraton ERS polymers are the best modifiers of polyolefins as an alternative for PVC in various applications

- Wide formulating latitude;
- Wide working temp. range;
- Non-hazardous;
- Clear.
- Recyclable;
- Safe;
- Overmolding to PO;
- Adhesion to PO layer.
Kraton™ ERS modified PP in Medical - IV Bag

- **Technology**
  - **Multi-layered co-extrusion film, cast & blown**

Example of IV bag made through co-extrusion film

**Outer layer (printing layer)**
- **Main material**: PP (+ ERS)
- **Requirements**: heat stability, scratch resistance, printability

**Mid-layer**
- **Main material**: PP (+ ERS)
- **Requirements**: flexibility, clarity

**Inner layer (sealing layer)**
- **Main material**: PP (+ ERS)
- **Requirements**: low seal initiation temp, high seal strength
Kraton™ ERS modified PP in Medical - IV Bag

- **Market Trend**
  - Switching from glass bottle to plastic bottle and from PVC to polyolefin based.

- **Requirements**
  - Transparency;
  - Resistance to sterilization (Steam: 121°C 20～30min);
  - Flexibility and low temp impact;
  - Resistance to different fluids;
  - Heat sealability (150°C～170°C 1～2 sec)

- **Technology**
  - Multi-layered co-extrusion film, cast & blown.

- **Opportunity**
  - PP/ERS blends;
  - Starting point
    Blend with G1645 or G1643.
• Kraton G1645 polymer successfully passes all ISO 10993 biological toxicity testing for use in medical applications and is USP VI approved;

• Plasticizer-free G1645-RCPP combinations provide a wide operating window for flexible medical tubes and are potentially able to replace soft PVC when considering:
  - Extrusion technology (mono- versus multi-layer);
  - Type of PP;
  - G1645-PP ratio.

• Depending on the type of PP the same sterilization techniques are applicable to G1645 based blends as to PVC;

• Surface tackiness can be resolved with the addition of slip agent;

• Laser welding recommended for medical device assembly with PP-based parts. Kraton-based formulations are not recommended for joining to plasticized PVC.
Kraton™ ERS Modified PP in Medical - More Examples

Features

- Clean
- Clear
- Impact resistance at room & low temperature
- Mechanical strength
- Low extractable
- Sterilizable

Opportunities

- Syringe devices
- IV Bottles
- Drug bottle/containers
- Medical device containers

(Kraton SBC polymer based elastomeric compounds also applicable for flexible medical parts, e.g. syringe gasket)
Kraton™ ERS modified PP in Transparent Consumer Goods Applications

PP modification with innovative ERS Kraton polymers result in a good balance of transparency, stiffness, and impact strength.

**Features**
- Transparency
- Impact resistance
- Mechanical Strength
- Wide service temperature range
- Processability
- Compatibility with other polymers
- Low relative gravity

**Opportunities**
- Food container
- Baby bottle
- Water bottle
- Containers
- Ice-trays
- Home appliance parts
Due to health concerns regarding BPA based PC Kraton investigated alternatives.

**Kraton Polymers’ approach:**
- Replace BPA containing PC with Random Copolymer PP (RCPP). Nucleated RC PP is widely accepted in food industry, is quite transparent, rigid and resistant to sterilization temperatures. Transparent RC PP however lacks impact resistance at room temperature and fridge temperatures.

**Kraton Polymers’ solution:**
- Use 7-10% of Kraton™ G1643 in nucleated transparent RCPP. Most advanced nucleated RCPP are required to get maximum transparency.

**Kraton G offers:**
- Easy to inject, BPA-free solution;
- Improved PP impact at room and fridge T;
- Effectiveness not impacted by sterilization;
- Cost reduction versus PC.
Impact Modification for Transparent PP Containers

Problem:
- Totes and bins made of transparent PP tend to crack during shipment to retailers and during early customer use.

Approach:
- Many customers assume that metallocene modifiers would be the cheapest solution. But metallocene level tends to be 20% while Kraton™ G at 3%-10% loading levels is OK.

Solution:
- Use of Kraton G as a modifier in PP storage bins resulted in cost reduction and performance gains for customers.

Kraton G offers:
- Improved impact;
- Improved transparency;
- Cost reduction via lower concentration levels.
Features

Kraton polymers can help polyolefins to meet higher performance in films:

- Maintain clarity, low haze;
- Increase toughness;
- Help to achieve Low modulus /flexibility;
- Boost impact and puncture resistance;
- Increase MD tear strength;
- Tough tie layer in co-ex films;
- Lower initial seal temperature.

Opportunity

- PP/ERS blends;
- Starting point:
  - PE films: G1657, G1645, G1643
  - PP films: G1645, G1643, G1657
Enhanced Rubber Segment ERS and Applications - Summary

- Enhanced Rubber segment Grades have a better compatibility with PP than the conventional SEBS grades;
- FDA and USP VI approved for food / medical applications;
- High stiffness and impact allows for reduced wall thickness;
- Can be added at the machine, no need to pre-compound;
- Can be used in injection molding, sheet extrusion and blow molding.
Kraton™ Adhesive Compounds for Protective Film Applications
Kraton™ Polymers in Protective Film Applications

Kraton melt extrudable products allow one step co-extrusion to save cost and provide superior performance for metal and plastic surfaces.

Example Applications
- LCD panel;
- Prism film;
- White goods;
- Window/mirror;
- New auto protection.

Key features and benefits
- Lower system costs;
- Superior Protection;
- High Flexibility and Customizable Peel Strength;
- Haze and residue-free;
- VOC-free.
Lower system costs

- One-step co-extrusion process using pelletized compounds;
- Eliminates multi-step coating and drying steps required of conventional, solvent cast films;
- Purchase/production of backing film (as used in the coating process) is not required;
- Does not require expensive ovens.

Features and benefits

- Sustains tack on curved and textured surfaces;
- Tailored peel strength (~ 0.9-6.5 N/25mm);
- Adheres to a wide variety of substrates chemistries and topographies.
### Protective Films: Film Structure Recommendation

<table>
<thead>
<tr>
<th>Kraton™ Adhesive Compounds (5-15 µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE/PP Backing (40-50 µm)</td>
</tr>
<tr>
<td>PE/PP + Antiblock (5-10 µm)</td>
</tr>
</tbody>
</table>

- A typical PF film is 3 layers (A+B+C) 50 - 70µm thick;
- A - adhesive layer usually 5 - 10 µm thick;
- B - core layer (LDPE/PP) 40 - 50 µm thick;
- C - outside layer (PP, HDPE or LDPE/HDPE blend 5 - 10 µm thick; This layer can also contain anti-block. The use of HDPE and anti-block in this layer will aid in the unwinding of the finished roll.

Rheology match is needed for each individual layer of the film!!
## Kraton™ Protective Film Compounds: Overview

<table>
<thead>
<tr>
<th>Property</th>
<th>MD6741</th>
<th>MD6718</th>
<th>MD6649</th>
<th>MD6729</th>
<th>MD6666</th>
<th>MD6748</th>
<th>MD6700</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFR - @ 190°C/2.16 kg</td>
<td>4.5</td>
<td>16.0</td>
<td>17.0</td>
<td>17.0</td>
<td>21.0</td>
<td>4.8</td>
<td>6.5</td>
</tr>
<tr>
<td>MFR - @230°C/2.16/ kg</td>
<td>20.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>0.91</td>
<td>0.90</td>
<td>0.92</td>
<td>0.92</td>
<td>0.94</td>
<td>0.94</td>
<td>0.94</td>
</tr>
<tr>
<td>Hardness, Shore A</td>
<td>49</td>
<td>36</td>
<td>37</td>
<td>37</td>
<td>37</td>
<td>31</td>
<td>30</td>
</tr>
<tr>
<td>G’ @ 23°C, Pa</td>
<td>10.4x10^5</td>
<td>5.4x10^5</td>
<td>8.3x10^5</td>
<td>8.5x10^5</td>
<td>9.9x10^5</td>
<td>11.8x10^5</td>
<td>10.0x10^5</td>
</tr>
<tr>
<td>DMA Tg, °C</td>
<td>-30</td>
<td>-27</td>
<td>-9</td>
<td>-7</td>
<td>11</td>
<td>15</td>
<td>21</td>
</tr>
</tbody>
</table>

**LDPE/Kraton Film**<sup>1</sup> 180° Peel, N/25mm

<table>
<thead>
<tr>
<th>Material</th>
<th>after 20 min. @ 25°C</th>
<th>after 7 days @ 25°C</th>
<th>after 20 min. @ 75°C</th>
<th>after 7 days @ 75°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless Steel</td>
<td>2.2</td>
<td>1.8</td>
<td>3.2</td>
<td>5.0</td>
</tr>
<tr>
<td>PMMA</td>
<td>2.7</td>
<td>2.6</td>
<td>4.3</td>
<td>5.5</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>1.7</td>
<td>2.7</td>
<td>3.8</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>4.1</td>
<td>5.2</td>
<td>5.1</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>4.4</td>
<td>4.9</td>
<td>5.9</td>
<td>6.2</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>2.2</td>
<td>2.5</td>
<td>3.8</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>4.8</td>
<td>6.5</td>
<td>6.7</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>6.5</td>
<td>7.2</td>
<td>7.5</td>
<td>7.3</td>
</tr>
</tbody>
</table>

(1) Thickness: 51 micron LDPE / 25 micron adhesive

(2) Arkema Plexiglas™ V052-100 (Plexiglas is a trademark of Arkema France Corp.)

(3) Sabic Lexan™ LS2-111 (Lexan is a trademark of Sabic Innovative Plastics)
Kraton™ Adhesive Compounds for Protective Film Applications - Summary

- Kraton adhesive compounds for co-extrusion consist of rubbery, free-flowing pellets;

- Adhesives can be made having a broad range of tack and adhesion, adhesion to both polar & non-polar surfaces;

- One-step co-extrusion process, lowers overall system costs;

- Compatible on polyolefin backings (PE or PP) to make removable protective films;

- Kraton adhesive compounds for co-extrusion provide the following, as a finished protective film:
  - Superior Protection
  - High Flexibility and Customizable Peel Strength
  - Clean Film
Cariflex™ Polyisoprene Rubber and Applications
What is Cariflex™ Polyisoprene (IR)?

Polyisoprene elastomers are:
- Synthetic;
- Predominantly stereoregular;
- Resembling natural rubber in molecular structure and properties.

There are two major synthetic polyisoprene types with high cis-1,4 content:
- Ziegler-Natta (high cis) IR, polymerized in the presence of a titanium/aluminum catalyst;
- Anionic IR, polymerized with an alkyl-lithium initiator.

Different polyisoprene production processes give different products:

<table>
<thead>
<tr>
<th>Natural Rubber</th>
<th>Ziegler-Natta IR</th>
<th>Cariflex IR</th>
</tr>
</thead>
<tbody>
<tr>
<td>No catalyst</td>
<td>Titanium/Aluminum catalyst</td>
<td>Alkyl-lithium catalyst</td>
</tr>
<tr>
<td>Branched product</td>
<td>Branched product</td>
<td>Linear product</td>
</tr>
<tr>
<td>Wide Molecular Weight Distribution</td>
<td>Wide Molecular Weight Distribution</td>
<td>Narrow Molecular Weight Distribution</td>
</tr>
<tr>
<td>98+ % cis content</td>
<td>96+ % cis content</td>
<td>90+ % cis content</td>
</tr>
<tr>
<td>High gel content</td>
<td>High gel content</td>
<td>Intrinsically NO gel</td>
</tr>
<tr>
<td>Contains natural impurities</td>
<td>Catalyst residuals</td>
<td>Low impurity level</td>
</tr>
</tbody>
</table>
Cariflex™ IR & IR Latex Applications

- Electronic coatings;
- Printing inks;
- Glues;
- Medical stoppers and other medical rubber pieces;
- Stoppers for IV bags;
- Dental dams;
- Needle shields;
- Catheters (heart, urinary);
- Condoms;
- Surgical gloves;
- Physiotherapy bands;
- Medical bandages;
- Cold seal adhesives for food & medical packaging;
- Marine coatings;
- IR solid material:
  - Pure
  - Transparent
  - Elastic
  - Soft
  - Strong

- Transparent shoe soles
- Cariflex IR
Potential Applications for Transparent Vulcanized Compounds by Cariflex™ IR

- Baby nipple
- KICT TR series
- Formulating technology
- Cariflex IR
- Transparent shoe soles
- Transparent rubber seal for Y-injection site
- Transparent keyboard cover
- Rubber tubing for medical pump
- Compression-molded tube

Cariflex™ Polyisoprene Products
Summary

- Kraton™ polymers offer a wide range of flexibility in polymer design and formulations that are suitable to diverse applications;

- Kraton ERS grades have a better compatibility with PP than the conventional SEBS grades, offering a wide range of applications including PVC replacement:
  - FDA and USP VI approved for food / medical applications;
  - High stiffness and impact allows for reduced wall thickness;
  - Can be added at the machine, no need to pre-compound;
  - Can be used in injection molding, sheet extrusion and blow molding.

- Kraton adhesive compounds for protective film applications allow one step co-extrusion to save cost and provide superior performance for metal and plastic surfaces;

- Cariflex™ IR is an unique polyisoprene rubber giving many advantageous performance over the conventional rubber systems in PURE - SOFT- STRONG applications.
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