Cariflex®
Polyisoprene Products

Transparent Rubber Compound for Footwear Applications

December 2015
Cariflex® Polyisoprene (IR) – Pure – Strong - Soft

Cariflex IR

Ziegler-Natta IR (ZN-IR)

NR

Polyisoprene microstructure models.

- Cis 1,4-Bonds
- Trans 1,4-Bonds
- 3,4-Bonds
- Phospholipid / Fatty acid
- Proteins

Natural Rubber

Competitive IR

Cariflex® IR

Cariflex Isoprene Rubber features

- Anionic polymerization
- No protein
- Low residual metals
- Low gel content (~0 %)
- No odour
- Excellent transparency due to high purity
Kraton customers have used Cariflex® IR and IRL in the following applications:

- **Electronic coatings**
- **Printing inks**
- **Glues**
- **Marine coatings**
- **Medical stoppers and other medical rubber pieces**
- **Catheters (heart, urinary)**
- **Dental Dams**
- **Condoms**
- **Transparent shoe soles**
- **Stoppers for IV bags**
- **Needle shields**
- **Cold seal adhesives for food & medical packaging**
- **IR Latex material**
  - Pure
  - Transparent
  - Elastic
  - Soft
  - Strong

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**Cariflex® Transparent Rubber Compounds**

Kraton Polymers has developed Cariflex® Transparent Rubber Compounds, using Cariflex® IR307 as an ingredient.

**Cariflex® TRC**
- can provide “crystal-clear” transparency over a wide range of hardness with good purity and mechanical strength, including abrasion resistance and soft touch. To our knowledge, no other rubber can provide the same balance of properties.
- can offer excellent clarity and sharp coloring
- can be processed with most conventional rubber compounding technology.
- can be sterilized with most sterilization methods without, or with limited performance deterioration.

We have identified potential applications for Cariflex® TRC in Footwear, both for the outer sole and the inner sole.

Key features for this material are:
- Fits the fashion trend of transparent shoes
- Excellent clarity and sharp coloring possible
- Better abrasion resistance than TPE soles
- Good UV stability

Optimization of the technology is still ongoing.

Please note, that Kraton has filed patent applications on the Cariflex® TRC technology and related applications described in this presentation.
### Cariflex® TRC - Comparison with other materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cariflex® TRC</td>
<td>- Cariflex® TRC has excellent transparency and mechanical performance compared with other types of rubber</td>
</tr>
<tr>
<td>ZN-IR</td>
<td>- Competitive ZN-IR is hazy</td>
</tr>
<tr>
<td>Urethane</td>
<td>- Urethane has good transparency, but suffers from poor heat, hydrolytic and UV stability (discoloration)</td>
</tr>
<tr>
<td>Silicone</td>
<td>- Silicone can come close in transparency, but is costly (LSR), or weak in tear strength and adherence issues in laminate structures</td>
</tr>
<tr>
<td>EPDM</td>
<td>- EPDM is somewhat hazy, and much less elastic</td>
</tr>
</tbody>
</table>
Transparent Rubber Compounds – The Landscape

- **Water clear**
  - TPE’s
  - Cariflex® TRC Conventional
  - Liquid Silicone Rubber
  - EPDM Clear Grade

- **Transparency**
  - Poor abrasion & permanent set
  - Conventional
  - Low tear & abrasion
  - Low tear, adhesion
  - Low stability, yellowing

- **Hazy**
  - Urethane Rubber
  - Solid Silicone Rubber
  - Cariflex® TRC Footwear / abrasion (IR/RB blend)
  - Cariflex® TRC High Strength (IR/MD blend)

- **Mechanical Strength**
  - Low
  - Tear strength
  - Tensile strength
  - Conventional
  - ZN-IR
  - NR
  - ZN-IR
  - NR

- **High**
  - Footwear / abrasion (IR/RB blend)
  - Low tear & abrasion
  - Urethane Rubber
  - Solid Silicone Rubber
  - Cariflex® TRC High Strength (IR/MD blend)

- **Cariflex® TRC Silicone**

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Generic formulation for a Carilfex® Transparent Rubber Compound

<table>
<thead>
<tr>
<th>Ingredients</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polymers</strong></td>
<td></td>
</tr>
<tr>
<td>Polyisoprene - Carilfex® IR307</td>
<td></td>
</tr>
<tr>
<td>Syndiotactic-1,2-polybutadiene, JSR RB820</td>
<td></td>
</tr>
<tr>
<td><strong>Curing agent</strong></td>
<td>Peroxide (2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane) (like: Trigonox® 101, Luperox® 101, Perhexa® 25B)</td>
</tr>
<tr>
<td><strong>Curing co-agent</strong></td>
<td>Ethylene glycol dimethacrylate (EGDMA)</td>
</tr>
<tr>
<td><strong>Anti-oxidant</strong></td>
<td>Irganox® 1726 (4,6-bis(dodecylthiomethyl)-o-cresol)</td>
</tr>
</tbody>
</table>

The amount of each ingredient can be tailored to suit the mechanical properties and transparency requirements of the application.
For footwear we typically recommend 50 phr of polyisoprene and 50 phr of JSR RB820 to achieve an abrasion resistance of < 100 mm³
## Cariflex® TRC processing

<table>
<thead>
<tr>
<th>Process</th>
<th>Steps</th>
<th>Details</th>
<th>Processing Parameters</th>
<th>Storage Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compounding</strong> (in 2-Roll Mill OR Internal Mixer)</td>
<td>Step 1</td>
<td>Mix masterbatch using Cariflex® IR307, JSR RB820 and Anti-oxidant (AO)</td>
<td>Temperature: Blend RB820 and AO into IR at 120°C (max 130°C)</td>
<td>• Limit exposure to oxygen and UV light</td>
</tr>
<tr>
<td></td>
<td>Step 2</td>
<td>Mix green compound using masterbatch of Step 1, peroxide and co-agent</td>
<td>Temperature: about 75°C</td>
<td>• Shelf-life = 3 weeks at max. T of 60°C</td>
</tr>
<tr>
<td><strong>Molding</strong></td>
<td></td>
<td>Compression Molding</td>
<td>Temperature: 160°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Injection molding also possible</td>
<td>Time: 6 – 7 minutes</td>
<td></td>
</tr>
</tbody>
</table>

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# Cariflex® TRC FW properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>CF - TRC</th>
<th>CF - TRC – aged *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abrasion (mm³) – 6mm</td>
<td>51 - 100</td>
<td>90 - 110</td>
</tr>
<tr>
<td>Transparency (%) – 6mm</td>
<td>87</td>
<td>87 - 89</td>
</tr>
<tr>
<td>Haze (%) – 6 mm</td>
<td>9.4 – 14.5</td>
<td>~ 15</td>
</tr>
<tr>
<td>Yellowness Index – 6 mm</td>
<td>&lt; 5</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Tensile (MPa)</td>
<td>10.7 – 11.6</td>
<td>TBD</td>
</tr>
<tr>
<td>Modulus 100% (MPa)</td>
<td>3.8 – 5.8</td>
<td>TBD</td>
</tr>
<tr>
<td>Elongation@Break (%)</td>
<td>147 - 201</td>
<td>TBD</td>
</tr>
<tr>
<td>Tear (kN/m)</td>
<td>24 - 27</td>
<td>TBD</td>
</tr>
<tr>
<td>Shore A 0 sec</td>
<td>71 - 72</td>
<td>69</td>
</tr>
<tr>
<td>Shore A 30 sec</td>
<td>67 - 68</td>
<td>66</td>
</tr>
<tr>
<td>Stickiness</td>
<td>None</td>
<td>None</td>
</tr>
</tbody>
</table>

* Properties of cured sheets that had been aged for 1 month at 40 °C

No yellowing of cured sheets is observed after 1.5 hr at 120 °C
Further aging tests still underway
Cariflex® TRC – Further Developments Ongoing

High-Abrasion Resistant Transparent Rubber Compounds

• Recently adapted a Cariflex® TRC formulation targeting even lower abrasion resistance
• Achieved by addition of 1-4 phr of a trans-polyoctenamer - Vestenamer® 8012
• As amount of Vestenamer increases, the abrasion resistance improves (to below 50 mm³), but slightly at the expense of transparency

High-Strength Transparent Rubber Compounds

• By blending Cariflex® IR307 with a unique Kraton developmental polymer grade, we can tailor the formulations to have improved mechanical properties, specifically tensile and tear strength. This goes at the expense of abrasion resistance
• This technology will be valuable for softer Transparent Rubber Compounds with requirements of improved strength for which abrasion resistance is not critical

Vestenamer® is a trademark of Evonik Degussa GmbH
Cariflex® TRC - Summary

- Cariflex® IR is a unique polyisoprene rubber with proven track record in applications requiring PURE - STRONG – SOFT properties.

- Cariflex® TRC, using Cariflex® IR as ingredient,
  - can provide “crystal-clear” transparency over a wide range of hardness with good purity and mechanical strength, incl. abrasion and soft touch. No other rubber can provide the same balance of properties.
  - can be processed with most conventional rubber compounding technology.
  - can be sterilized with most sterilization methods without, or with limited performance deterioration.
  - can meet requirements of medical and food applications requiring high level of purity (subject to adequate regulatory assessment, compound recipe, and processing conditions).

- JP provisional patent was published on Aug 28, 2014

- Potential applications are footwear/shoe soles, baby nipples, stoppers for transfusion bottles, vial stoppers, medical tubes such as joint drain tubes, high voltage insulation material incl. silicone rubber replacement, photo-curable rubbers, nice looking consumer goods.
Other potential developments

Kraton Polymers has unique Polymer Development Capabilities. Anionic polymerization allows for precise control over polymer molecular structure. For Cariflex® Polymers we could envision developing alternative rubber structures with specific property attributes.

<table>
<thead>
<tr>
<th>Design Tools</th>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>Melt viscosity</td>
<td>Adhesion</td>
</tr>
<tr>
<td>PS/BD/Isoprene Ratio</td>
<td>Solution parameters</td>
<td>Compatibility</td>
</tr>
<tr>
<td>Block structure Types</td>
<td>Hysteresis</td>
<td>Clarity</td>
</tr>
<tr>
<td>Block structure Length</td>
<td>Modulus</td>
<td>Strength</td>
</tr>
<tr>
<td>Vinyl Content</td>
<td>Strength</td>
<td>Softness/Hardness</td>
</tr>
<tr>
<td>Monomers</td>
<td>Glass Transition $T_g$</td>
<td>Processability</td>
</tr>
<tr>
<td>Phase Matrix</td>
<td>Temperature Resistance</td>
<td>Post reactivity (curing)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Viscosity enhancement</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Compression Set</td>
</tr>
</tbody>
</table>
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