Thermoplastic Styrene/Butadiene Elastomers: from Product Innovation to new Applications

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Thermoplastic styrene/butadiene elastomers: from product innovation to new applications

1. Introduction: Styroflex® – a unique S-TPE Elastomer based on innovative chemistry
2. Structure/property relationship of S-TPE
3. Blends of Styroflex® with thermoplastic polymers: compatibility and impact modification
4. Innovative applications driving customer value
5. Outlook
1. Styroflex® – a unique S-TPE Elastomer based on innovative chemistry

Styrene-based thermoplastic elastomers (TPE-S) as part of the TPE family
1. **Styroflex®** – a unique S-TPE Elastomer based on innovative chemistry

**Control of morphology**

source: B. Schmitt; Angew. Chem. 91, 286 (1979)

Phase volume ratio of S/B block copolymers determines character

- **Styroflex®** – a unique S-TPE Elastomer based on innovative chemistry

**Control of morphology**

Phase volume ratio of S/B block copolymers determines character

Styroflex® – a unique S-TPE Elastomer based on innovative chemistry
1. Styroflex® – a unique S-TPE Elastomer based on innovative chemistry
S-TPE are manufactured by anionic polymerization

Production of SBC by living anionic polymerization of the monomers styrene and butadiene in cyclohexane (solvent)

![Chemical structure and reaction scheme]

I = Initiator sec Butyl-Li

= styrene monomer

= butadiene monomer

Polybutadiene-block
Polystyrene-block
1. Styroflex® – a unique S-TPE Elastomer based on innovative chemistry
Anionic „living“ polymerization allows control of molecular architecture in a broad range

**Architecture**

**molecular weight distribution**
- narrow to multimodal

**block sequence**
- diblock to multiblock

**block transition**
- sharp to tapered to random

**molecular shape**
- linear, branched, star, comb

**Copolymerization and Microstructure**

- **cyclohexane / BuLi**  styrene/butadiene mixture
  - B-S block; 9% 1,2-vinyl

- **cyclohexane / THF / BuLi** (>0.25 vol% THF)
  - S/B random; 30% 1,2-vinyl

- **cyclohexane / BuLi / KOR**
  - S/B random; 12% 1,2-vinyl
1. Styroflex® – a unique S-TPE Elastomer based on innovative chemistry

Styroflex® structure determines unique properties

Special Soft Phase:
- Medium polarity
- $T_g - 40^\circ C$
  - Printability
  - Adhesion to styrenics, polyolefins and to a range of other thermoplastics
- Comparably high thermal stability due to low 1,2-vinyl content
1. Styroflex® – a unique S-TPE Elastomer based on innovative chemistry

ODT of 150 °C ensures flow and good processability at common melt processing temperatures

![Graph showing reduced storage modulus G' and temperature relationship]

- ODT: 145 °C
- Reference temperature: $T_0 = 190$ °C
- Reduced frequency: $\omega_r = 3 \text{s}^{-1}$
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2. Structure/property relationship of S-TPE

Styroflex®: high elasticity and thermal stability

Stress-strain diagram

- Rubber-like behavior
- High elongation
- Low stiffness
- No yield point

Thermal stability

- High thermal stability
- Low gel formation
- Good processability

Measurement: increase in pressure needed to extrude a strand at a constant rate
In contrast to other elastic materials, Styroflex® recovers almost back to the initial length, even when stretched repeatedly.
2. Structure/property relationship of S-TPE

Styroflex® has medium polarity, allowing high compatibility with many other thermoplastics.
2. Structure/property relationship of S-TPE

High free soft phase volume plus easy processing => Styroflex® features high O₂ and H₂O permeability
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Styroflex® can be used in combination with polystyrene and can help to optimize characteristics or finished parts according to the requirements of applications. Important: control of morphology via control of process conditions necessary!

- Styroflex® increases toughness (elongation at break, impact strength)
- Styroflex® improves environmental stress cracking resistance (ESCR)
- While punching or cutting, fewer micro notches occur
- Easy mixing directly at the extruder is possible
- Styroflex® is easily processable thanks to its high thermostability
3. Blends of Styroflex with thermoplastic polymers

Styroflex® / Styrolux® / Polystyrene: the versatile blend system
3. Blends of Styroflex with thermoplastic polymers

**Styroflex® / Styrolux® / Polystyrene: mechanical and optical properties**

![Graph showing the relationship between Modulus, Transparency, and Elongation at break versus % Styroflex®.](image)
3. Blends of Styroflex with thermoplastic polymers

Styroflex® in ABS – electron micrograph of morphology

Terluran HH 106

Terluran HH 106 + 4% Styroflex

Higher elongation @ break through “bridging effect”
### Applications Advantages

| PE and PP modification | • Thickness reduction through increased toughness (puncture and tear propagation resistance)  
| | • Compatibility optimization between different PE types  
| | • Compatibilization to styrenic polymers  

| HIPS modification | • Increase of toughness, also for low temperatures  
| | • Improvement of environmental stress cracking resistance (ESCR)  
| | • Enhanced tear strength  
| | • Good printability  
| | • Easy processing (extrusion, thermoforming)  

| Blend Styroflex® / HIPS / GPPS | • Increase of stiffness / toughness ratio  
| | • Easy processing  
| | • Enhanced tear strength  
| | • Good printability  

3. Blends of Styroflex with thermoplastic polymers

Styroflex® Blends: multiple options to create customized properties
3. Blends of Styroflex with thermoplastic polymers

**Styroflex® Blends: multiple options to create customized properties**

<table>
<thead>
<tr>
<th>Applications</th>
<th>Advantages</th>
</tr>
</thead>
</table>
| XPS modification      | • XPS with increased toughness  
                        |   • Foldable XPS  
                        |   • Carton board-like properties, but resistant to moisture  
                        |   • Easy processing  
                        |   • Cheaper and lighter than carton board |
| ABS modification      | • Highly effective impact modification  
                        |   • Improvement of flow properties  
                        |   • Improvement of stress crack resistance |
| Compatibilization     | • Compatibilizer between PS + PE  
                        |   • Compatibilizer between PS + ABS  
                        |   • Compatibilizer between PS, ABS, PE + PP  
                        |   • Useful for waste recycling |
3. Blends of Styroflex with thermoplastic polymers

**Styroflex® Blends: multiple options to create customized properties**

<table>
<thead>
<tr>
<th>Property</th>
<th>HIPS</th>
<th>ABS</th>
<th>SBC</th>
<th>PET</th>
<th>PPE</th>
<th>PMMA</th>
<th>XPS/PSP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impact resistance &amp; elongation</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Impact resistance at cold temp.</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>ESCR &amp; chemical resistance</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
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<td>↑</td>
<td>↑</td>
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<td>Flow</td>
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<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
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<tr>
<td>Stiffness</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>Recycling/Compounding</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
</tbody>
</table>

**Other benefits**
- e.g. compatibilization, tear initiation
- e.g. gloss retention after recycling
- e.g. tri-blend with GPPS
- e.g. compatibilization
- e.g. cost down
- e.g. improvement of cutting behavior
- e.g. formability, less gel formation

<table>
<thead>
<tr>
<th>Variation</th>
<th>&gt;+10%</th>
<th>Up to +10%</th>
<th>No change</th>
<th>Up to -10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impact resistance &amp; elongation</td>
<td>↑</td>
<td>↑</td>
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<td>Stiffness</td>
<td>↓</td>
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*Examples of benefits: compatibilization, gloss retention, improved tear initiation, etc.*
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4. Innovative applications driving customer value

Modification of high impact polystyrene (HIPS) with Styroflex® for example in packaging applications

→ Significant increase of environmental stress cracking resistance of HIPS through Styroflex® 2G66

170 mm radius, 24 h
Medium: air
Medium: olive oil/oleic acid

Increase of ESCR
4. Innovative applications driving customer value

Modification of high impact polystyrene (HIPS) with Styroflex® for example in extruded film

- Increased tear strength
- Improved impact resistance, also for low temperatures
- Increased environmental stress cracking resistance
- Good printability
- Easy to process (extrusion, thermoforming)

Important: control of Styroflex/HIPS morphology crucial; properties dependent on morphology!
4. Innovative applications driving customer value

Modification of plastics with Styroflex® allows a huge variety of applications

<table>
<thead>
<tr>
<th>Additive for improved mechanics</th>
<th>Plastic Pallet</th>
<th>Toughness modifier for: HIPS, ABS, PE</th>
<th>Compatible with: PET, PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexible Film</td>
<td>Stretch Hood</td>
<td>Toughness Processability Transparency Polarity Compatibility Elasticity</td>
<td></td>
</tr>
<tr>
<td>Compounds</td>
<td>Soft Touch</td>
<td>Softness Polarity Toughness Elasticity Surface properties</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Recycling</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
KEY benefits of Styroflex:

- Low content of additives
- Excellent bonding
- Density advantage (20-30%) vs PVC
- Good kink resistance
- Process ability
- Clarity/color

Application:

- Multi-layer tubing
- IV tubing
- Multi-lumen tubing
- Corrugated tubing
Due to its high styrene content and its low-med polar soft phase, Styroflex® adheres to different polymers:

- Styrenic polymers: HIPS, GPPS, SBS, ABS, MABS
- Engineering polymers: PET, PET-G, PC, PMMA
- Polyolefins: PE, PP
### 4. Innovative applications driving customer value

**Styroflex® in soft-hard 2-component injection molding applications**

<table>
<thead>
<tr>
<th>Hard component</th>
<th>Soft component</th>
<th>Peel strength [N/mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS 156 F (GPPS)</td>
<td>Styroflex® 2G66</td>
<td>No break</td>
</tr>
<tr>
<td>Styrolux® (SBS)</td>
<td>Styroflex® 2G66</td>
<td>No break</td>
</tr>
<tr>
<td>Terlux® (MABS)</td>
<td>Styroflex® 2G66</td>
<td>17.7</td>
</tr>
<tr>
<td>PC</td>
<td>Styroflex® 2G66</td>
<td>17.4</td>
</tr>
<tr>
<td>PMMA</td>
<td>Styroflex® 2G66</td>
<td>16.4</td>
</tr>
<tr>
<td>Luran® KR 2636 (SAN)</td>
<td>Styroflex® 2G66</td>
<td>10.8</td>
</tr>
<tr>
<td>PETG</td>
<td>Styroflex® 2G66</td>
<td>10.5</td>
</tr>
<tr>
<td>PET</td>
<td>Styroflex® 2G66</td>
<td>9.1</td>
</tr>
<tr>
<td>PS 156 F (GPPS)</td>
<td>Styroflex® 2G66 (Shore A 30)</td>
<td>No break</td>
</tr>
<tr>
<td>Styrolux® (SBS)</td>
<td>Styroflex® 2G66 (Shore A 30)</td>
<td>No break</td>
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Styroflex® future projects

- Even stronger focus on investigating options in the medical market for Styroflex
- Making use of specific, unique property combinations like: permeability, elasticity/recovery and transparency
- Styroflex as sustainable solution (thinner film, more impact efficiency in blends with plastics, recycling)
- Styroflex as modifier for thermoplastics
THANK YOU!

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