Selecting medical materials for enteral pump applications

Developments in SEBS for medical and other valuable applications

Simulated service testing of liquid silicone rubber based thermal insulation coatings

When a butterfly holds a smartphone: Innovative design and production concept
Developments in SEBS for medical and other valuable applications

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Thermoplastic elastomers (TPE) show optimal characteristics for the plastic and elastomers industries, as they exhibit similar behavior to crosslinked polymers at room temperature; but at higher temperatures commonly used in industrial processes, they are able to flow as thermoplastic polymers.

Styrene ethylene butylene styrene (SEBS) TPE block copolymers achieve market demands, mostly due to their better compatibility with polyolefins (polypropylene, polyethylene), their excellent weathering resistance and thermal stability, and the possibility for chain modification to be adapted to obtain materials with low hardness, high elasticity, softness and high optical properties.

New SEBS grades have been launched into the market to cover many of the requirements customers in the medical field need to fulfill with their materials in order to introduce their products in these markets. One objective could be the substitution of other polymers (such as PVC, olefin elastomers, silicones, etc.). Another objective could be to achieve performance that cannot be reached with other polymers.

Calprene H6180X, Calprene H6181X and Calprene H6182X have been designed to be used in applications such as elastic films, elastic tubing, and elastic fibers and nonwoven fabrics. Hydrogenated styrenic block copolymers have also been designed for improved performance in TPE compositions, specifically offering better processability, resealability and low permeability to oxygen. These materials are particularly useful in the production of medical articles, such as stoppers and pharmaceutical seals.

This article covers the main characteristics and key parameters of these new SEBS materials, as well as their performance in the applications of films, extruded tubes, medical stoppers and nonwoven fabrics.

**SEBS characteristics and key parameters**

SEBS is a block copolymer with hard polystyrene domains and a soft hydrogenated polybutadiene domain (figure 1).

The SEBS grades were synthesized by anionic polymerization using a lithium initiator, and the 1,4 or 1,2 vinyl groups are controlled by the addition of Lewis bases, followed by hydrogenation with a metallocene-type catalyst. The concentration of vinyl units controls the amount of crystallinity in the system (ref. 1).

The vinyl content in SEBS has a big influence on the thermal transition of the polymer. When vinyl content level is low, SEBS behaves as a semi-crystalline material, and the glass transition temperature \( T_g \) moves to lower values. When vinyl content level is over 55%, the copolymers show an amorphous behavior and the \( T_g \) moves to higher values (figure 2) (ref. 1).

The increase in vinyl content in the SEBS also leads to a better transparency, particularly when combined with polypropylene. The presence of these amorphous copolymers in the polypropylene affects the morphology of the system by reducing the domains’ size, smaller than the light wavelength, offering higher transparency (when compared to standard SEBS grades), and also affecting the polypropylene crystallization speed, showing excellent flexibility, and scratch and impact resistance compared to pure polypropylene (ref. 2).

With these considerations in mind, Dynasol Group has developed Calprene H6180X, Calprene H6181X and Calprene H6182X (table 1). These new high vinyl content SEBS products were designed to respond to market requirements, such as better transparency, higher elasticity, low migration and low hardness.

The increase in the vinyl content of the SEBS copolymers leads to a reduction in the solution viscosity and to a higher flowability (figure 3). As seen in figure 3, Calprene C-H6182X is the material that exhibits the lowest viscosity, particularly at low shear rates, the area where the extrusion process occurs.

Table 1 also shows some characteristics of an experimental SEBS grade designed for medical stoppers. This new material combines high vinyl content with chainlinking, which provides special features such as low viscosity compared with linear SEBS grades of equivalent molecular weights.

**Figure 1 - phase separation in SEBS**

**Figure 2 - effect of butylene composition on the glass transition temperature \( T_g \) of the midblock phase (styrene 30%); the dashed line represents the \( T_g \) of amorphous ethylene butylene copolymers**
Advantages of using TPE materials for medical applications

TPEs containing SEBS offers several advantages compared to PVC, including the absence of plasticizers, a low level of extractables, excellent sealability and adhesion performance, softness, flexibility, dimensional stability, weather resistance and recyclability. SEBS materials used for medical compounds also comply with FDA regulations and USP Class V1.

Regarding the chemical resistance and compared to PVC and silicones, TPE materials based on SEBS show excellent performance in the presence of fluids (table 2).

Flexible TPE medical films and tubing: Mechanical and optical properties

Polyvinyl chloride (PVC) based films and tubing are used in numerous medical products. The material is easy to formulate and process, is relatively inexpensive and performs well in most applications. However, there are concerns related to its disposal, and to the generation of chlorinated by-products after incineration. Moreover, there is a trend in the medical industry to replace PVC for issues related to phthalate plasticizers used to prepare flexible PVC.

SEBS/polypropylene (PP) compounds are a good alternative to replace PVC.

In contrast to flexible PVC, SEBS/PP compounds have the following advantages:

- Plasticizer free (low migration)
- Halogen free (no chloride emissions)
- Recyclability
Table 3 - mechanical properties of Calprene C-H6180X/PP homopolymer compounds

<table>
<thead>
<tr>
<th>Properties</th>
<th>Test method</th>
<th>C-H6180X/PP homopolymer (80/20)</th>
<th>C-H6180X/PP homopolymer (70/30)</th>
<th>C-H6180X/PP homopolymer (60/40)</th>
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<tbody>
<tr>
<td>Elongation at break, %</td>
<td>ASTM D412</td>
<td>785</td>
<td>645</td>
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<tr>
<td>Tensile strength, MPa</td>
<td>ASTM D412</td>
<td>9.3</td>
<td>8</td>
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<td>Hardness, durometer A</td>
<td>ASTM D2240</td>
<td>64</td>
<td>69</td>
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<td>Specific gravity, g/cc</td>
<td>ASTM D792</td>
<td>0.89</td>
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</table>

Table 4 - mechanical properties of Calprene C-H6180X/rPP1 homopolymer compounds

<table>
<thead>
<tr>
<th>Properties</th>
<th>Test method</th>
<th>C-H6180X/rPP1 (80/20)</th>
<th>C-H6180X/rPP1 (70/30)</th>
<th>C-H6180X/rPP1 (60/40)</th>
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<tr>
<td>Elongation at break, %</td>
<td>ASTM D412</td>
<td>816</td>
<td>797</td>
<td>798</td>
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<tr>
<td>Tensile strength, MPa</td>
<td>ASTM D412</td>
<td>11.1</td>
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<td>Hardness, durometer A</td>
<td>ASTM D2240</td>
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Table 5 - mechanical properties of Calprene C-H6180X/rPP2 homopolymer compounds

<table>
<thead>
<tr>
<th>Properties</th>
<th>Test method</th>
<th>C-H6180X/rPP2 (80/20)</th>
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<tr>
<td>Elongation at break, %</td>
<td>ASTM D412</td>
<td>694</td>
<td>590</td>
<td>571</td>
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<td>Tensile strength, MPa</td>
<td>ASTM D412</td>
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<td>Hardness, durometer A</td>
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<tr>
<td>Specific gravity, g/cc</td>
<td>ASTM D792</td>
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Table 6 - SEBS/PP compounds evaluation in applications for medical stoppers

<table>
<thead>
<tr>
<th>Hardness, durometer A</th>
<th>TPE-S0</th>
<th>TPE-S1</th>
<th>Ref. 1</th>
<th>Ref. 2</th>
<th>Ref. 3</th>
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</thead>
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<tr>
<td></td>
<td>Ref. 1</td>
<td>Ref. 1</td>
<td>radial</td>
<td>radial</td>
<td>linear</td>
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<tr>
<td>Compression set, % at 25°C for 22 hours</td>
<td>55</td>
<td>20</td>
<td>46</td>
<td>39</td>
<td>40</td>
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<tr>
<td>Compression set, % at 70°C for 22 hours</td>
<td>3</td>
<td>4</td>
<td>11</td>
<td>17</td>
<td>19</td>
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<tr>
<td>Average permeability to CO2, cc-mil/m²/day/atm</td>
<td>45,500</td>
<td>96,000</td>
<td>85,000</td>
<td>92,000</td>
<td>99,000</td>
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<tr>
<td>E-beam</td>
<td>OK</td>
<td>OK</td>
<td>OK</td>
<td>OK</td>
<td>OK</td>
</tr>
<tr>
<td>MFI, g/10 minutes at 230°C/5 kg</td>
<td>6.3</td>
<td>25</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Oil bleeding, 50°C, 10 days</td>
<td>OK</td>
<td>OK</td>
<td>OK</td>
<td>OK</td>
<td>OK</td>
</tr>
<tr>
<td>Oil, % weight</td>
<td>29</td>
<td>45</td>
<td>45</td>
<td>45</td>
<td>45</td>
</tr>
</tbody>
</table>

Optical properties evaluation
One of the parameters to consider when developing SEBS/PP compounds (80/20, 70/30 and 60/40) were processed in a Berstorff twin screw extrusion line (L/D: 36) to obtain cast films 1.2 mm thick.

Results for compounds developed utilizing the Calprene C-H6180X are shown in tables 3 and 4. Overall, films having Calprene C-H6180X show hardness values ranging from 61 to 80 durometer A, thus covering the demands of peristaltic tubing and intravenous tubing. Moreover, tensile strength can be modified depending on the ratio and the type of polypropylene grade chosen. The best elasticity value is given by the combination of C-H6180X with rPP1.

The rheological curves of the developed compounds are shown in figures 4 through 6. Most blends behave similarly to PP homopolymer and to rPP2; though, in the case of rPP1 (figures 4 through 6), this material shows lower viscosity at all the evaluated shear rates in all the combinations studied.

**Mechanical properties evaluation**

- Low temperature resistance
- Lower density

Formulations based on PP homopolymer (Isplen PP031G1E from Repsol Química S.A.), PP random copolymer (Isplen PR264G1F from Repsol Química S.A.) and PP random copolymer (PPM R021 from Total Petrochemicals) have been used to develop new SEBS grades Calprene C-H6180X, Calprene C-H6181X and Calprene C-H6182X, which in turn have been used to test new films and tubing samples.
transparent, clear materials is the refractive index (RI) of the components of the blend. The RI values of neat polyolefin and SEBS used to prepare blends are:

• PP homopolymer: 1.493
• rPP1: 1.494
• rPP2: 1.497
• C-H6180X: 1.493
• C-H6181X: 1.494
• C-H6182X: 1.492

All RI values are quite close to each other. This resulted in optically transparent SEBS/PP compounds.

The opacity values were quite low, mostly in combinations with rPP grades and C-H6182X. With respect to haze values, the combinations of C-H6180X and rPP1 and rPP2 exhibited the best performance.

The transparency of the processed tubes with SEBS and PP (figures 7 and 8) was quite good, and like that of PVC tubing available on the market.

**SEBS evaluation in medical stoppers**

SEBS-1 grade, described in table 1, was used to prepare compounds with PP, and evaluated in applications for medical stoppers. TPE-S0 and TPE-S1 compounds, shown in table 6, were prepared with SEBS-1 with two different levels of oil. All other compounds shown in table 6 had the same composition as TPE-S1, and were prepared with SEBS available on the market.

TPE-S1 and TPE-S0 compositions comprising radial, high vinyl content SEBS copolymer exhibit acceptable hardness and good resistance to compression, improving barrier properties to oxygen, while keeping good dimensional stability. These compositions also show good chemical and sterilization resistance,
screw extruder (Coperion ZSK 18, MegaLab), while nonwoven fabrics were made in a melt blown pilot plant (Reicofil) equipped with a spinneret having 1.041 orifices (external diameter 0.3 mm). Extrusion temperatures ranged from 235°C to 275°C.

Elastic properties were determined in an Instron 3343, and were obtained following the profile shown in figure 9.

As seen in table 7, standard PP or PP/PE core/sheath bicomponent bico nonwoven fabrics exhibit low elongation at break (ref. 3), while SEBS/PP fabrics elongate around 10 times more. SEBS/PP nonwovens have lower permanent set and higher recovered energy than PP or PP/PE bicomponent fabrics. Moreover, nonwovens containing SEBS are biaxial, exhibiting similar stretch values in machine direction (MD) and cross machine direction (CD).

All these results lead to an elastic fabric with good elastic recovery and with a comfortable softness, suitable for hygienic and medical applications.

Conclusions
In this article, we have demonstrated that the new SEBS series materials developed by Dynasol (Calprene C-H6180X, Calprene C-H6181X and Calprene C-H6182X) are suitable candidates to replace plasticized PVC as a raw material for production of medical devices.

Combinations of the new SEBS materials, especially Calprene C-H6182X with polypropylene random copolymer, enhance the transparency and good optical properties of the polypropylene, and it is possible to obtain products that combine good elongation and tensile strength properties, resulting in a tough material suitable for withstanding processes such as peristaltic flow.

When comparing these tubes with the others available on the market made from PVC, the transparency is equivalent. Combinations of Calprene C-H6182X with polypropylene homopolymer and random copolymer show the lowest kink resistance values, having at the same time good elastic recovery without any marking on the tubes after testing.

(continued on page 41)
permanently cold water outside. Such created thermal gradient is significantly reducing, compared to small scale tests, the heat impact on the silicone rubber insulation.

Conclusions
Multiple simulated service tests using the DowSil XTI-1003 RTV silicone rubber insulation material were performed. Key findings of this study show that, even after a full year of 180°C/300 bar aging, the silicone rubber maintains its elastomeric behavior. The expected changes in mechanical properties are related to post-cure effects typical for room temperature curing silicone elastomers. Thermal performance of the silicone rubber remains unchanged. Comparing the SST system test results with the small scale tests, it becomes obvious how contradictory the obtained information can be. While the SST is best at reflecting the real subsea conditions, the generated test results on aged rubber can be used to predict the lifetime expectation on insulation systems.

References
7. W.D. Inman, Jr., “Post-curing of silicone elastomers: When is it necessary?” Dow Corning Corporation, Form No. 52-1265-01.

SEBS for medical applications
(continued from page 34)

New radial SEBS compounds having high vinyl content and combined with polypropylene are suitable to prepare medical stoppers with properties as good as other SEBS products available on the market.

Nonwovens containing SEBS show a much lower set and a higher recovered energy versus standard existing nonwovens.

The new SEBS nonwovens presented in this article exhibit excellent strength, elasticity and high elongation at break, and are also biaxial, exhibiting similar stretch values in machine and cross machine directions.

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References