Modifiers for Adhesion Improvement in TPE-S Overmolding Compounds
Background

Thermoplastic Elastomers
Thermoplastic elastomers (TPE) are an interesting class of materials that combine the properties of thermoplastics and elastomers, as indicated by their name. Not only can these materials be processed cost-effectively like thermoplastics but they also have material properties similar to that of elastomers. Two main groups are distinguished based on the structure of TPE. The first group comprises block copolymers that consist of blocks of elastomers and thermoplastics. The thermoplastic segments may be crystalline or amorphous and melt reversibly when the glass transition temperature is exceeded. This permits thermoplastic processing. In the solid state below the glass transition temperature, the properties of the material are determined by the elastomeric segments.

The second group comprises polymer blends consisting of a thermoplastic polymer matrix and one or several embedded elastomeric component(s).

The component ratio in this type of blend can vary widely depending on the desired properties.

TPE materials based on styrene block copolymers (TPE-S or TPS) have come to be widely used. One reason for this is the lower manufacturing cost as compared to other thermoplastic elastomers as well as their broad versatility. This group of materials is traditionally used as a replacement for vulcanized rubber in a wide range of applications such as shoe soles, medical items, cable insulation material, automotive parts, etc.

Overmolding
The term “overmolding” refers to a method in which hard plastics are completely or partially overmolded with elastomeric plastic. In addition to plastics, other hard materials such as glass or metal can also be used as the hard component. TPE-S, for example, is used as the elastomeric component in this method. By combining hard and soft materials, the grip of tools, medical instruments and many items for daily use can be improved and a surface with soft touch can be obtained.

If the hard component is a thermoplastic material as well, processing can occur by multicomponent injection molding (multi-shot) and the hard and soft components are processed successively in an injection molding system. In the insert method, on the other hand, the hard substrate is manufactured first and subsequently overmolded with the soft component in a second process step using a standard injection molding system (single-shot).

The quality of such hard-soft combinations is critically dependent on the good adhesion of the soft component to the hard component. Adhesion problems occur in combinations of TPE-S with polycarbonate (PC), polyamide (PA) and acrylonitrile butadiene styrene (ABS) that must be solved either by structural modification or by using adhesion promoters (adhesion modifiers).
SCONA Adhesion Modifiers in TPE-S Overmolding Compounds

Styrene Block Copolymers for TPE-S Overmolding Compounds

Typical styrene block copolymers for use in overmolding compounds are shown in figure 1. The SCONA adhesion modifiers are based on the same block copolymers but are functionalized with maleic anhydride (MAH) to achieve better adhesion. The use of these types of adhesion modifiers means that a portion of the TPE-S is substituted by functionalized TPE-S.

In practice, TPE-S is not used as the only component in overmolding compounds. Instead, the formulations usually also contain white oil as an extender, which has a plasticizing effect, and polypropylene to adjust hardness. Figure 2 shows such a model formulation based on SEBS.

In this case not only a portion of the SEBS must be substituted by MAH-grafted SEBS but also a portion of the PP by MAH-grafted PP. A combination of two modifiers is therefore used in this scenario.

Model Formulation of a TPE-S Overmolding Compound

<table>
<thead>
<tr>
<th>Base Formulation without Adhesion Modifier:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>100 Parts SEBS</td>
<td>(thermoplastic elastomer)</td>
</tr>
<tr>
<td>100 Parts White Oil</td>
<td>(paraffinic oil, extender with a plasticizing effect)</td>
</tr>
<tr>
<td>30 Parts PP</td>
<td>(to adjust hardness)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>With Adhesion Modifiers for Improving Adhesion:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>50 Parts SEBS</td>
<td></td>
</tr>
<tr>
<td>50 Parts SCONA TSKD 9103</td>
<td></td>
</tr>
<tr>
<td>100 Parts White Oil</td>
<td></td>
</tr>
<tr>
<td>20 Parts PP</td>
<td></td>
</tr>
<tr>
<td>10 Parts SCONA TPPP 2112 GA</td>
<td></td>
</tr>
</tbody>
</table>
Chemistry of the Modifiers
SCONA modifiers are always base polymers (often non-polar) that are functionalized with diverse monomers in a grafting process. The base polymers SEBS and PP are among the products that are used as adhesion modifiers in TPE-S overmolding. Both are primarily functionalized with maleic anhydride (MAH) (figure 3).

All SCONA products are grafted using a patented solid phase process, whereas the standard procedure is to graft the polymers with the monomers in the melt. In solid phase grafting, a greater degree of functionalization is achieved, resulting in a lower required concentration of modifier in the compound. The content of volatile organic compounds (VOC) is extremely low in products manufactured using this method. Moreover, the low process temperature causes less damage to the base polymer and the resulting higher molecular weight is reflected in the improved mechanical properties of the compound.

Another option is to graft high molecular weight SEBS and SEEPS block copolymers, which would not be possible in conventional melt grafting.

More details on SCONA modifier technology are presented in brochure TP-TI 2 “Technology of SCONA Plastic Modifiers”.

The technology also offers the possibility to graft in a two-stage process. A solid phase grafting takes place in the first stage and is followed by melt grafting in the second stage (figure 4). An even greater degree of grafting can be achieved by using this combination.

“SCONA TP...” products are SCONA modifiers that are manufactured by the solid phase process only.

“SCONA TS...” products are modifiers that are manufactured by the combined process.
Mechanism of Action
The improvement of adhesion of the soft TPE-S to the hard substrates (PC, PA, ABS, glass, metal) is always based on the chemical bonding of the MAH groups of the adhesion modifiers to the polar groups of the substrates.

In formulations that also contain PP for adjustment of hardness, PP is usually primarily present in a finely dispersed form and these PP particles can impair or totally prevent adhesion. In this case, PP must therefore also be grafted with maleic anhydride. The high molecular weight PP previously available on the market contained only low concentrations of MAH (no more than 0.3 %). This meant in practice that the entire PP portion had to be substituted by grafted PP. With the introduction of the new high molecular weight and highly grafted PP modifiers (SCONA TPPP 2112 FA, SCONA TPPP 2112 GA, SCONA TPPP 8112 FA, SCONA TPPP 8112 GA and SCONA TPPP 2003 GB), only a portion of the PP component must be substituted.

Advantages of Using SCONA Modifiers
Figure 5 illustrates the good performance of SCONA TSKD 9103 as compared to a standard adhesion modifier (both based on SEBS). The results obtained from the standard were each set to 100. By using our unique grafting technology, we are capable of obtaining a higher grafting degree of the various types of TPE-S such as SEBS or SEEPS while maintaining the high molecular weight. Our customers can therefore obtain better adhesion to hard substrates and can also achieve an improved (lower) compression set when using high molecular weight TPE-S. Grafted high molecular weight types of SEBS and SEEPS are available and can be supplied on special request.

### Table: Comparison of SCONA TSKD 9103 with Standard Adhesion Modifier

<table>
<thead>
<tr>
<th>Employed Adhesion Modifier</th>
<th>Hardness Shore A</th>
<th>Tear Resistance</th>
<th>Adhesion to PA</th>
<th>Adhesion to PC</th>
<th>Adhesion to ABS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>61</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>300</td>
</tr>
<tr>
<td>SCONA TSKD 9103</td>
<td>61</td>
<td>111</td>
<td>186</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Standard</td>
<td>29</td>
<td>100</td>
<td>100</td>
<td></td>
<td>262</td>
</tr>
<tr>
<td>SCONA TSKD 9103</td>
<td>31</td>
<td>106</td>
<td></td>
<td>100</td>
<td>262</td>
</tr>
<tr>
<td>Standard</td>
<td>70</td>
<td>100</td>
<td>100</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>SCONA TSKD 9103</td>
<td>73</td>
<td>145</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Each test was performed using the same formulation with varying degrees of hardness.

### Table: Base SEBS

<table>
<thead>
<tr>
<th>Base Polymer</th>
<th>Grafting</th>
<th>MVR (230 °C/5 kg)</th>
<th>MAH Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCONA TSKD 9103</td>
<td>Solid phase + melt</td>
<td>15-35 cm³/10 min.</td>
<td>1,3 %</td>
</tr>
</tbody>
</table>

### Table: Base PP

<table>
<thead>
<tr>
<th>Base Polymer</th>
<th>Grafting</th>
<th>MFR (190 °C/2,16 kg)</th>
<th>MAH Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCONA TPPP 2003 GB</td>
<td>PP Copolymer</td>
<td>3-8 g/10 min.</td>
<td>0,9-1,3 %</td>
</tr>
<tr>
<td>SCONA TPPP 2112 FA</td>
<td>PP</td>
<td>2-7 g/10 min.</td>
<td>0,9-1,2 %</td>
</tr>
<tr>
<td>SCONA TPPP 2112 GA</td>
<td>PP</td>
<td>4-8 g/10 min.</td>
<td></td>
</tr>
<tr>
<td>SCONA TPPP 8112 FA</td>
<td>PP</td>
<td>&gt; 80 g/10 min.</td>
<td>1,4 %</td>
</tr>
<tr>
<td>SCONA TPPP 8112 GA</td>
<td>PP</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FA = Powder, GA, GB = Granular Material
Products and Applications

BYK Additives

Product Range Additives:

- Additives to improve surface slip, leveling, and substrate wetting
- Adhesion promoters
- Defoamers and air release agents
- Processing additives
- Rheological additives
- UV absorbers
- Viscosity depressants
- Wax additives
- Wetting and dispersing additives for pigments and extenders

Application Areas:

Coatings Industry
- Architectural Coatings
- Automotive Coatings
- Industrial Coatings
- Can Coatings
- Coil Coatings
- Wood & Furniture Coatings
- Powder Coatings
- Leather Finishes
- Protective & Marine Coatings

Plastics Industry
- Ambient Curing Systems
- PVC Plastisols
- SMC/BMC
- Thermoplastics

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- Flexo Inks
- Gravure Inks
- Inkjet Inks
- Silk Screen Inks
- Offset Inks
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