Basic Principles

Polypropylene is one of the most significant plastics of all in terms of quantity. This is due firstly to the diverse application possibilities and secondly, to the extremely attractive manufacturing costs. In the past, polypropylene was mainly used for inexpensive tasks which were not particularly demanding. But for some time now this interesting material has tapped into more and more fields of application which were previously reserved for the so-called technical thermoplastics, such as polyamides, ABS, etc. This has been made possible by factors including the use of functional fillers such as talc and glass fibers. Now glass fibers are being used, so today we see more and more coupling agents (adhesion promoters) also being employed, enabling the chemical bonding of the sized glass fibers to the polymer matrix (figure 1). This has given rise to a substantial improvement in the mechanical property profile of the resulting compounds, which have been able to replace technical thermoplastics in the most diverse applications as a result of their continuously increasing level of properties.

A key field of application for glass fiber-reinforced polypropylene is automotive engineering. Figure 2 shows a typical example of the induction manifold of a combustion engine which was previously manufactured out of metal. Later on, technical thermoplastics (polyamide/GF) were used and finally the product is now produced using the considerably cheaper and, equally important, lighter PP/GF solution.
SCONA Modifiers in Glass Fiber-reinforced PP and PA

Improving Mechanical Properties by Using a Coupling Agent

Coupling agents are used in glass fiber-reinforced compounds to increase the incorporation of the fibers in the polymer matrix, thereby significantly improving the compound’s mechanical properties. Figure 3 shows this by means of selected characteristics.

In industry it is also important for the coupling agents to raise the thermal stability (according to DIN EN ISO 75-1, -2, method A) from 70 °C to above 130 °C (in some cases even > 145 °C), which substantially broadens the application possibilities of the compound.

Chemistry of the Modifiers

The SCONA modifiers are always non-polar base polymers, which are functionalized with different monomers in a grafting process (figure 4). With regard to the modifiers used as couplers in glass fiber-reinforced polypropylene and polyamide, it is the base polymer PP that is mainly functionalized with maleic acid anhydride (MAH).

All SCONA Products are grafted in the solid phase according to a patented method, whereas usually the monomers are melt-grafted to the polymers. Greater levels of functionalization can be achieved in solid phase grafting, which results in lower quantities of the modifier being used in the compound. The content of volatile organic compounds (VOC) in the products manufactured according to this method is extremely low. In addition, the lower process temperature means that the base polymer is less damaged and consequently a higher molecular weight is noticeable in the improved mechanical characteristic values.

More details on the technology of SCONA modifiers can be found in the brochure TP-TI 2 “Technology of the SCONA plastic modifiers”.

Chemistry of the SCONA Coupling Agents for Glass Fiber-reinforced PP and PA

MAH = Maleic Acid Anhydride  AA = Acrylic Acid  St = Styrene
The technology also provides the possibility of grafting in a two-stage process. In the first stage, a normal solid phase grafting is carried out, which is then followed by a melt grafting in the second stage (figure 5). This combination enables even greater grafting levels to be achieved.

SCONA modifiers that were produced solely according to the solid phase process are the „SCONA TP...“ products. The combined process produces the „SCONA TS...“ products.

**Mechanism of Action**

As already mentioned and also shown in figure 1, the coupling agent brings about a stronger incorporation of the glass fibers in the polymer matrix, for which it must interact with the glass fibers. In fact, this interaction does not take place directly with the glass surface, but as the glass fibers produced are all provided with a surface coating (size) for strength purposes, the interaction is with this size. Specifically in the present case, this means a reaction of the MAH groups of the coupling agent with the amino groups of the silane of the size. The reaction results in an extremely stable imide structure.

**Advantages of SCONA Modifiers**

One of the most important fields of application for PP/GF is automotive engineering. For years now it has been increasingly important to reduce VOC (Volatile Organic Compounds) emissions. A not inconsiderable contribution to reducing these emissions is made by PP/GF compounds and, in particular, the coupling agents used. Coupling agents which were melt-grafted contain large quantities of cleavage products, both of the base polymer and the peroxide, which is required for the grafting reaction. As a result of the special SCONA manufacturing technology, we are able to significantly reduce the VOC content, since the chemical reaction is followed by a flushing process in which the volatile components (VOCs) are flushed out (figure 7).

Figure 8 shows a comparison of SCONA TPPP 9012 FA (solid phase grafting) with different competitive products, which were all melt grafted.

**Comparison of VOC Content of Coupling Agents**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>VOC (Mean Value) µg/g*</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCONA TPPP 9012 GA</td>
<td>88</td>
</tr>
<tr>
<td>SCONA TPPP 8112 GA</td>
<td>127</td>
</tr>
<tr>
<td>PP-g-MAH (Melt Grafting)</td>
<td>158</td>
</tr>
<tr>
<td>PP (non-grafted)</td>
<td>34</td>
</tr>
</tbody>
</table>

*based on VDA 277

**Comparison of Different Coupling Agents for Glass Fiber-reinforced Polypropylene**

<table>
<thead>
<tr>
<th>Modifier</th>
<th>Grafting</th>
<th>MFR g/10 min (190 °C/2.16 kg)</th>
<th>MAH content %</th>
<th>Yellowness Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCONA TPPP 9012 FA</td>
<td>Solid phase</td>
<td>123</td>
<td>0.98</td>
<td>0.02</td>
</tr>
<tr>
<td>Sample 1</td>
<td>Melt</td>
<td>260</td>
<td>0.95</td>
<td>0.71</td>
</tr>
<tr>
<td>Sample 2</td>
<td>Melt</td>
<td>280</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>Sample 3</td>
<td>Melt</td>
<td>380</td>
<td>0.8</td>
<td>0.69</td>
</tr>
</tbody>
</table>

**Combined Solid Phase/Melt Grafting**

**Reaction of the Coupling Agent with the Glass Fiber Size**

**Comparision of VOC Content of Coupling Agents**

**Comparison of Different Coupling Agents for Glass Fiber-reinforced Polypropylene**
Better Impact Strength as a Result of the Coupling Agent having a higher MAH Content

Figure 9 illustrates this once again by example of the impact strength and notched impact strength. The high content of free MAH in the competitor’s products is responsible for the high VOC emissions of these products. Furthermore, the free MAH also naturally reacts with the glass size, thereby coating the surface without actually contributing to the bond between the glass and the polymer matrix.

The lower yellowness index is also a consequence of the solid phase grafting, since the temperature load in this manufacturing method is significantly lower. The high temperature and short dwell times of melt grafting generally give fluctuating results in terms of the MAH content and the molecular weight; the solid phase technology can be better controlled and provides a more consistent coupling agent quality.

Figure 9 also shows that there is an optimum for the mechanical properties. Greater coupling agent quantities do not lead to any improvement or a slight deterioration is even observed. Nevertheless, it may sometimes be necessary to use a fractionally greater quantity because in the case of specific applications, such as suds containers for washing solutions in washing machines (white goods, suds discharge), it is only in this way that the necessary alkali resistance be achieved (figure 10).

Product Recommendations for Glass Fiber-reinforced PA and PP

<table>
<thead>
<tr>
<th>Coupling Agents for Polyamide</th>
<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 TSEB 2113 GB</td>
<td>Ethylene Butylacrylate Copolymer</td>
<td>Solid phase + melt</td>
<td>3-8 cm³/10 min.</td>
<td>0.6 %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coupling Agents for Polypropylene</th>
<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 TPP 9012 FA</td>
<td>PP</td>
<td>Solid phase</td>
<td>50-110 g/10 min.</td>
<td>&gt; 0.9 %</td>
</tr>
<tr>
<td>Scona TPP 9012 GA</td>
<td>PP</td>
<td>Solid phase</td>
<td>70-120 g/10 min.</td>
<td>&gt; 1 %</td>
</tr>
<tr>
<td>Scona TPP 9112 FA</td>
<td>PP</td>
<td>Solid phase</td>
<td>10-110 g/10 min.</td>
<td>&gt; 1 %</td>
</tr>
</tbody>
</table>

FA = Powder   GA = Granulate
Products and Applications

BYK Additives

Product Range Additives:

• Additives to improve surface slip, leveling, and substrate wetting
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This issue replaces all previous versions – Printed in Germany