Background

A number of additives are used during the processing of plastics in order to optimize the processing itself and to improve the quality of the finished plastic parts. Additives for the wetting of solid particles, air release agents, plasticizers, UV stabilizers, antioxidants and flame retardants are only a few of those used. BYK Kometra has focused in this segment on a very specific group of products that are marketed as SCONA Plastic Modifiers for use in thermoplastic materials. Depending on the area of application, they are also referred to as coupling agents, adhesion promoters, compatibilizers or impact modifiers.

The significantly lower density of plastics as compared to many other materials can help achieve significant weight reductions in many applications, thereby lowering energy consumption and reducing energy costs. The low mechanical strength of plastic material can be significantly improved by a combination with mineral fillers or fibrous reinforcement materials (glass fibers, natural fibers). Reinforced plastics have conquered many fields of application that were previously the sole domain of metallic materials. The successful use of these plastics in the automotive industry as materials for structural components clearly illustrates this. In filled and reinforced plastic materials, the SCONA modifiers are used to distribute the fillers and fiber materials more evenly in the polymer matrix and to increase the mechanical bonding strength between the two. Compounding of the plastic material is facilitated and the mechanical properties of the finished parts are improved.

Even chemical reactions between the modifiers and the other materials involved take place during this process in certain cases. The modifiers act in this case as a coupling agent or adhesion promoter. This results in a significant and measurable improvement in the mechanical properties of the compound consisting of the thermoplastic polymer and the filling/reinforcement materials.

Important markets of this kind (figure 1) for SCONA Plastic Modifiers are wood plastic compounds (WPC) and glass fiber-reinforced PP or PA. WPCs are wood fiber-reinforced PP and PE materials that are used, for example, for decking, railing and fencing. The modifiers contribute significantly to the good weather resistance of these compounds. Glass fiber-reinforced PP and PA are used primarily in the automotive industry and the SCONA modifiers not only result in a significant improvement in the mechanical properties but also result in lower emissions (VOC) as compared to conventionally manufactured products.

The modifiers are also used in non-filled plastics, for example, to increase the impact strength of polyamide, as compatibilizers for blends of polyamide with other polymers and to increase the tear resistance of PET bands. Another special application involves a process known as overmolding, in which hard plastic surfaces are coated (overmolded) partially with soft and elastic plastic materials. The process improves the grip on tool handles, tooth brushes and medical instruments. SCONA modifiers are used in this process as adhesion promoters between the hard and soft polymers.

Important Markets for SCONA Plastic Modifiers

- Wood Plastic Composites (WPC)
- Glass Fiber-reinforced PP, PA
- Impact Modification of PA, PET
- TPE-S Overmolding

Figure 1
SCONA Plastic Modifier Chemistry

Polymers and Monomers for Graft Copolymers

<table>
<thead>
<tr>
<th>Base Polymers</th>
<th>Homopolymers</th>
<th>Copolymers</th>
<th>Block Copolymers</th>
<th>Natural Products</th>
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</thead>
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<tr>
<td>PE</td>
<td>EVA</td>
<td>SEBS</td>
<td></td>
<td>Starch</td>
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<td>PP</td>
<td>POE</td>
<td>SEPS</td>
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<td>Cellulose</td>
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<td>SPS</td>
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Graft Monomers

Maleic Anhydride (MAH) – Styrene – Acrylic Acid – Methyl Methacrylate – Vinyl Acetate
Glycidyl Methacrylate – Methacrylic Acid – Vinyl Silane – Butyl Acrylate – Hydroxyethyl Acrylate

Even though SCONA Plastic Modifiers may be used in a variety of applications, the utilized basic chemical structure is always quite similar. The modifiers are always grafted polymers, meaning that a relatively non-polar base polymer (e.g. PE or PP) is chemically functionalized with various graft monomers (grafting).

The introduction of such functional or reactive groups leads to polymers that can better interact or even react with specific components of the plastic compound (e.g. the fillers) due to these active centers. It is obvious that this permits a change in the properties of the compound and the objective always is to improve the compounding process itself and finally also the properties of the manufactured plastic parts.

Figure 2 shows a selection of the base polymers and graft monomers that can be used for this purpose. The most frequently used base polymers are PP and PE and MAH is clearly the frontrunner for monomers. But it also becomes obvious that there are many additional possibilities that can be implemented depending on the objective. Figure 3 shows a schematic that illustrates the structure of such graft copolymers.

Figure 2

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Schematic Structure of the SCONA Plastic Modifiers

<table>
<thead>
<tr>
<th>MAH = Maleic Anhydride</th>
<th>GMA = Glycidyl Methacrylate</th>
<th>BA = Butyl Acrylate</th>
</tr>
</thead>
<tbody>
<tr>
<td>St = Styrene</td>
<td>REA = Hydroxyethyl Acrylate</td>
<td>AA = Acrylic Acid</td>
</tr>
<tr>
<td>Vs = Vinyl Silane</td>
<td>MAA = Methyl Methacrylate</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3
These types of graft copolymers are usually manufactured by a reactive extrusion process in which the polymer is melted in the extruder and then reacts with the graft monomers using a catalyst.

BYK Kometra has developed a patented method in which the grafting reaction occurs not in the melt but in the solid phase (solid phase grafting). One key advantage of this method is that the chemical reaction occurs at a lower temperature under more gentle conditions and the damage to the polymer is therefore less pronounced (thermal degradation). The schematic in figure 4 shows the possible reactions that can occur during the grafting of PP with MAH. Unlike melt grafting, in which step (3) is the only reaction pathway, the reaction in solid phase grafting can be directed in such a manner that a predefined molecular weight is obtained.

The polymer degradation can be observed by measuring the melt flow rates MFR and MVR. Figure 5 shows that high molecular weight products (= low MFR) can be obtained by melt grafting, but that the MAH content is very low as a result of this process (< 0.7 %). Although products with high MAH content (up to 1 %) can also be achieved in this method, the MFR will be significantly higher (= low molecular weight) in this case due to the degradation of the polymer. Solid phase technology, in contrast, allows a high MAH content (> 1 %) to be obtained while achieving a low MFR at the same time. Such high molecular weight products with high MAH content cannot be manufactured by melt grafting. In practical use, this means that modifiers grafted in the solid phase achieve better mechanical properties of the compounds and also improve other important properties such as, for example, a reduction in the water uptake of highly filled WPC compounds. Using this unique manufacturing process, BYK Kometra is capable of setting the MFR and therefore the molecular weight in a more or less specific manner. Furthermore, the dosage of the modifiers in the compound can also be reduced due to the significantly higher MAH contents.
An additional advantage of the solid phase process is that the content of Volatile Organic Compounds (VOC) can be reduced by a nitrogen flush process. This is an aspect that is already important today and the reduction in emissions will gain in importance in the future.

The modifiers also exhibit less discoloration due to the more gentle process, which is of particular relevance when used in transparent compounds. And, finally, modifiers can be obtained by solid phase grafting of non-melting polymers, which would not be feasible through melt grafting.
Solid Phase Grafting

Grafting in Semicrystalline Polymers

In solid phase grafting, the polymer to be grafted is used as a fine powder to provide as large a surface as possible to allow for an efficient chemical reaction. As an additional requirement, amorphous segments must exist in the polymer into which the graft monomers can diffuse (figure 6). Grafting occurs primarily in the amorphous segments, since the free space in the crystalline segments is very small due to the strong orientation of the polymer.

A solid phase grafting plant is shown in figure 7 along with the individual process steps.

Schematic of a Solid Phase Grafting Plant and the Individual Process Steps
Since the polymer to be grafted in solid phase grafting is used as a powder, the grafted product (the ready for sale modifier) is also in powder form. Many customers prefer to work with granulated material instead of a powder, however. For this purpose, the modifier is subsequently processed to granulated material through an extrusion process.

The technology finally also offers the additional option to graft in a two-stage process. A solid phase grafting takes place in the first stage and is followed by a melt grafting in the second stage (figure 8). Even greater degrees of grafting can be achieved by means of this combination.

“SCONA TP…” products are SCONA modifiers that are manufactured through the solid phase process only. “SCONA TS…” products are modifiers manufactured through the combined process.

A schematic overview of the available options is shown in figure 9.
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