Silane Crosslinking of Low Voltage Wire and Cable Applications of ENGAGE
ENR 7256.00 / LLDPE Blend

ENGAGE
Polyolefin Elastomers

Introduction
One process option of Silane crosslinking of a polyolefin involves the grafting of a vinyl alkoxy silane onto the polymer chain by means of a radical initiator such as a peroxide. In the cable industry this step is usually performed in a single screw extruder having a specially designed screw to optimize the silane grafting efficiency. Subsequent cure is accomplished off-line by condensation of the hydrolyzed alkoxy silane grafts, usually in the presence of a tin catalyst. The fact that the cure reaction occurs off-line, in a step essentially independent of the extrusion process itself, allows the processor of cable insulation to achieve a high line speed or throughput. Indeed, this is one of the main reasons behind the success of the Monosil process, jointly patented by BICC and Maillefer over 30 years ago, and widely used to produce silane crosslinked polyolefin insulation.

The development of the silane crosslinking process continues today with arguably the greatest boost to the continuing success of the silane process in wire and cable applications coming in the form of innovative polyolefin elastomers (POEs) with designed molecular architecture. Foremost among these resins are the polyolefin elastomer families synthesized using constrained geometry (metallocene) catalysts; resins such as ENGAGE™.

The Monosil Process
In general, the suitability of a polymer for the Monosil process can be described by 3 critical properties: a) resin processability; b) grafted resin cure performance; and c) final product physical properties.

Processability can mean different things to different people, but the most important aspects may be line speed or polymer throughput. Although the polymer microstructure is modified during the grafting process (for example resin melt index is reduced and molecular weight distribution is broadened), the processability of the polymer can be estimated from the unmodified polymer rheology. With regard to ENGAGE products having a standard narrow molecular weight distribution, processability can be defined as the maximum line speed achievable before the onset of surface defects in the insulation such as melt fracture. In general, the line speed achievable increases as the melt index of the polymer increases. This is illustrated in Figure 1 below.

Figure 1. Shear Stress at the Die as a Function of Wire Extrusion Speed and the Melt Index of ENGAGE. (Onset of melt fracture estimated to occur at 1.25 MPa shear stress).

The apparent cure rate of a silane grafted polymer is inversely proportional to the polymer melt index: high melt index products take longer to cure (monodisperse systems). This is illustrated in Figure 2, which shows the time to reach 175% hot set elongation (T175) as a function of the melt index of ENGAGE for 0.870g/cm³ density resins.

Figure 2. Hot Set Performance as defined by T175 of Silane
Some cable producers require not only a high line speed but also the fast cure of the grafted insulation. Not only does the cable producer need to balance line speed and cure rate, the physical properties of the final cable also need to be taken into consideration. In this respect, more and more cable producers are expressing a desire for more flexible insulation than that currently offered by Low Density Polyethylene (LDPE) and blends with Very Low Density Polyethylene (VLDPE) or VLDPE blends with Linear Low Density Polyethylene (LLDPE). However, this wish for enhanced flexibility insulation must be tempered by the ability of the insulation to resist permanent deformation, both upon windup of the insulation and any subsequent cable jacketing process. And the insulation must also achieve target tensile strength properties.

**Introducing ENR 7256.00 Blends for Silane Cured Low Voltage Insulation**

ENR 7256.00 can be used in combination with current LLDPE insulation products. This novel ethylene-butene product has been specifically designed with a broadened molecular weight distribution and long chain branching to enhance resin processability while maintaining fast cure of the grafted polymer by virtue of the starting polymer molecular weight. Further, when combined with LLDPE the relatively low crystallinity of this product provides a more flexible insulation product. The choice of a 40/60 ENR 7256.00/LLDPE blend composition retains deformation resistance of the insulation and has the ability to exceed the tensile strength target of 10 MPa.

**Processability**

Figure 3. 190°C Rheology of ENR 7256.00 and LLDPE Reference System.

The RDA-II rheology of ENR 7256.00 and a LLDPE cable resin reference are presented in Figure 3.

Figure 3 shows that the polyolefin elastomer has higher viscosity at low shear rates which will a) aid insulation green strength; b) allow the insulation to resist deformation and sag; and c) minimize any tendency to yield thin spots in the insulation. The polyolefin elastomer has a significantly greater degree of shear thinning behavior than the traditional LLDPE resin.

**ENR 7256.00/LLDPE Blend Rheology**

Figure 4. Capillary Rheology of the 40/60 ENR 7256.00/LLDPE Blend and the LLDPE Reference System: Shear Viscosity as a Function of Shear Rate at 190°C.

Figure 4 shows the shear viscosity as a function of shear rate for an ENR 7256.00.00/LLDPE blend which is the focus of this technical bulletin. In this capillary experiment the rheology of the ENR 7256.00.00/LLDPE 40/60 blend at 190°C is compared to that of the reference LLDPE.

This figure illustrates that at the 40/60 blend composition chosen, the ENR 7256.00.00/LLDPE blend exhibits similar processability at high shear rates to that of the reference LLDPE.
Figure 5 presents the hot set cure performance of the blend versus a current LLDPE cable offering. This data reveals that the addition of ENR 7256.00 leads to a slight but measurable increase in the apparent rate of silane cure of the LLDPE resin. We also find that the addition of ENR 7256.00 to the LLDPE increases the final state of cure of the reference (as defined by the final hot set figures and the resin gel level, see Table 1).

Table 1- Comparison of the Mechanical Properties of a 40/60 ENR 7256.00/LLDPE Blend and a Reference LLDPE Cable Resin

<table>
<thead>
<tr>
<th>Resin</th>
<th>40/60 Blend (ENR 7256.00/LLDPE)</th>
<th>LLDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I$_2$ Melt Index (ungrafted) g/10 min, 190°C</td>
<td>2.2</td>
<td>2.8</td>
</tr>
<tr>
<td>Density, g/cm$^3$</td>
<td>0.905</td>
<td>0.918</td>
</tr>
<tr>
<td>Tensile Strength, MPa</td>
<td>15.9</td>
<td>20.1</td>
</tr>
<tr>
<td>Elongation at Break, %</td>
<td>564</td>
<td>682</td>
</tr>
<tr>
<td>Flexural Modulus, MPa</td>
<td>150</td>
<td>280</td>
</tr>
<tr>
<td>Hot Set, time to 175%, hr</td>
<td>7</td>
<td>11</td>
</tr>
<tr>
<td>Final Hot Set, %</td>
<td>70</td>
<td>85</td>
</tr>
<tr>
<td>Gel Content, %</td>
<td>82</td>
<td>72</td>
</tr>
</tbody>
</table>

ENR 7256.00/LLDPE Blend Product Properties

The physical properties of the silane crosslinked ENR 7256.00/LLDPE blend are presented in Table 1. This data demonstrates that not only does the ENR 7256.00/LLDPE blend possess tensile properties well above the target 10 MPa (G7 cable norm), but that the blend has significantly increased flexibility as defined by the polymer flexural modulus. This enhanced flexibility allows the cable producer the potential to offer high performance flexible, user friendly cable solutions.

(Note: for the grafting formulations see Table 2.)

Table 2- Laboratory Silane Grafting Formulation

<table>
<thead>
<tr>
<th>Formulation</th>
<th>wt%</th>
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<tbody>
<tr>
<td><strong>Blend Composition</strong></td>
<td></td>
</tr>
<tr>
<td>ENR 7256.00</td>
<td>40</td>
</tr>
<tr>
<td>LLDPE, 2.8 I$_2$;0.918 g/cm$^3$</td>
<td>60</td>
</tr>
<tr>
<td><strong>Silane Graft Package</strong></td>
<td></td>
</tr>
<tr>
<td>Vinyl trimethoxy silane (VTMOS)</td>
<td>1.5</td>
</tr>
<tr>
<td>Dicumyl peroxide</td>
<td>0.1</td>
</tr>
<tr>
<td>Dibutyl tin dilaurate</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Summary

The addition of substantial amounts of polyolefin elastomers such as ENR 7256.00 to conventional LLDPE low voltage insulation formulations not only allows the cable producer to offer cost effective low voltage insulation with excellent processability and cure performance but also enables delivery of a cable system with a significantly increased level of flexibility.
Appendix:

Recommendations for Monosil Extrusion with ENR 7256.00/LLDPE Blends

For laboratory grafting experiments the silane graft package contained in Table 2 was employed.

Alternatively, commercial silane grafting solutions such as Silcat® VS 735/1 which are fully formulated for low/medium voltage copper cables can be used. Additional levels of this product should be around 1.5 wt% according to the supplier, GE Advanced Materials.

In most cases, the reactive extrusion can be performed on a single screw extruder, preferably fitted with a barrier screw. When performing reactive extrusion using vinyl silane/peroxide, care should be taken to match the extruder temperature profile and the residence time in the extruder to ensure complete decomposition of the peroxide.

Trials with blends of ENGAGE have also been performed on an 80 mm 30/L/D Monosil extruder with a grooved barrel and a Penelope screw. The extruder temperature profile was set at 80°C/80°C/140°C/170°C/220°C/220°C.

Experiments have been performed using the dry silane XL-Pearl® masterbatch XL-Pearl® 31 HDPE 40 available from GE Advanced Materials. In this case, suitable gravimetric feeding systems are needed to ensure accurate dosing of the silane/peroxide solution. For current blends of ENGAGE, XL-Pearl® 31 HDPE 40 masterbatch addition levels are recommended by the supplier to be around 3 wt% with respect to the total polymer content.
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