Introduction

ENGAGE™ Polyolefin Elastomers (POEs) cover a range of melt index and comonomer content (density) for use in several applications. The cost effectiveness of ENGAGE is limited by the combination of reduced flowability and/or softness requirements. The ability to extend ENGAGE with conventional process oils allows greater flexibility to the compounder to tailor the performance of the product to meet the application requirements. Two benefits of oil incorporation are increased processability and reduced hardness of the compounds. These benefits will be described later in more detail.

Process oil incorporation and its effect on physical and mechanical properties depend on several parameters associated with the type of oil and the grade of ENGAGE. ENGAGE is often used as the elastomeric component in a broad range of compounds. Since ENGAGE is usually used in compounds, this bulletin illustrates the properties and processability characteristics that can be achieved, and also describes the key process oil parameters and the major effects of oil addition on the physical properties of ENGAGE.

Background

Process oils used in elastomer compounding are considered processing aids when they are added at levels below 20 parts per hundred rubber (phr) or 16.67 weight percent (wt%). Above this level, they are considered extenders. The selection of an oil to be used in a compound of ENGAGE depends on the performance requirements of the application.

Many of the properties associated with the polymer and oil have, in some cases, significant tradeoffs in performance. For example, in order to achieve a low hardness, more than 30 wt% oil needs to be added. At this level, the mechanical properties at room or elevated temperatures are significantly reduced.

The following sections describe typical process oil physical properties and the effect on ENGAGE based compound performance.

Oil Composition—The three main classes of petroleum oils include:

- **aromatic** which contain mostly unsaturated rings,
- **naphthenic oils** which contain mostly saturated rings, and
- **paraffinic oils** that are made up of saturated molecules with side chains.

Paraffinic oils contain unbranched n-paraffin molecules that tend to form a wax at low temperatures. An abundant amount of these structures can cause an increase in the pour point temperature of the oil and may contribute to the perceived “oil loss” at subambient temperatures. Naphthenic oils do not contain as much if any wax-like molecules. For this reason, the pour point of the naphthenic oils is significantly lower than the paraffinic oils.

Based on the carbon type analysis, paraffinic chains are designated as \( \text{C}_p \); Naphthenic chains are designated as \( \text{C}_n \); and aromatic molecules as \( \text{C}_a \). The analysis lists these values as weight percents.

The classifications are made based on the amount of each type of component in the oil. Typically, paraffinic oils have a \( \text{C}_p \geq 50\% \); naphthenic oils have a \( \text{C}_n \) between 30\% and 40\% and higher; and an oil is classified as aromatic if the \( \text{C}_a \) >35\% by weight. Increasing the level of naphthenic and aromatic components in oil can increase or decrease the compatibility of the oil in the polymer, decrease the ability to cure the polymer with organic peroxides and promote color after aging. Paraffinic and lightly naphthenic oils are suggested for use in ENGAGE.
At the same viscosity, naphthenic oil typically has higher specific gravity, volatility and refractive index and a lower molecular weight compared to paraffinic oil. This is partially due to the compact nature of the naphthenic oil molecules. This tends to give the oil higher viscosities at lower average molecular weight compared to paraffinic oil (see Table 1).

### Table 1
Effect of Oil Type on Physical Properties of the Oil (at Similar Viscosity)

<table>
<thead>
<tr>
<th>Property</th>
<th>Paraffinic</th>
<th>Naphthenic</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Cn</td>
<td>32</td>
<td>47.6</td>
</tr>
<tr>
<td>% Cp</td>
<td>68</td>
<td>52.4</td>
</tr>
<tr>
<td>Viscosity, SUS at 38°C</td>
<td>360</td>
<td>351</td>
</tr>
<tr>
<td>Viscosity, cSt at 40°C</td>
<td>70</td>
<td>67</td>
</tr>
<tr>
<td>Viscosity, cSt at 100°C</td>
<td>8.9</td>
<td>7.4</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>0.870</td>
<td>0.8911</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.476</td>
<td>1.4833</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>249</td>
<td>204</td>
</tr>
</tbody>
</table>

**Oil Compatibility**—The compatibility of an oil in a polymer depends on the oil composition, viscosity, the polymer type (polar or nonpolar) and the polymer molecular structure (amorphous or semicrystalline). Oil loss by “bleed-out” or increased volatility could be signs of an incompatibility.

At elevated temperatures, such as in compounding, a higher density polymer is able to incorporate oil with no signs of incompatibility (free liquid in mixer or on the mixing chamber surface). When the polymer melts, there are no crystals present and the material is completely amorphous. The oil will “bleed-out” when the higher density polymer solidifies if the driving force to crystallize and re-entangle is greater than the swelling force imposed by the oil.

In general, lower molecular weight oils tend to incorporate into the polymer matrix at a higher rate and amount when compared to higher molecular weight oils. This is explained in the next section.

**Oil Viscosity**—The viscosity of the oil affects the volatility, processability, physical properties and hardness of the plasticized polymer. Increasing the molecular weight of the oil increases the oil viscosity and decreases the oil’s volatility. Unavoidably, increasing the molecular weight of a non USP or FDA oil also changes the color (yellow to brown) of the oil. The main factor to keep in mind when selecting the oil is the performance of the compound at the desired processing or service temperature. The goal is to select the oil that will minimize volatility issues during compounding/processing and remain in the compound during the service life.

The change in oil viscosity with temperature can influence the compound properties. For example, the effect of temperature on the oil viscosity is illustrated in Figure 1. HV refers to High Viscosity (>600 SUS at 38°C) and P or N refers to Paraffinic or Naphthenic, MV = Mid Viscosity (300–600 SUS at 38°C) and LV = Low Viscosity (<300 SUS at 38°C).

**Figure 1. Effect of Temperature on Oil Viscosity**

As the temperature increases, the viscosity of the oil decreases. The effect is more pronounced as the viscosity of the oil increases. Other general trends with changing viscosity include: at the same temperature, a slight increase in a compound’s tensile strength and hardness is expected when the viscosity of the oil is increased or as the temperature is reduced (at the same viscosity).
Oil Thermal Stability—Thermogravimetric analysis (TGA) of selected oils is shown in Figures 2 and 3. The test conditions were heating rate = 10°C/min in a nitrogen atmosphere.

At the same viscosity, paraffinic oils have greater thermal stability as shown in Figure 1. The temperature at which the oils begin to volatilize will depend on processing conditions, oil viscosity and molecular weight distribution. A good rule of thumb is the processing temperature should not exceed the point at which the oil loss exceeds 3–5% by weight measured by TGA.

The oil viscosity will also impact the processing temperature at which oil volatility becomes an issue. Oil volatility decreases as the viscosity of the oil increases.

The oil’s flash point can be used to approximate the upper processing temperature. The oil will “smoke excessively” at approximately 10–21°C below the flash point temperature.

Oil Specific Gravity—Paraffinic oils typically have the lowest specific gravity (SG) or density of the types of oils available, followed by naphthenic then aromatic. The aromatic content of the oil is a large contributor to the oil’s gravity. This becomes a factor when oils are switched based on price or availability. For example, a 30 wt% loading of a naphthenic oil (0.90 SG) occupies as much volume as 29 wt% of a paraffinic oil (0.87 SG). Adjustment in the oil loading may be necessary to account for the difference in the oil’s specific gravity. The effect becomes more apparent as the level of oil in the compound increases or as the difference in gravity of the two oils increases. Table 2 lists the amount of oil needed to reach equivalent loading expressed in weight % at different SGs. The results were calculated using the following equation

$$\frac{\text{wt\% Oil 1}}{\text{SpGr Oil 1}} = \frac{\text{wt\% Oil 2}}{\text{SpGr Oil 2}} = \frac{\text{wt\% Oil 3}}{\text{SpGr Oil 3}}$$

<table>
<thead>
<tr>
<th>Oil, wt%</th>
<th>Oil 1, SG = 0.9</th>
<th>Oil 2, 0.87</th>
<th>Oil 3, 0.85</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>10</td>
<td>9.66</td>
<td>9.40</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
<td>19.33</td>
<td>18.88</td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>29.00</td>
<td>28.33</td>
</tr>
<tr>
<td>40</td>
<td>40</td>
<td>38.67</td>
<td>37.78</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>48.33</td>
<td>47.22</td>
</tr>
</tbody>
</table>

Oil Pour Point—The pour point of oil is reached approximately 3–5°C above the temperature at which the oil maintains fluidity. The pour point of paraffinic oil is reached when the inherent waxes in the oil crystallize and restrict the flow. Lowering the wax content of the oil will reduce the pour point. The occurrence of a cloud point, the point at which the wax crystals begin to form, is inherent in paraffinic oils only. Naphthenic oils contain little or no wax and reach the pour point through an increase in viscosity.
Oil Cost—Typically, naphthenic oils are less expensive than paraffinic oils. Prices should be obtained from the manufacturer or supplier and could change based on quantity and availability. Generally, the oils within a class become more expensive as the level of processing increases to remove the ring (aromatic) structures. Another general rule is the oil’s price increases as the viscosity increases. Oil Volatility is a critical performance parameter for many applications so low volatility oils are desirable and typically cost more.

General Properties of Oil Filled Polyolefin Elastomers

Methods of Compounding of ENGAGE

Compounding of ENGAGE can be accomplished in a variety of ways including batch and continuous methods. ENGAGE is supplied in pellet form which offers better dispersion of material with lower energy input, improved material handling (eliminates the need to reduce the material from bale to flake), and the ability to use automated methods of feeding which allows the use of continuous compounding equipment.

Batch mixing of ENGAGE can be accomplished through commercially available internal compounding mixers. An upside-down mixing procedure is recommended with high oil loadings (>30%) achieved by multiple additions of oil during compounding.

Continuous compounding of POEs has been accomplished using single and twin screw extruders. It is recommended that high oil loadings >30% be made in two or more additions along the compounder to avoid flooding the extruder.

Effect of Polymer Density and Oil Viscosity

The amount of oil that can be added to ENGAGE depends on the crystallinity or density of the elastomer and the viscosity of the oil. Table 3 lists the range of oil incorporation that has been observed experimentally at 23°C for various density POEs with oil. The data shown in Table 3 should serve as a guide only. Actual values will depend on polymer morphology after processing (injection molding extrusion etc.) and the oil specific gravity. The oil incorporation limit decreases as the polymer density increases as shown in Table 3.

<table>
<thead>
<tr>
<th>Polymer Density g/cc</th>
<th>Oil Viscosity, SUS at 38°C</th>
<th>Oil Viscosity, SUS at 38°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High, &gt;600 SUS</td>
<td>Low, &lt;300 SUS</td>
</tr>
<tr>
<td>0.863</td>
<td>&lt;55%*</td>
<td>&lt;60%*</td>
</tr>
<tr>
<td>0.87</td>
<td>&lt;45%</td>
<td>&lt;50%</td>
</tr>
<tr>
<td>0.885</td>
<td>&lt;15%</td>
<td>&lt;27%</td>
</tr>
<tr>
<td>0.895</td>
<td>na</td>
<td>&lt;13%</td>
</tr>
</tbody>
</table>

*Estimates based on limited data.

A 0.87 g/cc POE will accept up to 45% by weight of a high viscosity paraffinic oil (HVP) with no signs of bleed-out at 23°C. A significant difference in the oil’s specific gravity could affect the results. The tradeoff is that physical properties decrease faster as the viscosity of the oil decreases. A 0.885 g/cc POE will accept up to 15% HVP oil by weight. The level increases to almost 30% when the viscosity of the oil decreases (LVP).

Effect of Service Temperature

The level of oil that can be added to ENGAGE will decrease as the service temperature decreases. Table 4 lists the results of studies that showed the effect of temperature on the hardness and oil loss by bleed-out.

Two of the samples bled oil within 24 hours at 0°C. This suggests a lower oil loading for 0°C service, or a higher service temperature. The data shown in Table 4 should serve only as a guide; the actual level of oil will depend on the performance required and the actual service temperature.
Table 4
Effect of Temperature on the Oil (LVP) Incorporation Limits (wt% oil in polymer)
Observed Experimentally after 24 hours at 0°C

<table>
<thead>
<tr>
<th>Polymer MI</th>
<th>Polymer MI</th>
<th>Wt% Oil Target</th>
<th>Oil Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>0.895</td>
<td>11.6</td>
<td>No</td>
</tr>
<tr>
<td>1</td>
<td>0.885</td>
<td>9.1</td>
<td>No</td>
</tr>
<tr>
<td>1</td>
<td>0.885</td>
<td>16.6</td>
<td>No</td>
</tr>
<tr>
<td>1</td>
<td>0.87</td>
<td>23.1</td>
<td>Yes</td>
</tr>
<tr>
<td>1</td>
<td>0.87</td>
<td>54.5</td>
<td>Yes</td>
</tr>
</tbody>
</table>

It has also been observed that dual density blends of ENGAGE could increase the oil incorporation limit compared to the same melt index and density single polymer.

To the f-PVC molder compounds of ENGAGE offer a 30% reduction in density, superior cold temperature flexibility and reduced gloss with favorable processing.

Effect of Oil Loading and Viscosity on Mechanical Properties

The mechanical properties of ENGAGE and oil depend mainly on the molecular weight and density of ENGAGE and the viscosity of the oil. The elongation to break typically increases as more oil is added and the tensile strength decreases. Increasing the viscosity of the oil, at the same loading, increases the tensile strength and decreases the elongation to break. Figure 4 shows some of the relationships described above.

The samples shown in Figure 4 were compression molded and cut from plaques using an ASTM D-1708 die. The test rate was 5 inches per min.

Increasing the polymer molecular weight improves the strength characteristics of the compound that has to be balanced with processability and oil compatibility limits previously described.

Figure 4. Effect of Oil Loading and Viscosity on Mechanical Properties

Effect of Polymer Density, Oil Loading and Temperature on the Durometer Hardness (Type A)

Two contour plots were generated showing the effect of POE density and oil loading on compound hardness at 23°C and –5°C. The contour plot allows quick determination of the level of oil needed to achieve a desired hardness at each temperature, using different POEs. For example, a higher density POE with oil compound would be desirable if slightly higher temperature resistance is desired compared to the same hardness non-oil-filled POE. The higher density POE compensates for the added oil and the compound still melts at a higher temperature. The higher density POE compound also solidifies at a higher temperature. This is an important property for injection molding applications.
If the base polymers have the same melt index, the higher density POE with oil process more easily. Another way to look at this is one can start with a higher density, lower melt index POE and add oil to achieve equivalent hardness. This will not sacrifice the processability compared to the higher melt index POE without oil. The increased molecular weight of the lower melt index, higher density POE will help retain the physical properties after oil addition.

Figure 5. Effect of Polymer Density and MVN Oil Level on the Hardness of a 1 MI ENGAGE Compound at 23°C

Compound hardness increases with decreasing temperature due to increased crystallinity of the POE. The compound hardness will also be affected by the change in the oil viscosity with temperature. The change in hardness due to increased oil viscosity at lower temperatures was assumed small compared to the changes noticed with increased POE crystallinity.

Figure 6. Effect of Polymer Density and MVN Oil Level on the Hardness of a 1 MI ENGAGE Compound at –5°C

Effect of Polymer Melt Index and Oil Loading on the Final Melt Index (190°C)
The effect of oil loading on the polymer melt index was determined for several grades from a 0.5 MI to a 30 MI polymer. The results of the study are shown in Figure 7.
Figure 7 shows the amount of oil necessary to achieve a desired compound melt index. For example—an application requires a melt index of 5.0. Adding 30% oil to a 0.5 MI POE or adding ~20% oil to a 1 MI POE will produce a compound with a melt index of 4.3. Again, the advantages and disadvantages of using a straight 5 MI polymer with no oil versus the oil filled polymers will depend on the final application.

The oil uptake rate (the speed of incorporation during mixing) increases as the viscosity of the oil decreases and the melt index of the POE increases.

**Effect of Oil Loading on the Low Shear Rate Viscosity (93°C)**

Oil addition reduces the compound viscosity as shown in Figure 8.

**Effect of Oil Loading on the Melting and Crystallization Behavior**

Addition of process oils will decrease the melting and solidification temperatures compared to the non-oil filled POE and lower the Tg (glass transition temperature).

**Table 5**

<table>
<thead>
<tr>
<th>POE</th>
<th>% Oil</th>
<th>Tg, °C</th>
<th>Tm, °C</th>
<th>Tc, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 MI, 0.87 g/cc</td>
<td>0</td>
<td>–53.8</td>
<td>59.5</td>
<td>46.4</td>
</tr>
<tr>
<td>MVN</td>
<td>10.5</td>
<td>–60.73</td>
<td>58.26</td>
<td>44.9</td>
</tr>
<tr>
<td>MVLN</td>
<td>32.5</td>
<td>–64.81</td>
<td>56.37</td>
<td>40.0</td>
</tr>
<tr>
<td>MVLN</td>
<td>46.3</td>
<td>–67.71</td>
<td>55.50</td>
<td>36.9</td>
</tr>
<tr>
<td>MVP</td>
<td>11.4</td>
<td>–57.62</td>
<td>57.90</td>
<td>45.1</td>
</tr>
<tr>
<td>MVP</td>
<td>32.6</td>
<td>–64.52</td>
<td>56.74</td>
<td>41.3</td>
</tr>
<tr>
<td>MVP</td>
<td>46.6</td>
<td>–65.0</td>
<td>55.78</td>
<td>38.6</td>
</tr>
</tbody>
</table>
**Dual Density Blends**

The ability to oil extend ENGAGE can be increased by using a blend of lower and higher density POEs. The effect is illustrated in *Figure 9*.

*Figure 9. The Ability to Oil Extend*

![Graph showing oil loss in blends](image)

*The compounds were produced on Haake system 90 torque rheometer.*

The single component 1MI, 0.885 g/cc POE shows signs of oil loss at room temperature when the oil loading reaches approximately 23 wt%. The same MI and density blend of POE’s does not show any signs of oil loss until approximately 40 wt% of a LVP oil. This technique also provides faster set up times and reduced cycle times in injection molded parts compared to non-blended ENGAGE based compounds. Other improvements in the physical properties of the dual density blend compound include higher service temperature and improved abrasion resistance.

**References**

US Patent 6005053—Dual Density Blends  
Sunoco Product Literature  
Shell Lubricants Product Literature  
Witco Corporation (now Crompton) Product Literature  
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