Evaluation of rubber process oils in winter tires

By Mika Lahtinen

Kamyr Alavi, Patrik Salomonsson, Herbert Fruhmann and Anna Eriksson

Nynäs A.B.

Performance improvement of tires has led in recent years to huge steps in the development of reinforcing fillers, tire polymers and their coupling to each other. Tire oils, however, have sometimes been overlooked in tire compound development. Oil is often one of the best tools in improving the winter and all-season tire performance. It is often used in large quantities and in many different tire compounds, and it has a significant effect on most compound properties such as mechanical strength and stiffness, processing performance, and dynamic behavior.

Research and development of winter tires require experience and time. Often a lot of luck is also needed in tire testing as weather conditions during testing may affect significantly the results and schedules. Winter tire development is to a large extent relying on dynamic mechanical analysis (DMA) of tire tread compounds. It is often justified as winter traction is one of the materials that are used in winter tires, and they meet the European tire oil legislation’s requirements for the low temperature of about -7°C. Braking distance on ice and snow at a testing temperature is not.

Naphthenic tire oils are often favored as they are known to be used in winter tires, and they all meet the European tire oil legislation’s requirements for the low temperature of about -7°C. Braking distance on ice and snow at a testing temperature is not.

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### Evaluation

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**SPECIAL REPORT—Process Oils**

**Table 4:** Results from snow and ice braking tests.

<table>
<thead>
<tr>
<th>Tire 1 (Naphthenic Black Oil)</th>
<th>Tire 2 (TDAE)</th>
<th>Tire 3 (RAE)</th>
<th>Tire 4 (Heavy Naphthenic Oil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Snow braking distance (m)</td>
<td>9.10</td>
<td>9.09</td>
<td>9.45</td>
</tr>
<tr>
<td>Ice braking distance (m)</td>
<td>10.80</td>
<td>11.07</td>
<td>11.42</td>
</tr>
<tr>
<td>Snow braking index</td>
<td>100.0</td>
<td>100.1</td>
<td>96.3</td>
</tr>
<tr>
<td>Ice braking index</td>
<td>100.0</td>
<td>98.2</td>
<td>98.3</td>
</tr>
<tr>
<td>Dynamic tensile modulus at -25°C (MPa)</td>
<td>84.7</td>
<td>97.1</td>
<td>126.8</td>
</tr>
<tr>
<td>Tan delta at -25°C</td>
<td>0.282</td>
<td>0.290</td>
<td>0.370</td>
</tr>
</tbody>
</table>

**Table 5:** Wet traction and RR test results.

<table>
<thead>
<tr>
<th>Tire 1 (Naphthenic Black Oil)</th>
<th>Tire 2 (TDAE)</th>
<th>Tire 3 (RAE)</th>
<th>Tire 4 (Heavy Naphthenic Oil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet braking index</td>
<td>1.41</td>
<td>1.42</td>
<td>1.32</td>
</tr>
<tr>
<td>RR</td>
<td>6.54</td>
<td>9.78</td>
<td>8.53</td>
</tr>
<tr>
<td>RR rating</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
</tbody>
</table>

**Table 6:** Recipe and variables in the ESBR study.

<table>
<thead>
<tr>
<th>Material</th>
<th>High PHR</th>
<th>Mid PHR</th>
<th>Low PHR</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESBR, Buna SE 1500</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Carbon Black, N234</td>
<td>90</td>
<td>75</td>
<td>60</td>
</tr>
<tr>
<td>Nylax 4700</td>
<td>40</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.5</td>
<td>1.75</td>
<td>1</td>
</tr>
<tr>
<td>CBBS, Vulkanit CS</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Vulkanit ZBEC</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>6PPD, Vulkanit 4020</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>TMQ, Vulkanox HS</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Wax, Anslina 654</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

The compound recipe for ESBR compounds can be seen in Table 2. The variables were statistically varied with maximum and minimum values with the addition of three midpoint formulations that helped to describe the validity and reproducibility of the test series. A tool was then created using Simca P and M0dulie 10.1.0 software. The goal was to use a run to minimize the systematic error that could potentially disturb the result of the measurements and analysis of the data.

**Results and discussion**

An essential feature of all season and winter tires is their traction in cold winter weather. The driver needs to control the vehicle even if there is a sudden change in weather conditions and only moderate or poor traction.

Winter tire requirements differ remarkably from summer tires: tread compounds need to remain soft and rubbery at extremely low temperatures. It, however, should exhibit sufficient stiffness when the temperature gets again higher and road surfaces are again dry.

In a typical DMA of tire tread compounds, Tg of both polymers and oils affects the dynamic behavior of rubber. Higher Tg leads typically to a higher compound viscosity. The difference between rubber compounds with different Tg is often found in the modulus at low temperature, the better the traction. The higher the modulus at low temperature, the better the traction.

Naphthenic black oil was used as a plasticizer in the recipe development window. To create the model, emulsion- and solution-polymerized styrene-butadiene rubber (ESBR and SSBR, respectively) based compounds were prepared again using a 1.5 liter intermeshing mixer at Deutsches Institut für Kautschuk. SBR/BR ratio, filler loading, plasticizer/resin ratio and content of sulfur were varied in a relatively large window in the compounding.

Rubber properties were determined in a similar manner to what was done in the other part of the study. Naphthenic black oil was used as a plasticizer in the compounding.

Wet traction and RR results are presented in Table 2. It can be seen that correlation of tensile stress with winter traction is poor. Shear modulus at -25°C has a good correlation with winter traction, and with ice traction in particular.

In many regions and countries such as the U.S. and South Korea, there are four seasons, but they are very common. Consumers have just one set of tires, so there is no need to change tires in the fall and again in the spring. The tires, however, should perform well in all temperatures and weather conditions.

With naphthenic oils the traction at the most difficult conditions is improved. Therefore, they provide an excellent tire compounding tool to manufacturers of winter and all season tires.

In this study we looked at typical tread compounds used in the industrial compounding, as well as selected properties of compounds that are presented in the typical compound. Target values for Shore A hardness, modulus at 300 percent extension and dynamic modulus and complex modulus are determined prior to the compounding. Traction in winter conditions is strongly affected by the compound hardness, and thus identical hardness was targeted for each compound.

In addition, a typical drawback of excellent winter traction is a lack of sufficient stiffness and slow steering response on dry and warm roads and a high driving speed. Therefore, a target was set for moduli in both static and dynamic conditions.

The moduli and hardness of compounds indicated that scale-up from laboratory mixer to a production-scale mixer was successful. Target values for Shore A hardness and static and dynamic moduli were obtained. In addition, differences in compound viscosities and curing rates were small, so processing yields to tire tread rubber is equivalent without any problems. Tires were built in several different sizes to get extensive data about how they perform in real road conditions mounted to both smaller and larger vehicles.

Results of snow and ice braking tests are shown in Table 4. Braking performance was also indexed using naphthenic black oil as a reference. Dynamic stiffnesses of tread compounds are presented in the same table. As expected, the higher stiffness of RAE compound at low temperature led to longer braking distances on both ice and snow. It took place even if oil content was the highest in RAE tire. The three other oils exhibited significant differences in braking. Their weather corrected braking distance was within centimeters.

In the winter conditions, there were larger differences in performance. Naphthenic oils and especially the heavy naphthenic oil were 6 percent worse than heavy naphthenic oil. One can certainly argue what is a significant difference in a braking test.

In the testing conditions (20 km/h to 5 km/h) the difference between heavy naphthenic oil and RAE was only 70 cm. At any higher speeds such as 60-100 km/h, which are common in Northern Europe even in the harshest winter conditions, the difference would be several meters and better performance might save lives. An experienced winter tire compounder would thus definitely welcome this approach.

In the literature and in tire confer- ences the most commonly used winter performance predictor is tensile stress of tread compound at -25°C. Only recently, dynamic stiffness has become more common. The compound recipe for ESBR compound properties. The compound recipe for ESBR compounds is often concluded from established studies is often concluded from test results and correlations are typically not shared.

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Evaluation

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compound recipes. Yet it might be even more fruitful to develop compounds which are not modified as often as tread compounds (e.g. sidewall or steel cord rubberizing compound). Main raw materials in them may remain unchanged from one tire generation to another, and creating a model would enable optimizing easily the desired properties for each tire generation. Both ESRB and SSBR based compounds were studied using an n-1 factorial analysis. A series of compounds was prepared with varying contents of the raw materials shown for ESRB in Table 6. The n-1 factorial analysis helped to reduce the number of compounds needed to create the model to 19. The software calculated a run order to minimize the variance error that could potentially disturb the result of the measurements and analysis of the data.

When the 19 rubber compounds had been prepared, the SIMCA method was used in creating the models. SIMCA is a classification technique that minimizes assumptions about the linearity of relationships between descriptors within and between classes. All responses were analyzed one by one to find the most preferable setting. The OPLS loading plot (Fig. 1) can be interpreted by drawing a line from the response of interest through the origin, and then the line should be looked upon as a seesaw. The farther away the factors are from the origin, the more significant the contribution. Factors that lay close to the line have a greater impact.

The study was extensive, and only selected data are presented in this paper. A typical SIMCA result plot is shown in Figs. 2 and 3. In the bottom left chart, the effects of variables on tan delta and dynamic modulus of ESRB compounds are shown. Significance of variable can be assessed by looking at the size and sign of the columns. For instance, as can be seen in Fig. 2, increasing oil content reduces tan delta slightly at -25°C. On the other hand, increase of sulfur loading increases tan delta, i.e. improves winter traction.

Reliability and reproducibility of model can be concluded from the chart in the top right corner. The green column B2 gives information of how well the data fit the model and the blue column Q2 about how accurately an unknown value can be estimated. Both of them are high, so the model is good.

Yet increasing sulfur leads almost certainly to increased compound stiffness— and thus loss of traction in wintry conditions. It indicates that tan delta is not a good predictor for winter traction. The result is evident in line with tire test results and compound property measurements carried out using the tire test compounds.

In a similar manner, ESRB SIMCA plot for dynamic modulus indicates that higher carbon black loading increases dynamic stiffness. It is naturally the expected result: higher filler loading reduces winter traction.

Conclusions

Nynas’ tire test program confirmed that naphthenic black oil and heavy naphthenic oil can improve tire performance. Winter traction improvement was achieved without compromising any other part of tire performance.

Improvement of traction compared with RAE might even save lives in harsh winter conditions and moderate to high driving speeds. It also was found that tire oils can affect rolling resistance of tires and therefore improve the fuel efficiency of vehicles.

Multivariate analysis technique may save time and investments needed in rubber compound development. The relatively small amount of work enables testing a model that can be used to estimate compound properties of any rubber formulation within the selected compounding window.
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