Combining performance and sustainability in truck tires

By Federico Grasso, Piera De Marco, Fabio Bacchelli, Barbara Pellizzari, Giovanni Cuder, Thomas Wu and Salvatore Coppola
Versalis S.p.A.

Fuel expenses are one of the major costs encountered by the trucking industry. In recent years, many modifications have been implemented to make trucks more energy efficient. Furthermore, in particular, better fuel efficiency is being attained by implementing a more aerodynamic design, which offers a lower coefficient of drag. Improved fuel efficiencies can also be attained by designing tires capable of providing less rolling resistance.

In order to reduce the rolling resistance of a tire, rubber compounds having high rebound can be used in making the tire treads. It has also been found that the rolling resistance and tire wear characteristics of truck tires can be improved by using a dual-filler approach and by incorporating specifically designed raw styrene-butadiene rubber, with a significant reduction of natural rubber in the tread recipe.

The traditional problem associated with this approach is that the tire wet traction and skid resistance characteristics are typically compromised. In order to balance these two viscoelastic properties, the mixtures of various types of synthetic and natural rubber are normally used in tire treads. However, such blends are not completely satisfactory for all purposes.

Moreover, present and upcoming regulations for reducing greenhouse gas emissions are requiring national authorities to significantly limit CO2 emissions and tire producers to improve tire traction properties. The reduction of rolling resistance, included in the regulation represents an important aspect of sustainability, which helps to reduce fuel consumption and related emission.

In this frame, the market of industrial and truck tires also requires a performance improvement, together with the development of polymers able to reduce the impact of natural rubber.

Besides the improvement of polymer performance, a major challenge for rubber and tire makers is the replacement of process oils following the ground-breaking European legislation to ban Polymeric Aromatic Hydrocarbons. In this frame, Versalis is following a “go green” strategy looking for new sources of materials that are derived from agricultural or sustainable feedstock.

The use of biomaterials may offer several benefits, including reduced dependence on foreign oil, competitive pricing, improved environmental footprint and optimized performance.

Experimental

Natural rubber, a commercial CV60, synthetic rubbers used for producing tread compounds, are Versalis commercial grades (Europrene). Polymer properties are summarized in Table 1. In particular, SOL R 71420 is a functionalized solution SBR designed for carbon black compounds, while Intene C30 is a star branched low-cis lithium BR obtained by continuous polymerization and specifically designed for tires. In order to debate on the macromolecular characteristics of raw SBR grades, a DMA test in torsion was applied, using an Anton Paar Physica MCR rheometer.

Test temperature was set to 110°C and the measurement was carried out in the range of frequencies 0.01-100 rad/s in strain control mode, to respect the linear viscoelastic limit of the materials. Frequency sweep curves were further extended in the frequency sweep curves were further extended in the range of frequencies 0.01-100 rad/s in strain control mode, to respect the linear viscoelastic limit of the materials.

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tended to lower frequency decades by apply-
ning a 60°C rubbery test with the MCR rheometer, at the same temperature. Creep data were then converted to visco-
estatic modulus (storage and loss modulus) by using Schwarzl relationships. A new generation of bio-sourced plastics obtained from vegetable feed-
stock and commercialized under the name Matrilox-brand, is reported in the present paper. The polyols are produced through a bio-refining process by Matrica, a joint venture between Versa-
lis and Novamont, a major player in the bioplastics market.

Matrix PF grades have been specifically
designed for the tire and rubber industry with the aim of partially or totally replacing oil of fossil origin. Matrilox vegetable oil derivatives are based on a complex mixture of triglycerides and esters of polyols, compr-
isng allogenic structure of the type R2-O-(C(O)-R3)-O-C(O)-CH(2)-O-R2, where R substituents are C2-, C4-, C6- carboxylic acid resi-
dues and alkyl groups. Part of the residual carboxylic acid component is esterified with monohydric alcohols.

Naphthenic oils with different glass transition temperature were kindly sup-
plied by Nynas. Oil properties are report-
ed in Table 2.

Rubber compounds were prepared in three steps by dry mixing using a labo-
atory internal mixer (50 cc) equipped with Banbury rotors. The adopted truck tread formulation for medium severity service is reported in Table 3. Physical and mechanical data of rubber compo-
nounds were measured according to ASTM or ISO standards.

Dynamic-mechanical measurements on vulcanized specimens were per-
fomed using a torsional har geometry in the temperature range -130 to 100°C, at 1Hz oscillation frequency and 0.1 percent dynamic strain. Rolling Resis-
tance index was determined at 60°C, 10 Hz, 5 percent strain.

Results and discussion

Frequency sweep data of raw polymers are arranged in Fig. 1 to represent a reduced Van Gurp-Palmen plot. This plot representation is widely adopted in the literature as a valuable way to identify the material response, inde-
pendently of test temperature, relax-
ation time, chemical composition and average molecular weight.

This approach was deeply investigat-
ed in a previous work, with solution SBR and emulsion SBR of significantly dif-
f erent macromolecular structure. In the reported picture, the phase angle δ is represented as a function of a normal-
ized rheological parameter, namely the ratio of the complex modulus |G*| and the rubbery plateau modulus. For values of the x-axis<1, the phase angle δ is significantly lower for materials with enhanced elastic properties. In the present case, SBR polymers feature very dif-
f erent macromolecular structures. The curves of SOL R C2525 and SBR1500 are quite distant one from the other, as a con-
sequence of the different relaxation spec-
trum. That is mainly due to the polymer-
ization technology, which ultimately entail different architectures in terms of both molecular weight distribution (broader for SBR1500) and presence of branching (nearly absent in SOL R C2525).

On the contrary, the curve relating to the hatch polymerized S-SBR (SOL R 71420) is showing two local peaks on the right hand region of the graph. Such behavior is due to a bimodal polymer structure featuring a combi-
nation of linear molecules with star-
branched chain population.

A representation of mixing efficiency is shown in Fig. 2, where the Mooney torque of the final compound is reported, together 
with the normalized Mooney variation between polymer matrix and compounded rubber. The latter parameter is calculated according to the following equation: (Mooney compound - Mooney polymer) / (Mooney polymer + Mooney compound). Therefore, it indicates the percentage increase of Mooney due to the com-
pounding step with respect to the poly-
mer itself. Because of the lower amount of BR (10 phr) variations related to the change in mixing efficiency between low-cis and high-cis polybutadiene can-
not be properly addressed. Compounds are then classified based on different combinations of polymers and different types of plasticizers. According to Tokita and Pliskin, the lowest viscosity is observed for the Mooney containing emulsion SBR, characterized by a very broad molecular weight distribution, while the fn-SBR, produced through batch technology with a very narrow molecular weight distri-
bution shows higher Mooney compound.

Part of this gap is recovered using low Tg oils, namely the bio-sourced PF801R (finite value comparable to that of contin-
uous S-SBR) and the naphthenic Nytex 810. Despite the low viscosity, no partic-
ular issues were observed during the oil feeding step. To be pointed out is that the compound containing Matrilox PF801R shows a Mooney variation be-
tween SBR matrix and final compound very close to that of the mixture contain-
ing SBR1500, accounting for a superior plasticization ability.

The formulation based on the continu-
ous S-SBR is characterized by the less

### Table 1: Polymer properties. Synthetic rubbers are commercial grades from Versalis.

<table>
<thead>
<tr>
<th>Polymer grade</th>
<th>Mooney 1+4 (°C)</th>
<th>Tg (°C)</th>
<th>Mooney (°C)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR (10 phr)</td>
<td>60</td>
<td>-50</td>
<td>50</td>
<td>-50</td>
</tr>
<tr>
<td>NR</td>
<td>30</td>
<td>-30</td>
<td>20</td>
<td>-30</td>
</tr>
<tr>
<td>SBR1500</td>
<td>50</td>
<td>-40</td>
<td>40</td>
<td>-40</td>
</tr>
<tr>
<td>SBR1500</td>
<td>50</td>
<td>-40</td>
<td>40</td>
<td>-40</td>
</tr>
</tbody>
</table>

### Table 2: Oil properties. Matrilox PF801 is a bio-refined plasticizer. Nytex is a naphthenic oil.

<table>
<thead>
<tr>
<th>Component</th>
<th>Viscosity (mPa.s)</th>
<th>Density (g/mL)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrilox PF801</td>
<td>1000</td>
<td>0.92</td>
<td>7.5</td>
</tr>
<tr>
<td>Nytex</td>
<td>100</td>
<td>1.05</td>
<td>7.0</td>
</tr>
</tbody>
</table>

### Table 3: Truck tread formulation for medium severity service.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>phr</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrile</td>
<td>50</td>
<td>25</td>
<td>20</td>
<td>15</td>
<td>10</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>20</td>
<td>15</td>
<td>10</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Silane</td>
<td>5</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

### Table 4: Curing behavior of the investigated compounds (MDR, 160°C).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mooney polymer</th>
<th>Mooney compound</th>
<th>Mooney variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOL R 2525</td>
<td>50</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>SBR1500</td>
<td>60</td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>SBR1500</td>
<td>60</td>
<td>25</td>
<td>35</td>
</tr>
</tbody>
</table>

### Table 5: Tensile properties of the investigated compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Elongation at break</th>
<th>Ultimate tensile strength</th>
<th>Tensile modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOL R 2525</td>
<td>500</td>
<td>25 MPa</td>
<td>5.5 GPa</td>
</tr>
<tr>
<td>SBR1500</td>
<td>600</td>
<td>30 MPa</td>
<td>6.0 GPa</td>
</tr>
<tr>
<td>SBR1500</td>
<td>600</td>
<td>30 MPa</td>
<td>6.0 GPa</td>
</tr>
</tbody>
</table>

### Table 6: Mechanical properties of the investigated compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hardness Shore A</th>
<th>Rebound %</th>
<th>Tensile strength</th>
<th>Elongation at break</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOL R 2525</td>
<td>80</td>
<td>65</td>
<td>25 MPa</td>
<td>500</td>
</tr>
<tr>
<td>SBR1500</td>
<td>75</td>
<td>55</td>
<td>30 MPa</td>
<td>600</td>
</tr>
<tr>
<td>SBR1500</td>
<td>75</td>
<td>55</td>
<td>30 MPa</td>
<td>600</td>
</tr>
</tbody>
</table>
Continued from page 25

pronounced variation of the compound viscosity vs SBR matrix, not being helped by physical or chemical variables in terms of filler dispersion. Finally, a beneficial effect is obtained when switching from SOL R C2525 to SOL R 71420. This is a possible combined effect of functionalization and polymer architecture, leading to a different filler dispersion together with a different morphology of immiscible polymer phases between NR, BR and S-SBR. This latter topic will be further discussed.

Vulcanization behaviors are depicted in Table 4. Variations in crosslink density (maximum torque) are small, as confirmed by hardness, listed in Table 6 and lying in the close range 65-67 for all the investigated compounds. The compounds containing bio-sourced plasticizers (based on the same polymer blend) show some differences related to the oil chemistry. In particular, the Matrilox grade characterized by higher iodine number (PF801D) gives lower MH, as suggested in previous studies[10-11] and reported in the literature.[12-13]

During the vulcanization of rubbers in the presence of unsaturated bio-based oils, double bonds could possibly be co-vulcanized in the presence of unsaturated bio-based oils, double bonds and functional groups with common practice with vegetable derivatives. Tensile properties of the compounded rubber are listed in Table 5. As already stated, due to the low content of BR and the particular choice of a special type of low-cis-polybutadiene (Inteza C30), tensile properties of functionalized S-SBR do not significantly change by replacing the high-cis-BR with the low-cis one. The stress-strain curves of compounds containing reference naphthenic oil (Nytex 4700) are shown in Fig. 2, confirming the good performance of functionalized S-SBR and E-SBR.

A different curve is found for SOL R C2525, due to lower stiffness and slightly higher values of elongation at break (no significant difference in the tensile strength). The batch functionalized S-SBR can achieve stiffer behavior vs. the continuous one due to a combined effect of macromolecular architecture and functionalization. As it will appear more clearly in the following and as already anticipated when discussing about the normalized Mooney compound, such effect also can be due to a different distribution of SBR in the partially immiscible rubber matrix. Stress-strain curves with the same polymer matrix and various oils are depicted in Fig. 4. A slightly worse performance is observed for the compound containing bio-oil PF801D, probably due to a lower state of cure related to higher unsaturation level of the plasticizer.

Other physic-mechanical properties are reported in Table 6. It is well known that tear test may produce noisy data. In this case, using two different geometries (Delft and Die C), inconsistent trends are observed, leading to the conclusion that there is no formulation with significantly better performance. On the contrary, as expected, the DIN abrasion test shows an interesting improvement while using functionalized S-SBR and low Tg oils.

To complete the characterization, specimens of all compounds were heat aged in an air oven at 100°C for 72 hours (Fig. 5). No oil migration or exudation was observed after air aging or specimen storage for all investigated compounds, including those based on polar bio-oils. Among compounds based on low viscosity and low Tg oils, the ones prepared with Matrilox bio-sourced plasticizers show more aging stability, accounting for negligible mass loss, with results very close to the reference, containing the same polymers, but the much heavier process oil Nytex 4700.

The batch prepared with the low viscosity naphthenic oil (Nytex 810), characterized by a good performance in the previously described tests, shows worse aging resistance, most probably due to the loss of light fractions. In this frame, an important benefit of the bio-sourced product (Matrilox) is related to a decrease in the plasticizer diffusion coefficient, due to the average larger size of oil molecules, as a result of the bio-refinery process technology. Moreover, as reported by Li et al.15 there is also a possible chemical interaction of bio-oils double bonds and functional groups with compound...
pounding ingredients, leading to a reduced migration in the rubber matrix.

It is well known that polar vegetable oils like Matrixol show reduced compatibility10 with the non-polar rubber matrix and the shift of compound Tg may be shorter than expected. This remark accounts for the small differences observed between compounds containing Matrixol PP801R and low Tg naphthenic oil (Nytex 810).

Despite the different glass transition temperature of the plasticizer, the final compound Tg determined by loss modulus, is of -58.6°C and -58.2°C respectively. In Fig. 6 the loss modulus (G") is shown, in the range of temperatures related to the glass transition temperature of the compound, represented by the peak value. A shift of the peak from -57.5°C to -55.8°C can be observed when switching from high to low-cis polybutadiene. This is expected, despite the low BR content, as low-cis-BR and high-cis-BR have a polymer Tg of -94°C and -106°C, respectively. However, it is interesting to remark that the combination of low-cis-BR and Matrixol PP801R (lowest Tg among the investigated process oil) lead to the compound Tg of -58.6°C, very close to the one observed in the case of the traditional formulation containing Nytex 4700 naphthenic oil and high-cis-BR (-57.5°C).

Fig. 7 reports the comparison between SOL R C2525 and SOL R 71420 in terms of loss tangent curve (tanδ). Strong difference in the shape of the curve is observed in the peak region. Especially, in the case of SOL R C2525 the tanδ peak shows an asymmetric profile, which is not occurring for SOL R 71420. This result is in line with data reported in Fig. 8, which recalls previously published measurements15 in terms of tanδ vs temperature for unfilled S-SBR/NR compounds with 50-50 ratio.

More precisely, the authors used two different SBR grades with the same chemical composition: One continuous-polymerized nearly linear S-SBR and a batch-polymerized elastomer with a macromolecular structure combining linear/star branched population. DMA curves showed very different curves in the region of the tanδ peak.

Therein, the authors voluntarily adopted unfilled cured specimens, in order to be able to stress on differences in the morphology between partially miscible polymer phases in the compounds, the thermodynamic compatibility being the same. TEM imaging (not reported here) showed that larger domains were obtained for the continuous S-SBR together with a bimodal peak in the tanδ curve in the transition region.

On the contrary, a better phase dispersion between NR and SBR was achieved when using the batch S-SBR. Due to corresponding molecular architectures, such result is qualitative compatible with the asymmetry of the curve shown in Fig. 7 of the present investigation.

Higher performance in terms of hysteresis can be achieved when using S-SBR vs. E-SBR, as pointed out in an earlier reference. See Tires, page 28.
Tires

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early work of Kern and Futamura,14 where the authors show, in a 100 percent SBR formulation, that the hysteretic properties are strongly depending on the molecular weight of the polymer primary chain. More precisely, E-SBR results negatively affected in terms of hysteresis due to its intrinsic macromolecular structure, with S-SBR showing improved performance in terms of rolling resistance, traction and wear properties. Based on this, hysteretic properties of S-SBR compounds are summarized in Figs. 9 and 10. The improvement in Rolling Resistance index (at 60°C), associated with chemical function-alization and narrow molecular weight (HBU), reveals to be helpful for adjusting processability, mechanical properties and hysteresis (Rolling resistance predictor, HBU, Rebound RT).

The addition of a low Tg safe oil (sustainable/bio-sourced or fossil/naphthenic) reveals to be helpful for adjusting processability, mechanical properties and abrasion. Among the investigated low Tg plasticizers, the highly sustainable bio-refinery grade Matrilox PF801R shows excellent thermal stability and aging resistance, together with a promising combination of other properties, for a more sustainable approach to the truck tire concept.

Conclusions
A dual filler truck tread formulation (medium severity) with increased content of SBR vs. NR were investigated. The combination of functionalized S-SBR and low-cis BR show promising results vs. traditional combinations (E-SBR/high-cis BR, S-SBR/high-cis BR), with a good trade-off between processability, mechanical properties and hysteresis (Rolling resistance predictor, HBU, Rebound RT).

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15. F. Bacchelli, S. Coppola, L’Industria della Gomma, 572 (2009), 35.

Fig. 9: Hysteretic properties of compounds of comparable composition, containing functionalized batch S-SBR and continuous S-SBR.

Fig. 10: Hysteretic properties of compounds of different composition, containing functionalized batch S-SBR.

Linglong signs agreement to build Serbian tire plant

BELGRADE—Shandong Linglong Tire Co., Ltd. has signed an investment framework agreement with the Serbian government covering the Serbian tire plant project announced in August, but the parties did not disclose details.

The agreement was signed by Linglong Chairman Wang Feng and Sinisa Mali, Serbia’s finance minister. Serbian president Aleksandar Vucic also attended the signing and, according to Linglong, said he would “fully support Linglong’s Serbian project to complete construction and start operation as soon as possible.”

The Chinese tire maker announced plans in August to build a $994 million car and light truck tire plant in Serbia’s Zrenjanin Free Trade Zone in Serbia. The construction of the Serbian manufacturing base will further develop the company’s European markets, according to Linglong.

“Direct sales from Serbian factory to OEMs and retail distributors in and around Europe will serve customers faster and more effectively and reduce logistics costs,” it added.

Linglong said the Serbian project also can promote the deeper cooperation between Linglong and some European auto makers, such as Volkswagen AG and VW’s Audi brand.

Linglong expects to start construction work on the plant—the company’s first European unit—next April. The six-year project will be completed in three phases, and at full capacity the factory will be rated at 13.6 million units a year: 12 million passenger car, 1.6 million truck/bus and 20,000 off-the-road units.

Full completion of the three phases is set for 2025.

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