TECHNICAL UPDATE





BENEFITS

- High wet traction and improved rolling resistance performance
- Improved silica dispersion
- Excellent process aid
- Compatible with a variety of common elastomers
- Abrasion resistance

TARGET MARKETS/ APPLICATIONS

• Silica tire tread compounds

ADDITIONAL INFO

• SDS: Ricon® 603

Ricon® 603 for High Wet Traction and Rolling Resistance Performance in Silica-Filled Tire Tread Compounds

Introduction

Cray Valley has developed a portfolio of products for the tire industry. Hydrocarbon resins and liquid polybutadiene resins are established as performance-enhancing additives for tire performance. The resins are used to modify the viscoelastic response of the tread compound to provide improvements to wet traction and rolling resistance of summer tires or ice traction of winter tires.

Cray Valley has developed a silane-modified polybutadiene resin, Ricon® 603, for silica tread applications. Non-functionalized additives partition mainly into the elastomer phase, while conventional silane coupling agents interact with the silica particle surfaces and elastomer phase. Silane-functional Ricon 603, when used with conventional silane coupling agents, wets the silica particle surfaces while bridging between them, without agglomeration. The result is an enhanced balance between wet traction and rolling resistance.

Materials and Tread Compound Preparation

The typical properties of Ricon 603 are presented in Table 1. The tread compounds were prepared using an internal mixer and a two-roll mill between mixing stages; recipe and preparation conditions are shown in Table 2. For the study, the controls were a low-Tg TDAE process oil (Plaxolene TD346, TotalEnergies Special Fluids) and an unfunctionalized polybutadiene resin.



Table 1: Typical values

| Resin | T _g ,°C | M _n , g/mol | Brookfield Viscosity |
|--------------------------------|--------------------|------------------------|----------------------|
| Ricon 603 | -41°C | 3500 | 18 Pa.s @ 25°C |
| Unfunctionalized polybutadiene | -40°C | 3900 | 40 Pa.s @ 25°C |

Table 2: Tire tread test formulations and preparation conditions

| Silica tread formulation (phr) - Shore A Hardness 63 ±1 | | |
|----------------------------------------------------------------|--------------|--|
| First stage: internal mixing 150-155°C / 5 min | | |
| SSBR (Buna* VSL 5025-2HM, Arlanxeo) | 75 | |
| High-cis BR (Buna® CB22, Arlanxeo) | 25 | |
| Amorphous silica (Zeosil* 1165MP, Solvay) | 60 | |
| Silane coupling agent on Carbon Black (Z-6945, Dow Corning) | 6.5 | |
| Resin or Process Oil* | 20 | |
| Second stage: internal mixing 90-100°C / 4 min | | |
| Sulfur | 2.2 (+0.3)** | |
| ZnO | 2.3 | |
| Stearic acid | 2.3 | |
| TBBS | 1.7 (+0.2)** | |
| Third stage: open mill mixing 60°C / 5 min | | |
| Homogenization and calendering | | |
| Curing: 160°C / 25 min in heated press | | |

^{*} Additive Resins (see Table 1) or Process Oil (Plaxolene TD346, TotalEnergies Special Fluids)

Tread Compound Evaluation

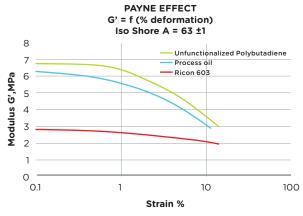
To evaluate the effectiveness of silica dispersion, elastic modulus G' as a function of strain deformation (the Payne effect) was measured by dynamic mechanical analysis (DMA Q800, TA Instruments). At low deformation, decreased interaction between silica particles results in a lower G' value, indicating improved wetting of the silica surface and better dispersion. Comparisons are provided in Figure 1.

It is common in the industry to use $\tan \delta$ as a performance indicator; a high value of $\tan \delta$ at 0°C is associated with improved wet traction and a low value of $\tan \delta$ at 60°C with lower rolling resistance. Tan δ curves of the cured silica-based rubber specimens were obtained via DMA and are shown in Figure 2.

Additionally, tensile properties and abrasion resistance were measured and are shown in Figures 3 and 4.

^{**} Sulfur adjustment on formulation with Ricon 603 to maintain iso-hardness

Dynamic Properties



Tan $\delta = f(T^{\circ}C)$ Iso Shore $A = 63 \pm 1$ - Unfunctionalized Polybutadiene Process oil Ricon 603 0.40.3 02 0.1-60 -50 -40 -30 -20 -10 0 10 20 30 40 50 °C

Figure 1: Payne effect

Figure 2: Tan δ vs. Temperature

Figure 1 shows the elastic modulus as a function of strain deformation measured by DMA. In the low deformation region, Ricon 603 has a significantly lower G' modulus which is correlated to lower silica-silica interaction. In the high deformation region, the interaction of the functional groups leads to a similar elastic modulus. Ricon 603 provides enhanced interaction with the silane coupling agent at the silica surface and can help to improve the dispersion of the silica agglomerates due to its molecular structure and silane functionality.

In Figure 2, the silica dispersion provided by Ricon 603 results in a highest dynamic response in $\tan \delta$ for the tire compound characterized by a high $\tan \delta$ at 0°C and a low $\tan \delta$ at 60°C. Following the $\tan \delta$ indicators for tire performances, the Ricon 603 leads to a high wet traction and a good fuel efficiency.

Physical properties

Effect on mechanical properties is shown in Figures 3 and 4. For a similar hardness, Ricon 603 provides a higher tensile modulus. Based on M300/M100, the compound containing Ricon 603 provides a higher interaction between the filler phase and the elastomer phase. Ricon 603 reacts with silica/silane particles via the silane functionalities and with the elastomeric phase via the poly(butadiene) unsaturation and subsequent sulfur vulcanization.

Also noted is an improved abrasion resistance when incorporating Ricon 603 compared to the unfunctionalized resin.

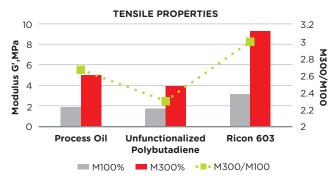


Figure 3: Tensile modulus

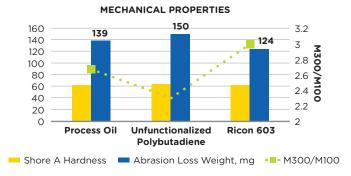


Figure 4: Hardness and abrasion

Summary

Ricon 603 provides improved silica dispersion with decreased silica-silica interaction. It was also demonstrated that Ricon 603 reacts both with silica and the elastomeric phase. These parameters lead to dynamic mechanical performance characterized by increased wet traction and fuel efficiency. Additionally, abrasion resistance is improved. These results suggest that Ricon 603 is ideally suitable for high-performance silica tire tread applications.

Appendix: Test Methods

| Property | Comments |
|------------------------------------------|------------------------------------------------------------------------------------------------------------|
| Dynamic mechanical analysis | Shear on round sample, sandwich clamp, 10 Hz frequency, 0.1% deformation (linear domain for tan δ) |
| Tensile strength and elongation at break | Tensile machine with extensometer |
| Abrasion resistance | Abrasion DIN5441 |

About Cray Valley

As part of the TotalEnergies family, Cray Valley is the premier global supplier of specialty chemical additives, hydrocarbon specialty chemicals, and liquid and powder tackifying resins used as ingredients in adhesives, rubbers, polymers, coatings and other materials. Cray Valley has pioneered the development of these advanced technologies, introducing hundreds of products that enhance the performance of products in energy, printing, packaging, construction, tire manufacture, electronics and other demanding applications.

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