



Unlocking the potential of sulfur as a reinforcing strategy in rubber compounds

By Yusheng Chen,
Frederick Ignatz-Hoover
and Jonathan Penney
Flexsys America L.P.

Rubber materials have unique properties, such as high elasticity, low stiffness and high energy absorption, making them useful in various applications, including tires, hoses, belts, vibration isolators, gaskets, seals and adhesives.¹

TECHNICAL NOTEBOOK

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However, to meet the diverse requirements of these applications, rubber materials often need reinforcement using various methods.² Addition of fillers (carbon black and silica) is a widely used reinforcement strategy due to the fillers' high reinforcing efficiencies, low costs and wide availabilities. For example, carbon black can greatly enhance the mechanical properties of rubber, such as stiffness, tensile strength, tear strength and abrasion resistance.³

Curable resins increase the modulus of the rubber material and can improve adhesion between rubber and other materials.⁴ Sulfur crosslinking strengthens rubber compounds by covalently binding together the rubber polymer chains and creates a three-dimensional network that offers enhanced mechanical properties and durability.⁵

In this paper, we will compare different reinforcement strate-

Executive summary

This paper evaluates various reinforcement strategies for rubber materials and highlights sulfur crosslinking as an optimal approach. Comparisons between fillers, resins and sulfur crosslinking reveal the advantages of sulfur crosslink in terms of modulus softening and hysteresis in rubber compounds.

Two practical tire compound examples (belt and apex) demonstrate the comprehensively balanced rubber performance with a resin system replaced with high sulfur loading. The introduction of the highly stable sulfur allotrope cyclododecasulfur (S_{12}) further addresses the limitations associated with high sulfur loading, resulting in the potential for increased sulfur loading in rubber compounds.

These research findings provide valuable insights for compounders to optimize rubber product performance.

gies and analyze the distinctions between various compounding approaches. Moreover, we will review the hysteresis effects and introduce the softening effects observed in different reinforcement strategies. Through these discussions, we aim to illustrate the advantages of utilizing sulfur crosslinks versus resins for reinforcement.

Two practical examples will be provided to demonstrate the feasibility of replacing resin reinforcement with sulfur crosslink. Additionally, a highly stable sulfur allotrope, S_{12} (cyclododecasulfur), will be introduced as a tool to unlock the reinforcement compounding strategy of sulfur crosslinking while improving processing efficiency.⁶⁻⁷

Fig. 1 illustrates a rubber formulation to compare various reinforcement strategies. The goal was to increase the modulus of the control compound by about 30

percent, or approximately 3 MPa, by adjusting the loading of resin, sulfur or carbon black. Filled rubber compounds show non-linear reinforcement behavior, that is the stiffness is strain dependent. Not only that, but some reinforcement behaviors may be transient and not reproducible.

For example, in **Fig. 2 (left)**, the RPA strain sweep tests similarly reveal that the low strain modulus of the second sweep is significantly lower than that of the first sweep. Interestingly, when comparing the difference in modulus between the first and second sweep, such as modulus at 5-percent strain, it was observed that the modulus reduction of the resin formulation was significantly larger compared to other compounding strategies. This suggests that the reinforcement network of resin has been compromised more severely than that of carbon

black or sulfur crosslinking.

Reinforcement often comes at the cost of increased hysteresis, where in tires this results in higher rolling resistance and fuel consumption. High hysteresis generates excessive heat and increases the operating temperature within dynamically flexed rubber compounds. This effect reduces fatigue life, mechanical properties and often the longevity of the rubbery material.

When selecting an appropriate reinforcement strategy, hysteresis should be carefully considered. **Fig. 2 (right)** illustrates that an increase in filler (carbon black) or resin content results in significantly higher $\tan \delta$ values (hysteresis) when compared to the control. Conversely, the use of sulfur crosslinking leads to lower hysteresis.

After considering both reinforcement softening and hysteresis factors, it can be deduced that the resin reinforcement strategy may not be the optimal compounding approach for reinforcement, especially when compared to sulfur and carbon black (although the latter may introduce more hysteresis). Thus, it could be advantageous to replace the resin reinforced network with a sulfur crosslink strategy to enhance the stability and durability of rubber compounds. Two examples are presented to demonstrate the improved rubber compound performance resulting from the replacement of resin in the tire belt and apex compounds, respectively.

Resorcinol and resorcinol-formaldehyde (RF) resin have long been utilized in the rubber industry to enhance mechanical reinforcement and adhesion performance. Despite their extensive industrial use, recent studies have identified potential health risks associated with these materials.⁸

In **Fig. 3**, the belt compound's resin network, previously formed with RF resin and HMMM, was supplanted with an additional sulfur network. The performance radar map indicates that the high sulfur loading strategy can provide comparable mechanical properties to RF resin/HMMM network. Moreover, the high sulfur compound exhibited exceptional hysteresis performance, evidenced by a low $\tan \delta$, higher rebound percent and lower surface temperature. This shows that a high sulfur

loading can effectively replace the RF resin/HMMM network and provide improved compound performance.

The use of phenolic resin and HMMM in various products has raised concerns regarding workplace exposure.⁹ Phenolic resin and HMMM have been commonly applied in apex compound formulations to enhance compound stiffness. The results in **Fig. 4** demonstrate that a high sulfur loading can serve as a substitute for phenolic resin and HMMM while providing similar mechanical properties. In a manner similar to the replacement of RF resin/HMMM in the belt compound (**Fig. 3**), substituting phenolic resin and HMMM with high sulfur loading demonstrates significant reduction of hysteresis in terms of the low $\tan \delta$.

The two examples presented highlight the potential of utilizing high sulfur loading as a reinforcement strategy to replace resin. However, it is noted that a high level of sulfur loading can potentially induce sulfur bloom, where excess soluble sulfur migrates to the surface, forming a powdery film. Sulfur blooming can result in loss of surface tack and poor interply adhesion.

Previous experiences indicate that blooming may occur when the soluble sulfur level exceeds ~0.7 wt percent in a natural rubber compound. **Fig. 5 (left)** demonstrates that loading 8 phr of insoluble sulfur (HD OT 20) into the belt compound resulted in a soluble sulfur level of 0.5 wt percent after 5 minutes and 0.9 wt percent after 10 minutes of processing time, respectively, at 120°C.

When the insoluble sulfur loading was maintained as 4 phr and a high processing temperature of 130°C, an internal rubber temperature achievable during mixing, the soluble sulfur level reached 0.9 wt percent after 1 minute. Therefore, it is imperative to introduce a more stable insoluble sulfur to leverage the benefits of high sulfur loading without the risk of sulfur bloom.

S_{12} (cyclododecasulfur) is a highly stable sulfur allotrope, with a unique molecular structure, as shown in **Fig. 6A** insert. S_{12} has low solubility in rubber compounds and a high melting point (m.p. 161°C), making it the second most stable allotrope of the sulfur family after S_8 (also known as soluble sulfur, rubber maker's sulfur).

Compared to conventional insoluble sulfur, such as HD OT 20 (m.p. 120-125°C), S_{12} 's high stability allows it to resist reversion to S_8 even at 115 °C for 15 minutes (**Fig. 6B**). DSC tests further demonstrate that after several sweeps (from 0°C to 125°C), there is almost no soluble sulfur formed, while HD OT 20 shows nearly complete formation of soluble sulfur under the same conditions.

Because of its stability, S_{12} (green) exhibits an increased re-

Fig. 1: Comparison for rubber reinforcement strategies.

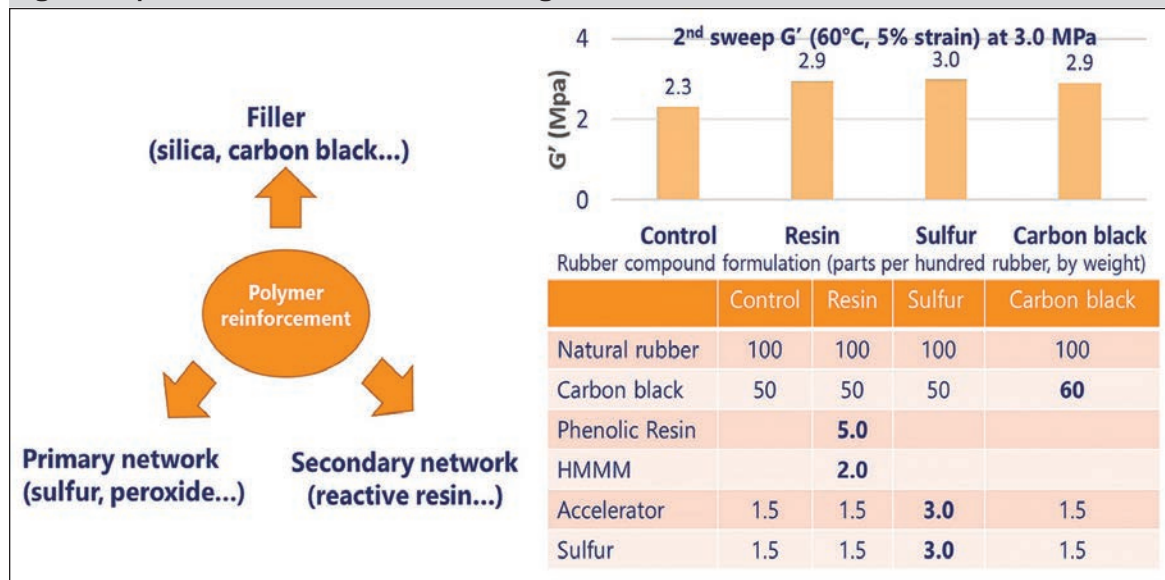
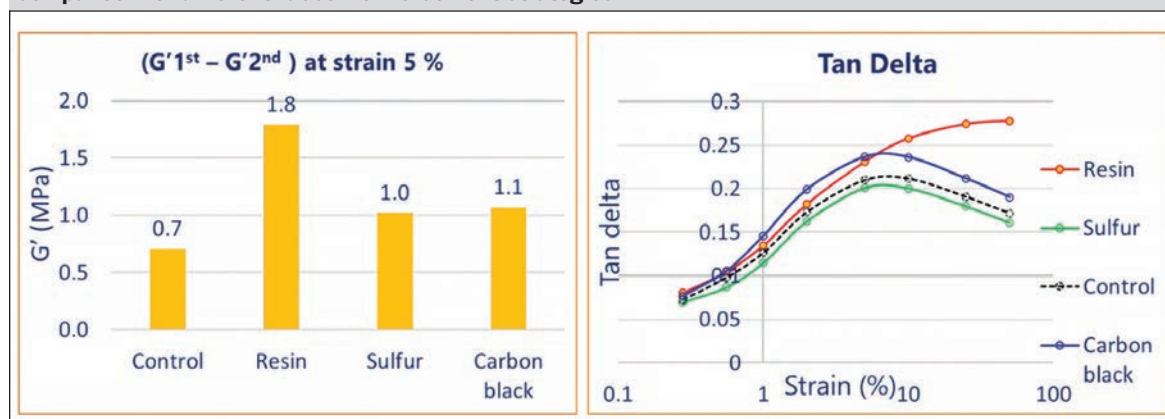


Fig. 2: At left is the modulus softening for different rubber reinforcement strategies. At right is a hysteresis comparison for different rubber reinforcement strategies.



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The authors

Yusheng Chen is a senior application scientist for Flexsys America L.P. He received his doctorate from the University of Akron and bachelor's from Tianjin University. He has 10 years of experience in the tire/rubber industry with expertise in compound design, manu-

facturing and testing.

Chen's interests focus on rubber materials research and applications, with 22 peer reviewed papers and one patent. He previously was secretary of the Tire Society and is currently serving in the Tire Society Award Committee and ACS Rubber Division Program Planning Committee.

Fred Ignatz-Hoover is a technology fellow at Flexsys America. He has more than 30 years of experience working with accelerator and antidegradant chemistry, as well as carbon black dis-



Chen

person.

Ignatz-Hoover earned his doctorate from the University of Akron. He is a member of the ACS Rubber Division and was the recipient of the Rubber Division's Melvin Mooney Award. He has served as editor of Rubber Chemistry and Technology and is an inaugural member of the Advisory Board at the Florida Center for Heterocyclic Compounds at the University of Florida, the Industrial Advisor Board for the Center of the Advanced Polymer Composites Engineering at Ohio State University, and



Ignatz-Hoover

the Industrial Advisor Board at the University of Akron's Department of Chemistry.

Jonathan Penney, a Ph.D. recipient who has been with Flexsys America for two years, has over 20 years of industrial experience in synthetic chemistry and chemical process development. For over a decade, he has been leading high-value R&D projects at various stages of the innovation pipeline. Since 2016, he has been leading technology efforts to develop and promote chemicals in the tire additives space.



Penney

Fig. 3: An example of a belt compound with a high sulfur reinforcement strategy to replace reactive resin reinforcement (RF resin/HMMM).

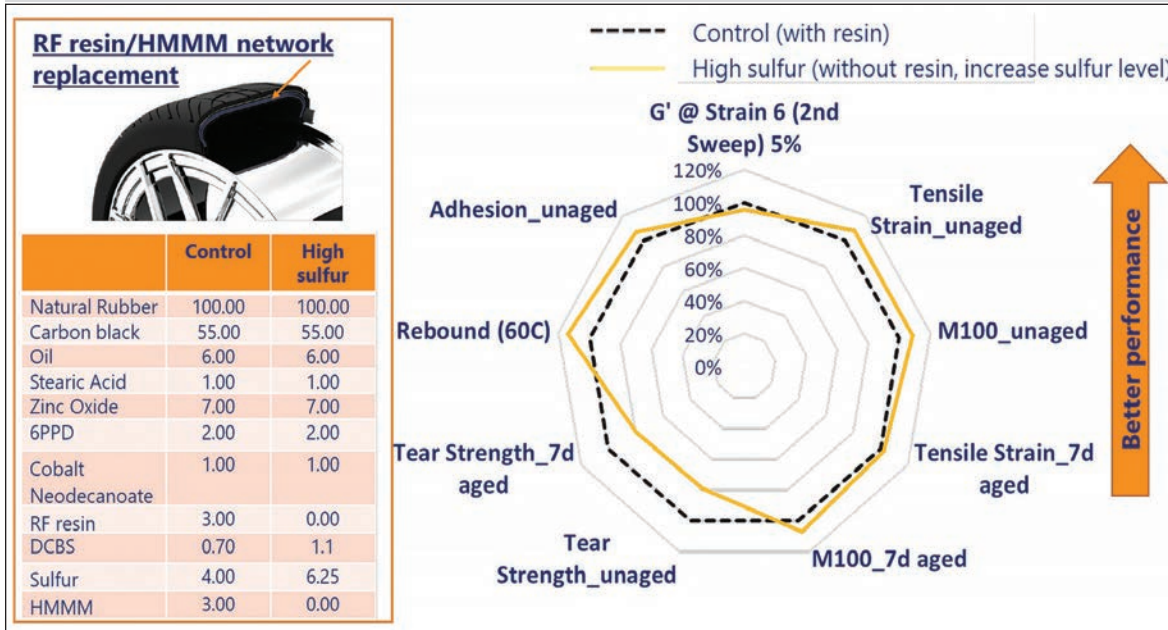


Fig. 4: An example of an apex compound with a high sulfur strategy to replace reactive resin reinforcement (phenolic/HMMM).

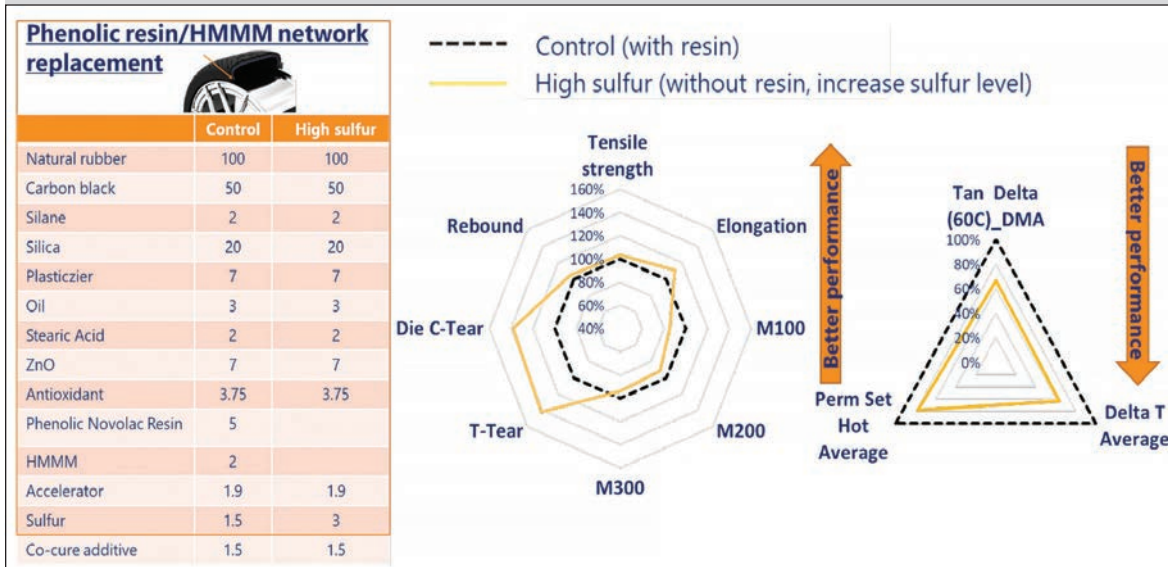
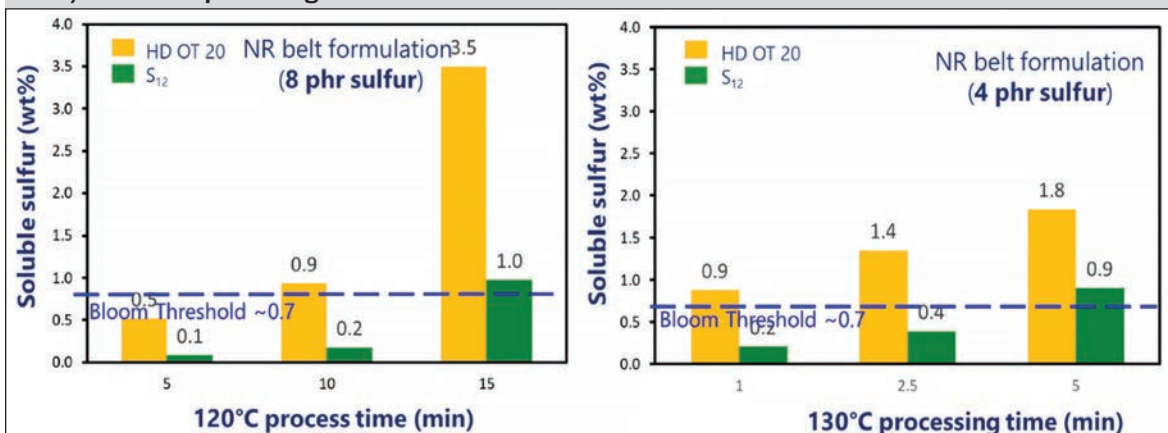


Fig. 5: RPA process simulation studies show, at left, soluble sulfur wt% for belt compound (100 phr NR/8 phr sulfur) in different processing time at 120°C. At right is soluble sulfur wt% for belt compound (100 phr NR/4 phr sulfur) in different processing time at 130°C.



stance to bloom in rubber compounds than HD OT 20 under a variety of conditions, as shown in Fig. 5. Therefore, S₁₂ is ideally suited for compounding strategies to achieve high reinforcement with lower hysteresis using high sulfur loadings.

Conclusion

This paper compares different reinforcement strategies and concludes that sulfur crosslinking may be an optimal compounding approach. Two examples demonstrate the improved rubber compound performances achievable by replacing resin with sulfur crosslinking in tire belt and apex compounds.

The utilization of S₁₂ in rubber reinforcement offers several advantages over conventional insoluble sulfur due to its exceptional stability. S₁₂ can maintain a high stability against reversion to soluble sulfur even in severe processing conditions, which makes S₁₂ an ideal component to produce highly reinforced rubbery products with improved processing efficiency.

Those results also present compounders with an opportunity to use high sulfur loading as a reinforcement strategy without concerns about blooming, thereby unlocking new applications

for high sulfur loading in rubber compounds.

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Fig. 6: (A) SEM picture of S₁₂ sulfur crystal (insert: ball and stick model of S₁₂ molecular structure). (B) insoluble sulfur weight percent surviving after 15 min. pre-warming process under 105°C and 115°C respectively. (C) and (D) DSC spectrum of HD OT 20 and S₁₂ after 6 sweeps (1st - 5th sweep, from 0°C to 125°C; 6th sweep, from 0°C to 200°C).

