A little extra

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Chemical curatives and solid fillers are present in almost every rubber formulation that’s currently used for tires. When the chemical curatives in the cure system react together during high-temperature curing, they provide dimensional stability for the final article.

“Solid fillers – for instance, carbon black and silica – impart good mechanical and dynamic properties to the rubber vulcanize,” notes Dr Ali Ansarifar, senior lecturer in the Department of Materials at Loughborough University, UK. “But there’s a better and more efficient way to use chemical curatives that offer the same kind of result – or even better.”

Ansarifar’s most recent research has focused on health, safety, cost and environmental issues related to the excessive use of chemical curatives in the sulfur vulcanization of rubber compounds. As a result, he and his team have developed a new method that measures the exact amount of chemical curatives in sulfur vulcanization for optimal effect in each type of rubber.

He argues that there are currently too many chemical curatives, at too great a concentration, in rubber formulations. He suggests this can be reduced to two or three chemicals and, in some cases, by 70-80% by weight, without compromising the rubber’s properties. “You could say that there isn’t so much the need to produce more effective or more suitable additives, rather that we should use current additives more efficiently,” he states.

New combinations
A major improvement in health and safety in the workplace and less damage to the environment, as well as lower costs, can also result from these changes. Most chemicals currently used in rubber formulations are petroleum-based, so their sustainability is uncertain. As a remedy to this and other issues, Ansarifar suggests replacing the traditional carbon black and
silica with cheaper and safer mineral fillers. “Research on the effect of mineral fillers such as kaolin (China clay) and organoclay on the properties of a range of commercial rubbers has shown very promising results. However, to make these fillers more reinforcing at high loading, which is the requirement of tire manufacturers, remains a challenge for researchers.

Our recent work has shown that when kaolin is used at very high loading in some hydrocarbon rubbers, it’s exceptionally effective as a reinforcing filler – almost as good as carbon black and silica. Fortunately all the signs are that these fillers are more cost-effective and much safer to handle than traditional fillers.”

Ansarifar suggests that industry R&D should explore more effective ways to combine additives: “For instance, when kaolin is treated with sulfur-bearing silanes, it produces a single product known as cross-linking filler. Our long-term research at Loughborough University has shown excellent results when sulfur-bearing silanized fillers are used to cross-link and reinforce rubber. For example, we saw a major improvement in the properties of some SBR/BR rubber blends for passenger car tire tread compound in spite of reducing the amount of chemical curatives in the formulation by almost 60% by weight.

“Therefore I cannot see any reason why chemical curatives cannot be either physically diffused together or chemically bound into single products. This would make their mixing with rubber a lot simpler and reduce the mixing cycle time.”

A supplier’s perspective on the additives market is provided by Colin Clarke, director of technical sales, rubber chemicals and release agents, at Schill + Selichar Struktol, which produces a range of process additive chemicals that improve the efficiency, uniformity and quality of various process steps, ranging from compound mixing to extrusion, mold flow and release.

Discussing current industry trends, he explains, “We see increased demand for functional additives, rather than simple process aids, which was the historic view of this sector. Additives should offer a benefit in terms of processability and a contribution toward tire properties.”

This, he says, has been achieved by Struktol in a number of applications, such as new peptizers that reduce NR viscosity efficiently while reducing hysteresis. “In the past lowering viscosity was often at the expense of worsening the tire dynamic properties,” he comments, “but such a compromise is no longer

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Dr Ali Ansarifar, senior lecturer, Department of Materials, Loughborough University
inevitable. This enables process efficiency in terms of mix time, the number of stages needed and even polymer blend uniformity while achieving a better tire performance, with lower heat build-up for example."

Looking ahead, Clarke predicts that changes in production technology – for instance, the wider use of continuous mixing and higher shear extrusion involving gear pumps and other technologies – will place greater demand on tire formulations. "Additives that can influence specific regions in a continuous process will be required," he suggests. "That might involve simply changing the physical form to enable automated dosing at any point in the process, or it may lead to more complex development of multicomponent additives having delayed or targeted actions."

Legislative impact
Meanwhile Mike Rowlinson, owner of Mike Rowlinson Technology, a rubber chemical market consultancy, suggests that a fundamental driver to change in the use of additives is regional legislation, which he says "is typically kickstarted by the inclusion of an additive on a 'substance of high concern' list." Indeed, legislation is currently driving changes in the use of resorcinol, accelerators (DPG) and cobalt bonding agents, to name a few. "The approach to replacement can vary from a simple modified alternative to complete replacement by using a different compounding approach."

Another key driver to change that Rowlinson highlights is the level of sophistication employed by tire manufacturers, which can include differing requirements based on mixing technology, tire-building processes and end-product requirements. "Perhaps the most exciting and technologically advanced changes," he comments, "are happening in the increasingly competitive high-value goods area. Each segment of that arena has its own specialist requirements. As these high-value segments typically offer a premium in terms of return, there's clearly more room for innovation."

With regard to high-value consumer tires, he stresses that the competition for differentiation in the UHP, winter and all-season categories is intense, especially with OE fitments where automotive manufacturers are demanding increasingly stringent targets for rolling resistance while maintaining or improving other performance characteristics.

Additives are playing an increasingly important role in enabling tire manufacturers to fine-tune performance to meet these requirements, as Rowlinson explains: "Historically an additive may have been employed to enhance an individual processing or performance property. Today they are expected to form part of an integrated system with measurable differences in multiple processing and/or performance aspects."

Examples of this can be found in specialist resins that are used to partially replace plasticizers while optimizing specific traction-performance requirements with equivalent or improved rolling resistance. "And while performance may trump sustainability in this area, there's also a drive toward the use of sustainable feedstocks."

Silane development is a good example of this multifaceted approach to compound optimization. The latest-generation silanes now offer improved processing and tire performance, while eliminating VOC emission and the need for DPG.

Rowlinson adds, "The importance of process optimization shouldn't be ignored as it also plays a role in performance modification. The combination of specialist resins and/or silanes, MANUFACTURER’S VIEW

Hendrik Stevens, head of R&D materials, for Apollo Tyres Global, presents a tire manufacturer's view on the use of key additives, suggesting developments that would benefit the industry in the coming years. He highlights the importance of accelerators, commenting, "They need to be safe for users. To this end, none of today's tire manufacturers, including Apollo/Vredestein, uses accelerators that may release nitrosamines, which are considered to be carcinogenic."

Regarding the demands placed on accelerator manufacturers, he says, "New accelerators have to offer an advantage over existing products on the market, giving a faster cure rate and better scrunch safety."

He reveals that he hasn't seen viable alternatives to sulphenamide accelerators in development in recent years. To compete, an alternative would have to offer "better scrub resistance, higher curing speed, lower cost, and be safe to handle with no health risks."

With regard to process aids, he explains that highly filled silica compounds are somewhat troublesome in processing. As a result, process aids are used to improve filler dispersion and extrudability, and decrease mill sticking. The process aids are mostly a combination of surface-active substances that improve the mixing behavior and extrusion.

Stevens adds, "For these to improve, we need to see improved extrusion behavior of compounds, smoother surface, higher extrusion speeds and better cost-effectiveness."