Coal-Derived Graphene: A Safer Antiozonant for Tires

The global tire industry is under mounting pressure to find safer alternatives to the additive 6PPD [N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylenediamine], a widely used antiozonant that protects rubber from ozone-induced degradation. Concerns have escalated following studies showing that 6PPD-quinone, a degradation byproduct, is highly toxic to aquatic life. The U.S. Tire Manufacturers Association recently conducted a Stage 1 Alternatives Analysis (AA) to evaluate functionally acceptable and technically feasible substitutes, with graphene emerging as a promising candidate.

Despite extensive research, finding a viable replacement for 6PPD remains a formidable challenge. 6PPD's self-sacrificial mechanism efficiently scavenges ozone but gradually forms harmful quinones, necessitating continuous replenishment from the tire's interior. Attempts to chemically modify 6PPD to prevent quinone formation may generate new toxic compounds.

A breakthrough may be on the horizon. In 2024, the Industry-University Cooperative Research Center for Tire Research (CenTiRe), supported by the U.S. National Science Foundation (NSF), funded a project to explore the use of coal-derived biocompatible reduced graphene oxide (rGO) as a potential substitute for 6PPD. Graphene's exceptional antioxidant and antiozonant properties, combined with its inherent biocompatibility and mechanical reinforcement capabilities, make it an attractive candidate. Leading tire manufacturers like Vittoria and Goodyear have already demonstrated graphene's benefits in enhancing speed, grip, durability, and puncture resistance, underscoring its compatibility with tire production processes.

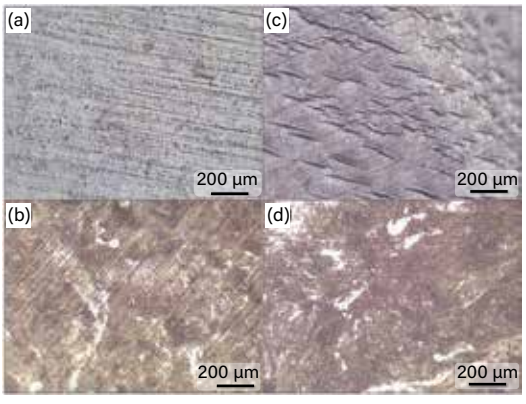
Beyond performance, this research, led by Professor Roop L. Mahajan of Virginia Tech, addresses a critical industrial bottleneck: global dependence on natural graphite, the primary precursor material for the synthesis of graphene, which is overwhelmingly controlled by China. Mahajan's team has developed a novel, environmentally friendly, and cost-effective method for producing graphene from coal rather than from graphite. This innovative process bypasses the conventional Hummers' method and enables the use of domestic coal.

The team hypothesized that coal-derived graphene — with its unique structure, including fewer layers, smaller particle size, and trace nitrogen doping — could serve as a safer and cost-effective alternative to 6PPD. Moreover, they proposed that with appropriate functionalization, coal-rGO, either fully or partially reduced, could deliver both antioxidant and antiozonant properties in tires, while simultaneously enhancing durability and grip.

Initial tests are highly promising. When coal-rGO was dispersed into a natural rubber matrix at the same parts per hundred rubber (phr) as 6PPD, it achieved approximately 80% of 6PPD's kinetic scavenging efficiency against ozone reactions. Furthermore, tire rubber coupons subjected to static ozone conditions demonstrated superior durability, attributed to graphene's gas barrier properties. By creating a tortuous gas diffusion path, graphene slows ozone permeation within the rubber matrix, effectively preventing cracks and outperforming conventional 6PPD-based formulations.

Looking ahead, the team will focus on optimizing performance by increasing coal-rGO loading, adjusting the ratio of fully and partially reduced GO fillers, and exploring different functionalization approaches. The material will be rigorously tested in accordance with ASTM standards, followed by aquatic toxicity evaluations. The ultimate goal is to develop a safe and cost-effective alternative to 6PPD — one that not only meets performance requirements but also extends tire lifespan.

Lawrence Rittman, Principal Research Scientist at American Triangle Tire Technologies, says, "This is exactly the type of research we hope to see from the university projects sponsored by CenTiRe. This work could prove instrumental in the journey to find a nontoxic replacement solution of 6PPD for the entire tire industry." CEP



◀ Here, 3D optical profilometry images of tire rubber coupons treated with 6PPD and coal-rGO are shown before (a, b, respectively) and after (c, d) ozone exposure under static conditions with 20% strain. Crack formation is observed in the 6PPD-treated rubber (c), whereas the coal-rGO sample (d) remains intact, highlighting the superior ozone resistance of coal-rGO in preventing rubber degradation.

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