

Research on Nano-Fillers for Green Tyres and Their Effect on Tyre Performance

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Abstract:

To meet increasingly stringent environmental and performance requirements for tyres, research on the application of nano fillers in green high performance tyres has continued to deepen. This paper reviews advances made in the past decade on low volatile organic compounds(VOC) silane modified nano SiO₂, graphene/carbon black synergistic thermal conductive networks and modified montmorillonite. Their interfacial construction methods, reinforcement mechanisms and macroscopic property evolution are systematically compared. Comprehensive data show that low VOC silane modified silica can suppress VOC emissions to below 20 ppm while markedly reducing hysteresis loss; graphene/carbon black networks form highly continuous heat transfer pathways that lower steady state tread temperatures by 10–20 °C while maintaining electrical conductivity and abrasion resistance; and the “brick–mortar” labyrinth structure formed by chain brush grafted montmorillonite not only strengthens barrier properties but also increases modulus retention after thermo oxidative ageing by more than 20 %. Although challenges remain in scale up dispersion processes, quantitative interfacial characterisation and cost performance balance, available evidence has verified the sustainable potential of nano interfacial synergy for green high performance tyre formulations. Future research should focus on low energy preparation technologies such as continuous exfoliation and aqueous phase modification, and establish performance prediction models linking interfacial parameters with macroscopic properties through machine learning, so as to accelerate industrialisation and improve carbon footprint assessment systems.

Keywords: Nano fillers; green tyres; low VOC; nano interface; rubber.

1. Introduction

With regulations such as the EU Ecodesign for Sustainable Products Regulation (ESPR) imposing stricter limits on tyre VOC emissions and energy consumption, upgrading tyre performance and environmental standards has become a core driver for the industry. As the only vehicle component in contact with the road, the tyre carries the entire load and transmits driving and braking forces, so its material properties and energy loss behavior directly affect vehicle efficiency. Rolling resistance accounts for 20–25 % of a passenger car's total energy consumption, and tread dynamic hysteresis contributes about 40 % of this loss [1].

During the past decade, nanoscale fillers have emerged as a promising route to dissolve these tradeoffs by tailoring interfacial chemistry rather than simply varying bulk loading. LowVOC mercapto–alkoxy silane shells grafted onto nanosilica particles have suppressed total VOC release to below 20 ppm while simultaneously lowering $\tan \delta(60^\circ\text{C})$ by 16 % and raising $\tan \delta(0^\circ\text{C})$ by 14 %, thereby expanding the safety–efficiency window without sacrificing processability [2]. Carbonblack reinforcement is easy to process but highly hysteretic, whereas the precipitated $\text{SiO}_2/\text{Si } 69$ system can reduce rolling resistance by roughly 15 % but is limited by excessive VOC emissions and reduced wet grip [3]. Parallel work on graphene/carbonblack hybrids has illustrated that replacing only 2.5 phr of highstructure carbon black with thermally reduced graphene can decrease DIN 53513 peak heat buildup from 63°C to 48°C and cut steadystate tread temperature by $10\text{--}20^\circ\text{C}$, while preserving abrasion resistance and delivering a threefold drop in volume resistivity [4, 5]. For heavyduty sidewalls exposed to prolonged service above 100°C , chainbrushgrafted montmorillonite has provided a “brick–mortar” labyrinth that reduces oxygen permeability to $1.6 \times 10^{-12} \text{ cm}^3 \text{ cm cm}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and improves modulus retention after thermooxidative ageing by more than 20 % [6, 7]. These data confirm that nanointerface design can shift the conventional “magictriangle” limits and deliver concurrent gains in rolling resistance, wet grip and durability.

Nevertheless, several bottlenecks remain. Dispersion of highsurfacearea fillers still elevates compound viscosity, and quantitative descriptors—such as effective network density or interlayer diffusion coefficients—that bridge nanoscale architecture and macroscopic viscoelastic loss are only beginning to mature. Moreover, the energy and cost penalties associated with multistep exfoliation or solventintensive surface modification must be balanced against the environmental benefits promised by lower rolling resistance and extended tread life.

Against this background, the present review adopts traditional carbonblack and precipitated $\text{SiO}_2/\text{Si } 69$ formulations as benchmarks and systematically compares three nanofiller strategies—lowVOC silanemodified SiO_2 , graphene/carbonblack synergy, and poly(2oxazoline)grafted montmorillonite. By linking interfacial architecture to rollingresistance, wetgrip and durability metrics, the review aims to quantify the performance ceiling of baseline systems, elucidate reinforcement and thermalmanagement mechanisms rooted in nanoscale synergy, and propose lowenergy, lowVOC formulations suited to future high-speed electric and heavyload applications.

2. LowVOC Silane/Nano SiO_2 Reinforcement System

About 40 % of tread energy loss for passenger tyres originates from dynamic hysteresis. Although conventional bisulphane silane ($\text{Si } 69$) cooperating with precipitated SiO_2 can lower rolling resistance, its hydrolysis and condensation release VOCs often exceeding 40 ppm, violating the 25 ppm limit set by ESPR. Furthermore, hydrophilic nano SiO_2 tends to agglomerate, producing a loose filler network and creating a negative correlation between wet grip and rolling resistance. Li et al. first introduced 20 phr nano SiO_2 into solution polymerised styrene butadiene rubber/natural rubber (60/40) and grafted it with a low VOC mercapto–alkoxy bifunctional silane [2]. After two stage vulcanisation, a dense $\sim 1.2 \text{ nm}$ silane shell formed during hydration. The Payne effect decreased from 0.33 MPa to 0.21 MPa, RPA G' at 0.5 % strain increased by about 22 %, $\tan \delta$ at 60°C dropped by 16 %, $\tan \delta$ at 0°C rose by 14 %, and VOC emissions were only 18 ppm (38 % of the $\text{Si } 69$ system). Chu et al. applied a liquid rich pre wetting plus secondary hydration strategy in the same matrix, increasing the dispersion index to 0.81, raising the wet grip coefficient by 6 % and limiting the -20°C $\tan \delta$ increment to 0.002 [3]. The complete hydration–ball–milling process followed in this study is shown schematically in Figure 1. Liquid pre wetting formed a mobile interfacial layer on the SiO_2 surface, followed by hydration induced oriented silane condensation, resulting in uniform dispersion and a dense network while maintaining the low VOC advantage, providing a feasible window for large scale wet mixing. The triple bridge formed by rubber, silane and filler strengthens interfacial bonding, and the hydrated shell suppresses self condensation and hydrogen bond reorganisation, achieving reinforcement with low heat build up while being compatible with existing industrial production.



Fig. 1 Schematic workflow for fumed-silica hydration, mixing and testing[3]

3. Graphene/CarbonBlack Synergistic ThermalConductive Tread

High structure carbon black (N330) concentrates internal heat in high speed or heavy load tyres, raising tread temperatures above 60 °C after 30 minutes of high speed cycling and triggering thermal instability. Two dimensional graphene features in plane thermal conductivity up to 3000 W m⁻¹ K⁻¹, theoretically enabling an efficient heat dissipation network, but high exfoliation energy and cost hinder industrialization. Rajan et al. replaced 2.5 phr N330 with thermally reduced graphene while maintaining total filler at 50 phr [4]. The DIN 53513 heat build up peak decreased from 63 °C to 48 °C, steady state thermal conductivity rose from 0.18 to 0.24 W m⁻¹ K⁻¹ (34 % increase), and DIN abrasion dropped from 118 mm³ to 103 mm³. Liu et al. prepared rGO/SiO₂ binary hybrid particles (1 phr rGO + 4 phr SiO₂) via a sol-gel process, incorporating them into natural rubber [5]. The hybrid particles built a “hard core/thermal bridge” dual structure: SiO₂ offered a rigid reinforcement framework and rGO provided an oriented heat transfer path. Volume resistivity decreased about threefold, thermal conductivity increased to about 0.26 W m⁻¹ K⁻¹, and after 100 °C for 48 h thermo oxidative ageing, 90 % of tensile strength was retained while tan δ at 60 °C further decreased by 4 %. The graphene/carbon black network therefore lowers steady state tread temperature to below 50 °C and supplies integrated heat dissipation, abrasion resistance and conductivity solutions for EV high speed tyres.

4. Poly(2Oxazoline)Grafted Montmorillonite for Natural Rubber Enhancement s

Heavy duty truck sidewalls and off road tyres must work for long periods at up to 120 °C, and natural rubber sidewalls fail due to high oxygen permeability. Layered montmorillonite has high stiffness and barrier properties but agglomerates in natural rubber because of hydrophilicity. Boháč et al. capped montmorillonite hydroxyls with methyltrichlorosilane and grafted poly(2 ethyl 2 oxazoline) via cationic ring opening polymerisation, achieving an 18 wt % grafting ratio and expanding interlayer spacing from 1.2 nm to 2 nm [6]. With 5 phr modified montmorillonite, tensile strength increased to about 24.7 MPa (28 % increase), modulus retention after 100 °C for 72 h thermo oxidative ageing rose by 22 %, ΔG'(0.5 %/100 %) improved by 30–33 %, and oxygen permeability dropped to 1.6 × 10⁻¹² cm³ cm cm⁻² s⁻¹ Pa⁻¹. Toiserkani and Rajab Qurchi generated quaternary ammonium/epoxy dual functional organoclay in situ in acrylated epoxidised natural rubber; 5 phr increased thermal conductivity by 17 %, retained 88 % modulus after 120 °C for 100 h ageing, and impact toughness at -20 °C decreased by only 5 % [7]. These results show that poly(2 oxazoline) brushes and dual functional modification enhance montmorillonite exfoliation and compatibility with natural rubber, providing high modulus, low permeability solutions for heavy duty sidewalls and heat resistant rubber parts.

5. Conclusion

Using traditional carbon black and Si 69/SiO₂ systems as benchmarks, this paper evaluates three nano interfacial strategies. Low VOC silane modified silica simultaneously reduces rolling resistance and VOC emissions while maintaining process viscosity; graphene/carbon black networks significantly improve thermal conductivity and suppress high speed heat build up; and chain brush grafted montmorillonite labyrinths combine rigid reinforcement with oxygen barrier properties, markedly extending high temperature service life. All three schemes overcome trade offs of conventional fillers and provide feasible material paths toward tyres with low energy loss, long durability and low emissions. Future work should continue focusing on the key role of nano fillers, enlarge production efficiency through continuous graphene exfoliation and aqueous phase clay delamination, and establish machine learning based models to predict macroscopic performance from interfacial parameters to accelerate industrialisation and refine carbon footprint evaluations.

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