



## SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> decorated with POSS units: unconventional filler systems for upgrading mechanical properties and thermal conductivity of rubber composites

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The reinforcement of elastomers by addition of inorganic filler is a practice widely exploited in tire industry. In particular, the control of SiO<sub>2</sub> nanoparticles (NPs) morphology, surface functionalities, and their networking within the rubber matrix plays a key role in achieving desired mechanical properties. Besides, the employ of high thermal conductive ceramics, like Al<sub>2</sub>O<sub>3</sub> NPs, has recently attracted the attention of researchers and companies in order to upgrade also the heat transfer in tires which, working under dynamic service conditions, experience remarkable heat build-up scarcely dissipated by the low thermal conductive elastomeric matrix. However, high filler loadings and improved filler compatibility are typically necessary this target dissipation pathways in tires, dramatically affecting the mechanical behavior of the final materials.

These considerations suggest that the utilization of fillers with tailorable structure and functionalities, able to simultaneously enhance the networking and the interaction with rubber, may be a promising strategy. In this context, polyhedral silsesquioxanes (POSS), a unique family of hybrid materials composed of a rigid core of cage-like silicon oxide and a shell of tailorable R organic groups imparting, if included in composites, a number of beneficial properties (e.g. thermal and mechanical stability), seem to be suitable candidates.

Stimulated by this background, SiO<sub>2</sub>@POSS and Al<sub>2</sub>O<sub>3</sub>@POSS hybrid filler, where oxide NPs and POSS units belong to the same functional structure, was synthesized by grafting tiny amounts of OctaMethacrylPOSS onto silanized commercial silica and alumina<sup>1,2</sup>. Upon incorporation in elastomeric matrices (SBR or PB), elastic modulus, hysteretical properties and thermal conductivity remarkably increase, even at relatively low loadings of thermally conductive filler (15-10 v/v %). These effects originate from the peculiar structure of the hybrid filler, constituted by NPs aggregates partially interconnected and decorated by POSS nanounits which, besides assuring the compatibility and interaction between the filler and the polymer host at the nanoscale, imparts an homogeneous distribution and continuous networking of the filler<sup>1,2</sup>.

The above results along with the moderately low costs of the material, foreshadow the potential application of these hybrid filler in large-scale formulations of rubber composites for tires.

### References

[1] M. D'Arienzo et al. *Mater. Chem. Front.* **2017**, 1, 1441–1452.

[2] L. Mirizzi, M. D'Arienzo et al. *Composites Science and Technology* **2023**, 236, 109977