

Sepiolite-Based Anisotropic Nanoparticles: A New Player in the Rubber Reinforcement Technology for Tire Application

Luciano Tadiello *, Silvia Guerra and Luca Giannini

Pirelli Tyre S.p.A., Research and Development, Viale Piero e Alberto Pirelli 25, 20126 Milan, Italy; silvia.guerra@pirelli.com (S.G.); luca.giannini@pirelli.com (L.G.)

* Correspondence: luciano.tadiello@pirelli.com

Abstract: Elastomer reinforcement with nanofillers has been a main rubber technology topic since the discovery of rubber vulcanization. Starting from carbon black, many researchers studied the correlations between the reinforcement of rubber and the colloidal properties of the reinforcing filler. The advent of silica allowed the experimentation of a playground of chemistries at the filler-rubber interface. In the increasing complexity of nowadays car manufacturer requests, reinforcing fillers play a pivotal role in determining the set of properties, which make a specific compound suitable for its applications. This effort of continuous improvement of rubber compound properties is pushing the tire industry towards novel solutions, and the silica/CB filler reinforcing technology will likely soon accept at least a third reinforcing filler as a major constituent of rubber compounds. While all major tire manufacturers build continuous knowledge on candidates such as carbon allotropes and 2-D nanoclays, Pirelli is paving the way for Sepiolite-derived nanofillers. Being Sepiolite naturally sourced, safe, and chemically playful, this unique 1-D phyllosilicate bears the promise of changing the game of elastomer nano-reinforcement, with the optional characteristic of giving mechanical anisotropy to the rubber compound. In this review, the historical progress on rubber reinforcement with sepiolite will be summarized, with an example of application in a commercially available Pirelli product, progenitor of the Smart-Net Silica® technology.

Keywords: nanofiller; nanoparticle; nanocomposite



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1. Introduction

As the vulcanization process is the most known chemical reaction associated with rubber, it is not the definitive method to determine the final properties of rubber goods. Elastomer reinforcement with fillers defines, together with the basic properties of the elastomeric matrix, the target application of a rubber formulation, or rubber compound. Carbon black is the most classical reinforcing filler in the tire industry, and its colloidal characteristics such as Specific Surface Area (SSA) and agglomerate particle structure represented by Oil Adsorption Number (OAN) are strictly correlated with the synthetic methodology employed [1]. Nowadays, the most industrially produced carbon black grades are standardized by ASTM and the resulting properties in the model compound are included in the standard as well; in other words, it is relatively easy to predict the mechanical effect of a certain grade of CB inside a rubber compound. The advent of silica in rubber formulations in the mid-1980s stimulated further research on the understanding of the relation between reinforcing filler characteristics and compound properties [2]. To mitigate the high level of hydrophilicity in silica, the use of a coupling agent became necessary to obtain a good level of dispersion. This also allowed the insertion of a specific surface chemistry thanks to the industrial availability of different alkoxysilanes bearing diverse functional groups [3]. The currently mostly employed silane in rubber compounding is able not only to disperse but also to covalently bind the polymer chains, allowing a further tuning of mechanical properties.

Nanoclays are also well-known raw materials in materials science [4–6] and more specifically in rubber compounding. The basic structural unit is the T-O-T sandwich of two T (tetrahedral) silicate sheets with O (octahedral) coordinated cation in between. The TOT silicate sandwich is found in several combinations in nature since the geological conditions together with the availability of specific elements yield diverse particulate materials [4]. The most common structures are lamellar nanoclays, such as bentonite and montmorillonite, consisting of 2D foils of TOT sandwiches stacks into pillared structures, with exchangeable cations balancing the TOT layer negative charge, as in Figure 1.

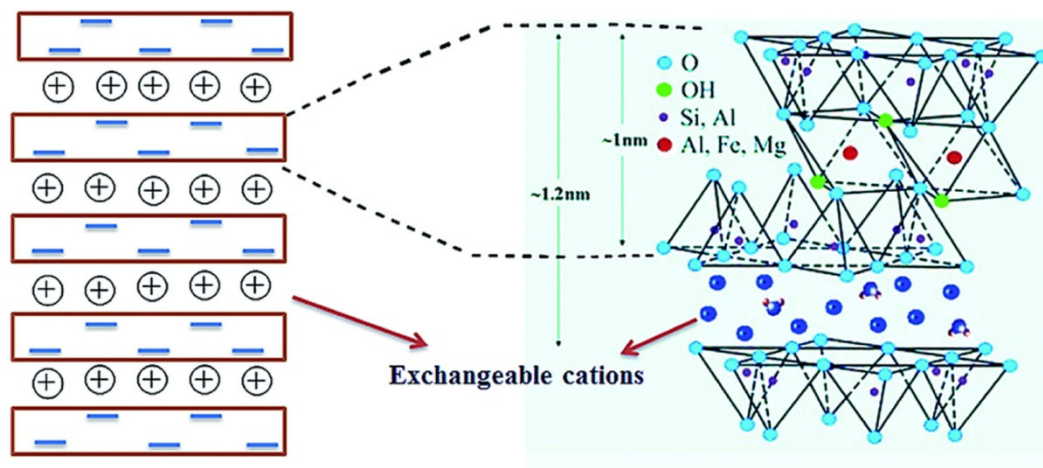


Figure 1. Nanometric (left) and atomic (right) structure of layered phyllosilicates from Ref. [7].

Lamellar nanoclays possess high specific surface area, and thanks to the presence on the surface of exchangeable cations (Na, Ca, Mg, Fe . . .) it is relatively easy to apply different chemical modifications simply by choosing adequate quaternary ammonium or phosphonium salts [4]. The industrial use of lamellar clays exploits the filler ability to reduce gas diffusion through rubber goods, thanks to the generation of tortuous paths, which hinder the permeation of small molecules. This characteristic found application in tire inner liner, but also gas masks, high pressure, and high vacuum rubber sealings, and others [8]. Another possibility for nanoclay particle shape is rod-like, among which attapulgite, palygorskite, imogolite, wollastonite, and sepiolite clays were chosen for literature studies [4].

2. Sepiolite as a Reinforcing Filler

Sepiolite is an Mg-silicate belonging to the class of phyllosilicate, differing from the others by the fact that the typical T-O-T structure is prominently elongated into one of the two directions as represented in Figure 2. These elongated platelets of TOT silicates are then fused by the edges into needle-like arrays of approx. $20 \text{ nm} \times 40 \text{ nm} \times 1\text{--}2 \text{ }\mu\text{m}$ which constitute the sepiolite primary nanoparticle structure [9]. In the native form, these nanoparticles appear strongly agglomerated into micrometric bundles, held together by hydrogen bonds. To obtain readily dispersible sepiolite nanoparticles, cation exchange with quaternary ammonium salts is the method of selection [4]. Like most of the other phyllosilicate-based clays, sepiolite belongs to the class of cationic clay, meaning that its surface is negatively charged in neutral water therefore its particle charge must be compensated by a cation. The original exchangeable cation of sepiolite is predominantly Mg^{++} , but it can be replaced with a more affine one as a quaternary ammonium organic salt (Q^+X^-). Unlike 2-D lamellar phyllosilicates, sepiolite cannot be exfoliated into its TOT original structure, because of the edge conjunction; hence, quaternary ammonium exchange results mainly in an external surface modification [10]. Since the primary particle is made of edge-bonded elongated lamellae, about half of the nanoparticle volume consists of regular microporous cavities, normally filled with coordinated water. This microporous structure is

responsible for about 2/3 of the original Sepiolite specific surface area (SSA), and quaternary ammonium salt treatment hinders access to the microporous channels and drastically reduces the measured SSA [10]. The zeolitic water might be not the exclusive guest of sepiolite microporous channels: host-guest interactions were studied for the classical case of the maya blue pigment [11] and some published work suggests that this interaction could be exploited to specifically locate functionalization at the nanoparticles tips [12].

Exchange of Sepiolite Mg^{++} cation with Q^+X^- generates a class of organomodified clays (OC) that are well studied in the literature and could be represented by the commercial material Pangel B5 produced by Tolsa. This specific sepiolite grade is characterized by a controlled shape (diameter about 40 nm, length about 1 μm , aspect ratio about 23) and modified with 25% wt of N,N-didodecyl-N-methyl-benzylammonium. Similar to other OCs, Pangel B5 is compatible with several apolar polymer matrixes [13], and since it does not tend to stack like intercalated 2-D OCs [14] it is easy to disperse. Literature reports applications of organomodified sepiolites in thermoplastics, polyolefin and rubber compositions [15–17]. Some application is also reported for non-modified sepiolite nanoparticles, particularly for waterborne compositions [18] or with polar matrixes [19].

Apart from an exchange with organic moieties, the Mg^{++} cation on the sepiolite surface can also be leached in acidulated water, transforming the surface silicate anions into silanol moieties. This simple yet powerful approach allows generating a silanol-rich surface, which can be consequently modified by reaction with silane coupling agents [20]. Bare sepiolite is easily dispersible but has a poor capability of reacting with silanes [21] leaving little room for surface modification during melt mixing. The silanization ability is the key for boosting filler-rubber interaction and consequent compound properties in silica-based rubber compounds [22].

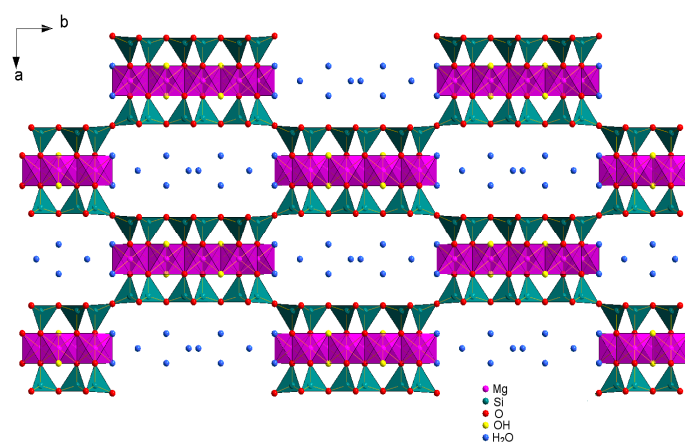


Figure 2. The crystalline structure of sepiolite, where thin phyllosilicate TOT layers are bonded by the edges in the typical checkerboard pattern. From ref. [23].

3. Sepiolite Hybrid Network Properties

3.1. Filler Network Properties

When a reinforcing filler is present in sufficient amount and it is well dispersed without zones lacking filler, a filler network is formed. Seen at the electronic microscope, it looks like a pattern of filler extended throughout the whole image, building up a single macroscopic structure out of an assembly of many nanometric particles. When a filled compound reaches the minimum concentration to form a particle network, materials properties change abruptly, and the obtained materials have hybrid characteristics between the filler and the matrix [24]. It is called a nanocomposite, because it combines the basic properties of its constituent like in macroscopic composite materials (reinforced concrete, prepegs etc.) but exploits an interaction at the nanometric level. This implies the formation of an extended interfacial area whose properties characterize the nanocomposite behavior, together with the particulate network structure.

In the effort of separating structure contribution from the interfacial behavior, few phenomenological studies attempted to correlate macroscopic mechanical properties with the nanocomposite chemical structure [25,26]. To quote one for all, the work of Payne is still considered the reference approach to explain network and interface effects on the behavior of a filled elastomer [27]. In brief, the shear modulus of a filled elastomer presents a low deformation regime (strain lower than 1% strain amplitude) where the filler network is intact and contributes to reinforcement. At the higher deformation regime (1–10% strain) the physical network contribution of the filler structure is gone, and only hydrodynamic and interface filler/rubber chemical interactions contribute to the mechanical reinforcement. The study of elastic modulus G' at low strain (G'_0) and high strain (G'_∞) allows separating those contributions which can be related to the nanocomposite structure.

The quantitative relation between particulate filler characteristics and consequent modulus enhancement is given by constitutive equations, the most popular being the Guth–Gold–Smallwood equation:

$$G/G_0 = 1 + 0.67f\varphi + 1.62f^2\varphi^2 \quad (1)$$

where, G and G_0 are the initial moduli of filled and unfilled material, respectively, φ is the filler volume fraction, the quadratic term accounts for the mutual disturbance caused by the spherical particles and f is a shape factor that allows the application of the equation to non-spherical fillers.

3.2. The Silica-CB Network

Studying reinforcement effects of different fillers proved significant structure properties relations. For instance, silica coupled with sulfurated silane, with respect to CB, interacts covalently with the elastomeric matrix, reducing the filler structure contribution to reinforcement and lowering the energy dissipation in driving conditions, known as rolling resistance. Nowadays, using different grades of commercially available silica and carbon black allows tuning the formulation properties according to a given target. Some authors pointed out that the concurrent use of silica and carbon black in rubber compounds may give non-additive or synergistic effects like reductions of the Payne effect, which would testimony for a reduced particles network strength [28]. Direct network observations with 3D TEM techniques described the Silica-CB hybrid network as formed of several interactions between silica and CB particles, without segregation of single filler islands [29].

3.3. Filler Networks with Other Nanofillers

Even with the help from the synergies between silica and CB, rubber scientist struggle to create compounds with a new set of properties, and other nanofillers have found room in both patent and journal publications. Since silica and carbon black are relatively tunable in terms of nanoparticle size and surface chemistry, promising alternatives come from non-spherical particles. Nanofiller shape effect on rubber reinforcement was modeled in terms of constitutive equations similar to the rheological effect predicted by the Guth–Gold–Smallwood equation [30] and its implication on mechanical reinforcement was demonstrated in terms of increase of static and dynamic modulus of the rubber compound [31]. Furthermore, anisotropic fillers are able to form a particulate network at concentrations lower than spherical fillers providing effective reinforcement or other additional properties like electrical conductivity, gas barrier, and others [4]. The reciprocal interactions between the network formed depend on the three key parameters of the fillers: size, shape, surface structure. For instance, lamellar organomodified clays tend to wrap around carbon black nanoparticles [32] thanks to the hydrophobic interaction but in virtue of the reciprocal shapes. In a study based on SBR/silica compounds, rod-like silica sol-gel nanoparticles showed a tendency to align into self-assembled domains [33] rather than distributing randomly, giving a measurable and effective bound rubber reinforcement effect. This occurred despite the amorphous polymeric matrix and the use of a non-orienting process such as melt compounding in an internal mixer. Similarly, rod-like silica nanoparticles

obtained by leaching of pristine sepiolite distribute homogeneously through the matrix forming self-assembled domains as seen in Figure 3. The resulting increase in bound rubber has proved a beneficial effect on compound hysteresis [34].

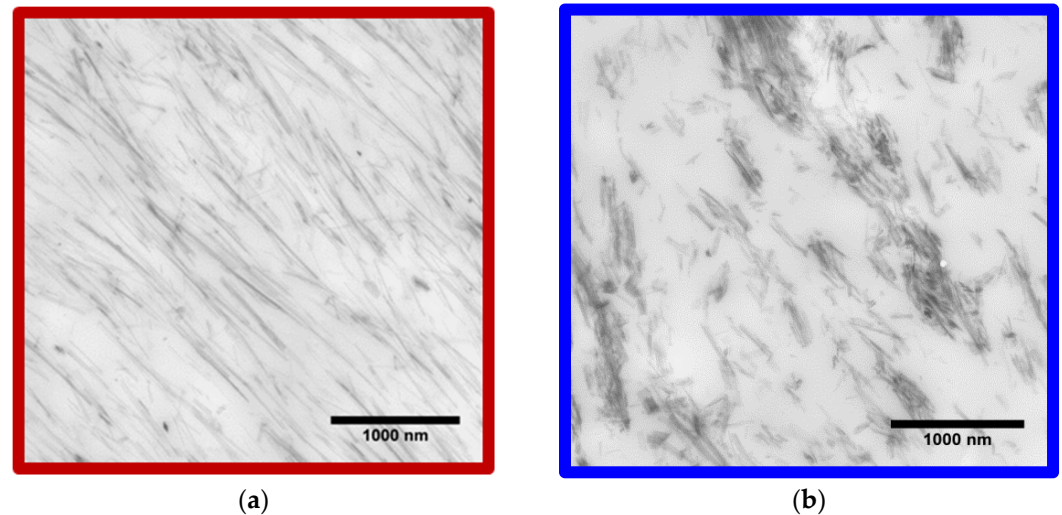


Figure 3. (a) Organomodified sepiolite (Pangel B5) as a single filler in rubber compound; (b) Smart-net Silica® featuring stronger interparticle attraction. From ref. [35].

4. Hybrid Filler Networks in Compounds for Tire Application

The effect of filler network structure is quantified with rheology and mechanical measurements and rationalized with the help of constitutive equations and models. For instance, in ref [36] the authors utilize a hybrid silica/sepiolite filler to tune the mechanical properties of natural rubber formulations. The Payne effect, or the magnitude of G' reduction upon strain, is related to the energy dissipation during the low-strain dynamic solicitation, representative of the compound contribution to tire rolling resistance. In Figure 4, the trend of G' for SepS9 and REF-SepS9 shows a lower reinforcing effect but also a lower Payne effect for SepB5 and REF-SepB5. The authors attribute this behavior to the filler network structure, which presents larger aggregated structures for SepB5 and REF-SepB5 materials, responsible for a higher stiffness on the unstrained network that eventually breaks down giving an undesirably higher Payne effect.

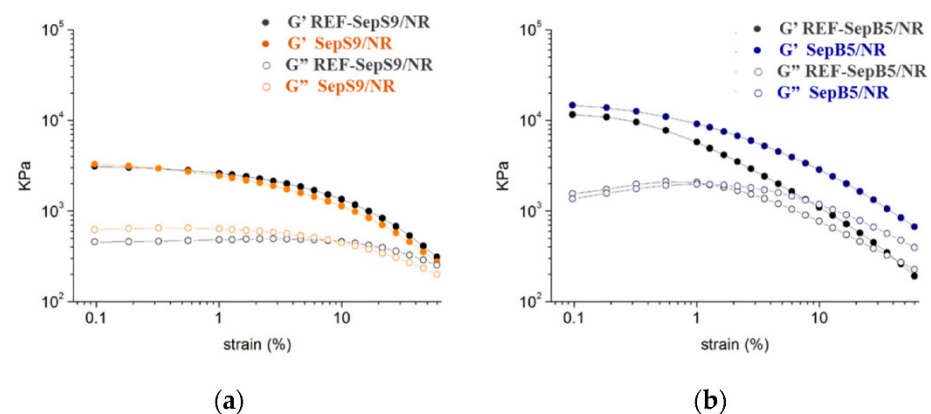


Figure 4. Strain dependency of elastic (G') and viscous (G'') moduli for natural rubber silica/sepiolite nanocomposites from ref. [36]. (a) the trend of G' for SepS9 and REF-SepS9. (b) the trend of G' for SepB5 and REF-SepB5

Compounds for tire applications shall contribute with their mechanical properties to the overall tire behavior. It is generally acknowledged that the tread compound contains the whole ‘magic’ of the tire grip on the surface, with little interest in the other components

that are supposed to have only secondary functions (e.g., inner liner compound for air retention, sidewall for ozone protection, etc. . . .). The tread compound indeed features the most demanding overall set of properties, which has increased in complexity over the last few years: the magic triangle of properties, largely reported in the tread compound literature, shall be more realistically replaced by a ‘magic dodecagon’. Nevertheless, the tire technologist understands how deep is the interaction between tread pattern, tread compound, and tire structure, and in this holistic picture mechanical properties of each structural compound are expected to play a role. For that reason, the filler or mixture of fillers used in each component determines the main mechanical indicators, in particular in a function of (1) the stability of filler network upon strain, which determine the compound hysteresis, or its capability to dissipate heat under cyclic deformation (2) the stability of the filler network in the temperature range, which is relevant for the consistency of properties in the different conditions in which the tire is operating.

The possibility of testing novel nanofillers in the particulate-filled networks of tire compounds has allowed Pirelli to discover new properties trade-off, which can become a precious development tool for the most diverse applications. This is the result of long-standing collaborations with selected universities, which allowed the development of specific knowledge and competencies to study key elastomeric materials topics that can be declined in everyday tire technologist’s work of winning rubber compounds trade-offs.

A basic example of this concept is patent application WO2012164433 [37] where a novel set of properties was claimed. The innovative formulation containing derivatives of Sepiolite together with the mixture of silica and carbon black showed a steep increase of dynamic modulus while keeping good tensile properties, as shown in Table 1. This allowed using stiffer undertread formulations for better handling performances without compromising high-speed safety. This was demonstrated on two different undertread compounds, to testify the generality of the approach.

Table 1. Properties of formulation for tire undertread taken from ref. [38].

	Reference	Hybrid
Natural Rubber	100	100
Carbon Black	63	56
Sepiolite Pangel B5		9
Tensile modulus at 100% strain (MPa)	4.5	6.5
Tensile Strength (MPa)	19.5	20.1
Elongation at break (%)	374	350
E' (70 °C, 100 Hz), MPa	16.9	20.6
tanD (70 °C, 100 Hz)	0.19	0.188

Another example is WO2014068451 [38] where the real challenge for a new filler network takes place: high modulus compounds. The apex compound is a little insert in the tire structure but with a relevant impact on driving performance and some applications demand a very stiff compound for quick response under little deformation. Nevertheless, given the peculiarities of apex compound processing, the filler mixture used shall not imply an increase in compound viscosity. Using Sepiolite derivatives inside the filler mixture allowed a significant increase in the dynamic stiffness of the component without compromising the processability of the formulation. Nonetheless, the hysteresis value remained under control, to avoid excessive heat build-up in extreme conditions. This improved hysteresis behavior resulted from the improved filler network stability under strain, which is responsible for a lower Payne effect.

The concept of temperature stability of the filler network assumes different meanings according to the specific application considered. Property stability at high temperature results in improved driving in extreme handling conditions, as for WO2014049516 [39] where Sepiolite derivatives allowed this achievement without implying any loss of struc-

tural strength or other properties correlated. Looking at the lower end of the possible tire operating temperature range, patent WO2019106562 [40] describes an application for a Sepiolite-derived material where the temperature stability of the modulus is verified over a wider temperature range, where wet, dry, and high-performance behavior can be evaluated. The use of Sepiolite derivatives provokes a decrease of compound stiffness temperature instability, keeping a high level of dynamic reinforcement, good mechanical properties, and low hysteresis in standard driving conditions, as reported in Table 2.

Table 2. Properties of tire base compound taken from ref. [41].

	Reference	Hybrid
Polyisoprene Rubber	100	100
Precipitated Silica	50	27
Sepiolite Pangel B5	5	27
Tensile modulus at 100% strain (MPa)	4.04	4.84
Tensile Strength (MPa)	21.20	21.24
Elongation at break (%)	518	492
E' (23 °C, 100 Hz), MPa	15.9	19.7
E' (100 °C, 100 Hz), MPa	11.0	14.4
Delta E' (23–100 °C), %	45%	40%

Sepiolite has playful chemistry and when its surface is specifically modified, the trade-off game moves to one of the biggest challenges of the last 20 years in tire technology: decreasing the tire rolling resistance, which represents the tire contribution to the overall car fuel consumption as a result of its interaction with the road. The study of sepiolite surface modification led to the industrialization of a family of Pirelli customized materials represented by the Smart Net Silica® registered brand. When the Sepiolite is covalently bonded to the polymeric matrix, a huge advantage in hysteresis is achieved, as testified by patent applications WO2018207068 [41], EP3289013 [42], WO2018116125 [43] that cover different applications from tread to structural compounds (Table 3). Aside from the performance indicators, the approach is environmentally sustainable and represents a strategic asset for the tire developments of the next decades, in the frame of the company sustainability approach [44].

Table 3. The use of sepiolite in hybrid networks with silica and carbon black allows reducing compound hysteresis, the main contributor of the tire rolling resistance coefficient. Filler amounts expressed in parts per hundred rubber (p.h.r.). Full recipe available in ref. [40].

	Reference	Sep Hybrid
Carbon Black	25	25
Silica	30	20
Modified Sepiolite	-	8.29
E' [MPa] 23 °C 100 Hz	8.41	8.55
E' [MPa] 70 °C 100 Hz	8.44	8.65
Tan Delta 23 °C 100 Hz	0.094	0.075
Tan Delta 70 °C 100 Hz	0.066	0.052

5. Conclusions

The use of Sepiolite derivatives seems so attractive to the tire technologist because it wins typical rubber compound trade-offs, improving diverse types of tire components. The benefits vary according to the application, from the basic compromise between stiffness versus toughness to the fine-tuning of the modulus in different temperature ranges to the decrease of compound hysteresis for reduction of fuel consumption. This all goes through the formation of a homogeneous filler network that connects the nanometric structure of the particle to the macroscopic characteristics of the compound. What is specific of

Sepiolite-based materials is the potential of obtaining mechanically anisotropic compounds thanks to the nanoparticle rod-like shape. This approach crystallizes in the Smart-Net Silica[®], a specific application in a high-performance bicycle tread compound where the compound mechanical anisotropy has a peculiar effect on tire handling. Being stiffer in longitudinal vs. transverse direction, the tire is soft on the lean and stiff on the straight, combining low cyclist effort with curve stability. The Smart-Net Silica[®] name testifies for a technology that encompasses nanomaterial to rubber compound to tire, all being held together by the particulate filler network.

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