Nanostructured SiO₂ material: synthesis advances and applications in rubber reinforcement

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Silica is a commercially significant material due to its extensive use in widespread applications and products. Synthetic amorphous silica (SAS) is a form of SiO₂ that is intentionally manufactured and has been produced and marketed for decades without significant changes in its physico-chemical properties. The industrial production of nanostructured SiO₂ is nowadays challenged by the expensive raw material use and high energy consumption. The search for non-petroleum-based fillers such as nanostructured SiO₂, which are environmentally friendly, cheap, abundant, renewable, and efficient, has been initiated nowadays. Therefore, a large number of research activities have been carried out so far for the preparation of SAS from potential alternate precursors, i.e., synthetic chemicals, biogenic, and mineral ore resources. Reinforcement of rubbers with nanostructured SiO₂ fillers is a process of great practical and technological importance for improving their mechanical, dynamic, and thermal properties. The efficiencies of SiO₂ reinforcement correlate with different factors such as filler structure, surface area, rubber–filler interactions, and filler–filler interactions with their effects. This review paper discusses the recent synthesis advances of nanostructured SiO₂ from synthetic chemicals, biogenic and mineral ore resources, their physical characteristics, and applications in rubber reinforcement, overcoming challenges. Finally, summary and future work recommendations have been mentioned well for future researchers.

1. Introduction

With the rapid emergence of the field of nanotechnology, regulations specific to nanomaterials are under development. One of the key issues hindering regulation is a lack of agreement on the definition of what constitutes a nanomaterial. Currently, the most comprehensive and internationally recognized definition of nanomaterials is presented by the International Standards Organization (ISO). The ISO definition distinguishes between two subgroups, nano-objects and nanostructured materials, and defines them as:¹ nano-objects are materials that exist in a defined singular form that have at least one dimension in the nano-scale (<100 nm), which includes nano-particles (3D in nano-scale), nanofibers (2D in nano-scale), and nano-plates (1D in nano scale). Nanostructured materials are materials that have structural features on the nano-scale but whose particle size is typically greater than 100 nm. Examples of these are materials that primarily exist in aggregated and/or agglomerated forms.

Silica is a commercially significant material due to its extensive use in widespread applications and products. The base unit of the structure of the macromolecular network nSiO₂ is the [SiO₄]¹⁻ tetrahedron. Synthetic amorphous silica (SAS) is a form of SiO₂ that is intentionally manufactured and has been produced and marketed for decades without significant changes in its physico-chemical properties. SAS is in the form of white dry powders or dispersions of these powders are used in a multitude of industrial applications, i.e., an additive in rubber. It is also approved to be used in consumer products, i.e., food, cosmetics, and pharmaceuticals. To define, SAS in powder form is a nanostructured material according to the technical specification of ISO TS 80004-1. The aggregate is the smallest indivisible unit upon dispersion. There are three types of synthetic amorphous SiO₂ produced at the industrial scale: fumed SiO₂, precipitated SiO₂, and SiO₂ gel. Of these three types of amorphous SiO₂, precipitated SiO₂, whose production started in the 1940s, has the greatest commercial importance. Precipitated SiO₂ is a finely divided white powder sparingly soluble in water and composed of aggregates up to approximately 1 mm in diameter.

The current commercial precipitated SiO₂ is produced by a wet SiO₂ production route or sol–gel process, in which an aqueous alkali metal silicate solution is neutralized with acid (e.g., H₂SO₄), releasing SiO₂ and H₂O in a reaction tank to produce a slurry of SiO₂. The most commonly used aqueous alkali silicate is water glass (Na₂O.nSiO₂; n = 2–4), which is produced by melting quartz sand with soda at about 1300 °C.² Reaction conditions are manipulated according to the particle size required. Hydrogen bonding among particles will form...
clusters or aggregates, and these aggregates may loosely bond as
agglomerates. Fumed silica [SiO₂], also known as pyrogenic
silica (SiO₂), is mainly produced by reacting any SiO₂ source
with any carbon source in an electric arc furnace at approxi-
mately 1900 °C undergoing carbothermal reduction to meta-
lurgical grade silicon, Si (met), which is then treated with HCl to
produce SiCl₄. The SiCl₄, in turn, is combusted in a hydrogen–
oxygen flame to produce fumed SiO₂ plus byproduct HCl. Both
synthetic amorphous silica commercial processes require
expensive precursor use, corrosive, toxic and polluting side
product generation, the need for tailoring properties of pro-
ducts, high-temperature and energy-intensive steps make
production processes expensive in which further synthesis
advancement has been the subject of much of the ongoing
researches. Many researchers have devoted studies to replace
the expensive source of synthetic silica with one that is cheaper
and renewable, i.e., biogenic and mineral ore resources. In
addition to this, researchers extensively worked on the promo-
tion of widespread preparation methods with an emphasis on
sol–gel synthesis parameter optimization to tailor the nano-
structured SiO₂ product physicochemical properties for specific
applications, particularly for rubber reinforcement.

Elastomers or rubbers, whether natural or synthetic, are not
usually used in their pure form due to insufficient practical
physico-mechanical properties. Fillers are extensively used in
the rubber industry to improve service efficiency and ease of
processing, and their addition results in a fundamental change
in the properties of rubber. According to the kinetic theory of
elasticity, the rubber modulus (with no fillers) increases with
the rise of temperature; the addition of fillers significantly
changes the temperature coefficient of modulus and may even
alter the sign of the coefficient, resulting in a decrease of the
modulus with increasing temperature.

Fillers are classified based on chemical composition and
their influence on rubber properties. Further, in rubber com-
ounding, they can be divided primarily into three categories in
accordance with their reinforcing effect: inactive, semi-active,
and very active. The term active signifies the degree of rein-
forcement, i.e., the influence of the filler on the viscosity of the
compound and the resulting mechanical properties. The main
characteristics that determine the reinforcing effect of fillers are
their structure and surface properties. Active fillers have a large
relative surface area and high structure, providing strong
physical and chemical interaction between the filler and poly-
mer. However, a highly active filler surface leads to strong
interparticle forces, which negatively influence the processing
behavior as a result of the agglomeration of filler particles
during mixing and storage.⁴ Common to composites’ prepara-
tion and modification mechanisms, several factors influence
the property profiles, which lie between those of pure rubber
and filler or processability. These include volume fraction,
particle dimension and geometry, dispersion quality, the
interaction between rubber and fillers or among fillers, and, if
applicable, the degree of orientation of fillers for anisotropic
properties. These factors, in turn, affect one another, and
synergy is achieved if an optimum balance is reached.⁵

The most common fillers used in the rubber industry are the
carbon family of materials (carbon black, carbon fiber (CF),
carbon nanotubes (CNTs), graphite and graphene), inorganic
particles (nanoclays, polyhedral oligomeric silsesquioxane
(POSS), SiO₂, calcium carbonate (CaCO₃), talc, zinc oxide (ZnO),
titanium oxide (TiO₂), alumina (Al₂O₃), halloysite, and bio-
fillers (cellulose, husk, wood, coir).⁶ However, the large volume
applications of rubber, certainly those involving high elasticity
and mechanical properties, including stiffness, strength,
toughness, abrasion resistance, anti-scratching property, or
friction behavior, etc., are reinforced by carbon black and
precipitated SiO₂ as the dominant fillers. Even if both carbon
black and nanostructured silica are the dominant fillers for
rubbers, the search for non-petroleum based filler and a prom-
ising efficiency for reducing the rolling resistance of rubber
nanocomposites in tire tread makes nanostructured silica an
important and economical filler in the rubber industry. The
potential of lowering the rolling resistance makes silica a
promising reinforcement in the fabrication of green tire
tread.⁹ Modern fuel-saving tire treads are commonly reinforced
by silica due to the fact that this leads to lower rolling resistance
and higher wet grip compared to carbon black-filled alterna-
tives, which may have the potential to improve tire performance
further.

Very limited review works have been reported yet on the
synthesis advances of nanostructured SiO₂ material from cheap,
renewable potential precursors and characteristic features of
SiO₂ filler for rubber reinforcement. This paper highlights the
synthesis advancement of nanostructured silica from potential
precursors with emphasis on soft template based synthetic
chemical precursors, biogenic, and mineral ore resources. The
review also describes the reinforcement of rubber with nano-
structured SiO₂ fillers due to its mechanical, dynamic, and
thermal properties and correlates with different factors like
filler structure, surface area, filler–filler, and rubber–SiO₂ filler
interactions effects on SiO₂ filled rubber nanocomposites with
the overcoming challenges, which are reported in different
works published so far.

2. Research advances for the
synthesis of nanostructured SiO₂

The widespread preparation methods, e.g., hydrothermal, sol–
gel, precipitation, etc., generally tend to yield spherical or
slightly irregular nanostructures, which may or may not be manip-
ulated to design different physical shapes (e.g., elongated
structures⁸ and rods of different aspect ratios, etc.). SiO₂ nano-
fibers have been produced by electro spinning⁹ or by chemical
vapor deposition (CVD).¹¹

The properties of SAS are strongly dependent on the
parameters of synthesis, such as the reactant concentration,
reaction temperature, time of precipitation, pH range, type and
addition of surfactants, solvents, and modes of washing and
drying. These parameters influence the development of the size
and uniformity of the SiO₂ particles, their morphology, aggre-
gation, pore dimensions and volume, and specific surface area.
These, in turn, influence the properties of the designed structures and the consideration of the properties along with the high surface area enables their use for a wide range of applications. The preparation of amorphous SiO2 nanostructures has been studied by various research groups using different categories of precursors: synthetic chemicals, biogenic, and naturally occurring mineral resources. The research efforts in these three categories are briefly discussed in the following sections.

2.1. Synthesis of SAS using synthetic chemicals

Dispersed, amorphous, and uniform SiO2 nanostructures are of interest due to their simple preparation and potential applications in various industries as they may be used as effective materials for improving the strength, flexibility, durability, workability, etc. The most common precursors used at the laboratory scale are tetraethyl or tetra methyl orthosilicate (TEOS or TMOS) or inorganic sodium silicate. Different synthetic strategies have been applied to prepare these structures: the modified Stober method,12-16 combustion techniques,17 chemical vapor deposition,18 aerosol spray,19 and emulsion20,21 methods. Various types of morphologies such as hexagonal, cubic, lamellar, and wormhole-like mesostructures have been synthesized using these methods and TEOS or TMOS as precursors. It is well-known that spherical dispersed silica nanoparticles can be prepared using the sol-gel method with TEOS or TMOS or sodium silicate precursors.

The main advantage of the sol–gel method is the control of the particle size at the nano level and morphology development of SiO2 nanostructures by changing the concentration of reagents, type of catalyst, temperature, reaction conditions, etc. Many efforts have been made to control the particle size and morphology of SiO2 nanoparticles through the use of different types of surfactants as templates. In the synthesis of mesoporous materials (such as SiO2), organic surfactant molecules play an important role in generating porosity within the building blocks and thus act as the endotemplate or structure directing agent (SDA). In this regard, the soft templating method has been the most successful pathway for the synthesis of ordered and disordered mesoporous matrices.

The SDAs can be of different types: (i) surfactants may be employed as SDA, wherein the essential feature is the coexistence of chemically bonded non-polar hydrocarbon ‘tail’ and a polar ‘head’ group in a molecule. These molecules have high molecular weight and form aggregates in the solvent to form self-assembled micelles,22-24 (ii) non-surfactant single molecules, which may or not form self-assembly bearing hydrophobic–hydrophilic groups in a single molecule, but act as templates in the design of mesopores in a material;25 and (iii) dendrimers or polymers (macromolecular single molecule having high molecular weight).26,27 All three types of templates are soft templates. Fig. 1 shows the classification of soft templates,28 some of which are used to study structure development in SiO2 nanostructures.

Different SDAs, depending on their structure and nature, have different critical micelle (CMC) values in water or solvent.29,30 Beyond the CMC values, the self-assembly of micelles occurs to form a 3D spherical or 2D rod-like array with further increasing concentration, and this self-assembly helps in pore generation (Fig. 2). These self-assembled micelles are formed by the association of individual amphiphilic templating molecules bonded through weak forces like van der Waals, hydrogen bonding, etc., but without covalent linkage between the amphiphiles.31

Thus, SDA molecules are placeholders: what becomes the void space to produce a nanoporous material. They not only allow controlling the variation of pore size but also the shape of
the pores, i.e., the total architecture of the template molecule whose size and shape are imprinted in the porous solid, as shown in Fig. 3.\textsuperscript{32}

The concentration of SDA also influences the shape and size of the nanostructures, as shown by the example of using CTAB as SDA in Fig. 4.\textsuperscript{33,34}

The hydrothermal method, actually a sol–gel process, consists of a number of steps. Initially, the formation of surfactant self-assembly occurs via the true liquid crystal template (TLCT) mechanism to form a homogeneous surfactant solution in an aqueous solvent media. Then, the silicate precursor, TEOS or TMOS or sodium silicate, is added to the surfactant solution when it gets hydrolyzed under the acidic or basic conditions to form a silicate oligomer sol. These oligomers then condense with surfactant micelles via cooperative assembly and aggregation to form an inorganic–organic hybrid, which eventually precipitates in the form of a gel. The gel is treated hydrothermally for further condensation, solidification, and reorganization of the material to an ordered arrangement.\textsuperscript{35,36} After a certain time of ageing, the resultant product is cooled, filtered, washed, and dried. The process is shown in Fig. 5.\textsuperscript{34,37} Ordered mesostructured \(\text{SiO}_2\) material is obtained from this as-synthesized solid after the removal of surfactant through calcination or solvent extraction.

Some of the research efforts using different precursors and without and with SDAs are summarized in Table 1.

2.2. Extraction and preparation of amorphous \(\text{SiO}_2\) from biogenic sources

Much of the world’s agricultural waste contains \(\text{SiO}_2\), and the search for a practical way to extract it stretches back almost 80 years. The extraction of amorphous \(\text{SiO}_2\) from biogenic sources, especially the third category of biomass, i.e., true bio-waste, which means they are generated as a byproduct of another useful resource, is a hot area of research. Research focus has and is on approaches to find the source of \(\text{SiO}_2\) that is safe,
cheap, and more environmentally friendly as an alternative to the commercial activities of production. Research efforts have involved the use of agricultural waste such as rice husk, rice straw, coffee, cane husk, etc., as precursors for the preparation of pure SiO₂ in either the amorphous or crystalline form. Table 2 shows the ash and SiO₂ content of some plants. The major biogenic source of research is rice husk and its ash. The world paddy production in 2017 was 769.65 million tons (503.6 million tons, milled basis) and is produced in many regions of the world. On average, 28% of the rice paddy is husk, giving an annual total global production in excess of 212.5 million tons. The rice husk (rice hull) is formed from hard materials, including SiO₂ and lignin, which protect the seed. Each kilogram of milled white rice results in roughly 0.28 kg of rice husk as a by-product of rice production during milling.

![Fig. 4](image1.png) Arrangement of anions around CTAB cylindrical micelle (section) (a); phase diagram of the shape of CTAB micelles, (b) structure and size development with SDA concentration.

![Fig. 5](image2.png) Stepwise formation of mesoporous SiO₂ material.
| Sl No. | Precursor                          | BET surface area (m² g⁻¹) | Particle size (nm) | Pore size (nm) and volume (cm³ g⁻¹) | Method and Details                                                                 |
|--------|-----------------------------------|---------------------------|--------------------|------------------------------------|----------------------------------------------------------------------------------|
| 1      | Sodium silicate solution          | 160.29                    | —                  | 0.57                               | Sol-gel method<br>Precipitation by HCl<br>Precipitation by H₂SO₄ at pH 4, 7, and 9 |
| 2      | Sodium silicate solution          | —                         | —                  | —                                  | —                                                                                |
| 3      | Tetraethylorthosilicate           | —                         | —                  | —                                  | —                                                                                |
| 4      | Tetraethylorthosilicate           | —                         | 60 to 100          | —                                  | —                                                                                |
| 5      | Tetraethylorthosilicate           | —                         | —                  | —                                  | —                                                                                |
| 6      | Tetraethylorthosilicate           | —                         | ~150 to 190        | —                                  | —                                                                                |
| 7      | Tetraethylorthosilicate           | 0 CTAB: 45 H₂O: 7.8        | 0.1 CTAB: 45 H₂O: 308 | 0 CTAB: 45 H₂O: size: spheres 700–800 | Sol-gel method<br>Precipitation from wet-gel<br>DTAB: 100 to 350 with an average of 212 |
|        |                                   |                           | 0.1 CTAB: 45 H₂O: 600–700 | 0.1 CTAB: 45 H₂O: size: 2.9; volume: 0.21 | Cationic surfactants<br>- CTAB<br>- DTAB<br>- TTAB<br>- CTAB |
| 8      | Tetraethylorthosilicate           | —                         | Average: 79.68 to 87.35 | —                                  | —                                                                                |
| 9      | Water glass                       | —                         | Less than 100: avg ~25–43 | —                                  | —                                                                                |
| 10     | Tetraethylorthosilicate           | Reaction parameters dependant: 515.4 to 1164.9 | — | Reaction parameters dependant<br>- Pore size: 2.7 to 4.9<br>- Pore vol: 0.6 to 1.5 | —                                                                                |
| 11     | Sodium silicate                   | —                         | CTAB: 90 to 250 with an average of 148 | —                                  | —                                                                                |
|        |                                   |                           | DTAB: 100 to 350 with an average of 212 | —                                  | —                                                                                |
| 12     | Tetraethylorthosilicate           | —                         | DTAB: ~140          | —                                  | —                                                                                |
|        |                                   |                           | TTAB: ~95           | —                                  | —                                                                                |
| 13     | Tetraethylorthosilicate           | n-SiO₂: 5.5               | CTAB: ~55           | —                                  | —                                                                                |
|        |                                   |                           | Span 60: ~80        | —                                  | —                                                                                |
Over the years, different preparation procedures have been investigated: the dry bio-digestion process involving the anaerobic digestion of rice straw to produce both bioenergy and SiO$_2$ enriched solids followed by calcination and washing to obtain high purity SiO$_2$,\textsuperscript{52,53} precipitation method (before and after calcination of the precursor),\textsuperscript{55} sol–gel process using rice husk ash as a low cost precursor and chitosan as template for the preparation of bimodal macroporous SiO$_2$ (BPS),\textsuperscript{56} pre and post strong acid leaching and alkali treatment of rice husk followed by calcination to prepare relatively pure activated SiO$_2$,\textsuperscript{57,58} SiO$_2$ gel from rice husk derived sodium silicate and neutralization by microwave heating,\textsuperscript{59} combustion of rice husk in a fluidized bed to obtain SiO$_2$ white higher in quality than that of GB-precipitated SiO$_2$ and approaches that of pyrogenic SiO$_2$ except for specific surface area and iron content\textsuperscript{60} and high-purity SiO$_2$ from rice husks using a carboxylic acid and citric acid leaching process followed by calcination,\textsuperscript{59,61} etc.

Some representative research efforts utilizing different biogenic precursors for the extraction of amorphous SiO$_2$ are summarized in Table 3.

### 2.3. Extraction and preparation of SAS from mineral ores

The extraction of SAS from mineral ores is a thematic research area with efforts aimed at developing sustainable economic processes compared to the current commercial processes, which are energy intensive and considered less environmentally friendly. The motive of the research efforts is to develop extraction and transformation processes from suitable lower cost silicious mineral ore materials, which can significantly reduce the costs of production. Silicates constitute approximately 95 percent of the Earth’s crust and upper mantle, occurring as the major components of most igneous rocks and also in substantial quantities in sedimentary and metamorphic varieties. Of the nearly 600 known silicate minerals, only a few dozen—a group that includes the feldspars, amphiboles, pyroxenes, micas, olivine’s, feldspathoids, and zeolites—are significant in the rock formation. In these minerals, SiO$_2$ exists in both crystalline and amorphous forms. The crystalline form with limited applications due to low activity is more abundant in the Earth’s crust compared to the amorphous form. Siliceous materials are either SiO$_2$-rich or silico-aluminate rich materials.

| Sl No. | Precursor | BET surface area (m$^2$ g$^{-1}$) | Particle size (nm and volume (nm$^3$ g$^{-1}$)) | Method Ref. |
|-------|-----------|---------------------------------|-----------------------------------------------|------------|
| 14    | Sodium silicate | $n$-SiO$_2$ (Span 20): 6.2 | Majority of primary particles: 15 to 30 nm; tendency to form bigger particles (aggregate) | Precipitation by oxolation with H$_2$SO$_4$ | 51 |
| 15    | Sodium silicate | $n$-SiO$_2$ (Span 40): 9.1 | Majority of primary particles: 15 to 30 nm; tendency to form bigger particles (aggregate) | Precipitation by oxolation with H$_2$SO$_4$ | 51 |
| 16    | Sodium silicate | $n$-SiO$_2$ (Span 60): 11.5 | Majority of primary particles: 15 to 30 nm; tendency to form bigger particles (aggregate) | Precipitation by oxolation with H$_2$SO$_4$ | 51 |
| 17    | Sodium silicate | Up to 110 | Majority of primary particles: 15 to 30 nm; tendency to form bigger particles (aggregate) | Precipitation by oxolation with H$_2$SO$_4$ | 51 |

### Table 2 Ash and SiO$_2$ content of some plants

| Plant | Part of plant | Ash% | Silica% | Reference |
|-------|---------------|------|---------|-----------|
| Cane  | Husk          | 08.00| 93.00   | 52        |
| Coffee| Husk          | 12.00| 93.00   | 53        |
| Bagasse| —             | 73.00| 93.00   | 52        |
| Bamboo| Nodes (inner portion) | 57.40| 81.80 | 52        |
| Bread fruit tree| Steam | 8.64| 81.80 | 52        |
| Corn  | Leaf sheath   | 64.32| 81.80   | 52        |
| Lantana| Leaf and stem | 23.38| 81.80 | 52        |
| Rice husk | —           | 93.00| 81.80   | 52        |
| Rice straw | —           | 82.00| 81.80   | 52        |
| Sorghum| Leaf sheath epidermis | 88.75| 81.80 | 52        |
| Sl. No. | Biogenic precursor | BET surface area (m² g⁻¹) | Particle size (nm) | Pore size (nm) and pore volume (cm³ g⁻¹) | Method | Ref. |
|--------|--------------------|---------------------------|-------------------|------------------------------------------|--------|-----|
| 1      | Palm oil mill ash  | pH 8.75 to 8.80; 140.75 to 79.91 pH 9.5; RT to 95 °C: 50–140 | 10.67 ± 1.44 µm | — | Sol gel precipitation Gel destabilization by CO₂ Mechanical defragmentation of SiO₂ cake | 62 |
| 2      | Barley grain waste | Acid treated barley, 700 °C: 323 | ~150 | Pore size: 22 Pore volume: 1.045 | Waste washed, dried and dried powdered into fine particles | 63 |
| 3      | Sugarcane waste ash | 131 | <20 | — | Ash pretreatment with acid, washing and sieving Formation of Na₂SiO₃ at 400 °C Co-condensation to form SiO₂ NPs using H₂SO₄ Surfactant: CTAB | 64 |
| 4      | Rice husk | — | Ball Milled 18 to 36 h: <3 µm Ball milled 72 h: < 1 µm | — | RH washing, drying and burning at up to 700 °C Acid leaching using H₂SO₄, HNO₃ or HCl, washing, filtration and drying to powder Ball milling of powder | 65 |
| 5      | Rice husk ash | Thermal treatment at 700 °C: 1 to 3 h: ~2.83 to 2.74 at 800 °C: 1 to 3 h: ~1.70 to 1.46 Acid leach: ~2.97 Alkali: ~290.03 | Thermal treatment at 700 °C: 1 to 3 h: ~17.72 to 18.53 at 800 °C: 1 to 3 h: ~22.55 to 22.78 Acid leach: ~20.10 Alkali: ~205.10 | — | Thermal treatment of RHA with no pretreatment at 700 °C and 800 °C for 1, 2, and 3 h Acid leaching and drying - Heating treatment at 800 °C Extraction in boiling NaOH and precipitation by HCl at low temperature Acid leaching with HCl; calcination at 600 °C Boiling with NaOH to Na₂SiO₃ Resin-exchange-alkali-catalysis following solvent exchange, surface modification, and drying Calcination | 17 |
| 6      | Wheat husk | 513 to 587 | — | Pore size: 9–15 Pore volume 2.3–4.0 | — | 66 |
| 7      | Equisetum arvenses | Acid wash 1; 2, pH 7: No calcination: ~74.08; 83.45 K: ~74.08; ~330.63; 823 K: ~296.40; 296.40; 873 K: ~274.64 to; 250.73 | Acid wash 1; 2, pH 7: No calcination 36.65; 32.54; 773 K: 9.16; 8.21; 823 K: 9.89; 9.16; 873 K: 11.77; 10.83 | — | — | 67 |
derived primarily from geological sources. To ensure adequate levels of activity, these materials must be mainly amorphous. Given their geological origin, many amorphous SiO₂ sources contain small proportions of crystalline SiO₂ minerals (quartz and Cristobalite), which must be considered in the efforts to extract amorphous SiO₂ from them. The variety of mineral rock sources of amorphous SiO₂ materials results in a wide range of material properties and reactivities. The properties reflect their diverse sourcing and generally involve several independent parameters that govern the extraction process. These parameters must be optimized to improve the efficiency of SiO₂ production as well as its purity for any meaningful technological and large-scale applications.

The global efforts to extract amorphous SiO₂ involve the use of indigenous mineral rock resources as precursors found in the respective regions. This aspect assumes importance as any selection of siliceous raw material for commercial production will be directly influenced by a plethora of techno-commercial factors such as its abundance, consolidated availability, cost, transport, and the types and relative concentrations of impurities. In general, the wet process with due modification of individual process steps (ore dependent) is used for the extraction of SiO₂. The process steps make use of different lixiviants (e.g., acids/bases and their salts) to extract SiO₂ in the form of either H₄SiO₄ or solutions of Na₂SiO₃ or K₂SiO₃, which are then neutralized to produce amorphous SiO₂. The process does not require excessively high-temperature reaction input, and hence, the energy demand is less. An elevated temperature conditioning step, post extraction of amorphous SiO₂, is optional depending on the target application.

Some representative research efforts utilizing different mineral ores as precursors for the extraction of amorphous SiO₂ are summarized in Table 4.

## 3. SiO₂ fillers in the rubber industry

### 3.1. Classes of SiO₂ and rubber reinforcement

In the polymer industry, two classes of silica are generally used: fumed SiO₂, whose main use is to reinforce silicone rubber since its cost limits more general application to rubbers and precipitated SiO₂. A third class being viewed as a possible internal substitution for precipitated SiO₂ by manufacturers of SiO₂ is colloidal SiO₂.

The primary particles of reinforcing fillers, such as carbon black and SiO₂, are spherical and tend to aggregate or agglomerate due to self-association of the active functionalities present on their surface during production. Similar to carbon black, precipitated SiO₂ exists as aggregates, but unlike fumed SiO₂, the aggregates tend to be more highly clustered, with some having the appearance of fragments of silica gel. A primary SiO₂ particle ranges in cross-sectional dimensions from 5–100 nm, but aggregates formed by chemical and physical interactions of these particles range from 100–500 nm. The aggregates are quantified according to the specific surface area of primary particles, their geometrical arrangement, and the number of primary particles. The combination of these three gives rise to the structure (a general measure of the aggregate) of SiO₂.

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Table 3 (Cont’d.)

| Sl. No. | Biogenic precursor | BET surface area (m² g⁻¹) | Particle size (nm) | Pore size (nm) and pore volume (cm³ g⁻¹) | Method | Ref. |
|---------|--------------------|---------------------------|-------------------|-------------------------------------------|--------|-----|
| 8       | Teff Straw          | – Water and acid washing under pressure | – Calciation at 773 K | – Ball milling to 10 to 20 mm | Acid wash 2, pH 4: No calcination: 39.03; 773 K: ~12.2 K, 39.0 K: ~216.91; 773 K: ~228.03 | 69, 70, 71 |
Table 4  Physical characteristics of nanostructured silica extracted from mineral ore precursors

| Sl. No. | Precursor      | BET surface area (m² g⁻¹) | Particle size (nm) | Pore size (nm) and pore volume (cm³ g⁻¹) | Yield (%)       | Method                                                                 | Ref. |
|---------|----------------|---------------------------|-------------------|------------------------------------------|-----------------|------------------------------------------------------------------------|------|
| 1       | Silica sand    | —                         | 10 to 50          | —                                        | —               | Wet process<br>  - NaOH and silica sand mass ratios of 1:1, 1:5:1 and 2:1 homogeneously mixed in DI water under ultrasound waves (32 kHz, 100 W)<br>  - Mixed mass heated at 500 °C for 100 min<br>  - Resulting vitreous compounds dissolved in hot H₂O to Na₂O(SiO₂)ₓ·xH₂O followed by H₂SO₄ titration<br>  - NPs obtained by adding NH₄OH to form gel<br>  - Gel washed, dried and calcined at 300, 400, 500, 600, 700, 800, and 900 °C | 74   |
| 2       | Pumice rock    | 422                       | 8                 | 5.50<br>0.65<br>Optimal: 95.83            | 15–96           | Leaching process<br>  - Activated poweder activated at 500 °C<br>  - Activated powder mixed with different molar ratio of NaOH to silica at different temperature and time to form Na₂SiO₃<br>  - Aqua gel formed by addition of H₂SO₄ filtered, washed and dried, purified with HCl, filtered, washed, dried and calcined at 800 °C | 75   |
| 3       | Olivine Mg₂SiO₄(s) | 670.8               | <10               | 5.59<br>0.95<br>5                        | 86.8            | Leaching process<br>  - Dissolution of ball milled olivine with NaOH and KOH solution to obtain a dense slurry<br>  - Slurry heated to fixed reaction temperatures and times; solid products obtained<br>  - Dissolution of solid products in DI water to extract soluble Species<br>  - Solid products separated by vacuum filtration and filtrate solution reacted with HCl to Precipitate amorphous SiO₂ | 72   |
| 4       | Desert sand    | —                         | —                 | —                                        | —               | Reaction at 120 °C for 60 minutes; ~80% Na₂SiO₃<br>  - Alkali fusion process<br>  - Sand washed, dried, ground and sieved into different fractions of 850, 600, and 425 μm<br>  - Each fraction reacted with NaOH at weight ratios of 1.5, 2.0 and 2.5 and temperatures of 80, 100 and 120 °C for different times of 30, 40, 50, and 60 min<br>  - After the reaction, mixtures leached with distilled water and the residue removed by filtration, washed with hot water, and dried<br>  - SiO₂ precipitated by H₂SO₄ filtered, washed, dried, and well ground | 76   |
Table 4 (Contd.)

| Sl. No. | Precursor | BET surface area (m² g⁻¹) | Particle size (nm) and pore volume (cm³ g⁻¹) | Yield (%) | Method | Ref. |
|---------|-----------|----------------------------|---------------------------------------------|-----------|--------|------|
| 5       | Quartz sand (whole rock) | - | A: pH 3, 6, 10: 194, 91, 33; B: pH 3, 6, 10: 133, 58, 24; C: pH 3, 6, 10: 178, 86, 31 | At pH 3, 6, 10: 0.5 to 8 μm | 86.8 | Wet process | 77 |
|         |           |   | A: pH 3, 6, 10: 194, 91, 33; B: pH 3, 6, 10: 133, 58, 24; C: pH 3, 6, 10: 178, 86, 31 | Pore size, A: 111, 79, 129, B: 127, 85, 22, C: 107, 83, 115 | | - Silicate formed by heating at 1060 °C, a mixture of Na₂CO₃ and burdigalian or barremian quartz sand (molar ratio, n, of SiO₂/Na₂O equal to 1.5 or 3) | |
|         |           |   | C: pH 3, 6, 10: 178, 86, 31 | Pore vol, A: 0.53, 0.23, 0.12, B: 0.46, 0.14, 0.06, C: 0.50, 0.20, 0.09 | | | |
| 6       | Pyrophyllite ore | - | <50 nm | - | - | Wet process | 78 |
|         |           |   | - Ball milled 180 μm pyrophyllite refluxed with 3 M NaOH to form Na₂SiO₃ | - Na₂SiO₃ titrated with 5 M H₂SO₄ (5 M) to obtain SiO₂ gel | - Gel aged, filtered, washed to remove sulfate and dried followed by 1 M HCl leaching under reflux | | - SiO₂ separated by centrifuge, washed, dried, and calcined at 800 °C | |
| 7       | Pumice rock | 422 | 5 to 15 | Pore size: 2 to 6 avg: 5.5 | - | Wet process | 79 |
|         |           |   | - Washed, dried and size reduced pumice activated at 500 °C for 3 h | - Refluxed with 3 M NaOH to form Na₂SiO₃ slurry, filtered and washed with boiling H₂O | - Filtrate solution acidulated to neutral with 5 M H₂SO₄ to form SiO₂ gel | | - SiO₂ leached with 1 M HCl, filtered, washed, dried before being filtered and washed |
Table 4  (Contd.)

| Sl. No. | Precursor  | BET surface area (m² g⁻¹) | Particle size (nm) | Pore size (nm) and pore volume (cm³ g⁻¹) | Yield (%) | Method | Ref. |
|---------|------------|---------------------------|-------------------|----------------------------------------|-----------|--------|------|
| 8       | Perlite    | Closed reaction system    | Closed reaction system | NaOH/SiO₂ = 2.4 molar ratio at 120 °C within 60 min: ~98        | —         | —      | Wet process          | 80 |

- Perlite washed, dried, and calcined at 800 °C
- Reacted with NaOH: time 0 to 60 min; molar ratio of NaOH/SiO₂, 0.6 to 2.4 and reaction temperature, 60-120 °C to form Na₂SiO₃
- Na₂SiO₃ solution filtered and washed with boiling distilled H₂O and titrated with 5 N H₂SO₄ to neutral to form SiO₂ gel and aged
- Gel washed to remove sulphate and dried
- Dried gel leached with 1N HCl under reflux, washed and dried
Aggregates condense into agglomerates in the range of 1–40 μm. During compounding, they more or less disintegrate to the size of aggregates or even primary particles (rare) (Fig. 6). The efficiency of the distribution, dispersion, and disintegration of agglomerates into aggregates depends on the degree of shear afforded by the mixing equipment: internal mixers are the most efficient (and are the work horse of the rubber industry) compared to two roll mills. This higher structure gives a greater reinforcing effect than carbon black, but the higher specific component of the surface energy of the SiO\textsubscript{2} filler results in difficulty in dispersion in rubbers and even re-agglomeration post mixing. Nonetheless, excellent properties have been obtained in rubber compounds especially tires with precipitated SiO\textsubscript{2}, by improving the bonding to rubber, either by activating the SiO\textsubscript{2} or by the addition of coupling agents.\textsuperscript{82,83}

Grades of precipitated SiO\textsubscript{2} are generally classified as semi-reinforcing or reinforcing, similar to carbon black. Further, due to the considerable diversity in the types of SiO\textsubscript{3}, because of the different production processes and in-process variations, these fillers are of various types, as shown in Table 5.\textsuperscript{85}

Colloidal SiO\textsubscript{2} is an alternative to carbon black, although typically, the polarity difference between SiO\textsubscript{2} and common rubbers gives deficient reinforcing properties unless coupling agents are employed.

### Table 5 Various classes of silica depending upon precipitation conditions\textsuperscript{85}\textsuperscript{a}

| Category        | Required pH | Drying time | Dispersibility |
|-----------------|-------------|-------------|----------------|
| Conventional silica | High        | Long        | Bad            |
| Semi-HD silica  | Low         | Long        | Moderate       |
| HD silica       | High        | Short       | Good           |

\textsuperscript{a} HD: highly dispersible.

As for the structure, conventional silica has a typical dibutylphthalate (DBP) adsorption value of 175/100 g while for highly dispersible (HD) SiO\textsubscript{2}, it is 200/100 g or even more. These higher values show that the structure of HD SiO\textsubscript{2} is less fragile than conventional silica. Improvement in the dispersion behavior of HD SiO\textsubscript{2} is explained by their high aggregate porosity, surviving for longer times than conventional SiO\textsubscript{2} under high shear during compounding. The result is that the polymer has more space and time to penetrate into the voids present in HD SiO\textsubscript{2} compared to conventional SiO\textsubscript{2} with more compact structures. The aggregates of HD SiO\textsubscript{2} have a more branched structure; with three to four major branches on average.\textsuperscript{86} These branched structures also improve the dispersion characteristics of the HD SiO\textsubscript{2} during the mixing process.
and at the same time, reflect a bimodal distribution of the aggregates. Compared to conventional SiO$_2$, the amount of small aggregates is relatively high in HD SiO$_2$.

Bulky particulate materials like calcium carbonate can be employed just to reduce the cost of the final material without any improvement of properties. In this case, they can be simply called extenders or non-reinforcing fillers. On the other hand, there are fillers like precipitated silica, as observed in Fig. 7, with a reduced nano size scale, which can reinforce the rubber, known as active fillers.24

3.1.3. SiO$_2$ surface chemistry and characteristics. Silica particles generated from the polymerization of silicic acid form complex amorphous polycyclic ring structures. Because of internal defects in these ring structures, silanol groups (||=Si–OH) and siloxane groups are generated on the surface of the particles. The surface is mainly characterized by the (i) number of silanol groups, (ii) degree of hydration, (iii) amount of adsorbed water, and (iv) its surface acidity. The silanols are classified into three categories depending on the precipitation conditions shown in Fig. 8.86-88

These groups display a strong affinity for water molecules, especially the geminal type of silanol groups. In HD SiO$_2$, the geminal content is less than 20%. Silanol groups on the silica surface also improve the bond ability of new rubber compounds with older rubber, e.g., retread compound with old rubber. The polar component of SiO$_2$ is relatively high due to the presence of a large number of polar groups on the filler surface and the difference in the solubility parameters of the polymers and the filler is responsible for the degree of wetting of fillers by polymers.89,90 The Hildebrand solubility parameters of some polymers and silica are shown in Table 6.84

From Table 7, it may be seen that in comparison to the polymers listed and carbon black, the high solubility parameter of SiO$_2$ leads to difficulty in blending SiO$_2$ fillers with polymers. Based on the studies of the interactions of SiO$_2$ surfaces with low molecular weight analogs of elastomers, the level of interaction has been classified as:89

NBR > SBR > NR ≥ BR > HV-BR > EPR > IIR

3.2. Bound rubber model of SiO$_2$-filled rubber

During the processing of SiO$_2$-filled rubbers, various chemical reactions occur, and generally, there exist two components: (i)
occluded rubber in SiO2 aggregates and (ii) cross linked polymer due to polymer chain scission and recoupling reactions. These two phenomena are responsible for the bound rubber of SiO2-filled rubber and a model of the SiO2/silane reinforcement based on the hydrodynamic–occlusion–interaction theory is shown in Fig. 9.

The large polarity difference between the SiO2 filler and the rubber matrix leads to the ease of formation of a filler–filler network, with part of the matrix occluded in the filler network. This occluded rubber is both physically and chemically immobilized within the filler network. Under high deformation, the filler network partially breaks down, and with the increase in deformation of the rubber, the occluded rubber within the filler network reduces, followed by a deformation of the matrix. Due to the chemical bonding via a silane coupling agent, the occluded rubber and rubber on the SiO2 surface remain immobilized and still contribute to the modulus even at high deformations. The chemically immobilized rubber is the in-rubber structure.

The mechanisms of components of bound rubbers directly contacted to silica surface are in terms of multiple contact rubber chain, insert rubber chain, chemically bonded rubber chain, and single contact rubber chain, as shown in Fig. 10.

3.3. Effects of filler–filler and SiO2 filler–rubber interactions

The filler–rubber interaction depends on the particle size and shape, surface characteristics of the filler, as well as the chemical nature of the polymer. It increases with the filler dispersion and with the extent of the organic/inorganic interface. Many studies have also demonstrated that the filler-rubber interaction induces the formation of a polymer layer around filler particles (the so-called bound rubber) with a consequent slowdown of the dynamics of the rubber chains interacting with the particle surface. The stronger the interaction, the more tied the polymer layer.

Filler–filler interaction is due to the strong tendency of silica particles embedded in rubber to interact with each other by surface silanol condensation. This favors a strong inter-particle aggregation, which contrasts the filler–rubber interaction and lowers the homogeneous distribution of the filler. This drawback can be ridden out by using suitable coupling agents (e.g., silanes), which form chemical bonds between the polymer chains and the oxide, improving the compatibility with the rubber matrix.

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Fig. 9 Model of the silica/silane reinforcement (a): no deformation; (b): after large deformation.

Fig. 10 Components of bound rubbers directly in contact with the silica surface. (a) Multiple contact rubber chain, (b) insert rubber chain, (c) chemically bonded rubber chain, and (d) single contact rubber chain.

Fig. 11 Stress–strain curve of SiO2 filled rubber nanocomposite: strain-dependent and strain independent contributions to the Payne effect are differently colored.
The control of both filler-filler and filler-rubber interactions plays a key role in determining the filler reinforcing action. In fact, the reinforcement due to filler-rubber interaction is almost independent of the strain amplitude. On the other hand, the filler-filler interaction enhances the modulus at low strain, but breakdowns at high strain. This causes a drop in the modulus (Payne effect), which is associated with an energy dissipative process and Mullen’s effect as well.97

3.3.1. Payne effect. Payne effect and its associated weak overshoot are of importance for understanding and regulating the softening of rubber nanocomposites under large amplitude oscillations. Rubber nanocomposites widely used in the industry demonstrate the Payne effect, also named as Fletcher–Gent effect, under large amplitude oscillations, depicting softening and dissipation behavior is usually accompanied by a weak overshoot of loss modulus ($G''$) depending on the dispersity of the filler and its weak forces like H-bonds and van der Waals interactions with the rubber matrix. The Payne effect and its associated weak overshoot are usually attributed to the breakdown of the filler network and the desorption of bound chains from the filler surface, and strain softening phenomenon is known as the Payne effect, and the components of reinforcement are readily separated, as shown in Fig. 11, while recent studies show that the filler amplified viscoelastic deformation of the matrix is crucial.97–99

The vulcanized nanocomposites of diverse compositions demonstrate the Payne effect and weak overshoot behavior being dominated by the viscoelastic deformation of the rubber matrix with defective crosslinking network. The filler amplifies the microscopic strain of the matrix, which is more significant for the silicious than the carbonaceous fillers. While both the silicious and carbonaceous fillers tend to lower the intensities of the weak overshoot, and the serious agglomeration of silica may cause interparticle friction to intensify the overshoot at high filler loadings. On the other hand, the interaction between silica and rubber based on covalent bonding from silanization tends to intensify the strain amplification effect and filler–rubber interfacial friction. Payne effect at small strain shear deformation and other strain independent contributions (strong filler–rubber interaction) on reinforcement degree of rubber by SiO$_2$ filler can be reduced by surface modification of either the filler or polymer due to covalent bonds existing at the

![Diagram of different dissipative mechanisms associated to the Mullins effect](image)
polymer–particle interface (through coupling agents), and in the in-rubber structure (sulfur crosslinks).38

3.3.2. Tensile tests and Mullins effect. From the macroscopic point, the interface stability (associated with filler–rubber interactions) can also be evaluated by mechanical measurements that explore higher strain regimes than the Payne effect: tensile tests and Mullins effect. In tensile tests, the material is stretched at strain values 20–50 times higher than for the Payne effect, and the high-strain effects can be attributed to filler–rubber interactions that play a complex but important role in tuning the breakage mechanism. The Mullins effect, in turn, refers to a particular aspect of the mechanical response in filled rubbers in which the stress–strain curve depends on the maximum loading previously encountered. The Mullins effect can be evaluated by a series of tensile traction and retraction tests until the break, in which a lag time between cycles allows to restore reversible deformations, while pseudo-permanent deformations cannot be restored.

Besides the tensile test, it is possible to evaluate the energy losses localized at different strain intervals, allowing the material to restore between one cycle and the other, separating permanent (purely viscous) losses from reversible (viscoelastic) losses with the hysteresis measured in each cycle considered as an indicator of these losses.100 The dissipative effect at different strain levels has been related to different physical phenomena, as shown in Fig. 12.33,101

3.3.3. Failure properties of SiO2 filled rubber. Particulate fillers improve the strength and fatigue resistance of rubber. This is illustrated in Fig. 13, showing substantial decreases in tensile strength, even for a filler such as calcium carbonate that provides minimal actual reinforcement. The strength of rubber increases with filler content, attaining a broad maximum at high concentrations. The majority of applications of rubber, certainly those involving mechanical properties, require reinforcement with carbon black and precipitated silica, the dominant fillers. Reinforcing fillers increase the viscosity and modulus by a hydrodynamic effect, augmented by rubber occluded within the filler. The ultimate properties (tensile strength, fatigue life, abrasive wear, etc.) are an important aspect of reinforcement, although the magnitude of the improvements and the relevant mechanisms are not always well understood.102

The mechanical properties of SSBR composites filled with SiO2/CB exhibited a “synergistic effect.” Among these, the composite with SiO2/CB (20/50) showed good filler dispersion with low heat generation, as shown in Table 7.103

3.4. Overcoming difficulties in the use of SiO2 fillers

Mixing SiO2 filler into rubber is a challenge. The dispersive part, a component of surface free energy, is low, i.e., weak interaction between the filler particles and rubber, resulting in a low reinforcing effect. However, the specific part, the second component of surface free energy, is high, i.e., a strong filler–filler interaction leading to a substantial increase in the viscosity of SiO2–rubber compounds. The interparticle forces between filler particles must be overcome during mixing so that a satisfactory dispersion of filler particles can take place and a link between the SiO2 particles and rubber may be established. For a homogeneous distribution of filler aggregates within a matrix, intensive contact between filler particles and rubber is a necessary criterion for efficient mixing. The two most important characteristics that determine the contact between the surface of the filler and the rubber matrix are the surface area of the filler and its wettability.104,105

Wettability is significant when using SiO2 fillers as there exists a mismatch between the solubility parameters of the polar SiO2 filler and nonpolar rubber. This mismatch affects both its compatibility with non-polar elastomers and the cure characteristics of the compounds. The high structure of SiO2 filler (aggregates and agglomerates) is characterized by a high surface area and a high percentage of the void volume within the structure. Since a direct interaction between the filler and polymer is low, polymer chains are physically entrapped in the voids of the filler structure. To enhance the polymer–SiO2 filler interaction, the filled structure has to be broken to an optimum level during mixing.106

From an industrial perspective, it has been observed that reinforcing by carbon black was more efficient than SiO2 until silane coupling agents were introduced to reduce the polarity differences between the polar filler and nonpolar rubbers. These agents are able to react with both the SiO2 surface and the polymer forming a chemical linkage between the filler particles and rubber, thus overcoming the problems of both increased viscosity and dispersion. The result is the enhancement of the properties of the final product.107 They may be premixed or pre-reacted with the SiO2 particles or may be added to the rubber mix during mixing with consideration that the coupling agents then combine in situ with SiO2.108

Different types of coupling agents have been developed over the years to improve the compatibility and dispersion of SiO2

![Fig. 13](image-url) Tensile strength of SBR unfilled (line), with 0.13 volume fraction (45 phr) calcium carbonate (squares) and with 0.13 volume fraction (30 phr) HAF carbon black and precipitated SiO2, as a function of crosslink density.102
fillers in different polymer matrices. Some commonly used silane coupling agents include, e.g., bis(triethoxysilylpropyl) tetrasulfide (TESPT): the polysulfide part of which reacts with the polymer, and the ethoxyisilyl groups on the silicon atom react with the hydroxyl groups present on the surface of SiO₂. The average sulfur rank of the polysulfide is 3.86 and is unstable at high shear or high temperature. During rubber processing, the TESPT molecules split and release reactive sulfur moieties in the compounds, thus performing as a sulfur donor.

Another silane that releases sulfur during processing is bis(triethoxysilylpropyl) disulfide (TESPD: Si₂66/Si75), which comprises mixtures of polysulfides and has an average sulfur rank close to 2. This silane is more stable at high shear or high temperatures compared to TESPT, and therefore, rubber compounds are less sensitive to scorch. But, due to its lower sulfur content, additional elemental sulfur needs to be incorporated into rubber to achieve comparable reinforcement to TESPT.

There are also other types of silane coupling agents commercially available and are used based on the type of the polymer matrix and target application of the SiO₂–rubber compound. They are used to reduce the emission of volatile organic compounds such as ethanol during the mixing process or product lifetime, e.g., tires.

The reaction mechanism of silanization is exemplified by that of TESPT in Fig. 14(a) and (b). In the primary step, the reaction of the first alkoxy group of the silane with silanol groups on the SiO₂ surface takes place via two possible mechanisms (Fig. 14(a)): a direct reaction of the silanol groups on the silicon with the alkoxysilane group of TESPT and hydrolysis of the alkoxysilane group to form a reactive silanol with the release of ethanol.

These reactions occur slowly on the SiO₂ surface in the presence of water. The rate constant of hydrolysis increases with increasing temperature in the presence of a catalytic agent such as an acidic or alkaline medium. Post hydrolysis, the activated silane is capable of reacting with silanol groups on SiO₂. The rate constant of this reaction is relatively faster than hydrolysis, i.e., the hydrolysis reaction is the rate determining step for silanization. Just after the primary reaction, a secondary reaction (Fig. 14(b)), and an intermolecular condensation between the silanes on the SiO₂ surface caused by the unreacted ethoxy groups of the silanes occur. The rate of reaction is, however, slower than the primary reaction and may be accelerated by water accompanied by an increase in temperature. For an optimal level of reinforcement, it is preferred to have a low degree of intermolecular condensation.

![Fig. 14 Reaction mechanism of silanization](image_url)
The degree of silanization can be significantly improved and accelerated by 1,3-diphenylguanidine (DPG) or by accelerators such as amines, enamines (R=RC = C-NR3), and aldimines (R-CH = N-R) in combination with DPG.121,122

4. Summary and future recommendations

The search for nonpetroleum-based fillers, which are environmentally friendly, cheap, abundant, and renewable, has been raised nowadays. Literature reports published so far evidenced the improving physicochemical properties of nanostructured SiO2 and reduction of the cost of production by searching for potential precursors, and low energy consuming methods is an important research area. The main bottleneck problem for the application of sol–gel processes at a larger scale is the use of expensive alkoxide precursors in the liquid state. Therefore, in the near future, alternative precursors from local materials are an urgent call to researchers.

Other parameters that play a crucial role in the performance of rubber materials are size, surface chemistry, surface area, and aspect ratio of nanofillers. Owing to their large availability, low cost, high surface area, green and possible sol–gel preparation from sodium silicate precursors, nowadays, nanosilica structures with different physicochemical characteristics and aspect ratios have attracted huge interest as reinforcing agents for rubber materials. Despite the fact that rare studies have been conducted so far on the effect of nanosilica structure on rubber nanocomposites, a larger scope exists in the development of novel rubber products using different nanostructures of silica synthesized from natural sources, i.e., biogenic and mineral ore resources.

Nanofillers, particularly anisotropic silica, show great promising results, and their commercial potential is significant. However, the dispersion problem of SiO2 nanostructures, encountered in the use of all reinforcing fillers, remains a major obstacle to the utilization of nanoparticles in the rubber industry. Recent works showed that the surface modification of silica with silane coupling agent made it competitively applied to rubber industries. Recently, researchers tried some investigations on the effect of anisotropic silica on rubber reinforcement, Payne and Mullen’s effects reduction, and parameter optimized sol–gel synthesized spherical and rode shaped silica becomes a promoted rubber reinforcement filler but very rarely investigated yet. Therefore further studies in all aspects of nanostructured SiO2 material for rubber reinforcement efficiency is a hot research area of study.

Conflicts of interest

The authors declared that they have no conflict of interest.

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