**REVIEW ARTICLE**



# **Investigating the potential of sustainable use of green silica in the green tire industry: a review**

Behnaz Shoul<sup>1</sup> • Yousef Marfavi<sup>2</sup> • Banafsheh Sadeghi<sup>1</sup> • Elaheh Kowsari<sup>2</sup> • Peyman Sadeghi<sup>3</sup> • Seeram Ramakrishna<sup>4</sup>

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#### **Abstract**

Undoubtedly, with the increasing emission of greenhouse gases and non-biodegradable wastes as the consequence of over energy and material consumption, the demands for environmentally friendly products are of signifcant importance. Green tires, a superb alternative to traditional tires, could play a substantial part in environmental protection owing to lower toxic and harmful substances in their construction and their higher decomposition rate. Furthermore, manufacturing green tires using green silica as reinforcement has a high capacity to save energy and reduce carbon dioxide emissions, pollution, and raw material consumption. Nevertheless, their production costs are expensive in comparison with conventional tires. In this review article, by studying green tires, the improvement of silica-rubber mixing, as well as the production of green silica from agricultural wastes, were investigated. Not only does the consumption of agricultural wastes save resources considerably, but it also could eventually lead to the reduction of silica production expenses. The cost of producing green silica is about 50% lower than producing conventional silica, and since it weighs about 17% of green silica tires, it can reduce the cost of producing green rubber. Accordingly, we claim that green silica has provided acceptable properties of silica in tires. Apart from the technical aspect, environmental and economic challenges are also discussed, which can ultimately be seen as a promising prospect for the use of green silica in the green tire industry.

**Keywords** Green silica · Green tire · Tire reinforcement · Agricultural waste · Sustainability · Carbon footprint

## **Introduction**

Due to the increase in population and the growth of consumer demand, both qualitatively and quantitatively, the demand for cars is increasing. Due to this need, the tire as a consumable

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 $\boxtimes$  Elaheh Kowsari Kowsarie@aut.ac.ir

- $\boxtimes$  Seeram Ramakrishna seeram@nus.edu.sg
- <sup>1</sup> Amirkabir University of Technology, Mahshahr Campus, P.O. BOX, Mahshahr 63517-13178, Iran
- <sup>2</sup> Department of Chemistry, Amirkabir University of Technology, No. 424, Hafez Avenue, Tehran 1591634311, Iran
- <sup>3</sup> Faculty of Polymer and Chemical Engineering, University of Tehran, P.O. Box, Tehran 13145-1384, Iran
- <sup>4</sup> Department of Mechanical Engineering, Center for Nanofbers and Nanotechnology, National University of Singapore, Singapore 119260, Singapore

and depreciable material increases (Singh et al. [2019](#page-18-0); Kawajiri et al. [2020](#page-16-0)). Global tire consumption was 2.9 billion tons in 2017 and is growing at an annual rate of 0.4%, which is worth about 258 billion dollars, and by the end of 2025, it is expected to be about 2.5 billion tones (Bockstal et al. [2019](#page-15-0); Chen et al. [2019](#page-15-1); Symeonides et al. [2019\)](#page-18-1). In recent decades, with the emergence of environmental crises due to the increasing emission of nonbiodegradable waste and the growth of greenhouse gas emissions due to the high consumption of energy and materials, the need for greener products is more than ever (AliAkbari et al. [2020](#page-14-0); Pervez et al. [2021;](#page-17-0) Sadeghi et al. [2021a](#page-17-1), [b](#page-17-2), [c](#page-17-3)). The production processes of traditional tires resulted in high pollution, and raw materials used in their manufacturing are sourced from unsustainable resources. Considering that tires are a consumable commodity and create a large amount of non-biodegradable waste, this causes an increase in environmental crises such as an increase in microplastics in the marine environment and an increase in greenhouse gases due to higher tire production (Wu et al. [2020](#page-18-2); Sadeghi et al. [2021a,](#page-17-1) [b](#page-17-2), [c\)](#page-17-3). With the forthcoming trend, it is expected that in 2030, we will have about 5 billion scrubbed tires and 1.2 billion discarded tires (Abbassi and Ahmad [2020](#page-14-1)).

One of the solutions to reducing the damage caused by scrubs and rubber waste in the environment is recycling waste tires and their usage in diferent industries. More than 4 billion waste tires are accumulated worldwide, of which 1.8 billion will be generated by 2020. Public intervention and industry innovation has made recycling the main method of waste management in Europe and increased the recycling rate from 13 to 39% of all waste tires (Kole et al. [2017](#page-16-1); Pilkington [2021](#page-17-4)). Xu et al. compared the replacing commercial carbon black with pyrolytic residue from the waste tire. They reported that adding a small amount of pyrolytic carbon black can decrease the cost of raw materials and con-sumption of fossil energy (Xu et al. [2021\)](#page-18-3).

Another solution is to produce and use green tires. Green tires are an excellent option to replace traditional tires due to removing some toxic and harmful substances in their construction and their higher rate of decomposition in the environment (Marimin et al. [2018](#page-17-5); Tian et al. [2021](#page-18-4)). The most important advantages of green tires compared to conventional tires are 3 Rs, and for this reason, they are also called eco-friendly tires, and they are rolling resistance (RR), raw materials, and recycling (thenewautomag [2022](#page-18-5)). Therefore, according to what has been said, the green tire can be defned briefy as follows: the green tire is a tire with lower fuel consumption due to RR, also lighter, recyclable, has a longer lifespan, and is produced from renewable materials with less energy consumption, so the green tire industry is part of the overall tire industry that is rapidly growing (smithers [2020](#page-18-6)).

Green tires are produced with less energy-intensive methods and are designed to reduce fuel consumption over the life of the tire due to less RR (Dong et al. [2020\)](#page-15-2). Kumar et al. reported that green tires have longer longevity than conventional tires (Cao et al. [2016](#page-15-3)). The production processes of traditional tires resulted in high pollution, and raw materials used in their manufacturing are sourced from unsustainable resources. Considering that tire waste is a consumable commodity and creates a large amount of non-biodegradable waste, this causes an increase in environmental crises such as an increase in microplastics in the marine environment and an increase in greenhouse gases due to higher tire production. (Canepari et al. [2018;](#page-15-4) Wu et al. [2020](#page-18-2)). According to research conducted by the US National Research Council, a 10% reduction in RR can reduce the fuel consumption of passenger cars by 1 to 2% (Consumers [2006\)](#page-15-5). So, green tire consumers will beneft from less fuel consumption, which will save cost and money in the long term. Because of these benefts and advantages that will be mentioned in the following sections, global green tire consumption is on the rise; in 2010, 1.2 billion green tires were sold worldwide, while in 2015, this amount reached 1.4 billion. Therefore, the share of green tire sales in the total tire manufacturer's sales increased from 10 to 30% (Devineni et al. [2011](#page-15-6)).

Researchers in recent years have conducted a variety of research on tires, tire waste, and health effects (Chuang et al. [2015;](#page-15-7) Labaki and Jeguirim [2017;](#page-16-2) Lai et al. [2018\)](#page-16-3). De Toledo et al. ([2019](#page-15-8)) used bioremediation to reuse scrap tires. Fahad et al. ([2015a,](#page-15-9) [b\)](#page-15-10) used rubber ash for zinc fertilization treatment. In some studies, activated carbon was prepared using waste tires (Gupta et al. [2013;](#page-15-11) Belgacem et al. [2014\)](#page-15-12). Zhang et al. ([2018a](#page-18-7), [b\)](#page-19-0) investigated the applicability of recycled rubber tire-sand mixtures as the lightweight backfll in base/ subbase applications. In some studies, waste rubber was used as the immobilization matrix to remove toxic substances (Lu et al. [2015](#page-16-4), [2017](#page-17-6)). In addition, green tires are made from more durable and recycled materials (Zhang et al. [2021a,](#page-19-1) [b](#page-19-2)). In this review article, the reinforcement used in green rubber tread and the potentials and challenges of using silica from agricultural waste as a circular economy-based material to produce a greener product are examined.

#### **Green production process of tires**

The green tire was introduced by Michelin about 30 years ago. Michelin is one of the largest manufacturers in the tire industry. Its management control strategy is focused on improving its main product, tires, in terms of safety, durability, and decreased environmental impact (Baker et al. [2018](#page-14-2)). Green tires are essential for driving safety, reducing fuel consumption, and thus reducing air pollution; for example, by reducing the RR of the green tire by 22–35%, fuel consumption is reduced about 3–8% and, as a result, helps to save more fuel in vehicles and reduce  $CO<sub>2</sub>$  pollutions in the environment (Weng et al. [2020](#page-18-8); Zhang et al. [2021a](#page-19-1), [b](#page-19-2)). The RR of a tire can afect the fuel consumption of a vehicle as well as its  $CO<sub>2</sub>$  emissions (Soica et al. [2020](#page-18-9)). A green tire is a tire that has less RR due to the diferent design of the tread compound and therefore consumes less fuel (Dominic et al. [2020](#page-15-13)).

When a car travels on the road, part of the mechanical energy that drives the wheels is stored in the tires, while the other part is disintegrated as heat build-up and called hysteresis loss (Luo et al. [2020](#page-17-7)). RR is a scale measuring the mechanical energy changing to heat by moving the tires on the road (Lolage et al. [2020a,](#page-16-5) [b](#page-16-5)). The importance of green tire technology is that a tire must have a high grip for high safety. For this purpose, a high hysteresis rubbery compound for high frequencies is needed that absorbs high-energy surfaces (Esmaeeli [2020](#page-15-14); Sibeko et al. [2020](#page-18-10)). On the other hand, to achieve low RR, a low hysteresis rubbery compound for low frequencies is needed that absorbs low surface energy (Lovison et al. [2021](#page-16-6)). Because of the inverse nature of the two, it decreases one with the addition of another and vice versa. It is impossible to gain this technology with the same materials and machinery. Compounds can be designed to present higher hysteresis at high frequencies and lower hysteresis at low frequencies, but this is not the case with CB, although this is possible with silica (Ten Brinke [2002](#page-18-11)). From what has been said, the importance of using silica in the manufacture of green tires is evident, and it is that the use of silica in the tread compound of passenger car tires can reduce RR and improve the wet resistance (Weng et al. [2019](#page-18-12)). So, the focus is specifcally on silica. In addition to using the materials used to make rubber, green production also requires the highest quality standards and safety measures (Katarzyna et al. [2020](#page-16-7)). In addition to reducing the emission of harmful chemical gases into the environment, proper wastewater management, and waste control, these methods help ensure adherence to high-quality production standards (Narayanamurthy et al. [2020](#page-17-8)).

To achieve green tire technology, it is necessary to compound specifc polymers, precipitated silica, and coupling agent to bond the two (Grunert et al. [2020\)](#page-15-15). These essential ingredients used in the green tire are discussed below:

#### **Rubber**

Styrene-butadiene rubber (SBR) has many applications in the rubber industry, and it is still the predominant rubber in car tire treads (Nowakowski and Król [2021](#page-17-9)). Although emulsion styrene-butadiene rubber (ESBR) is commonly used in the rubber industry, solution styrene-butadiene rubber (SSBR) is better used in green tires because of its better RR and wet skid resistance than ESBR (Hwang et al. [2019](#page-16-8)). SSBR is synthesized anionic polymerization with SnCl4, ethoxysily, and 3-mercaptopropinic acid (Song [2020](#page-18-13)).

#### **Silica**

The use of sustainable and recycled materials is essential for producing green tires. Many materials are used in the production of tires, but most attention has been focused on silica (Joseph et al. [2020](#page-16-9); Parker et al. [2020;](#page-17-10) Banerjee et al. [2021](#page-14-3); Lovison et al. [2021\)](#page-16-6). Silica is a versatile and durable material made of sand, glass, and quartz that acts as a bonding agent in tires. Also, the widespread use of recycled materials in the production of this type of tire is not surprising. Therefore, due to the importance of silica in the production of green tires, the paper will focus on green silica after a general explanation of silica.

#### **Conventional silica**

Silica is generally divided into two types, crystalline and amorphous (He et al. [2019](#page-16-10)). The crystalline type often does not have reinforcing properties. Amorphous silica, which is divided into two models, precipitated and fumed, has reinforcing properties. Fumed silica has the smallest particle size among all types of silica. However, due to processing problems and high prices, it is not generally used in the tire industry. Therefore, precipitated silica is often used in rubber compounds used in the tire industry (Hewitt [2007\)](#page-16-11). For green tire manufacturing, amorphous precipitated silica is used as a reinforcing fller in the tire tread recipes (Lolage et al. [2020a,](#page-16-5) [b](#page-16-5)). Physical interactions between elastomers and fller particles are essential for rubbers reinforcement. The number and kind of active functional groups, the surface energy, and the diferent crystallinity of the fller surfaces afected surface activity. In general, this leads to the distribution of active sites to adsorb polymer segments on the surface of reinforcing particle fllers (Laskowska [2014](#page-16-12)). As shown in Fig. [1,](#page-2-0) CB, as used in conventional tire, has numerous active sites on the surface and can be compatible with a variety of rubbers without the need for a surface modifer (Hewitt [2007\)](#page-16-11). Unlike CB, silica is hydrophilic and has highly polar functional groups silane (Si-OR) and acidic silanol (Si–OH) on the surface. So it cannot interact well with nonpolar elastomers (Laskowska [2014](#page-16-12)).

Unlike CB, the polar nature of silica has made it incompatible with nonpolar hydrocarbon elastomers (Grunert et al. [2020](#page-15-15)). Incompatibility between the fller and the elastomer prevents the fller particles from dispersing in the elastomeric matrix (Song [2020\)](#page-18-13). On the other hand, the viscosity of the rubber increases due to the interaction between the fller-fller containing the silanol groups and complicates the rubber process (Xiao et al. [2020\)](#page-18-14). As a result, it usually reduces the properties of silica-flled compounds compared



<span id="page-2-0"></span>**Fig. 1** Diferent active groups available on the surfaces of **a** silica and **b** CB (Hewitt [2007](#page-16-11))

to CB-flled compounds (Khanra et al. [2020](#page-16-13)). The compound recipe, mixing process, and equipment often afect the silica dispersion quality (Grunert et al. [2020](#page-15-15)). The solutions to this problem will be discussed in the following and after the green silica section.

#### **Green silica**

Nowadays, more attention has been paid to the use of plant materials to produce green silica as an eco-friendly method. The advantages of this trend are its availability, the low cost of agricultural waste, the elimination of chemical substances, and the decrease in energy consumption (Abolghasemi et al. [2019](#page-14-4)). One of the very cheap sources for preparing silica is rice husk ash (RHA); silica content in RHA is 90%; 700 million tons of rice are produced annually, of which 22% of the weight is rice husk, which is obtained during rice milling (Shen [2017](#page-18-15)). The use of this rice husk as boiler fuel for energy production produces a large amount of RHA, the disposal of which is an environmental problem (Nazar et al. [2021\)](#page-17-11). Rice husk is also used as a material for animal husbandry, but in many cases, it is considered rice mill waste and dumped in barren lands (Jembere and Fanta [2017](#page-16-14)). Therefore, the use of this RHA and being a cheap and available source for silica production can partially solve this environmental problem. There has been a lot of research on green silica, some of which is summarized in Table [1.](#page-4-0)

The most common agricultural waste for the production of green silica is RHA, which contains 85–95% silica (Chun and Lee [2020](#page-15-16)). Also, sugarcane bagasse contains an amount of high silica, 92.5%, which is the same as the amount of silica produced from RHA (Sapawe and Hanaf [2018](#page-17-12)). Bamboo leaf can provide a high silica percent that is about 61% (Silviana and Bayu [2018](#page-18-16)). Corn stalks were used as a source of nano-silica by the modifed cell gel method (Adebisi et al. [2019,](#page-14-5) [2020\)](#page-14-6). Other agricultural waste such as bamboo culm, oil palm ash, sugarcane bagasse ash, wheat straw, and corncob ash can synthesize silica (Okoronkwo et al. [2016](#page-17-13); Sapawe and Hanafi [2018;](#page-17-12) Surayah Osman and Sapawe [2019](#page-18-17); Farirai et al. [2021](#page-15-17); Ravindran et al. [2020\)](#page-17-14). The structural properties of silica have led to its use in various felds of science and technology (Costa and Paranhos [2020](#page-15-18)). Green silica is a potential reinforcement in the tire that has many advantages such as heat resistance, high modulus, hardness, tear strength, abrasion resistance, improved RR, decrease in heat buildup, and rapture resistance (Jembere and Fanta [2017\)](#page-16-14). As Jembere and Fanta ([2017\)](#page-16-14) reported, if the size of green silica particles is large, the dispersion of these particles will be weaker. It cannot improve the rubber products' mechanical properties compared to the commercial silica fller. On the other hand, the silicone functional group reacts better on the green silica surface and leads improved modulus, hardness, abrasion resistance, and rheological properties. Also, it can minimize the beginning time of vulcanization (Jembere and Fanta [2017](#page-16-14)). Lolage et al., [2020a,](#page-16-5) [b,](#page-16-5) by synthesis and reinforcement application of highly dispersible green silica in a basic tire tread rubber formulation of a passenger car tire and comparison with the conventional silica, demonstrated that the green silica led to lower Mooney viscosity and much better dispersion as well as better reinforcement factor. Also, tensile strength (TE) and elongation at break (EB) are increased for green silica. Finally, it can be argued that the low-temperature process and a suitable route for converting agricultural waste into a high-value product such as green silica can be beneficial in green tire tread compounds (Lolage et al. [2020a, b](#page-16-5)).

#### **Coupling agent**

Since silica has hard dispersion with nonpolar rubbers due to its acidic nature, high surface energy, and strong polar functional groups such as silanol and siloxane on its surface; the main issue is the good dispersion of fller in the rubber and fller-rubber interaction (Jin et al., Hassanabadi et al. [2020](#page-16-15), Song [2020](#page-18-13), Tureyen et al. [2021](#page-18-18)). The main reason for the unequal and challenging dispersion of silica particles in rubber compounds is the tendency of these particles to aggregate, which is also because of the presence of silanol groups on the surface of silica particles that may cause hydrogen bonds. For this reason, the interaction between fller-rubber is hugely weaker than the interaction between fller-fller in silica compounds in comparison to CB (Kohjiya et al. [2020\)](#page-16-16). To solve this problem, some methods have been used including the use of bifunctional organosilane coupling agents such as bis-(triethoxysilylpropyl) tetrasulfde (TESPT) or bis-epoxypropyl polysulfde (BEP) as a popular coupling agent in the tire industry which efectively increases the wettability and compatibility of silica with hydrocarbon elastomers and promotes polymer-fller interactions via the formation of covalent chemical linkages (Ye et al. [2020\)](#page-18-19).

#### <span id="page-3-0"></span>**TESPT**

TESPT is a coupling agent through the ethoxy-groups in [TESPT](#page-3-0) molecules to silanol groups of silica on the one hand and rubber during the vulcanization reaction on the other, leading to the generation of chemical bonds between silica and rubber (Yrieix et al. [2016\)](#page-18-20). Due to the tetrasulfde structure, TESPT emits a large C2H5OH silanization reaction during mixing, which poses an environmental challenge. Therefore, some silanes such as 3-octanoylthio-1-propyltriethoxysilane (NXT) and 3-mercaptopropyl-di(tridecan-1-oxy-13-penta(ethyleneoxide)) ethoxysilane (VP Si-363) have been considered too (Sengloyluan et al. [2016](#page-17-15)).

Source	Description	Ref
Rice husk	$\bullet$ H <sub>2</sub> O <sub>2</sub> and NaOH were used as extractors · Optimum condition for maximum silica and minimum solid loss: 8% NaOH, $1\%H_2O_2$ in 20 °C, and removal of silica is about 88% • Optimum operating conditions taking into account the cost aspect: 5.29% NaOH, $1\%$ H <sub>2</sub> O <sub>2</sub> in 20 °C, and removal of silica is 88.47% and removal of silica is about $75%$ All optimization of concentration and temperature values was performed by response surface methodology (RSM) and Box-Behnken design (BBD)	Bazargan et al. (2020)
Rice/paddy straw	• In three steps, acid hydrolysis, alkaline peroxide treatment $(1.5\%H_2O_2, 2\%$ NaOH), and precipitation (with $H_2SO_4$ , PH = 6.5), silica was extracted from paddy straw powder • Extraction of pure nano-silica with a relatively uniform shape with a size of about 17 nm was performed in a relatively inexpensive manner	Kauldhar and Yadav (2018)
Rice husk	• Amorphous silica was extracted from the rice husk, and the reaction conditions Santana Costa and Paranhos (2018) such as temperature, time, and NaOH concentration that was the extractor were studied • 1 M HCl was used for acid treatment of RHA, and 5 M $H_2SO_4$ was used for silica deposition • High specific surface area of silica was obtained • Optimal extraction conditions: $[NaOH] = 4 M$ , time = 4 h, extraction yield ~ $80 - 99\%$ • Optimal calcination conditions: time = 2 h, $T = 700$ °C	
	Cassava periderm (CP) $\bullet$ CP was washed, dried, and leached with 40 ml of HCl. Then it was rinsed with Ahmed et al. (2021) distilled water • Concentration and time have a great effect on acid pretreatment of cassava periderm, and temperature has a lesser effect • Optimum treatment condition was 1.59 M of HCl, $45 \pm 5$ °C, and 85 min	
Rice hull ash (RHA)	• RHA was milled in dilute HCl, placed in yttria-stabilized zirconia, and HCl solution (3.7 wt% HCl). After 48 h, acid-milled RHA was recovered by suction filtration through a Buchner funnel and then washed with DI water and finally was dried, and this powder was added to the $HG + KOH$ solution. The mixture was heated, and during silica depolymerization after 24 h, 40–50 wt% of the silica is extracted as the spirosiloxane • The spirosiloxanes provide access to high purity silica in multiple forms which can replace other alkoxysilanes that are currently produced from silicon metal	Temeche et al. $(2020)$
Rice husk	• Amorphous silica was extracted from rice husks obtained from different regions of Kazakhstan by three procedures of HCl pretreatment, citric acid pretreatment, and without pretreatment • 2 M HCl and citric acid was used for the acid pretreatment of rice husk • Calcination condition: time = 4 h, $T = 600$ °C • Silica extraction condition: [NaOH] = 2 M, temp = 90 °C, time = 2 h • Variation was observed in the properties of the synthesized silica, but the best properties obtained were as follows: 99.96% purity, 20% yield, and 980 m 2/g surface area	Azat et al. (2019)
Wheat husk and spike	• Crystalline silica was extracted from the wheat husk and spike ash, with a thermal reduction method • Initially, two thermal regions were applied one hour at 500 $\degree$ C, and then calci- nation occurred at 2 h at 800 °C, and finally 23% wheat ash was prepared. Then thermal treatment was carried out by NaOH 2.5 N for 12 h, after that, HCl 6 N added dropwise to the solution, the reaction occurred between evaporated mag- nesium and SiO2, then the product was washed with HCl 1 N and then with 5% HF to obtain pure silica • The highest efficiency of silica extraction was obtained at 550 $\degree$ C, low tem- perature of magnesium reduction	Hernández-Martínez et al. (2020)

<span id="page-4-0"></span>**Table 1** Recent studies to extract of silica from agricultural waste

#### **Table 1** (continued)



#### **NXT**

NXT has better scorch safety than TESPT because of an octanoyl-blocked mercaptosilane. Also, the apparent activation energy of the vulcanization reaction of a compound with NXT is less than that of TESPT, and the apparent activation energy of both compounds reduces with enhancing silane concentration (Wang et al. [2020a](#page-18-22), [b](#page-18-23)).

#### **VP Si‑363**

Another coupling agent is VP Si-363 or 3-mercaptopropyldi (tridecan-1-oxy-13-penta (ethyleneoxide)) ethoxysilane which is a mercaptosilane containing 1 ethoxy-group and 2 long alkoxy groups that is due to containing the thiol group or the long alkoxy groups in its structure the reaction rate between silica and silane enhances (Sengloyluan et al. [2016](#page-17-15)). In addition, long alkoxy chains containing oxygen atoms can increase silane uptake at the silica surface, thus speeding up the silane-silica reaction (Ngeow et al. [2019\)](#page-17-17). Compounds containing VP Si-363 compared with TESPT in tire compounds improved the RR and reduced Volatile organic compounds (VOC) (Blume et al. [2019\)](#page-15-20). Figure [2](#page-6-0) shows the silanization process by the coupling agent schematically.

#### **Improving silica dispersion in the green tire**

Silica-polymer compounds have been studied for many years, due to their excellent properties such as mechanical, electrical, optical, thermal, and inimitable fame retardant, and all these properties are in case the dispersion of silica in the polymer matrix are done well (Kierys et al. [2020;](#page-16-19) Wang et al. [2020a,](#page-18-22)

[b](#page-18-23)). Improving silica dispersion in silica-rubber compounds can reduce RR and increase wet traction (Weng et al. [2020](#page-18-8)). As mentioned in the previous sections, mixing silica with rubbers is complicated and is done with the help of coupling agents. Improving silica mixing is the key to achieving the desired properties in silica compounds. Until today, various solutions have been proposed to solve this problem, the most common of which are silane coupling agents, which bind silica particles and polymer molecules together by covalent bonding (Maghami [2016\)](#page-17-18). Since the coupling agent reacts with some acidic silanol groups on the silica surface, the presence of an alkaline substance such as diphenylguanidine (DPG), which acts as a secondary accelerator in the vulcanization reaction, can neutralize these residual acid groups on the silica surface; on the other hand, by adsorbing on the silica surface, it reduces the polarity of the silica (Roshanaei et al. [2020\)](#page-17-19). Also, during the reaction of silane and silica, ethanol is released, which is not easy to recycle in industrial production. Because ethanol vapor is harmful to nature, many countries have strict regulations for the release of VOCs, so studies have been performed on designing a new VOC-free bonding agent containing epoxy groups to react with silanol-silica groups instead of silane (Yang et al. [2020](#page-18-24); Ye et al. [2020\)](#page-18-19). This coupling agent uses sulfde bonds to improve the reaction of silica with rubber (Ye et al. [2020](#page-18-19)).

Several physical and chemical modifcations, such as an interface or bulk conversion, have been applied to improve the compatibility of silica with the polymer matrix (Wang et al. [2020a,](#page-18-22) b). The polymer-fller interaction is improved by functionalizing the polymer chain; thus, the silica dispersion increases (Hassanabadi et al. [2020](#page-16-15)). Researchers are trying to design functional elastomers, especially SSBR, to

<span id="page-6-0"></span>**Fig. 2** Schematic silanization reaction on the silica surface in the presence of diferent coupling agents (Sengloyluan et al. [2016\)](#page-17-15)



reduce SBR hydrophobicity for more excellent compatibility of hydrophilic silica with SBR (Das et al. [2020](#page-15-22); Hassanabadi et al. [2020\)](#page-16-15). Rubbers with phosphonium compounds to silica-containing formulations can improve the dispersion and increase surface interaction, showing lower RR (Bockstal et al. [2019](#page-15-0)). Also, petroleum resin efectively improves wet traction; therefore, modifed phosphonium styrene resin can solve both green tire needs (Weng et al. [2020\)](#page-18-8).

Zinc acts as a pair factor by reacting as a silanol-silica and alkoxy-silane groups and is the most common bonding agent for strong adhesion between silica and rubber (Song [2020](#page-18-13)). Nanomaterials such as carbon nanotubes and graphene have been used in the rubbery compound to maintain wear resistance besides improving RR and wet grip (Guo et al. [2020](#page-15-23); Hao et al. [2020](#page-15-24); Kumar et al. [2020\)](#page-16-22). Nanomaterials improve the properties of the rubbery compound by their essential properties like excellent aspect ratio. Meanwhile, carbon nanotubes with rough surfaces have a higher dispersion than smooth carbon nanotubes and have stronger surface interactions (Kang et al. [2021\)](#page-16-23).

Plasticizers can be used as an aid to the process as well as improving the dispersion of the fller in the elastomeric compound (Xu et al. [2020](#page-18-25); Huang et al. [2021\)](#page-16-24). One of the problems with the plasticizers is their migration to the surface, which is problematic for human health and the environment (Hassan et al. [2020](#page-15-25)). The compatibility of polymerized soybean oil (SBO) with polymers and thermal stability is higher than SBO and oils as plasticizers (Ifijen et al. [2021](#page-16-25)), but polymerizing SBO into large molecules reduces their plasticizing capability. Due to its high purity and active bonds  $C = C$ , it is considered as a suitable alternative to aromatic oils (Hassan et al. [2019\)](#page-15-26). SBO improves processing, provides a better fow rate, faster dispersion, and the incorporation of fller with the polymer network, and endows thermal stability (Karmalm et al. [2009](#page-16-26)). The demonstration of coupling interaction of silanized plasticizer (SP) as an interfacial compatibilizer into SBR/silica system during cross-linking is shown in Fig. [3](#page-7-0) (Hassan et al. [2020](#page-15-25)).

Recent measures taken to improve the silica dispersion in the rubber matrix and thus improve the physical–mechanical and dynamical properties of silica-flled rubber compounds used in the tread of the green tires are listed in Table [2](#page-8-0).

The compound of high-performance tire tread should have the following characteristics: for snow traction should have a gentle elastic modulus amount at low temperatures, for wet traction should have high loss modulus from 0 to 20C, for dry stability should have rigid complex modulus from 20 to 30C, for RR should have low hysteresis at high temperatures, and also for wear resistance should have a low glass-transition temperature. On the other hand, these ideal properties are challenging to achieve due to the restriction of high loading silica-flled compounds (Kang et al. [2021](#page-16-23)). Silane grafting onto the rubber can be used in the tire industry, as with improved silica dispersion, the physico-mechanical properties of rubber could be better.

The functional groups, capable of shaping hydrogen bonds with silica silanol groups, increased the interaction between silica and polymer and decreased silica agglomerates (Weng et al. [2019;](#page-18-12) Hassanabadi et al. [2020\)](#page-16-15). It is also possible to

<span id="page-7-0"></span>**Fig. 3** Schematic image of coupling interactions of SP in SBR/silica compound after vulcanization reactions (Hassan et al. [2020\)](#page-15-25)



improve the dispersion of silica particles in the rubber matrix by anionic polymerization of polybutadiene rubber and oxidized soybean oil (Kim et al. [2015](#page-16-27)). Silica surface modifcation can also have a signifcant efect on its dispersion in rubber compounds, leading to better performance of rubber compounds (Zhang et al. [2018a,](#page-18-7) [b;](#page-19-0) Zhang et al. [2019](#page-19-3)).

RS-CNTs improve the wet traction and dry stability of rubber due to their rough surface and provide good RR due to their good dispersion and surface interactions between the polymer and CNTs. Besides, soybean oil can increase the snow traction of tires due to its mild elastic modulus and suitable glass-transition temperature. So, the RS-CNT/soybean oil compound showed the highest strength based on the synergistic efects of carbon nanotubes and soybean oil. The synergistic effects of mixing these two materials produce high wear resistance tires on an industrial scale (Kang et al. [2021](#page-16-23)).

SP has excellent potential for improving the overall performance of silica-flled SBR compounds used for the green tire industry affordably and environmentally friendly (Hassan et al. [2020\)](#page-15-25). Today, by converting agricultural waste into a valuable product such as silica, the green tire reinforcement fller has been produced. Still, by recycling this waste, which is also challenging to dispose of, a greenway has been used to protect the environment (Lolage et al. [2020a](#page-16-5), [b](#page-16-5)).

## **Environmental assessment of green production process**

As mentioned in the previous sections, green tires are more environmentally friendly than regular tires in some respects, which are given below:

#### **Environmental assessment of CB replacement with silica**

Because CB is produced through the incomplete combustion of heavy petroleum products, as a result of this incomplete combustion, toxic and dangerous gases are released into nature. In addition, hazardous waste is generated as a result of this process (Dominic et al. [2020](#page-15-13)). Therefore, it is necessary to replace CB with environmentally friendly and renewable fllers such as silica in the rubber industry to prevent the occurrence of environmental damage also health problems (Baan [2007\)](#page-14-9). In addition, the use of renewable biomass resources is easier to access, has environmental benefts, and is also economical to use to be given more attention in the future (Stegmann et al. [2020;](#page-18-26) Zhang et al. [2021a](#page-19-1), [b](#page-19-2)).

#### **Reducing GHG emission**

In response to the increase in global GHG emissions and thus the increasing pressure on climate change management, the need for highly efective and innovative strategies to reduce that in all industries has been considered (Hertwich and Wood [2018](#page-16-28); Metson et al. [2020;](#page-17-20) Liu et al. [2021](#page-16-29)). For example, in 2013, China launched a practical plan to prevent and control air pollution to reduce GHG emissions, improve air quality, and protect public health (Lu et al. [2019\)](#page-17-21). In the tire industry, they could realize an annual reduction of up to 45 million tons of CO2 emissions and could be realized in the USA alone with the addition of precipitated silica to tire treads ([www.reportsanddata.com](http://www.reportsanddata.com) [2020](#page-18-27)). Therefore, integrating these tires over the traditional ones can signifcantly decrease carbon footprint.

#### **Reducing fuel consumption**

One of the main environmental effects in the lifetime of a tire is RR during use. Twenty percent of car fuel consumption and 30 to 40% of truck fuel consumption is due to RR (Barrand and Bokar [2008\)](#page-15-27). On the other hand, the US National Research Council conducted a study that showed that a 10% reduction in RR reduces the fuel consumption of passenger cars by 1 to 2% (Consumers [2006](#page-15-5)). The US Environmental Protection Agency also found that reducing RR on-highway vehicles reduced fuel consumption and GHG emissions, as well as reduced NOx (Bachman et al. [2006\)](#page-14-10).



<span id="page-8-0"></span>Table 2 Recent studies to improve the silica dispersion in the green tires **Table 2** Recent studies to improve the silica dispersion in the green tires



**Table 2** (continued)



**Table 2** (continued)

Table 2 (continued)

#### **Reducing accumulated agricultural waste**

## Due to the increase in world population, various industries have increased their productions, including agricultural and food industries (Ng et al. [2020](#page-17-22); Ortiz-Gonzalo et al. [2021](#page-17-23)). These industries often supply the required raw materials through agriculture, and after producing the fnal product, a lot of waste is made. In fact, agricultural wastes are plant remainder that is not processed into food and edible (Donner et al. [2021](#page-15-28)) and often disposed of the unscientifc way in the environment, that is considered an environmental problem (Ravindran et al. [2020\)](#page-17-14). On the other hand, incineration of agricultural waste through GHG emissions causes severe pollution in the environment (Adebisi et al. [2019](#page-14-5), [2020](#page-14-6)). About 140 billion tons of the world's remaining biomass is produced annually from agriculture (Martirena and Monzó [2018](#page-17-24)). In all rice-producing countries, rice husk, an agricultural by-product, is abundantly produced. It is estimated that over 120 million tons of rice husk are produced annually (Su et al. [2020](#page-18-28)).

#### **Reducing CO2 emissions from conventional silica production**

As mentioned in the "Silica" section, carbon dioxide, sodium sulfate, and effluents will be generated during the conventional silica production process, and environmentally this process is a challenge (Zarei et al. [2021\)](#page-18-29). Maier (Maier [2012\)](#page-17-25) reported the result of the emission factor of fused silica, which makes from fusing quartz sand, which can be seen in Table [3.](#page-11-0)

In fact, fumed silica is a by-product of the production of silicon and ferrosilicon, and the amount of CO2 resulting from its production is given in Table [3.](#page-11-0) Gao et al. ([2017](#page-15-29)), with a synthesis of a green olivine nano-silica, evaluated the carbon footprint, and they reported a reduction of the CO2emission between 20.4 and 29.0%. Mellado et al. [\(2014\)](#page-17-26) used RHA-based silica and reported a 50% decrease in  $CO<sub>2</sub>$ emission (Mellado et al. [2014](#page-17-26)).

#### **Recycling of agricultural waste containing silica**

Because a large amount of agricultural waste contains silica, it can be recycled and produced green silica. Among them is RHA which contains 85–95% silica (Chun and Lee [2020](#page-15-16)), sugarcane bagasse which contains 92.5% silica (Sapawe and Hanafi [2018](#page-17-12)), bamboo leaf which contains about 61% silica (Silviana and Bayu [2018](#page-18-16)), and corn stalks (Adebisi et al. [2019](#page-14-5), [2020\)](#page-14-6). And other agricultural waste such as bamboo culm, oil palm ash, sugarcane bagasse ash, wheat straw, and corn cob ash can recycle and synthesize silica (Okoronkwo et al. [2016](#page-17-13); Sapawe and Hanafi [2018;](#page-17-12) Surayah Osman and Sapawe [2019;](#page-18-17) Farirai et al. [2021](#page-15-17)).

#### **Tire half‑life**

Green tires, which are known to have lower fuel consumption due to lower RR than conventional tires, also have more extended longevity (Wu et al. [2019a,](#page-18-30) [b\)](#page-18-31).

### **Economic assessment of green production process**

#### **Green tire production costs**

Despite the environmental and economic incentives to use silica technology in the rubber industry, it should be noted that the issue of silica dispersion in the rubbery matrix is more costly than CB (Lolage et al. [2020a](#page-16-5), [b\)](#page-16-5). Due to the silanization reaction, which is the connection of the silane with the silica in the mixer, and the silane connection reaction to the rubber simultaneously in the production of a green tire tread compound, the cost, and energy consumption of using silica instead of CB is higher. So it takes time, and it must spend more energy (Sengloyluan et al. [2014;](#page-17-27) Kaewsakul et al. [2015\)](#page-16-31). In addition, the uses of special rubbers such as SSBR (Hassanabadi et al. [2020;](#page-16-15) Weng et al. [2020](#page-18-8); Ye et al. [2020\)](#page-18-19) to help improve the dispersion of silica and reduce RR are other factors that increase the cost of green tire production.

#### **Reduce costs due to reduced fuel consumption**

Green tire consumers will beneft from better fuel economy in the longtime. Shah ([2012\)](#page-17-28) based on European usage refects calculated that a car owner traveling 12,500 km/ year could easily save up to  $\epsilon$  100 of fuel/year. Also, the extra investment of  $\epsilon$  20 to  $\epsilon$  50 per tire saves every 2 years. The global green tires market size is estimated to reach USD 178.07 billion from USD 80.48 billion in 2019, delivering a compound annual growth rate of 10.4% through 2027 ([www.](http://www.reportsanddata.com) [reportsanddata.com](http://www.reportsanddata.com) [2020\)](#page-18-27).

## **Reduce costs by replacing commercial silica with waste‑based silica**

One of the main components of the green tire is silica, which is the main production process from natural sources. In

<span id="page-11-0"></span>**Table 3** Carbon footprint for fused silica

Carbon foot- print for quartz sand (kg $CO2/t$ ) $CO2/t$ )	Specific melt- ing energy (kg)	Specific elec- trode consump- tion (kg $CO2/t$ )	Total ( $kg CO2/t$ fused silica)
29	620.46	36	685.46

addition to reducing natural resources, this process is associated with high energy consumption and high cost (Surayah Osman and Sapawe [2019\)](#page-18-17). Few studies have compared the cost of commercial and waste-based silica. Tong et al. ([2018\)](#page-18-32) investigated the production of a low-cost, low environmental impact sodium silicate solution from RHA and reported a 55% lower cost than commercial silicate solution.

Therefore, comparing the cost of green tires produced by commercial silica with green tires made by silica obtained from agricultural bio-waste in the rubber industry may be necessary. For this purpose, in the following, we performed a preliminary cost estimate of using green silica in the green tire industry instead of commercial silica to determine the economic benefts of using it. As mentioned in the "Green production process of tires" section, sodium silicate is used to make silica, which is typically obtained by melting quartz rock at 1300 °C with sodium carbonate. This process is both costly and time-consuming (Kamari and Shahbazi [2020](#page-16-32)). Maybe that is why the reported price for a ton of commercial silica on an industrial scale is \$ 600 to \$ 900 (alibaba [2022](#page-14-11)), while the price of silica extracted from agricultural waste, such as rice husk, has been reported \$ 340 per ton (indiamart [2022](#page-16-33)).

A tire is not a simple object but is made up of diferent components to make the tire. These components include tread, inner liner, nuts, and straps (Weyssenhoff et al. [2019](#page-18-33)), and therefore, the weight of a tire consists of the weight of each of these components. Table [4](#page-12-0) shows the weight percentage of each component of a tire (p2infohouse [2020\)](#page-17-29).

As shown in Table [4](#page-12-0), more than half of the tire weight (54.5%) is made up of tread and sidewall compounds, and in green tires, silica roles as reinforcement agents. Typically, the weight of a passenger tire is 12 kg. According to what has been said, about 4 kg of its weight is related to the tread compound, and about 2.5 kg of its weight is the sidewall compound. Based on the tread and sidewall formulation (Ten Brinke [2002](#page-18-11); Ghosh et al. [2012\)](#page-15-30) reported, and what has been said above, about 1,400 g of silica is used in the tread and 650 g in the sidewall of green passenger tires. According to research and analysis performed, at least 2 kg of silica has been used to manufacture each green passenger tire. The efect of using the agricultural bio-waste silica instead of commercial silica on the manufacturing cost of each tire (\$/tire) in the green tire industry is shown in Table [5.](#page-12-1)

Table [5](#page-12-1) compares prices on an industrial scale, as you can see if the manufacturer uses agricultural bio-waste silica. It saves about 1\$ per tire on production costs. Therefore, the efect of changing the commercial silica to bio-waste type on the fnal price of each tire for the consumer will be more than 1\$ price reduction.

<span id="page-12-0"></span>**Table 4** The weight percentage of each component of a tire



<span id="page-12-1"></span>**Table 5** Effect of using the commercial and bio-waste types of silica on the cost of each green tire manufactured



#### **Perspective**

In order to expand the market for green products, the ratio between price and quality in the manufactured products must be considered. This means that these types of green products can compete in the consumer market with products made from raw materials (Sadeghi et al. [2021a](#page-17-1), b, c). In today's world, sustainable raw materials are being used to make economic processes greener (AliAkbari et al. [2021b](#page-14-12)). In the assessment of Qiao and Su ([2021](#page-17-30)), assuming that the price of the new green product and the previous conventional product was constant, the original equipment manufacturer showed a preference for a higher quality product, which reduced the cannibalization efect. In other words, by producing a new green product with relatively high quality, the producer can move to gain market share and make a new consumer market. The efect of reducing profits can be offset by increasing market share. Another efective strategy for a large enterprise can be to reduce prices to increase market share (McColl et al. [2020\)](#page-17-31).

Renewable portfolio standard plays a catalytic role in expanding the green market (Marfavi et al. [2022](#page-17-32)). These standards were examined in the regulated and deregulated markets in the USA by Shayegh et al. In summary, the study found that in deregulated markets, the need for subsidies is lower for markets with low penetration rates. In contrast, the need for donations for markets with high market share is minimized in regulated markets (Shayegh and Sanchez [2021](#page-18-34)). As a result, in the case of our study, the green tire industry, the target market structure should be identifed, and supportive standards should be maintained in accordance with the industry and market structure.

Understanding new social issues in the successful design of the market is another issue that plays a crucial role in the production and expansion of the market (Langley [2020\)](#page-16-34). For example, with the development of the industry 4.0 Concept, production has shifted towards more personalization. This issue was confrmed in the study of Saniuk et al. ([2020](#page-17-33)), and it was proved that consumers, in addition to price and quality, have a great tendency to personalize products and are willing to pay more for the personalized product. The consumer pays this type of payment to satisfy the sense of uniqueness, which increases consumer loyalty. On a large scale, material consumption and waste production are reduced. The question is whether the above issues, including the implementation of support standards in accordance with the structure of the target market and product personalization, can be applied to the green tire market? In the case of customer personalization of the purchase, in the process of selling vehicles, the options available in selecting more details of the tire by the customer, chosen options such as soft, hard, medium, and even elements of the tire appearance such as size and color, can be activated if the customer selects the green tire. In this method, the consumer receives more personalization as an incentive option if he chooses the green tire. Of course, this method requires supporting standards and laws. Or in the discussion of customer taste design, it can be through customer mental stimulation that education and advertising are among the main stimuli of mental stimulation that can be used to create more customer desire for greener products. Therefore, in addition to quality and economic issues, the customer also considers environmental responsibilities (Poels and Dewitte [2019](#page-17-34); Stocchi et al. [2021;](#page-18-35) Yang et al. [2021](#page-18-36)).

The market growth is due to the climbing awareness about adverse efects on the environment and human health caused by vehicular emissions and the cumulative number of pollutants emitted by the automobile industry. Green tires have gained popularity because of lower fuel consumption, and the price of diesel and gasoline has increased this popularity. The growth of autonomous vehicles and substitute powertrains (hybrid & electrical) leads to increased green tire deployment (Baskar et al. [2021](#page-15-31)). Integrating these tires over the traditional ones can signifcantly decrease carbon footprint. For example, an annual reduction of up to 45 million tons of  $CO<sub>2</sub>$  emissions could be realized in the USA alone with the addition of precipitated silica to tire treads [\(www.reportsanddata.com](http://www.reportsanddata.com) [2020\)](#page-18-27).

Since silica is the main fller in the tread of green tires, the use of agricultural waste as an alternative source of silica seems necessary. The attractiveness of these sources is the meager material value, stability, high silica content, and the ability to produce amorphous silica (Surayah Osman and Sapawe [2019](#page-18-17)). Based on raw materials, the silica incorporated rubber segment is estimated to witness major demand in the coming years as the high silica content in the rubber permits tires to attain low RR, thereby reducing fuel consumption as well as harmful vehicular emissions.

## **Conclusion**

Attention to the future of the world environment is increasing day by day (Bigdelo et al. [2021\)](#page-15-32). This attention can be seen in a variety of industries that use cleaner raw materials and production methods that are less harmful to the environment while maintaining higher profits (Aliakbari et al. [2021a\)](#page-14-13).

Tires are one of the most common products globally, not only the tires themselves but the production process of which causes a lot of pollution. In recent years, research and implementation of cleaner, environmentally friendly production processes and the use of more sustainable raw materials for tire production have been considered, so the production of green tires using silica as a signifcant reinforcing fller increased worldwide. This green claim is made because silica helps save more fuel in vehicles and reduces  $CO<sub>2</sub>$  emissions (Lolage et al. [2020a](#page-16-5), [b\)](#page-16-5). The use of agricultural waste to produce silica reinforces the claim that these tires are green.

This article reviews recent studies on silica production from agricultural wastes and their properties as reinforcement in tires are investigated. Based on these studies, it can be concluded that a low-temperature process and a suitable path for converting agricultural waste into a highvalue product such as green silica can be useful in green tires. The advantages of using green silica in a green tire are as follows:

- CB, the main fller in conventional tires, is a petrochemical product derived from petroleum, but silica, the main filler in green tires, is abundant on earth (Kohjiya et al. [2020](#page-16-16)).
- Silica improved wet traction that is used in winter tires. It also shortens the brake line, which contributes a lot to safety (Ten Brinke [2002\)](#page-18-11).
- The use of silica in rubber tread recipe is reducing RR by 20–30%, and the result is fewer GHG emission (Lolage et al. [2020a](#page-16-5), [b\)](#page-16-5).
- The use of silica and reducing RR, which is the most crucial feature of the green tire, has greater stifness modulus values which provide tensile strength, abrasion resistance, and tear resistance to the tread compound (Grunert et al. [2020;](#page-15-15) Kang et al. [2021](#page-16-23); Song [2020](#page-18-13); Ye et al. [2020](#page-18-19)).
- While CB fller reduces the overall performance of tires in cases such as fuel consumption, tread life, and safety

throughout all seasons while increasing both energy consumption and environmental issues, silica fller improves all of this (Wu et al. [2019a](#page-18-30), b).

- Green silica will have competitive properties against the common silica on the market as a filler in the green tire.
- The cost of green silica is lower, so it is justified in the green tire industry.
- Agricultural waste is used optimally based on a circular economy. There are also disadvantages that are summarized below:
- The challenges of using silica in rubber formulation are the problem of silica dispersion in the rubber matrix (Zhu et al. [2019](#page-19-4)).
- Removing the by-product produced during the silanization process in manufacturing green tires from the mixer (Kim et al. [2019](#page-16-35)).
- Silica flled rubbers have a low wear resistance compared to carbon-black-flled ones (Kang et al. [2021\)](#page-16-23).
- Another problem with silica-flled tires is static electricity, which is not present in CB-flled tires (Wu et al. [2019a,](#page-18-30) b).

To implement agricultural waste to provide the materials needed by industry, additional research on economic and technical optimization can be very efective.

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