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Synthesis of mesoporous silica with superior properties suitable for green tire

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ABSTRACT

In this article we report synthesis of mesoporous silica with superior properties for application in green tire (environmentally friendly tire) as filler. The synthesis was done using a newly innovated apparatus which produce mesoporous silica with superior properties. The desired superior properties are big pore size, optimum BET, large pore volume, uniform properties, and improved performance in real application as tire filler. Mesoporous silica was characterized by BET method and final product with a pore diameter of up to 37 nm was obtained without using surfactants. This is unprecedented step toward synthesis of silica that is suitable for tire industry.

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1. Introduction

The growing interest in nanostructured materials calls for the development of processing techniques that allow for the tailoring of specific features of the nanometer size. One method for engineering such structures involves the chemical manipulation of nano-building blocks. Several sol–gel strategies have been successfully used to engineer nanostructure materials as broadly reviewed by Mackenzie and Bescher [1]. Some of the processes take advantage of the versatility and complexity of the hydrolysis and condensation reactions of metal alkoxides. Others exploit the nanoporosity of gels as a host for various molecules or inorganic clusters. In all cases, the chemistry of the systems is the main controlling factor for the resulting nanostructure. However, the reported sol–gel strategies are inadequate to manufacture superior products that are suitable as filler for tire industry. The manufacturing apparatus has a significant contribution to the properties of the final products.

The mesoporous architecture may be tailored for connectivity, orientation, arrangement, or size and exploited for various applications, such a chromatography columns, sensors, catalyst support, low dielectric constant materials, or controlled release of reactants. A very good review by Klein and Woodman lists the many different methods that can be used to control the processing parameters on the porosity of silica products [2]. In the design of complex nanoarchitectures, the main advantage of the sol–gel process is the versatility in the control of size, distribution, and arrangement of nanopores, for example through self-assembly. Furthermore, through careful heat treatment and dependent upon the chemistry of the starting solution and the thermal treatment, many kinds of nanoparticles can be manufactured. Previous studies have reported several methods of manufacturing silica that are currently used in tire industry [3,4]. The major drawbacks of the previous studies can be pinpointed to the properties of their final product. Normally, the silica that was produced had small pore size, poor dispersion in rubber, and the synthesis method was non-economical. That is why silica is not yet widely accepted as filler for tire to completely replace the carbon black which is commonly used. In addition to the sol–gel strategies, a careful design of the manufacturing apparatus can be employed to advance the properties of the final products that are desired for a particular application. Thus, in this study we are improving the properties of silica to make it more suitable as green tire filler.

Silica has been used in the treads of tires for more than twenty years in order to reduce the fuel consumption of vehicles, thus contributing to a reduction in vehicle emissions of greenhouse gases [5, and references therein]. According to Rhodia [6], until now, the best silica have made it possible to reduce rolling resistance by approximately 25%, bringing about a reduction in fuel consumption and vehicle CO_2 emissions by an estimated 5%. Moreover, the company claims that its new Zeosil® Premium enables rolling resistance to be further reduced by almost 10%, making silica 'the most environmentally friendly filler option' for tire tread. Studies conducted demonstrate that the impact of the

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tire on health and the environment is very largely due to the fuel consumption caused by rolling resistance [6]. It was reported that, after 40,000 km a tire containing silica in its tread gives a gain of five eco-points, or 11%, in comparison with one that contains only carbon black. This gain is equivalent to the total environmental impact of the tire production and the raw materials from which it is made. A current report indicate that the world production of amorphous precipitated silica is 1.3 million tons of which one-third is used in tire production [5]. According to the Freedonia Group, Inc. 2007, USA, there is a huge market for silica products. The annual global market is estimated to be $1 Billion at present, with an approximate annual growth rate forecast of 5%. Because of the strict environmental and safety regulations, manufactures and silica markets are obliged to invest in silica products with the following merits: low cost, high quality (uniform properties), "green" i.e. environmentally friendly/less CO_2 emission. Our new innovation is targeting to and suitable for satisfying these conditions.

One of the main reasons why silica is not fully adopted as inorganic tire fillers is due to its inhibitive production cost [4]. Thus, mesoporous silica is normally very expensive compared to the carbon black. However, the cost of silica production can be significantly reduced by various approaches such as by utilizing inexpensive precursors, for example sodium silicate, and by conducting reaction at room temperature to save energy. In addition to those approaches, in this study, we have systematically examined the impact of aging time (polymerization time) in order to minimize time and energy consumption when silica is dried in an oven. It should be noted that the properties of silica is directly related to the aforementioned factors; and the level of its performance in the final product is determined by its properties. For instance, the mesoporous silica with uniform properties have the following advantages: it enables production of products with reproducible quality (for tire, beverages, food), good transparency property (for tooth paste), easy and excellent dispersibility (for tire, paints), excellent coloring properties are obtained (for paper), and a beautiful finish (for films).

In the present study, the synthesis of mesoporous silica was performed in a newly innovated manufacturing apparatus. This apparatus was designed by the researchers of E&B Nanotech Co. Ltd, Republic of Korea in collaboration with the Hanyang University, South Korea. It produces mesoporous silica with uniform and superior properties by enabling uniform mixing of source materials at an accurate predetermined ratio. The apparatus is comprised of high-speed instantaneous reactor equipped with nozzles that generate an eddy current of the source materials (precursors); this enables uniform control of physical properties of the final product. The precursors are then mixed at an accurate predetermined ratio (40 wt.% H_2SO_4 and 24 wt.% $Na_2O{\cdot}SiO_2$). The physical (surface and pore structure) and textural properties of the obtained mesoporous silica are reported. The final product has suitable properties for industrial application as reinforcing filler for the green tire.

2. Experimental procedures

2.1. Preparation of mesoporous silica from $Na_2O{\cdot}3.4\ SiO_2$ and H_2SO_4

Mesoporous silica was prepared from an aqueous sodium silicate solution by the sol–gel method. Sodium silicate solution 24 wt.% $Na_2O{\cdot}3.4\ SiO_2$ (Shinwoo Materials Co., Ltd., Korea) and 40 wt.% H_2SO_4 (Duksan Pure Chemicals Co., Ltd., Korea) were rapidly mixed within a nozzle at a constant flow rate of 60 ml/min so that the reaction occurred homogeneously. The flow rate of precursors was controlled by using chemical feed pumps and air chambers to prevent rapid gelation, as demonstrated in Fig. 1.

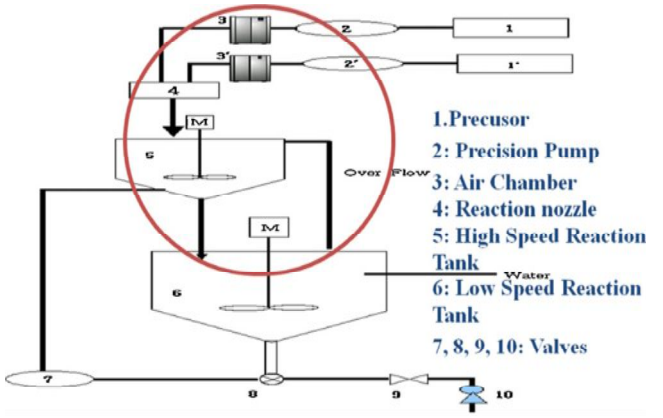


Fig. 1. A diagram showing a new innovative apparatus developed by the Hanyang University and E&B Nanotech Co. Ltd, Republic of Korea, for the production of mesoporous silica.

When sodium silicate solution and H_2SO_4 were mixed, hydrolysis of SiO_2 takes place and is followed by the polymerization. Thus, mesoporous silica was formed according to the reactions (1) and (2):

$$Na_2O{\cdot}nSiO_2 + H_2SO_4 + (2n-1)H_2O \rightarrow nSi(OH)_4 + Na_2SO_4 \quad (1)$$

$$nSi(OH)_4 \rightarrow Si_nO_{(4n-nx)/2}(OH)_{nx} + \frac{4n-nx}{2}H_2O \quad (2)$$

where x is the ratio of OH/Si which relates to the density of silanol terminal groups.

The reaction was carried out at room temperature and after aging for 8 h the product was moved to an auto controlling system where it was instantaneously washed and aged for a predetermined duration (1–7 h) at 150 °C as demonstrated in Fig. 2. The final products were labeled depending on the aging time: S-1 (aged for 1 h), S-2 (aged for 2 h), S-3 (aged for 3 h), S-4 (aged for 4 h), S-5 (aged for 5 h), S-6 (aged for 6 h), and S-7 (aged for 7 h). The comparisons of the properties of the final products are summarized in Table 1. These properties are tunable to wider range depending on the processing conditions which are: pH, reaction speed, reaction temperature, and (in the case of the present study), the aging time.

2.2. Characterization methods

The specific surface area and pore size distributions (PSDs) of the final product were analyzed using Brunauer–Emmet–Teller (BET) and BJH nitrogen gas adsorption and desorption method (ASAP 2020, Micromeritics, USA). BET analysis from the amount of N_2 gas adsorbed at various partial pressures (five points $0.05 < p/p_0 < 0.3$, nitrogen molecular cross sectional area = 0.162 nm^2) was used to determine the surface area, and a single condensation point ($p/p_0 = 0.99$) was used to determine the pore volume. Before N_2 adsorption, the sample was degassed at 200 °C. Pore size distributions were calculated from the desorption isotherms.

3. Results and discussion

3.1. Formation of mesoporous silica with superior properties

The mesoporous silica with superior properties was successfully manufactured by the aforementioned method; that is by using the newly innovated apparatus. The apparatus and other processing conditions were carefully utilized to manipulate the properties of the final product that is obtained through the chemical reactions presented in Eqs. (1) and (2). The mechanism of

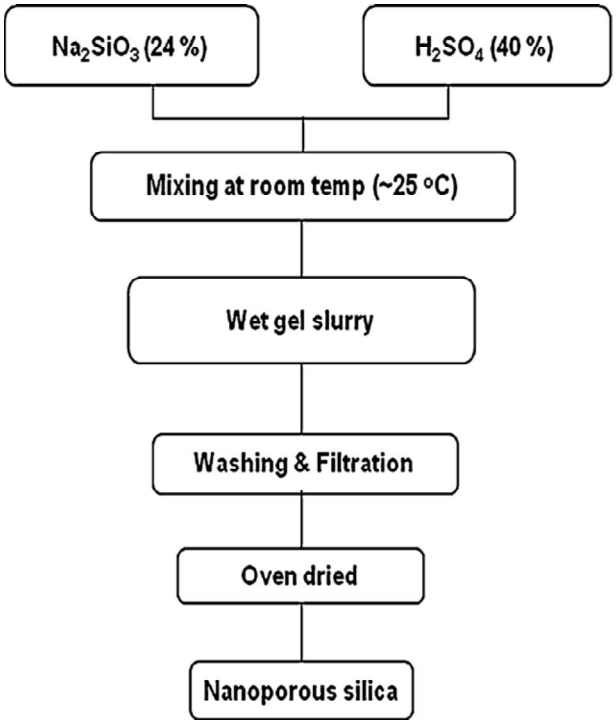


Fig. 2. A flow chart of the experimental procedures for the production of mesoporous silica with superior properties suitable for tire industry.

the formation of mesoporous silica can be briefly explained as follows: First of all, the unstable monomeric silicic acid is formed when H_2SO_4 reacts with $Na_2O{\cdot}SiO_2$. Then it undergoes condensation and polymerization to develop siloxane links and instantaneously the primary nanoscale particles (from approximately 2 to 40 nm) of a very short lifespan are formed [7]. Silanol contained in monomers or weakly branched oligomers are most likely to be protonated. As a result, silica clusters aggregate to form a three dimensional porous silica network clusters with approximately 100–500 nm in size [7]. Finally, the aggregates are subsequently bound together by electrostatic bonds to form agglomerates from 1 to 40 μm. Electrostatic bonds, while weaker than covalent bonds, cannot be broken from normal use; breaking these bonds requires the use of a dispersant. Therefore, mesoporous silica has superior properties and does not cause health hazards because of these aggregates and agglomerates.

3.2. Structural properties/porosity of mesoporous silica

The porosity of the obtained mesoporous silica was examined by using N_2 adsorption/desorption physisorption technique [8]. The results obtained are summarized in Table 1. The average pore diameter resides at the range of 22.2–37.0 nm; this confirms that

Table 1
Comparison of the properties of mesoporous silica obtained after aging for 1–7 h (S-1 to S-7). These properties are tunable to wider range depending on the processing conditions which are: pH, reaction speed, reaction temperature, and (in the case of the present study), the aging time.

	Surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
S-1	180	37	1.45
S-2	214	31.3	1.16
S-3	221	25.3	1.0
S-4	244	22.2	0.96
S-5	262	25.9	1.01
S-6	271	26.7	1.25
S-7	292	24.7	1.35

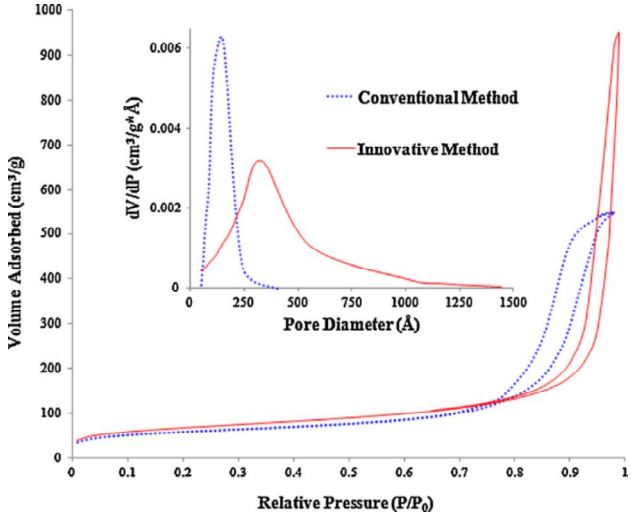


Fig. 3. Comparison of the isotherms and pore size distribution curves of mesoporous silica prepared through our innovative method (red, full line) and conventional product (blue, doted line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

the obtained silica is mesoporous and has extremely superior properties suitable for tire industry which require silica with large pore size. The BET surface area and pore volume ranges from 180 to 292 m^2/g and 0.96 to 1.45 cm^3/g, respectively. Silica with BET surface area of 175 m^2/g was reported to be highly dispersible in tire [9]. Thus, mesoporous silica can be used effectively as filler for green tire since it demonstrates highly superior properties such as large pore diameter (up to 37 nm) and has wide range of useful BET surface area. The nitrogen adsorption-desorption isotherms and pore size distribution of the conventional product compared to mesoporous silica which is synthesized using our innovative method is shown in Fig. 3. According to the IUPAC classification [10], both products exhibit characteristic type IV curves with capillary condensation that signify the presence of mesopores. Moreover, Fig. 3 demonstrates that the mesoporous silica has larger pore size and broader PSD compared to the conventional product. The mesoporous silica obtained at smaller aging time (S-1) has the largest pore size and optimum BET surface area. This product (S-1) is more suitable as economic tire filler because it requires only 1 h as its aging time. Moreover, Table 1 reveals that the BET surface area gradually increase with the increase in aging time. This is attributed to growth of the silica grain and the degree of aggregation which affect the porosity of the final product. Nevertheless, the pore volume is not highly affected by the aging time (even up to 7 h, S-7) indicating that there is no significant further change in silica internal structure. Generally, there are no significant changes in silica properties as the aging time is increased; hence S-1 is sufficient as mesoporous silica with suitable properties for green tire industry.

3.3. Comparison of mesoporous silica with the conventional products used as tire fillers

Tires are complex composites made of mixtures of rubber with metal and textile reinforcements [11]. The primary reinforcing fillers used for the production of rubber articles (such as tire) are precipitated amorphous silica (such as Zeosil® Premium from Rhodia) and carbon black. Tires have a wide range of performance requirements. They must carry the load of the vehicle, have sufficient grip on the road, transmit steering forces to guide the vehicle, provide dampening between the road and the vehicle, have durability that enables their use at high speeds and over long time periods, and have as low as possible impact on fuel

Table 2
Competitive strengths of mesoporous silica (tunable properties) compared with commercial products (Zeosil® Premium and carbon black).

Parameter	Mesoporous silica	Carbon black	Commercial silica
Technology	**Cheap/new innovation**	Conventional	Expensive/Traditional method
Synthesis duration	**Short (minimum energy, temp., etc.)**	Moderate	Long (max. energy, temp., etc.)
Overall operation cost	**Low**	Moderate	High
Relative cost/price	**15–25% cheaper**	Moderate	Expensive
Specific characteristics			
Quantity required	Same	Same	Same
Pore/particle size	Tunable/**wide range/uniform (up to 40 nm)**	28 nm/not tunable	Tunable/limited range
Bulk density	0.11–0.32 g/cm^3	~0.32 g/cm^3	0.19–0.32 g/cm^3
BET surface area	**Tunable (up to 300 m^2/g)**	120 m^2/g	215 m^2/g
Oil absorption	Up to 300 ml/100 g	~100 ml/100 g	150–300 ml/100 g
Performance characteristics			
Tire durability	Good	**Excellent**	Good
Fuel economy	**Fuel-efficient**	High fuel consumption	Fuel-efficient
Manufacturing complexity	Moderate	**Simple**	Moderate
Environmental concern	**"Green" tire/Less CO_2 emission**	Environmentally unfriendly	"Green" tire/less CO_2 emission
Dispersibility in rubber	**Excellent**	**Excellent**	Good
Processing	**Excellent**	**Excellent**	Good
Handling	Excellent	Excellent	Premium
Waste released	Na^+ and SO_4^{2+} ions (**harmless**)	CO_2/CO (contribute global warming)	Na^+ and SO_4^{2+} ions (harmless)
Health concern	**Harmless**	Carcinogenic (Group B)	Harmless
Other characteristics	**Low** rolling resistance, **very good** wet traction, and good wear resistance	High rolling resistance, poor wet traction, and **excellent** wear resistance	Low rolling resistance, good wet traction and wear resistance

consumption. The reinforcing fillers used in tire compounding are critical to achieving the performance requirements. This is especially true for the tread compound with its large number of requirements and emphasis on wear resistance. The fillers provide a large degree of strengthening of the rubber network, resulting in a substantial increase in stiffness, tensile strength, and resistance to abrasion [12]. The reinforcing fillers achieve this via a high level of chemical links with the polymer network. Without reinforcing fillers, tires would need to be replaced considerably more often, resulting in an increased burden on end-of-life-tire (ELT) management and an increase in tire manufacturing energy requirements and greenhouse gas emissions per vehicle. Another benefit of the fillers strength is its ability to transmit forces through the tread area (or footprint) of the tire. The most important aspect of this is improving traction and reducing stopping distance for the vehicle [13]. Without well adapted reinforcing fillers, vehicles would not be able to stop as quickly as they currently can, causing safety concerns for drivers.

In order to empirically demonstrate the superiority of the mesoporous silica (as a desired tire filler), it was compared with its counterparts that are currently available in the market (conventional products). Various characterization methods (summarized in Table 2) demonstrate that the mesoporous silica has superior properties compared to its commercial/conventional counterpart. The observed differences can be associated with the microstructure of the products. For example, though the isotherm and pore size distributions patters are similar, the two products have demonstrated notable differences, as demonstrated in Fig. 3. Mesoporous silica has larger pore size and pore size distribution that are suitable for tire applications and for other applications that require silica with those properties. Silica with big pore size can be easily dispersed in rubber/tire. It improves the longevity of the tires, in terms of overall load bearing, durability, and tread-wear performance.

Moreover, Table 2 demonstrates striking superiority of mesoporous silica compared to the products that are currently available in the market of silica for tire. For instance, the manufacturing process of mesoporous silica is 15–25% cheaper than commercial products since the synthesis duration was shorter and there was significant cost serving (energy, time, labor, etc.). The porosity of mesoporous silica was superior and highly tunable compared to other products. For example, the BET surface area of the mesoporous silica can be tuned up to 292 m^2/g and the pore diameter can be raised up to 37 nm. Normally, this is not possible without using surfactant/templates. A detailed comparative-description of the properties reported in Table 2 is beyond the scope of this article.

4. Conclusion

The synthesis of inexpensive mesoporous silica with superior properties using a newly innovated manufacturing apparatus is reported in this study. The innovated apparatus, together with careful manipulation of the reaction conditions, can be utilized to produce mesoporous silica with wider range of suitable properties as filler for green tire. The mesoporous silica developed in this study has superior properties such as large pore diameter (up to 37 nm) and optimum BET surface area (tunable) suitable for tire industry. The approach reported in this study is more economical and it produces mesoporous silica with superior properties compared to its commercial counterparts that are currently available in the market of fillers for tire. The project on scale-up of the apparatus for mass production is in progress.

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