Using Silica from Rice Husk as a Reinforcing Filler in Natural Rubber

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The objective of this research was to reinforce natural rubber with silica prepared from rice husk. Rice husk was cleaned with tap water, then treated with 0.4M hydrochloric acid at 105°C for 3 hours. The treated rice husk was burnt at 600°C for 6 hours. The resulting white ash contained as high as 99.6% silica. The ash was ground with a jet mill and tested for its properties. It was found that silica from rich husk ash (RHA silica) had higher silica content, higher specific surface area and lower moisture content than commercial silica commonly used in rubber industries. RHA silica was then used as a reinforcing filler in natural rubber. The curing characteristics of natural rubber products using RHA silica and commercial silica were examined with an oscillating disk rheometer and a Mooney viscometer. Mechanical properties, namely, tensile strength, tear strength and hardness were determined. The results indicated that products reinforced with RHA silica had shorter curing times compared to those with commercial silica. Overall mechanical properties, i.e. tensile strength, tear strength, abrasion resistance, compression set and resilience, of rubber products reinforced with RHA silica are better than those with commercial silica. However, the hardness was inferior to those reinforced with commercial silica. Therefore, the products are suitable for applications in which hardness is not the major concern but other mechanical properties are desirable.

Key words: Natural rubber, silica, rice husk, reinforcement, composites.

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การใช้ซิลิกาจากแกลบเป็นสารตัวเติมเสริมแรงในยางธรรมชาติ

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งานวิจัยนี้เป็นการทดลองเสริมแรงยางธรรมชาติด้วยซิลิกาที่เตรียมได้จากแกลบ โดยนำแกลบที่ล้างด้วยน้ำแล้วไปทำปฏิกิริยากับกรดไฮโดรคลอริกความเข้มข้น 0.4 โมลาร์ ณ อุณหภูมิ 105 องศาเซลเซียส เป็นเวลา 3 ชั่วโมง แล้วนำไปเผาที่อุณหภูมิ 600 องศาเซลเซียส เป็นเวลา 6 ชั่วโมง จะได้เถ้าสีขาวที่มีปริมาณซิลิกาสูงถึงประมาณร้อยละ 99.6 นำเถ้าซิลิกาที่ได้ไปบดให้เป็นผงด้วยเครื่องบดแบบใช้กำลังลม เมื่อทดสอบสมบัติของซิลิกาที่เตรียมได้ พบว่านอกจากจะมีปริมาณซิลิกาและพื้นที่ผิวจำเพาะสูงกว่าซิลิกาทางการค้าที่ใช้ในอุตสาหกรรมยาง ยังมีปริมาณความชื้นต่ำกว่าด้วย และเมื่อนำผงซิลิกาที่เตรียมจากแกลบนี้ไปใช้เป็นสารเสริมแรงในยางธรรมชาติแล้วตรวจสอบพฤติกรรมการคงตัวของผลิตภัณฑ์ด้วยเครื่องวัดการไหลแบบออสซิเลตติงดิสก์ และเครื่องวัดความหนืดแบบมูนนีย์ รวมทั้งทดสอบสมบัติเชิงกลต่างๆ ได้แก่ ความทนแรงดึง ความต้านทานการฉีกขาด ความต้านทานการสึกหรอ การคืนตัว และการกระดอน เทียบกับผลิตภัณฑ์ที่เสริมแรงด้วยซิลิกาทางการค้า พบว่ายางธรรมชาติสูตรที่ใส่ซิลิกาจากแกลบมีสมบัติเชิงกลโดยทั่วไปดีกว่า อีกทั้งใช้เวลาในการคงรูปสั้นกว่าด้วย อย่างไรก็ดี เนื่องจากผลิตภัณฑ์ที่เสริมแรงด้วยซิลิกาจากแกลบจะมีความแข็งต่ำกว่าผลิตภัณฑ์ที่ใช้ซิลิกาทางการค้า จึงเหมาะที่จะนำไปทำเป็นผลิตภัณฑ์ที่ต้องการสมบัติเชิงกลด้านอื่นนอกจากความแข็ง

คำสำคัญ ยางธรรมชาติ ซิลิกา แกลบ การเสริมแรง วัสดุเชิงประกอบ

INTRODUCTION

Rice has been one of the most important agricultural products of Thailand since ancient time. It was cultivated not only for domestic consumption but also for export. Consequently, several million tons of rice husk, which can be considered as agricultural waste, is obtained every year. It was found that when rice husk is burnt, the resulting black ash contains silica. However, this silica from rice husk carries too many impurities and exhibits some inferior properties. As a result, research have been carried out to convert this rice husk into high purity amorphous silica. Several methods for preparing silica from rice husk have been proposed.[1,2]

Another economically important agricultural product is natural rubber, of which Thailand is currently the world's largest producer. Its price has dropped markedly during the past years. Research and development plays an important role as a remedy for this worsening situation.[3]

Prior to curing, raw natural rubber is mixed with various chemicals including vulcanizing agents, accelerators, activators, age resistors, plasticizers, reinforcing fillers and inert fillers. Two common reinforcing fillers for natural rubber are carbon black and silica. Since the products reinforced with carbon black will be, obviously, black in color, it is suitable only for applications where aesthetic appearance is not important. In applications in which color is important, it is common to use silica as a reinforcing filler owing to the fact that silica is a non-black filler that has the highest reinforcing capability. However, the price of commercially available silica is so high that the products reinforced with silica are uneconomical.[4]

Some research has been carried out in order to explore the possibility of using silica from rice husk ash as a filler in rubber.[2,5,6]

The objective of this research is to replace commercial silica commonly used in natural rubber industries as a reinforcing filler with high purity silica prepared from rice husk (RHA silica). Several important mechanical properties, i.e. tensile strength, tear strength, abrasion resistance, resilience and hardness, of rubber products reinforced with RHA silica was investigated and compared with those of products reinforced with commercial silica. The effect of aging on mechanical properties was also taken into account. Apart from increasing the value of rice husk, it is also desirable to promote the use of natural rubber by reducing its raw material cost.

MATERIALS AND METHODS
Silica Preparation

Rice husk was thoroughly cleaned with tap water using a washing machine (Mitsubishi CW224E). The cleaned husk was mixed with 0.4M HCl in the ratio of 100g husk per 1 litre acid and heated until boiled for 30 minutes. Then the mixture was maintained at $105^{o}C$ for 3 hours. During this step, the color of the husk gradually changed from yellow to dark brown. After the reaction, the acid was completely removed from the husk by washing with tap water. It was then dried overnight in an oven at $110^{o}C$. The treated husk was burnt in an electric furnace by controlling the temperature so that it reached $600^{o}C$ in one hour. After burning at $600^{o}C$ for 6 hours, silica was obtained in the form of white ash. The shape of the silica is similar to the shape of the husk but smaller in size. In order to reduce its size, a jet mill was used to grind the silica. Then some physical properties of obtained silica were investigated and compared with commercial silica. Particle size distribution of the prepared silica was also examined using a centrifugal particle size analyzer

(Simadzu SA-CP2). A SEM (Jeol JSM-35CF) was employed to investigate the particle appearance.

Rubber Compounding

Natural rubber compounds were prepared according to the formula shown in Table 1. Natural rubber STR 5L was obtained from Bangkok Rubber Co. Zinc Oxide and stearic acid, used as activators, were supplied by Unithai Oxide Co. and Imperial Thai Co., respectively. Paraffinic oil was purchased from Esso and was used as a plasticizer. Paraphenylene diamine (PPD) acquired from Sunny World Co. was used as a protective agent. Mercaptobenzothiazyl disulphide (MBTS) and Diphenyl guanidine (DPG) were used as accelerators and were provided by Kijpaibul Co. and Gujarat Co., respectively. Sulphur, obtained from Siam Chemical Co., was used as a vulcanizing agent. Three batches of rubber compounds were prepared,: one without silica, one with commercial silica and one with RHA silica. The weight of each batch was approximately 1220g. All chemicals were industrial grade and used as received.

Table 1. The compounding formula.

Chemicals	Amount (phr)		
	I	II	III
Natural Rubber STR 5L	100	100	100
Zinc Oxide	5	5	5
Stearic Acid	2	2	2
RHA silica		40	
Commercial silica			40
Paraffinic oil	5	5	5
PPD	1	1	1
MBTS	1.8	1.8	1.8
DPG	0.25	0.25	0.25
Sulfur	3	3	3

*phr: parts per hundred of rubber

The rubber and all chemicals except sulfur were first mixed in a banbury mixer. Then, sulfur was added and the mixing was performed using a two-roll mill.

The mixed compounds were kept overnight then cured by a hydraulic compression moulding machine (Carver Laboratory Press model 2625) at 150°C with a pressure of 16,500 pounds. The curing time of each batch was acquired previously using a Monsanto oscillating disk rheometer (ODR) model MDR2000 based on ASTM D2084-93. Mooney viscosity and scorch time of raw rubber compounds were also assessed using a Mooney Viscometer (Shimadzu SMV-201) based on ASTM 1646-81.

The cured products in the form of rubber sheets were cut using a specimen cutting machine. These specimens were later used for tensile strength test (Lloyd LR5K), tear strength test (Lloyd LS500),

hardness test (Lever Loader Hardness Tester Model 917) and resilience test (Wallce Dunlop Tripsometer). The compressed rubber compounds, in the form of cylindrical products, were prepared for abrasion resistance test (DIN abrader) and compression set test (ASTM 395-89).

Some tests (i.e. tensile strength, tear strength, hardness, resilience and compression set) were also performed after the compressed rubber products had undergone aging using an Ueshima rubber aging oven according to ASTM D573.

RESULTS AND DISCUSSION
Silica Obtained from Rice Husk

The particle size distributions of RHA silica and commercial silica were examined by dispersing silica in 0.1M calgon solution (sodium hexametaphosphate). As shown in Figure 1, it was observed that, while size distributions of both types of silica were spread, most of the RHA silica particles were finer. Further information about silica morphology was obtained by scanning electron microscopy.

Figure 1. Size distribution curve for silica from rice husk and commercial silica.

Evidently, from the SEM micrographs shown in Figure 2 and 3, commercial silica had a circular shape because it was obtained by precipitation. The size of RHA silica was obviously smaller but the shape was not circular due to its preparation method.

Table 2. Physical properties and chemical composition of silica used in this experiment.

	Commercial Silica	RHA silica
<u>Physical Properties</u>		
Specific surface (m^2/g)	170	182
pH	6.84	5.70
% Humidity (2hrs/105°C)	7.50	0.60
Density (g/cm^3)	1.95	2.20
Bulk density (g/cm^3)	0.26	0.27
Oil absorption (g/g)	1.90	1.92
Dustiness index	1.60	1.77
<u>Chemical Composition</u>		
Silica (SiO_2) %	> 88	99.6
Al_2O_3 %	< 0.5	0.05
Fe_2O_3 %	<0.1	< 0.001
Na_2O_4 %	< 2.0	-

Figure 2. A SEM micrograph of commercial silica.

Figure 3. A SEM micrograph of RHA silica.

Some physical properties and the chemical composition of silica both from rice husk and the commercial one are shown here in Table 2. The specific surface area of RHA silica was found to be higher than that of commercial silica. This is probably due to the fact that RHA silica consists of more fractions of finer particles. Higher silica content was also found in RHA silica, comparing with the commercial silica.

Viscosity and Curing Characteristics of Rubber Products

Mooney viscosity of raw compounds is related to the hardness of the cured products. As the Mooney viscosity increases, the hardness also increases.[7] Mooney viscosity of each raw rubber compound was investigated and the results are shown in Table 3. Mooney viscosity of reinforced products was found to be higher than that of unreinforced products. Moreover, commercial silica reinforced products had a greater Mooney viscosity than products with RHA silica.

Scorch times for these products, as shown in Table 3, were also obtained using the Mooney viscometer. Scorch time was longest in the case of products with commercial silica, while unreinforced products had the shortest scorch time. The scorch time of products reinforced with RHA silica was between these two values. Commercial silica had an ability to absorb

activators used in the compound thus prolonging the scorch time.

An oscillatating disk rheometer was used to determine 90% and 98% curing time, respectively denoted by $T_c(90)$ and $T_c(98)$, of each mixed rubber compound. The results are shown in Table 3.

Table 3. Curing characteristics of rubber compounds.

Properties	No Silica	RHA Silica	Commercial Silica
Mooney viscosity	39.4	63.4	104.93
Scorch time			
T_5	11.95	18.61	23.20
T_{35}	15.15	24.82	28.73
Curing time			
$T_c(90)$	5	9.89	28.81
$T_c(98)$	7.98	15.50	45.46

The rubber products reinforced with RHA silica showed an interesting effect on curing times. The products reinforced with silica had a considerably longer curing time than the products without silica. Furthermore, the curing times of the products reinforced with RHA silica were much shorter than those reinforced with commercial silica.

In this experiment, commercial silica was prepared by precipitation as well as silica prepared from sand by combustion, it has a more active surface than silica from rice husk.[5] The highly active surface can absorb the activators used in the compound, thus delaying the curing time. Longer curing times are undesirable in rubber industries since they are both time and energy consuming.

Mechanical Properties of Rubber Products

As expected, the rubber products reinforcing with silica showed better overall mechanical properties when compared with unreinforced products.

The products reinforcing with RHA silica had a higher tensile strength than the products reinforced with the commercial silica. The results are shown in Figure 4.
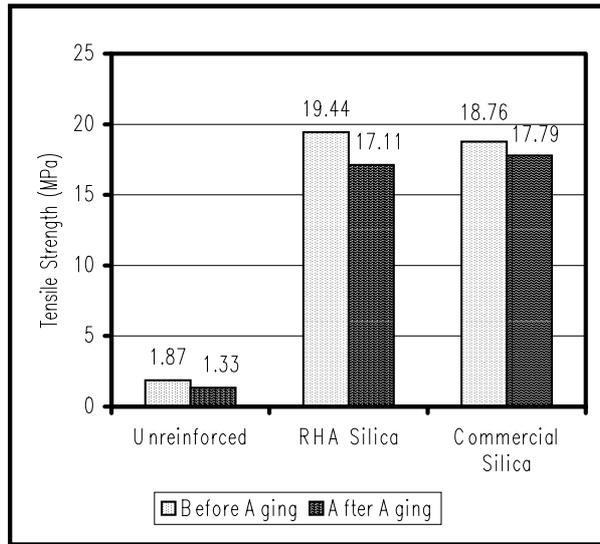
Figure 4. Tensile strength of the rubber products.

The products reinforced with RHA silica also showed highest tear strength as presented in Figure 5.
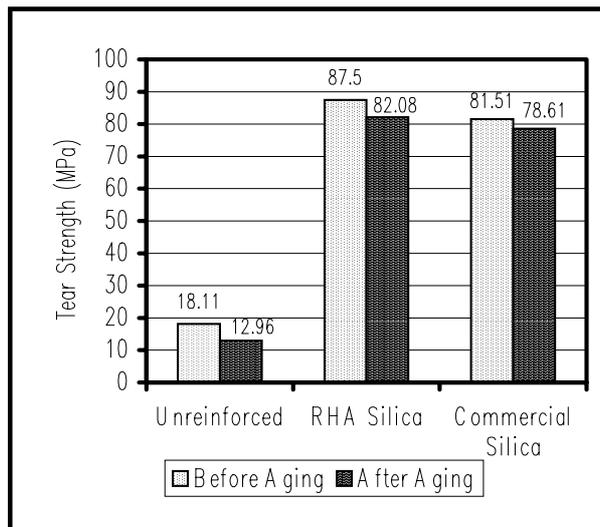

Figure 5. Tear strength of the rubber products.

The abrasion resistance was highest when silica from rice husk were used as the reinforcing filler as shown in Figure 6.
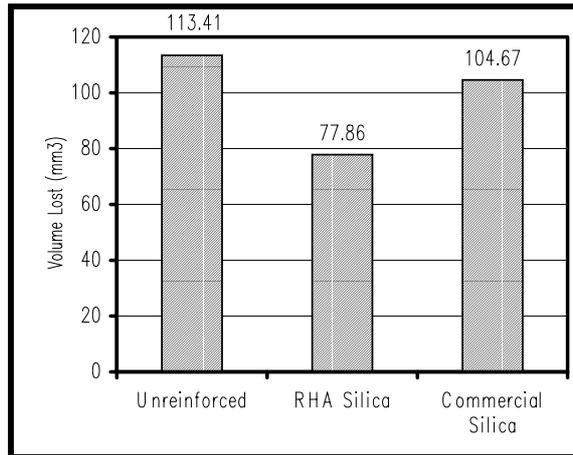
Figure 6. Abrasion resistance in term of volume lost.

Figure 7 shows the results of the compression set test. It was found that products reinforced with RHA silica demostrated excellent compression set, compared with unreinforced products and products with commercial silica.
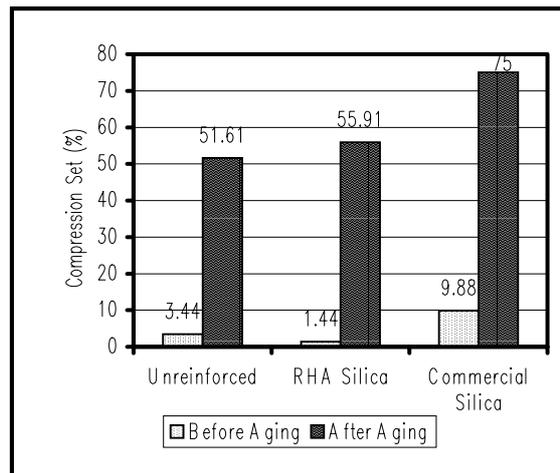

Figure 7. Compression set test of the rubber products.

Resilience of the rubber products exhibited the same trend as tensile strength, tear strength, abrasion resistance and compression set. Again, the products reinforced with silica from rice husk showed the highest resilience as demonstrated in Figure 8.
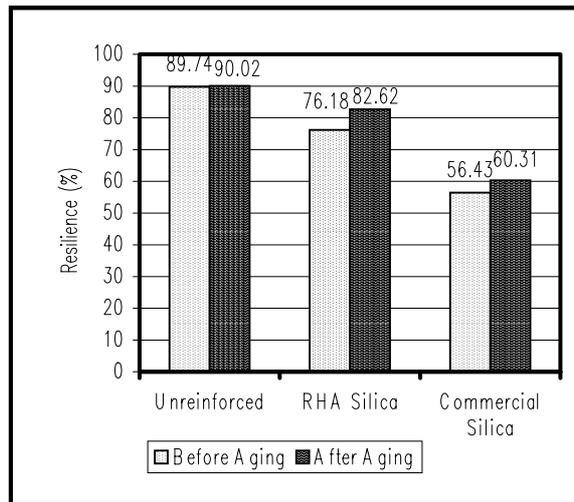
Figure 8. Resilience of the rubber products.

The Higher purity of RHA silica, as opposed to commercial silica, may be an important reason that overall mechanical properties are superior.   Theoretically, mechanical properties would be improved upon increasing of the amount of silica. As the same amounts of filler were added, RHA silica contained more silica than commercial silica thus improving the mechanical properties of the products. The particle size of the filler also affects the mechanical properties of rubber products. Generally, the reinforcing power is greaten when the particle size of the filler is smaller.[8]   As a consequence, with finer particle size, RHA silica offers more reinforcing effects to the product. Surface area also plays an important role in reinforcing rubber as discussed in previous work.[9-11]   In our case, RHA silica has higher specific surface area thus giving better mechanical properties to the products.

Hardness normally increases upon incorporation of fillers, especially when the particle sizes of the fillers is large. Large filler particles obstruct the movement of the rubber matrix when the matrix is subjected to indentation. Consequently, indentation hardness is increased.[7,12] The result as shown in Figure 9 is in agreement, that is, the hardness is obviously lower when RHA silica was used, as it has smaller size.
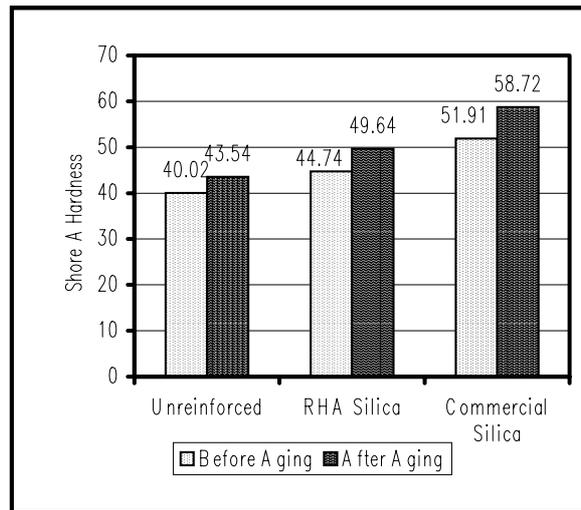
Figure 9. Hardness of the rubber products.

Effect of Aging on Mechanical Properties

Aging displayed an important effect on the mechanical properties of the rubber products. Tensile strength and tear strength were found to be slightly decreased after aging. Compression set was clearly worsened after the products underwent aging. Contrarily, resilience and hardness were increased again to a small extent. The results are shown in Figures 4, 5, 7, 8 and 9.

CONCLUSIONS

High purity silica prepared from rice husk was used as a reinforcing filler in natural rubber. The Mechanical properties of the rubber products were investigated to find an alternative application for silica from rice husk. The indirect objective was to reduce the cost of natural rubber products by replacing expensive commercial silica with silica from rice husk.

Silica prepared from rice husk contained a higher percentage of silica. Particles of silica prepared from rice husk were smaller and had greater specific surface area compared to particles of commercial silica. These properties affect greatly the curing characteristics and mechanical properties of rubber compounds.

The curing time of products with RHA silica is shorter than products with commercial silica. From the industrial viewpoint, this is an advantage since time and energy consumption during production could be reduced.

The overall mechanical properties of products with RHA silica were found to be higher than products with commercial silica. These properties are tensile strength, tear strength, abrasion resistance, compression set and resilience. However, the hardness was lower when RHA silica was used.

Thus, RHA silica has great potential for use as a reinforcing filler in natural rubber products where hardness is not the major consideration while other mechanical properties are desirable.

In this research, the silica loading was the same amount as used in the industrial compounding formula. Further study can be done in order to study the effect of silica loading on the mechanical and physical properties of natural rubber products.

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