

# CURE CHARACTERISTIC, MECHANICAL PROPERTIES AND MORPHOLOGY OF IN-SITU SILICA-GEL/NR COMPOSITES

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## 1 Introduction

Natural rubber (NR) is an important economical material. Thailand is the most natural rubber exporter in the world. For scientific term, Natural rubber can be made from rubber latex, colloid form which has molecular weight in the range of 100,000 to 1,000,000. Density and glass transition temperature ( $T_g$ ) of NR is about  $0.93 \text{ g/cm}^3$  at  $20^\circ\text{C}$  and  $-72^\circ\text{C}$ , respectively. Interestingly, it has good properties in elasticity toughness and abrasion resistance that prevent penetration of water and air. NR can be used in wide temperature by using vulcanization process and reinforcing agents to improve its properties.

There are many reinforcing agents for NR such as carbon black, silica, fly ash, calcium carbonate, clay and etc. Carbon black and silica are the most popular fillers in natural rubber composites. Silica can make NR obtain high abrasion resistance. Nevertheless, there are some agglomerations of silica particles in NR matrix because of their high polarity surface.

When silica is added into rubber at high concentration, it tends to form a secondary network, alternatively called "filler-filler networks". This would cause an increase in compound viscosity giving rise to difficulty in processing. The chemical treatment of silica surface has become the most successful method to improve rubber-filler interaction and reduce filler-filler interaction [1].

Rice husk ash (RHA) contains over 60% silica and can be an economically valuable raw material for the production of silicates and silica [2]. The amorphous nature of RHA silica makes it extractable at lower temperature, and hence provides a low energy method as an alternative to the current high energy method. A low energy method was developed to produce pure silica (93% with 2.6% moisture) from RHA with 91% extraction yield. Silica gel is a rigid three-dimensional network of colloidal silica, and is classified as aquagel (pores are filled with water), xerogel (aqueous phase in the pores is removed by evaporation) or aerogel (solvent

is removed by supercritical extraction) depending on how they were made.

In this study, rubber system containing Si-Gel formed in-situ was studied in detail. It was found that the Si-Gel content at 30 phr behaved similar to rubber containing precipitated silica (PSi) at the same silica content. The interconnected rubber and Si-Gel cluster phenomena was currently shown in this study.

## 2 Experimental Procedure

### 2.1 Materials

*Rubber and curative:* Natural rubber latex (60%DRC) was purchased from Resin arts, Bangkok, Thailand. The curative additives, were kindly supplied by Chemical Innovation LTD., Bangkok, Thailand.

*Reinforcing Filler:* Precipitated silica (PSi) was purchased from Siam Silica, Bangkok, Thailand.

*Stabilization Chemical:* Igepal CO-890 was purchased from SIGMA-ALDRICH, Inc., Steinheim, Germany.

### 2.2 Preparation Si-Gel in-situ reinforced NR

$1000 \text{ cm}^3$  of Natural Rubber latex (60 % DRC) was diluted to 30 % DRC before stabilized with 3 % wt Igepal. The stabilized NR latex was then gently stirred with mechanical stirrer for 24 hour. Sodium silicate solution was prepared by extraction 10 grams rice husk ash in 300 ml of 1 M NaOH for 17 hours. Silicate solution was then mixed with stabilized 30 % DRC NR latex with various ratios to obtain various contents of Si-Gel in dried rubber. The mixtures were left to mix thoroughly for 24 hours. After that 5 %  $\text{H}_2\text{SO}_4$  solution was added drop-wise to the latex mixture to adjust pH of the mixture to 7. The coagulated NR containing various Si-Gel formed was washed with flowing water while milling on a mini two roll mill to obtain rubber sheet (or crumble depending on the Si-Gel contents). Leached water was frequently tested with  $\text{Ba}(\text{NO}_3)_2$  in order to investigate the leached  $\text{SO}_4^{2-}$ . The clean rubber sheet was then dried at  $50^\circ\text{C}$  in a hot air oven for 24 hours or until dry. TGA analysis

indicated that the silica content was found to be 5, 10, 15, 20, 25, 30, 35 and 40 phr with respect to NR.

### 2.3 Preparation and Vulcanization of Rubber Compounds

The dried NR sheet with in-situ Si-Gel/PSi was masticated on a two roll mill (Hong Yow, China) until form banding, then the following additives was added stepwise: 5 phr. of ZnO, 2 phr. of stearic acid, 0.5 phr. of MBT and 0.2 phr. of DPG. 3 phr. of sulfur was then added at the end of compounding process. The compound was then mixed thoroughly. Cure characteristic properties were investigated using Moving Die Rheometer (MDR, Model GT-M2000, GOTECH Testing Machine, Ind., Taiwan) at 160 °C resulting minimum and maximum torques, scorch and cure times. The compounds were subsequently compressed in a compression molding (Lab Tech. Co. Ltd Bangkok Thailand) to a 90 % cure, with the hydraulic pressure of 1500 Psi, at 160 °C, with cure time obtained from MDR.

### 2.4 Testing of Rubber Vulcanizates

Tensile properties of the vulcanized rubber composites were monitored in terms of tensile modulus, tensile strength and elongation at break, according to ASTM D412-03 using dumbbell-shaped samples and tear strength according to ASTM D624-00, the tests being carried out using the universal testing machine (Model Autograph AG-I, SHIMADZU, JP.) with the testing speed of 500 mm/min. The morphology of the vulcanizates was evaluated using scanning electron microscope (CamScan, Bruker, UK).

## 3 Results and Discussion

### 3.1 Morphology of precipitated NR containing in-situ Si-Gel

It was found that the content of bound rubber in dried NR containing in-situ Si-Gel increased with the contents of Si-Gel, as elucidated in **Table 1**. This could be explained by the interconnected rubber network formed between Si-Gel clusters as appear in morphological structure, elongated matrix, shown in **Figure 1**. The cartoon illustrating in **Figure 2** shows inter connecting phenomena between the polymer chains and Si-Gel during coagulation of rubber and gelation of silicate solution. As the figure exhibits elongated like rubber matrix, it is therefore proposed here that during the gelation of silica, rubber particle suspended in the latex also coagulated and would result in Si-gel interconnected with rubber molecules. Generally, if rubber molecule penetrated through the porous Si-Gel, after coagulation of rubber and gelation of silicate solution, bound rubber can be presented. The bound rubber content

of dried coagulated NR containing Si-Gel in Table 1 was also found to increase with the content of in-situ silica-gel up to the content of in-situ silica-gel at 20 phr, **Figure 3**. At higher content of Si-Gel, it tended to agglomerate in large particle size and interconnected Si-Gel-rubber-Si-Gel particles tend to agglomerate, explained by cartoon in **Figure 4**, and constant up to the Si-Gel content of 40 phr.

After thermally degrade polymer molecule under TGA's furnace at 300 °C, the porosity of the Si-Gel can be observed, as shown in **Figure 5**. The pores left on Silica debris indicated pore sites where rubber molecules used to be. The figure also shows that the pore size of the site and Si-Gel debris, where polymer chain used to stay, increase with the Si-Gel content.

### 3.2 Cure Characteristic of NR containing in-situ Si-Gel compound

The cure characteristic parameters of NR/Si-Gel compound were studied in comparison with NR/PSi compound and those properties are presented in **Figure 6-7**. As can be seen, cure characteristic times; scorch and cure time, in **Figure 6** were increase with the content of Si-Gel. This is explained by the absorption of vulcanizing accelerator and led to slow curing reaction and hence scorch and cure time. The effect was found to be more intense than PSi case in which the porosity is far lower than the previous case.

The present of Si-Gel clusters also obstructed flow of the rubber compound during melting state. As expected, the minimum and maximum torques, **Figure 7**, increased with the contents of Si-Gel. At low contents of Si-Gel, due to polarity and high porosity of Si-Gel, the vulcanization was retarded resulting in lower crosslink density.

### 3.3 Tensile Properties of NR containing in-situ Si-Gel

As explained in the previous section that crosslink density of NR containing Si-Gel vulcanizate would be lower showing by low maximum torque and this would result in low in tensile modulus at 100 % strain, tensile strength, and also elongation at break, as shown in **Figure 8**. Considering tear strength, in **Figure 9**, the properties of the vulcanizate was also low, in comparison with the vulcanizate containing PSi. However, higher contents of Si-Gel, the tensile properties were increased and comparable to PSi. The properties are slightly higher than latter case, for high Si-Gel contents. This supported the effect of interconnection between rubber and Si-Gel cluster on properties of rubber vulcanizates, as elucidate in **Figure 1-2**.

## 4 Conclusion

The result from this study shows that Si-Gel formed in-situ while NR coagulated from latex behaves as interconnection between rubber molecules and Si-Gel cluster result in Si-Gel-rubber-Si-Gel cluster. And at some certain content, Si-Gel could reinforce NR in rubber vulcanizates. It was

also found that the effect was comparable with using PSi as filler in NR.

Formulae	Bound rubber (%)	Minimum Torque (dN-m)	Maximum Torque (dN-m)	Scorch Time (m:s)	Cure Time (m:s)
0phr.Si-Gel/NR	0.00	1.13	27.54	0:35	2:53
5phr Si-Gel/NR	26.11	1.42	19.34	1:34	3:03
10phrSi-Gel/NR	51.43	2.35	8.15	2:20	8:24
15phrSi-Gel/NR	64.80	3.59	9.70	4:40	14:27
20phrSi-Gel/NR	71.20	6.00	15.71	2:57	14:41
25phrSi-Gel/NR	63.01	9.41	24.11	2:22	12:32
30phrSi-Gel/NR	68.58	12.07	27.42	1:50	11:27
35phrSi-Gel/NR	62.77	13.42	30.16	1:55	11:05
40phrSi-Gel/NR	70.36	18.88	37.64	1:41	9:36

Table 1 The properties of dried Si-gel/NR composite: bound rubber, cure characteristic properties.

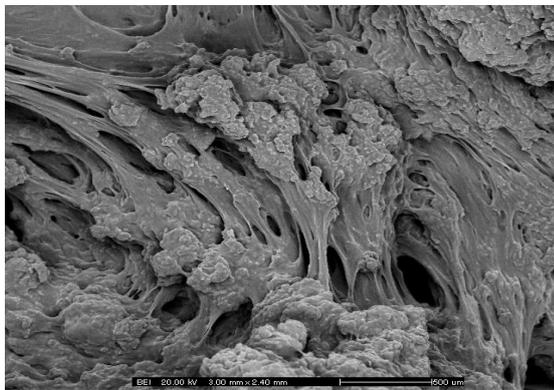


Figure1 SEM Micrograph of dried rubber

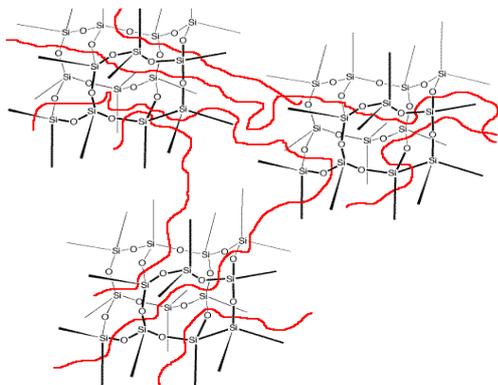


Figure 2 Interconnected Si-Gel-rubber-Si-Gel cluster

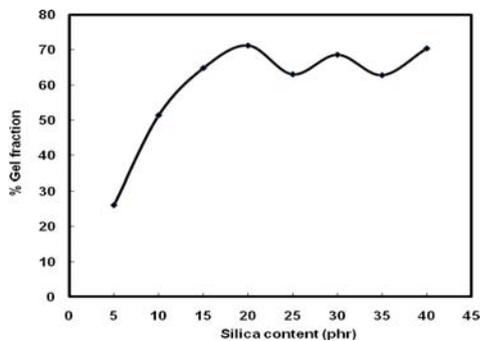


Figure 3 Bound rubber content occur by the interconnected Si-Gel-rubber-Si-Gel cluster

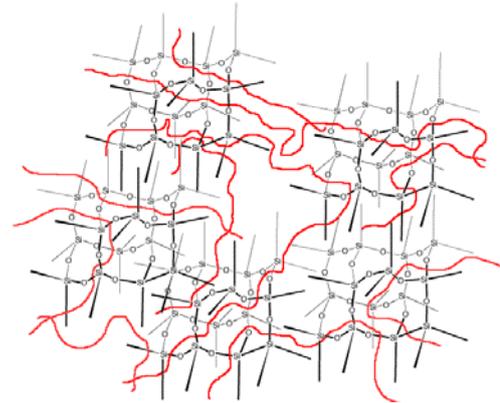
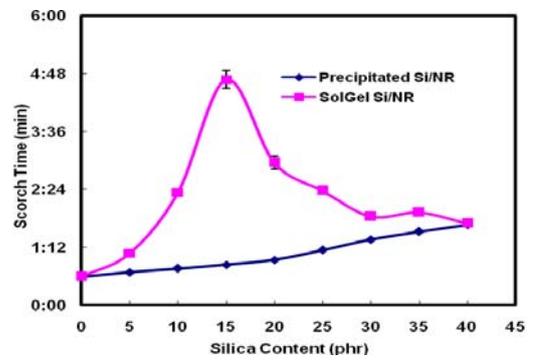
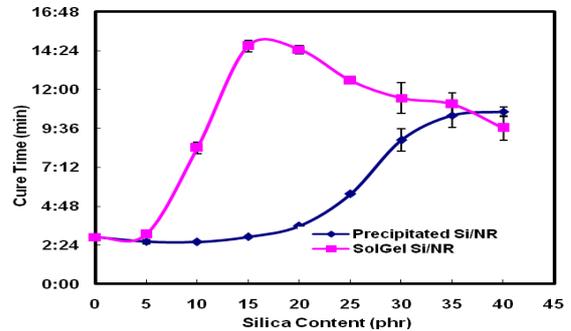


Figure 4 Coagulated Si-Gel-rubber-Si-Gel

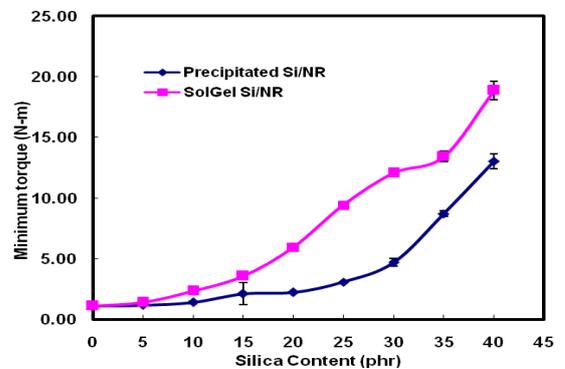


(a)

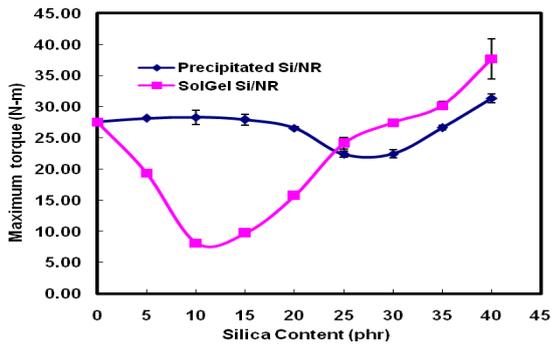


(b)

Figure 6 (a) Scorch time and (b) cure time of NR compounds

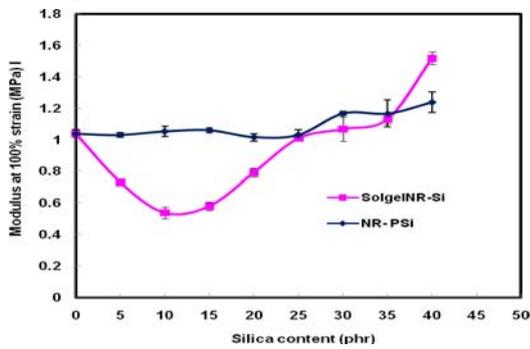


(a)

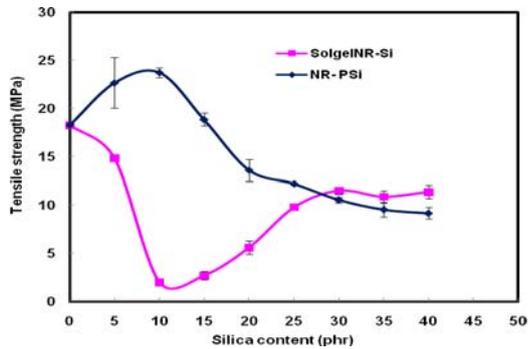


(b)

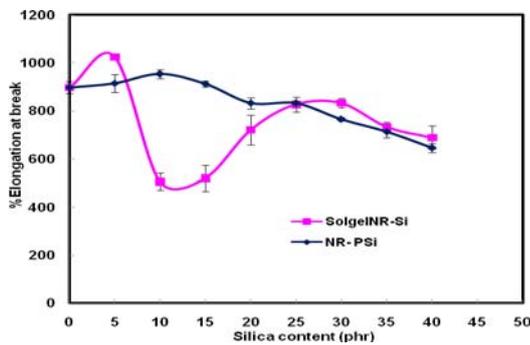
Figure 7 (a) Minimum and (b) maximum torque of NR compounds



(a)



(b)



(c)

Figure 8 (a) Modulus at 100 % elongation (b) tensile strength and (c) elongation at break of NR vulcanized

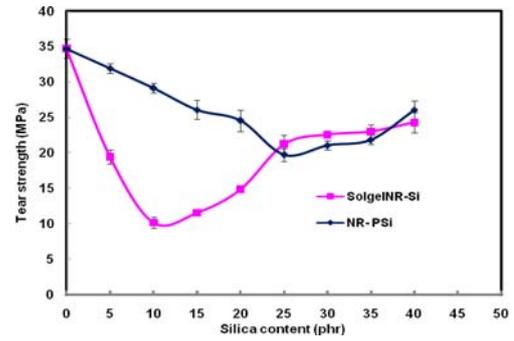


Figure 9 Tear strength of NR vulcanizates

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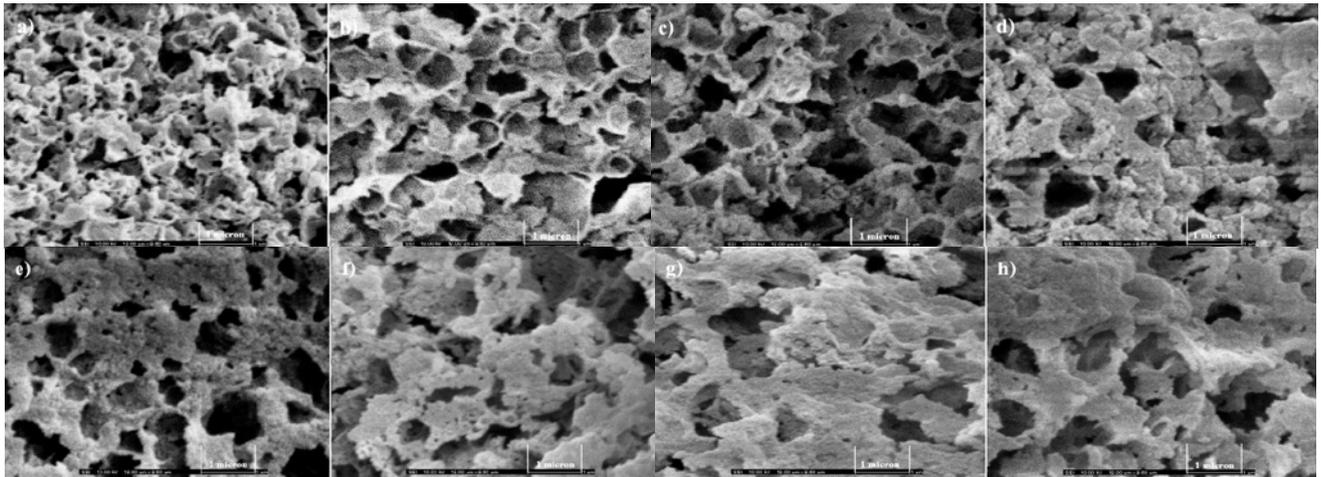


Figure 5 SEM micrographs of Si-Gel debris from TGA test at various contents of Si-Gel in dried NR: (a) 5 phr, (b) 10 phr, (c) 15 phr, (d) 20 phr, (e) 25 phr, (f) 30 phr, (g) 35 phr and (h) 40 phr.