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The Effect of Excess Silane-69 used for Surface Modification on Cure Characteristic and Mechanical Properties of Precipitated Silica filled Natural Rubber (PSi/NR)

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Abstract

This research is concentrated on the effect of concentration of silane-69 used for surface modification on precipitated silica (PSi), on cure characteristic and mechanical properties of PSi filled NR. The PSi content in this study was fixed at 20 phr in order to reveal the effect of silane used to modify PSi, on NR compound and vulcanizate. Moving Die Rheometer (MDR) was used to characterize cure characteristic of rubber compounds. Generally, scorch and cure time of NR would increase with the addition of PSi due to the absorption of accelerator on its surface whereas the addition of Si-69 modified PSi would reduce both scorch and cure time. It was found in this research that the excess amount of Si-69 used increased scorch and cure time of rubber compounds. This was thought to be that the excess of Si-69 led to the formation of polysiloxane clusters which could absorb accelerator in rubber compound and resulted in a prolonged scorch and cure time. In term of vulcanized rubber, it was found that maximum torque increased with the concentration of Si-69 up to 6 %. The polysiloxane formed during the cure characterization test was responsible for the slightly decreased torque after 6% of Si-69 treatment. Nonetheless, even with high concentration of Si-69 used, torque was still higher than that of untreated PSi filled NR. This is widely understood that sulfur atoms in Si-69 molecule are able to participate in the bonding between rubber and silane molecules resulted in the enhancement of crosslink density of the vulcanizate rubber. The increased of modulus at 200 % elongation, tensile strength under tension, with the silane concentration, was evidence of the crosslink enhancement. Tear strength and hardness of the vulcanizates exhibiting the increment, with the silane used, also clearly confirmed the bonding between Si-69 and rubber molecules. It was elucidated from the research that excess of Si-69 would lead to polysiloxane formation, cluster form of silane and crosslinking density. Scanning Electron Microscope (SEM) micrographs and swelling test are also presented to confirm the phenomena.

Introduction

In general, silica reinforced rubber was not concentrated much for various application due to filler-filler interaction which is responsible for its difficulty to disperse in the rubber matrix [1-7]. Considering the unique properties of silica filler, such as tear strength, abrasion resistance, aging resistance and adhesion properties, the use of silica as a filler in NR was still in demands. The surface modification was brought about to ease the dispersion and compatibility between NR and silica. It has been widely accepted that the modification of silica using silane coupling agent, especially Si-69, help dispersing and coupling silica in rubber matrix [8]. Hybrid filler is another direction to use more than one filler in order to sustain the advantage of individual filler. Silica has the advantages over carbon black in many aspects such as tear resistance, abrasion resistance, ageing resistance and adhesion properties. The hybrid system between silica and carbon black was

studied [9]. It was found that the amount of silane used for the silica modification was the important factor to control both cure characteristic and mechanical properties. Many researches reported [10] that silica particles could be generated in-situ via sol-gel process of the tetraethoxysilane (TEOS). It is therefore very interesting to study effect of amount of silane used, i.e. excessive amount of Si-69, to modify precipitated silica (PSi) surface. The effect of excess Si-69 on cure characteristic and mechanical properties will be studied in this research.

Experimental Procedure

1. Materials

- *Rubber and curative additives*: Natural rubber (NR, STR 20) was received from Sinthong Thai Rubber Ltd. All curative additives were kindly supplied by Chemical Innovation Ltd. Bangkok, Thailand.
- *Reinforcing Fillers*: The precipitated silica (PSi) was purchased from Siam Silica, Bangkok, Thailand
- *Modification Chemical*: PSi surface was chemically modified using bis (3triethoxysilylpropyl) tetrasulfane (Si-69), kindly supplied by Innovation Chemical Ltd., Bangkok, Thailand, as a surface modifying agent.

2. Surface Modification of Precipitated Silica (PS) with Si-69

In this research, the surface modification was performed at various percentage of Si-69, i.e. 3, 6, 9, 12, 13.5 and 15 % wt. of PSi. The modification method was carried out as follow: the require amount of Si-69 was thoroughly dissolved in 400 cm^3 of ethanol and stirred with mechanical stirrer for 30 minutes then 50 grams of PSi was added slowly with stirring until PSi was very well dispersed in ethanol. The slurry was then mixed under stirring for further 15 minute before drying in a hot air oven at 100 °C for 12 hours. This part of experiment will result in various percentage of Si-69 treated PSi.

3. Preparation and Vulcanization of Rubber Compounds

The rubber compounds were prepared using a Two Roll Mill (Hong Yow, China). The compound formulations are given in **Table 1**. The rubber compounding was carried out by masticating the NR on a two roll mill (Hong Yow, China) for 5 minutes or until soft, the prepared fillers and chemicals stated in **Table 1**, except sulfur, were then masticated for further 20 minutes. The required sulfur was then added at the end of this state of compounding process and masticated for further 5 minutes. After mixing, cure characteristic properties of the compounds, i.e. minimum and maximum torques, scorch time and cure time, were evaluated in a Moving Die Rheometor (MDR, Model GT-M200, GOTECH Testing Machine, Ind., Taiwan) at 160 °C. The compounds were then compressed in a compression molding (Lab Tech. Co. Ltd Bangkok Thailand) to a 90 % cure, with the hydraulic pressure of 170 kg/cm2, using 160 °C cure temperature and the cure time resulted from cure characteristic test, to obtain vulcanized rubber composites.

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 D412-98 (1998) using dumbbell-shaped samples, the tests being carried out using the universal testing machine (Model LR50K, LLOYD Instruments, UK.) with the testing speed of 500 mm/min. Tear strength was determined according to ASTM D624-00 (2000) using angle- specimens (die C). The test was carried out under universal testing machine (Model LR50K, LLOYD Instruments, UK.) and with the testing speed of 500 mm/min. A hardness durometer (Shore A) Model 475, PTC instruments, (MA, USA) was used for hardness tests, the test conditions being in accordance with ASTM D 2240-03 (2003).

Result and Discussion

The effect of Si-69 amount treated on PSi surface, on the cure properties of PSi/NR was presented in **Fig. 1**. It was found, same as other research, that Si69 modified PSi improved the dispersion of PSi and compatibility of PSi and NR matrix leading to the reduction of both t_s and t_{c90}. Surprisingly, both characteristic times of the compound increased again after level off at the Si-69 content of 6 %. It was well understood that the silane coupling agent could self polymerize and form polysiloxane. In this case, excess of Si-69 used for silica treatment would be able to form polysiloxane. The polymer also contains –OH polar group on their surface and are able to absorb polar curative additive such as accelerator and activator and consequently prolong the curing reaction time.

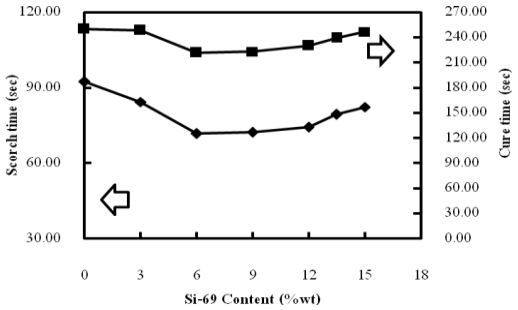

Figure 1 Scorch and cure time of Si-69 modified PSi/NR compound.

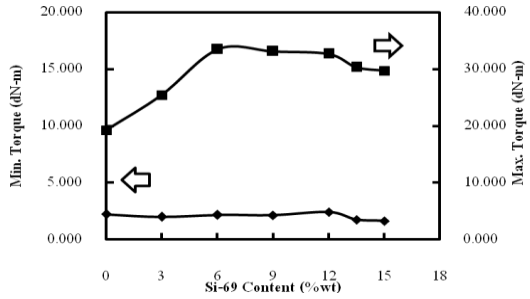

Figure 2 Minimum and Maximum torques of Si-69 modified PSi/NR compound.

In terms of torques, in **Fig. 2**, i.e. minimum and maximum torques, the results clearly showed the increased in ability to disperse and compatibility of PSi in NR matrix with the amount of Si-69 up to 6%, and this also result in better crosslinking in the NR matrix, confirming by the increasing of maximum torques. Sulfur containing in Si-69 could also be able to take part in sulfur vulcanization, crosslink density was therefore increased with the amount of Si-69 used for PSi treatment [8]. However, at Si-69 content higher than 6 phr, the torque start to reduce again but the increased of t_{c90}. In such a complex phenomena occuring here, it must be useful to point out that there are many factors govern the properties of vulcanized rubber. For example, the agglomeration of polysiloxane which could function as in-situ formed silica in rubber matrix and resulted in polar curative absorption subsequently retard the curing reaction and lower crosslink density, as indicated by the increasing t_s and t_{c90} and the decreasing of maximum torque. Nonetheless, even with high concentration of Si-69 used and such phenomena occurred, torque was still higher than that of untreated PSi filled NR, indicating the higher crosslinking in rubber vulcanizate. This could be the responsibility of reinforcement effect of the silica, both by the PSi and in-situ formed silica in rubber matrix, including the crosslinking enhancement by sulfur atoms in Si69, as could be seen by the steadily increasing of modulus at 200 % elongation and tensile strength, in **Fig. 3a** and **3b**.

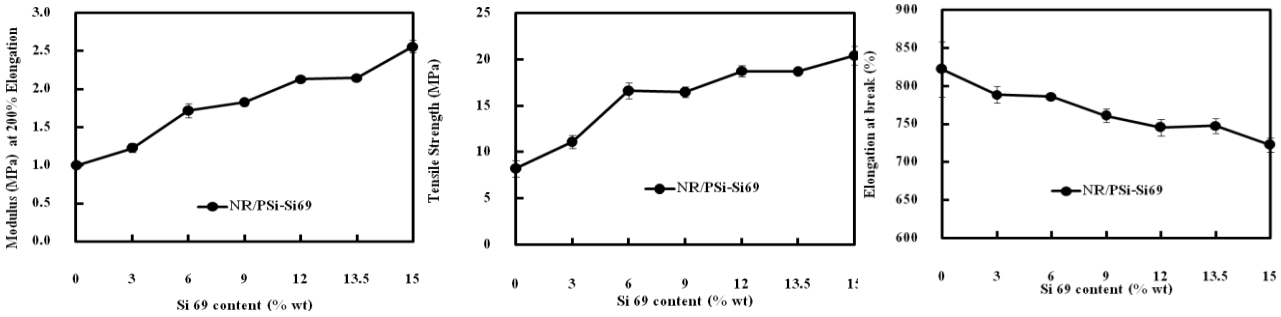

Figure 3 Modulus at 200 % elongation (a), tensile strength (b) and elongation at break (c) of Si-69 modified PSi/NR vulcanizates.

The present of polysiloxane formed by the excess of Si-69 would reduce tensile strength of the vulcanized rubber due to the plasticization effect of polysiloxane [8]. However, the effects mentioned earlier govern the characteristic increased of the tensile strength. It was notable that the reinforcement effect overruled the plasticization caused elongation at break to reduce with the increased amount of Si-69 used, as seen in **Fig. 3c**. The confirmation of crosslinking enhancement was confirmed by the steadily increased of the tear strength in **Fig. 4**. The well dispersion and

compatibility of the Si-69 treated PSi, confirmed by SEM micrographs in **Fig. 5**, and the effect of excess Si-69 on crosslinking enhancement also improved hardness of the vulcanizates, **Fig. 6**.

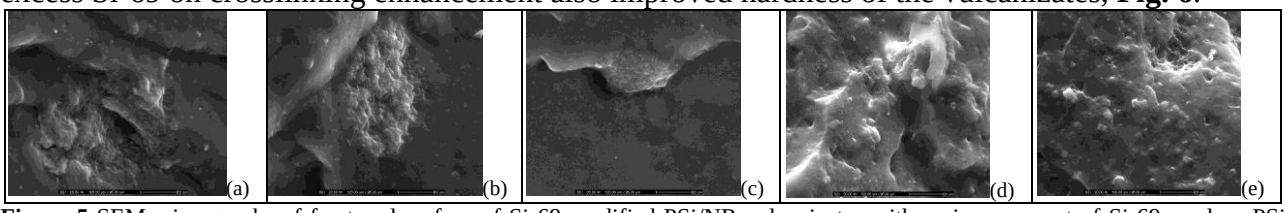

Figure 5 SEM micrographs of fractured surface of Si-69 modified PSi/NR vulcanizates with various amount of Si-69 used on PSi surface, (a) 3, (b) 6, (c) 9, (d) 12 and (e) 15% wt of PSi.

Conclusions

The excessive amount of Si-69 used for modification resulted in excessive crosslink in the matrix, Silica particles formed in situ can prolong cure characteristic time and curing efficiency. However, crosslink density was still higher than those of the untreated PSi. The excessive Si-69 could contribute sulfur to crosslink and raise secant modulus. Polysiloxane and aggregated polysiloxane could function as plasticizer and reinforcement. These factors responsible for the mechanical behavior of the vulcanized rubber. The decreased elongation confirmed reinforcing effect.

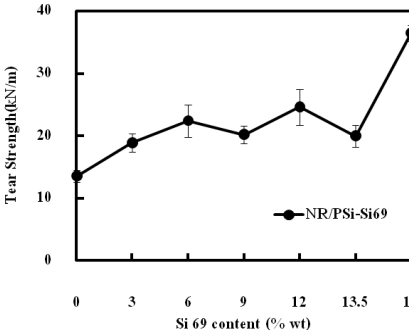

Figure 4 Tear strength of Si69 modified PSi/NR vulcanizates.

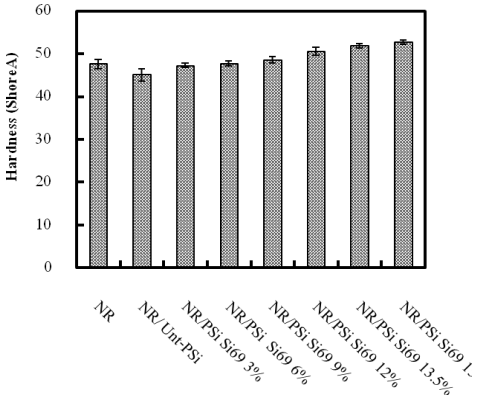

Figure 6 Hardness of Si69 modified PSi/NR vulcanizates.

Table 1 Compounding Formulation

Additives and Filler	Content (phr)
Natural Rubber (STR 20	100
ZnO	5
Stearic acid	2
Sulfur	3
MBT	0.5
DPG	0.2
PSi modified with Si-69 3, 6, 9, 12, 13.5, 15 % wt. of PSi	20

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