

EFFECT OF FILLER SURFACE TREATMENT ON PROPERTIES OF FLY ASH/NR BLENDS

*S. Thongsang and N. Sombatsompop**

Polymer Processing and Flow (P-PROF) Group

School of Energy & Materials

King Mongkut's University of Technology Thonburi (KMUTT)

Bangmod, Bangkok 10140, THAILAND

**Email: narongrit.som@kmutt.ac.th*

Abstract

Silica contents in fly ash particles of 30 and 60phr were introduced as reinforcing filler in NR compound with varying Si69 coupling agent contents. It was found that the scorch and cure times of the NR/FA vulcanizates slightly increased with a decrease in crosslink density when increasing Si69 contents. The decrease in crosslink density was compensated by chemical bonding between the rubber and the fly ash particles as a result of Si69. Concentrations of 2.0 and 4.0 wt% Si69 coupling agent were recommended for the improvement of the tensile modulus and tear strength of the NR/FA composites. The tensile strength did not change with Si69 content.

Introduction

In rubber industry, the silica is widely used as a reinforcing filler due to its fine particle size (high specific surface area), its performance in improving the mechanical properties of the vulcanizates, particularly tensile strength, tear resistance, abrasion resistance and hardness [1]. The silica is available from the precipitation of an aqueous sodium silicate solution: precipitated silica, the pyrogenic process: fumed silica, and from natural resources (e.g. rice husk ash and fly ash). Nowadays, many attempts have been made to use silica from the natural resources as alternative reinforcing filler in natural rubber because of cost savings, good mechanical properties (if properly used), better dimensional stability, and environmental issue. There have been many attempts investigating effects of the addition of rice husk ash into rubbers [2-3], but only a few considering the properties of rubbers containing fly ash as a filler in rubber materials [4-6]. Sombatsompop *et al* [6] introduced untreated fly ash particles into NR vulcanizates, and found that the mechanical properties of fly ash-filled NR vulcanizates appeared to be very similar to those of commercial silica-filled vulcanizates at silica contents of 0-30phr. Above these concentrations, the properties of the fly ash-filled compounds remained unchanged, the fly ash particles being used as an extender. The treatment of filler surface can be made by the several methods. Different treatment methods will lead to the different characteristics of filler, such as changes in particle size and shape, surface area, and functional groups on filler surface. The widely

surface treatment method is to use a silane coupling agent or multifunctional additive (MFA) which is suitable in the case where the rubber and the filler is incompatible or non-interactive. The most commonly used silane coupling agents are bis-(3-triethoxysilylpropyl)tetrasulfane (Si69) and γ -mercaptopropyltrimethoxysilane. Both silane coupling agents and MFA have proven to enhance the filler-rubber interaction [1, 4-5, 7-13].

In this work, fly ash (FA) particles were introduced into natural rubber (NR) compound, as a result of having hydroxyl group on the surface [5], and Si69 was chosen as a chemical silane coupling agent to improve the properties of the FA/NR vulcanizates. The aim of work is to seek the optimum content of the coupling agent content to be added into the NR vulcanizates by considering various properties such as cure characteristics, crosslink density, tensile properties, tear strength and hardness.

Experimental

Raw materials

The rubbers used in this work were NR (STR20) supplied by Huay Chuan Co., Ltd. (Bangkok, Thailand). The silane coupling agent used was bis-(3-triethoxysilylpropyl) tetrasulfane (Si69), $[(C_2H_5O)_3Si-(CH_2)_3-S_4-(CH_2)_3-Si-(C_2H_5O)_3]$, supplied by JJ-Degussa (Bangkok, Thailand) Co., Ltd. The fly ash particles were supplied by Mae Moh Power Station of KNR Group Co.,Ltd. (Lampang, Thailand). The chemical compositions of the fly ash particles listed in Table 1 were experimentally determined through X-Ray Fluorescence Spectrometer (Horiba Model MESA-500W, Japan). The particle size of the fly ash used was less than 250 micron. In this study, we intended to examine the reinforcing effectiveness of silica from fly ash in NR compounds with regard to 30 and 60 phr of silica content. Therefore, the required silica content in the fly ash particles added to the rubber compounds had to be calculated with the information on the fly ash chemical compositions as also given in Table 1.

Surface treatment of fly ash by silane coupling agent

The silane content was varied from 0 to 8 percent by weight (%wt) of the fly ash. The silane solution was prepared by mixing with ethanol [5]. For instance, for silane content of 2%wt, 2g of the Si69 was mixed with 100 ml of ethanol, and then stirred for 30 minutes. 100g of fly ash were then added into the solution with a further 15 minute stirring, in order to ensure a uniform distribution of the coupling agent on the ash surface. The treated fly ash was then dried at 100°C for 12 hrs in an oven until a constant weight was achieved. Similarly, 4, 6 and 8%wt of silane coupling agents on the ash surface were prepared by varying the initial Si69 contents for 100g fly ash using the same procedure as described above.

Rubber sample preparation and rubber vulcanization

The formulation of the rubber compounds was as follows: 100 phr rubber, 5.0 phr zinc oxide (ZnO), 2.0 phr stearic acid, 0.5 phr mercaptobenzthiazole (MBT), 0.2 phr diphenylguanidine (DPG), and 3.0 phr sulfur. In the mastication step, the rubber was masticated on a laboratory two-roll mill (Yong Fong Machinery Co., Ltd., Samutsakon, Thailand) for 5 min and was then mixed with a specified content of treated fly ash for another 15 min. In the compounding step, the rubber and filler were compounded with prepared vulcanization chemicals on the two-roll mill for another 10 min, and the compounds were then kept at 25°C at 50% humidity before further use. The resultant rubber compound was then compression-molded to a 90% cure with a hydraulic press (LAB TECH Co., Ltd., Bangkok, Thailand) at 170 kg/cm² with a 160°C cure temperature to produce vulcanized rubber. The cure time used for any individual compound was pre-determined by an Oscillating Die Rheometer (Model ODR GT 70-70, GOTECH Testing Machine, Inc., Taiwan) before the vulcanization process proceeded.

Characterization

Cure and crosslink characteristics: Scorch time and cure time values of the rubber compounds were detected with the Oscillating Die Rheometer (Model ODR GT 70-70, GOTECH Testing Machine, Inc., Taiwan) at a test temperature of 160°C. The determination of the crosslink density of the vulcanized rubber compounds was carried out with a swelling method, whose experimental procedure can be obtained elsewhere [6].

Mechanical properties: The tensile properties (modulus at 200% elongation, tensile strength, and %elongation at break) of the rubber vulcanizates were tested according to ASTM D 412-92 (1998) with dumbbell-shaped samples; the tests were carried out with a universal testing machine

(Autograph AG-I, Shimadzu, Tokyo, Japan). Tear strength was determined according to ASTM D 624-00 (2000) with angle-shaped samples and a Shimadzu tear strength testing machine. Both the tensile and tear properties were tested at a speed of 500 mm/min.

Results and discussion

Figure 1 shows the effect of Si69 loading on the scorch time and cure time for NR containing 30 and 60 phr of silica in fly ash (FASi). It can be observed that the addition of Si69 had a significant effect on the scorch and cure times, while the fly ash content had a small effect. The scorch time and cure time appeared to increase with Si69 content. The increases in scorch time and cure time indicate some interference effect to the crosslink formation of the rubber caused by the presence of the Si69. This can be explained using a chemical reaction between Si69-treated fly ash and the being-vulcanized rubber (FA-Si69-NR) as shown in Scheme 1. It can be seen that the reactive sites (radicals) on the rubber occurring during the mastication process may have to form a chemical linkage (C-S linkage) with the Si69 [12]. This would automatically reduce chances to form sulphur-crosslinking within the rubber molecules. Another reason could be due to a formation of longer chains of Si69 which consists of triethoxysilylpropyl groups on its ends. These bulky groups probably resulted in a steric hindrance for rubber crosslinking, this view being supported by Poh *et al* [8]. As a result, the scorch time and cure time were prolonged. This means that the scorch and cure times were more dependent on Si69 content rather than fly ash content. This was why the fly ash content had a little effect on the changes in scorch and cure times. If the above explanation for scorch and cure time changes was true, one would expect to see a decrease in crosslink density of the vulcanizates decreased with increasing Si69 content. The crosslink density results of the NR vulcanizates with varying Si69 contents are shown in Figure 2. As can be observed the crosslink density of the vulcanizates reduced with increasing Si69 contents from 6.0-8.0%wt. However, at 2.0-4.0%wt Si69, the crosslink density increased. An increase in the crosslink density may be caused by additional C-S linkages formed by the chemical reaction between the rubber and Si69. This could be said that the Si69 could act as a crosslinker in the vulcanizates.

Figure 3 shows the minimum and maximum torques of the NR compounds containing different Si69 contents. It was found that the minimum torque did not much change with Si69 contents while this was not the case for maximum torque. The decrease in maximum torque with increasing Si69 was expected and may be linked with the decrease in crosslink density of the vulcanizates as stated in Figure 2. It should also be noted that for any given Si69 content, the maximum torque for FASi60 filled vulcanizates was greater than that for FASi30 vulcanizates.

This was associated with a change in rigidity of overall vulcanizates, as a result of different fly ash content and quantity of the FA-Si69-NR network in the vulcanizates.

Figures 4 and 5 show the tensile modulus, ultimate tensile strength and elongation at break of NR composites with FASi30 and FASi60 for different Si69 contents, respectively. It can be seen that the tensile modulus in Figure 4 increased with Si69 content up to 2-4%wt and then started to decrease at higher Si69 loadings. This indicates that the FA/NR reinforcement with Si69 reduced at high Si69. This could be reasoned by a self-condensation reaction of the Si69, resulting in a formation of mono- and poly-layers of polysiloxane molecules on the fly ash surface [14], which could act as a plasticizer between the fly ash and the NR molecules [1], and thus decreasing the rubber modulus. The change in modulus of the NR/FA vulcanizates was corresponded with that in elongation at break as shown in Figure 5 with varying Si69 contents as the vulcanizates became more rigid (resistance to higher stress at lower elongation) up to the optimum content of the Si69. It was interesting to observe that the tensile strength of the vulcanizates did not change with Si69. This could be explained by C-S bonding occurring in the rubber vulcanizates. The C-S bonding could be achieved through two sources, one with the Si69 and the other in with the added sulphur. During the vulcanization reaction, any reactive site on the rubber molecules which has formed the C-S bond with the Si69 meant a loss in C-S linkage with the added sulphur. This was why there was no improvement of the tensile strength of the vulcanizates with varying the Si69 contents.

The tear strength of the NR composites containing FASi30 and FASi60 with varying Si69 contents is illustrated in Figure 6. It was found that the tear strength of the NR composites with FASi30 was greater than that with FASi60. The changes in tear strength with varying Si69 contents were every similar to those in tensile modulus, the optimum Si69 contents being around 2-4%wt. The changes in tear strength should be discussed in terms of continuity of rubber phases by the presence of Si69. It can be expected that NR composites with higher silane content tend to produce more continuous phases as a result of chemical bondings between the rubber and the fly ash particles. However, above the optimum Si69 contents, the tear strength worsened. This may be due to the plasticization effect of the Si69 as discussed earlier.

Conclusion

The effect of Si69 content on the cure and mechanical properties of the NR vulcanizates containing FASi30 and FASi60 was studied. The results suggested that the scorch and cure times marginally increased with a decrease in crosslink density when increasing Si69 contents. The decrease in crosslink density was compensated by

chemical bonding between the rubber and the fly ash particles due to the presence of Si69. This work recommended concentrations of 2.0 and 4.0 wt% Si69 to be introduced into the NR/FA composites for the improvement of the tensile modulus and tear strength of the NR/FA composites with unchanged tensile strength.

Acknowledgements

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Key words

Natural rubber, fly ash, mechanical properties, rubber reinforcement, composites.

Table 1. The chemical compositions of fly ash particles

Chemical composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	TiO ₂	Pb ₂ O ₅
Content (%)	35.05	20.14	9.13	9.56	2.28	1.18	1.91	1.39	0.33	0.36

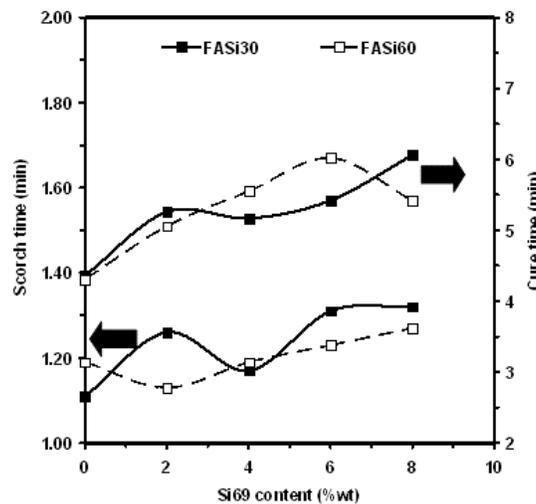
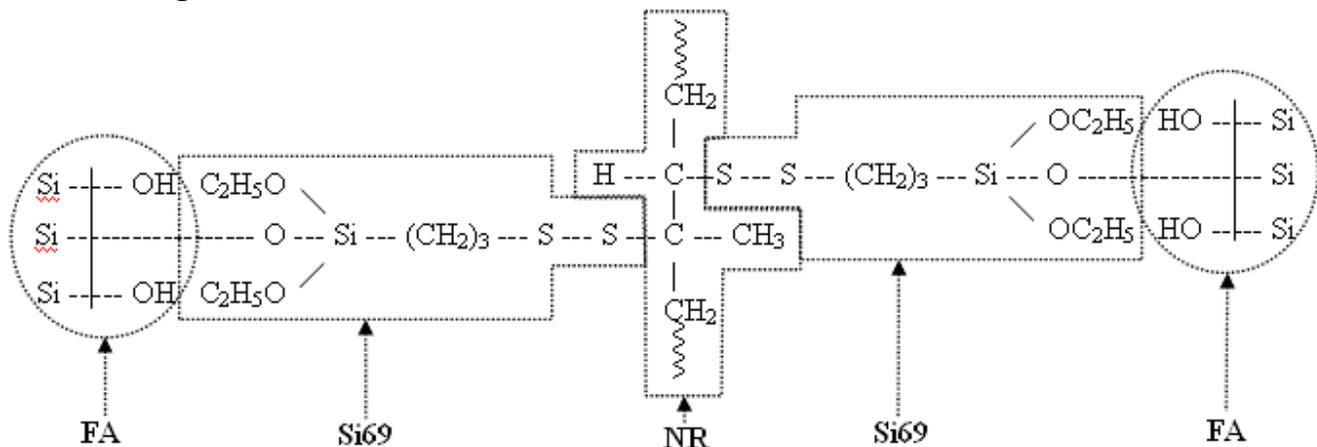


Figure 1. Scorch and cure time of NR/FA vulcanizates with various Si69 contents



Scheme 1. A chemical reaction between Si69-treated FA and NR

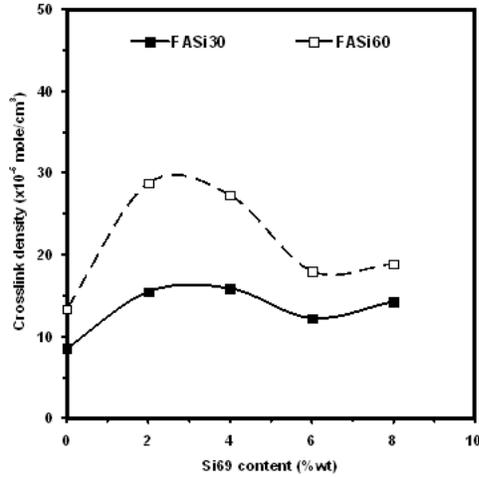


Figure 2. Crosslink density versus Si69 content for NR/FA vulcanizates

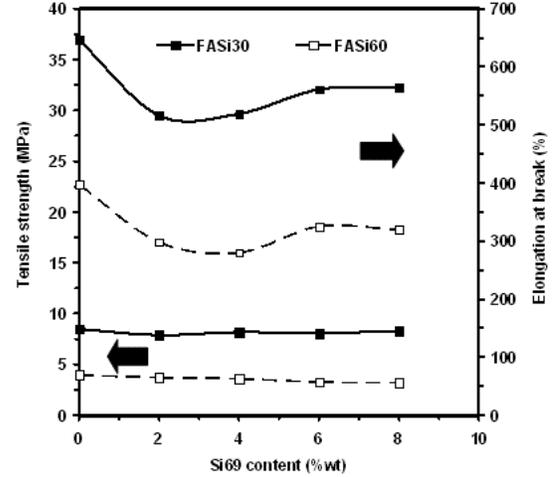


Figure 5. Tensile strength and elongation at break with various Si69 contents of NR/FA vulcanizates

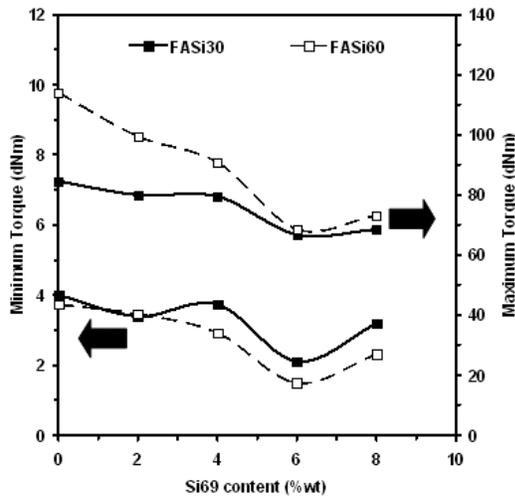


Figure 3. Minimum and maximum torques of NR/FA vulcanizates with various Si69 contents

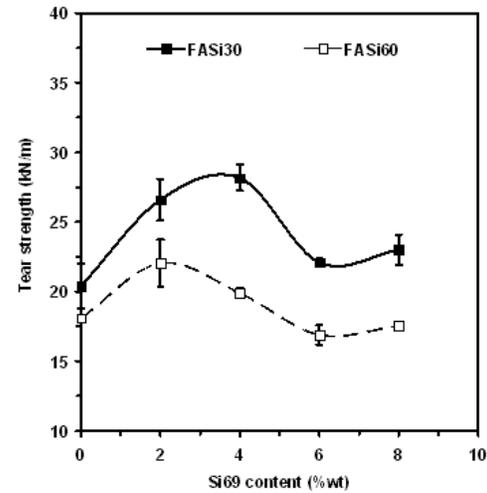


Figure 6. Tear strength as a function of Si69 content for NR/FA vulcanizates

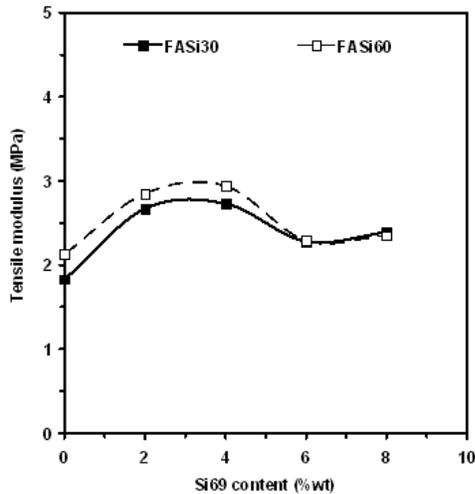


Figure 4. Tensile modulus as a function of Si69 content for NR/FA vulcanizates