Aminopropyltriethoxy silane in natural rubber/silica composites: Torque and vulcanization properties

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Abstract. The performance of rubbers composites in engineering application depend on the compatibility between reinforcing fillers and rubbers. It is a concern especially when forming rubbers composites with much contrasting of polarities between the rubbers matrix and the reinforcing fillers. However, correct compatibilizer will settle the poor interactions. This study; natural rubber (NR)/precipitated silica (PSi) composites were compounded together with aminopropyltriethoxy silane (AS) as a compatibilizer. The AS is one type of silane coupling agents and it was compounded into the composites of NR/PSi with varied doses i.e. one to seven phr. It was found that the AS significantly affected the torque and vulcanization properties of the NR/PSi composites. The AS decreased the viscosity/minimal torque but raised the maximal torque and torque differentiation. It was also found that the AS increased the rate of vulcanization. The increases in the torque and vulcanization properties were presumably attributed to the enhancement in rubber to filler interactions originating from coupling bonds formation in the presence of AS as a compatibilizer. Besides, the AS also role as a plasticizer which increased the degree of filler dispersion of PSi. Therefore, the addition of AS had a considerable potential to compatibilize the non-polar NR and PSi filler.

1. Introduction
The precipitated silica (PSi) and carbon blacks have been universally utilized to enhance the physical/tensile/mechanical properties of rubbers systems/compounds (Refs). The PSi offers one unique combination of strengths, abrasion and ageing resistances and adhesion properties to rubbers vulcanisates/products [1]. PSi is a polar filler because of the surface of its particles are fully with a lot of silanol groups and hence, it will not suitable/compatible to natural rubber (NR) as one of non-polar rubbers [2-3]. Researchers have been trying to address this deficiency of PSi by some methods to enhance its compatibility. These include utilizing silane coupling agents or compatibilizing agents [4] or processing/dispersant aid [5-7].

One further study on the affection of aminopropyltriethoxy silane (AS) on the torque and vulcanization properties of the NR/PSi composites was carried out. The AS is a type of commercial silane coupling agents. As presented in Figure 1, it has amine component within its molecule. The AS was incorporated into NR/PSi composites at from one to seven phr. The torque and vulcanization properties of NR/PSi composites with and with no AS were studied.
2. Materials and methods

2.1. NR and other Ingredients

NR was used as the matrix. Other ingredients i.e. AS (C₉H₂₃NO₃Si) as the compatibilizer, IPPD as the antioxidant, PSi (Vulcasil-S) as the reinforcing filler, Sulphur (S) as the cross linker, MBTS as the accelerator, zinc oxide/ZnO as the activator and stearic acid as the co-activator were used as supplied.

2.2. Preparation of NR Composites

A semi-efficient vulcanization formulation (Table 1) was applied in the preparation of NR/PSi composites. The composites preparation procedures were done on a 2 roll mill based on ASTM D 3184/80. The system of the NR/PSi composites with and with no AS is displayed in Table 1.

| Table 1. The system of NR/PSi composites with/with no AS |
|---------------------------------------------------------|
|                  | NR and other ingredients | Phr |
| NR               |                          | 100 |
| ZnO              |                          | 5   |
| S                |                          | 1.5 |
| MBTS             |                          | 1.5 |
| PSi-Vulcasil S   |                          | 30  |
| Stearic acid     |                          | 2   |
| IPPD             |                          | 2   |
| AS               |                          | 1; 3; 5; 7 |

2.3. Torque and Vulcanization Properties

The torque and vulcanization properties of the NR/PSi/AS composites were determined using MDR 2000/Monsanto Moving Die Rheometer based on ISO 3417. The composites were Vulcanized at 150 °C. The torque properties were Tₘ as minimal torque, Tₜ as maximal torque and (Tₜ – Tₘ) as torque change. The vulcanization properties were ts₂ as time to scorch and t₉₀ as optimum vulcanization time.

3. Results and Discussion

3.1. The Torque Properties

Figure 2 presents the minimal torque (Mₘ) of the NR/PSi systems in the existence of AS with various doses. It was observed that the Mₘ values of NR composites with AS were lower than that of NR system with no AS. The AS decreased the Mₘ. The Mₘ announces the filler to filler inter agglomeration [8]. It can estimate the viscosity of a rubber system, relatively [9]. The higher the Mₘ value means the stronger the filler to filler interaction is and hence, the AS decreased the filler to filler interaction that led to improve the process ability of the NR/PSi systems.
Figure 2. The $T_L$ of the NR composites in the existence of AS.

Figure 3 presents the $T_H$ of the NR/PSi composites plus AS with various doses. As observed, the $T_H$ of the NR/PSi composites with AS till five phr were higher compared to the reference composite. The $T_H$ value estimates relatively the stock modulus that was raised in this investigation. It was connected to the nature of rubber to filler interaction i.e. intercalation and exfoliation [2]. These interactions were further raised if the doses of AS were further raised also till five phr. It was connected to the role of AS as compatibilizer for the NR/PSi composites.

Figure 3. The $T_H$ of the NR composites in the existence of AS.

Figure 4 presents the torque change i.e. $(T_H - T_L)$ of the NR/PSi composites with various AS doses. The $(T_H - T_L)$ of composites of NR/PSi with AS till five phr were higher compared to the reference composite.
Figure 4. The (TH – TL) of the NR composites in the existence of AS.

The (TH – TL) value indicates the crosslinks level of a system of rubber [10]. The lower the value means the lower the level. The total crosslinks are the amount of sulphide crosslinks and physical crosslinks [11]. The addition of AS till five phr increased the (TH – TL). It was connected to the role of AS as a compatibilizer. The hydrophobic PSi (because of the incorporation of AS) stored the performance of ZnO in stimulating the accelerator that speed up the vulcanization and enhanced the state of the sulphide crosslinks. The more hydrophobic the PSi, the more compatible it was to NR. As a consequence, the AS reduced the filler-filler interaction but raised the rubber to filler interaction; getting to to form NR-AS-PSi coupling bonds that were defined as a different type of crosslinks and hence, further raised the total crosslinks of NR systems.

The decline in (TH – TL) after the five phr of AS dose was connected to the dilution affection of the enormous amounts of AS that reduced the crosslinks.

3.2. The Vulcanization Properties
The vulcanization properties of the NR/PSi plus AS composites i.e. scorch (t2) and optimum vulcanization (t90) times are shown in Figs. 5-6. As observed, the bigger the dose of AS was in the NR/PSi composites, the lower t2 and t90 were. It was connected to the amine ingredient inside AS. As presented in Fig. 1, the AS has an amine within its molecule. Amine is an accelerator activator that increases the vulcanization rate [12].
If PSi is compounded with non-polar rubbers; PSi reacts with ZnO and forms PSi bound zinc that is unable to stimulate the accelerator and hence, the zinc action was reduced and the vulcanization was decelerated, respectively [13]. Compared to the reference composite, the $t_{90}$ of the NR/PSi composites with AS was lower than that of reference composite. The AS acted as a compatibilizer because the polar parts of the AS has chemically-reacted with the silanol groups of PSi and changed the hydrophilic PSi into hydrophobic PSi that combined relatively less with ZnO. Therefore, the achievement of ZnO in turning on the accelerator was maximised.

4. Conclusions
The rheology and vulcanization properties of natural rubber/PSi composites were improved by the incorporation of aminopropyltriethoxy silane as a compatibilizer. The aminopropyltriethoxy silane promoted the dispersion of PSi filler in the natural rubber matrix was connected to its waxy character.
It was clearly demonstrated that the utilizing of aminopropyltriethoxysilane decreased the viscosity of the natural rubber compounds but improved filler to filler interactions as well as the crosslinks level/torque change, providing great benefits to the processing aspect. This conclusion contributed to sense the role of aminopropyltriethoxysilane as a compatibilizer for natural rubber/PSi composites and could be an important information for producing such materials.

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