The effects of aminopropyltriethoxy silane on tensile and rheometric properties of silica-filled natural rubber vulcanizates

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Abstract. By using a semi-efficient vulcanization system; the effects of aminopropyltriethoxy silane on rheometric and tensile properties of silica-filled natural rubber (NR) composites were investigated. The NR composites were filled by silica filler at a fixed loading at 30.0 parts per hundred rubber (phr). The aminopropyltriethoxy silane was incorporated into the silica-filled NR composites. The aminopropyltriethoxy silane loadings were 1.0, 3.0, 5.0 and 7.0 phr. It was found that aminopropyltriethoxy silane functioned as a co-curing agent which reduced the scorch and cure times of the silica-filled NR composites. The higher the aminopropyltriethoxy silane loading, the shorter the scorch and cure times were. It was also found that aminopropyltriethoxy silane caused improvements in modulus and tensile properties, exclusively up to a 5.0 phr of loading. The 5.0 phr of aminopropyltriethoxy silane was the optimum loading.

1. Introduction
The rubber compounding is an operation that mixes a type of raw rubbers with rubber additives. Each ingredient of the rubber compound offers specific usage either in the mixing process, vulcanization or properties of the rubber vulcanizates [1]. The raw material of rubber offers rubbery behaviour to the vulcanizates; rubber chemicals include vulcanizing agent vulcanizes rubber molecules; accelerators improve the function of a vulcanizing agent to enhance vulcanization rate; and plasticizers reduce viscosity but increase deformability and also shift properties.

The chemicals of rubber include non curative chemicals and curative chemicals. Curative chemicals impact rheometric properties of compounds of rubber. The most popular curative chemicals are stearic acid, accelerators, zinc oxide and sulphur [2].

The examples of non curative chemicals are reinforcing fillers and non-reinforcing ones. The prime purpose of the use the fillers is to increase mechanical or physical properties of composites or vulcanizates include tearing and flexing, abrasion resistance, tensile strength or decreasing the production cost. Besides the black filler (carbon black), silica as a white filler is one of the most applicable fillers in rubber mixing and it is applied to strengthen the vulcanizates. It is polar and relatively hydrophilic filler. During rubber mixing, the filler particles tend to reach out each other physically and create agglomeration of filler that poor filler dispersion. To handle the specific problem, another rubber chemical includes processing/dispersant aid, oil/oily chemical is added during rubber mixing.

Organosilanes are utilized to increase silica dispersion degree and consequently increase tensile/physical properties of rubber vulcanizates [3]. They are reactive and usually utilized in a relatively small quantity, less than 2 phr [4] [5]. They modify the silica surfaces [6] and modified
silica, as the product, offers silica surfaces with more active. These active surfaces contribute significantly during vulcanization and give some coupling bonds between silica - organosilane - raw rubber [7] [8]. There are a lot of pieces of evidence [9] [10] proving the existence of such type of bonds. In all these cases marked improvement in rubber properties was noted [4] [9] [11].

The aminopropyltriethoxy silane is one type of organosilanes. This research work, it was applied to handle the poor degree of silica dispersion and hence, the aminopropyltriethoxy silane influences on properties of compounds of silica-filled natural rubber (NR) include rheometric and tensile were investigated.

2. Methodology
2.1. Raw rubber and rubber chemicals
NR (SMR 3) and other rubber chemicals such as aminopropyltriethoxy silane (C₅H₃NO₃Si), N-isopropyl-N'-phenyl-p-phenylenediamine, precipitated silica (vulcasil-s), sulphur, mercaptobenzothiazolyl disulfide, zinc oxide and stearic acid were supplied by rubber Lab of Engineering Campus of Universiti Sains Malaysia, Malaysia. All materials were consumed as supplied.

2.2. Rubber Mixing
A semi-efficient recipe/system, as presented in Table 1, was applied in the rubber mixing process. All of the mixing procedures were done to follow the ASTM D 3184/80. The process of rubber mixing was conducted on a lab scaled of two roll mill.

| Rubber/chemicals                        | Amount (parts per hundred rubber/phr) |
|----------------------------------------|---------------------------------------|
| SMR 3                                  | 100                                   |
| Zinc oxide                             | 5                                     |
| Sulphur                                | 1.5                                   |
| mercaptobenzothiazolyl disulfide       | 1.5                                   |
| Silica                                 | 30                                    |
| N-isopropyl-N'phenyl-p-phenylenediamine| 2                                     |
| Stearic acid                           | 2                                     |
| Aminopropyltriethoxy silane            | 1; 3; 5; 7                            |

2.3. Rheometric properties
The rheometric properties of NR samples were collected utilizing an MDR 2000/Monsanto Moving Die Rheometer at 150°C. The ts₂ as time to scorch, ts₀ as optimum time to cure, Mₘᵢₙₐₓ as minimum torque, Mₘₐₓ as maximum torque and Mₘₚₐₓ - Mₘᵢₙ as torque difference was determined according to ISO 3417.

2.4. Tensile properties
NR samples with dumbbell-formed (ISO 37) were tested to know tensile properties include tensile moduli (M100, M300), tensile strength (TS) and also elongation at break (EB). The tests were conducted at a universal tensile machine (Instron3366) with a five hundred (mm.min⁻¹) of crosshead speed.

3. Results and discussion
3.1. The influences of aminopropyltriethoxy silane on rheometric properties
The relationship between aminopropyltriethoxy silane and ts₂, scorch and ts₀, optimum cure times of NR composites are presented in Table 2. Because of its specific surface chemistry, the polar filler silica always causes cure retardation. Its surface is a relatively high polarity; causing silica reacted chemically with the activator (ZnO) during vulcanization and created silica bound zinc and because of
that the activator unable to activate the accelerator. As a consequence, the activity of zinc was diminished and the process of vulcanization was retarded [12] [13]. Whenever compared to control composite, the aminopropyltriethoxy silane additions reduced both the cure and scorch times. The aminopropyltriethoxy silane might be classified as a co-curing agent since its polar parts interacted with silanol (the polar groups) to convert hydrophilic silica to less hydrophilic one. The less hydrophilic silica interacted relatively weaker with ZnO. Therefore, the ability of the activator in activating the MBTS was enhanced.

Table 2. The influences of aminopropyltriethoxy silane on rheometric properties.

| Filled NR compounds | Aminopropyltriethoxy silane loadings |
|---------------------|--------------------------------------|
|                     | 0 phr / Control                      |
|                     | 1 phr                               |
|                     | 3 phr                               |
|                     | 5 phr                               |
|                     | 7 phr                               |
| ts₂ (minutes)       | 4.95                                |
|                     | 2.72                                |
|                     | 1.52                                |
|                     | 0.87                                |
|                     | 0.62                                |
| t₈₀ (minutes)       | 9.67                                |
|                     | 6.74                                |
|                     | 4.27                                |
|                     | 3.31                                |
|                     | 2.32                                |
| Mₘₐₓ. (dN.m)        | 10.34                               |
|                     | 10.43                               |
|                     | 10.90                               |
|                     | 11.48                               |
|                     | 9.43                                |
| Mₘᵲₙ. (dN.m)        | 1.23                                |
|                     | 0.95                                |
|                     | 0.69                                |
|                     | 0.54                                |
|                     | 0.33                                |
| Mₘᵡ₋ₘᵰₙ. (dN.m)    | 9.11                                |
|                     | 9.48                                |
|                     | 10.21                               |
|                     | 10.94                               |
|                     | 9.10                                |

As shown in Table 2, the aminopropyltriethoxy silane affected ts₂ and t₈₀. The more the loading of aminopropyltriethoxy silane, the lower was both times. It was because of the amine-content (NH₂₂) of the aminopropyltriethoxy silane. Amine is one of the activators for accelerators and it is an alkaline chemical that enhances the rate of cure [14]. It may also be applied to handle the problem of cure retardation due to the silica reinforcement for rubber [13] [14] [15].

From Table 2, the aminopropyltriethoxy silane reduced the minimum torque (Mₘᵲₙ.) that indicates the interaction of filler to filler [16] [17] and Mₘᵲₙ. is the relative the rubber compound viscosity [18] [19] [20] [21] [22]. A lower Mₘᵲₙ. tends to diminish the filler to filler interaction. Therefore, the aminopropyltriethoxy silane diminished the filler to filler interaction which enhanced the processability of the NR composites.

From Table 2, the addition of the aminopropyltriethoxy silane at 1.0 phr, into control composite, the upturned difference in torque. The aminopropyltriethoxy silane additions up to a 5.0 phr further upturned difference in torque; however, it was started to reduce after a 5.0 phr of loading of the additive. The difference in torque is the rubber composite crosslink density [23] [24]. A greater difference in torque means a higher crosslink density. Total crosslink density is the sum of sulphide/chemical and physical crosslinks [25] [26]. The aminopropyltriethoxy silane additions up to a 5.0 phr upturned the difference in torque. It was because of the action of aminopropyltriethoxy silane which not only changed the hydrophobic silica into hydrophilic one but also kept the performance of ZnO in activating accelerator. The more hydrophobic silica was produced and it was more compatible with NR. Consequently, the aminopropyltriethoxy silane additions diminished the interaction of filler to filler and also upturned the interaction of rubber to filler; causing in the creating of aminopropyltriethoxy silane with - NR - silica coupling bonds which were classified as another type of crosslinks.

The decrease in torque difference beyond a 5.0 phr addition of the additive was because of dilution affection of the more amount of aminopropyltriethoxy silane that reduced the crosslink density.

3.2. The influences of aminopropyltriethoxy silane on tensile properties

Table 3 tabulates the relationship between aminopropyltriethoxy silane and tensile properties of filled NR. The aminopropyltriethoxy silane additions up to a 5.0 phr upturned the tensile moduli but reduced them with further increase in the amount. The TS result had the same trend.

It is popular that tensile moduli of a rubber vulcanizate depend on the total of crosslink density [27] [28], enhancements in tensile moduli up to 5.0 phr were because of a greater crosslink density as result of forming of aminopropyltriethoxy silane - NR - silica coupling bonds. The bonds of coupling were
considered as another type of crosslink [14] that upturned the total crosslink density of NR composites. Therefore, aminopropyltriethoxy silane caused an upturn in crosslink density. The discussion agreed with result of difference in torque as tabulated in Table 2. The torque differences of filled NR composites plus aminopropyltriethoxy silane were greater compared to filled composite without the additive.

Table 3. The influences of aminopropyltriethoxy silane on tensile properties.

| Filled NR vulcanizates | Aminopropyltriethoxy silane loadings |
|------------------------|--------------------------------------|
|                        | 0 phr / 1 phr / 3 phr / 5 phr / 7 phr |
| M100 (MPa)             | 0.79 / 0.97 / 1.15 / 1.30 / 1.29     |
| M300 (MPa)             | 2.29 / 2.36 / 2.67 / 2.90 / 2.40     |
| TS (MPa)               | 18.0 / 18.4 / 19.6 / 21.2 / 19.9     |
| EB (%)                 | 826.5 / 840.0 / 831.7 / 774.7 / 793.3 |

The decrease in tensile modulus after a 5.0 phr addition of the additive was because of excessive amount of aminopropyltriethoxy silane which reduced crosslink density. It was assumed that the more amount of aminopropyltriethoxy silane created some layers which bounded parts of the curatives-silica system and hence, deterioration in sulphide and coupling bond crosslinks formation. Again, this discussion was suitable with data as presented in Table 2.

As shown in Table 3, the aminopropyltriethoxy silane additions reduced the EB up to a 5.0 phr of loading and began to upturn whenever aminopropyltriethoxy silane loading was further upturned. The EB properties depend principally on crosslink density [28]. The decreases in EB up to a 5.0 phr was because of a higher crosslink density that immobilized NR chains from silica surface. Improvement in EB after a 5.0 phr was because of crosslink density deterioration.

4. Conclusions

From the results, some conclusions can be drawn:

1. The aminopropyltriethoxy silane was a curative rubber chemical for silica-filled natural rubber vulcanizates. It upturned rate of vulcanization process but diminished scorch time. The addition of aminopropyltriethoxy silane upturned the level of silica reinforcement on natural rubber. Both tensile strength and moduli were upturned, exclusively up to a five phr of aminopropyltriethoxy silane.

2. The aminopropyltriethoxy silane presumably was a coupling agent for silica-filled natural rubber vulcanizates. It upturned torque difference, tensile moduli and tensile strength. The five phr of aminopropyltriethoxy silane was an optimum loading for silica-filled natural rubber vulcanizates.

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