The utilization of aminopropyltriethoxy silane as a rubber additive in improving the degree of filler dispersion of natural rubber/precipitated silica composites

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Abstract. The performance of aminopropyltriethoxy silane (AS) as an additive in improving the filler dispersion of natural rubber (NR)/precipitated silica (PSi) was observed. The NR was loaded with PSi at thirty phr. The AS was mixed with the NR/PSi composites with various dosages (one to seven phr). The NR/PSi/AS composites were vulcanized at 150 °C. The rheometric behaviours of the NR/PSi/AS composites were determined by applying a curemeter. The AS role as a plasticizing additive. It cut down the minimal torque (viscosity) but raised the maximal torque and torque changes. The bigger the AS dosage; the lower the viscosity of the NR/PSi/AS composites. The incorporations of AS till five phr raised the maximal torque and torque changes. Based on the torque behaviours; the degree of PSi dispersion was observed. It was revealed that the AS raised the degree of PSi dispersion. Presumably, in the relation to the plasticizing affection of AS on the NR/PSi systems; the AS plasticized or soften the NR/PSi composites and hence, made easier the dispersion process of PSi into the NR systems, raised the PSi dispersion in the NR composites, jointly. The bigger the AS dosage, the better was the PSi dispersion.

1. Introduction
The rubber mixing is a mixing process which combines a particular form of raw rubbers with suitable additives. At the final stage of the mixing process; output as the rubber compounds/systems are accomplished. Then, the rubber systems are heated/cured/vulcanized to producing vulcanizates of rubbers with utmost physical (mechanical) properties and excellent elasticity. Therefore, the vulcanizates of rubbers are not changeable with other materials [1].

The raw rubbers can be synthetic or natural ones. As a very favoured raw rubber, the vulcanizates of natural rubber (NR) has relatively stronger properties even the vulcanizates are compounded with no filler or gum NR vulcanizates. Similar to the other types of rubber, their unfilled vulcanizates properties (physical/tensile/mechanical) can be farther raised by the addition of reinforcing into their compounds at the middle of the mixing process [2].

A particular filler of those reinforcing fillers is precipitated silica (PSi). The PSi is a white filler, because of it has a micron-sized of particles and whenever has to be appilicated at relatively bigger dosage; the PSi particles are possible to form several agglomerations and turn to a poor degree of PSi dispersion that can destruct the properties of the NR/PSi systems/vulcanizates. To clear up the PSi handicap; one particular rubber ingredient is added in the middle of the rubber mixing process. In this observation, aminopropyltriethoxy silane (AS) as one type of organosilanes, was applied to clear up the
poor degree dispersion of the PSi. The AS has the oily nature and hence, it has the chance to be applied as one type of plasticizing ingredient to raising the degree of PSi dispersion. Therefore, this observation examined the influence of AS dosage on the degree of PSi dispersion in the composites of NR.

2. Experiments

2.1. NR and rubber additives
NR was used as the raw rubber. The PSi was used as the particular reinforcing filler. Other rubber additives namely stearic acid, AS, (C₉H₂₃NO₃Si)/AS, sulphur/S, zinc oxide/ZnO, antioxidant/IPPD and accelerator/MBTS were needed.

2.2. NR compounding
A particular vulcanization formulation (Semi Efficient) was needed for the process of compounding of NR/PSi/AS composites were executed on a 2-roll mill (Model XK-160). Table 1 shows the system of the NR/PSi/AS systems.

| NR/additives | Parts per hundred rubber |
|--------------|--------------------------|
| NR          | 100                      |
| Stearic acid| 2                        |
| ZnO         | 5                        |
| S           | 1.5                      |
| MBTS        | 1.5                      |
| PSi         | 30                       |
| IPPD        | 2                        |
| AS          | 1 to 7                   |

2.3. Torque behaviour
The torque behaviours namely maximal torque (Tx), minimal torque (Tn) and change in torque (Tx – Tn) were figured out based on ISO 3417 applying one Rheometer/MDR 2000). The vulcanization temperature was at 150 °C.

3. Results and discussion

3.1. The rheometric behaviours
Fig. 1 presents the max (M_H) and min (M_L) torques of the NR composites in the existence of AS with various doses. As observed, the M_L values of NR composites with AS were lower than that of NR composite with no AS. The AS decreased the M_L. The M_L announces the filler-filler inter agglomeration [3] and equal with the relative viscosity of a composite [4]. The low the M_L, the weak the filler-filler interaction is; causing in lowering the viscosity of the NR/PSi/AS composites. Therefore, the AS decreased the filler-filler interaction that led to a lowering the viscosity, improving the process ability of the NR/PSi/AS composites.

From Fig. 2, the max torque (M_H) of the NR/PSi composites with various dosages of AS. It was observed that the M_H of the NR composites with AS till five phr were higher compared to NR reference composite. The M_H was connected to the nature of filler to rubber interaction namely intercalation and exfoliation [5-6]. The raise in M_H got more significant if the AS dosage was higher. In this observation, the AS behaviour as a plasticizing ingredient that boosted the degree of PSi to NR interaction.

Fig. 2 visualizes the torque differentiation, (M_H – M_L), of the NR composites in the existence of AS with various doses. As observed, the (M_H – M_L) values of NR/PSi composites with AS till five phr were higher than that of NR/PSi composite with no AS. The AS raised the (M_H – M_L). The (M_H – M_L) is the NR/PSi/AS composites cross-linking. A greater (M_H – M_L) means a higher cross-linking level. Total
cross-linking is the sum between sulphide, chemical and physical cross-linking [7-8]. The AS inclusion with dosage till a five phr upturned the (MH – ML). It was connected the roles of AS as PSi modifier that changed the PSi into a more hydrophobic one. The more hydrophobic PSi was relatively more compatible with NR and hence, the AS inclusion lowered the filler-filler interaction and also raised the rubber-filler interaction; forming the NR-AS-PSi coupling bonds. The latter is another form of crosslinks.

The deterioration in (MH – ML) after five phr of the additive was connected to the affection of dilution of the more dosage of AS that lowered the crosslinks.

![Figure 1](image1.png)

**Figure 1.** The max and min torques of the NR/PSi/AS

![Figure 2](image2.png)

**Figure 2.** The torque differentiation of the NR/PSi/AS composites

### 3.2. Measurement the degree of filler dispersion

The degree of PSi dispersion within the composites can be determined calculated by Equation 1 as follows [9]:

\[
\text{Eq. 1: Degree of dispersion} = \frac{\text{Torque at AS dosage}}{\text{Torque at 0 phr AS}} \times 100%
\]
\[ L = \frac{Q_r}{P_r} - P_r \]  

where \( Q_r = \frac{T_{Lr}}{T_{Hr}} \) and \( P_r = \frac{T_{Hr}}{T_{Hr}} \); and \( T_{Lg} \) and \( T_{Hg} \) were the minimal and the maximal torques of the filled rubber. The \( T_{Lg} \) and \( T_{Hg} \) of the gum NR compound were 0.07 and 4.88. The lower the value of \( L \) at a particular filler dose, the better the degree of PSi dispersion within the NR.

Fig. 3 presents that the values of \( L \) for the NR/PSi composites with AS were than that of the NR/PSi with no AS. It was observed that the value of \( L \) of the composite of NR/PSi with No AS was the biggest. It was connected to the surface of PSi which was full of hydrophilic silanol groups, and its relatively weak interaction with NR. The PSi particles also had a relatively strong interaction and created bigger agglomerates [10]. As a consequence, the PSi dispersion became poor. The inclusion of AS with a dosage of one phr decreased the value of \( L \). It was connected to the polar parts of AS that had a strong interaction with PSi that changed the filler into a hydrophobic one and hence, improved the dispersion. The bigger the dose of the AS, the lower the value of \( L \); the better the PSi dispersion.

![Figure 3. The L value of the NR/PSi/AS composites](image)

4. Conclusions

The aminopropyltriethoxy silane was a curative additive for the natural rubber/precipitated silica composites. It declined the minimal torque but raising in maximal torque, torque change and degree of precipitated silica dispersion. The bigger the aminopropyltriethoxy silane dosage, the better was the degree of the precipitated silica dispersion. It was related directly to the plasticizing behaviour of aminopropyltriethoxy silane that has the ability to reducing the viscosity of the natural rubber/precipitated silica composites. It was assumable that the molecule structure of the AS declined the viscosity.

References

[1] Yang RQ, Song YH and Zheng Q 2017 Polymer 116 pp 304-13
[2] Surya I, Ismail H 2019 IOP Conference Series: Materials Science and Engineering 523 1 012063
[3] Manna A K, De P, Tripathy D, De S and Peiffer DG 1999 POLY SC 74 2 389
[4] Ismail H, Nordin R and Noor A 2002 Polym Test 21 5 565
[5] Lautenschlaeger F and Edwards K 1980 Rubber Chem Technol 53 1 27
[6] Ranney M and Pagano C 1971 Rubber Chem Technol 44 4 1080
[7] Kraus G 1965 Rubber Chem Technol 38 1070
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