The Natural Rubber/Silica/Silane Composites: Study on Hardness, Tensile and Morphology Behaviours

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Abstract. Applying a favorite semi-efficient method, the influences of a typical silane coupling agent, named aminopropyltriethoxy Silane (APTES), on morphology, hardness, and tensile strength behaviors of the natural rubber/silica composite were examined. As a natural-based rubber, the natural rubber (NR) was filled with a reinforcing filler (silica) at a fixed amount, i.e., 30 parts per hundred rubber (phr). As an additive for rubber compounds, the APTES Silane has been incorporated into the NR/silica system with varied amounts such as 1, 3, 5, and 7 phr. The APTES Silane could potentially be used as an agent that improved the degree of filler distribution of silica. The morphology study found that the APTES Silane incorporations produced SEM images with larger matrix tearing and matrix breaking lines; clearly, the APTES Silane caused hardness, modulus, and tensile improvements from 1 to 5 phr of incorporations. The 5 phr of APTES Silane was chosen as the APTES Silane optimum amount.

Keywords: Natural Rubber · Silica · Silane · Hardness · Tensile Behaviours · Morphology

1 Introduction

The vulcanization process changes the base rubbers into rubbers vulcanizates with wanted mechanical properties [1]. A further enhancement in rubbers vulcanizates properties can be achieved by adding a certain dose of a reinforcing filler [2, 3]. The main purpose of exploiting the reinforcing fillers is to enhance the physical or mechanical behaviors of vulcanized rubbers. The enhancement in those properties depends on factors, including the type, quantity, or dose of chosen reinforcing filler and compatibility between the base rubbers and the reinforcing fillers [4].

For many years, there have been two types of popular reinforcing fillers. They are carbon black (CB) and precipitated silica (silica) [5]. The CB is a black filler, and silica is a white filler. Silica has been used as one of the reinforcing fillers in the rubber industry

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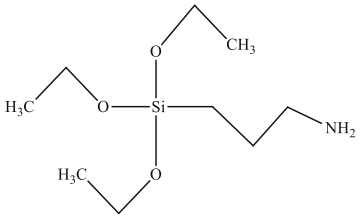

Fig. 1. The molecule structure of aminopropyltriethoxy Silane (APTES Silane)

in producing rubbers vulcanizates with light colors. It is a hydrophilic or polar filler, so many silanol groups exist on its particle surfaces. Hence, it makes the reinforcing filler relatively unsuited to natural rubber (NR) as a hydrophobic or nonpolar rubber [6–8]. Recently, many research workers have been examining to study intensively on this silica deficiency by some trying to enhance the silica-NR compatibility. Tries include applying coupling agents [7] or compatibilizers [8], or processing/dispersant aid [3, 9].

Another examination of the effects of APTES Silane, as an abbreviation of aminopropyltriethoxy Silane, on the morphology and tensile behaviors of the NR/silica composite was examined. The APTES Silane is typical of commercialized silane coupling agents. Referring to Fig. 1, the amine element is shown inside the APTES Silane material. As an additive, the APTES Silane was added into the NR/silica system with varied amounts, i.e., 1.0 to 7.0 phr. The influences of APTES Silane incorporations on morphology, hardness, and tensile behaviors of NR/silica with and without APTES Silane were examined.

2 Method

2.1 The Rubber and Other Rubber Chemicals

NR was used as the base rubber. The APTES Silane ($C_9H_{23}NO_3Si$) was used as the additive for the NR/silica composites, Isopropyl-N'-phenyl-p-phenylenediamine as an antioxidant, vulcanite-s (precipitated silica) as the material to reinforce the composite, sulfur as the material to crosslink the base rubber, mercaptobenzothiazolyl disulfide as the material to accelerate the curing process and zinc oxide/stearic acid as the activator and co-activator. The base rubber and the rubber materials were exploited as supplied.

2.2 Rubber Composite Preparation

She was referring to one typical semi-efficient formulation, the NR/silica composite was prepared. The rubber composites were prepared on a 2-roll mill (ASTM D 3184/80), and Table 1 tabulates the formulation of the rubber composites with no/with APTES Silane.

2.3 Crosslinks Level Measurement

The crosslinks level of NR/silica/APTES Silane was measured by its torque behaviors, i.e., delta torque and maximum and minimum torques of the NR composite. The delta torque equals maximum torque minus minimum torque, and the delta torque value indicates the crosslinks level. The less the delta torque, the lower the crosslinks level.

Table 1. The NR and rubber material for NR/silica composite preparation

NR, rubber materials	Amount-phr.
NR	100
Zinc oxide	5
APTES Silane	1; 3; 5; 7
Sulfur	1.6
Mercapto-benzothiazolyl disulfide	1.6
Silica	30
Stearic acid	2.1
Isopropyl-N'-phenyl-p-phenylenediamine	2.1

2.4 Hardness Behaviour

The hardness behavior in Shore A was determined by ISO 7691-I using the Durometer (Shore Type A).

2.5 Elongation at Break, Tensile Moduli, and Strength Behaviours

The dumbbell-shaped NR/silica/ APTES Silane samples (ISO 37) were tested to examine tensile behaviors. Stresses at low (100%), elongation at break, and strength at break. The tests were performed on an Instron (Instron3366) with speed at a 500 ($mm.min^{-1}$) crosshead speed and installed on a computer. The sample specimens with a dimension width of 10 mm, length of 100 mm, and thickness of 2 mm were prepared from press-cured sheets using a cutter. For each sample, at least 5 specimens were tested.

2.6 Morphology Behaviour

The morphology behavior of the NR composites with a size of about (1 cm × 1 cm) was prepared beyond the tensile test. Every specimen was carefully put on double-sided scotch tape, and a very thin gold layer was coated onto the surface. The morphology behavior of the fractured surface of the films was studied under a Zeiss Supra-35VP - scanning electron microscope (SEM) to have the information relating to the filler distribution level and to examine the available formation of some micro-defects.

3 Results and Discussion

3.1 Delta Torque/Crosslink Behaviours

Since the delta torque is used to indicate the crosslinks level of a rubber vulcanizate/compound/composite [10–12]. The less the delta torque value, the lower the crosslinks level. Therefore, the crosslinks behavior of the NR/silica/APTES Silane composite was studied based on its delta torque behavior. Figure 2 demonstrates the torque behavior of NR/silica/APTES Silane, including delta, maximum and minimum torque. The delta torque is the difference between the maximum torque and minimum torque.

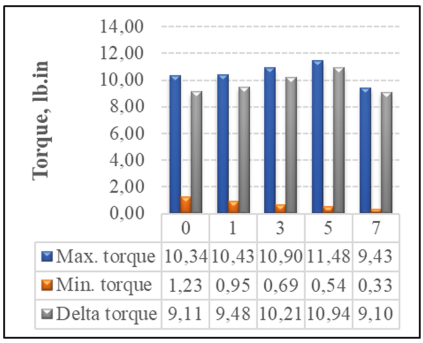

Fig. 2. The torques vs. APTES Silane amount

From Fig. 2, adding APTES Silane up to 5.0 phr into the NR/silica compound shifted the delta torque. It was clearly because of the function of the APTES Silane that converted the hydrophobic silica into a hydrophilic one. This latter type of silica became more compatible with NR. Hence, the incorporation of APTES Silane weakened the filler-to-filler interaction and shifted the rubber-to-filler interaction, causing an increase in the crosslinks level. The diminishing of the delta torque beyond the 5.0 phr of APTES Silane was positive because of any dilution influence of the excessive amount of the additive, which diminished the crosslinks.

3.2 The Tensile Behaviour

Figures 3, 4, 5 demonstrate the tensile behaviors of the NR/silica composites with no/with APTES Silane with various amounts. As shown in Fig. 3, the EB - elongation at break of NR/silica composites with some APTES Silane till 5 phr was lower than that of NR composite with no APTES Silane.

The EB was increased continuously with further increase of AS amount after 5 phr. Since the EB behavior calculate mainly on crosslinks density [11]. The decrease in EB till a 5 phr resulted from greater total crosslinks that retarded the NR chains' mobility from the surface of silica. The increase in EB after a 5 phr resulted from crosslinks devastation.

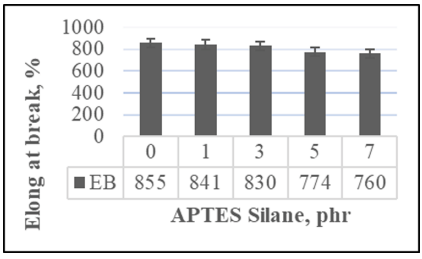

Fig. 3. The elongation at break vs. APTES Silane amount

Figures 4 and 5 show the tensile strength (TS) and moduli at 100% elongation (M 100), respectively. As seen, the TS and M100 of NR/silica composites with the doses of APTES Silane till 5 phr were greater than that of NR composite with no APTES Silane. Those properties started to decrease with a further increase in the APTES Silane dose at 7 phr. The TS and tensile moduli results had the same trend.

Since the TS and M 100 of a composite are equal to the level of crosslinks [11], the tensile moduli enhancement with the additions of APTES Silane till 5 phr were presumably a result of greater total crosslinks as a response of creating of NR - APTES Silane - silica coupling bonding that increased the level crosslinks of the NR/silica composites. Therefore, APTES Silane made the crosslinks level enhancement.

The deterioration in TS and M 100 above a 5 phr dose of the APTES Silane resulted from the excessive amount of the additive, which decreased crosslinks. The more APTES Silane presence created the APTES Silane layers, which rounded the curatives system and diminished the crosslinks.

Figure 6 demonstrates the hardness behavior of NR/silica/APTES Silane composites. As seen, the hardness performs a similar behavior with M 100, indicating the vulcanizate's stiffness. Both tensile moduli and hardness depend principally on the level of crosslinks [10]. The enhancement in hardness up to 5.0 phr of APTES Silane was because of a higher crosslinks level, and any deterioration in hardness beyond 5.0 phr was because of a lower crosslinks level.

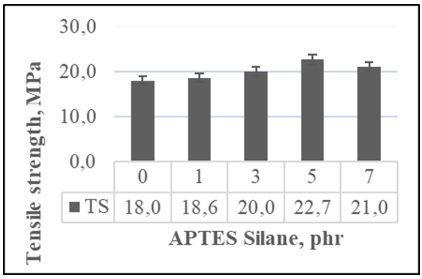

Fig. 4. The tensile strength vs. APTES Silane amount

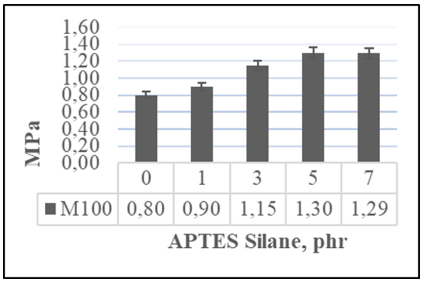

Fig. 5. The modulus at 100% elongation (M 100) vs. APTES Silane amount

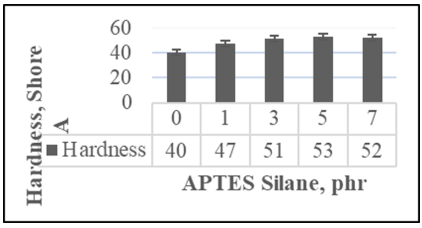

Fig. 6. The hardness vs. APTES Silane amount

3.3 The Morphology Behaviour

The scanning electron microscopy (SEM) images are visualized in Fig. 7, showing the fractured surfaces of NR/silica with/without APTES Silane at a 500x magnification. The images showed the homogeneity of the silica distribution because of the APTES Silane incorporations. The silica distribution was the poorest homogeneous in (I), which showed larger silica flocs (see the signs in Fig. 7 (I). The image of (a) also looked relatively even compared to the others. It means that (I) was less malleable than the others. But, the image for (III) phosphoresces the largest matrix breaking line and surface roughness when compared to (II) and (IV). A better filler distribution in (III) changed the crack path, leading to an enhanced crack-resistance process and hence, caused the moduli and TS improvements. The rupture energy enhancement was probably because of a better filler distribution of silica, and it relates to the state of roughness and matrix tearing form of the broken specimen. An enhancement in rupture energy is due to the roughness and matrix tearing line of the broken surface of rubbers composites samples [13]. But the matrix tearing rows and surface roughness of (I) and (IV) were smoother compared to (II) and (III), which produced less tensile strength.

The tensile strength and tensile moduli (tensile behaviors) of the natural rubber/silica composites were increased, but the addition of APTES Silane as a rubber additive reduced elongation. The APTES Silane offered a phenomenon from the filler degree of distribution to crosslink enhancement by coupling bonds between the natural rubber - APTES Silane - silica. The scanning microscopy electron (SEM) analysis proved that the APTES Silane incorporations improve the filler distribution of silica within the natural rubber matrix. This finding offers to understand the function of APTES Silane as a rubber additive in natural rubber/silica composites, and it might be a source of useful information for manufacturing such composites.

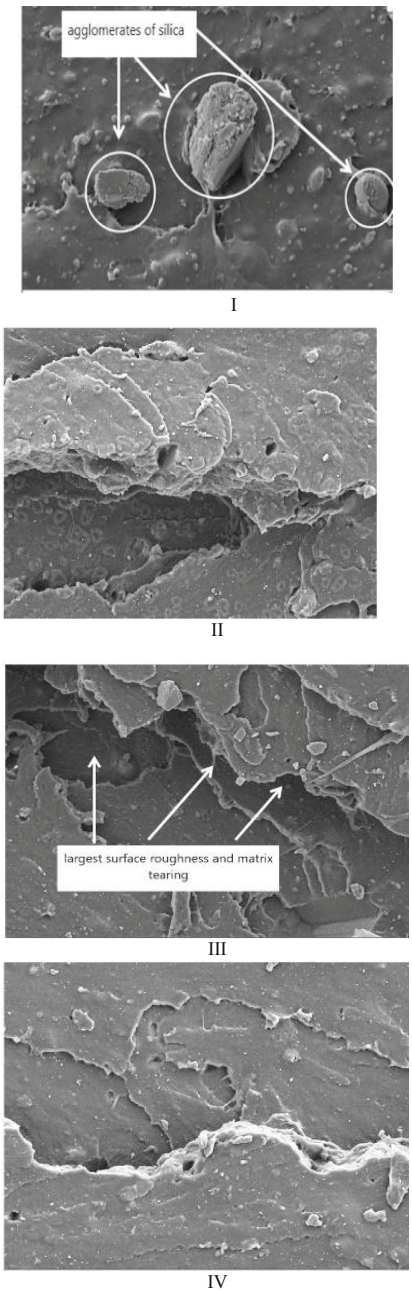

Fig. 7. Scanning electron microscopy images of the failed fracture of NR/silica composites with/with no APTES Silane, at a magnification of 500x: (I) No APTES Silane, (II) APTES Silane at 3 phr, (III) APTES Silane at 5 phr, and (IV) APTES Silane at 7 phr.

4 Conclusion

The tensile strength and tensile moduli (tensile behaviours) of the natural rubber/silica composites were increased but elongation was reduced by the addition of APTES Silane as a rubber additive. Assumably, the APTES Silane offered a phenomenon from the filler degree of distribution to crosslink enhancement by formed of coupling bonds between the natural rubber - APTES Silane - silica. The scanning microscopy electron (SEM) analysis proved that the APTES Silane incorporations improve the filler distribution of silica within the natural rubber matrix. This finding offers to understand the function of APTES Silane as a rubber additive in natural rubber/silica composites and, it might be a source of useful information for manufacturing such composites.

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