Mechanical properties improvement in silica-filled natural rubber composites using stearyl alcohol

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Abstract. Mechanical properties improvement in silica-filled natural rubber (NR) composites through the use of stearyl alcohol (SA) was carried out. The SA was palm kernel oil based fatty alcohol. The NR was filled by precipitated silica at a certain concentration (thirty parts per hundred rubbers, phr). The SA-fatty alcohol was added into composites from 1.0 to 4.0 phr. Due to its functions as a curative additive and internal plasticiser; the SA improved torque difference, crosslink density and also tensile strength up to a 2.0 phr of addition. Morphology study proved that a 2.0 phr of SA was the optimum addition where a fractured surface image of silica-filled NR composite with 2.0 phr of SA exhibited the greatest surface roughness and matrix tearing lines.

1. Introduction

The enhancement of stiffness, tensile and tear strengths and also abrasion resistance of the rubber products due to the addition of reinforcing fillers are defined as rubber reinforcement [1]. Fillers are reinforcing, semi and non-reinforcing [2, 3]. Non reinforcing fillers cheapen the cost of rubber products.

The carbon blacks (CBs) and silicas are popular to be utilised as reinforcing fillers in manufacturing rubber products. Mechanical properties of vulcanizates which are reinforced by silicas are inferior to those of CBs, even though they have similar in particle-sizes [4, 5]. It is because of the surface of silica is hydrophilic and highly polar and hence, it is relatively incompatible with NR causing in weak filler to rubber interactions. Becoming worse, silica particles likely interact with each other to create bigger aggregates. All of this will cause in a poor degree of silica dispersion.

Numerous technologies have been launched to increase the silica to NR interactions and one of them is silane-modified silica which shows a significant increase in performance compared to normal silica. For some applications, it has been suggested as alternatives to the lower reinforcing grades of CB. However, in practical applications the performance of the silane-modified silica has not been clearly defined, the high cost of the silane is the disadvantage.

A new effort to solve the weakness of silica was applying to stearyl alcohol (SA). The chemical originally comes from palm kernel oil. Because of its oily matter and since oil is a type of plasticising agent [2, 3], it has the potential to improve the degree of silica dispersion in NR composites. Therefore, this research work reports the mechanical properties improvement in silica-filled NR composites through an application of SA as a plasticizing agent.
2. Materials and methods

2.1. Materials for research
PPTPN 7, Bandar Lampung, Indonesia supplied the SIR 3L-grade NR. PT. Industri Karet Deli (IKD), Medan, Indonesia supplied the IPPD (antioxidant), sulfur, ZnO, stearic acid, MBTS (mercaptobenzothiazole disulfide) and precipitated silica. PT. Ecogreen, Batam, Indonesia supplied the SA-fatty alcohol, \( CH_3(CH_2)_{16}CH_2OH \).

2.2. The compounding of rubber composite
A typical semi-efficient curing was applied in preparing the NR composites. All procedures of composite preparing were performed according to ASTM D 3184-80. The composites preparing was made on an XK-160 Model of a two-roll mill. Table 1 lists the recipe of composites of NR without and with SA-fatty alcohol.

| Materials                  | Composition (parts per hundred rubber, phr) |
|----------------------------|---------------------------------------------|
| NR                         | 100.0                                       |
| ZnO                        | 5.0                                         |
| Stearic acid               | 2.0                                         |
| IPPD                       | 2.0                                         |
| MBTS                       | 1.5                                         |
| Sulphur                    | 1.5                                         |
| Precipitated silica        | 30.0                                        |
| SA-fatty alcohol           | 0.0; 1.0; 2.0; 3.0; 4.0                     |

2.3. Cure properties
The cure properties of NR composites without and with SA based on the recorded data of an MDR 2000-Rheometer that was operated to produce the data such as scorch time and cure time, minimum and maximum torques, the difference in torque (maximum torque minus minimum torque) based on ISO 3417. The respective samples of composites were cured at 150°C.

2.4. Swelling percentage behaviour
The swelling behaviour of the composites was determined in toluene (ISO 1817). Vulcanized composites with the dimension of (30mm x 5mm x 2mm) were weighed utilizing a balance and then swollen in toluene until an equilibrium state is reached (72 hours at ambient temperature). The samples of composites were taken from the liquid and the toluene was removed from surfaces of the samples and then weights were determined. Mass changing is calculated using Equation 1.

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\text{Swelling percentage (\%)} = \frac{100 \% \ (W_2 - W_1)}{W_1}
\]

in which \( W_1 \) = initial gram of specimen; \( W_2 \) = gram of specimen after immersion

2.5. Hardness and tensile properties
Hardness tests of the composites were performed utilizing a Shore A type manual durometer (ISO 7691-I). Dumbbell-shaped of composites samples were cut from moulded and vulcanized sheets. The testing of tensile properties was done at a cross-head speed of 500 mm/min using an Instron 3366 universal tensile machine (ISO 37). The tensile strength (TS), stresses at 100\% and 300\% elongations (M100 and M300) and elongation at break (EB) were determined.
2.6. The morphology study
The tensile fractured surfaces of composites were tested utilizing a Zeiss Supra-35VP SEM for information regarding the possible presence of micro-defects. The fractured pieces were coated with a gold layer to eliminate electrostatic charge build-up during the testing.

3. Results and Discussion

3.1. Cure properties
The cure properties of composites without and with SA are shown in Figures 1-3. As shown in Fig. 1, scorch times of the composites with SA were higher compared to without SA (the control composite). The higher the SA addition, the higher were scorch times. In this case, the SA acted as a scorch delay agent. The SA reduced cure times. It was because of the function of SA as a curative ingredient in the cure process.

![Figure 1. Cure and scorch times of silica-filled NR composites with various SA loadings.](image)

From Fig. 2, SA reduced the minimum torques. It was because of the function of SA as a plasticizing agent in the cure process. The SA increased torque difference up to 2.0 phr and reduced torque difference after the addition. The torque difference is a degree of crosslinking density of a composite [6-9]. Increases in crosslink density up to an optimum SA loading was attributed to hydroxyl groups which might activate chemically not only the rubber but also elemental sulphur/curatives and formed some intermediate complexes that attached them to chains of rubber with more efficient [2, 10]. Because of its oily matter, SA reduced viscosity of the composites. As a consequence, silica dispersion degree and rubber to silica interactions are improved, respectively. The silica to rubber interactions are defined as physical crosslinking, and together with sulphide crosslinking contributed to composites totally crosslinking density [11, 12]. Decreases in torque differences, after the optimum addition, was attributed to the excessive amount effect of SA which absorbed silica, other curatives and coated them together. Perhaps, this process reduced the crosslinking density.

3.2. Swelling percentage behaviour
The swelling behaviour of the composites without and with SA is shown in Figure 3. It is widely believed that swelling test relates to crosslinking density of a network chain [13], a more toluene penetration into composites resulting a lower crosslinking density.
Figure 2. Torque properties of silica-filled NR composites with various SA loadings

The 1.0 phr of SA decreased swelling percentage of the control composite. Increases SA addition up to a 2.0 phr caused a further decreased in swelling percentage. Beyond the addition started to increase swelling percentage. The increasing of crosslinking density was because of the acting of SA as a plasticizing agent [14, 15] that reduced viscosity of the composites. A lower viscosity makes easier silica dispersion and increased rubber to filler interactions, respectively. The NR to silica interactions are considered as additional physical crosslinking; together with sulphides crosslinking, contributed to the totally crosslinking density [1, 13, 16].

Figure 3. Swelling percentage of silica-filled NR composites with various SA loadings

3.3. The mechanical properties

The mechanical properties of composites without and with SA are shown in Table 2. The SA reduced M100, M300 and hardness. Increases SA concentration caused in a further reducing in M100, M300 and hardness. The M100, M300 and also hardness indicate stiffness of a composite [1, 5] and hence, SA caused in softness to the composites. It was because of the plasticizing effect of SA.
Table 2. Mechanical properties of silica-filled NR composites with SA loadings

| Silica-filled NR composites | SA loadings (phr) |
|-----------------------------|-------------------|
|                             | 0                | 1    | 2    | 3    | 4    |
| M100 (MPa)                  | 0.79             | 0.75 | 0.73 | 0.70 | 0.68 |
| M300 (MPa)                  | 2.22             | 2.03 | 1.94 | 1.90 | 1.87 |
| TS (Mpa)                    | 15.5             | 16.18| 17.90| 16.40| 15.10|
| EB (%)                      | 685.0            | 727.5| 732.5| 740.0| 765.0|
| Hardness (Shore A)          | 35.0             | 34.5 | 34.0 | 33.0 | 32.0 |

From Table 2, the TS improved up to optimum SA loading, 2.0 phr, and then reduced with further increasing SA addition. The improvement in TS was due to higher degrees of silica dispersion and crosslinking density. Those decreases in TS beyond a 2.0 phr loading were because of curative absorbing effect of excessive SA that reduced the crosslinking density. A 1.0 phr of SA caused increasing in EB. Increases the addition of SA caused further increases in EB. Of course, it was because of the function of SA a plasticizing agent.

3.4. Morphology study

Figure 4 shows SEM images with 340X magnification of fractured surfaces of NR composites without and with SA. The images of NR composites with SA (Figs. 4b and 4c) show a greater surface roughness and matrix tearing lines compared to NR composite without SA (Fig. 4a).
The rough surface indicated that matrix tearing relates to TS value. A rougher surface indicated higher TS \cite{17,18,21,22}. A rupture energy improvement was because of a stronger rubber to filler interactions within the composites. The 4b image of NR composite with 2.0 phr of SA showed the greatest surface roughness and matrix tearing. This indicated the crosslinking density was in highest degree which altered interactions between rubber segments into strongest ones and hence, causing in TS improvement.

The images of tensile fractured surfaces were in line with the results from the previous researchers who claimed that an increase in rupture energy was equal to surface roughness and matrix tearing lines \cite{17,18}.

4. Conclusion
Stearyl alcohol decreased cure time, minimum torque, tensile modulus and hardness but increased scorch time and elongations at break of silica-filled natural rubber composites.
Stearyl alcohol also increased torque difference, crosslinking density and tensile strength of silica-filled natural rubber composites. The 2.0 parts per hundred rubbers of stearyl alcohol was optimum loading for the silica-filled natural rubber composites. The stearyl alcohol produced a softer silica-filled natural rubber composite with a higher tensile strength and elongation at break.

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