Silica dispersion enhancement in natural rubber composites utilising stearyl alcohol

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Abstract. Silica dispersion enhancement in natural rubber (NR) composites utilising stearyl alcohol (SA), a type of fatty alcohol, was carried out. The effects of SA-fatty alcohol on curing, swelling behaviour and silica dispersion degree of NR composites were studied. The commercial grade of SA-fatty alcohol was utilised and added into NR composite which was filled by filler (silica) at 30.0 phr. The SA-fatty alcohol is a derivative material from palm kernel oil and it was mixed into the composites of NR as an additive of rubber. The SA-fatty alcohol concentrations were from one to four phr. From the results, the SA-fatty alcohol functioned not only as a curative but also as a plasticizing agent. As a curative agent, SA-fatty alcohol decreased the cure time but increased scorch time of the composites of NR. The higher the loading of SA-fatty alcohol, the shorter the cure time and the longer the scorch time was. As a plasticizing agent, SA-fatty alcohol reduced minimum torque and increased degree of silica dispersion in NR. The 2.0 phr was the optimum concentration of SA-fatty alcohol.

1. Introduction
The compounding is defined as the mixing of raw rubber and additives of rubber. Each of both raw rubber and additives has a specific usage [1]. Additives of rubber are non-curative and curative. Curative additives influence the curing. The popular ones are sulfur or other curing materials, accelerators and also stearic acid with zinc oxide. The non curative additives, fillers, are exploited to increase the mechanical properties of composites. Both silicas and carbon blacks (CBs) are the most exploited reinforcing fillers in the making of various rubber products [2]. But, at a relatively higher addition, their micron-sized filler particles tend to form bigger aggregates and poorer the filler dispersion degree. In practical, to solve the filler-agglomeration, a type of processing aid or dispersant aid is used.

Stearyl alcohol (SA) is a type of fatty alcohol which comes from palm kernel oil and it potentially to be utilised as a plasticiser to handle the filler dispersion problem. Oily material is a type of plasticiser [3-4] therefore; SA-fatty alcohol may plasticise/soften the NR composites and increase the silica dispersion degree in NR.

This research investigates the effects of SA-fatty alcohol on the curing, swelling property and silica dispersion degree of NR composites.

2. Experimental

2.1. Materials
The PPTPN 7, Bandar Lampung, Indonesia supplied the SIR 3L-grade NR. PT. Industri Karet Deli (IKD), Medan, Indonesia supplied the IPPD (N-isopropyl-N’-phenyl-p-phenylenediamine), sulfur, ZnO (zinc oxide), stearic acid, MBTS (mercaptobenzothiazole disulfide) and precipitated silica. PT. Ecogreen, Batam, Indonesia supplied the SA-fatty alcohol, CH₃(CH₂)₁₆CH₂OH.

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. The recipe for composites of NR without and with SA-fatty alcohol is shown in Table 1.

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

2.3. Curing

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

2.4. Swelling percentage

The swelling measurement was done in toluene according to ISO 1817. The cured samples of dimension (30 mm x 5 mm x 2 mm) were weighed utilising an electrical balance and swollen in toluene until equilibrium at room temperature (took 3 days). The swollen samples were removed from the toluene and the toluene was removed from the surfaces of the samples and the weight was determined. The change in mass is calculated as follows;

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

where \(W_1\) : initial mass of sample (gram) and \(W_2\) : mass of sample (gram) after immersion.

3. Results and Discussion

3.1. The curing

The effects of SA-fatty alcohol on cure time and scorch time of the NR composites are visualized at Figure 1. Scorch times of the NR composites with SA-fatty alcohol were higher compared to composite without SA-fatty alcohol. The more the SA concentration, the higher were the scorch times and SA-fatty alcohol caused in scorchy to the composites.
Figure 1. Effect of SA on cure and scorch times of NR composites

Figure 1 also presents that the addition of 1.0 phr of SA fatty alcohol into the control composite reduced curing time. A shorter curing time is a higher curing rate. The SA caused improvement in the cure. A higher SA addition, a more pronounced was the cure improvement. In this way, SA fatty alcohol was a co-curing agent in cure process.

From Figure 2, one phr of SA fatty alcohol reduced the minimum torque of the control composite. The minimum value of torque indicates viscosity [6-9]. A lower value indicates a lower viscosity. Decreases in viscosity of the composites of NR were due to an additional usage of SA fatty alcohol as a plasticising agent. It reduced the viscosity of the composites of NR. The higher the SA fatty alcohol concentration, the lower the viscosity was.

Figure 2. The effect of SA on the minimum torque of NR composites
Figure 3 shows one phr of SA-fatty alcohol enhanced the control composite torque difference. The addition of SA-fatty alcohol up to two phr further increased the value and after 2.0 phr started to decrease the value. A difference of torque reflects the crosslink density degree of a composite; a greater value, a higher the crosslink density is [10-13]. Enhancement in crosslink density up to 2.0 phr concentration of SA-fatty alcohol (two phr) was due to the molecule properties of SA-fatty alcohol. The hydroxyl groups of SA-fatty alcohol activated chemically the NR, curatives and sulfur-crosslinker during curing and hence, formed some intermediate complexes that attached the sulfur-crosslinker to rubber chains efficiently [4]. This caused in a higher cure degree.

![Graph showing torque values](image)

**Figure 3.** Effect of SA on maximum and difference torques of NR composites

Surely, the oily property of SA-fatty alcohol makes it a plasticiser. The previous discussion, SA-fatty alcohol reduced viscosity of NR composites. It enhanced the silica dispersion degree and also rubber to filler interactions. The NR to filler interactions are physical crosslinking [6, 8], together with chemical crosslinking contribute to totally crosslinking density of a composite of NR [14-16].

The torque difference decreases after the optimum concentration. It was due to the excessive concentration of SA-fatty alcohol that formed several oily layers, which absorbed parts of both silica and curatives. In this way, the total crosslink density was reduced.

3.2. The swelling behaviour

The effect of SA-fatty alcohol on percentage of swelling of the composites is visualized in Figure 4. The five samples of the composites of each NR composite were weighed utilising a balance and swollen in toluene till equilibrium, which took 3 days at room temperature. It is accepted that swelling corresponds to degree of crosslink of a crosslinked chains of composites [17], a more toluene in the composites indicating a lower crosslink density degree.
Figure 4. Effect of SA on swelling percentage of NR composites

The addition of one phr of SA-fatty alcohol reduced the swelling percentage of the control composite. Increases SA-fatty alcohol concentration up to a two phr caused a further decreased in swelling percentage. After the two phr started to increase the swelling percentage. The improvement in crosslink density was attributed to the function of SA-fatty alcohol as a plasticizer [6, 8] which reduced viscosity of NR composites. A lower viscosity makes improve silica dispersion and also rubber to silica interaction. The NR to silica interaction is physical crosslinking [8-9] and, together with sulfide crosslinking, surely have the contribution to totally crosslinking density [15-16].

3.3. 

Silica dispersion degree in the composite of NR (based on torque properties) can be calculated quantitatively using Equation (2) [7, 17].

\[ L = \eta_r - m_r \]  

In which: \( \eta_r \) is [\( T_{L_r} / T_{H_r} \)], and \( m_r \) is [\( T_{H_r} / T_{H_g} \)]; in which \( T_{L_r} \) and \( T_{H_r} \) are the minima and maxima torques of the composites and \( T_{L_g} \) and \( T_{H_g} \) are the minima and maxima torques of the gum NR. A higher L value, at a certain silica utilisation, means a lower silica dispersion degree. The minima and maxima torques of gum NR were 0.05 and 4.85, respectively.

Figure 5 shows the silica dispersion degree in NR matrix at various SA loading. As can be examined, the L values of silica-filled composites with SA were lower compared to silica-filled composite without SA. The higher the SA loading, the lower was the L value. It was due to the plasticizing effect of SA which reduced viscosity, improved the silica dispersion degree, respectively.
Figure 5. The effect of SA on the L value of NR composites

4. Conclusions
Utilisation of stearyl alcohol, a type of fatty alcohol, caused decreases in cure times and minimum torque and increases in scorch times of silica-filled natural rubber composites. The stearyl alcohol-fatty alcohol acted as both plasticising and curative agent. The higher the fatty alcohol concentration, a more pronounced was the acceleration of cure and plasticizing effects.
The stearyl alcohol-fatty alcohol caused increases in the torque difference up to the optimum concentration. A two parts per hundred rubber was the optimum concentration of stearyl alcohol-fatty alcohol for natural rubber composites which filled by silica.
The stearyl alcohol-fatty alcohol also caused improving in silica dispersion degree. Increases the fatty alcohol loading caused further increases in the silica dispersion degree.

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