Effects of lauryl alcohol addition on cure characteristics and tensile properties of silica-filled natural rubber composites

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Abstract. By using a semi-efficient vulcanisation system; the effects of the lauryl alcohol (LA) addition as a new rubber additive on cure characteristics and tensile properties of silica-filled natural rubber (NR) composites were investigated. The NR composite was filled with silica filler with a fixed loading, 30.0 phr. The LA is a fatty alcohol based on palm kernel oil and added into the silica-filled NR composites. The LA loadings were 1.0, 2.0, 3.0 and 4.0 phr. It was found that LA functioned as a co-curing (curative) and internal plasticiser. As a co-curing agent, LA increased the crosslink density and tensile strength up to 3.0 phr of loading. As an internal plasticiser, LA decreased the modulus tensile and increased elongations at break of silica-filled NR composites. The 3.0 phr of LA was the optimum loading.

1. Introduction
Generally, the definition of filler reinforcement is the improvement of mechanical properties, such as stiffness, tensile strength, tear and abrasion resistances of the rubber products resulting from the addition of filler. Fillers are usually used to enhance the mechanical properties of rubber vulcanisates such as tensile strength, resistance to abrasion, tearing and flexing or cheapen the cost of the product. Based on their reinforcement effect on rubber properties, fillers are divided into three groups: reinforcing, semi, and non-reinforcing fillers. Reinforcing filler improves tensile strength, modulus, resistance to abrasion, tearing and flexing. Non-reinforcing filler reduces the cost of a product and improves the processability.

Besides carbon blacks (CBs), silicas of varying forms and particles-sizes have been widely utilised as reinforcing fillers in rubber industry today. In general, the properties of silica-reinforced rubbers are usually inferior to those of carbon blacks, even when they are of comparable size (1). It is due to the surface properties of silica cause several difficulties in using it as reinforcing filler, particularly in hydrocarbon rubbers such as natural rubber (NR). The surface of silica is highly polar and hydrophilic as the presence of numerous silanol groups. These silanol groups relatively incompatible with NR, and interaction between them is weak. On the other hand, the silica particles tend to interact each other to form aggregates. Since the silica - NR interaction weaker than the silica-silica interaction; the results are the formation of large agglomerates, a poor degree of silica dispersion.

Numerous technologies have been done to improve the reactivity of silica with the NR phases. One of them is the silane-modified silica. This product shows significant improvement in performance
compared to its base material. 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.

An alternative method to solve the deficiency of silica was the utilisation of lauryl alcohol (LA). The LA is a material comes from palm oil kernel and it has the potential to be utilised as a plasticiser agent which solves the deficiency of silica. Physically, it is an oily material with both polar and non-polar functional groups. Oil is one type of plasticising agents (2-3) and hence, LA has the potential to lubricate, plasticise or soften the silica-filled NR composites and improve the degree of silica dispersion in the NR matrix. Therefore, this study reports the effects of LA addition on the cure characteristics and tensile properties of silica-filled NR composites.

2. Experimental

2.1. Materials

NR grade SIR 3L was obtained from PPTPN VII, Bandar Lampung, Indonesia; Sulphur was obtained from Miwon Commercial Co. Ltd, South Korea; Zinc oxide was obtained from P.T. Intancitra Logamindo, Medan, Indonesia; Stearic acid was obtained from P.T. Socimas, Medan, Indonesia; N-isopropyl-N’-phenyl-p-phenylenediamine (IPPD) was obtained from Jiangsu Sinorgchem Chemical Co. Ltd., China; Mercaptobenzothiazole disulfide (MBTS) was obtained from Shandong Sunshine Chemical Co. Ltd., China; Silica was obtained from P.T. JJ Degusha Hulls, Jakarta, Indonesia; and lauryl alcohol (LA) was obtained from P.T. Ecogreen Batam, Indonesia. The chemical formula of LA is \(\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OH}\).

2.2. Compounding

A semi-efficient vulcanisation system was used for the rubber compounding. The compounding procedure was done in accordance with the American Society for Testing and Material (ASTM) – Designation D 3184 – 80. The compounding was performed on a two-roll mill (Model XK-160). Table 1 displays the compound formulation of silica-filled NR composites with various LA loading.

| Ingredients | Content (phr)* |
|-------------|----------------|
| SIR-3       | 100.0          |
| Zinc oxide  | 5.0            |
| Stearic acid| 2.0            |
| IPPD        | 2.0            |
| MBTS        | 1.5            |
| Sulphur     | 1.5            |
| Silica      | 30.0           |
| LA          | 0.0; 1.0; 2.0; 3.0; 4.0 |

* parts per hundred rubber

2.3. Cure characteristics

The cure characteristics of the silica-filled NR composites with and without LA were obtained using a Monsanto Moving Die Rheometer (MDR 2000) which was employed to determine the scorch time \((t_{52})\), cure time \((t_{90})\), minimum torque \((M_L)\), maximum torque \((M_H)\) and torque difference \((M_H-M_L)\) according to ISO 3417. Samples of the respective compounds were tested at 150°C.

3. Results and discussion

3.1. Characterization of lauryl alcohol

Figure 1 shows the typical infrared spectrum of the LA. The strong broadband at 3320 cm\(^{-1}\) is an O–H stretch. Peak spectrum at 2920 cm\(^{-1}\) indicates C–H (refer to C–H stretching). Peak spectrum at 2851, 1123, 1055 and 720 cm\(^{-1}\) sequentially confirm the presence of a methyl group CH\(_3\) (refer to CH\(_3\)
symmetric), C–C (refer to C–C stretching), C–O and CH$_3$ (refer to CH$_3$ bending) (4). The spectrum clearly shows the presence of wavenumbers of the functional group of LA with molecular equation, CH$_3$(CH$_2$)$_{10}$CH$_2$OH.

![Figure 1](image.png)

**Figure 1.** The infrared spectrum of lauryl alcohol

### 3.2. The cure characteristics

The effects of LA addition on the cure characteristics of the silica-filled NR compounds are shown in Table 2. The cure characteristics were measured at 150 °C including scorch and cure times, minimum and maximum torques and torque differences.

As shown in Table 2, the scorch times of silica-filled NR compounds with LA were higher than those of without LA (control compounds). The higher the LA loading, the higher were the scorch times. The LA functioned as a scorch delay agent.

| Silica-filled NR composites          | 0.0 (Control) | 1.0 | 2.0 | 3.0 | 4.0 |
|-------------------------------------|---------------|-----|-----|-----|-----|
| t$_{95}$, min.                      | 1.65          | 1.64| 1.62| 1.57| 1.50|
| M$_H$, dN.m                         | 11.38         | 10.43| 10.61| 11.30| 9.70|
| M$_L$, dN.m                         | 2.74          | 2.33| 2.22| 2.15| 2.02|
| M$_H$–M$_L$, dN.m                   | 8.64          | 8.10| 8.39| 9.15| 7.68|

From Table 2, it can be seen that the addition of 1.0 phr of LA into the control compounds decreased the cure time. Lower cure time means higher cure rate and hence, a cure enhancement phenomenon was observed. It was attributed to the function of LA as a co-curing agent in the curing or curing process.

It was also can be seen that the higher the LA loading, the more pronounced the cure enhancement. It was simply attributed to a higher amount of hydroxyl groups in the silica-filled NR compounds.

As shown in Table 2, the additions of 1.0 phr of LA decreased the minimum torques (M$_L$) of control compounds. The M$_L$ value is used to measure the viscosity of a rubber compound (5-6). The lower the M$_L$ value, the lower is the viscosity. The addition of LA reduced the viscosity of the silica-filled NR compounds. This was attributed to the additional function of LA as an internal plasticiser.
which plasticised, softened and reduced the viscosity of the filled NR compounds, respectively. The higher the LA loading, the lower was the viscosity.

Table 2 also shows that the addition of 1.0 phr of LA increased the torque difference ($M_H - M_L$) values of control compounds. The torque difference was further increased with the addition of LA up to 3.0 phr and decreased beyond the loading. The torque difference indicates the degree of crosslink density of a rubber compound (7-8). The greater the value, the higher is the crosslink density. The increasing of torque difference or crosslink density up to the optimum loadings of LA (3.0 phr) was attributed to the chemical and physical properties of LA. The hydroxyl groups of LA activated chemically not only the rubber but also the elemental sulphur during sulphuration or curing reaction. Together with the others curatives, hydroxyl groups could form intermediate complexes which attached the available elemental sulphur to rubber chains more efficient (9-12), causing a higher degree of cure.

Physically, LA is an oily material and has the function as an internal plasticiser agent. As discussed earlier, LA decreased the viscosity of the silica-filled NR compounds. It improved the silica-dispersion and rubber-filler interaction/bond, respectively. The rubber-filler bond is defined as additional physical crosslinks (8), and together with sulphide crosslinks contribute to total crosslink density of a rubber vulcanisate (8, 10).

The decrease of the torque differences, beyond the optimum loading, was most probably due to the dilution effect of the excessive amounts of LA which formed some oily layers. These layers might absorb a part of silica filler and other curatives and coated them together. By this mechanism, the total crosslink density was decreased.

3.3. The tensile properties

The effects of LA on tensile properties of silica-filled NR composites are shown in Table 3. It can be seen that LA decreased the M100 and M300. The higher the LA loading, the lower were the M100 and M300. LA produced silica-filled NR composites with lower tensile modulus. It was due to the function of silica as an internal plasticiser.

It also can be seen that TS increased slightly up to optimum LA loading (3.0 phr) and then decreased with further increasing the LA loading. The enhancement in TS, up to 3.0 phr LA loading, might be due to the improvement of silica dispersion in NR phase and a higher degree of crosslink density due to the presence of LA. The deterioration of TS beyond a 3.0 phr loading was most probably due to the curative absorbing effect of the excessive LA, which caused a lower in crosslink density.

The addition of a 1.0 phr of LA into a silica-filled NR composite produced a silica plus LA-filled NR composite with a higher EB. Increasing the ALK loading caused further increases the percentage of EB. Again, it was due to the function of LA as an internal plasticiser to the silica-filled NR composite. Plasticiser is a compounding material used to enhance the deformability of a polymeric compound, and one of the sources from which it is made is natural oil/fat (2-3). However, the LA is oily and originated from kernel palm oil, a type of natural oil. Increasing the LA loading has the same effect as an increase in the amount of plasticiser in the NR composites that will enhance the deformability by increasing the extensibility of the silica-filled NR composite.

| Table 3. Tensile properties of silica-filled NR composites at various LA loadings |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| Silica-filled NR composites     | 0.0 (Control)   | 1.0             | 2.0             | 3.0             | 4.0             |
| M100, MPa                       | 0.79            | 0.74            | 0.70            | 0.67            | 0.64            |
| M300, MPa                       | 2.22            | 1.94            | 1.90            | 1.86            | 1.72            |
| TS, MPa                         | 15.5            | 17.0            | 17.4            | 19.1            | 16.7            |
| EB, %                           | 685.0           | 737.5           | 775.0           | 780.0           | 810.0           |
4. Conclusions
From this study, the following conclusions were drawn:
1. Lauryl alcohol can be function as a co-curing agent and internal plasticiser in silica-filled natural rubber composites. It increased the scorch time and decreased cure time and minimum torque of the silica-filled natural rubber composites. The higher the loading, the more pronounced the cure-acceleration and plasticising effects.
2. Lauryl alcohol decreased the tensile modulus of the silica-filled natural rubber composites. The higher the loading, the lower were the tensile modulus at 100% and 300% elongations.
3. Lauryl alcohol increased the torque difference and tensile strength of the silica-filled natural rubber composites up to the optimum loading. A 3.0 phr was the optimum loading of lauryl alcohol for silica-filled natural rubber composites.
4. Lauryl alcohol also increased the elongations at break. Increasing the lauryl alcohol loading further increased the elongations at break.

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