Improvements in filler dispersion and tensile properties of natural rubber vulcanizates applying lauryl alcohol

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Abstract. Lauryl alcohol as one type of fatty alcohols was used to raise degree of silica filler dispersion and also tensile properties of silica filled natural rubber (NR) applying a system of semi efficient vulcanization. The NR was reinforced by silica filler with a settled loading at thirty phr. The lauryl alcohol was incorporated into the silica filled NR at one, two, three and four phr. The results showed that lauryl alcohol expanded the time to scorch but reduced time to cure and minimum torque. Lauryl alcohol also reduced tensile modulus but expanded elongation at break. The other properties such as crosslink density, torque difference and tensile strength were expanded up to three phr of lauryl alcohol. The swelling properties confirmed that three phr of lauryl alcohol was an optimum concentration where silica filled NR vulcanizate with three phr of lauryl alcohol showed the highest tensile strength. As a plasticizing agent, lauryl alcohol expanded tensile strength by increasing the degree of silica dispersion.

1. Introduction

By definition, rubber reinforcement is the growth of mechanical properties like modulus, abrasion resistance, tear/tensile strengths of a vulcanizate as the impact of reinforcing filler addition [1,2]. Likewise, carbon blacks (CBs), silicas with particles-sizes and varying forms have been widely applied as reinforcing fillers in reinforcement of rubber. Usually, mechanical properties of silica vulcanizates are inferior to those of CBs, although both of them have similar sizes [3]. It is because of the surface properties of silica offer some obstacles in applying it as the reinforcing filler, especially within non polar natural rubber (NR).

Polarity of silica filler is very high because of existence of many silanol groups. Those silanol groups are less compatible to NR and hence, the rubber to filler interaction is weak. Differently, between silica particles has the trend to connect with every other and build some bigger aggregates of filler. Because of filler to rubber interaction is weaker than that of filler to filler interaction; the results are the forming of larger agglomerate, poorer degree of silica dispersion and deterioration in mechanical properties.
A lot of methods have been offered to increase susceptibility of silica to matrix of NR. The conventional one was the silane modified silica [4]. It demonstrates a compelling improvement in achievement compared to its basic form. For much utilization, it has been offered as an alternative to a lower reinforcing effect of CBs. Yet, in factual utilization, the achievement of silane modified silica has not been determined; expensive cost of the additive is a detriment.

One different method was offered to clarify the problem of low degree of silica dispersion applying lauryl alcohol. The lauryl alcohol was a rubber chemical whatever derived based on palm kernel oil. It is an oily chemical and oil is one type of plasticizers [5,6] that can develop degree of filler dispersion of a vulcanizate. Therefore, this study describes the developments in degree of silica dispersion and properties of tensile of silica filled NR vulcanizates applying lauryl alcohol. The effects of lauryl alcohol on degree of silica dispersion, curing and tensile properties of silica filled NR vulcanizates were investigated.

2. Chemicals and methodology

2.1. Chemicals

SIR 3L of NR grade and other rubber chemicals like sulphur, ZnO, IPPD, MBTS, precipitated silica were prepared by PT. Industri Karet Deli, Indonesia. Lauryl alcohol was procured by PT. Ecogreen Batam, Indonesia. Lauryl alcohol is CH\(_3\)(CH\(_2\))\(_{10}\)CH\(_2\)OH.

2.2. Rubber compounding

The NR and other compounds ingredients were compounded based on a semi-EV cure system. The sequences of rubber compounding were done based on ASTM D3184-80 on a lab-type 2-roll mill. Table 1 presents the compound recipe for rubber compounding.

| Chemicals       | Content (phr.) |
|-----------------|---------------|
| SIR 3L          | 100           |
| MBTS            | 1.5           |
| IPPD            | 2             |
| Stearic acid    | 2             |
| S               | 1.5           |
| ZnO             | 5             |
| Lauryl alcohol  | 0; 1; 2; 3 and 4 |
| Silica          | 30            |

2.3. Curing properties

The NR curing properties include (ts\(_2\), scorch time), (ts\(_0\), cure time), max. torque (Mx), min. torque (Mn), difference in torque (Mx - Mn) (based on ISO 3417) were delivered by the use of a Rheometer (MDR 2000). The compounds/samples of NR were cured at 150°C.

2.4. Tensile properties

Tensile properties include (TS, tensile strength), (M300/M100, tensile moduli) and (EB, elongation at break) of NR vulcanizates were determined using a tensometer (Instron-3366) based on ASTM D-882.
3. Results and discussion

3.1. Curing properties

The effect of lauryl alcohol additions on curing properties of silica filled NR vulcanizates is demonstrated in Table 2. The time to scorch of vulcanizate without lauryl alcohol was lower. The higher the lauryl alcohol concentration, the higher times to scorch was. At this point, lauryl alcohol was a curative additive and function as a scorch delay additive.

| NR vulcanizate | Lauryl alcohol (phr) |
|----------------|----------------------|
|                | 0        | 1        | 2        | 3        | 4        |
| Time to scorch, min. | 0.72     | 0.73     | 0.74     | 0.79     | 0.81     |
| Time to cure, min.    | 1.65     | 1.64     | 1.62     | 1.57     | 1.50     |
| Maxim. torque, dN.m   | 11.38    | 10.43    | 10.61    | 11.30    | 9.70     |
| Minim. torque, dN.m   | 2.74     | 2.33     | 2.22     | 2.15     | 2.02     |
| Difference torque, dN.m| 8.64    | 8.10     | 8.39     | 9.15     | 7.68     |

As demonstrated in Table 2, the incorporation of one phr of lauryl alcohol shortened the time to cure. The additive lauryl alcohol caused by curing enhancement. It was because of its function as a curative rubber chemical in vulcanization process. The higher lauryl alcohol loading, the higher the cure rate was.

The one phr addition of lauryl alcohol reduced minimum torque whatever expresses viscosity of a vulcanizate [7,8]. The higher the value, the higher viscosity is. Lauryl alcohol decreased the viscosity of vulcanizates. It was because of supplementary usage of lauryl alcohol as a plasticizing chemical which reduced viscosity of the vulcanizates. The higher lauryl alcohol content, the lower viscosity was.

The addition of one phr of lauryl alcohol raised torque difference of reference vulcanizate. The torque difference was further raised with the incorporation of lauryl alcohol up to a three phr and reduced after the concentration. Torque difference expresses the degree of crosslink density of a vulcanizate [9,10]. The lower the value, the lower degree of crosslink density is. The raises of crosslink density up to the three phr of lauryl alcohol were because of its chemical and physical properties. Presumably, its hydroxyl groups stimulated chemically both the NR and elemental sulfur at the same time as vulcanization. Those hydroxyl groups and curatives created intermediate complexes whatever linked available elemental sulfur to NR more effectively [11-14], causing a higher state of curing.

Substantially, lauryl alcohol is an oily chemical and has competence as an internal plasticizer. From the past discussion, lauryl alcohol diminished viscosity of vulcanizates. It could improve degree of silica dispersion and silica to NR interaction, commonly. The silica to NR interaction is characterized as supplementary physical crosslinks. These types of crosslinks with sulphide crosslinks give total crosslink density of a vulcanizate [12,13].

The drop in torque difference, after the three phr of lauryl alcohol, was because of the dilution consequence of more amount of lauryl alcohol whatever created some oily layers. These layers absorbed silica and curatives and kept them together. Through formation of the system, total crosslink density was diminished.

3.2. The degree of filler dispersion

Based on its curing properties, degree of silica dispersion in NR compounds was counted applying Equation (1) [9,10,13,15].

\[ L = \eta r - m r \]  

(1)
where: \( \eta_r = \frac{\text{ML}_f}{\text{ML}_g} \), and \( m_r = \frac{\text{MH}_f}{\text{MH}_g} \); where \( \text{ML}_f \) and \( \text{MH}_f \) were minimum and maximum torques of filled vulcanizate and \( \text{ML}_g \) and \( \text{MH}_g \) was minimum and the maximum torques of the unfilled vulcanizate. A lower value of \( L \), at certain silica, means a better silica dispersion [15]. As determined previously, minimum and maximum torques of unfilled vulcanizate were 0.05 and 4.85, commonly.

Figure 1. visualizes degree of silica dispersion at various lauryl alcohol concentrations. As visualized, the \( L \) values of NR vulcanizates with lauryl alcohol were lower compared to NR composite with no lauryl alcohol. It was because of the lauryl alcohol plasticization effect which diminished viscosity and hence, raised the degree of silica dispersion.

![Graph showing L values vs lauryl alcohol (phr)](image)

**Figure 1.** Effects of lauryl alcohol on \( L \) values of NR vulcanizates

### 3.3. The tensile properties

Effects of lauryl alcohol on tensile properties of silica filled NR vulcanizates are demonstrated in Table 3. Lauryl alcohol reduced tensile moduli (\( \text{M}_{100} \) and \( \text{M}_{300} \)). The higher lauryl alcohol, the lower the tensile moduli were. Lauryl alcohol caused in silica filled NR vulcanizates with a lower tensile modulus. It was because of the function of lauryl alcohol as the internal plasticizing chemical.

The tensile strength (TS) raised slightly up to three phr of lauryl alcohol and then reduced with a further increase in lauryl alcohol loading. The enhancement in TS was because of improvements in degrees of dispersion and crosslink density. The drop in TS above a three phr of lauryl alcohol was because of curative absorbing the consequence of more amount of lauryl alcohol whatever diminished crosslink density.

The one phr of lauryl alcohol raised percentage of elongation at break (EB) and higher lauryl alcohol caused in a further increase in EB percentage. Once again, it was because of the action of lauryl alcohol as an internal plasticizing chemical. Plasticizing material is a rubber chemical applied to level up durability of a vulcanizate and one of the sources of plasticizer natural fat/oil [5,6]. Its oily properties raised elasticity of silica filled NR vulcanizates.
Table 3. Tensile properties of NR vulcanizates

| NR vulcanizate | Lauryl alcohol (phr) | 0     | 1     | 2     | 3     | 4     |
|----------------|----------------------|-------|-------|-------|-------|-------|
| M300, Mega Pascal |                      | 2.22  | 1.94  | 1.90  | 1.86  | 1.72  |
| M100, Mega Pascal |                      | 0.79  | 0.74  | 0.70  | 0.67  | 0.64  |
| TS, Mega Pascal |                      | 15.5  | 17.0  | 17.4  | 19.1  | 16.7  |
| EB, Percent |                      | 685.0 | 737.5 | 775.0 | 780.0 | 810.0 |

4. Conclusion
From the discussion, some conclusions were compiled:
1. Lauryl alcohol was a co-curing rubber chemical for silica filled natural rubber vulcanizates. It raised time to scorch but reduced time to cure and minimum torque. The higher the concentration, the faster was cure rate.
2. Lauryl alcohol was an internal plasticizer for silica filled natural rubber vulcanizates. It reduced tensile modulus but raised elongations at break and degree of silica dispersion. The higher the loading, the more significant was plasticizing effect.
3. Lauryl alcohol raised torque difference and tensile strength of silica filled natural rubber vulcanizates up to a three phr of concentration.
4. The three phr was the optimum loading of lauryl alcohol for silica filled natural rubber vulcanizates.

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