The properties of unfilled natural rubber in the existence of alkanolamide: rheological and crosslink density properties

I Surya* and Philbert

Engineering Faculty, Universitas Sumatera Utara, Medan, Indonesia

*E-mail: indradanas@yahoo.com, isurya@usu.ac.id

Abstract. Using a semi-efficient vulcanization system; a study was carried out on the utilization of alkanolamide as a curative additive in natural rubber (NR) compounds. The alkanolamide was incorporated into the unfilled-NR compound at 0.2, 0.4, 0.6, 0.8, and 1.0 phr. The effect of alkanolamide on rheological and crosslink density properties of the NR compounds were observed. It was found that the addition of the alkanolamide exhibited shorter scorch and cure times and higher elongation at break of the NR compounds. The alkanolamide also exhibited higher torque differences and crosslink density of up to 0.6 phr of alkanolamide loading and then decreased with further increases in the alkanolamide loading.

1. Introduction

In the rubber industry, rubber compounders’ daily activities are believed performing the science & art of rubber technology. They determine useful rubbers recipes or rubber formulations by selecting raw rubbers, chemicals and also their appropriate quantities. The rubbers recipes are process able, fulfill or exceed the customer’s needs and wants in rubber products, and of course must be competitively priced [1].

Rubbers recipes are considered as heart of compounding that has a combination of raw rubber - rubber chemicals. Rubber chemicals are curative and non-curative ones. The curative chemicals are agents of vulcanizing such as zinc oxide, sulphur, accelerators and stearic acid.

Several researchers have investigated on curative chemicals; Coran investigated on effect of stearic acid on natural rubber or NR [2] [3] and found; specific rate of curing process was reduced if stearic acid concentration was increased. Poh & Tang reported; time to scorch raised with content of stearic acid for all studied rubbers [4]. Hart & Barton reported; modulus was improved as content of lauric acid increases. The lauric acid addition also raised physical properties of the vulcanizates [5]. Ruhaizat & Ismail; palm oil fatty acid concentration affected both cure and mechanical properties of calcium carbonate filled NR and unfilled NR [6] [7].

Based on our knowledge; there were no efforts have been done so far to use alkanolamide as curative chemical in compounds of unfilled NR. The alkanolamide synthesized from waste of cooking oil production and diethanolamine and hence, this study was aimed to investigate on the effects of alkanolamide on rheological and crosslinks properties of compounds of unfilled or gum NR.
2. Methodology

2.1. Raw rubber and rubber chemicals
NR (SMR 3) and other rubber chemicals such as N-isopropyl-N’-phenyl-p-phenylenediamine or IPPD, sulphur, mercaptobenzothiazolyl disulfide, zinc oxide and stearic acid were supplied by rubber Lab of Engineering Campus of Universiti Sains Malaysia, Malaysia. The alkanolamide was lab-prepared.

2.2. Rubber mixing
A semi-efficient recipe/system, as presented in Table 1, was applied in the rubber mixing process. All of the mixing procedures were done to follow the ASTM D 3184/80. The process of rubber mixing was conducted on a lab scaled of 2 roll mill and, Table 2 tabulates designation of the NR systems used in this observation.

| Table 1. The system of NR. |
|---------------------------|
| Rubber/chemicals | Amount (parts per hundred rubber/phr) |
| SMR 3 | 100 |
| Zinc oxide | 5 |
| Sulphur | 1.5 |
| mercaptobenzothiazolyl disulfide | 1.5 |
| Silica | 30 |
| IPPD | 2 |
| Stearic acid | 2 |
| Alkanolamide | 0.2 to 1.0 |

| Table 2. Designation of NR systems. |
|---------------------------|
| Designation | Composition | Unfilled NR/alkanolamide |
| A/0.0-Control | Unfilled NR | 100/0.0 |
| B/0.2 | Unfilled NR/Alkanolamide | 100/0.2 |
| C/0.4 | Unfilled NR/Alkanolamide | 100/0.4 |
| D/0.6 | Unfilled NR/Alkanolamide | 100/0.6 |
| E/0.8 | Unfilled NR/Alkanolamide | 100/0.8 |
| F/1.0 | Unfilled NR/Alkanolamide | 100/1.0 |

2.3. Rheological properties
The rheological properties of NR samples were collected utilizing an MDR 2000/Monsanto Moving Die Rheometer at 150°C. The $t_{52}$ as time to scorch, $t_{90}$ as optimum time to cure, $M_{\text{min}}$ as minimum torque, $M_{\text{max}}$ as maximum torque and $M_{\text{max}} - M_{\text{min}}$ as torque difference was determined according to ISO 3417.

2.4. Calculating of crosslinks density
The swelling method was applied to calculating NR vulcanizates crosslinks density. The cured test samples with dimension 30 mm × 5 mm × 2 mm were swollen in toluene until equilibrium for three days at room temperature. The samples were taken out from toluene and weights were determined. Then, the samples were dried in an oven at 70 °C till the constant weights were reached. The results of swelling were applied in calculating the molecular weight between 2 crosslinks ($M_c$) by using the Equation of Flory-Rehner [8].

$$M_c = \frac{-\rho_p V_s V_r^{1/3}}{\ln(1-V_r) + V_r + \chi V_r^2}$$ (1)
In which; the density of the NR ($\rho_p = 0.92\ g\cdot cm^{-3}$), the toluene molar volume $V_s = 106.4\ cm^3\cdot mol^{-1}$, $V_r$ is NR volume fraction in swollen specimen. $Q_m$ is increment weight of the samples in toluene and $\chi$ is parameter of rubber network-solvent interaction ($\chi$ of NR = 0.393). The level of crosslinks density is given by:

$$V_r = \frac{1}{1 + Q_m}$$  \hspace{1cm} (2)

$$V_C = \frac{1}{2M_C}$$  \hspace{1cm} (3)

3. Results and discussion

3.1. Effects of alkanolamide on rheological

The effects of alkanolamide on rheological properties of compounds of unfilled-NR can be observed in Figures 1 and 2. Figure 1 presents that times to scorch and cure were reduced with raising alkanolamide concentration. It was a cure rate improvement, indicating that alkanolamide was a co-curing chemical for compounds of unfilled-NR. The cure improvement was because of the amine of alkanolamide. Amine is an alkaline chemical that turns rubber compound more basic and improves cure rate since acidic material tends to retard the accelerator [9]. Increasing the concentration of alkanolamide is increasing the amine amount and hence, the bigger the concentration of alkanolamide, the higher the cure rate.

Bateman [10] and Ismail & Ng [11] reported that an appropriate organic chemical with atom of nitrogen would accelerate the process of curing and was responsible for enhancing cure states and rate of rubber compound.

As shown in Figure 2, the alkanolamide additions of up to 0.6 phr increased values of maximum torque minus minimum torque ($T_{max} - T_{min}$). Further increases in alkanolamide concentration reduced the ($T_{max} - T_{min}$) values. Theoretically, the values of ($T_{max} - T_{min}$) represent crosslinks density of a rubber

![Figure 1. The $t_2$ & $t_{90}$ vs alkanolamide concentration.](image-url)
compound [12] [13]. The alkanolamide additions into unfilled-NR compound affected the value of (T\text{max}-T\text{min}) or crosslinks density. The affection was because of the alkanolamide action as an extra accelerator during the process of cure. Even tough an accelerator always constitutes a very little amount of a rubber compound; it has a significant effect on nature of crosslinks.

\textbf{Figure 2}. The (T\text{max} – T\text{min}) of the unfilled-NR compounds at various alkanolamide loadings.

3.2. Effects of alkanolamide on crosslinks density
The crosslinks density of the vulcanizates of unfilled-NR was determined by Equation (1). Figure. 3 visualizes that the alkanolamide additions increased crosslinks density up to maximum value at 0.6 phr and then, reduced with further raises alkanolamide concentration. This result agreed with the result of (T\text{max} – T\text{min}). The enhancements in crosslink density up to 0.6 phr of alkanolmide were because of the action of alkanolamide as an extra accelerator. Based on Ignatz-Hoover & To, atoms of nitrogen can act as a hydrogen acceptor and amine activates elemental sulphur and/or rubber for the reaction of crosslinking.
Figure 3. The crosslinks density vs alkanolamide concentration.

The crosslinks density reduction after 0.6 phr loading, was due to the lubricating effect of the more amount of alkanolamide which reduced crosslinks density. It was a phenomenon of dissolving of elemental sulphur partly and hence, less sulphur was attached to NR chains.

4. Conclusions
Alkanolamide was a curative chemical for compounds of unfilled-natural rubber. It acted as an extra accelerator and a plasticizer for compounds of unfilled natural rubber. The alkanolamide incorporations raised cure state and rate and also elongations at break but diminished scorch time. The alkanolamide incorporations also raised crosslinks density of vulcanizates of unfilled natural rubber specially up to the 0.6 phr.

Acknowledgement
Many thanks to the rubber lab of Universiti Sains Malaysia for performing research activities.

References
[1] Dick J S, Annicelli R A 2001 Rubber technology, Compounding and testing for performance, Hanser Gardner Publications p 1
[2] Coran A 1964 Rubber Chem Technol 37 (3) 679-88
[3] Coran A 1965 Rubber Chem Technol 38 (1) 1-14
[4] Poh B, Tang W 1995 J appl Polym Sci 55 (3) 537-42
[5] Barton B C, Hart E J 1953 Rubber Chem Technol 26 (3) 510-21
[6] Ismail H, Ruhaizat T 1998 POLYM-PLAST TECHNOL ENG 37 (4) 483-94
[7] Ismail H, Ruhaizat T A 1997 Iran Polym J 6 97-104
[8] Flory P J, Rehner J Jr 1943 J Chem Phys 11 521
[9] Ismail H, Ng C 1998 *Journal of Elastomers and Plastics* 30 (4) 308-27
[10] Surya I and Ismail H 2019 IOP Conf. Ser. Mater. Sci. Eng. 523 012063
[11] Surya I and Siswarni M Z 2019 *IOP Conf. Ser. Mater. Sci. Eng.* 505 012113
[12] Long H 1985 Basic Compounding and Processing of Rubber, Rubber Division American Chemical Society Inc. The University of Akron, Ohio, USA
[13] Rodgers B 2004 Rubber Compounding, Chemistry and Applications, CRC