The properties of unfilled natural rubber in the existence of alkanolamide: swelling, mechanical and morphological properties

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Abstract. A study was carried out on the utilization of alkanolamide as a new curative additive in natural rubber (NR) compounds by using a semi-efficient vulcanization system. The alkanolamide was derived from the waste of cooking oil and incorporated into the unfilled-NR compound at 0.2, 0.4, 0.6, 0.8, and 1.0 phr. The effect of alkanolamide on swelling percentage, mechanical and morphological properties of the NR compounds were observed. It was found that the addition of the alkanolamide increased elongation at break of the NR compounds. The alkanolamide also increased tensile modulus, tensile strength, hardness and crosslink density of up to 0.6 phr of alkanolamide loading and then decreased with further increases in the alkanolamide loading. Scanning electron microscopy (SEM) micrographs proved that 0.6 phr loading of alkanolamide in the NR compounds exhibited the greatest matrix tearing line and surface roughness which correlated to a higher tensile strength of the NR compounds.

1. Introduction

The main jobs of rubber compounders include performing science and art of technology of rubber and also determining applicable rubber formulations by choosing rubbers and chemicals with their appropriate amounts. The rubber formulation should be processable, offer customer’s needs and wants in rubber articles and of course, should be competitive in price [1].

Rubber formulation is heart of rubber mixing that has a type of raw rubber and chemicals. Rubber chemicals can or cannot affect the rheological properties of compounds of rubber. A lot of investigations on rubber chemicals have published by several researchers. Ismail and Ruhaizat published that fatty acid influenced both mechanical and rheological properties of gum and CaCO$_3$-filled NR vulcanizates [2] [3]. The salt of diamine and fatty acid could also be used as a rubber chemical for compounds of filled NR. The salt improved rheological and mechanical properties of compounds of NR which filled by silica and white rice husk ash [4].

In our knowledge, there are no researches have been performed so far to utilize alkanolamide as a rubber chemical in NR compounds. The additive ingredient is prepared from diethanolamine and stearin. This article describes the study on the utilization of alkanolamide as a rubber chemical for compounds of unfilled-natural rubber (NR). Effect of alkanolamide concentration on properties of swelling, mechanical and morphological of compounds of unfilled-NR was reported.
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 systems of NR used in the observation.

| 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 |
|-------------|----------------------------------|--------------------------|
| A0.0-Control| Unfilled NR                      | 100/0.0                  |
| B0.2        | Unfilled NR/Alkanolamide         | 100/0.2                  |
| C0.4        | Unfilled NR/Alkanolamide         | 100/0.4                  |
| D0.6        | Unfilled NR/Alkanolamide         | 100/0.6                  |
| E0.8        | Unfilled NR/Alkanolamide         | 100/0.8                  |
| F1.0        | Unfilled NR/Alkanolamide         | 100/1                    |

2.3. Determining optimum cure time
The cure time of compounds of NR was determined by applying a Monsanto Moving Die Rheometer.

2.4. Compression molding
The NR samples were vulcanized at 150 ºC with the respective optimum cure time applying a hot press. The samples with 2 mm thickness sheets were molded.

2.5. The swelling properties
Swelling behaviours were determined in toluene, based on ISO 1817. The (30 mmx5 mmx2 mm) samples were weighed and swollen in toluene for 72 h at room temperature. The samples were removed from toluene and the weights were determined. The percentage of swelling:

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

In which, \(W_1\) is the beginning mass (g) and \(W_2\) is the swollen mass (g).
2.6. Hardness and tensile properties
Properties of hardness of unfilled-NR vulcanizates were determined based on ASTM D 2240 applying Durometer Shore A. Unfilled-NR samples with dumbbell-formed (ISO 37) were tested to know tensile properties include tensile moduli (M300/M100), tensile strength (TS) and also elongation at break (EB). The tests were conducted on a universal tensile machine (Instron3366) with a five hundred (mm.min\(^{-1}\)) of crosshead speed.

2.7. Morphological properties
The surfaces of tensile fractured of unfilled-NR vulcanizates were observed by applying a Zeiss Supra-35VP SEM. The surfaces were covered by gold to protect electrostatic charging during tests.

3. Results and discussion
3.1. The swelling properties
The influence of alkanolamide loadings on percentage of swelling of unfilled-NR is visualized in Fig. 1. Percentage of swelling relates to crosslink density of a compound of rubber [5] [6] [7] [8]. A less toluene penetration into rubber compound sample indicates a greater degree of crosslinks.

![Swelling percentage vs alkanolamide concentration.](image)

Figure 1. The swelling percentage vs alkanolamide concentration.

As seen in Figure. 1; the incorporations of alkanolamide from 0.2 to 0.6 phr. caused in decreasing the swelling percentage or increasing crosslink density of control NR compound. The further additions of alkanolamide after the 0.6 started to increase the swelling percentage or reduce crosslinks level.

The reducing in crosslinks level was because of the curative effect of alkanolamide which improved crosslinks level. The decreases in crosslinks level might be due to the excessive loading of alkanolamide which isolated the curatives from the NR and deteriorated crosslink density.
3.2. The hardness and tensile properties

The influences of alkanolamide incorporations on properties of tensile/hardness of unfilled NR vulcanizates are visualized in Figures 2-5. As visualized in Figure 2, the incorporation of 0.2 phr alkanolamide into unfilled-NR system produced vulcanizate B/0.2 with longer elongation at break.

![Figure 2. The EB vs alkanolamide concentration.](image)

Increases alkanolamide concentration affected further increases in percentage of elongation at break. It was because of the action of alkanolamide as a plasticizing agent which is a compounding ingredient used to improve rubber compound processing, modify hardness and flexibility of rubber vulcanizate [9] and, one of the sources from which it is produced is natural oil [10]. Because of its waxy properties, it would provide free volumes which allowing NR chains to move freely. Increasing alkanolamide concentration affected increases in free volumes that increases the flexibility of vulcanizates of unfilled NR.
Figure 3. The tensile modulus vs alkanolamide concentration.

From Figure 3, the alkanolamide incorporations increased the tensile moduli slightly up to the highest value at 0.6 phr and then reduced with further increases in concentration of alkanolamide. Results of hardness and tensile strength also exhibited similar trends (Figures 4 and 5). The tensile moduli are typical measures hardness or stiffness of a vulcanizate [11] [12].

Figure 4. The TS vs alkanolamide concentration.
Figure 5. The hardness alkanolamide concentration.

According to Ismail & Chia [13] tensile moduli and tensile properties depend only on level of crosslinks. The improvements in tensile moduli and strength and also hardness up to 0.6 phr of alkanolamide were because of the higher level of crosslinks (Figure. 1). The deteriorations in those properties after 0.6 phr was because of the lower level of crosslinks and the more significant the affections of softening and plasticizing of alkanolamide.

3.3. The morphological properties
Figure. 6 provides the SEM micrographs of surfaces of tensile fractured of the control compound, A-0.0 [Figure. 6A], and the unfilled-NR compounds with 0.4, 0.6, and 0.8 phr of alkanolamide. The surfaces of C-0.4 and D-0.6 showed a lot of larger discontinuous slip tear lines with path deviation than surface of A-0.0. It meant; higher energy was needed for failure. The surface of E-0.8 exhibited the least surface roughness and matrix tearing that presumably related to the presence of the more amount of alkanolamide in vulcanizate of E-0.8.
Figure 6. SEM micrographs of surfaces of tensile fractured of vulcanizates of unfilled-NR with the magnification of 200X; [A] A-0.0, [B] C-0.4, [C] D-0.6 and [D] E-0.8.

4. Conclusions
Alkanolamide was a curative rubber chemical for compounds of unfilled natural rubber. It has increased elongations at break. The hardness and tensile properties were also increased especially up to 0.6 phr of alkanolamide concentration.

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