The effect of alkanolamide addition on cure and tensile properties of unfilled natural rubber compounds

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Abstract. Effect of alkanolamide (ALK) addition on cure and tensile properties of unfilled natural rubber (NR) compounds was investigated. The ALK was synthesized from Refined Bleached Deodorized Palm Stearin (RBDPS) and diethanolamine, and incorporated into the unfilled-NR compound as a new rubber additive. The ALK loadings were 0.2, 0.4, 0.6, 0.8, and 1.0 phr. It was found that the addition of ALK exhibited shorter scorch and cure times and higher elongation at break of the unfilled NR compounds. The ALK also exhibited higher torque differences, tensile modulus and tensile strength of up to 0.6 phr of ALK loading and then decreased with further increases in the ALK loading. Scanning electron microscopy (SEM) proved that 0.6 phr loading of ALK in the NR compounds exhibited the greatest matrix tearing line and surface roughness which correlated to a higher tensile strength of the NR compound.

1. Introduction

In rubber technology, rubber recipe is the heart of rubber compounding which contains a group of base rubber and rubber additives [1]. Each of them has a specific function either in processing, curing, or end use of the rubber products. Rubber or blend of rubbers will provide rubbery behavior to the compound; rubber additives such as fillers can cheapen the cost of rubber products, modify modulus and processing properties; plasticisers are used to reduce viscosity, enhance deformability and alter properties; vulcanizing agents can crosslink the rubber chains; and accelerators are something that improve the action of vulcanizing agents to speed up the resultant crosslinking.

Rubber additives are classified into curative and non-curative additives. Curative additives play an important role in determining the cure characteristics of rubber compounds. They affect the rate and nature of the vulcanization process. In rubber technology, the popular curative additives are sulphur or other vulcanizing agents, zinc oxide, stearic acid and accelerators.

A lot of studies on curative additives have been reported by some researchers. Coran studied on concentration effect of stearic acid, a palm oil fatty acid, on NR [2-3]. He found that the specific rate of vulcanization is decreased if the concentration of stearic acid is increased. Poh and Tang reported that the scorch time increases with the stearic acid content for all the rubbers investigated [4]. Barton and Hart reported that modulus values improve as the lauric acid content increases. The addition of lauric acid also improved the physical properties of the vulcanisates [5]. Ismail and Ruhaizat reported...
that the concentration of palm oil fatty acid affected not only the curing characteristics and but also the mechanical properties of the unfilled and calcium carbonate filled NR compounds [6-7]. The diamine salt of fatty acid, referred to as a multifunctional additive (MFA), can also be utilised as curative additive in filled NR compounds. The MFA improved the cure characteristics and mechanical properties of the silica-filled NR compounds [8] and white rice husk ash-filled NR compounds [9].

In this study, the effect of the addition of Alkanolamide (ALK) on the cure and tensile properties of the unfilled-NR compounds was investigated. The ALK is considered as a relatively new rubber additive, and it was prepared from Refined Bleached Deodorized Palm Stearin (RBDPS) and ethanolamine. Compared to others, this additive has unique nature of molecule which is structured by the combination of hydrophobic long chain hydrocarbon and hydrophilic amide as visualized in Figure 1.

2. Experimental Method

2.1. Materials

NR grade SMR L was used and obtained from Guthrie (M) Sdn. Bhd., Seremban, Malaysia. Other compounding ingredients such as sulphur, zinc oxide, stearic acid, N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD) and Mercapto Benzothiazolyl disulfide (MBTS) were supplied by Bayer (M) Ltd., Sdn. Bhd., Petaling Jaya, Selangor, Malaysia. All materials were used as supplied. The ALK was synthesized in laboratory using Refined Bleached Deodorized Palm Stearin (RBDPS) and diethanolamine. Its molecular structure is shown in Figure 1.

![Figure 1. The molecular structure of alkanolamide](image)

2.2. Compounding

A semi-efficient vulcanization system was used for the compounding. The recipe for the preparation of the NR compound is given in Table 1.

| Ingredients     | Content (phr)* |
|-----------------|-----------------|
| NR (SMR L)      | 100.0           |
| Zinc oxide      | 5.0             |
| Stearic acid    | 2.0             |
| IPPD            | 2.0             |
| MBTS            | 1.5             |
| Sulphur         | 1.5             |
| ALK             | 0.0; 0.2; 0.4; 0.6; 0.8; 1.0 |

*parts per hundred parts of rubber
The compounding procedure was done in accordance with the American Society for Testing and Material (ASTM) – Designation D 3184 – 80. The compounding was done on a two-roll mill. Table 2 shows the designation and composition of the NR-based recipes used in this study.

| Designation | Composition     | Unfilled NR/ALK (phr) |
|-------------|----------------|-----------------------|
| A/0.0 (Control) | Unfilled NR    | 100/0.0               |
| B/0.2       | Unfilled NR/ALK | 100/0.2              |
| C/0.4       | Unfilled NR/ALK | 100/0.4              |
| D/0.6       | Unfilled NR/ALK | 100/0.6              |
| E/0.8       | Unfilled NR/ALK | 100/0.8              |
| F/1.0       | Unfilled NR/ALK | 100/1.0              |

2.3. Cure Characteristics

The cure characteristics of the rubber compounds were obtained using a Monsanto Moving Die Rheometer (MDR 2000) which was employed to determine the scorch time (\(t_{s2}\)), cure time (\(t_{90}\)) and torque difference (\(M_{H}-M_{L}\)) value according to ISO 3417. Samples of the respective compounds were tested at 150°C. The rubber compounds were subsequently compression-moulded using a stainless steel mould at 150°C, with a pressure of 10 MPa and applying a laboratory hot-press based on respective curing times.

2.4. Tensile Properties

Dumbbell-shaped samples were cut from the moulded sheets according to ASTM D 412-93. Tensile tests were performed at a crosshead speed of 500 mm/min. Tensile tests were carried out with a universal tensile machine Instron 3366 to determine the tensile properties in terms of tensile strength (TS), stresses at 100% and 300% elongations (M100, M300) and elongation at break (EB).

2.5. Scanning Electron Microscopy (SEM)

The tensile fractured surfaces of the compounds were examined by using a Zeiss Supra-35VP scanning electron microscope (SEM). All the surfaces were examined after first sputter coating with gold to avoid electrostatic charging and poor image resolution.

3. Results and Discussion

3.1. Effect of Alkanolamide on Cure Characteristics and Crosslink Density

Effect of ALK on the cure characteristics of the unfilled NR compound is showed in Table 3. The scorch and cure times decreased with increased ALK loading. It was a cure enhancement which indicated ALK acted as a co-curing agent (secondary accelerator) in the curing. The amine content of
the ALK caused the rubber compound more basic. Alkaline substances tend to improve the cure rate [10].

Table 3. The cure characteristics and tensile properties of unfilled NR compounds with and without ALK

| Compounds | Cure characteristics | Tensile properties |
|-----------|----------------------|-------------------|
|           | ts2, min. | t90, min. | \(M_H-M_L\) (dN.m) | M100 (MPa) | M300 (MPa) | TS (MPa) | EB (%) |
| A/0.0     | 4.59      | 7.13      | 4.77              | 0.538      | 1.235      | 17.7     | 1070.0 |
| B/0.2     | 4.52      | 7.05      | 4.85              | 0.544      | 1.236      | 19.3     | 1095.7 |
| C/0.4     | 4.24      | 6.65      | 4.97              | 0.561      | 1.311      | 19.5     | 1116.5 |
| D/0.6     | 3.96      | 6.45      | 5.21              | 0.586      | 1.364      | 20.1     | 1141.5 |
| E/0.8     | 3.74      | 6.00      | 5.12              | 0.545      | 1.267      | 18.4     | 1154.0 |
| F/1.0     | 3.73      | 5.83      | 4.89              | 0.516      | 1.231      | 16.5     | 1172.0 |

Note: \(M_L = \text{Minimum torque}; M_H = \text{Maximum torque}; M_H-M_L = \text{Torque difference}. \) A/0.0 = Unfilled NR without ALK B/0.2; C/0.4; D/0.6; E/0.8; F/1.0 = Unfilled NR with ALK.

The addition of up to 0.6 phr of ALK increased the torque difference \((M_H-M_L)\). Further increases in the ALK loading decreased the torque difference. Torque difference represents shear dynamic modulus which indirectly related to the crosslink density of a rubber compound [11-14]. The addition of ALK affected the torque difference of the rubber compounds or the crosslink density of the rubber vulcanisate. It was due to the action of the ALK as a secondary accelerator which enhanced the state of curing process.

The reduction of crosslink density beyond 0.6 phr loading was due to the softening or lubricating effect of the excessive ALK which dissolved a part of the elemental sulphur and hence reduced crosslink density. This explanation was supported with the morphology study of the tensile fractured surface of the E/0.8 with excessive ALK. In Figure 2(D), it seemed smooth with a less matrix tearing and surface roughness. It indicated the more pronounced lubricating effect of the excessive ALK (15).

3.2. Effect of Alkanolamide on Tensile Properties

Effect of ALK loading on the tensile properties of the unfilled NR vulcanisates is shown in Table 3. The addition of 0.2 phr ALK produced vulcanisate B/0.2 with higher EB. Increasing the ALK loading caused further increases in the percentage of EB or the extensibility of the rubber vulcanisate. This was due to the function of ALK as an internal plasticiser which modified flexibility or distensibility of rubber vulcanisate.

The addition of ALK increased the M100 and M300 up to maximum level at 0.6 phr and decreased with further increases in the ALK loading. The results of tensile strength also exhibit similar trend. Tensile modulus and tensile strength are dependent only on degree of crosslink [8, 13]. The improvement of those properties was attributed to higher degree of crosslink (as indicated by a higher
value of torque difference). The deterioration of those properties was due the excessive amount of ALK which dissolved other curatives and hence reduced degree of crosslink density (as indicated by a lower value of torque difference). As discussed earlier, crosslink density of a rubber compound is indicated by torque difference value. The greater the torque difference, the higher is the degree or total crosslink density [11, 13].

3.3. Scanning Electron Microscopy (SEM)

Figure 2 shows the SEM micrographs of the tensile fractured surfaces of the unfilled NR compounds with and without ALK. Compared to A/0.0 (Figure 2A), the fractured surfaces of C/0.4 and D/0.6 (Figure 2B and 2C, respectively) show many larger discontinuous slip tear lines with path deviation indicating a higher energy requirement to cause failure. As a consequence, it led to increased resistance to crack propagation and thus, caused an increase in crosslink density. Otherwise the fractured surface of E/0.8 (Figure 2D) exhibits the least matrix tearing and surface roughness which presumably correlated lower crosslink density due to the existence of the excessive ALK in the E/0.8 compound. The micrographs of the tensile fractured surfaces were in line with results obtained by Ismail et al. and Nabil et al., (2013)[15]. They reported that an increase in crosslink density was responsible for the roughness and matrix tearing line of the fractured surface.

Figure 2. SEM micrographs of the failure fracture surface of unfilled NR compound at a magnification of 200 X, (A) A/0.0, (B) C/0.4, (C) D/0.6, and (D) E/0.8

It was demonstrated that ALK can be utilised as a new curative additive in unfilled NR compounds. ALK can be function as secondary accelerator which enhanced the cure rate. ALK also
enhanced the torque difference, crosslink density, tensile modulus and tensile strength especially up to 0.6 phr. ALK also can be function as internal plasticiser which enhanced the EB.

4. Conclusions
Alkanolamide can function as a curative additive in unfilled natural rubber compounds. Results indicate that alkanolamide can be utilized as a secondary accelerator and a plasticiser in the unfilled natural rubber compounds. The incorporation of alkanolamide enhanced the cure rate, reduced the scorch time and improved the flexibility by increasing the elongation at break. The incorporation of alkanolamide also enhanced tensile properties and crosslink density of the unfilled natural rubber vulcanisate especially up to 0.6 phr loading.

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