

# Studies on cure index, swelling behaviour, tensile and thermo-oxidative properties of natural rubber compounds in the presence of alkanolamide

I Surya<sup>1,2\*</sup>, L Sukeksi<sup>1</sup> and N Hayeemasae<sup>3</sup>

<sup>1</sup>Department of Chemical Engineering, Universitas Sumatera Utara, Medan, 20155, Indonesia

<sup>2</sup>Sustainable Energy and Biomaterial Center of Excellence, Faculty of Engineering, Universitas Sumatera Utara, Medan, 20155, Indonesia

<sup>3</sup>Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani Campus, 94000, Pattani, Thailand

\*E-mail: indradanas@yahoo.com

**Abstract.** The studies on cure index, swelling behaviour, tensile and thermo-oxidative properties of unfilled natural rubber (NR) compounds in the presence of alkanolamide (ALK) were carried out. As a rubber additive, the ALK was added into the NR compounds at various loadings (0.2, 0.4, 0.6, 0.8, and 1.0 phr). It was found that the cure indexes of NR compounds with ALK were higher than that of NR compound without ALK (control compound). It was also found that ALK exhibited higher tensile modulus and tensile strength up to 0.6 phr of loading and then decreased with further increases in the loading. The swelling test revealed that 0.6 phr of ALK in the unfilled NR compound exhibited the highest degree of crosslink density which correlated to the highest tensile modulus and tensile strength of the NR vulcanisates. The ALK increased the heat aging resistance of the NR vulcanisates.

## 1. Introduction

Rubber compounding is an activity that performs the art and science of rubber technology. The rubber compounds, as the output of rubber compounding, are composed by a group of base rubber and rubber additives with their suitable quantities. Each of them has a particular function either in compounding, vulcanisation or end use of the rubber articles. The base rubber will give some rubbery characteristics; rubber additives cause in a wide range of physical, chemical and mechanical properties to the rubber articles.

Rubber additives are curative and non-curative additives. Curative additives affect the cure characteristics of rubber compounds. They are sulphur or other curing agents such as zinc oxide, stearic acid, and accelerators.

Alkanolamide (ALK) is considered as a new rubber additive, relatively. It can be prepared from Refined Bleached Deodorized Palm Stearin (RBDPS), a by-product of cooking oil production, and diethanolamine. It improved the cure characteristics and tensile/mechanical properties of the unfilled NR compounds [1], silica [2] and carbon black filled NR compounds [3]. It also can be utilised as a coupling agent in silica reinforcement of NR [4] and as a curing agent of CB filled chloroprene rubber compounds [5].

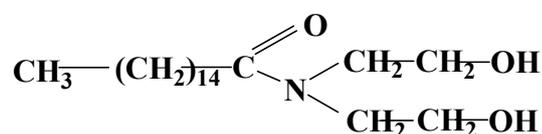


It is important to explore more about the function and application of ALK in NR compounds. Therefore, this study reports the cure index, swelling behaviour, tensile and thermo-oxidative properties of unfilled NR compounds in the presence of ALK.

## 2. Materials and Methods

### 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 Benzothiazolil disulfide (MBTS) were supplied by Bayer (M) Ltd., Sdn. Bhd., Petaling Jaya, Selangor, Malaysia. All the materials were freshly supplied and utilised as supplied. The ALK was prepared in laboratory utilising Refined Bleached Deodorized Palm stearin (RBDPS) and diethanolamine. The reaction procedures and molecular characterisations of the ALK were given in our previous report [2]. The molecular structure of ALK is presented in Fig. 1.



**Figure 1.** The molecular structure of alkanolamide.

### 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. 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 1 also shows the designation and composition of the NR-based recipes used in this study.

**Table 1.** The composition and designation of the NR compounds

Ingredients	Content (phr)*	Designation					
		A/0.0 (Control)	B/0.2	C/0.4	D/0.6	E/0.8	F/1.0
SMR L	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0
IPPD	2.0	2.0	2.0	2.0	2.0	2.0	2.0
MBTS	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5
ALK	0.0 – 1.0	0.0	0.2	0.4	0.6	0.8	1.0

\*parts per hundred parts of rubber

### 2.3. Cure characteristics

The cure characteristics of the NR compounds were obtained using a Monsanto Moving Die Rheometer (MDR 2000) which was employed to determine the scorch time ( $ts_2$ ) and cure time ( $t_{90}$ ) according to ISO 3417. Samples of the respective compounds were tested at 150 °C. The NR 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. The cure index or cure rate index (CRI) of the compounds was calculated as follows:

$$\text{CRI} = \frac{100}{(t_{90} - t_{s2})} \quad (1)$$

#### 2.4. Swelling behaviour

The swelling test was performed in toluene according to ISO 1817. Cured test pieces of the compounds of dimension (30 mm x 5 mm x 2 mm) were weighed using an electrical balance and swollen in toluene until equilibrium, which took 72 h at room temperature. The samples were removed from the liquid, the toluene was removed from the samples surfaces, and the weight was determined. Calculation of the change in mass is as follows;

$$\text{Swelling (\%)} = \frac{W_2 - W_1}{W_1} \times 100\% \quad (2)$$

where  $W_1$  is the initial mass of specimen (gram) and  $W_2$  is the mass of specimen (gram) after immersion.

#### 2.5. Tensile properties

Dumbbell-shaped samples were cut from the moulded sheets. The tensile test was performed at a cross-head speed of 500 mm/min using an Instron 3366 universal tensile machine, according to ISO 37. The tensile strength (TS), stress at 100% elongation (M100), stress at 300% elongation (M300), and elongation at break (EB) were determined.

#### 2.6 Thermo-oxidative Ageing.

The thermo-oxidative ageing tests were done according to ASTM D573-04. Test samples were placed in an air circulating oven at 100 °C for 48 hours. At the end of the period, test samples were removed from the oven, cooled for 30 minutes at room temperature and allowed to rest from 16 to 96 hours before determination of the tensile properties. Five specimens were used and the average was determined and reported. Retention in tensile properties was calculated as follows:

$$\text{Retention (\%)} = \frac{\text{Value After Ageing}}{\text{Value Before Ageing}} \times 100 \quad (3)$$

### 3. Results and Discussion

#### 3.1. The cure index and swelling behaviours

The cure index and swelling behaviour of the NR compound with and without ALK are shown in Table 2. The cure rate index (CRI) is a measurement of the cure rate based on the differences between the optimum cure time ( $t_{90}$ ) and incipient scorch time ( $t_{s2}$ ) [6]. The CRI of the NR compound with ALK was higher than that of the NR compound without ALK. It indicated that the rate of curing increased slightly with increasing the ALK loading. It was due to the function of ALK as an additional accelerator [2, 7] which increased in the number of reactive sites on the rubber molecules used for the cross-linking reactions.

**Table 2.** The cure index and swelling behaviour of NR compounds with and without ALK.

CRI and Swelling Properties	NR Compounds					
	A/0.0 (Control)	A/0.2	A/0.4	A/0.6	A/0.8	A/1.0
CRI, min.	39.4	39.5	41.5	42.2	44.2	47.6
Swelling, %	396.2	395.9	395.2	375.5	384.8	399.2

As shown in Table 2, ALK decreased the swelling percentage of NR compounds up to 0.6 phr. Further increases in the ALK loading (0.8 phr) increased the swelling percentage. It is believed that the swelling percentage is directly related to the crosslink density of a rubber vulcanisate [6]. The less is the percentage; the higher is the crosslink density. The ALK affected the crosslink density of the NR vulcanisate. It was attributed to the action of the ALK as an additional accelerator during the curing of the NR compounds [2-4, 7]. The amine constituent of the ALK activated not only the rubber but also the elemental sulphur during curing. The amine and others curatives formed intermediate complexes which attached the available elemental sulphur to rubber chains more efficient [8], causing a higher degree of crosslink density.

The decrease in crosslink density beyond a 0.6 phr loading of ALK was most probably due to the excessive amount of ALK which dissolved a part of the elemental sulphur and as a consequent, a less sulphur was attached to the NR chains.

### 3.2. The tensile properties

The tensile properties of the NR vulcanisates with and without ALK are presented in Table 3. As shown, the EB of B/0.2-vulcanisate was higher than that of A/0.0-vulcanisate. Increasing the ALK loading caused further increases in the EB of the NR vulcanisate.

**Table 3.** The tensile and thermo-oxidative aging properties of NR compounds with and without ALK

Compounds	Tensile properties				Retention (%)		
	M100 (MPa)	TS (MPa)	EB (%)	EB Increment (%)	M100 (MPa)	TS (MPa)	EB (%)
A/0.0	0.538	17.7	1070.0	0.00	129.4	92.9	93.1
B/0.2	0.544	19.3	1095.7	2.40	133.1	93.9	92.4
C/0.4	0.561	19.5	1116.5	4.35	136.7	94.7	88.0
D/0.6	0.586	20.1	1141.5	6.68	137.5	97.5	78.5
E/0.8	0.545	18.4	1154.0	7.85	139.9	99.0	75.5
F/1.0	0.516	16.5	1172.0	9.53	147.5	99.1	74.2

It was attributed to the function of ALK as an internal plasticiser to the unfilled-NR compound [2-3, 7]. A plasticiser is a rubber additive which improves rubber compound processing and modifies hardness, flexibility or distensibility of a rubber vulcanisate [8]. The ALK plasticised and provided some layers in NR compound which provided free volume, thus allowing more mobility/flexibility for the NR chains [8-9]. Increasing the ALK amount has the same effect as an increase in free volume that enhanced the flexibility or the extensibility of the NR vulcanisates. Therefore, a higher ALK loading caused in a higher percentage of EB increment.

Table 3 shows that the ALK increased the M100 and M300 slightly up to a maximum level at 0.6 phr and then decreased with further increases in the loading. The TS also exhibit a similar trend. M100 and M300 are typical measures stiffness or hardness of a rubber vulcanisate [10-12]. Modulus or stiffness/hardness and tensile properties are dependent mainly on the degree of crosslink [9, 11]. The improvements in M100, M300, and TS up to 0.6 phr of ALK were due to a higher degree of crosslink density. The decreases in those properties, beyond 0.6 phr, were attributed to a lower degree of crosslink density and a more pronounced the plasticizing effect of the ALK.

### 3.3. The thermo-oxidative properties

The thermo-oxidative ageing properties of the NR vulcanisates with and without ALK were also studied. During the ageing process, NR vulcanisates were subjected to the hot air and this leads to the diffusion of oxygen into the outer part of NR vulcanisates. Some parts of the NR vulcanisates were immediately consumed by oxidation reaction to produce a further crosslinking, scission of rubber chains and/or crosslinking and combination of the reactions [13].

The ageing process is also like post-curing, the phenomenon clearly indicates that some microstructures such as the formation of new intermolecular bonds have taken place after ageing and resulted in higher crosslink density of the rubber vulcanisates.

The ageing properties of a rubber vulcanisate might be presented in terms of retention values (the property ratio of the aged to unaged specimens). The retention values of M100, TS, and EB of the NR vulcanisates with and without ALK are shown in Table 3, respectively. As shown in Table 3, the M100 of the aged vulcanisates increased due to the formation of some new crosslinks and enhancement the degree of crosslink density [13]. Hence, the increased in M100 was simply attributed to post-curing effect which enhanced the crosslink density of the aged unfilled NR vulcanisates.

It was also observed that the retention values of M100 of the aged vulcanisates with ALK were greater than that of the aged vulcanisate without ALK. The higher the ALK loading, the greater was the value of M100 retention. It was clearly due to the function of ALK as an additional accelerator which greatly affected the post-curing process of the unfilled NR compounds. Increasing the amount of accelerator of a Semi-EV curing system will have the same with changes the curing system into an EV system. The increase in the accelerator to sulphur ratio, as in EV system, is believed could reduce the main chain modifications, the formation of cyclic structures and rank of sulphur crosslinks and improve the vulcanisation efficiency and crosslink density [8]. These changes in microstructures have been correlated with improved of mechanical and ageing properties. According to Rattanasom et al. [14], a higher content of monosulphidic crosslinks of EV system would provide higher thermal stability. This contributes to increasing the retention of M100 with higher ALK loading for the unfilled NR vulcanisates with ALK.

Table 3 shows that the TS of the NR vulcanisates with and without ALK decreased after the ageing process. This was attributed to the degradation process of NR vulcanisates were dominant by the main chain scission which leading to the main chains modification which reduced the ability of NR vulcanisates to undergo strain-induced crystallization. This phenomenon decreased the EB of the aged NR vulcanisates.

It was also observed with the addition of ALK provided better TS retention to unfilled NR vulcanisates. The higher the ALK loading increased the TS retention. Again, this was due to the function of ALK as an accelerator which modified the microstructures of the aged unfilled NR vulcanisates during the post-curing process. The nitrogen atoms of ALK will react with sulphur atoms of disulphidic crosslinks and immediately formed more monosulphidic crosslinks in the aged vulcanisates which gives better ageing resistance compared to disulphidic crosslinks.

From Table 3, the EB of the NR vulcanisates with and without ALK decreased significantly after 3 days of thermo-oxidative ageing at 100 °C. The higher the ALK loading, the lower the EB retention was observed. It simply was attributed to the increased crosslink density which mobilized the rubber chains of the aged vulcanisates less freely. Similar with M100, EB also depends mainly on the degree of crosslink density [13,15].

#### 4. Conclusions

From the studies, the following conclusions were drawn:

1. Alkanolamide enhanced the cure index of unfilled natural rubber compounds. The cure indexes of natural rubber compounds with alkanolamide were higher than that of without alkanolamide. The higher the alkanolamide loading, the higher was the cure index.
2. Alkanolamide decreased the swelling percentage and increased the crosslink density of unfilled natural rubber compound up to 0.6 phr loading. The cure indexes of natural rubber compounds with alkanolamide were higher than that of without alkanolamide.
3. Alkanolamide enhanced the tensile properties of unfilled natural rubber vulcanisate up to 0.6 phr loading.
4. Alkanolamide enhanced the thermo-oxidative ageing resistances of unfilled natural rubber compounds.

### Acknowledgements

The authors would like to thank Universiti Sains Malaysia, for providing the research facilities for carrying out the experiment and for making this research work possible.

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