

## The effects of the addition of alkanolamide on carbon blacks filled natural rubber compounds

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**Abstract.** The effects of the addition of alkanolamide (ALK) on cure characteristics and filler dispersion of the two types of carbon black (CB) filled natural rubber (NR) compounds were investigated. The N-550 and N-220 types of CB were utilised, and each of them was incorporated separately into NR compound with a fixed loading, 30.0 phr. The ALK was synthesized from Refined Bleached Deodorized Palm Stearin and diethanolamine; and incorporated into the CB filled NR compounds as an additive ingredient. The ALK loadings were 3.0, 5.0, 7.0 and 9.0 phr. It was found that ALK could function as a secondary accelerator and also an internal plasticiser. As a secondary accelerator; ALK decreased the scorch and cure times of the N-550 and N-220 CBs filled NR compounds. The higher the ALK loading, the shorter the scorch and cure times. As an internal plasticiser; ALK decreased the minimum torque and improved the dispersions of both types of CB in NR phases. At a similar ALK loading; N-220 exhibited higher cure rate, minimum and maximum torques and torque difference values. However, degree of filler dispersion of N-220 was poorer.

### 1. Introduction

In rubber technology, a rubber compound contains a group of base rubber and rubber additives. Each of them has a specific function either in processing, curing or end use of the rubber products [1]. Rubber or blend of rubbers will provide rubbery behavior to the compound; rubber additives such as plasticisers are used to reduce viscosity, enhance deformability and alter properties; vulcanising agents can crosslink the rubber chains; and accelerators improve the action of vulcanising agents to speed up the cure rate.

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 vulcanisation process. The popular curative additives are sulphur or other vulcanising agents, zinc oxide, stearic acid, and accelerators.

Fillers are considered as non curative additives. The main purpose of utilising them is to enhance the mechanical properties of rubber vulcanisates such as tensile strength, resistances to abrasion, tearing and flexing or cheapen the cost of products. Carbon black (CB) is the most popular filler in manufacturing of various rubber products, and normally CB is used to reinforce the rubber compounds [2-3]. However at a relatively higher loading, the filler particles tend to form



agglomeration and will poor the filler dispersion. Practically, to overcome the filler dispersion problem, special additives such as processing aid, dispersant aid, oil etc. are used.

Alkanolamide (ALK) as a relatively new rubber additive is suggested to solve the filler dispersion problem. It was synthesized from Refined Bleached Deodorized Palm Stearin (RBDPS) and ethanolamine. RBDPS is one type of vegetable oils which comes from palm tree. Physically, the RBDPS-based ALK is an oily substance. Oil is one type of plasticising agents [4] and hence, ALK potentially can be utilised to lubricate, plasticise or soften the CB filled NR compounds and improve the CB dispersion in the rubber phases.

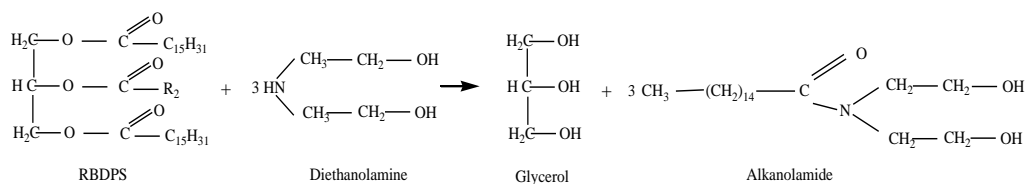
Some previous works on ALK have been reported. The ALK enhanced the mechanical properties of the silica-filled NR vulcanisates [5]. The enhancement of the properties was attributed to the improvement of silica dispersion and the excelling crosslink density that stemmed from the incorporation of ALK. The results also indicated that ALK could function as an accelerator and internal plasticiser. Studied on the comparison of ALK and aminopropyltriethoxy Silane (APTES)-silane coupling agent on the properties of silica-filled NR compounds [6], it was reported that due to its unique function as an accelerator and internal plasticiser, ALK produced a higher reinforcing efficiency than APTES at a similar loading. Studied on the effect of ALK loading on properties of CB-filled NR, epoxidised natural rubber (ENR) and styrene butadiene rubber (SBR) compounds revealed that ALK gave cure enhancement, better filler dispersion and greater rubber–filler interaction to three different types of rubbers [7].

In this study, the effects of ALK loading on the cure characteristics of CBs filled NR compounds and degree of CB dispersion in the filled NR compounds were investigated. Two types of CBs, N-550 and N-220, were used as the fillers. They are different in particle sizes. N-220 has smaller particle size than N-550 [4].

## **2. Materials and Methods**

### *2.1 Materials*

NR grade SMR-L was obtained from Guthrie (M) Sdn. Bhd., Seremban, Malaysia. N-550 and N-220 grades of CB were supplied by Cabot Corporation. 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 utilised as supplied. The ALK was synthesized in laboratory using RBDPS and diethanolamine. The chemical reaction of the preparation of ALK is presented in Figure 1.



**Figure 1.** Chemical reaction of the preparation of Alkanolamide.

## 2.2 Laboratory Preparation of Alkanolamide

The reaction was carried out at atmospheric pressure in a 1000 mL reaction vessel fitted with a stirrer. Typically 1.0 mol of RBDPS, and 3.0 mol each of diethanolamine, sodium methoxide and methanol (as catalysts) were placed in the reaction flask. The mixture was stirred and heated; the reaction temperature was kept constant at 70°C for about 5 h. The resultant mixture was extracted with diethyl ether and washed with saturated sodium chloride solution. The crude ALK was purified with anhydrous sodium sulphate and then concentrated by a rotary evaporator. The cream-coloured and oily ALK was characterized by Fourier transform infra-red (FTIR) spectroscopy. The infrared spectrum of ALK is presented in Figure 2.

## 2.3 Compounding

A semi-efficient vulcanisation system was used for the rubber compounding. The compounding procedure was done in accordance with the American Society for Testing and Material (ASTM) – Designation D 3184 – 80. The compounding was performed on a two-roll mill (Model XK-160). Table 1 displays the compound formulation of CBs filled NR compounds with various ALK loading.

**Table 1.** The composition of the CBs filled NR compounds.

Ingredients	Content (phr)*
SMR-L	100.0
Zinc oxide	5.0
Stearic acid	2.0
IPPD	2.0
MBTS	1.5
Sulphur	1.5
CB (N-220/N-550)	30.0
ALK	0.0; 3.0; 5.0; 7.0; 9.0

\* parts per hundred part of rubber

## 2.4 Cure Characteristics

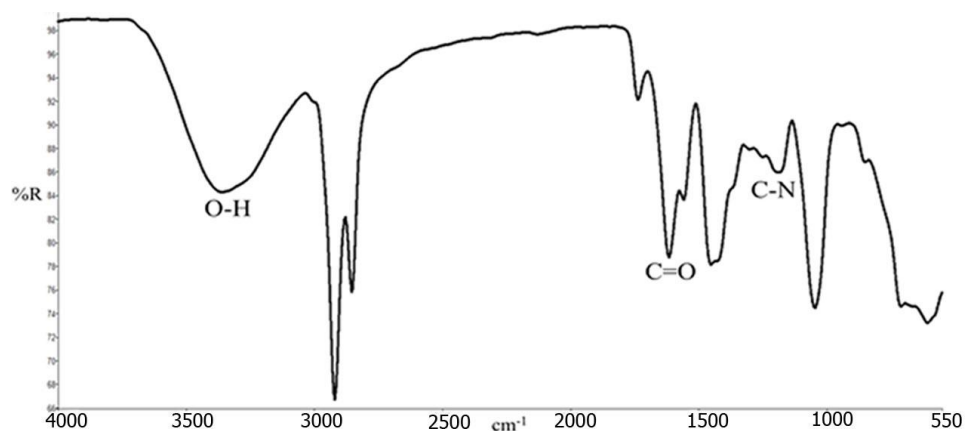
The cure characteristics of the CBs filled NR compounds with and without ALK were obtained using a Monsanto Moving Die Rheometer (MDR 2000) which was employed to determine the scorch

time ( $ts_2$ ), cure time ( $t_{90}$ ), minimum torque ( $M_L$ ), maximum torque ( $M_H$ ) and torque difference ( $M_H - M_L$ ) according to ISO 3417. Samples of the respective compounds were tested at 150°C.

### 3. Results and Discussion

#### 3.1 Characterization of ALK

Figure 2 shows the typical infrared spectrum of the ALK which was obtained from RBDPS and ethanolamine. The spectrum clearly shows the presence of wavenumbers of the functional groups of ALK such as O-H, C=O and C-N groups.



**Figure 2.** The infrared spectrum of ALK from RBDPS and ethanolamine.

#### 3.2 Cure Characteristics

The effects of ALK loading on the cure characteristics of the two different types of CBs (N-550 and N-220) filled NR compounds are presented in Table 2. The cure characteristics were measured at 150°C including scorch and cure times, minimum and maximum torques and torque differences.

Scorch time is the required time to reach the two torque units rise above the minimum torque. Scorch time is considered as the required time at which vulcanisation begins, and cure time is the required time for a rubber compound to reach 90% of the state of cure (8-9).

As presented in Table 2, it was observed that the scorch times ( $ts_2$ ) of CBs filled NR compounds with ALK were lower than those of without ALK (control compounds). The higher the ALK loading, the lower were the scorch times. The curing systems of those two rubber compounds used MBTS as the accelerator, and it is functionally classified as a primary accelerator which usually provides scorch delay to a rubber compound (4, 10). The lower the mass ratio of MBTS, the lower was the scorch safety. The addition of ALK reduced mass ratios of the base rubber (NR) and also rubber additives. This explained why the scorch times tended to slightly decrease when the ALK was added.

**Table 2.** Cure characteristics of CBs filled NR compounds at various ALK loadings

CBs filled NR Compounds	ALK Loadings (phr)				
	0.0 (Control)	3.0	5.0	7.0	9.0
<b>N-550 filled</b>					
ts <sub>2</sub> , min	3.36	1.79	1.35	1.20	1.14
t <sub>90</sub> , min	7.21	4.10	3.50	3.26	3.17
M <sub>H</sub> , dN.m	6.66	8.40	8.66	8.56	8.18
M <sub>L</sub> , dN.m	0.33	0.30	0.16	0.14	0.12
M <sub>H</sub> —M <sub>L</sub> , dN.m	6.33	8.10	8.50	8.42	8.06
<b>N-220 filled</b>					
ts <sub>2</sub> , min	2.13	1.42	1.26	1.12	1.08
t <sub>90</sub> , min	5.56	3.45	3.16	2.88	2.80
M <sub>H</sub> , dN.m	8.42	11.95	9.80	9.52	9.42
M <sub>L</sub> , dN.m	0.39	0.37	0.33	0.32	0.29
M <sub>H</sub> —M <sub>L</sub> , dN.m	8.03	11.58	9.47	9.20	9.13

From Table 2, it was also observed that the addition of each 3.0 phr of ALK into the control compounds decreased the cure time (t<sub>90</sub>). Lower cure time means higher cure rate and hence, a cure enhancement phenomenon was observed. It was attributed to the function of ALK as a curative agent (secondary accelerator) in the curing or vulcanisation process. In rubber compounding, amine is usually utilised not only as an accelerator but also an accelerator activator [7,11]. In the case of the cure enhancement phenomenon, the amine part of ALK together with zinc oxide and fatty acid, activated the MBTS-accelerator more pronouncedly and hence, improved the rate of sulphur reaction of CBs filled NR compounds. It was also observed that the higher the ALK loading, the more pronounced the cure enhancement. It was simply attributed to a higher amount or mass ratio of amine in the CBs filled NR compounds.

At a similar ALK loading, the scorch and cure times of N-220 were shorter than those of N-550. It was simply attributed to the difference in sizes of their particles. According to Fetterman [12-13], CB will react with sulphur during vulcanisation and form sulphur bonds that link the rubber chains and also rubber – filler bonds. The nature of rubber – filler bond is determined by some factors and one of them is the surface activity of filler. Greater surface area tends to provide greater surface activity [14]. N-220 has a smaller particle-size or greater surface area than N-550 [4] and hence, shorter scorch and cure times of N-220 were due to its greater surface activity which reduced time to complete the rubber – filler bonds formation.

Table 2 shows that the additions of 3.0 phr of ALK decreased the minimum torques (M<sub>L</sub>) of both control compounds. The M<sub>L</sub> value is used to measure of the viscosity of a rubber compound ([5]. The lower the M<sub>L</sub> value, the lower is the viscosity. The addition of ALK reduced the viscosity of the CBs filled NR compounds. This was attributed to the additional function of ALK as an internal plasticiser which plasticised, softened and reduced the viscosity of the filled NR compounds, respectively. The higher the ALK loading, the lower was the viscosity.

Table 2 also shows that the addition of each 3.0 phr of ALK increased the torque difference ( $M_H - M_L$ ) values of both control compounds. N-550 and N-220 have different trends of torque differences with further increases the ALK loading. The torque difference of N-550 was further increased with the addition of ALK up to 5.0 phr, and decreased beyond the loading. Whilst, the torque difference of N-220 was increased by the addition of 3.0 phr, and decreased beyond the loading. The torque difference indicates the degree of crosslink density of a rubber compound [7, 16]. The greater the value, the higher is the crosslink density. The increasing of torque difference or crosslink density up to the optimum loadings of ALK (5.0 phr for N-550; 3.0 phr for N-220) was attributed to the chemical and physical properties of ALK. The nitrogen atom or the amine constituent of ALK activated chemically not only the rubber but also the elemental sulphur during sulphuration or curing reaction. Together with the others curatives, amine could form intermediate complexes which attached the available elemental sulphur to rubber chains more efficient [4], causing higher degree of cure. The nitrogen atom also can act as a hydrogen acceptor and amine accelerators can activate the elemental sulphur and/or the rubber for the curing reaction [4].

Physically, ALK is an oily material and has the function as an internal plasticiser agent. As discussed earlier, ALK reduced the viscosity of the CBs filled NR compounds. It improved the CB dispersion and rubber - filler interaction/bond, respectively. The rubber – filler bond is defined as additional physical crosslinks [17], and together with sulphide crosslinks contribute to total crosslink density of a rubber vulcanisate [10, 18].

The reductions of the torque differences, beyond the optimum loadings, were most probably attributed to the dilution effect of the excessive amounts of ALK which formed some oily layers. These layers might absorb a part of CB filler and other curatives and coated them together. By this mechanism, the total crosslink density was reduced.

### 3.3 Filler Dispersion

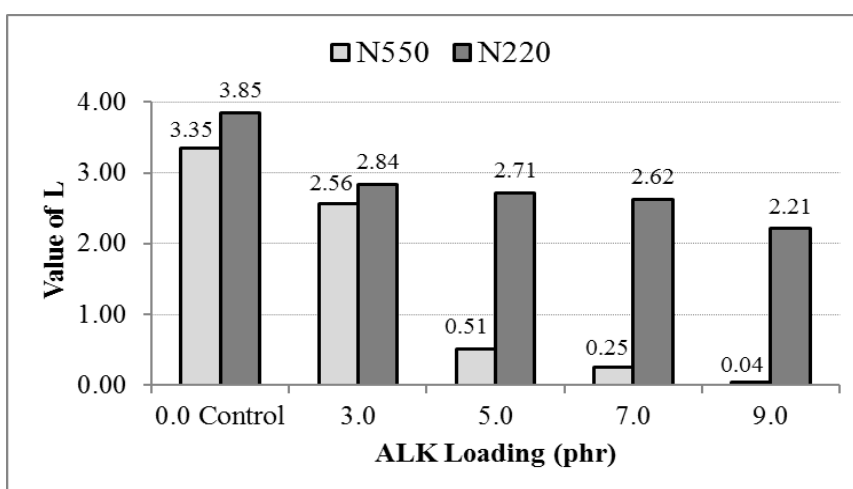
Based on torque properties data in Table 2, the degree of CBs dispersion in NR phases, with and without ALK, can be quantitatively calculated by Equation (1) [7, 19-20].

$$L = \eta_r - m_r \quad (1)$$

where:  $\eta_r = [M_{Lf} / M_{Lg}]$ , and  $m_r = [M_{Hf} / M_{Hg}]$ ; where  $M_{Lf}$  and  $M_{Hf}$  are the minimum and maximum torques of the filled compounds, and  $M_{Lg}$  and  $M_{Hg}$  are the minimum and the maximum torques of the unfilled/gum rubber compound. A lower value of  $L$ , at a particular CB loading, meant a better degree of CB dispersion. The minimum and maximum torques of gum NR compounds were 0.05 and 4.85, respectively.

Figure 3 shows the values of L for CBs dispersion in the NR phases at various ALK loading. It can be seen that the L values of CB-filled compounds with ALK were lower than those of CB-filled compounds without ALK. The higher the ALK loading, the lower was the L value. This was attributed to the plasticisation effect of ALK which reduced minimum torque or viscosity the rubber compounds and hence, improved the CB dispersion.

At a similar ALK loading, The L values of N-220 were higher than those of N-550. A higher value of L, meant a lower degree of filler dispersibility. Again, it was simply attributed to the particle-sizes of those CBs. According to Bhakuni [21], decreasing particle-size decreases the dispersibility of filler in a rubber compound. The N-220 has smaller particle-size than N-550 and hence, its smaller particle-size decreased its degree of dispersibility.



**Figure 3.** The effect of ALK loading on value of L of the carbon blacks filled NR compounds.

#### 4. Conclusions

From this study, the following conclusions were drawn:

1. Alkanolamide can be function as a curative additive in carbon blacks filled natural rubber compounds. It acted as a secondary accelerator and internal plasticiser in the carbon blacks filled natural rubber compounds. Alkanolamide reduced not only the scorch and cure times but also minimum torque of the carbon blacks filled natural rubber. The higher the loading, the more pronounced the acceleration of curing and plasticising effects.
2. Alkanolamide improved the torque difference of the carbon blacks filled natural rubber up to the optimum loadings. A 5.0 phr was the optimum loading of Alkanolamide for N-550, and 3.0 phr was for N-220 filled natural rubber compounds.



3. Alkanolamide also improved the filler dispersions of N-550 and N-220 in natural rubber phases. Increasing the Alkanolamide loading further increased the dispersion degrees of the fillers. At a similar Alkanolamide loading, the filler dispersion of N-220 was poorer than that of N-550.

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