

# Cure characteristics, crosslink density and degree of filler dispersion of kaolin-filled natural rubber compounds in the presence of alkanolamide

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**Abstract.** The effects of alkanolamide (ALK) addition on cure characteristics, crosslink density and degree of filler dispersion of kaolin-filled natural rubber (NR) compounds were investigated. The kaolin filler was incorporated into NR compounds with a fixed loading, 30.0 phr. The ALK was prepared from Refined Bleached Deodorized Palm Stearin (RBDPS), a waste product of cooking oil production, and diethanolamine. The ALK is an oily material and added into the filled NR compounds as a rubber additive at different loadings, 0.0, 3.0, 5.0 and 7.0. The kaolin-filled NR compounds with and without ALK were vulcanized using a semi-efficient vulcanization system. It was found that ALK decreased the scorch and cure times and improved filler dispersion of the kaolin-filled NR compounds. The higher the ALK loading, the shorter were the scorch and cure times. It was also found that ALK increased the crosslink density of kaolin-filled NR compound up to 5.0 phr of loading. Due to its oily properties, The ALK acted as an internal plasticizer which decreased the minimum torque and improved the degree of kaolin dispersion in NR phases. The higher the ALK loading; the lower the minimum torque and better the filler dispersion.

## 1. Introduction

The rubber compounds are prepared by mixing a base rubber and rubber additives. The base rubber or rubber gives rubbery characteristics to the compound and rubber additives plasticizers reduce viscosity, enhance deformability and alter properties; curing agent crosslinks the rubber chains; and accelerators enhance the action of curing agent to speed up the resultant crosslinking formation.

Rubber additives can be divided into curative and noncurative additives. Curative additives affect the cure characteristics of a rubber compound. Non-curative additives do not affect the rate and nature of the curing process. Fillers are non-curative additives. The main purpose of utilizing 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. Fillers can be divided into black and nonblack fillers. The black filler is carbon black (CB), and non-black fillers are calcium carbonate, kaolin clay, precipitated silica, talc, barite, wollastonite, mica, precipitated silicates, fumed kaolin and



diatomite. Of these, the three most widely used, by volume and by functionality, are calcium carbonate, precipitated silica, and kaolin. For many applications, kaolin and the other non-black fillers are not satisfactory alternatives to CB, because of their lower reinforcement levels. The basic problem is their surface chemistry which is more polar and hydrated than CB, and which cause them to be difficult to wet, disperse and interact with hydrocarbon rubbers. Some methods have been introduced to improve the reactivity of nonblack fillers with the rubber phases. The most popular one is the utilising of a silane-coupling agent. The coupling agent modifies the surface of polar fillers. The modified polar fillers provide chemically active surfaces that can participate in vulcanization, providing coupling bonds between silane and both the polar fillers and the rubber phases [1-3]. Those products show significant improvement in performance compared to their base materials.

Another alternative method to overcome the weakness of polar fillers, such as kaolin, is the using of alkanolamide (ALK). The ALK is prepared by reacting Refined Bleached Deodorized Palm Stearin (RBDPS) with diethanolamine with a certain condition. This study reports the effects ALK loading on cure characteristics, crosslink density and degree of filler dispersion of kaolin-filled NR compounds.

## 2. Materials and Methods

### 2.1. Materials

NR grade SMR-L was obtained from Guthrie (M) Sdn. Bhd., Seremban, Malaysia. Other compounding ingredients such as kaolin, 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 utilized as supplied. The ALK was prepared in the laboratory using RBDPS and diethanolamine [4]. The chemical formula of ALK is  $\text{CH}_3(\text{CH}_2)_{14}\text{CON}(\text{CH}_2\text{CH}_2\text{OH})_2$ .

### 2.2. Compounding

A sulphur-accelerated curing system was used for compounding. The recipe for the preparation of the kaolin-filled NR compounds 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. 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 kaolin-filled NR compounds

Ingredients	Content (phr)*	Designation				
		A/0.0 (Control)	B/1.0	C/3.0	D/5.0	E/7.0
SMR L	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
Stearic acid	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
MBTS	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
Kaolin	30.0	30.0	30.0	30.0	30.0	30.0
ALK	0.0 – 7.0	0.0	1.0	3.0	5.0	7.0

\*parts per hundred parts of rubber

### 2.3. Cure characteristics

The cure characteristics of the kaolin-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 ( $t_{s2}$ ), 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.

#### 2.4. Crosslink density

Swelling tests on the kaolin-filled NR vulcanisates were performed in toluene in accordance with ASTM D471-12a. The cured test pieces (30 mm × 5 mm × 2 mm) were weighed using an electric balance and swollen in toluene until equilibrium, which took 72 hours at room temperature. The samples were taken out from the liquid, the toluene was removed from the sample surfaces and the weight was determined. The samples were then dried in the oven at 70 °C until constant weights were obtained. The swelling results were used to calculate the molecular weight between two crosslinks ( $M_c$ ) by applying the Flory-Rehner equation [5-6].

$$M_c = \frac{-\rho_r V_s V_r^{1/3}}{\ln(1 - V_r) + V_r + \chi V_r^2} \quad (1)$$

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

where  $\rho$  is the rubber density ( $\rho_r$  of SMR-L = 0.92 g/cm<sup>3</sup>),  $V_s$  is the molar volume of the toluene ( $V_s = 106.4$  cm<sup>3</sup>/mol),  $V_r$  is the volume fraction of the rubber in the swollen specimen,  $Q_m$  is the weight increase of the vulcanisate in toluene and  $\chi$  is the interaction parameter of the rubber network-solvent ( $\chi$  of SMR-L = 0.393). The crosslink density is given by;

$$V_c = \frac{1}{2M_c} \quad (3)$$

### 3. Results and Discussion

#### 3.1. The effects of ALK on cure characteristics of kaolin-filled NR compounds

The effects of ALK addition on cure characteristics of the kaolin-filled NR compounds are shown in Table 2. The cure characteristics are the scorch time, cure time, minimum torque, maximum torque and torque difference. As shown in Table 2, the scorch times of kaolin-filled NR compounds with ALK were lower than that of without ALK (control compound). The higher the ALK loading, the lower were the scorch times. As shown in Table 1, rubber compounds used MBTS as the accelerator. It is functionally classified as a primary accelerator which causes a scorch delay to rubber compounds [7-8]. Whenever ALK was added to the filled-rubber compounds, the additive decreased the mass ratios of both rubber and non-rubber constituents. Therefore, ALK decreased the mass ratio of MBTS and consequently, decreased the effect of scorch safety.

**Table 2.** The cure characteristics of kaolin-filled NR compounds with and without ALK

Compounds	Cure characteristics				
	$t_{s2}$ , min.	$t_{90}$ , min.	$M_H$ , dN.m	$M_L$ , dN.m	$M_H - M_L$ , dN.m
<b>A/0.0</b>	5.94	9.89	5.34	0.39	4.95
<b>B/1.0</b>	4.45	7.61	6.49	0.13	6.36
<b>C/3.0</b>	3.71	6.31	6.59	0.11	6.48
<b>D/5.0</b>	2.98	5.40	7.57	0.09	7.48
<b>E/7.0</b>	1.47	3.38	7.21	0.03	7.18

As shown in Table 2, the addition of 1.0 phr of ALK decreased the cure time of control compound. A lower cure time means a higher cure rate and hence, a cure enhancement phenomenon was observed. In this case, the ALK acted as an additional accelerator in the curing process [8-9] and it was considered as a secondary accelerator for the kaolin filled NR compounds. The cure enhancement was due to the amine presence in ALK, together with zinc oxide and fatty acid, they activated the MBTS-accelerator more pronouncedly [10] and hence, improved the cure rate. It was also seen that increases the ALK loading caused in a more pronounced the cure enhancement and it was simply due to a higher amount of amine in the kaolin-filled NR compounds.

As shown in Table 2, the addition of 1.0 phr of ALK decreased the minimum torque of control compounds. Further increases the ALK loading decreased the minimum torque. The minimum torque relates to the viscosity of a rubber compound qualitatively [3, 11]. A lower minimum torque means a lower viscosity and vice versa. The ALK decreased the viscosity of the filled NR compounds because of its waxy properties [4, 8] which plasticised, softened and decreased the viscosity of the filled NR compounds, respectively. The higher ALK loading the lower was the viscosity.

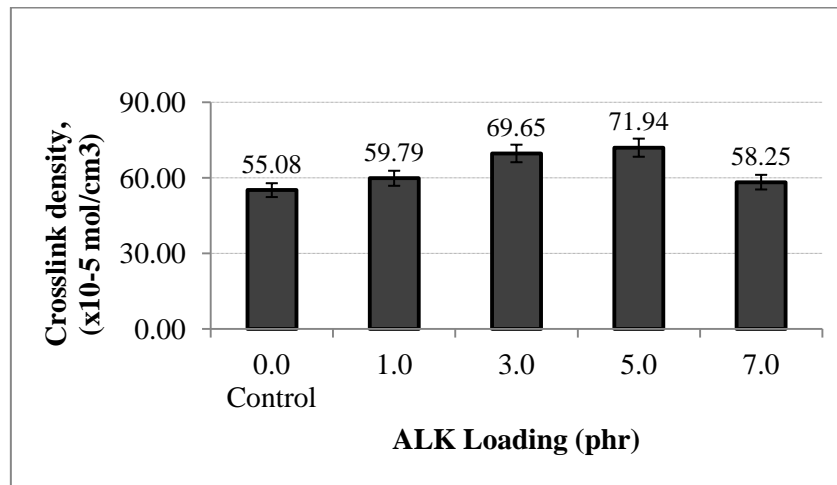
As shown in Table 2, the addition of 1.0 phr of ALK increased the maximum torque. The maximum torque relates to the value of stock modulus which increased in this case. It was due to the nature of rubber - filler interaction including intercalation and exfoliation [12]. The increases in maximum torque were more pronounced whenever the ALK loadings were further increased up to 5.0 phr and decreased beyond the loading. Therefore, the intercalation, exfoliation, and rubber - filler interaction were further increased also up to 5.0 phr of ALK. In this case, the ALK acted as a compatibilizer in the kaolin-filled NR compounds.

As shown in Table 2, the addition of 1.0 phr of ALK increased the torque difference ( $M_H - M_L$ ) value. The value was further increased by the addition of ALK up to 5.0 phr and decreased beyond the loading. Torque difference relates to the degree of crosslink density of a rubber compound [4, 13]. The greater the value, the higher is the crosslink density. The increases of torque difference or crosslink density up to the optimum loadings of ALK (5.0 phr) was due to the acting of ALK not only as an additional accelerator but also as a compatibilizer. As an accelerator, the amine constituent activated chemically both the rubber and elemental sulphur during curing reaction. Together with the others curatives, the amine formed intermediate complexes which attached the available elemental sulphur to rubber chains more efficient [8], causing in a higher degree of cure. As a compatibilizer, the oily properties of ALK decreased the viscosity of the filled NR compounds and hence, improved the kaolin dispersion or rubber-filler interaction. The rubber – filler interaction is defined as additional physical crosslinks [9], and together with sulphide crosslink contribute to total crosslink density of a filled rubber vulcanisates [8-9].

The decrease in torque difference (beyond the optimum loading) might be due to the excessive amount of ALK which formed some oily layers. The layers covered and coated the kaolin and other curatives and hence, decreased the total crosslink.

### *3.2. The effect of ALK on crosslink density of kaolin-filled NR compounds*

The effect of ALK on the total crosslink density of the kaolin-filled NR vulcanisates is shown in Figure 1. The total crosslink density was determined by the Flory—Rehner approach (Equation 1). The additions of up to 5.0 phr of ALK into the kaolin-filled NR compound increased the total crosslink density and further increase the ALK loadings decreased the total crosslink density. This observation is in line with the result of the torque difference as presented in Table 2. It surely confirms that torque difference indicates the degree of crosslink density of the filled NR compounds.



**Figure 1.** The effect of ALK loading on crosslink density of the kaolin-filled NR vulcanisates

### 3.3. The effect of ALK on degree of filler dispersion of kaolin-filled NR compounds

Based on the cure characteristics, the degree of kaolin dispersion in NR phases in the presence of ALK was determined qualitatively by using Equation 4 [9, 14,15].

$$L = \eta_r - m_r \quad (4)$$

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 rubber compound. A lower value of  $L$ , at a particular kaolin loading, means a better degree of filler dispersion. The minimum and maximum torques of unfilled NR compounds were 0.05 and 4.85, respectively.

Table 3 shows the values of  $L$  (degree of kaolin dispersion) of kaolin-filled NR compounds. The  $L$  values of kaolin-filled compounds with ALK were lower than that of control compound. The higher was the ALK loading, the lower was the  $L$  value. It was due to the plasticizing effect of ALK which decreased viscosity the filled NR compounds and hence, improved the kaolin dispersion.

**Table 3.** The values of  $L$  for kaolin-filled NR compounds

Dispersion parameter	Kaolin-filled NR compounds with ALK				
	0.0 phr	1.0 phr	3.0 phr	5.0 phr	7.0 phr
Minimum torque	0.39	0.13	0.11	0.09	0.03
Maximum torque	5.34	6.49	6.59	7.57	7.21
$\eta_r$	5.57	1.86	1.57	1.29	0.43
$m_r$	1.09	1.33	1.35	1.55	1.48
$L = \eta_r - m_r$	4.48	0.53	0.22	- 0.26	- 1.05

## 4. Conclusion

From this study, the following conclusions were drawn:

1. Alkanolamide acted as an additional accelerator in the curing process of kaolin-filled natural rubber compounds. It decreased scorch and cure times. The higher the alkanolamide loading, the lower were the scorch and cure times.

2. Alkanolamide acted as a compatibilizer in the kaolin-filled NR compounds. It increased the maximum torque and torque difference of the kaolin-filled natural rubber compounds up to an optimum loading. A 5.0 phr of alkanolamide was the optimum loading.
3. Alkanolamide also acted as internal plasticiser which decreased the minimum torque and improved filler dispersion of kaolin in natural rubber phases. Increases the alkanolamide loading further increases in degree dispersion of kaolin.

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