

## Effects of alkanolamide and epoxidation in natural rubber and epoxidized natural rubbers compounds

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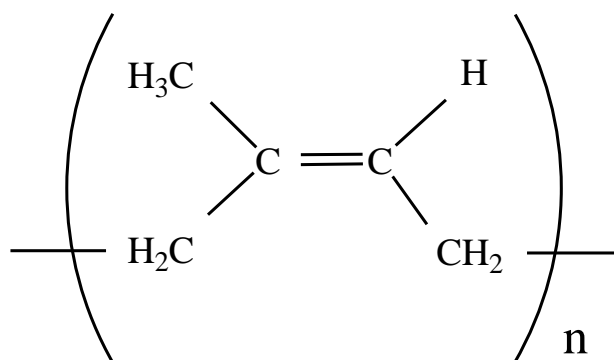
**Abstract.** The effects of alkanolamide (ALK) loading and epoxidation on cure characteristics, crosslink density and mechanical properties of unfilled natural rubber (NR) and epoxidized natural rubbers (ENRs) compounds have been investigated. The NR, ENR-25 and ENR-50 having 0, 25 and 50 mol % of epoxidation were utilised. It was found that the cure and scorch times decreased with increasing ALK loading. At similar ALK loading, ENR-50 possessed the lowest scorch and cure times followed by ENR-25 and NR compounds. Compared to the control compound (without ALK), the mechanical properties of the three rubbers have been enhanced by the ALK addition. However at a similar ALK loading, the mechanical properties viz. tensile modulus, tensile strength and hardness of ENR-50 vulcanisates were the highest followed by ENR-25 and NR vulcanisates. The superiority in mechanical properties of ENR-50 was due to its highest degree of crosslink density.

### 1. Introduction

Natural rubber (NR) is produced from the latex of the *Hevea brasiliensis* tree. Before coagulation, the latex was stabilized with preservatives such as ammonia, formaldehyde, sodium sulfite and hydroxylamine which are added to produce technically-specified, constant viscosity grades of NR. NR contains 93 to 95% of cis-1, 4 polyisoprene as shown in Figure 1. NR is widely used in general purposes, industrial and engineering applications which include hoses, seals, sealant, O-rings, safety boots, tires, bushing and mountings materials.

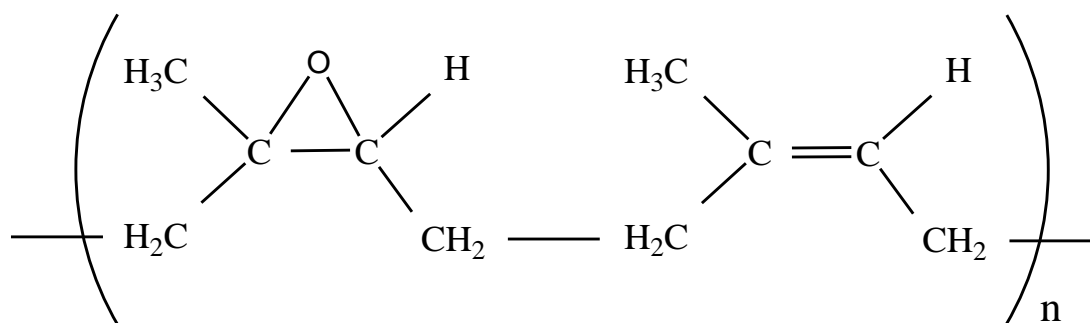
Epoxidised natural rubber (ENR) has been introduced to the rubber world as a chemically modified form of NR, in which some of the unsaturations are converted into epoxide groups which are randomly distributed along the NR chains as shown in Figure 2. Whenever NR is epoxidised, both its physical and chemical properties change according to the epoxidation degree. Commercially, ENR is available in 25 mol% epoxidation (ENR-25) and 50 mol% epoxidation (ENR-50). Many investigations on the preparation of ENR from NR latex and its characteristics have been reported and, practically up to 90 mol% epoxidation is possible [1]. Increasing the degree of epoxidation increases the glass transition temperature ( $T_g$ ) which results in decrease resilience (more damping) and air permeability, increase hysteresis and better wet traction. The epoxidation increases the polarity of the NR which improves its resistance towards hydrocarbon oils. ENR-25 and ENR-50 are strain crystallize [2], which reflected by their gum vulcanisates properties.





**Figure 1.** Molecular structure of natural rubber.

ENR, like NR, are cured by any sulphur accelerated vulcanisation system, but semi efficient (Semi-EV) system or efficient (EV) system type formulation is preferred [2-3]. In general, Semi-EV or EV vulcanisation of ENRs showed properties comparable to those of their NR counterparts. While Conventional (CV) system is not recommended for ENRs because of their poor ageing characteristics [4].



**Figure 2.** Molecular structure of epoxidised natural rubber.

This study reports the utilising of alkanolamide (ALK) as a rubber additive for NR and ENRs. The effects of ALK addition and degree of epoxidation on cure characteristics, crosslink density and mechanical properties of unfilled NR and ENRs compounds were investigated.

## 2. Materials and Methods

### 2.1. Materials

NR grade SMR-L was obtained from Guthrie (M) Sdn. Bhd., Seremban, Malaysia. ENR 25 and ENR 50 were supplied by the Rubber Research Institute Malaysia (RRIM). Other compounding ingredients such as sulphur (S), zinc oxide (ZnO), stearic acid, N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD), Mercapto benzothiazolyl disulphide (MBTS) were supplied by Bayer Co. (M) Sdn. Bhd., Petaling Jaya, Selangor, Malaysia. All materials were used as supplied. The ALK was synthesized in our laboratory using Refined Bleached Deodorized Palm Stearin (RBDPS) and diethanolamine. The reaction procedure and molecular characterization of the ALK was given in the previous report [5] and 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 and cure characteristics

A semi-efficient vulcanisation system was applied for the compounding. The compounding procedure was performed on a two-roll mill (Model XK-160). Table 1 displays the compound formulation of unfilled NR and ENRs compounds with and without ALK. The compounding ingredients were mixed using a laboratory two-roll mill, Model XK-160. The cure characteristics of the unfilled rubbers

compounds were determined at 150 °C using a Monsanto Moving Die Rheometer (MDR 2000). The respective scorch time ( $t_{s2}$ ), cure time ( $t_{90}$ ) and torque difference ( $M_H - M_L$ ) were obtained from the rheograph according to ISO 3417. The compounds were subsequently compression moulded using a stainless steel mould at 150 °C with a pressure of 10 MPa using a laboratory hot-press based on the respective curing times.

**Table 1.** Composition of the rubber compounds

Ingredients	Content (phr) <sup>a</sup>
Rubber <sup>b</sup>	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 and 1.0

<sup>a</sup> parts per hundred parts of rubber

<sup>b</sup> NR, ENR-25 or ENR-50

### 2.3. Tensile and hardness properties

Dumbbell-shaped samples were cut from the moulded sheets. Tensile tests were 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) and stress at 100% elongation (M100), stress at 300% elongation (M300) and elongation at break (EB) were investigated. The hardness measurements of the samples were obtained according to ISO 7691-I using a Shore A type manual Durometer.

### 2.4. Measurement of crosslink density

Swelling tests on the unfilled NR and ENRs 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 [6-7].

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

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

where  $\rho$  is the rubber density which are 0.92 g/cm<sup>3</sup> and 0.95 g/cm<sup>3</sup> respectively,  $V_s$  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 NR/ENRs = 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 addition on cure characteristics

The effects of ALK addition on cure characteristics of the unfilled NR and ENRs compounds are shown in Table 2. As can be seen, the additions of each 0.2 phr of ALK decreased the scorch and cure times of those control compounds. Cure enhancement phenomena were observed. It was due to the amine content of ALK [8-11], because amine is an accelerator for rubber compounds [8].

The higher the ALK loading, the lower were the scorch and cure times. It meant that increases the ALK loading caused increases in amount of amine and hence, the faster were the curing processes.

**Table 2.** The effects of ALK on cure characteristics and crosslink density of NR and ENRs compounds

NR / ENRs Compounds	ALK Loadings					
	0.0 (Control)	0.2	0.4	0.6	0.8	1.0
<b>SMR-L/NR</b>						
ts <sub>2</sub> , min.	4.59	4.52	4.24	3.96	3.74	3.73
t <sub>90</sub> , min.	7.13	7.05	6.65	6.45	6.00	5.83
M <sub>H</sub> —M <sub>L</sub> , dN.m	4.77	4.85	4.97	5.21	5.12	4.89
Crosslink dens.*	33.77	33.78	34.16	36.18	35.82	33.93
<b>ENR-25</b>						
ts <sub>2</sub> , min.	3.56	3.24	2.96	2.74	2.54	2.43
t <sub>90</sub> , min.	6.03	5.59	5.55	5.51	5.45	5.30
M <sub>H</sub> —M <sub>L</sub> , dN.m	5.12	5.19	5.25	5.79	5.44	5.24
Crosslink dens.*	34.05	34.17	35.62	38.15	37.42	34.34
<b>ENR-50</b>						
ts <sub>2</sub> , min.	2.53	2.47	2.44	2.38	2.33	2.19
t <sub>90</sub> , min.	5.46	5.38	5.34	5.26	5.20	4.99
M <sub>H</sub> —M <sub>L</sub> , dN.m	6.31	6.53	6.83	6.85	6.89	5.96
Crosslink dens.*	39.84	40.28	41.96	44.08	46.06	43.65

\* Crosslink density ( $\times 10^5$  mol/cm<sup>3</sup>)

At a similar ALK loading, the scorch and cure times of both ENRs were shorter than those of NR. It was due to the presence of epoxide groups in the ENRs molecules. The epoxide groups activated the adjacent double bonds and caused them a more susceptible and ready for curing [12]. Compared to ENR-25, ENR-50 has more epoxide groups. Therefore, the scorch and cure times of ENR-50 were shorter than those of ENR-25.

Table 2 also shows that the additions of each 0.2 phr of ALK into the control compounds increased the torque differences. NR and ENR-25 have similar trends of torque differences which were increased with the addition of ALK up to 0.6 phr, and decreased beyond the loading. In contrast to both rubbers, the torque differences of ENR-50 increased with the ALK addition at a relatively higher loading, 0.8 phr, and then decreased with further increase in the ALK loading.

Theoretically, torque difference represents shear dynamic modulus which indirectly related to the crosslink density of a rubber compound [9-12]. The increases of the torque difference up to ALK optimum loadings (0.6 phr for NR and ENR-25; 0.8 phr for ENR-50) were due to the function of ALK as a (secondary) accelerator during the curing of the rubbers compounds. Although an accelerator constitutes a very small part of a rubber compound, it has a profound influence on the nature of curing [8].

The decreases of the torque differences, beyond the optimum ALK loadings, were due to the excessive amount of ALK, which decreased the total crosslink density.

At a similar ALK loading, the torque differences of both ENRs were higher than that of NR. It was due to the degree of epoxidation which formed additional amine-epoxy crosslinks [12] in curing processes of the rubbers compounds. Compared to ENR-25, ENR-50 with more epoxide groups might form a higher degree of additional amine-epoxy crosslinks.

### 3.2. The effects of ALK addition on crosslink density

The crosslink density of the unfilled NR and ENRs compounds with and without ALK was determined by using Equations (1)-(3) [6] and the results are shown in Table 2. The results of crosslink density were in line with those of torque difference. The crosslink density increased up to the optimum ALK loadings, and then decreased beyond them.

The increases in crosslink density up to the optimum ALK loadings were due to the function of ALK as a secondary accelerator and the nature of the molecule. The nitrogen atom or amine constituent of ALK activated not only the rubbers but also the elemental sulphur during curing process. Together with the others curatives, the amine formed intermediate complexes which attached the available elemental sulphur to rubbers chains more efficient [13] causing higher in degree of crosslinking. The nitrogen atom also acted as a hydrogen acceptor and amine accelerators activated the elemental sulphur and/or the rubber for the crosslinking reaction [13].

The decreases in crosslink density beyond the optimum ALK loadings were most probably due to the softening or lubricating effect of the excessive ALK which caused in decreases in crosslink density. This can be due to the phenomenon of dissolving a part of the elemental sulphur into the excessive ALK, and as a consequent less sulphur was attached to the rubbers chains.

### 3.3. The effects of ALK addition on mechanical properties

The effects of ALK loading on mechanical properties of the unfilled NR and ENRs vulcanisates are shown in Table 3. As can be seen, the additions of each 0.2 phr ALK into the control compounds increased the elongation at break (EB). Increases the ALK loading further increased the EB or the extensibility of the rubbers vulcanisates. It might be due to the function of ALK as an internal plasticiser [5]. A plasticiser provides a monolayer in the rubbers compounds which causes in free volume and hence, allowing a more mobility/flexibility for the chains of the rubbers [13-14]. Increases the ALK loading have the same effect as increases in free volume that enhanced the flexibility or the extensibility of the unfilled rubbers vulcanisates. Therefore, as shown in Table 3; the higher ALK loading the higher were the EB.

**Table 3.** The effects of ALK on mechanical properties of NR and ENRs compounds

NR / ENRs Vulcanisates	ALK Loadings					
	0.0 (Control)	0.2	0.4	0.6	0.8	1.0
<b>SMR-L/NR</b>						
M100, MPa	0.538	0.544	0.561	0.586	0.545	0.516
M300, MPa	1.235	1.236	1.311	1.364	1.267	1.231
EB, %	1070.0	1095.7	1116.5	1141.5	1154.0	1172.0
TS, MPa	17.7	19.3	19.5	20.1	18.4	16.5
Hardness, Shore A	36	37	39	40	38	37
<b>ENR-25</b>						
M100, MPa	0.549	0.556	0.569	0.595	0.554	0.542
M300, MPa	1.334	1.391	1.403	1.454	1.366	1.350
EB, %	803.4	863.3	877.2	886.6	893.4	913.4
TS, MPa	18.0	19.7	20.2	20.9	19.7	19.4
Hardness, Shore A	37	38	40	41	39	38

<b>ENR-50</b>						
M100, MPa	0.637	0.721	0.732	0.753	0.760	0.692
M300, MPa	1.610	1.771	1.781	1.793	1.891	1.689
EB, %	772.5	825.0	837.5	842.9	865.0	869.8
TS, MPa	19.5	20.4	21.0	21.4	21.8	20.0
Hardness, Shore A	39	40	41	42	43	40

At a similar ALK loading, The EBs of both ENRs were lower than that of NR. It was due to decreases in degree of crystallinity as the mole % epoxidation increased from NR to ENR 50 [12]

As shown in Table 3, the ALK additions increased the M100, M300, TS and hardness slightly up to some maximum levels (at 0.6 phr for NR and ENR-25; and 0.8 phr for ENR-50). Beyond the loadings caused in decreases those mechanical properties. Tensile strength and hardness exhibited similar trends. Both M100 and M300 are typical measures stiffness or hardness of a rubber vulcanisate [15] Modulus or stiffness/hardness and also tensile properties are dependent mainly on degree of crosslink [16-18]. The increases in mechanical properties up to the ALK optimum loadings were due to a higher degree of crosslink density. The decreases in the properties beyond the ALK optimum loadings were due to a lower degree of crosslink density and a more pronounced softening effect of ALK.

At a similar ALK loading, the mechanical properties of both ENRs were higher than those of NR. Presumably, it was due to the specific chemical crosslinking taking place between the epoxy groups and ALK during cure process and hence, contributed to a higher degree of crosslink density.

#### 4. Conclusion

Alkanolamide can be utilised as a new curative additive in unfilled natural and epoxidized natural rubbers compounds. As an accelerator, it increased the cure rate. It was also increased the crosslink density, hardness and tensile properties up to 0.6 phr (for natural and epoxidized natural rubber 25% epoxidation); and up to 0.8 phr (for epoxidized natural rubber 50% epoxidation). The optimum loadings were 0.6 phr of alkanolamide for natural and epoxidized natural rubber 25% epoxidation; and 0.8 phr for epoxidized natural rubber 50% epoxidation. The alkanolamide also can be utilised as an internal plasticiser which increased the flexibility or elongation at break of the unfilled natural and epoxidized natural rubbers compounds.

#### Acknowledgement

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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