

Effects of alkanolamide addition on crosslink density, mechanical and morphological properties of chloroprene rubber compounds

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Abstract. The effects of alkanolamide (ALK) addition on crosslink density, mechanical and morphological properties of unfilled polychloroprene rubber (CR) compounds were investigated. The ALK was prepared from Refined Bleached Deodorized Palm Stearin (RBDPS) and diethanolamine and -together with magnesium and zinc oxides- incorporated into the unfilled CR compounds. The ALK loadings were 0.5, 1.0, 1.5 and 2.0 phr. It was found that ALK enhanced crosslink density, tensile modulus, tensile strength and hardness especially up to a 1.5 phr loading. Scanning Electron Microscopy (SEM) proved that the 1.5 phr of ALK exhibited the greatest matrix tearing line and surface roughness, due to the highest degree of crosslink density and mechanical properties.

1. Introduction

In curing process of polychloroprene rubber or chloroprene rubber (CR), the specialty rubber is traditionally cured by both magnesium oxide (MgO) and zinc oxide (ZnO), at satisfactory loadings of 4 and 5 phr, respectively. Besides MgO and ZnO, ethylene thiourea (ETU) is widely used as the curing accelerator for CR [1].

Nowadays, some newer curing agents such as thiophosphoryl disulfides, dimethyl l-cystine, and cetyltrimethylammonium maleate, have been reported [2-3]. Although there are many published papers on different curing agents for CR, the most practical curing agents are still ETU, MgO and ZnO, due to the superior mechanical properties of the CR vulcanisates. ETU is a toxic material and is suspected to be carcinogenic [4-5] and hence, the appearance of an alternative curing accelerator for CR, which is capable of providing CR vulcanisates equivalent or superior to those provided by the ETU and both metal oxides, has been in demand.

Some previous works revealed that alkanolamide (ALK) functioned as an accelerator in unfilled NR compounds [6-7], silica-filled NR compounds [8-9], carbon black-filled NR, SBR and ENR compounds [10-11]. Therefore, this study reports the utilising of ALK as an additive ingredient for unfilled CR compounds. The effects of ALK loading on crosslink density, mechanical and morphological properties of unfilled CR compounds were investigated.



2. Experimental

2.1. Materials

Polychloroprene rubber (CR) [Skyprene B-30] was purchased from TOSOH Co. (Japan). Other compounding ingredients such as MgO, ZnO, stearic acid and sulphur were all obtained from Bayer Co. (M). Sdn. Bhd., Petaling Jaya, Selangor, Malaysia. All materials were used as supplied. The ALK was prepared using RBDPS and diethanolamine. The procedure of the ALK preparation was given in our previous report [8, 11]. 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 CR 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 CR-based recipes used in this study.

Table 1. The composition and designation of the CR compounds

Ingredients	Content (phr)*	Designation				
		CR-A/0.0 (Control)	CR-A/0.5	CR-A/1.0	CR-A/1.5	CR-A/2.0
CR	100.0	100.0	100.0	100.0	100.0	100.0
MgO	4.0	4.0	4.0	4.0	4.0	4.0
ZnO	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0
Sulphur	2.0	2.0	2.0	2.0	2.0	2.0
ALK	0.0 – 2.0	0.0	0.5	1.0	1.5	2.0

* parts per hundred parts of rubber

2.3. Measurement of crosslink density

Swelling tests on the CR vulcanisates were performed in toluene in accordance with ISO 1817. The cured test pieces (30 mm × 5 mm × 2 mm) were weighed using an electrical 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 60 °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 [12-13].

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

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

Where ρ is the rubber density (ρ of CR = 0.96 g/cm³), V_s is the molar volume of the toluene (V_s = 106.4 cm³/mol), V_r is the volume fraction of the polymer in the swollen specimen, Q_m is the weight increase of the blends in toluene and χ is the interaction parameter of the rubber network-solvent (χ of CR = 0.4284). The degree of the crosslink density is given by;

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

2.4. 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 and stress at 100% elongation (M100), 300% elongation (M300), and elongation at break were investigated. The hardness measurements of the samples were performed according to ISO 7691-I using a Shore A type manual durometer.

2.5. Scanning Electron Microscopy (SEM)

The tensile fractured surfaces of the CR vulcanisates were examined using a Zeiss Supra-35VP scanning electron microscope (SEM) to obtain information regarding the possible presence of micro-defects. The fractured pieces were coated with a layer of gold to eliminate electrostatic charge build-up during the examination.

3. Results

3.1. The crosslink density

Table 2 shows the effect of ALK loading on crosslink density of CR compounds. As shown, the crosslink density of the CR-A/0.5 compound was higher than that of the control compound. The addition of 0.5 phr of ALK increased the crosslink density of CR compound significantly and hence, the ALK was considered as an additional vulcanising agent for the CR system. Increases the ALK loading up to a 1.5 phr caused a further increase in crosslink density. Beyond the loading started to decrease the crosslink density.

Table 2. Crosslink density dan mechanical properties of the unfilled-CR vulcanisates with/without ALK

Mechanical Properties	Unfilled CR vulcanisates				
	CR-A/0.0 (Control)	CR-A/0.5	CR-A/1.0	CR-A/1.5	CR-A/2.0
M100, MPa	0.72	0.78	0.82	0.83	0.78
M300, MPa	1.30	1.31	1.37	1.38	1.29
TS, MPa	13.7	15.5	17.2	18.9	17.8
EB, %	1,612.3	1,590.3	1,536.8	1,487.0	1,516.3
Hardness, Shore A	55	56	57	58	56
Crosslink density, ($\times 10^{-5}$ mol/cm ³)	10.37	16.95	19.92	23.79	13.96

3.2. The mechanical properties

Table 2 shows the effects of ALK loading on the mechanical properties of the CR compounds. As shown, the addition of up to 1.5 phr of ALK into the CR compound increased the M100 and M300, hardness and TS. However, further loading increases decreased those properties. The modulus (or stiffness/hardness) and tensile properties of a rubber vulcanisate are dependent mainly on the degree of crosslink density [11, 14-15]. The improvements of M100, M300, hardness and TS up to 1.5 phr were

due to the function of ALK as an additional curing agent, which increased the degree of crosslink density of the CR compounds. This explanation is in line with the crosslink density trend shown in Table 2 and the morphological properties as shown later on in Fig. 1.

The deterioration of properties beyond 1.5 phr was due to the excessive loading of ALK, which decreased the total crosslink density. Presumably, the excessive amount of ALK formed a boundary layer, which dissolved and coated a part of the curatives (S, MgO and ZnO); and hence, decreased the formation of crosslinking of CR by those curatives. This explanation is again in line with the result of crosslink density shown in Table 2.

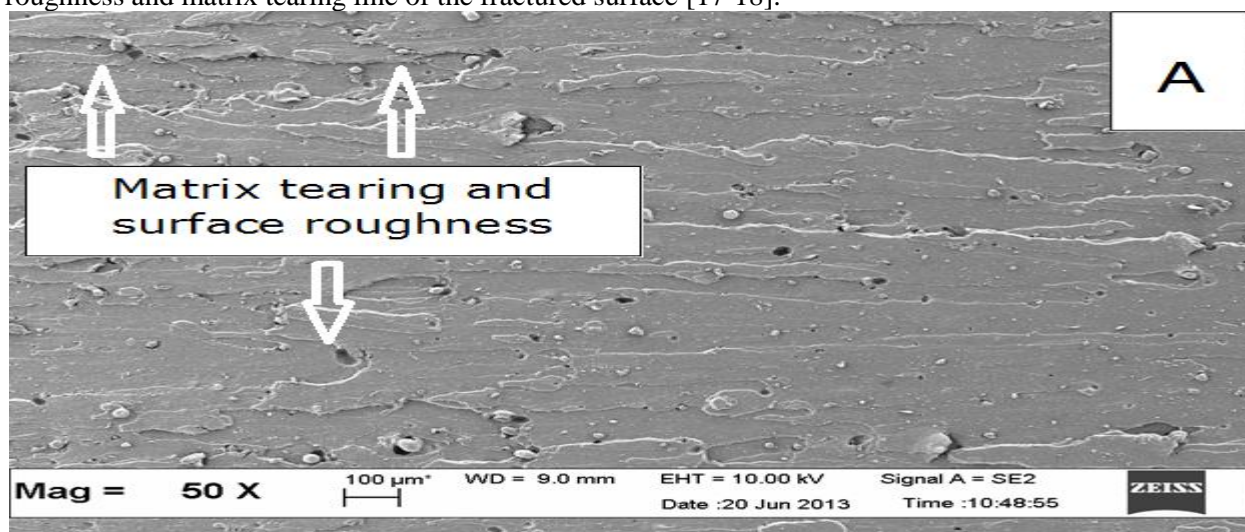
Table 2 shows the effect of ALK loading on the EB of the CR vulcanisates. As shown, ALK decreased the EB by up to 1.5 phr, and then increased it slightly as the loading further increased. EB depends mainly on the degree of crosslink density [14]. The reduction of EB by up to 1.5 phr was simply attributed to the higher degree of crosslink density; which immobilised the CR segments more pronounced. However, beyond the 1.5 phr of ALK loading, EB was found to increase. An explanation for this is again given by the excessive effect of ALK, which decreased the crosslink density and causes a more free movement of the CR segments.

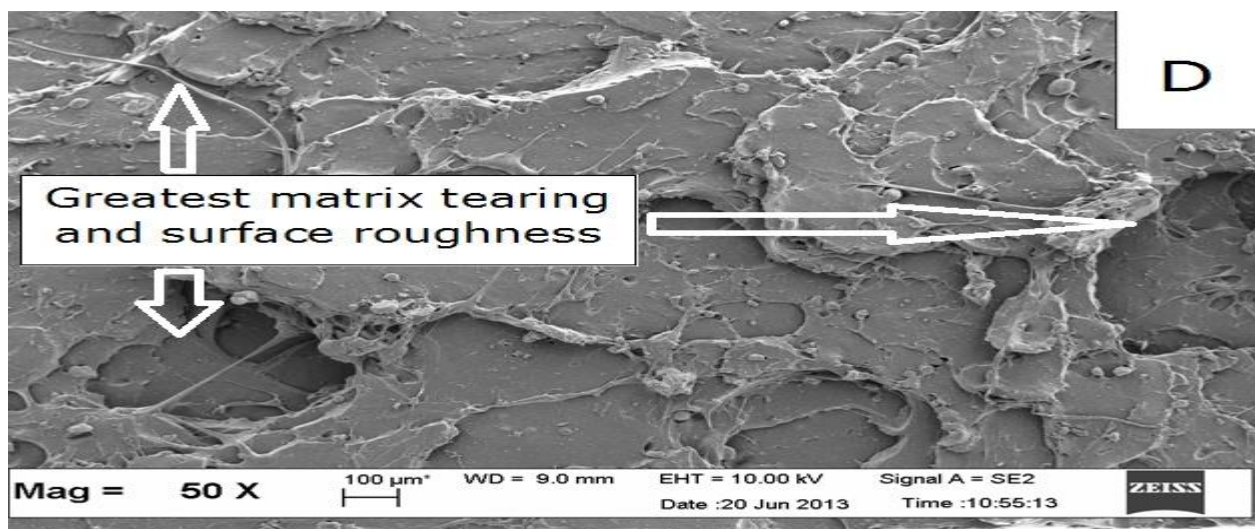
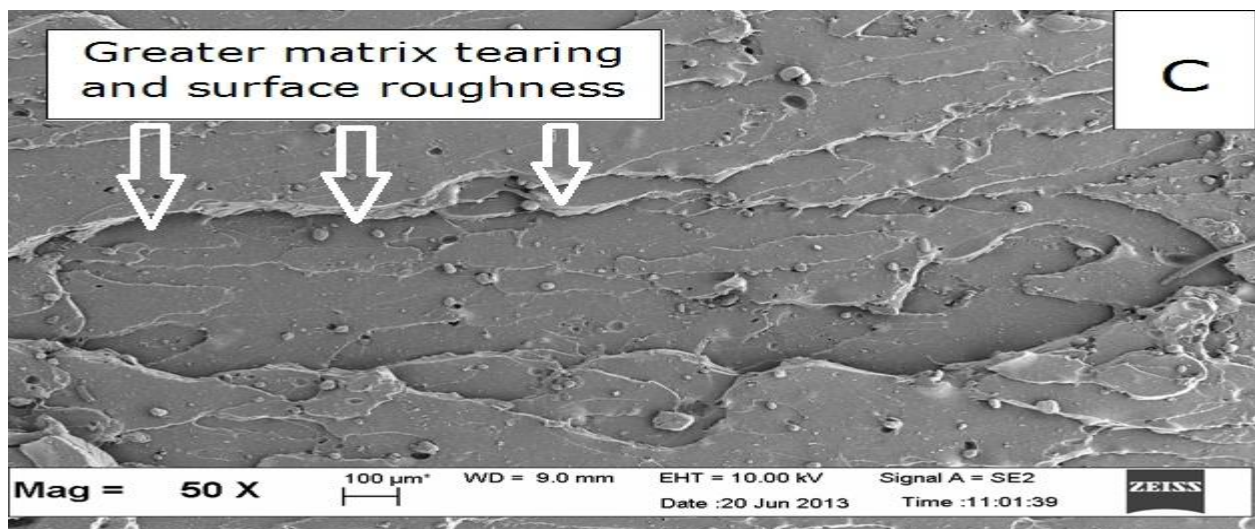
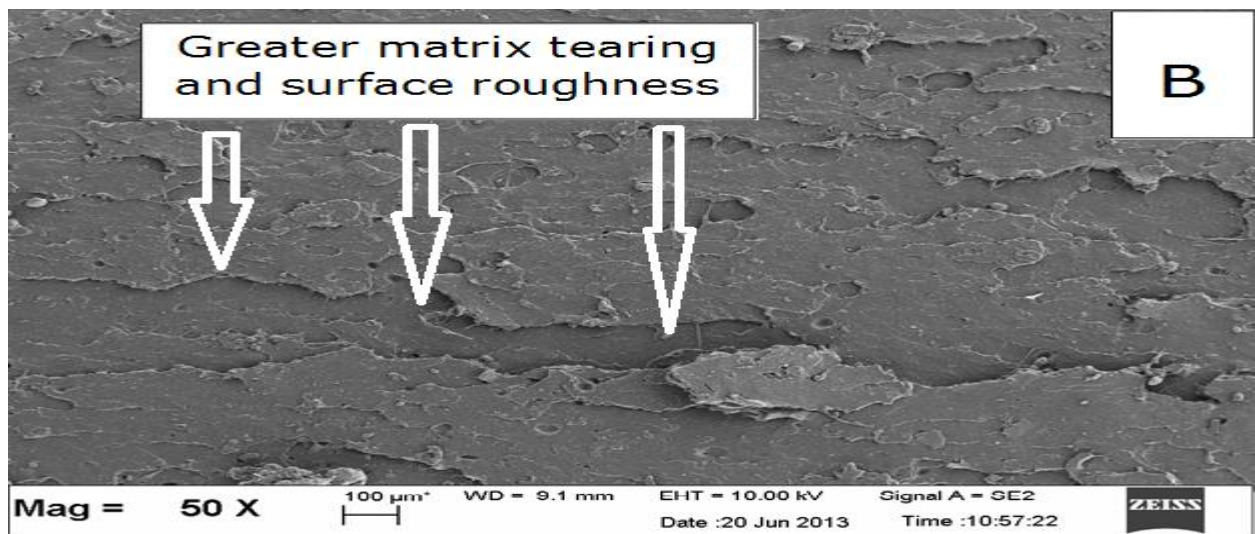
3.3. The morphological properties

Figure 1 shows SEM micrographs (magnification 50 X) of the fractured surfaces of the CR vulcanisates with and without ALK. It was clearly observed that the micrographs of CR vulcanisates with ALK (CR-A/0.5, CR-A/1.0, CR-A/1.5, and CR-A/2.0) – as shown in Figs. 1b, c, d, and e - exhibited a greater matrix tearing lines and surface roughness than that of the CR vulcanisate without ALK (as shown in Fig. 1a). The rough surface of a rubber vulcanisate indicates that the matrix tearing relates to the value of tensile strength (ref). The rougher the surface, the higher is the tensile strength [16-17]. As shown in Fig. 1, the rougher surfaces also indicated a stronger interaction within the CR segments and that the micrographs of the tensile fractured surfaces were in good agreement with the results of TS as shown in Table 2.

An enhancement in rupture energy (due to a stronger interaction within the CR segments) was responsible for the roughness and matrix tearing line of the fractured surface. The 1d-micrograph of unfilled CR vulcanisate with 1.5 phr of ALK (vulcanisate CR-A/1.5) exhibited the greatest matrix tearing and surface roughness. This indicates the highest degree of crosslink density, which altered the interactions between CR segments into the strongest ones; and thus, caused an increase in tensile strength.

The micrographs of the tensile fractured surfaces were in good agreement with the results obtained by previous workers. They reported that an increase in rupture energy was responsible for the roughness and matrix tearing line of the fractured surface [17-18].





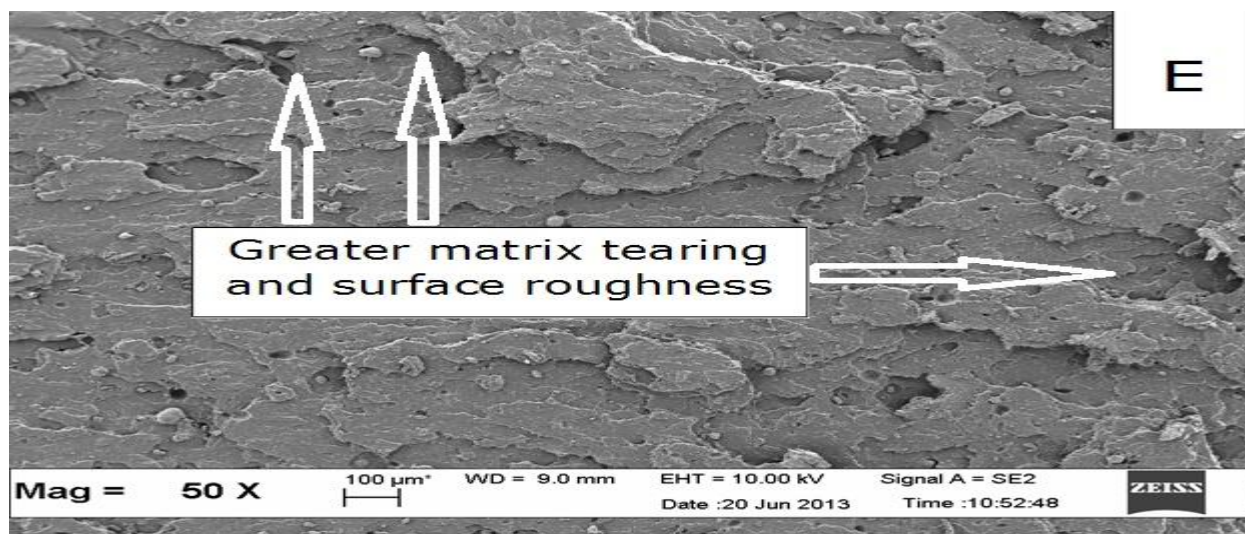


Figure 1. The SEM micrographs of CR vulcanisate failed fracture at a magnification of 50 X;
(A) CR-A/0.0 (B) CR-A/0.5 (C) CR-A/1.0 (D) CR-A/1.5 (E) CR-A/2.0

4. Conclusion

From this study, the following conclusions were drawn:

1. Alkanolamide increased the crosslink density and mechanical properties of magnesium-zinc oxides vulcanised unfilled chloroprene rubber compounds, especially up to a 1.5 phr loading.
2. The enhancements of the crosslink density and mechanical properties were due to the function of alkanolamide as a curative additive in unfilled chloroprene rubber compounds.
3. Morphological studies of the tensile fractured surfaces of the unfilled chloroprene vulcanisates indicated that alkanolamide interacted well with chloroprene rubber compounds.

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