The silica-filled polychloroprene rubber in the addition of alkanolamide: tensile and vulcanization properties

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Abstract. Alkanolamide as a type of fatty alcohols was compounded to improve the tensile and vulcanization properties of silica filled polychloroprene rubber (CR) using a system of semi efficient vulcanization. The CR was filled by silica filler with a certain concentration at thirty phr and the alkanolamide was compounded within silica-reinforced CR at varied amounts i.e. 0.0, 1.0, 3.0, 5.0 and 7.0 phr. The results showed that alkanolamide increased the times to optimum cure, maximum and minimum torques and torque change. It also reduced the tensile moduli but increased the breaking elongations. The tensile strength was increased up to a three phr of alkanolamide incorporation and, the three phr of alkanolamide was an optimum concentration where silica filled CR vulcanizate with three phr of alkanolamide concentration had tensile strength with the highest value.

1. Introduction

CR is widely known as Neoprene is an oil resistant synthetic rubber [1] and it is the most important specialty elastomer. As produced in 1932 firstly, CR has got an excellent position in market because the encouraging combination of engineering or technical properties of CR vulcanizates which are used chiefly within the industry of rubber [2].

The molecular structure of CR, as shown in Figure 1, is similar to that of natural rubber; excluding that atoms of chlorine has changed the methyl groups [3]. The existence of chlorine makes the vulcanization system of CR to be commonly different to other diene elastomers [3, 4]. The atoms of chlorine reduce the double bonds reactivity of the CR chains and hence, the sulphur reactivity becomes weaker. The oxides of metal, thiuram and ethylene thiourea (ETU) based vulcanization agents are popularly used as the vulcanization system for CR [4]. The ETU is used as the vulcanization accelerator and it is a toxic and carcinogenic chemical [5]. As diene elastomers are vulcanized by a single chemical such as peroxide or sulphur, while CR is traditionally vulcanized by both zinc oxide (ZnO) and magnesium oxide (MgO) with satisfactory concentrations of 5 and 4 phr, respectively [4].
And hence, this observation describes the development in CR vulcanization process in the presence of alkanolamide together with ZnO and MgO. The influences of alkanolamide incorporations on tensile and vulcanization properties of the vulcanizates of silica filled CR were observed.

2. Methodology

2.1. Rubber and rubber chemicals
CR, sulphur, ZnO, MgO, TBBS, stearic acid and precipitated silica were supplied by local company in Medan, Indonesia. Alkanolamide, \( \text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OH} \), was synthesized by reacting stearin and ethanolamine [6]

2.2. Rubber compounding
The CR and rubber chemicals were mixed based on a sulphur accelerated vulcanization system. The steps of rubber compounding were made based on ASTM D3184-80 on a lab-type two-roll mill and, Table 1 tabulates the recipe for CR compounding.

| Chemicals        | Content (phr.) |
|------------------|----------------|
| CR               | 100            |
| ZnO              | 5              |
| MgO              | 4              |
| Stearic acid     | 1              |
| Sulphur          | 2              |
| Precipitated silica | 30          |
| TBBS             | 1              |
| Alkanolamide     | 0; 1; 3; 5 and 7 |

2.3. Properties of vulcanization
The properties of CR vulcanizates include: \( t_{90} \) - optimum cure time; \( M_x \) - max. torque; \( M_n \) - min. torque; the change in torque (based on ISO 3417) and, were determined by a Rheometer (MDR 2000). The CR compounds were Vulcanized at 150 °C.

2.4. Properties of tensile
The properties of tensile of CR vulcanizates were observed based on ASTM D-882 using tensometer (rate of extension at 500 mm/minute).
3. Results and discussion

3.1. Properties of vulcanization
The influences of alkanolamide incorporations on vulcanization properties of silica filled CR vulcanizates are visualized in Figs. 2 to 5. As visualized at Fig. 2, the times to optimum cure of CR vulcanizates with alkanolamide were higher. A bigger alkanolamide concentration tent to increase the time to optimum cure and hence, the alkanolamide was a curative additive.

![Figure 2. Optimum cure time vs alkanolamide concentration.](image)

As visualized at Fig. 3, the one phr alkanolamide incorporation increased minimum torque whatever means the viscosity of a rubber vulcanizate [7] [8]. The increase in CR viscosity was because of supplementary usage of the alkanolamide as a curative agent. The higher alkanolamide content, the higher viscosity was.

![Figure 3. Minimum torque vs alkanolamide concentration.](image)
As visualized at Figs. 4 and 5, the incorporation of one phr of alkanolamide increased maximum torque and torque change of control vulcanizate of CR. The maximum torque and torque change were further increased by the incorporation of alkanolamide up to a seven phr. Torque change means the degree of crosslinks of a rubber vulcanizate [9][10]. The higher the value, the higher the crosslinks degree is. The increases in crosslinks up to the seven phr of alkanolamide were because of both physical-chemical properties of the additive. Assumedly, the chlorine groups triggered chemically both the CR-elemental sulphur during vulcanization and the hydroxyl groups-curatives interactions made some intermediate complexes whatever attached the sulphur to CR more densely, causing a higher state of vulcanization.

![Figure 4. Maximum torque vs alkanolamide concentration.](image1)

![Figure 5. Torque difference vs alkanolamide concentration.](image2)
Substantially, the oily properties of alkanolamide made it has the potential to be used as an extra plasticizer that improve degree of silica dispersion and silica to CR interactions, respectively. The silica to CR interactions are interpreted as auxiliary physical crosslinks and together with sulphide crosslinks determine the total crosslinks [11][12] [13] [14].

3.2. The tensile properties
The influences of alkanolamide incorporations on tensile properties of silica filled CR vulcanizates are tabulated in Table 2. Alkanolamide reduced M300 and M100. The bigger the alkanolamide concentration, the softer the tensile moduli were. Alkanolamide made softer the silica filled CR vulcanizates. It was attributed to the action of alkanolamide as the plasticizing rubber chemical.

The tensile strength or TS was enhanced slightly up to three phr of alkanolamide incorporation and then was diminished with a further increase in alkanolamide concentration. The increases in TS were attributed to improvement in degree of silica dispersion as well as crosslinks. The reduction in TS above a three phr of alkanolamide incorporation was attributed to curative absorbing affection that diminished crosslinks.

The one phr of alkanolamide incorporation increased percentage of breaking elongation or EB and bigger alkanolamide concentration caused in a further increase in EB. Repeatedly, it was attributed to the action of alkanolamide as a plasticizer which level up the durability of a rubber vulcanizate [6].

| CR vulcanizates | Alkanolamide in phr |
|-----------------|---------------------|
|                 | 0.0 | 1.0  | 3.0  | 5.0  | 7.0  |
| M300 - Mega Pascal | 5.66 | 4.75 | 4.43 | 4.06 | 3.63 |
| M100 - Mega Pascal | 2.39 | 2.10 | 2.08 | 1.84 | 1.76 |
| TS - Mega Pascal   | 16.7 | 17.1 | 19.5 | 18.0 | 16.8 |
| EB - Percent       | 706.7 | 743.3 | 753.3 | 783.3 | 816.7 |

4. Conclusion
1. As a co curing rubber chemical, the alkanolamide raised the time to optimum cure and minimum torque of the silica filled polychloroprene rubber vulcanizates. The bigger the alkanolamide concentration, the longer the time to optimum cure and the bigger the minimum torque were.
2. As a plasticizing rubber chemical, the alkanolamide reduced tensile modulus but increased the breaking elongations and degree of silica dispersion. The bigger the alkanolamide concentration, the more significant was the plasticizing affection.
3. Alkanolamide increased the torque change and tensile strength of silica filled polychloroprene rubber vulcanizates up to a three phr of incorporation.
4. The three phr was the optimum concentration of alkanolamide incorporation for silica filled polychloroprene rubber vulcanizates.

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