IOP Conf. Series: Materials Science and Engineering **309** (2018) 012104 doi:10.1088/1757-899X/309/1/012104

Effects of alkanolamide loading on swelling, rheometric and tensile properties of chloroprene rubber compounds

I Surya*[1,2], H Ismail[3]
[1]Department of Chemical Engineering, Universitas Sumatera Utara, Medan, 20155, Indonesia
[2]Sustainable Energy and Biomaterial Center of Excellence, Faculty of Engineering, Universitas Sumatera Utara, Medan, 20155, Indonesia
[3]School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300, Nibong Tebal, Penang, Malaysia

*E-mail: indradanas@yahoo.com

Abstract. The effects of Alkanolamide (ALK) addition on swelling, rheometric and tensile properties of unfilled chloroprene rubber (CR) compounds were investigated. The ALK was prepared from Refined Bleached Deodorized Palm Stearin and diethanolamine and -together with magnesium and zinc oxides- incorporated into the CR compounds. The ALK loadings were 0.5, 1.0, 1.5 and 2.0 phr. It was found that ALK enhanced the cure rate and torque difference of the CR compounds. ALK also enhanced the tensile modulus and tensile strength; especially up to a 1.5 phr loading. The swelling test proved that the 1.5 phr of ALK exhibited the highest degree of crosslink density which caused the highest in tensile modulus and tensile strength.

1. Introduction

Polychloroprene or chloroprene rubber (CR) is a popular specialty elastomer. Its areas of application within the rubber field are widespread such as transmission belts, conveyor belts, moulded goods, cable jackets, seals, coated fabrics, etc. It is excellent in mechanical properties, ozone and oil resistances, flame retardancy, weatherability, special cohesiveness, moderate resistance to most chemicals and ease of processability [1-4]. The molecular structure of CR is similar to that of natural rubber (ref); except that chlorine has replaced the methyl groups [5-6]. The presence of chlorine causes the cure system of CR to be generally different from that of NR [7]. The chlorine atoms decrease the reactivity of double bonds on the CR backbone and hence, the reactivity with sulphur becomes less.

Magnesium oxide (MgO), zinc oxide (ZnO) and ethylene thiourea (ETU) are always used as the cure system for CR. ETU is used as the curing accelerator for CR. It is a toxic material and suspected to be carcinogenic [8]. Therefore, 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.

This study reports the using of Alkanolamide (ALK) as a rubber additive for CR. The effects of ALK addition on crosslink density, rheometric and tensile properties of CR compounds were investigated.

IOP Conf. Series: Materials Science and Engineering **309** (2018) 012104 doi:10.1088/1757-899X/309/1/012104

2. Materials and Methods

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 [9].

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-0.0 (Control)	CR-0.5	CR-1.0	CR-1.5	CR-2.0
CR	100.0	100.0	100.0	100.0	100.0	100.0
Magnesium oxide	4.0	4.0	4.0	4.0	4.0	4.0
Zinc oxide	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. Rheometric properties
The rheometric properties of the CR compounds were determined at 150 °C using a Monsanto Moving Die Rheometer (MDR 2000). The rheometric properties such as scorch time (ts_2), cure time (t_{90}), minimum torque (M_L) and maximum torque (M_H) were measured according to ASTM D2084. The CR 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.

2.4. Tensile properties
Dumbbell-shaped samples were cut from the molded sheets according to ASTM D 412-93. Tensile tests were performed at a crosshead speed of 500 mm/min. Tensile tests were carried out with a universal tensile machine Instron 3366 to determine the tensile properties in terms of tensile strength (TS), stresses at 100% and 300% elongations (M100 and M300) and elongation at break (EB).

2.5. Swelling properties
The swelling test was performed in toluene according to ISO 1817. Cured test pieces of the compounds of dimension (30 mm x 5 mm x 2 mm) were weighed using an electrical balance and swollen in toluene until equilibrium, which took 72 h at room temperature. The samples were removed from the liquid, the toluene was removed from the samples surfaces, and the weight was determined. Calculation of the change in mass is as follows;

$$\text{Swelling (\%)} = \frac{W_2 - W_1}{W_1} \times 100\% \qquad (1)$$

Where W_1 is the initial mass of specimen (gram) and W_2 is the mass of specimen (gram) after immersion.

3. Results and Discussion

3.1. The rheometric properties

Table 2 shows the rheometric, swelling and tensile properties of CR compounds with and without ALK. The addition of up to 2.0 phr of ALK into the unfilled CR compound produced CR with ALK compounds with shorter scorch (ts_2) and cure (t_{90}) times, compared to the control compound (CR-0.0). The ALK acted as a curative additive since it affected the rheometric properties of unfilled CR compounds. It increased the cure rate and it was considered as an accelerator. Any rubber additive that improves the action of a curing agent to speed up the resultant cure, even though it constitutes a very small part of a rubber compound, is classified as an accelerator [10]. Amine is an accelerator ingredient of rubber compounds [10] and hence, the amine constituent of ALK caused in the cure enhancement [11-13].

The higher the ALK loading, the longer were the scorch and cure times. It was due to ALK functioning as an additional curing agent (discussed later).

The torque difference of the CR-A0.5 compound was higher than that of the control compound. The torque difference is used as an indication of the crosslink density of a rubber compound [12, 14-15]. The higher the torque difference value, the higher is the degree of crosslink density. The addition of 0.5 phr of ALK improved the torque difference of the unfilled compound significantly. The improvement in torque difference has the same meaning as improvement in crosslink density and hence, ALK was considered as an additional curing agent for the unfilled CR compounds.

As discussed earlier, increasing the ALK loading up to 2.0 phr increased the scorch and cure times. Simultaneously, the torque difference value increased with up to 1.5 phr, but decreased beyond this loading. These phenomena was due to the function of ALK as an additional curing agent. The higher the loading, the more was the amount of ALK in the CR compounds as a reactant, and the more pronounced was its action as a curing agent over that of as an accelerator and hence, a longer time was needed to finish the curing process.

The decrease in torque difference value after the 1.5 phr of ALK was most probably due to the excessive amount of ALK which decreased the crosslink density.

3.2. The tensile properties

As presented in Table 2, the addition of up to 1.5 phr of ALK into the unfilled CR compound increased the M100, M300 and TS. However, further increase the ALK loading decreased those properties. The tensile properties of a rubber vulcanisate are dependent mainly on the degree of crosslink density [12, 15-16]. Again, the improvements of M100, M300 and TS up to 1.5 phr were due to the action of ALK as an additional curing agent, which increased the degree of crosslink density of the unfilled CR compounds. This explanation was agree with the trend of swelling-test result as shown in Fig. 1. It is well-known that the swelling-test result is related to the crosslink density of a rubber vulcanisate. A less solvent uptake or penetration into the CR compounds indicating a higher crosslink density [17]. The addition of a 1.5 phr of ALK exhibited the lowest swelling percentage of CR vulcanisate. This indicates the highest degree of crosslink density, which altered the interactions between CR segments into the strongest ones and hence, caused an increase in tensile strength.

The decreases in properties after a 1.5 phr was due to the excessive amount of ALK, which decreased the degree of crosslink density. Supposedly, the excessive amount of ALK formed some boundary layers, which dissolved a part of the curative system and hence, decreased the degree of crosslink density. This explanation is again agree with the result of swelling-test as shown in Fig. 1.

Table 2. The rheometric properties, swelling and tensile properties of unfilled CR compounds

Compounds	Rheometric properties			Tensile properties			
	ts_2, min.	t_{90}, min.	M_H–M_L, dN.m	M100, MPa	M300, MPa	TS, MPa	EB, %
CR-0.0	11.29	28.28	7.91	0.72	1.30	13.7	1612
CR-0.5	3.74	25.31	14.90	0.78	1.31	15.5	1590
CR-1.0	6.68	27.09	15.56	0.82	1.37	17.2	1537
CR-1.5	7.16	27.43	15.59	0.83	1.38	18.9	1487
CR-2.0	7.58	27.96	12.63	0.78	1.29	17.8	1516

The ALK decreased the EB by up to 1.5 phr, and then increased it slightly as the ALK loading further increases. EB depends mainly on the degree of crosslink density [14]. The decreasing of EB by up to 1.5 phr was simply due to the higher degree of crosslink density; which immobilised the CR segments freely. However, after the 1.5 phr of ALK loading, the EB increased. An explanation for this is again given by the excessive amount of ALK, which decreased the crosslink density and caused in a more free movement of the CR chains.

3.3. The swelling properties

Effect of ALK loading on the swelling percentage of unfilled CR compounds is shown in Fig. 1. The swelling percentage was measured by toluene uptake until equilibrium swelling was reached at room temperature. It is widely used that the swelling is related to the crosslink density of a network chain [17], with a less toluene penetration into the blends indicating a higher degree of crosslink density. As shown in Fig. 1, the swelling percentage of unfilled CR compounds decreased with the addition of 0.5 phr of ALK and decreased with further increases in the ALK loading up to 1.5 phr. After the 1.5 phr of ALK loading, the swelling percentage increased. The increases in swelling percentage was due to the excessive amount of ALK which decreased the degree of crosslink density.

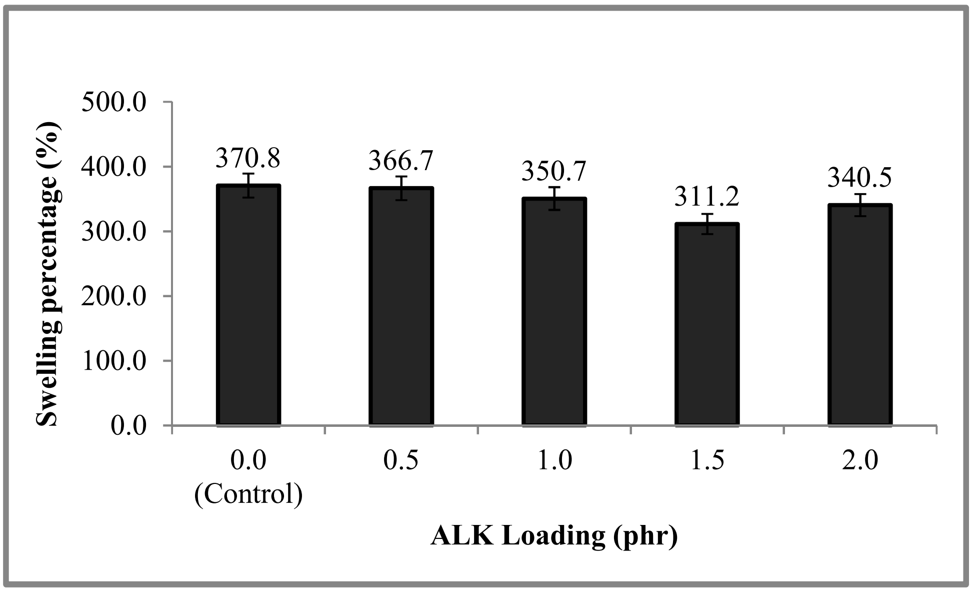

Figure 1. The effect of ALK loading on swelling percentage of unfilled CR compounds

4. Conclusions
From this study, the following conclusions were drawn:
1. Alkanolamide enhanced the cure rate of magnesium-zinc oxides vulcanised chloroprene rubber compounds.
2. Alkanolamide also enhanced the tensile properties and crosslink density of unfilled chloroprene rubber compounds especially up to 1.5 phr loading.
3. The enhancements of the cure rate, crosslink density and tensile properties were due to the function of ALK as a curative additive in unfilled chloroprene rubber compounds.

Acknowledgements
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. Authors - Indra Surya is grateful to the DRPM, Ministry of Research, Technology and Higher Education (Kemristekdikti) of the Republic of Indonesia, for research grant under Penelitian Hibah Bersaing scheme with contract No. 017/SP2H/LT/DRPM/II/2016, 17 February 2016.

References
[1] Rodgers B 2004 *Rubber Compounding: Chemistry and Applications* CRC
[2] Schatzel R, Cassell G 1939 Synthetic Elastic Polymers in the Cable Industry *Industrial & Engineering Chemistry* **31(8)** 945-949
[3] De S K, White J R 2001 *Rubber Technologists Handbook* Vol 1 Rapra Technology
[4] Ciesielski A 1999 *An introduction to rubber technology* William Andrew Pub
[5] Dick J S 2001 *Rubber technology : compounding and testing for performance* Hamser, Munich
[6] Surya I, Ismail H 2016 Alkanolamide as a novel accelerator and vulcanising agent in carbon black-filled polychloroprene rubber compounds *Plastics, Rubber and Composites* **45(7)** 287-293
[7] Akiba M, Hashim H 1997 Vulcanization and crosslinking in elastomers *Progress in polymer science* **22(3)** 475-521
[8] Smith D M 1984 Ethylene thiourea: thyroid function in two groups of exposed workers *British journal of industrial medicine* **41(3)** 362-366
[9] Surya I, Ismail H, Azura A 2013 Alkanolamide as an accelerator, filler-dispersant and a plasticizer in silica-filled natural rubber compounds *Polymer testing* **32(8)** 1313-1321
[10] Long H 1985 *Basic Compounding and Processing of Rubber, Rubber Division* American Chemical Society Inc The University of Akron, Ohio, USA
[11] Surya I, Ismail H, Azura A 2014 The comparison of alkanolamide and silane coupling agent on the properties of silica-filled natural rubber (SMR-L) compounds *Polymer testing*
[12] Surya I, Ismail H, Azura A 2015 The effect of alkanolamide loading on properties of carbon black-filled natural rubber (SMR-L), epoxidised natural rubber (ENR), and styrene-butadiene rubber (SBR) compounds *Polymer testing* **42** 208-214
[13] Surya I, Ismail H 2016 The effect of the addition of alkanolamide on properties of carbon black-filled natural rubber (SMR-L) compounds cured using various curing systems *Polymer testing* **50** 276-282
[14] Ismail H, Ng C 1998 Palm oil fatty acid additives (POFA's): Preparation and application *Journal of elastomers and plastics* **30(4)** 308-327
[15] Hayeemasae N, Surya I, Ismail H 2016 Compatibilized natural rubber/recycled ethylene-propylene-diene rubber blends by biocompatibilizer *International Journal of Polymer Analysis and Characterization* 1-12
[16] Ismail H, Chia H 1998 The effects of multifunctional additive and epoxidation in silica filled natural rubber compounds *Polymer testing* **17(3)** 199-210

[17] Nabil H, Ismail H, Azura A 2013 Compounding, mechanical and morphological properties of carbon-black-filled natural rubber/recycled ethylene-propylene-diene-monomer (NR/R-EPDM) blends *Polymer testing* **32(2)** 385-393