The cure and tensile properties of montmorillonite-natural rubber composites in the incorporation of alkanolamide

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Abstract. Effects of alkanolamide incorporation on cure and tensile properties of montmorillonite (MMT)-natural rubber (NR) composites were studied. The material of alkanolamide was synthesized from the waste of cooking oil production which was used as a rubber additive and incorporated into the NR compounds at 0, 1, 3, 5, 7 and 9 parts per hundred rubber (phr.). From the results, the alkanolamide decreased the times to scorch and cure but increased elongation at break. It was also found that the alkanolamide improved difference in torque, tensile strength and tensile moduli up to a five phr. of alkanolamide and decreased those properties with further increasing the alkanolamide loading. From the swelling test; the five phr. of alkanolamide loading was the optimum loading which causing the highest density of crosslink of the MMT composite of NR.

1. Introduction
The black and non black fillers are very common rubber additives which are incorporated into rubbers compounds in order to increase the mechanical or tensile properties of the final rubbers goods. The black fillers are carbon blacks (CBs) and non black ones such as CaCO\textsubscript{3}, montmorillonite (MMT) and precipitated silica. The CB is used to produce some rubbers goods with black colored and non black can produce rubbers products with unwanted black colored. Generally, the mechanical properties of rubbers goods filled with non black are always inferior compared to those of filled with CB. It is due to the surface chemistry of non black fillers which is a more hydrated and polar causing the fillers to be not easy to disperse and react with natural rubber (NR) as a non polar rubber [1].

The MMT, one type of polar fillers, is a nano-sized non black filler. It is very similar to others fillers with micron-sized particles, at relatively higher loading of using, the nano-sized MMT tends to make some bigger aggregates during mixing and causing in a relatively poorer degree of filler dispersion.

As an effort to solve such problems, a special rubber additive which is named as alkanolamide was added into the MMT-filled NR compounds. It is a chemical based on palm oil [2-6] and it was used in order to solve both the low level of mechanical properties enhancement and filler dispersion problems. The alkanolamide is an oily material [7] and oil can be used as a plasticizing agent [8] that improves the degree of filler dispersion.

This research-study investigated effects of the alkanolamide incorporation on the cure and also tensile properties of the composites of MMT-NR.
2. Methodology

2.1. Chemicals
The SMR L grade of NR, MBTS (N-cyclohexyl-benzothiazylsulfenamide), sulphur, IPPD (N-isopropyl-N'-phenyl-p-phenylenediamine), stearic acid and ZnO were supplied by the Rubber Lab of Universiti Sains Malaysia (USM), Malaysia. The alkanolamide, $\text{CH}_3(\text{CH}_2)_{14}\text{CON(CH}_2\text{CH}_2\text{OH})_2$ was prepared in the laboratory [3-4].

2.2. Compounding
The semi-EV formulation was applied for the preparation of MMT-NR-alkanolamide composites. The recipe for the making of composites is shown in Table 1. The procedures of the making of composites were conducted based on ASTM D-3184-80 using a laboratory two-roll mill.

| Chemicals | Composition, (phr) |
|-----------|-------------------|
| SMR L     | 100               |
| ZnO       | 5                 |
| MMT       | 8                 |
| Stearic acid | 2              |
| Sulphur   | 1.5               |
| TMTD      | 1                 |
| MBTS      | 1.5               |
| IPPD      | 2                 |
| Alkanolamide | 0; 1; 3; 5; 7; 9 |

2.3. The cure
The cure data of MMT-filled composites of NR were delivered by operating the MDR 2000 - Rheometer. It was operated for the data of times to cure and scorch and also the differences in torques based on ISO-3417. The composites of NR were vulcanized at a hundred and fifty degrees of Celsius. The composites were compression molded utilizing a stainless steel mold at fifty degree of Celsius, with a 10 MPa of the pressure of a hot press based on their optimum times to cure.

2.4. The swelling percentage
The swelling percentage test was performed in toluene based on ISO-1817. The (30 mm x 5 mm x 2 mm) sized of vulcanized NR was weighed using a balance and was then swollen in toluene for almost 72 hours at room temperature. The samples of composites were cleaned from the residue of toluene and the weight was determined. The change in mass is as follows:

Swelling percentage (%) = $100\% \left( \frac{W_2 - W_1}{W_1} \right)$  \hspace{1cm} (1)

In which $W_1$ is the beginning mass (gr.) and $W_2$ is the mass (gr.) after immersion in toluene.

2.5. The tensile properties
The dumbbell-shaped of composites samples were cut from the molded sheets based on ISO-37. Tensile tests were conducted at a crosshead speed of 500 mm/min. Tensile tests were performed on an Instron 3366 tensometer to determine tensile properties as TS (tensile strength), EB (elongation at break) and tensile moduli (M300, M100).
3. Results and discussion

3.1. The cure

The effect of alkanolamide on cure of the MMT-NR composites is shown in Table 2. As observed, both of the times to scorch and cure of MMT-NR composite with one phr. of alkanolamide were lower than those of the control composite. The alkanolamide caused improvement in the cure. The higher loading of alkanolamide caused in lowering the scorch and cure times and hence, the greater the affection of cure improvement. It was because of the action of alkanolamide as a co curing ingredient. In this case, the alkanolamide was an internal accelerator; presumably its amine part increased the rate of cure because amine is one of the accelerator ingredients for rubber compounds. [8-11].

| NR composites  | Scorch, min. | Cure, min. | MH-ML (dN.m) |
|----------------|-------------|------------|--------------|
| NR/Alkanolamide -0 | 2.79        | 4.69       | 5.89         |
| NR/Alkanolamide -1 | 2.91        | 4.98       | 6.02         |
| NR/Alkanolamide -3 | 2.60        | 4.53       | 6.69         |
| NR/Alkanolamide -5 | 2.16        | 3.92       | 6.92         |
| NR/Alkanolamide -7 | 1.75        | 3.20       | 6.75         |
| NR/Alkanolamide -9 | 1.37        | 2.67       | 6.70         |

Table 2. Curing data of MMT-filled composites of NR

MH-ML = Max torque minus Min torque

The torque difference or (MH-ML) value of MMT-filled NR composite with one phr. of alkanolamide was higher than that of MMT-filled NR composite with no alkanolamide. The alkanolamide increased the (MH-ML) value. Increasing the alkanolamide loading further increased the (MH-ML) value up to a five phr. of alkanolamide. After the five phr. of alkanolamide, the (MH-ML) started to decrease. The value of torque difference indicates modulus of shear dynamic and it corresponds to composite crosslink density [12-14]. The alkanolamide affected the MMT-NR composites crosslink density. Positively, it was because of the function of alkanolamide as a co curing agent that improved the cure state.

Decreases in crosslink density beyond the five phr. of alkanolamide loading were because of the excessive effect of alkanolamide which attracted parts of the curatives and as a consequence, a decrease of crosslink density was observed.

3.2. The swelling percentage

Result of swelling percentage test of MMT-NR composites is visualized in Fig. 1. Swelling percentage corresponds to the composite crosslink density [15-17]. The toluene with a less penetration into composite means a higher crosslink density. The incorporations up to five phr. of alkanolamide decreased swelling percentage/crosslink density of MMT-NR composites and after the five phr. of alkanolamide loading causing increases swelling percentage/crosslink density. Increases in percentage of swelling were because of excessive amount of alkanolamide that decreased crosslink density [15-17].
3.3. The tensile properties
The TS, tensile moduli and EB of the MMT-NR composites without and with alkanolamide are visualized in Figs. 2-4. As observed in Fig. 2, alkanolamide affected the EB of the MMT-NR composites. The one phr. of alkanolamide increased EB of the control composite (NR composite with no alkanolamide). The increases the alkanolamide loading caused further increases in the EB of NR composites. It was because of to the action of alkanolamide as a plasticizing material which modified EB of NR composites [18].
M300 and M100 and further increasing the alkanolamide loading started to decrease those properties. The results of TS showed a similar trend as can be seen in Fig. 4. The tensile moduli and TS relate to composite crosslink density [2-4]. The increases in those properties were because of a higher of crosslink density degree (higher torque difference indication in Table 2). The decreases in those properties were because of excessive amount of alkanolamide that decreased the composite crosslink density (lower torque difference indication in Table 2). See the previous discussion, the crosslink density degree of a composite can be indicated by its torque difference value. A higher in torque difference means a higher is crosslink density degree.

![Figure 3. Effects of alkanolamide on tensile moduli of MMT-filled NR composites](image3.png)

![Figure 4. Effects of alkanolamide on tensile strength of MMT-filled NR composites](image4.png)

4. Conclusions
Alkanolamide was a cocurative and internal plasticizing agent in montmorillonite-filled composites of natural rubber. Alkanolamide caused in the decreasing the times to scorch and cure but increasing the
elongation at break or extensibility. Alkanolamide improved crosslink density degree and tensile properties of montmorillonite-filled composites of natural rubber up to five parts per hundred rubber of loading.

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