The rheometric, mechanical and morphological properties of carbon black filled styrene butadiene rubber vulcanizates in presence of alkanolamide

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Abstract. Properties of carbon black (CB)-filled styrene-butadiene rubber (SBR) vulcanizates include rheometric, mechanical and morphological in presence of alkanolamide were studied. The synthetic rubber was filled by CB at a settled loading at thirty parts per hundred rubber (phr). The alkanolamide was derived from ethanolamine and refined bleached deodorized palm stearin and it was incorporated into CB-filled SBR at one, three, five and seven phr. From the results, it was found that alkanolamide was a rubber chemical as a co-curing and plasticizing material. As a co-curing material, it reduced the times to cure and scorch of filled SBR vulcanizates. As a plasticizing material, it reduced minimum torque or viscosity but raised the elongation at break. The properties of torque difference, tensile moduli, hardness, tensile strength and resilience of CB-filled SBR vulcanizates were also raised due to the presence of alkanolamide. The presence of a five phr of alkanolamide was the optimum concentration for CB-filled SBR whatever was tested by morphological study. The fractured vulcanizate of CB-filled SBR with the five phr of alkanolamide demonstrated greatest surface roughness and matrix tearing.

1. Introduction
Compounding is mixing a type of raw rubbers with some rubber chemicals. Raw rubber presents some rubbery behaviors; rubber chemicals include plasticizing agent cut down viscosity but enlarge deformability, and change properties; vulcanizing agent vulcanizes chains of raw rubber; accelerators raise vulcanization rate, and fillers to improve mechanical properties or reduce the production cost [1-2].

The filler reinforcement as defined as the raising of mechanical properties includes tensile moduli, tear and tensile strengths and resistances to abrasion of Vulcanized rubber occurring from the incorporation of reinforcing filler [3]. Carbon blacks (CB) and silica, because of their particles sizes are in micron meter, are widely applied as reinforcing fillers due to making rubber vulcanizates/products [4]. However, in the application with a relatively higher loading, the particles turn to make agglomeration of filler and hence, that phenomenon degrades the degree of filler dispersion and as a consequence, deterioration in some mechanical properties would happen. To clarify the problem, rubber chemicals with special usage include processing/dispersant aid or oil is used [4].
Alkanolamide (ALK) as a rubber chemical that can be derived from palm stearin and diethanolamine [3-6] can raise the degree of filler dispersion. At this current study, the properties of the vulcanizates of CB-filled styrene-butadiene rubber (SBR) include morphological, mechanical and rheometric in presence of alkanolamide were investigated.

2. Chemicals and methodology

2.1. Chemicals
The SBR and other compound ingredients include sulfur, zinc oxide, CB-330, IPPD, MBTS and stearic acid were given by the rubber lab of USM-Universiti Sains Malaysia, Malaysia. The alkanolamide was developed employing refined bleached deodorized palm stearin and diethanolamine. The steps of alkanolamide preparation were given in our reports previously [3,4,7] and its chemical formula is \( \text{CH}_3(\text{CH}_2)_{14}\text{CON(CH}_2\text{CH}_2\text{OH})_2 \).

2.2. Rubber compounding
The SBR and other compounds ingredients were compounded based on a semi-EV cure system. The sequences of rubber compounding were done based on ASTM D3184-80 on a lab-type 2-roll mill. Table 1 presents the compound recipe for rubber compounding.

| Chemicals       | Content (phr.) |
|-----------------|----------------|
| SBR             | 100            |
| Sulfur          | 1.5            |
| IPPD            | 2              |
| Stearic acid    | 2              |
| MBTS            | 1.5            |
| Zinc oxide      | 5              |
| Alkanolamide    | 0; 1; 3; 5 and 7|
| CB-N330         | 30             |

2.3. Rheological properties
The SBR rheological properties include (ts₂₂, scorch time), (t₉₀, cure time), max. torque (Mₓ), min. torque (Mᵧ), difference in torque (Mₓ - Mᵧ) (based on ISO 3417) were delivered by the use of a Rheometer (MDR 2000). The compounds/samples of SBR were cured at 150°C.

2.4. Mechanical properties
The values of the hardness of the SBR composites were obtained based on ASTM D2240-05 by the use of a Shore A type Durometer.

Tensile properties include (TS, tensile strength), (M₃₀₀/M₁₀₀, tensile moduli) and (EB, elongation at break) of the vulcanized SBR were determined using a tensometer (Instron-3366) based on ASTM D-882.

Resilience properties were determined by applying a Wallace Dunlop Tripsometer based on BS 903 Part A8. The properties of resilience were measured based on equation 1.

\[
\% \text{ Resilience} = \left( \frac{1 - \cos \theta_2}{1 - \cos \theta_1} \right) \times 100
\]

in which, \( \theta_1 \) is original angle of displacement (45°), and \( \theta_2 \) is maximum rebound angle.
2.5. Morphological properties
The SBR morphological properties were investigated by examining the tensile fractured surfaces of vulcanizates using a Zeiss Supra-35VP SEM to receive data respecting possible presence of micro-defects. The cracked pieces were coated with a layer of gold to erase electrostatic charge boost at the same time as a test.

3. Results and Discussion

3.1. The rheometric properties
Times to curing and scorch of filled SBR vulcanizates in presence of alkanolamide are demonstrated in Table 2 and the presence of one phr of alkanolamide reduced the times to scorch and cure. An increase in cure was observed and it was because of the alkanolamide action as a co-curing rubber chemical. The ingredient of amine of the alkanolamide caused the cure enhancement [3,4,8]. Presence of alkanolamide in a higher concentration caused a more pronounced in cure enhancement.

Table 2 also presents the properties of torque differences of the SBR composites in the presence of alkanolamide. The presence of one phr of alkanolamide increased the torque difference. The presences of alkanolamide up to a five phr further increased the properties of torque differences. The presence of alkanolamide after the five phr started to reduce those properties.

The reduction of torque difference after a five phr of alkanolamide was because of the effect of dilution of the more amount of alkanolamide tent to form some oily layers which absorbed/attracted CB plus some of curatives inside those oily layers and hence, diminished total crosslink density.

3.2. The mechanical properties
Properties include tensile moduli, resilience and hardness of filled SBR vulcanizates in presence of alkanolamide are demonstrated in Table 3. The presences of alkanolamide up to a five phr raised those properties and above the five of alkanolamide concentration diminished those properties. Tensile moduli and stiffness or hardness of a vulcanizate are depended only on properties of crosslink density [18]. The increases in tensile moduli and hardness up to the five phr of alkanolamide were because of the higher degree of crosslink density and deterioration in these properties was because of a lower degree of crosslink density.

Properties of elongations at break (EB) of filled SBR vulcanizates in presence of alkanolamide are also shown in Table 3. EB of filled SBR vulcanizates with alkanolamide was higher. The higher alkanolamide concentration the higher was EB.
Once again, it was because of alkanolamide action as an additional plasticizing rubber material which modified flexibility of the SBR vulcanizates. Perhaps, the alkanolamide provided some free volumes whatever granted more flexibility for the SBR chains to flow. The higher alkanolamide concentration, the greater was free volume and more flexible SBR. It could be assumed that free volume was in layers of extra plasticizing material [18].

| Table 3. Mechanical properties of SBR vulcanizates |
|-----------------------------------------------|
| CB-filled SBR vulcanizates | Alkanolamide, phr. | 0 | 1 | 3 | 5 | 7 |
| M100, Mega Pascal         | 1.31 | 1.34 | 1.39 | 1.43 | 1.35 |
| M300, Mega Pascal         | 3.18 | 3.89 | 4.47 | 4.73 | 3.58 |
| EB, Percent               | 770.9 | 776.1 | 782.1 | 829.2 | 866.7 |
| TS, Mega Pascal           | 18.2 | 18.8 | 19.1 | 19.8 | 17.8 |
| Hardness, Shore A         | 55 | 56 | 57 | 58 | 56 |
| Resilience, Percent       | 55.0 | 56.1 | 56.7 | 58.4 | 56.4 |

The properties of tensile strength (TS) of the filled SBR vulcanizates in presence of alkanolamide are also demonstrated in Table 3. The presences of alkanolamide up to a five phr raised the TS and after the concentration started to reduce the TS.

The TS enhancements up to the five phr were because of competence of alkanolamide to soften and plasticize filled SBR due to achieve a better CB dispersion and greater SBR to CB interaction. This discussion in line with SEM results of the SBR vulcanizates as shown in Fig.1. The micrograph of the SBR vulcanizate with the presence of the five phr of alkanolamide (see Fig. 1B) showed a more homogeneous of CB micro dispersion.

The deterioration in TS properties beyond the five phr of alkanolamide was because of the excessive amount of alkanolamide that more pronounced effect of softening, causing in a weaker SBR to CB interaction.

3.3. The morphological properties
Figure 1. displays scanning electron microscope (SEM) micrographs of cracked surfaces of the SBR vulcanizates in presence of alkanolamide whatever were arrested at magnification 50X. As can be seen, SBR vulcanizate with a five phr of alkanolamide (micrograph of Figure 1.B) showed some momentous surface roughness and matrix tearing lines whatever presented a greater matrix tearing lines and surface roughness compared to that of SBR vulcanizate without the presence of alkanolamide (Figure 1.A).
Figure 1. SEM micrographs of cracked samples of filled SBR vulcanizates at a magnification of 50X; (A) with no alkanolamide, (B) with five phr alkanolamide, and (C) with seven phr alkanolamide.
It was confirmed a greater SBR to CB interaction that changed the crack paths, leading to increase in resistance to crack propagations and hence causing an increase in properties to include tensile moduli, TS and stiffness or hardness. The rupture energy increment was because of a greater crosslink density, was responsible for roughness and the matrix tearing line of cracked surface [19,20]. Matrix tearing lines and surface roughness of micrograph of Figure 1.C was smoother than that of the micrograph of Figure 1.A which confirmed lower TS because of a more pronounced effect of lubricating/plasticizing of extra alkanolamide.

4. Conclusion
Alkanolamide was as a curative rubber chemical in carbon black-filled SBR vulcanizates. The times to scorch and curing of carbon black-filled SBR vulcanizates with presence of alkanolamide were lower than that of without presence of alkanolamide.

Alkanolamide was as an internal plasticizing rubber chemical in carbon black-filled SBR vulcanizates. It reduced minimum torque but raised elongation at break. The higher the alkanolamide loading, the lower was minimum torque but the higher was elongation at break.

Alkanolamide raised mechanical properties. The tensile moduli, hardness, resilience and tensile strength of carbon black-filled SBR vulcanizates with presence of alkanolamide were higher.

The five phr of alkanolamide was optimum concentration for carbon black-filled SBR vulcanizates. The cracked surface of carbon black-filled SBR vulcanizate with five phr of alkanolamide confirmed greatest matrix tearing and surface roughness.

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