Enhancing tensile strength of styrene butadiene rubber using alkanolamide

Indra Surya\textsuperscript{1*}, H Ismail\textsuperscript{2}

\textsuperscript{1}Chemical Engineering Department, Universitas Sumatera Utara, Medan, Indonesia
\textsuperscript{2}School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, Nibong Tebal, Penang, Malaysia
* Corresponding author: indradanas@yahoo.com

Abstract. Enhancing the carbon black (CB) dispersion and tensile strength of composites of styrene-butadiene rubber (SBR) using bio compatibilizer-alkanolamide (BALK) was carried out. The raw SBR was filled by N330 type of CB at a fixed concentration (thirty parts per hundred rubbers, phr). The BALK was Refined Bleached Deodorized Palm Stearin (RBDPS)-based additive, loaded into the composites at 1, 3, 5 and 7 phr. The BALK enhanced not only degree of CB dispersion but also tensile properties. It exhibited tensile and modulus enhancements, especially up to a five phr of addition. The morphological study proved that the five phr was the optimum BALK addition where the fractured surface of composites of SBR with five phr of BALK showed the greatest surface roughness and matrix tearing line.

1. Introduction
In achieving rubber composites with an ultimate level of strength, reinforcing fillers are used [1]. Silicas and carbon blacks (CBs) are the most well-known fillers that reinforce the rubber composites. CBs are used for manufacturing rubber composites with black-coloured, while silicas are used in multi-coloured composites. Those fillers can be used in a combination type for the aim of gaining some synergistic effects in order to manufacture better mechanical properties [2].

Due to the production of various rubber composites, both silica and CB are utilised in reinforcement of rubber composites. But, at a higher filler addition, particles of those fillers ready to form bigger aggregates that will decrease composites properties. In practical, to overcome such problem, some additives like dispersant aid or processing aid are utilised.

In this research-work, biocompatibilizer-alkanolamide (BALK) was used to overcome dispersion of CB in styrene butadiene rubber (SBR) composites. Therefore, effect of BALK addition on degree of CB dispersion, tensile moduli and tensile strength of SBR composites were carried out.

2. Materials and methods

2.1. Materials for research
A 1502 type of SBR was supplied by TSRC Taiwan-Corporation. An N330 type of CB was purchased from Cabot Corporation. Chemicals like sulphur, stearic acid, zinc oxide, benzothiazolyl disulfide (MBTS) and antioxidant (IPPD) were purchased from Bayer Co. (M) Sdn. Bhd., Malaysia. The BALK, CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{14}CON(CH\textsubscript{2}CH\textsubscript{2}OH)\textsubscript{3}, was prepared by utilising RBDPS, diethanolamine and Refined Bleached Deodorized Palm Stearin [3]
2.2. Compounding for SBR composites
Semi-efficient vulcanisation system was applied for compounding. The procedure of compounding was done on an XK-160 Model of a two-roll mill. Table 1 presents recipe of SBR composites without and also with BALK.

| Materials   | Content (phr) |
|-------------|---------------|
| SBR         | 100           |
| Stearic acid| 2             |
| ZnO         | 5             |
| MBTS        | 1.5           |
| IPPD        | 2             |
| Sulphur     | 1.5           |
| CB N330     | 30            |
| BALK        | 0; 1; 3; 5; 7 |

2.3. The curing characteristics
The curing characteristics of SBR composites were obtained utilising an MDR 2000-type of Monsanto Moving Die Rheometer, that was applied to know optimum cure time, scorch time and also torque difference (maxima torque – minima torque), in accordance with ISO 3417. The respective composites were tested at 150°C of temperature. The SBR composites were compression moulded utilising a stainless-steel mould at 150°C with 10 MPa of pressure and applying a laboratory hot press based on respective optimum curing times.

2.4. The tensile properties
Dumbbell-shaped samples of SBR composites were cut from moulded-sheets. Tensile measurements were performed at a cross-head speed of 500.0 mm per minute by utilising an Instron 3366 universal tensile machine in accordance with ISO 37. The TS (tensile strength), stresses at 100% and 300% elongations (M100 and M300) and also EB (elongation at break) were determined.

2.5. The scanning electron microscopy (SEM)
Fractured surfaces of tensile of the SBR composites were observed utilising a Zeiss Supra-35VP type of SEM to get any data relating CB dispersion, detecting possible presence of micro defects. The fractured samples were coated with a layer of gold to minimize electrostatic charge build up during testing.

3. Results and discussion

3.1. Torques of SBR composites
Table 2 exhibits torque properties SBR composites without and also with BALK. The addition of 1.0 phr of BALK produced an SBR composite with a higher value in torque difference. The value was further enhanced with BALK addition up to 5.0 phr and reduced after the loading.
Table 2. The torques and L value of SBR composites at various BALK loadings

| Torque and L value | Unfilled | 0     | 1     | 3     | 5     | 7     |
|--------------------|----------|-------|-------|-------|-------|-------|
| Maxi. torque, dN.m | 6.180    | 10.110| 11.900| 12.470| 12.960| 11.990|
| Mini. torque, dN.m | 0.720    | 1.290 | 1.270 | 1.230 | 1.210 | 1.080 |
| Maxi. – Mini., dN.m| 5.460    | 8.820 | 10.630| 11.240| 11.750| 10.910|
| L Value            | 0.16     | - (0.16)| - (0.31)| - (0.42)| - (0.44)|

The torque difference reflects crosslinking density degree of a composite [4-7]. A lower value of torque difference means a lower in crosslinking density degree. The BALK additions up to an optimum addition (five phr) enhanced torque differences of the composites. The plasticising effect of BALK softened the composites which resulted in decreasing viscosity, enhanced CB dispersion and also rubber to CB interactions, respectively. Such rubber to CB interactions can be categorized as additional physical crosslinking [8, 9], and together with sulphides crosslinking contribute to total crosslinking density [10].

The reducing in torque difference after the five phr, was due to excessive amounts of BALK that absorbed and also attracted CB-filler plus curatives within the BALK molecules and hence, reduced total crosslinking density.

3.2. The degree of CB dispersion

Degree of CB dispersion in the composites was calculated using Equation (1) [11].

\[ L = \eta_f - m_f \]  

in which: \( \eta_f = [T_{Lf}/T_{Lf}] \), and \( m_f = [T_{Hf}/T_{Hf}] \); where \( T_{Lf} \) and \( T_{Hf} \) were minima and maxima torques of the composites; and \( T_{Lf} \) and \( T_{Hf} \) were minima and maxima torques of unfilled SBR. A lower L value, at a certain BALK addition, means a higher degree of CB dispersion.

Based on data of torques, L values for CB-filler in SBR composites were determined using Eq. 1 and they were presented in Table 2. As presented, ALK decreased L values. The higher BALK loading, the lower was the L value which meant a higher degree of CB dispersion. The L value was a similar trend with minima torque which represents the filler to filler interaction [12] and it can be used to measure viscosity of a composite, relatively [13, 14]. A lower value means a lower viscosity of composite that caused an easier processability of CB dispersion and also weakened CB to CB interactions.

The decreases in L value and minimum torque were attributed to BALK function as a plasticising agent. As mentioned previously, the decreased viscosity enhanced CB-filler dispersion.

3.3. Tensile properties of SBR composites

Table 3 presents values of M100 and M300 of SBR composites. The incorporation of BALK up to five phr enhanced those properties into maximum values, and beyond those loadings displayed deterioration in the properties.

Tensile modulus of a composite depends on degree of crosslinking [6]. The improvement in M100 and M300 up to BALK optimum addition was due to a higher degree of crosslinking density and deterioration in M100 and M300 after BALK optimum loading was attributed to a lower crosslinking density.
Table 3. Tensile properties of composites of SBR without and with BALK additions

| SBR composites | BALK additions |
|----------------|---------------|
|                | 0  | 1  | 3  | 5  | 7  |
| M100 (MPa)     | 1.31 | 1.34 | 1.39 | 1.43 | 1.35 |
| M300 (MPa)     | 3.18 | 3.89 | 4.47 | 4.73 | 3.58 |
| E B (%)        | 770.9 | 776.1 | 782.1 | 829.2 | 866.7 |
| T S (MPa)      | 18.2 | 18.8 | 19.1 | 19.8 | 18.1 |

The effect of BALK on EB of SBR composites is presented in Table 3. EB enhanced with increasing of the BALK loading. It was due to the action of BALK as a plasticising agent that modified flexibility property of the composites. The TS of composites of SBR without and with is also presented in Table 3. The incorporations of BALK up to five phr enhanced TS and beyond the loading displayed a reduced trend of TS.

Improvement in TS up to the BALK optimum loading was due to the ability of BALK to plasticise the composites and hence, provided a greater rubber to filler interactions. This explanation was in agreed with the SEM micrographs of SBR composites as shown in Fig. 1. The micrograph with a five phr of BALK (Fig. 1b) exhibits the most homogeneous micro-dispersion of CB-filler as a result of BALK presence.

The TS decreases after a five phr of BALK was attributed to excessive loading of BALK that caused in a greater plasticising effect, causing in a weaker rubber to filler interactions.

3.4. Morphological study of SBR composites

Fig. 1 visualizes SEM micrographs of fractured samples of SBR composites without and with BALK, at magnification 300X. It is observed that the composites with optimum five phr of BALK (micrograph of Fig. 1(b)) exhibited a significant surface roughness and matrix tearing lines. It exhibits a greater surface roughness and matrix tearing lines compared to that of control composite (Fig. 1(a)). It indicates a stronger rubber to filler interactions that altered crack paths, leading to an improved resistance to crack propagations, and thus causing in enhancements in tensile modulus and tensile strength. The improvement in energy of rupture, attributed to a stronger rubber to filler interactions, was responsible for surface roughness and matrix tearing lines of fractured sample [15-17].

Matrix tearing lines and surface roughness of Fig. 1(c) micrograph was smoother than that of Fig. 1(b) micrograph that indicates a lower degree in crosslinking density.
Figure 1. SEM images of failed fracture of SBR composites with a 300X magnification: (a) without BALK, (b) with 5.0 phr of BALK, and (c) with 7.0 phr of BALK.

4. Conclusion
The alkanolamide improved carbon black degree of dispersion and also tensile properties of styrene-butadiene rubber composites. A five phr of alkanolamide addition was the optimum addition for styrene-butadiene rubber composites.

The alkanolamide improved both tensile strength and tensile modulus of styrene-butadiene rubber composites up to an optimum addition.

The morphology study proved that the styrene-butadiene rubber composites with alkanolamide at optimum addition exhibited greatest surface roughness and matrix tearing line due to a higher degree of carbon black dispersion.

Acknowledgement
The authors thank USM Malaysia for serving all research facilities for realizing this research-work.

References
[1] Bateman L 1963 The Chemistry and Physics of Rubber-like Substances: Studies of the Natural Rubber Producers' Research Association: Applied Science Publishers
[2] Rattanasom N, Saowapark T and Deepprasertkul C 2007 Reinforcement of natural rubber with silica/carbon black hybrid filler Polym. Test. 26 3 369-77
[3] Surya I, Ismail H and Azura A 2013 Alkanolamide as an accelerator, filler-dispersant and a plasticizer in silica-filled natural rubber compounds Polym. Test. 32 8 1313-21
[4] Boonstra B, Cochrane H and Dannenberg E 1975 Reinforcement of silicone rubber by particulate silica Rubber Chem. Tech. 48 4 558-76
[5] Cochrane H and Lin C 1993 The influence of fumed silica properties on the processing, curing, and reinforcement properties of silicone rubber Rubber Chem. Tech. 66 1 48-60
[6] Ismail H and Chia H 1998 The effects of multifunctional additive and epoxidation in silica filled natural rubber compounds Polym. Test. 17 3 199-210
[7] Teh P, Ishak Z M, Hashim A, Karger-Kocsis J and Ishiaiku U 2004 Effects of epoxidized natural rubber as a compatibilizer in melt compounded natural rubber–organoclay nanocomposites Eur. Polym. J. 40 11 2513-21
[8] Boonstra B and Taylor G 1965 Swelling of filled rubber vulcanizates Rubber Chem. Tech. 38 4 943-60
[9] Nunes R, Fonseca J and Pereira M 2000 Polymer–filler interactions and mechanical properties of a polyurethane elastomer Polym. Test. 19 1 93-103
[10] Polmanteer K and Lentz C 1975 Reinforcement studies—effect of silica structure on properties
[11] Lee B 1979 Reinforcement of Uncured and Cured Rubber Composites and Its Relationship to Dispersive Mixing—An Interpretation of Cure Meter Rheographs of Carbon Black Loaded SBR and Cis-Polybutadiene Compounds Rubber Chem. Tech. 52 5 1019-29

[12] Manna A K, De P, Tripathy D, De S and Peiffer D G 1999 Bonding between precipitated silica and epoxidized natural rubber in the presence of silane coupling agent J. App. Polym. Sci. 74 2 389-98

[13] Ismail H, Nordin R and Noor A 2002 Cure characteristics, tensile properties and swelling behaviour of recycled rubber powder-filled natural rubber compounds Polym. Test. 21 5 565-9

[14] Surya I, Ginting M and Ismail H 2017 The effects of the addition of alkanolamide on carbon blacks filled natural rubber compounds IOP Conf. Ser. Mater. Sci. Eng. 223 1 012006

[15] Ismail H and Mathialagan M 2012 Comparative study on the effect of partial replacement of silica or calcium carbonate by bentonite on the properties of EPDM composites Polym. Test. 31 2 199-208

[16] Nabil H, Ismail H and Azura A 2013 Compounding, mechanical and morphological properties of carbon-black-filled natural rubber/recycled ethylene-propylene-diene-monomer (NR/REPDM) blends Polym. Test. 32 2 385-93

[17] Surya I, Siregar S and Ismail H 2017 The effect of alkanolamide addition on cure and tensile properties of unfilled natural rubber compounds IOP Conf. Ser. Mater. Sci. Eng. 223 1 012012