The degree of filler dispersion, rheometric and mechanical properties of carbon black-filled styrene-butadiene rubber composites in the presence of alkanolamide

I Surya 1,2,*, H Ismail 3

1 Department of Chemical Engineering, Faculty of 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 degree of filler dispersion, rheometric and mechanical properties of carbon black (CB)-filled styrene-butadiene rubber (SBR) composites in the presence of alkanolamide (ALK) were investigated using a semi-efficient sulphur accelerated vulcanisation system. The ALK was prepared from Refined Bleached Deodorized Palm Stearin and diethanolamine and added into the CB-filled SBR composites at 1.0, 3.0, 5.0 and 7.0 parts per hundred rubber (phr). It was found that ALK decreased the scorch time, cure time and minimum torque of the CB-filled SBR composites. The ALK also increased the torque difference, tensile modulus, hardness, resilience and tensile strength; especially up to a 5.0 phr of loading. Due to its plasticising effect, ALK improved the degree of CB dispersion and increased the elongation at break of the CB-filled SBR composites. The crosslink density was increased by improving the degree of CB dispersion and rubber-filler interaction, respectively. The 5.0 phr of ALK was the optimum loading for CB-filled SBR composites which exhibited the highest values in tensile modulus, hardness, resilience and tensile strength.

1. Introduction

Various raw rubbers, rubber chemicals and fillers with their suitable amounts are mixed during the compounding operation [1] in order to achieve rubber composites. The raw rubbers provide rubbery properties to the composites; fillers reinforce the rubbers or reduce the cost of composites products; plasticisers decrease the viscosity, improve deformability and change properties; and accelerators enhance the rate of vulcanisation reaction[2, 3].

By vulcanisation, the weak and plastic raw rubbers are converted into strong elastic rubber vulcanisates. The strength and elasticity can be further enhanced by the addition of a type of reinforcing fillers into the rubber composites. The silica and carbon (CB) are the most famous reinforcing fillers in rubber reinforcement. Their particles are very fine and at a relatively higher filler loading. They tend to interact with each other and form filler agglomeration. The agglomeration will deteriorate the properties of the rubber composites and it is considered as a problem in filler

* Corresponding author: indradanas@yahoo.com
dispersion. In general, to solve the filler dispersion problem, a special additive such as processing aid or dispersant aid is added during compounding[4,5].

Therefore, in this study alkanolamide (ALK) was utilised for solving the filler dispersion problem of CB-filled styrene-butadiene rubber (SBR) composites. The ALK was prepared from refined bleached palm stearin (RBDPS) [6]. The degree of CB dispersion, due to the addition of ALK, was investigated. The rheometric and mechanical properties of CB-filled SBR composites without and with ALK were also investigated.

2. Experimental

2.1. Materials

Styrene-butadiene rubber (SBR), Taipol 1502, was purchased from TSRC Corporation, Taiwan. An N330-grade CB was supplied by the Cabot Corporation. Other compounding ingredients, such as sulphur, zinc oxide, stearic acid, N isopropyl-N'-phenyl-p-phenylenediamine (IPPD), and benzothiazolyl disulfide (MBTS), were supplied by Bayer Co. (M) Sdn. Bhd., Petaling Jaya, Selangor, Malaysia. All materials were utilised as supplied. The ALK was prepared using RBDPS and diethanolamine. The procedure of the ALK preparation was given in our previous report [6 - 9] and its chemical formula is CH$_3$(CH$_2$)$_{14}$CO(N(CH$_2$CH$_2$OH)$_2$.

2.2. Compounding

A semi-efficient sulphur-accelerated curing system was used for compounding. The recipe for the preparation of the CB-filled SBR composites is given in Table 1. The compounding procedure was done in accordance with the American Society for Testing and Material (ASTM) – Designation D3184 – 80. Compounding was done on a two-roll mill.

| Ingredients  | Content (phr, parts per hundred rubber) |
|--------------|----------------------------------------|
| SBR          | 100.0                                  |
| ZnO          | 5.0                                    |
| Stearic acid | 2.0                                    |
| IPPD         | 2.0                                    |
| MBTS         | 1.5                                    |
| Sulphur      | 1.5                                    |
| CB N330      | 30.0                                   |
| ALK          | 0.0; 1.0; 3.0; 5.0; 7.0                |

2.3. Rheometric properties

The rheometric properties of the CB-filled SBR composites were determined at 150 °C using a Monsanto Moving Die Rheometer (MDR 2000). The rheometric properties such as scorch time (ts$_2$), cure time (to$_90$), minimum torque (M$_L$) and maximum torque (M$_H$) were measured according to ASTM D2084. The CB-filled SBR composites without and with ALK 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, hardness and resilience properties

Dumbbell-shaped samples were cut from the moulded sheets. Tensile tests were performed at a cross-head speed of 500 mm/min using an Instron 3366 universal tensile machine according to ISO 37. The tensile strength and stress at 100% elongation (M100), 300% elongation (M300), and elongation at break were investigated. The hardness measurements of the samples were performed according to ISO 7691-I using a Shore A type manual Durometer. The resilience was studied using a Wallace Dunlop
Tripsometer according to BS 903 Part A8. The rebound resilience was calculated according to the following equation:

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

(1)

where, \( \theta_1 \) is the initial angle of displacement (45°), and \( \theta_2 \) is the maximum rebound angle.

3. Results and Discussion

3.1. The rheometric properties

The rheometric properties of the CB-filled SBR composites without and with ALK are shown in Table 2. The scorch and cure times of CB-filled SBR composites with ALK were lower than that of CB-filled SBR composites without ALK. The higher the ALK loading, the lower was the scorch and cure times. It was due to the amine part of ALK which contributed to the cure enhancement [4, 6, 7, 11].

The torque differences (\( M_{hf} - M_{lf} \)) of the CB-filled SBR composites with ALK were higher than that of CB-filled SBR composites without ALK. The ALK increased torque difference up to 5.0 phr and started to decrease beyond the loading.

| Rheometric properties | ALK loadings |
|-----------------------|--------------|
|                       | 0.0 | 1.0 | 3.0 | 5.0 | 7.0 |
| Scorch time, min.     | 5.07| 4.03| 2.89| 2.23| 2.09|
| Cure time, min.       | 12.76| 11.15| 8.15| 6.85| 6.13|
| Maximum torque, dN.m  | 10.11| 11.90| 12.47| 12.96| 11.99|
| Minimum torque, dN.m  | 1.29 | 1.27 | 1.23 | 1.21 | 1.08 |
| Torque difference, dN.m | 8.82 | 10.63 | 11.24 | 11.75 | 10.91 |

The torque difference relates to crosslinking density of a rubber composite[10, 12-14]. A greater torque difference means a greater crosslink density.

The decrease of the torque difference beyond 5.0 phr of ALK was due to the dilution effect of the excessive amount of ALK which most probably absorbed CB filler and part of curatives consequently decreased the total crosslink density.

3.2. The degree of filler dispersion

The degree of CB dispersion in the SBR composites, due to the addition of ALK, was determined quantitatively by Equation 2 [15],

\[
L = \eta_f - m_r
\]  

(2)

where: \( \eta_f = \frac{M_{lf}}{M_{lg}} \), and \( m_r = \frac{M_{hf}}{M_{hg}} \); where \( M_{lf} \) and \( M_{hf} \) are the minimum and maximum torques of the filled compounds; and \( M_{lg} \) and \( M_{hg} \) are the minimum and maximum torques of the unfilled/gum rubber compound. A lower value of \( L \), at a particular loading, means a better degree of CB dispersion.

Based on the torques properties data as shown in Table 2, values of \( L \) for CB dispersion in the SBR phase is shown in Figure 1. The ALK decreased the \( L \) value. The higher the ALK loading, the lower was the value of \( L \), which indicated better CB dispersion. The trends of \( L \) values were similar to those of minimum torque (\( M_L \)) in Table 2. The minimum torque represents the filler–filler inter agglomeration [16] and the value is used to measure the relative viscosity of a rubber compound [7]. The lower the value, the lower the viscosity of the compound which not only results in easier processability of filler dispersion but also weakened the filler–filler interaction.
The decreases in minimum torque and L value were due to the function of ALK as an internal plasticiser, as mentioned earlier, which decreased the viscosity of the filled SBR composites. A lower viscosity tent to make easier the filler dispersion and enhanced SBR-CB interaction, respectively. The SBR-CB interaction can be defined as additional physical crosslinks [18-19] and, together with sulphide crosslinks, contributed to total crosslink density [20-21].

![Graph showing the value of L vs ALK Loading](image)

**Figure 1.** The L values of CB-filled SBR composites without and with ALK

### 3.3. The mechanical properties

Table 3 represents the M100, M300, TS, EB, hardness and resilience of CB-filled SBR composites without and with ALK. The ALK increased M100, M300, TS, hardness and resilience up to 5.0 phr of loading; beyond the loading started to decrease those properties.

| CB-filled SBR composites | ALK Loadings | 0.0 | 1.0 | 3.0 | 5.0 | 7.0 |
|--------------------------|--------------|-----|-----|-----|-----|-----|
| M100, MPa                |              | 1.31± 0.09 | 1.34± 0.09 | 1.39± 0.12 | 1.43± 0.10 | 1.35± 0.09 |
| M300, MPa                |              | 3.18± 0.06 | 3.89± 0.07 | 4.47± 0.08 | 4.73± 0.08 | 3.58± 0.09 |
| EB, %                    |              | 770.9± 17.5 | 776.1± 18.9 | 782.1± 19.8 | 829.2± 19.2 | 866.7± 20.2 |
| TS, MPa                  |              | 18.2± 0.5 | 18.8± 0.5 | 19.1± 0.6 | 19.8± 0.6 | 18.4± 0.8 |
| Hardness, Shore A        |              | 55± 0.2 | 56± 0.2 | 57± 0.3 | 58± 0.3 | 56± 0.3 |
| Resilience, %            |              | 55.0± 0.4 | 56.1± 0.4 | 56.7± 0.6 | 58.4± 0.5 | 56.4± 0.6 |

Tensile modulus (M100 and M300) and hardness of a rubber composite are only dependent on the crosslink density [10]. Resilience is improved to some extent as the crosslink density rises [5]. The enhancements in tensile modulus, hardness and resilience up to the 5.0 of ALK loading were due to a higher crosslink density and the deteriorations in those properties beyond the loading were due to a lower crosslink density. This explanation is in line with the torque difference result in Table 2.

The EB of the CB-filled SBR composites with ALK was longer than that of without ALK. The higher the ALK loading, the longer was the EB. It was simply due to the function of ALK as an internal plasticiser which enhanced the flexibility of CB-filled SBR composites. The ALK provided free volumes which allowed a more flexibility for the rubber chains to move. The higher the ALK loading, the greater were the free volumes and the more flexible were the rubber chains. Presumably, the free volumes were in the layers of excessive ALK [10].

The ALK increased TS of CB-filled SBR composites up to 5.0 phr of loading and started to decrease the TS after the loading. The enhancement in TS up to a 5.0 phr of ALK was due to the
plasticizing effect of ALK which softened and plasticised the filled SBR composites achieving a better filler dispersion and greater rubber-filler interaction. The deterioration in TS after the 5.0 phr of ALK was due to the excessive amount of ALK which caused a more pronounced in softening-effect and weaker rubber-filler interaction, respectively.

4. Conclusions
From this study, the following conclusions were drawn:
1) Alkanolamide was as a curative additive which decreased the scorch and cure times of carbon black-filled styrene-butadiene rubber composites. The higher the alkanolamide loading, the lower were the scorch and cure times.
2) Alkanolamide was as an internal plasticiser which decreased the minimum torque but increased the elongation at break of carbon black-filled styrene-butadiene rubber composites. The higher the alkanolamide loading, the lower was the minimum torque but the higher was the elongation at break.
3) The plasticising effect of alkanolamide improved the degree of filler dispersion carbon-black filled styrene-butadiene rubber composites. The degree of filler dispersion further increased with increasing the alkanolamide loading.
4) Alkanolamide increased the mechanical properties of carbon black-filled styrene-butadiene rubber composites. The tensile modulus, hardness, resilience and tensile strength of carbon black-filled styrene-butadiene rubber composites with alkanolamide were higher than those of without alkanolamide.
5) The 5.0 parts per hundred rubber of alkanolamide was the optimum loading for carbon black-filled styrene-butadiene rubber composites.

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