Silica-filled styrene-butadiene rubber in the existence of palmitamide: vulcanization properties and reinforcement index

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Abstract. By applying one semi EV vulcanization system; the influences of palmitamide on vulcanization properties and reinforcement index of silica-filled styrene-butadiene rubber (SBR) compounds were observed. The palmitamide was lab-prepared from urea and palmitic acid and added into the silica-filled SBRt1, 3, 5 and 7phr. It was revealed that the palmitamide was a curative material which decreased the optimum cure time but increased the maximum and change in torques of the silica-filled SBR compounds. The bigger the palmitamide loading, the shorter was the optimum cure time. It was also revealed that palmitamide was an extra plasticizing material which decreased minimum torque. The reinforcement index, tensile moduli and tensile strength were increased up to a 3.0 phr of palmitamide concentration. The enhancement in those properties was due to the enhancement in crosslinks as well as cure state of the compounds of silica-filled SBR.

1. Introduction

Based on their sources, rubbers are classified as natural and synthetic rubbers. Natural rubber is produced from a rubber tree and synthetic rubbers are produced by applying the synthetic or polymerization process. As a popular synthetic rubber, styrene-butadiene rubber (SBR) is polymerized by free radicals of styrene and butadiene. It has excellent mechanical properties and processing behaviour but it is extremely susceptible to deterioration due to the presence of several double bonds in its main chains.

SBR is a non-crystallize rubber and hence, it is important to reinforce the rubber to have some useful mechanical properties. Therefore, filler reinforcement is needed. Normally; carbon blacks (CBs) or silicas are used for the filler reinforcement upon rubbers. Usually, at relatively bigger silicas or CBs concentration, those fillers particles form filler agglomeration [2] which degrade mechanical properties of the SBR articles [3]. Solving the problem, a specific rubber additive must be added into into-filled-SBR compounds practically.

Therefore, this study was aimed to solve the silica-particles agglomeration inside the SBR compounds through the utilizations of palmitamide. By adding the palmitamide while compounding, the degree of silica dispersion was improved and hence, a higher reinforcement effect of silica on SBR would be provided. The additive is oily and oil is a plasticizing agent [4] and it was the reason why the palmitamide was utilized to improving the silica dispersion. This study investigated the influences of palmitamide on vulcanization properties and reinforcement index of silica-filled SBR compounds.
2. Chemicals and methodology

2.1. Chemicals
The SBR and other compound ingredients include sulfur, zinc oxide, precipitated silica, isopropyl-N'-phenyl-p-phenylenediamine, mercapto benzothiazolyl disulfide and stearic acid were given by the rubber lab of the school of materials and natural resources, Universiti Sains Malaysia (USM), Nibong Tebal-Malaysia.

2.2. Rubber compounding
The SBR and other compounds ingredients were compounded based on the semi-EV cure system. Sequences of SBR 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            |
| Isopropyl-N'-phenyl-p-phenylenediamine | 2             |
| Stearic acid                      | 2              |
| Mercapto benzothiazolyl disulfide | 1.5            |
| Zinc oxide                        | 5              |
| Precipitated silica               | 30             |
| Palmitamide                       | 0; 1; 3; 5; and 7 |

2.3. Vulcanization properties
The SBR vulcanization properties include (t, optimum cure time), max. torque (M), min. torque (M), the change in torque (\(M_\text{c} - M_\text{n}\)) (based on ISO 3417) were delivered by the use of a Rheometer (MDR 2000). The vulcanization processes were held at 150°C.

2.4. Determination of tensile properties and reinforcement index
Tensile properties of vulcanized SBR were observed according to ASTM D-882 using tensometer with extension rate is of 500 mm/minute. Reinforcement index (RI) was calculated based on Equation 1.

\[
\text{RI} = \left( \frac{M_\text{300}}{M_\text{100}} \right) \times 100
\]  

(1)

3. Results and discussion

3.1. Vulcanization properties
The influences of palmitamide concentration on vulcanization properties of silica-filled SBR are visualized in Figs. 1-4. From Figure 1, that 1.0 phr of palmitamide incorporation decreased minimum torque. Since minimum torque indicates viscosity of rubbers compounds, the palmitamide decreased the SBR viscosity. The decreasing in viscosity was because of the oily property of palmitamide and, oil is a plasticizing agent[4]. As observed, the bigger the palmitamide loading, the lower was the viscosity or minimum torque. It was due to the more amount of palmitamide in the silica-SBR compounds and hence, the more significant the plasticizing affection.
From Fig. 2, the 1.0 phr of palmitamide incorporation increased the maximum torque. Since maximum torque indicates stock modulus that was raised in this observation. The increase in maximum torque due to the behaviour of rubber to filler interactions include intercalation and exfoliation [5]. The increase in maximum torque became more significant when the palmitamide concentrations were further increased up to a 3.0 phr. Therefore, the processes of intercalation, exfoliation and rubber to filler interactions were further raised.

From Fig. 3, the 1.0 phr of palmitamide incorporation increased the change in torque. Increases the palmitamide concentration up to a 3.0 phr further increases torque change. The torque change is the crosslinks level of a compound of rubber [6-7]. The bigger the torque change, the higher also cross links level. The total crosslinks is the summation of sulphide and physical crosslinks[8]. The palmitamide
incorporations up to a 3.0 phr increased the torque change. It was due to the increment of physical crosslinks which was improved through the greater rubber to filler interactions.

![Figure 3. Torque change vs palmitamide concentration.](image3)

From Fig. 4, the 1.0 phr of palmitamide incorporation decreased optimum cure time of control SBR compound. In this observation, palmitamide was a curative chemical that affected the vulcanization of SBR [9]. Since nitrogen atom is a type of accelerators [4]; positively, the amine part of palmitamide functioned as an extra accelerator causing in a more pronounced the acceleration performance of MBTS during vulcanization. The bigger the palmitamide loading, the lower was the optimum cure time. It was due to the bigger amount of palmitamide presented in the SBR compounds and hence, the more pronounced the acceleration affection was.

![Figure 4. Optimum cure time vs palmitamide concentration.](image4)
3.2. reinforcement index and tensile properties

Table 2 shows the reinforcement index (RI) and tensile properties of silica-filled SBR without and with palmitamide. The tensile properties include tensile moduli (M300 and M100) and tensile strength (TS). As observed in Table 2, the 1.0 phr of palmitamide incorporation increased the RI, M300, M100 and TS of the control compound of SBR. The enhancement in the above properties was due to the cross links increasing of SBR through the enhance mentin rubber to filler interactions or physical crosslinks[10-14]. The increases of palmitamide concentration up to a 3.0 phr further increase the RI, M300, M100 and TS and, after the incorporation of 3.0 phr of palmitamide, those properties started to reduce. The enhancement in those properties was due to cross links increasing, and the deterioration in those properties was due to crosslinks decreasing. This explanation agreed with the result of the change intorque as shown in Fig. 3.

| SBR compounds | Palmitamide loadings (phr.) |
|---------------|-----------------------------|
|               | 0.0 | 1.0 | 3.0 | 5.0 | 7.0 |
| M100, Mega Pascal | 0.82 | 0.98 | 1.03 | 0.99 | 0.89 |
| M300, Mega Pascal | 1.39 | 1.75 | 1.94 | 1.69 | 1.49 |
| TS, Mega Pascal | 10.90 | 15.37 | 21.87 | 18.20 | 17.70 |
| RI, % | 169 | 178 | 188 | 170 | 167 |

4. Conclusion

Based on the results; the palmitamide was a curative material for silica-filled styrene-butadiene rubber. It decreased the optimum cure time but increased torque difference. Palmitamide also increased the reinforcement index of the silica by enhancing the degree of silica dispersion as reducing the silica-filled styrene-butadiene rubber viscosity. The tensile moduli and tensile strength were enhanced specifically up to three phr of palmitamide concentration.

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