Enhancing the reinforcing efficiency of silica on styrene-butadiene rubber through the use of palmitamide

I Surya*1, M Ginting2
1Department of Chemical Engineering, Universitas Sumatera Utara, Medan, Indonesia
2Department of Chemistry, Universitas Sumatera Utara, Medan, Indonesia
E-mail: I. Surya (indradanas@yahoo.com; isurya@usu.ac.id)

Abstract. In this paper, enhancing the reinforcing efficiency of silica on styrene-butadiene rubber (SBR) compounds through the use of palmitamide was carried-out. The palmitamide was laboratory prepared from palmitic acid and urea and loaded into the silica-filled SBR compounds at 1, 3, 5 and 7 phr. It was found that palmitamide exhibited modulus and tensile strength enhancements; the tensile modulus at 100% and tensile strength were enhanced, especially up to a three phr of palmitamide concentration. It was revealed that the modulus and tensile enhancements were attributed to the enhancing of reinforcing efficiency of silica on the SBR through the use of palmitamide as a curative and plasticizing rubber chemical which increased the degree of silica dispersion, interactions SBR to silica as well as cure state. From scanning electron microscopy (SEM) or morphology test, it was proved that the SEM image of silica-filled vulcanizates with 3 phr of palmitamide exhibited the greatest matrix tearing lines that indicated the greatest degree of filler dispersion and interactions between SBR to silica.

1. Introduction
As a non-crystallize rubber; to have several useful mechanical properties, silica type of reinforcing filler can be added to the SBR compounds. But, at relatively a higher silica concentration, the silica particles turn to form agglomeration [1]. These silica agglomerations degrade tensile properties of the SBR vulcanizates [2]. It is usual to figure out the filler agglomerations problem by adding a specific chemical as dispersant/processing aid.

The degree of filler reinforcement provided by silica depends on the development of greater interactions of rubber and silica. The interactions depend on the surface area of silica particles [3]. The silica agglomerations positively reduce the available surface of the filler to interact with SBR.

The degree of reinforcement which is provided by silica can be determined by its reinforcing efficiency. High reinforcing efficiency has the meaning of great interactions of rubber to the filler that is affected by the degree of filler dispersion. A better degree of filler dispersion can provide greater interactions of rubber to filler. Therefore, this study aimed at enhancing the reinforcing efficiency of silica on SBR through the use of palmitamide.

2. Chemicals and method

2.1. Chemicals
The SBR and other compound ingredients include sulfur, zinc oxide, precipitated silica, isopropyl-N'-phenyl-p-phenylenediamine, mercapto benzothiazolyl disulfide, stearic acid were prepared by the rubber lab of P.T. Industri Karet Deli, Medan, Indonesia. The palmitamide was lab-prepared by reacting the palmitic acid with urea. The molecule structure of palmitamide is CH3(CH2)14CONH2.
2.2. SBR compounding
The SBR and other rubber chemicals were compounded based on the semi-EV vulcanization system. Sequences of SBR compounding were done based on ASTM D3184-80 on a lab-type 2-roll mill. Table 1 presents the recipe for SBR 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. Optimum cure time and torque properties
The optimum cure time ($t_{90}$) and torque properties include maximum torque ($M_x$), minimum torque ($M_n$) and change in torque ($M_x - M_n$) were determined based on ISO 3417 through the use of a Rheometer (MDR 2000). The vulcanization temperature was 150 °C.

2.4. Determination of tensile properties and reinforcement efficiency
Tensile properties of vulcanized filled SBR include tensile moduli ($M_{300}/M_{100}$) and tensile strength (TS) were determined based on ASTM D-882 through the use of tensometer with extension rate at 500 mm/minute. Reinforcement efficiency (RE) was calculated based on torque properties of the silica-filled SBR vulcanizates using Equation 1 [4].

$$RE \, (\%) = 100(M_x - M_n)_f - (M_x - M_n)_{uf} / (M_x - M_n)_{uf}$$  \(1\)

In which;

$$(M_x - M_n)_f = \text{Torque change of filled vulcanizate}; (M_x - M_n)_{uf} = \text{Torque change of unfilled vulcanizate}$$

2.5. Morphology properties
The morphology properties were tested applying a Zeiss Supra-35VP scanning electron microscope (SEM) to attain information concerning the available existence of micro-defects. The tensile fractured pieces were covered with a layer of gold to exclude electrostatic charge build-up at the same time as the testing.

3. Results and discussion

3.1. Optimum cure times and torque properties
The influences of palmitamide incorporations on vulcanization properties of silica-filled SBR include optimum cure time ($t_{90}$) and torque properties are shown in Table 2. As shown, an incorporation of one phr of palmitamide reduced the optimum cure time of control compound of SBR. It was observed that the palmitamide acted as a curative agent which interfered the vulcanization properties of SBR compound. Decreasing in optimum cure time has the same meaning with increasing in the rate of vulcanization process and; since nitrogen atom is one type of accelerators [5]; presumably, the amine ingredient of palmitamide has acted as an additional or extra accelerator, besides MBTS and hence, increased the performance of MBTS during the vulcanization process. A bigger concentration of palmitamide caused a lower optimum cure time. It was due to a more pronounced was the acceleration performance.
From Table 2, an incorporation of one phr of palmitamide reduced minimum torque (Mn). Since minimum torque relates to the rubber compound viscosity; The decreasing in viscosity was because of the oily behaviour of the palmitamide which decreased viscosity. In rubber technology, it is popular to used oil as a plasticizing agent. A bigger the palmitamide concentration caused a lower in minimum torque. It was because of the more pronounced the plasticizing performance of the palmitamide.

![Table 2. The influences of palmitamide t90 and torque properties of compounds of SBR](image)

From Table 2, an incorporation of one phr of palmitamide raised maximum torque (Mx). Since maximum torque indicates the stock modulus, the increase in maximum torque was because of action of palmitamide as compatibilizer which improved the processes of intercalation and exfoliation. The increase in maximum torque or intercalation and exfoliation processes was more pronounced whenever the concentration of palmitamide was further improved up to a three phr.

From Table 2, an incorporation of one phr of palmitamide increased change in torque (Mx - Mn) of SBR control compound. Increasing in the palmitamide concentration up to a three phr further increased torque change. Since torque change is the indication of crosslinks level of a rubber compound [6-7], the palmitamide increased the crosslinks of silica-filled SBR compounds and the increases the palmitamide concentrations up to a three phr caused in further increased the crosslinks. Since total crosslinks in a rubber vulcanizate are the summation of physical and sulphide crosslinks; the improvement in crosslinks was because of the improvement in physical crosslinks due to the action of palmitamide as a compatibilizing agent.

3.2. Filler dispersion properties

Based on torque properties, the filler dispersion properties for the silica inside the compounds of SBR was determined by applying Equation (2) [8].

\[ L = \eta_R - m_R \]  

(2)

In which: \( \eta_R \) is \([Mn_f / Mn_{uf}]\) and \( m_R \) is \([Mx_f / Mx_{uf}]\), in which Mn \( f \) and Mx \( f \) are the minimum and maximum torques of the filled SBR and Mn \( uf \) and Mx \( uf \) are the minimum and maximum torques of the unfilled SBR. A lower L value, at an appropriate silica concentration, is a better degree of silica dispersion. The minimum and maximum torques of unfilled SBR were 0.72 and 6.18, respectively [9].

The value of L at various palmitamide concentrations is shown in Fig. 1. As shown, the value of L filled SBR systems with palmitamide were lower than filled SBR systems with no palmitamide. The bigger the palmitamide concentration, the lower was the value of L and hence, it was because of the plasticizing affection of palmitamide that lowered viscosity and improved the degree of silica dispersion, respectively.
3.3. Reinforcement efficiency (RE)

Fig. 2 shows the reinforcing efficiency (RE) and Table 3 shows M100 and tensile strength (TS) of silica-filled SBR without and with palmitamide. As shown in Fig. 2 and Table 3, an incorporation of one phr of palmitamide raised the RE, M100 and TS of the SBR control compound. The raising of those RE and tensile properties was because of the crosslinks raising of SBR through improving the interactions between rubber and silica or physical crosslinks [10-13].

The increases of palmitamide concentration up to a three phr further increased the RE, M100 and TS and after the three phr of palmitamide concentration, RE and those tensile properties started to diminish. The enhancing in those tensile properties was due to crosslinks increasing; the deterioration in those tensile properties was due to crosslinks decreasing.
Table 3. The M100 and tensile strength of vulcanizates of SBR

| SBR vulcanizates | Palmitamide in phr |
|------------------|--------------------|
|                  | 0.0                | 1.0    | 3.0    | 5.0    | 7.0    |
| M100, Mega Pascal| 0.82               | 0.98   | 1.03   | 0.99   | 0.89   |
| TS, Mega Pascal  | 10.90              | 15.37  | 21.87  | 18.20  | 17.70  |

3.4. Morphology properties

The scanning electron microscopy or SEM images with 200X magnification of fractured surfaces of CB-filled SBR vulcanizates without and with palmitamide is shown in Fig. 3. The images of silica-filled SBR vulcanizates with palmitamide (Figs. 3B and 3C) showed a bigger matrix tearing lines than silica-filled SBR vulcanizates without palmitamide (Fig. 3A). The tearing lines correlate to the value of TS [14]. A bigger matrix tearing lines indicated a greater TS [14,15]. The rupture energy improvement was because of a greater interaction of rubber to filler. The 3b image of silica-filled SBR system with three phr of palmitamide showed the greatest matrix tearing lines which indicated the crosslinks were at the highest level, causing in TS enhancement.

Figure 3. The SEM images of silica-filled SBR compounds failed fracture at a 200X-magnification; (A) 0 phr of palmitamide (B) 3 phr of palmitamide (C) 5 phr of palmitamide.

4. Conclusion

The palmitamide enhanced the reinforcing efficiency of silica on silica-filled styrene-butadiene rubber.
The enhancing reinforcing efficiency was performed through improving the degree of filler dispersion and rubber to filler interactions, respectively. The enhancing in tensile moduli and tensile strength were attributed to enhancements in crosslinks as well as the cure state. The morphology test confirmed the three phr of palmitamide was the optimum concentration which produced a tensile fractured image with the greatest matrix tearing lines.

References
[1] Surya I and Ismail H 2018 MATEC Web Conf 197 12006.
[2] Surya I and Ismail H 2019 IOP Conf Ser Mater Sci Eng 509 012053.
[3] Boonstra B B 1973 Polymer 20 (6) 691-704.
[4] Hashim A S, Kohijiya S and Ikeda Y 1995 Polym Int 38 (2) 111-117.
[5] Rodgers B 2004 Rubber Compounding: Chemistry and Applications CRC.
[6] Ismail H and Ng C 1998 J Elastom Plast 30 (4) 308-27.
[7] Hayeemasae N, Surya I and Ismail H 2016 Int J Polym Anal Ch 21 (5) 1-12.
[8] Lee B 1979 Rubber Chem Technol 52 (9) 1019-29.
[9] Surya I, Ismail H and Azura A R 2015 Polym Test 42 208-14.
[10] Sianturi R W and Surya I 2018 J Phys Conf Ser 1116 (4) 042033.
[11] Surya I, Hayeemasae N and Ginting M 2018 IOP Conf Ser Mater Sci Eng 343 012009.
[12] Andriani F and Surya I 2018 J Phys Conf Ser 1116 (4) 042005.
[13] Surya I, Ginting M and Anto J 2018 AIP Conf Proc 2024 (1) 020061.
[14] Ismail H and Mathialagan M 2012 Polym Test 31 199-208.
[15] Nabil H, Ismail H and Azura A 2013 Polym Test 32 385-393.

Acknowledgement
The researchers thank PT. Industri Karet Deli (Medan – Indonesia) for the availability of research facilities.

Funding
This research work was supported by the PDUPT Scheme of DRPM Kemenristekdikti (2019).