

# Effects of palmitamide on cure and tensile properties of styrene butadiene rubber

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**Abstract.** A semi EV curing system was applied for studying the effects of palmitamide on cure and tensile properties of silica-filled styrene-butadiene rubber (SBR) compounds. The palmitamide was prepared from palmitic acid and urea. As an additive material, the palmitamide was added into the silica-filled SBR at 0.0, 1.0, 3.0, 5.0 and 7.0 parts per hundred rubber (phr.). It was found that the palmitamide acted as a curative additive material which decreased the scorch and cure times but increased the difference in torque of the silica-filled SBR compounds. The higher the palmitamide loading, the shorter the scorch and cure times were. It was also found that the palmitamide acted as an internal plasticizer material which decreased the minimum torque. The tensile moduli and tensile strength were increased but the elongation at break was decreased up to a 3.0 phr. of palmitamide loading. From the swelling test, the improvements in tensile properties were attributed to the improvements in crosslink density as well as the cure state of the silica-filled SBR compounds.

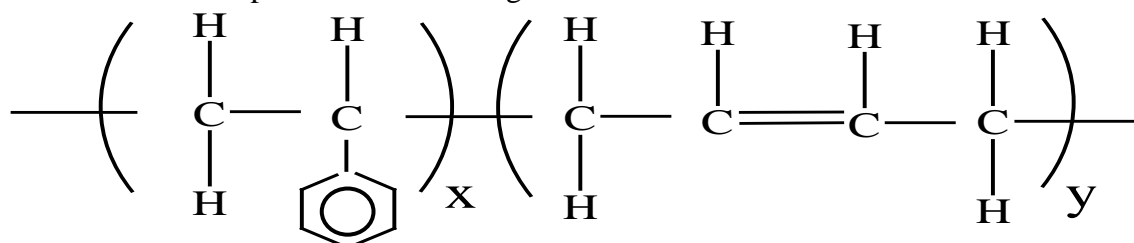
## 1. Introduction

As a synthetic rubber; the styrene butadiene rubber (SBR) is prepared by the free radicals polymerization of styrene and butadiene, resulting as a random co-polymer and irregular structure as shown in **Fig. 1**. SBR is a non-crystallize rubber. It possesses good mechanical properties and processing behavior, can be used like NR due to good abrasion, crack-initiation and flex resistances. Nevertheless; similar with unsaturated elastomers, it is extremely susceptible to deterioration, because of the presence of some double bonds in the main chains. Deterioration of SBR is accelerated by humidity, heat, light, radiation and ozone [1]. Some properties of SBR such as wear resistance, heat ageing and curing properties are better than NR due to the presence of styrene group in its backbone.

As a non-crystallize rubber; in order to have some useful mechanical properties, a type of reinforcing fillers must be added to the SBR compounds. Normally; reinforcing fillers include carbon black (CB) or precipitated silica is popularly used for the purpose. Nevertheless, at relatively higher silica or CB loading, the fillers particles turn to make agglomeration [2]. Filler agglomerations degrade properties of the elastomers articles [3]. Rationally, in order to handle the problem of filler dispersion, some specific additives include processing aid and dispersant aids are utilized.

In this study, a new rubber additive namely palmitamide will be used to solve the filler dispersion problem. The additive can be synthesized from palmitic acid and urea. Physically,

the palmitamide is an oily material and oil is utilized as a plasticizing agent [4] and hence, the palmitamide is a potential rubber additive which helps increase the degree of filler dispersion. Therefore in this study, it was added into silica-filled SBR while compounding operation through the use of a two-roll mill. The effects of palmitamide on cure and tensile properties of silica-filled SBR compounds were investigated.



**Figure 1.** Molecular structure of SBR.

## 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, 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.

**Table 1.** 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. Cure properties

The SBR cure properties include ( $ts_2$ , scorch time), ( $t_{90}$ , cure time), max. torque ( $M_x$ ), min. torque ( $M_n$ ), the difference in torque ( $M_x - M_n$ ) (based on ISO 3417) were delivered by the use of a Rheometer (MDR 2000). Compounds/samples of NR were vulcanized at 150°C.

## 2.4. Tensile properties

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.

## 2.5. Swelling behavior

Studying swelling behavior was conducted in toluene based on ISO 1817. The SBR vulcanized test pieces (30 mmx5 mmx2 mm) were weighed through the use of a balance and swollen in toluene for reaching an equilibrium that took 72 hours at room temperature. Samples of SBR were removed from the toluene and then rest of toluene was removed from SBR surfaces and then the weights were completed. The change in mass is:

$$\text{Swelling percentage (\%)} = 100\% (W_2 - W_1) / W_1 \quad (1)$$

Where,  $W_1$  is original mass (gram) and  $W_2$  is mass (gram) beyond immersion in toluene.

## 3. Results and discussion

### 3.1. The cure properties

The effects of palmitamide additions on the cure properties of silica-filled SBR are presented in **Table 2**. The cure properties include time to scorch ( $t_{s2}$ ), time to cure ( $t_{90}$ ), min. torque ( $M_N$ ) and max. Torque ( $M_X$ ). As presented in **Table 2**; whenever compared to the control SBR compound (silica-filled SBR compound with no palmitamide), the additions of palmitamide decreased the cure and scorch times of control SBR compound. The palmitamide can be considered as a curative agent because it affected the curing process of SBR [5]. Since nitrogen atom is one type of accelerators [4]; presumably, the amine content of the palmitamide acted as an additional accelerator which caused in a more pronounced the acceleration effect of primary accelerator (MBTS) during the curing process.

**Table 2.** The effect of palmitamide on cure properties of SBR

SBR compounds	Palmitamide loadings (phr.)				
	0.0	1.0	3.0	5.0	7.0
$t_{s2}$ , minutes	12.74	11.24	9.08	8.22	7.53
$t_{90}$ , minutes	25.84	24.41	21.43	19.13	17.94
$M_X$ , dN.m	7.83	8.52	9.50	9.30	8.90
$M_N$ , dN.m	1.87	1.82	1.72	1.69	1.49
$(M_X - M_N)$ , dN.m	5.96	6.70	7.78	7.61	7.41

The more the loading of palmitamide, the lower the time to scorch and time to cure were. It was because of the more and more amount of the palmitamide which causing in a more pronounced the acceleration effect of the accelerators.

The palmitamide addition of 1.0 phr. decreased min torque which corresponded to the viscosity of the SBR that was decreased in this study. It was due to the nature of the palmitamide which was an oily material. The material of oil is a plasticizing material that decreased the viscosity of a rubber compound [4]. As can be seen in **Table 2**, the more the loading of palmitamide, the lower the minimum torque was. It was because of the more the

amount of palmitamide inside the SBR compounds and hence, the greater was the palmitamide fraction inside the SBR compounds.

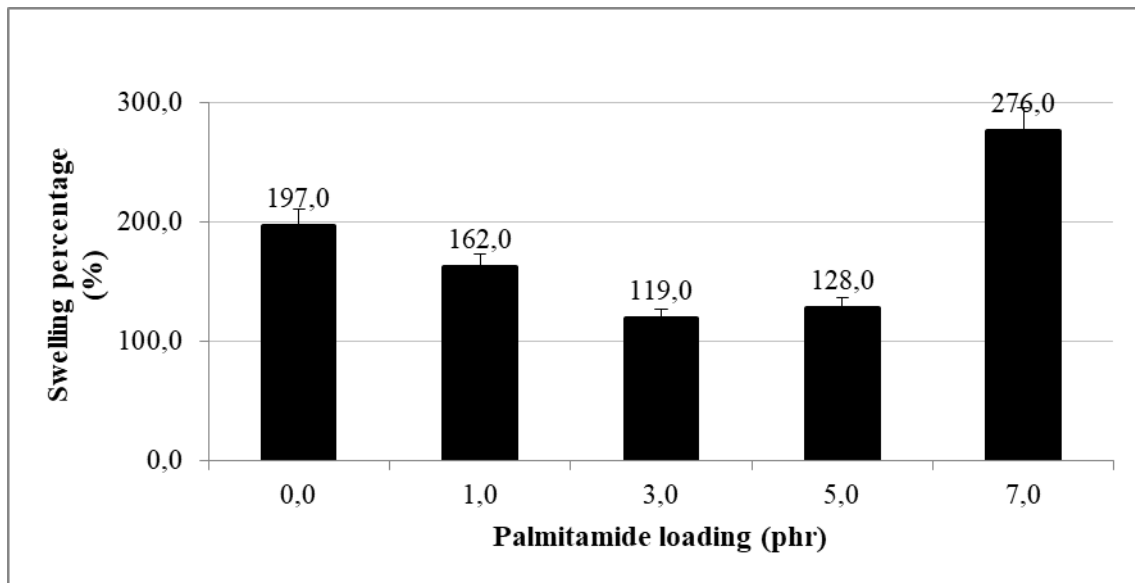
The palmitamide addition of 1.0 phr. increased the max torque which related to stock modulus that was enhanced in the investigation. It was because of the nature of rubber to filler interaction including intercalation and exfoliation [6]. The increases in max torque became more significant when the loadings of palmitamide were further enhanced up to a 3.0 phr. The intercalation together with exfoliation and also rubber to filler interaction were further enhanced.

The palmitamide addition of 1.0 phr. produced an SBR compound with a higher difference in torque compared to control SBR compound. The palmitamide additions up to a 3.0 phr. of loading further enhanced torque difference. The torque difference is the crosslink density of a compound of rubber [7-8]. The higher the torque difference value, the higher also crosslink density. The total crosslink density is the sum of sulphide crosslinks and physical crosslinks [8-9]. The palmitamide additions of up to a 3.0 phr. increased the torque differences of the SBR compounds. It was because of the increases of physical crosslinks which enhanced the formation of SBR to silica filler interaction.

### ***3.2. The swelling percentage***

The effect of palmitamide additions on swelling percentage of silica-filled SBR is presented in **Fig. 2**. The swelling percentage is the crosslink density of a rubber compound [9]. A less toluene infiltration into rubber compound sample means a higher degree of crosslink density. As presented in **Fig. 2**; the additions of palmitamide from 1.0 to 3.0 phr. caused in decreasing swelling percentage or increasing crosslink density of control SBR compound. The further additions of palmitamide beyond the 3.0 started to increase the swelling percentage or decrease crosslink density. These increases and decreases in crosslink density agreed with the result of the effects of palmitamide on torque difference of silica-filled SBR (see **Table 2**).

The increases in crosslink density were because of the plasticizing effect of palmitamide that improved the degree of silica dispersion and SBR to silica interaction, respectively. The deteriorations in crosslink density might be because of excessive loading of palmitamide which isolated silica from SBR and deteriorated rubber to filler interaction, respectively [10-11].



**Figure 2.** Effects of palmitamide on swelling percentage of silica-filled SBR compounds

### 3.3. The tensile properties

**Table 3** presents the effects of palmitamide additions on tensile properties of silica-filled SBR. The tensile properties include tensile moduli (M100 and M300), tensile strength (TS) and also elongation at break (EB). As presented in **Table 3**, the palmitamide additions affected tensile properties significantly. The palmitamide addition of 1.0 phr. increased the tensile moduli of the control SBR compound. The more the palmitamide loading, the higher were tensile moduli.

Because of tensile moduli depend on the crosslink density of a compound [12-14]. The improvements in tensile moduli were because of the increases in crosslink density of SBR. As discussed earlier, rubber to filler interaction between SBR and silica was considered as physical crosslink [15-18] and this type of crosslink together with sulphide crosslink gave to total crosslink density of SBR [19]. The more the loading of palmitamide, the denser the physical crosslink and as a consequence, some increases in tensile moduli of SBR were observed. The explanation agreed with the results of difference in torque in **Table 2** and swelling test in **Fig. 2**. The torque difference of SBR with a higher palmitamide loading was higher than that of SBR with a lower palmitamide loading.

**Table 3.** The effect of palmitamide on tensile properties of SBR

SBR compounds	Palmitamide loadings (phr.)				
	0.0	1.0	3.0	5.0	7.0
M100, Mega Pascal	0.82	0.98	1.23	1.17	1.07
M300, Mega Pascal	1.49	1.65	1.84	1.77	1.69
TS, Mega Pascal	10.90	15.37	21.87	18.20	17.70
EB, Percent	900	870	850	865	890

From **Table 3**, the additions of palmitamide affected the tensile strength (TS) of SBR compounds. The additions of palmitamide increased the TS up to a 3.0 phr. of loading and after the loading, the TS started to decrease. The improvements in TS were because of the

increases in crosslink density and the decrease in TS was because of the deterioration in crosslink density.

As seen in **Table 3** which presents the influence of palmitamide additions on the elongation at break (EB) of compounds of SBR; the additions of palmitamide decreased the EB up to a 3.0 phr. of palmitamide loading. It was because of the increases in crosslink density which immobilized the SBR chains.

The palmitamide addition after the 3.0 phr. of loading started to increase the EB. It was attributed to the more pronounced of the palmitamide effect as an internal plasticizing agent that decreased the crosslink density. As a consequence, the mobilization of the SBR chains became more freely.

#### 4. Conclusion

From the results and discussion can be concluded that:

The palmitamide acted as a curative material for silica-filled styrene butadiene rubber. It decreased the time to scorch and time to cure but increased torque difference. Palmitamide helped to increase the reinforcement effect of the silica by improving the degree of silica dispersion as decreasing the viscosity of silica-filled styrene butadiene rubber. The tensile properties were enhanced especially up to a three phr. of loading of palmitamide.

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