Renewable Compatibilizing Agent for Silica Reinforced Natural Rubber

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Abstract. The main problem in utilizing silica as an alternative reinforcing filler for natural rubber (NR) compounds is a weak rubber-filler interaction and poor filler distribution due to their incompatibility feature. The particles of silica have a strong tendency to filler interactions which leads to form silica agglomeration. To solve this drawback, this work has utilized ethanolamine-modified palm stearin (EMPS) as a renewable compatibilizer agent to improve NR-silica compatibility. The EMPS was prepared by a typical chemical reaction between ethanolamine and refined bleach-deodorized palm stearin (a byproduct of cooking oil production) on a laboratory scale. The influence of the EMPS on the improvement of rubber-filler interaction was investigated by studying the processing characteristics and the tensile properties of silica-reinforced NR compound (silica content was fixed at 30 phr). Compared to the silica-reinforced NR with no EMPS, it was found that EMPS caused a greater coefficient of vulcanization, tensile strength, and reinforcement effect for the silica-reinforced NR. It was due to an active reaction between silanol groups of silica with EMPS which increased the NR-silica compatibility, and the Fourier Transform Infra-Red (FTIR) analysis has confirmed the typical reaction.

1 Introduction

Referring to the best properties in rubberiness/elasticity, resilience, stiffness, toughness, and strengths, Natural rubber (NR) is widely used in manufacturing rubber goods and products. [1]. NR is a strain-induced crystallization material because it can crystallize whenever it is stretched. This strain-induced crystallization provides good and desirable mechanical properties of vulcanized NR. Moreover, NR also has very good tackiness and dynamic properties [2]. Generally, the compound of NR with a curing agent, activator and co-activator agents, accelerator, anti-degradant agent, and processing aids are processed and will provide NR vulcanizate with excellent mechanical properties [3]. These excellent mechanical properties are greatly further enhanced by adding reinforcing fillers, including carbon black (CB) or silica [4-6]. The choice of reinforcing filler type depends on the desired properties and specific application of the rubber product. The amount and reinforcing filler, along with other compounding chemicals, are carefully selected to design the desired balance of

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properties while considering factors including production cost, processing requirements, and environmental considerations.

CB is achieved by the incomplete combustion of natural gas or oil. It is used in producing black-coloured rubber products, whilst silica is used to produce light-coloured products [4]. Silica is utilized to improve the abrasion resistance, tear resistance, and tensile strength of rubber products. It is particularly important in producing vehicle tires, where these properties are crucial for safety and durability. In tire production, silica is often added to the tread compounds. This can enhance the tire's grip and traction on wet surfaces, making it safer in wet conditions. Silica, combined with other additives, like silane coupling agents, can enhance the dispersion of silica particles in the rubber matrix, ensuring a more even dispersion and better performance. Silica in rubber compounds also can help reduce rolling resistance in tires. Lower rolling resistance results in cheap fuel consumption and reduced carbon emissions, making vehicles more environmentally friendly.

Otherwise, the presence of silanol groups makes silica unsuitable or incompatible with NR, leading to poor silica distribution and reinforcement effect [5]. The structure of silica agglomerates in rubbers should be diminished by modifying the silica surface to achieve better miscibility of silica to rubber, higher filler distribution level, easier compound processability, and other vulcanizate properties [5].

Many researchers have modified the silica surface, including admicellar polymerization [7-8], plasma polymerization [2, 9], silane [10-11], and amide treatments [12-14]. In this examination, ethanolamine-modified palm stearin (EMPS) was utilized to improve the NR-silica interaction. The chemical reaction in producing EMPS is visualized in Fig. 1. Moreover, the optimum loading of EMPS was investigated to achieve a better mechanical property.

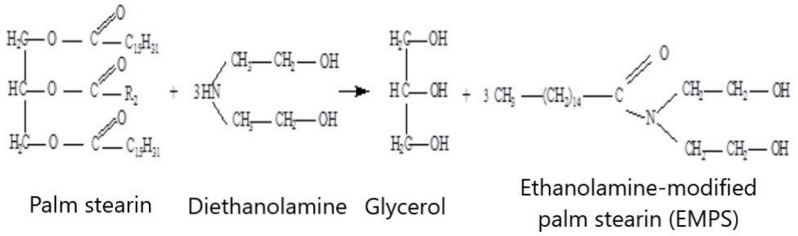

Fig. 1. Chemical reaction in producing EMPS [15]

2 Materials and Method

2.1 Materials

The EMPS was lab-prepared by performing the reaction between diethanolamine with palm stearin. NR (SMR/L), vulcasil S (precipitated silica), zinc oxide (ZnO), stearic acid, IPPD, MBTS, and sulfur were supplied by Rubber Lab, Engineering Campus of Universiti Sains Malaysia.

2.2 Laboratory preparation of EMPS

The preparation of EMPS was carried out in a stirred 1000 ml glass vessel. Raw materials of 1 mol of palm stearin, 3 mol of diethanolamine, natrium methoxide, and catalyst methanol were placed in the flask. The reaction temperature was kept at 70 ºC for 5 hours. The extraction and purification processes are visualized in Fig. 2.

2.3 Conventional rubber compounding on a two-roll mill

The NR reinforced with silica compounds were prepared relating to the rubber mixture shown in Table 1. The silica was loaded at 30 phr for each compound. NR and all rubber ingredients were compounded on a lab-scaled two-roll mill. The compounds must be rested for at least 24 hours before the vulcanization process and testing, such as tensile and processing properties, were carried out. The NR-Silica-EMPS compounding process is visualized in Fig. 3.

Table 1. Rubber mixture of NR-silica with and with no EMPS as a compatibilizer agent

Chemical substances	EMPS - (parts per hundred parts NR, phr)				
	0	**1**	**3**	**5**	**7**
NR	100	100	100	100	100
ZnO	5.1	5.1	5.1	5.1	5.1
Acid of stearic	2.2	2.2	2.2	2.2	2.2
Antioxidant	2.2	2.2	2.2	2.2	2.2
MBTS	1.7	1.7	1.7	1.7	1.7
Sulfur	1.7	1.7	1.7	1.7	1.7
EMPS	0	1	3	5	7
Silica	30	30	30	30	30

2.4 The processing characteristics

The determination of processing characteristics includes minimal torsion (T_L), maximal torsion (T_H), delta torsion ($T_H - T_L$), cure time (t_{90}), scorch time (t_{s2}) and rate of coefficient vulcanization (Rv). They were determined by applying the Oscillating Disk Rheometer based on the method of ASTM D2084. Samples of rubber approximately 5 grams were determined for its processing characteristics at a temperature of 150 ºC, with oscillating frequency = 100 cpm for 30 min.

2.5 The tensile properties determination

Determination of tensile properties was carried out according to ISO 37 using an ordinary tensometer or universal testing machine. The extension rate was 500 mm/min. The reinforcement index (RI) was determined based on tensile or torsion properties through the application of 2 equations, i.e., equations (1) and (2).

2.6 The determination of reinforcement index (RI)

The degree of silica reinforcement effect (RE) in the presence of EMPS compatibilize on NR was calculated using equations (1) [16] and (2) [17]. Equation 1 is based on torsion properties as follows,

$$RE = (T_H - T_L)\, f - (T_H - T_L)\, g \,/\, (T_H - T_L)\, g \quad (1)$$

Equation 2 is based on tensile properties as follows,

$$RE = (M300 \,/\, M100) \times 100\ \% \quad (2)$$

In which, M300 and M100 = stresses at 300% and 100% strains, respectively.

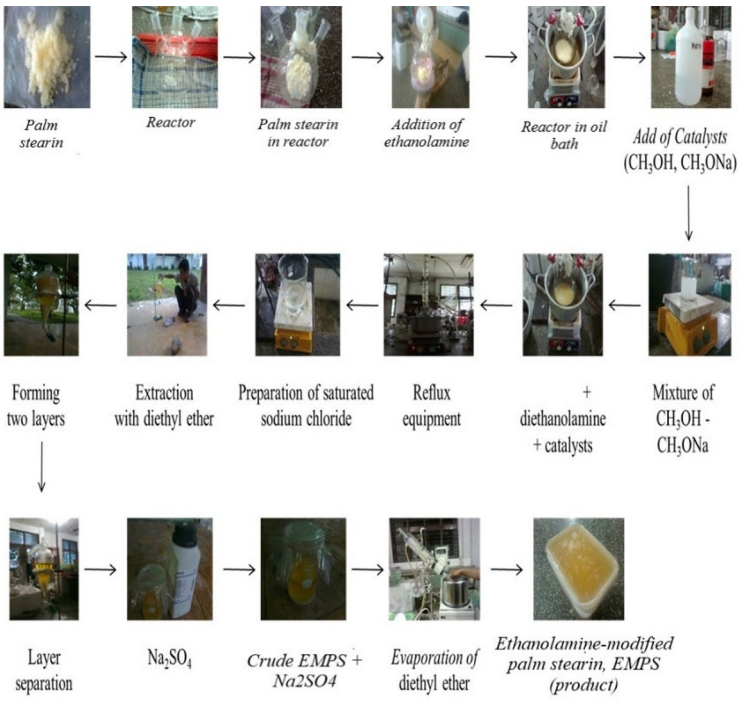

Fig. 2. The flow diagram of the preparation of EMPS

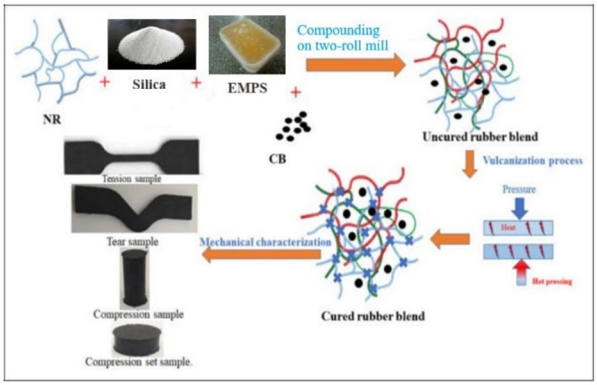

Fig. 3. The NR-Silica-EMPS compounding process

3 Results and discussion

3.1 Fourier Transform – Infra Red spectrum

The EMPS FTIR spectrum was characterized using an ATR or attenuated total reflection - FTIR spectrometer ranging from 4000 to 400 per cm. The FT-IR characterized of EMPS is visualized in Fig. 4. As visualized, the typical infrared spectrum of EMPS and the wavenumber belong to EMPS functional groups.

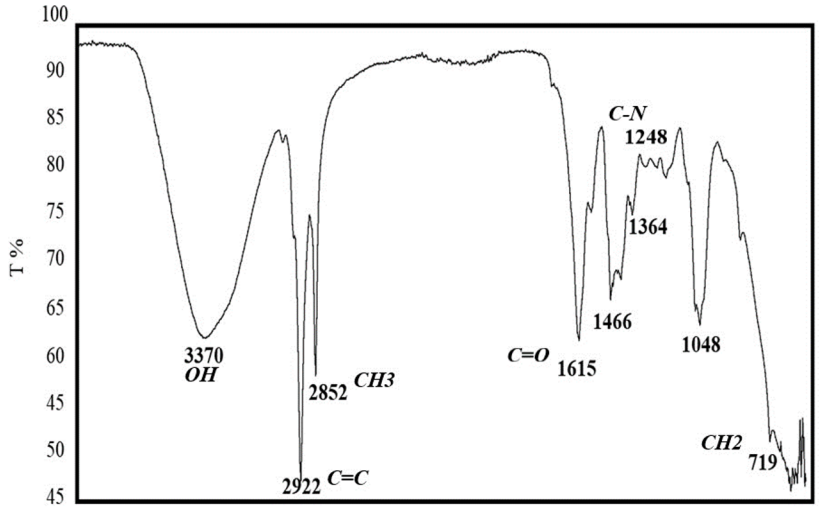

Fig. 4. FTIR spectra of EMPS

3.2 Processing characteristics

Processing characteristics of silica-reinforced NR with and without EMPS are tabulated in Table 2. Silica-reinforced NR with EMPS has a shorter cure time and scorch time than those of silica-reinforced NR with no EMPS. Greater EMPS concentration causes further shorter cure and scorch times. The rate coefficient of vulcanization (Rv) is visualized in Fig. 5, and, as observed, the EMPS additions increased the Rv value. It was because the EMPS functional groups were hydrolyzed to form a hydroxyl group and then overwhelmed the condensation reaction with the silica silanol groups [18], causing less adsorption of the accelerator.

Table 2. Processing characteristics of silica-reinforced NR with EMPS

NR compound	Composition (phr)	T_H, dNm	T_L, dN.m	Delta, dN.m	t_{90}, min.	t_{s2}, min.
Gum	-	4.88	0.07	4.81	-	-
Sil-filled	30	10.34	1.23	9.11	9.67	4.96
Sil-EMPS	1	10.29	0.78	9.51	8.72	4.60
	3	11.40	0.65	10.75	6.87	3.70
	5	11.60	0.51	11.09	5.19	2.57
	7	9.40	0.24	9.16	4.69	2.33

3.3 Determination of crosslink density

Table 2 presents the delta torsion of the compound silica-reinforced NR with EMPS. An addition of 1 phr EMPS into the compound NR-silica has produced a compound with a higher value of delta torsion, and the EMPS additions up to 5 phr have lifted the delta torsion. However, the delta torsion was decreased by the further increase of the EMPS (7 phr). The value of delta torsion is usually used to indicate the crosslink level or density of a compound [19], the crosslink properties of the compounds of NR-silica with varied EMPS would adopt their values of delta torsion. The crosslink density as a function of delta torsion is visualized in Fig. 6.

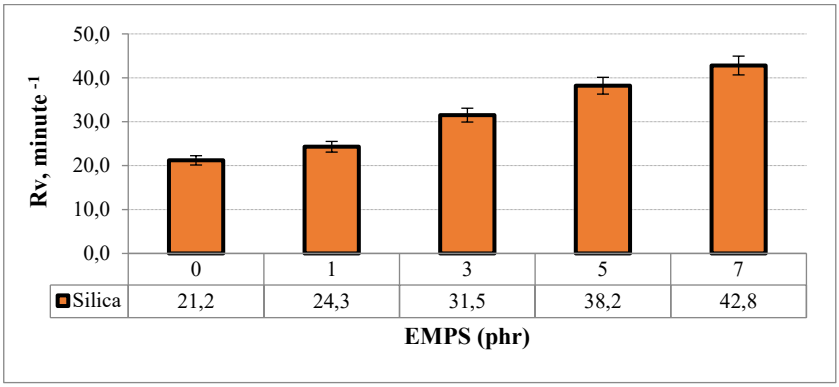

Fig. 5. Rv value vs EMPS concentration

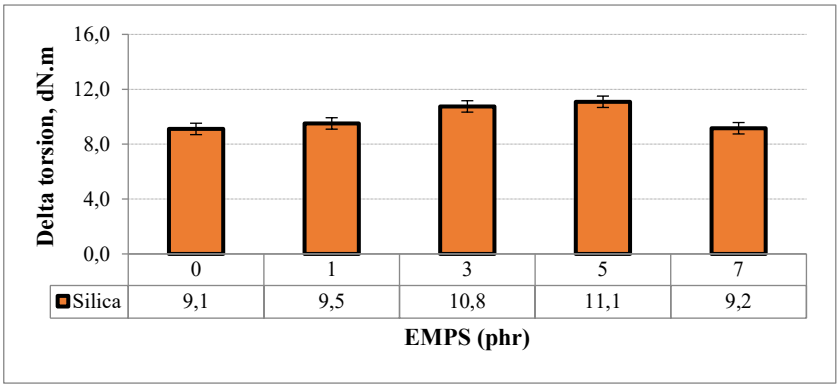

Fig. 6. Delta torsion vs EMPS concentration

A greater delta torsion means a level degree of crosslink density, and total or overall crosslink is the quantity of sulfide plus physical crosslink [20-21]. From the result, the 5 phr of EMPS addition has increased the maximal torsion minus minimal torsion. Therefore, it was positive due to the EMPS function, which changed the hydrophobic silica into more hydrophobic silica. The latter silica seems more compatible with NR. It is easy to understand that the incorporations of EMPS have weakened the filler-filler action but strengthened the rubber-filler action, respectively. This could be because of the formation of coupling bonding of NR-EMPS-silica, and this typical bonding could be assumed as another type of crosslink, which further improved the total crosslink of the compound NR-silica-EMPS. The reduction of the value of delta torsion beyond a 5 phr of EMPS incorporation was because of the excessive affection of EMPS amount, which diminished the crosslinking level.

3.4 Tensile properties

Tensile strength (TS), reinforcement index (RI), and elongation at break (EB) of vulcanizate NR-silica with and with no EMPS are visualized in Figs. 7-10, respectively. RI, EB, and TS of silica-reinforced NR with EMPS were greater than those of silica-reinforced NR with no EMPS. Enhancements in RI and EB were due to silica-reinforced NR with EMPS samples having higher crosslink density. The enhancement in EB was due to the effect of EMPS as a plasticizing substance, which allowed NR chains to move freely. The greater the amount of EMPS, the higher the RI, TS, and longer EB.

It can be observed that the RI, both based on torsion properties and tensile modulus properties, were increased with the addition of EMPS. The increased RI value means a greater interaction between NR and silica. It was observed that the EMPS presence had caused a higher RI of silica. It was because of a better degree of silica dispersion and a greater interaction of NR-silica as the presence of compatibilize EMPS. This discussion agrees with the results in Table 2.

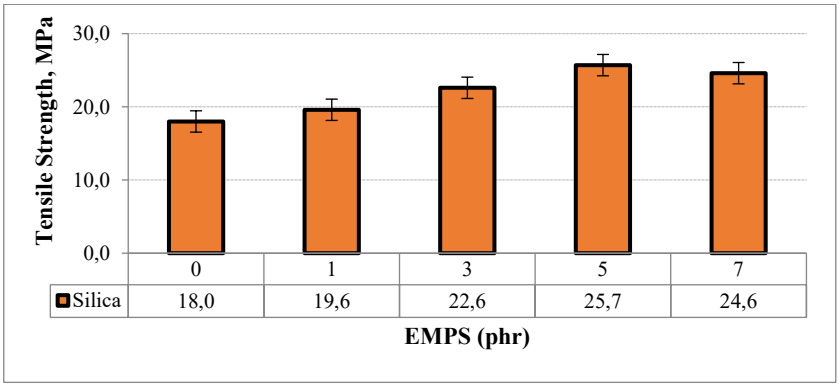

Fig. 7. Tensile strength vs EMPS concentration

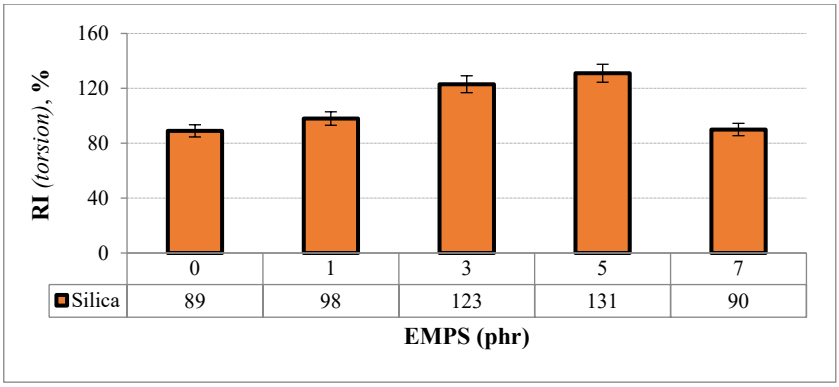

Fig. 8. RI (based on torsion) vs EMPS concentration

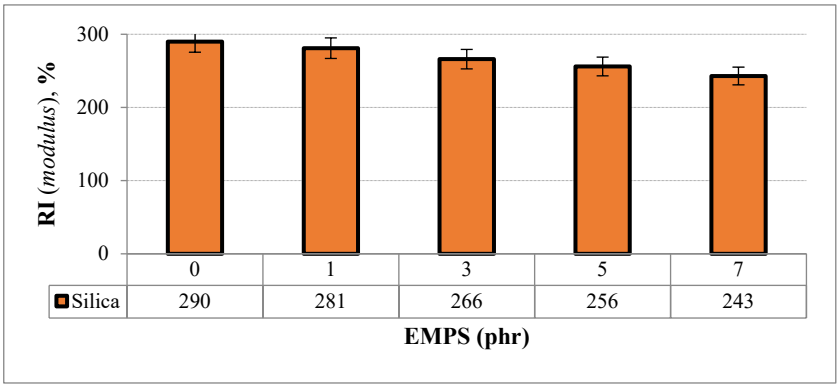

Fig. 9. RI (based on tensile modulus) vs EMPS concentration

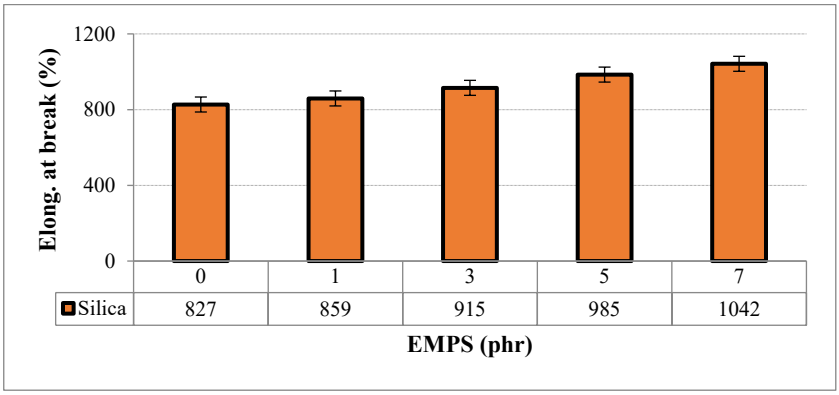

Fig. 10. Elongation at break vs EMPS concentration

4 Conclusion

Ethanolamine-modified palm stearin has been proven to be used as a plasticizing substance for silica-reinforced natural rubber compounds. The ethanolamine-modified palm stearin caused better processing characteristics, reinforcement index, and tensile properties. The rate coefficient of vulcanization was improved the ethanolamine-modified palm stearin addition. The bigger the ethanolamine-modified palm stearin concentration, the greater the value of the rate coefficient of vulcanization. The ethanolamine-modified palm stearin increased the reinforcing efficiency of silica on natural rubber. The bigger the ethanolamine-modified palm stearin concentration, the higher also the tensile strength of the silica-reinforced natural rubber vulcanizate.

This work was supported by the collaboration between Universiti Sains Malaysia (USM), Malaysia and Universitas Sumatera Utara (USU), Medan.

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