

Research article

Influence of benzyl esters of vegetable oils on curing, mechanical and dynamic properties of silica filled natural rubber and styrene-butadiene rubber compounds

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Abstract. Benzyl ester oils (BEO) were prepared by esterification of fatty acids from three different types of vegetable oils, *i.e.*, coconut, palm, and soybean oils using benzyl alcohol in the presence of an acid catalyst. They are then exploited as alternative rubber processing oils with the main aim to replace conventional aromatic oil. The influence of BEO on mixing, curing, viscosity, crosslink density, dynamic and mechanical properties is investigated in silica-filled natural rubber (NR) and styrene butadiene rubber (SBR) compounds. The rubber compounds with BEO exhibit lower mixing energy, higher cure rate index (CRI) and torque difference. Furthermore, the NR compounds with BEO have a lower Mooney viscosity than the one with aromatic oil, but the SBR compound has the opposed trend. Higher crosslink density and superior mechanical properties are observed in NR vulcanizates with the coconut benzyl ester oil. On the other hand, lower crosslink density and inferior mechanical properties are observed in the SBR vulcanizates with BEO as compared to the SBR compound with aromatic oil. It is therefore concluded that some types of the BEO could be possible as alternatives to be used instead of the typical aromatic oil in rubber compounds with some advantages.

Keywords: rubber, enyl ester oil, aromatic oil, natural rubber (NR), styrene-butadiene rubber (SBR)

1. Introduction

Silica-filled rubber compounds have been used in various applications in widely, particularly in tire manufacturing. This is due to the rolling resistance of tires which could be reduced by replacing carbon black with silica [1]. Silica is generally classified as a highly polar filler material because of the large number of silanol groups on the surface of the silica particles. The polar nature of silica causes negative effects on its compatibility and hence dispersion as well as distribution in nonpolar elastomers [2]. Likewise, strong hydrogen bonds between the silica particles themselves result in tight silica aggregates and agglomerates, causing poor dispersion of silica in the rubber compounds [3]. A good dispersion of the filler

in a rubber compound is a very important aspect that affects the mechanical and dynamic properties of rubber vulcanizates [3, 4]. The filler dispersion in silica-filled rubber compounds is generally worse than that of the carbon black counterpart due to its higher polarity. Moreover, when a large amount of silica is added, the viscosity is substantially increased, making the rubber compound more difficult to process, with high processing energy and causing wear of the processing equipment. Additionally, the fine silica particles tend to adsorb or, in some cases to, react with the polar chemicals in the rubber formulation, such as cure accelerators, which normally causes interference with the curing process by decreasing the cure rate and hence an increase in the cure

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time of rubber compounds. Because of these constraints, the use of silica in rubber compounds has been limited to certain products, including shoe soles, hot-water bottles, and rice polisher brake/rolls [5]. Chemical modification of the silica surface by bifunctional organosilanes is widely performed to overcome those drawbacks of silica. Such modified silica can be easily dispersed in a rubber matrix and has shown the maximum reinforcement effect [6, 7]. A number of organosilanes have been developed and evaluated in rubber compounding along with various types of silica [7]. Among these, bis(triethoxy silyl propyl) tetrasulfane (TESPT) has become the most widely used. It has been reported that the bifunctional organosilane, TESPT (Si-69) functions as a coupling agent in silica-filled nonpolar rubbers [8]. During mixing, one of the ethoxy silyl groups in the TESPT reacts with a silanol group of the silica. This is followed by a condensation reaction between pairs of neighboring silane molecules. At higher temperatures during vulcanization, a third reaction between the coupling agent and the rubber molecules takes place through added sulfur in the rubber compound or generated by disproportionation of the TESPT. Therefore, silica-filled rubber compounds prepared based on organosilane coupling agents show improvement in properties such as tensile and tear strengths, heat build-up, rolling resistance, and wet skid resistance [9].

Vegetable oils are gaining noteworthy importance to substitute petroleum-based carcinogenic oils in the rubber industry. The renewable epoxidized palm oil and polymerized soybean oil are suitable substitutes of petroleum-based distillate aromatic extract in carbon-black-filled NR/SBR composites [10]. Furthermore, it was found that soybean oil fatty acid (SBOFA) improved the flowability of the NBR compound and enhanced the thermal resistance of the NBR vulcanizate and showed a comparable plasticizing efficiency and mechanical strength with the DOP-plasticized NBR [11]. Furthermore, new vegetable oils, including Moringa oil (MO) and Niger oil (NO) was compounded with silica-filled natural rubber composite (NRC) in comparison with petroleum-based naphthenic oil (NTO). The results revealed that MO and NO exhibited higher thermal stability and better processability, tensile strength and low dynamic energy loss than NTO [12]. Moreover, in the bio-based blends of polyamide 1010 (PA1010) with 20 wt% of polylactide (PLA), four

different compatibilizers were used to enhance the miscibility and the performance. It was found that two multi-functionalized vegetable oils (maleinized linseed oil (MLO) and epoxidized linseed oil (ELO)) improved elongation at break and toughness, and two petroleum-derived glycidyl-based additives (epoxy styrene-acrylic oligomer (ESAO) and styrene-glycidyl methacrylate copolymer (PS-GMA)) provided excellent balanced properties [13]. In addition, palm oil was also used to prepare epoxidized palm oil (EOP) and then react with bisphenol A (BPA), through the epoxy fusion process. The reaction product could be used as modifiers of a commercial bisphenol A-based low molecular weight epoxy resin [14].

Benzyl ester oil (BEO), in the forms of coconut benzyl ester (CBE), palm benzyl ester (PBE), and soybean benzyl ester (SBE) is composed of benzyl ester head groups and unsaturated aliphatic hydrocarbon tails [15]. The benzyl ester oil can diffuse fast into silica agglomerates due to its low molecular weight. Hence, hydrophobization of the silica surface is achieved by adding benzyl ester oil. During mixing, the silica-silica network will be reduced and made more compatible to the nonpolar rubber and hence better filler dispersion. Additionally, silica-benzyl ester oil-rubber coupling might be formed during vulcanization, resulting in higher polymer-filler interactions [16]. In addition, reactions of sulfur with the unsaturation ($-C=C-$) in the benzyl ester oil molecules can also occur during vulcanization, forming linkages between benzyl ester oil and rubber molecules. Hence, there is a strong possibility that the benzyl ester oils can perform dual functions: as processing oil and as a bifunctional coupling agent in silica-filled compounds. In this work, the feasibility of exploiting the benzyl ester oil as a coupling agent and process oil in silica-filled natural rubber and styrene butadiene rubber compounds is investigated.

2. Materials and methods

2.1. Materials

The materials used in this work are presented in Table 1.

2.2. Compounding and characterization

Various types of benzyl ester oil (BEO) were first prepared by modification of fatty acids from three different types of vegetable oils, including coconut, palm, and soybean oils. This was done by esterification of

Table 1. Materials and suppliers.

Materials	Suppliers
NR (Air dried sheet, ADS)	Klongchang co-operative rubber Ltd, Khokpho, Pattani, Thailand
SBR (SBR 1502)	JSR-BST Elastomers Co., Ltd., Rayong, Thailand
Zinc oxide	Global Chemical Co., Ltd., Samut Prakan, Thailand
Sulfur	Siam Chemicals Co., Ltd., Samut Prakarn, Thailand
Stearic acid	Imperial Chemical Co., Ltd., Pathum Thani, Thailand
Silica (Ultrasil VN3)	Siam Silica Co., Ltd., Rayong, Thailand
Bis(triethoxy silyl propyl) tetrasulfane (TESPT)	Zhenjiang Wholemark Fine Chemical Co., Ltd, Jiangsu, China
<i>N,N'</i> -diphenyl guanidine (DPG)	DKSH Co., Ltd., Bangkok, Thailand
<i>N</i> -tert-butyl-2-benzothiazole sulfonamide (TBBS)	Flexsys America L.P., Ohio, USA
Benzyl alcohol	Lanxess Deutschland GmbH, Cologne, Germany
Coconut oil	Zun Heng Co., Ltd., Pattani, Thailand
Palm oil	Lam Soon Co., Ltd., Trang, Thailand
Soybean oil	Thai Vegetable Oil Co., Ltd., Nakorn Pathom, Thailand
Aromatic oil (ST-20A)	Sunoco (Thailand) Co., Ltd., Bangkok, Thailand

the fatty acids using benzyl alcohol in the presence of an acid catalyst under optimum reaction conditions. The details of the preparation techniques of the benzyl ester oils were reported elsewhere in our previous work [15, 17–19]. In the present work, the influence of benzyl ester oil on the properties of silica (Ultrasil VN3) filled NR and SBR compounds are investigated by using the rubber formulations, as shown in Table 2 with the corresponding mixing schedule indicated in Table 3. It is to be noted that two steps of mixing were performed, *i.e.*, masterbatch and final mix (Table 3). In the masterbatch, rubber and various chemicals were mixed in an internal mixer with a mixing capacity of 500 ml (Charoen Tut, Co., Ltd., Samut Prakarn, Thailand) at 60 °C and a rotor speed of 60 rpm. The rubber was first masticated for 2 min, and then the first half of the mixture between silica and silane was incorporated and mixed for about 5 min. Then, the second half of the mixture of the silica and silane together with the process oil was added into the mixing chamber and mixing was continued for another 5 mins. After that, zinc oxide, stearic acid and DPG were then sequentially incorporated and mixed for about 3 mins., and eventually, the rubber compound was dumped out of the mixing chamber. In the final mix, the masterbatch was mixed with curing agents (*i.e.*, TBBS and sulfur) on a two-roll mill (Chaicharoen Karnchang Ltd., Bangkok, Thailand) for about 0.5 and 4.0 min after adding TBBS and sulfur at room temperature. The compound

Table 2. Compounding formulations of silica filled NR and SBR compounds.

Ingredient	NR [phr]	SBR [phr]
Rubber	100.00	100.00
Zinc oxide	5.00	3.00
Sulfur	2.25	1.75
Stearic acid	2.00	1.00
Silica (Ultrasil VN3)	50.00	50.00
Silane [Bis(triethoxy silyl propyl) tetrasulfane, TESPT]	4.00	4.00
DPG	1.05	1.05
TBBS	0.70	1.00
Processing oil ^a	10.00	10.00

^aAromatic oil (AO), coconut benzyl ester (CBE), palm benzyl ester (PBE), soybean benzyl ester (SBE).

Table 3. Mixing schedule of silica filled NR and SBR compounds.

Step 1.	Master batch	Time [min]
	Rubber mastication	2.0
	1/2 Silica + 1/2 Silane	5.0
	1/2 Silica + 1/2 Silane + process oil	5.0
	Zinc oxide + Stearic acid + DPG	3.0
Step 2.	Final mix	Time [min]
	Master batch	3.0
	Accelerator (TBBS)	0.5
	Vulcanization agent (sulfur)	4.0
	Discharge	

was then discharged from the mill and conditioned overnight at room temperature before testing. The rubber compounds were tested in terms of mixing energy, curing characteristics, Mooney viscosity, crosslink density, dynamic and mechanical properties.

2.3. Testing of the rubber compounds before vulcanization

2.3.1. Mixing energy

Mixing energy [J] during rubber compounding was determined in the form of mixing torque at various mixing times by using the Equation (1) [20, 21]:

$$\begin{aligned} \text{Mixing energy} &= \\ &= \text{Mixing torque} \cdot \text{Mixing velocity} \cdot \text{Mixing time} \end{aligned} \quad (1)$$

2.3.2. Cure characteristics

The rubber compound was sheeted out and then conditioned at $25 \pm 2^\circ\text{C}$ for about 24 h in a closed container before determining the curing properties by using a moving die rheometer (rheoTech MD plus; Monsanto Inc., Ohio, USA) at 150°C for NR and at 160°C for SBR compounds. The scorch time (t_{s1}), optimum cure time ($t_{c,90}$), maximum torque (M_H), and minimum torque (M_L) were then evaluated from the curing curves. The cure rate index, CRI [min^{-1}] was determined from the Equation (2) [21]:

$$CRI = \frac{100}{t_{c,90} - t_{s1}} \quad (2)$$

2.3.3. Mooney viscosity

The Mooney viscosity and Mooney stress relaxation test of the rubber compounds were determined using a Mooney viscometer (Premier™ MV, Alpha Technology, Ohio, USA) at 120°C according to ASTM D 1646-94.

2.3.4. Dynamic mechanical properties

The dynamic mechanical properties of the rubber compounds were tested over a frequency range using a rubber process analyzer (RheoTech MDPT, TechPro, Inc., Ohio, USA) equipped with conical-shaped dies. Uniform shear strain was performed in the rubber samples as the deformation under a constant maximum strain. The sample was loaded into the lower die, and then the upper die was closed to form a constant volume of the compression mold. The oscillating frequency was set in the range of 0.1 to 30 Hz at a

constant maximum strain of 15% and at 120°C . The storage modulus, loss modulus, and loss tangent (*i.e.*, $\tan \delta$) were determined [22].

2.4. Testing of rubber vulcanizates

2.4.1. Crosslink density

The extent of crosslinking or crosslink density was determined by the swelling of rubber vulcanizates in toluene. Rubber samples with dimensions of $10 \times 10 \times 2$ mm were first immersed in toluene at 25°C for at least 24 h. The toluene was then refreshed to remove the extracted components, and extraction continued for another 24 h. The swollen rubber samples were then weighed, dried at 50°C for 48 h to remove the solvent, and weighed again [23]. The crosslink density was eventually determined based on the Equation (3) [23]:

$$\phi_p = \frac{V_p}{V} = \frac{1}{1 + \frac{m - m_d}{m_d}} \cdot \frac{\rho_p}{\rho_s} \quad (3)$$

where ρ_p is the density of the polymer, ρ_s is the density of the solvent, m is the mass of the swollen sample, m_d is the mass after drying of the sample, and ϕ_p is polymer volume fraction.

The ratio of total volume (V) of the swollen rubber sample and the volume (V_p) of the dry polymer sample can be used to determine the swell ratio Q , as Equation (4) [23]:

$$Q = \frac{V}{V_p} \quad (4)$$

It is noted that the reciprocal swell ratio Q^{-1} could be used as the measured crosslink density of the rubber vulcanizates.

2.4.2. Tensile and tear properties

Vulcanized rubber slabs were prepared by compression molding, and then dumbbell-shaped specimens were prepared from the molded sheets using an ASTM Die C. The tensile tests were then conducted by using a universal tensile testing machine (Hounsfield Test Equipment Co., Ltd., Surrey, England) at $25 \pm 2^\circ\text{C}$ according to ASTM D 412 [24]. The modulus at 300% elongation, tensile strength, and elongation at break were determined based on the stress-strain curves. The initial length of the specimens used was 25 mm, and the cross-head speed of the test was set at 500 mm/min. Five samples were tested for each condition. The median values from 5 replicate samples of tensile strength, modulus at 300% elongation and

elongation at break are reported with the relative errors below 5% an acceptable level. The tear strength of the rubber vulcanizates was also determined according to ASTM D 624 under the same condition as the tensile tests.

2.4.3. Rebound resilience

The rebound resilience of the rubber samples was determined by a Wallace Dunlop Tripsometer (H.W. Wallace Ltd., Croydon, England) according to BS 903 Part A8 [25]. The dropping angle of the pendulum was set at 45° and the rebound angle was read from the dial. The rebound resilience was calculated as Equation (5) [25]:

$$\text{Rebound resilience [\%]} = \frac{1 - \cos \theta}{1 - \cos 45^\circ} \cdot 100 \quad (5)$$

where θ is the rebound angle.

2.4.4. Heat build-up

Heat build-up was determined with a Goodrich Flexometer (Ueshima Seisakusho Co., Ltd., Tokyo, Japan) according to the method described in ISO 4666/3-1982(E). A cylindrical sample with 25 mm height and 17.5 mm diameter was tested at 100 °C for 25 min by applying a weight of 11 kg and 4.45 mm stroke at a frequency of 30 Hz. The increase in temperature (ΔT) from the beginning of the test (T_0) to 25 min test time (T_{25}) was recorded.

2.4.5. Abrasion loss

The wear resistance property of vulcanized rubber was determined by an Akron abrader (H.W. Wallace Ltd., Croydon, England) according to ASTM D 1630-16 [26]. The sample and the grinding wheel were set at a certain leaning angle and load. The

machine abraded the samples, and the weight loss during the test was taken as the abrasion loss.

In this work, the abrasion resistance index (ARI) was determined in terms of a measure of the abrasion resistance of a vulcanized rubber relative to that of a standard rubber compound under specified conditions.

3. Results and discussion

3.1. Influence of oil types on properties of silica filled NR and SBR compounds

3.1.1. Mixing torque

Figure 1 shows the mixing torques of the silica-filled NR and SBR compounds with four different types of oil and without oil. It is clearly seen that the mixing torque-time curves can be divided into four different zones. The first zone represents the mastication step of rubber, where a first maximum torque is observed after adding the rubber (*i.e.*, NR or SBR) into the mixing chamber. The torque thereafter gradually decreases with increasing mixing time due to the break down of the rubber molecular chains and the level of chain entanglement and also shear heating, causing the rubber to soften. The silica was added into the compound in two steps (Table 3), as indicated by the mixing torque-time curves in the second and third zones. This is to avoid and prevent excessive shear forces generated during the mixing operation of the rubber compounds. In the second zone, it can be seen that the torque is abruptly increased after the first half of the silica and silane were incorporated into the mixing chamber. Then, a slight decreasing trend of the mixing torque is observed at the end of this mixing zone. This might be possibly due to large silica agglomerates broken down to smaller aggregates and some individual particles that

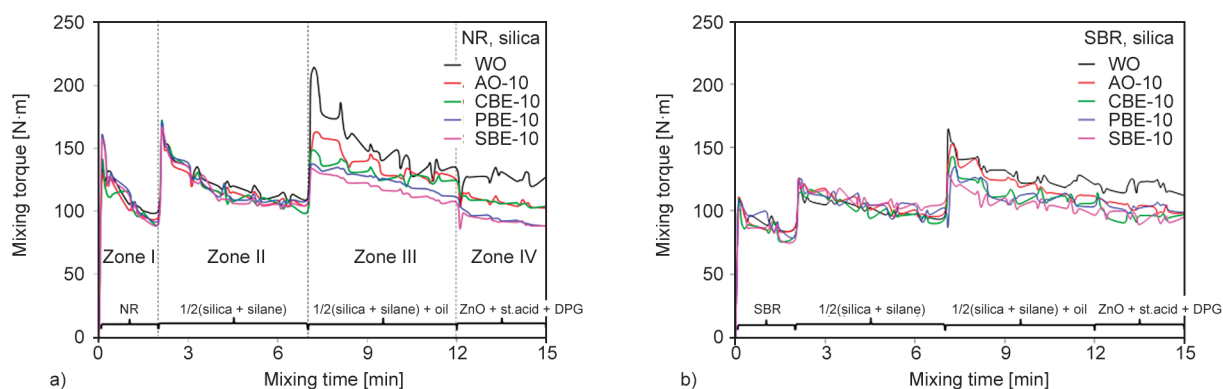


Figure 1. Mixing torque-time curves of silica filled NR (a), and SBR compounds (b), without (WO) and with various types of processing oil [*i.e.*, without oil (WO), aromatic oil (AO), coconut benzyl ester (CBE), palm benzyl ester (PBE) and soybean benzyl ester (SBE)] at a loading level of 10 phr.

are dispersed in the rubber matrix. Hence, the reduction of torque in the second zone could indicate the dispersion and distribution of silica in the rubber matrix. In the third zone, oil and the other half of silica with silane coupling agent were added into the rubber compounds. During the mixing operation, the rubber chains are forced into the interstices between agglomerates or aggregates of silica, and the process oil may contribute to improving chain mobility and wetting of the filler surfaces. As for mixing proceeds, the mixing torque progressively decreases in the third zone due to dispersion of the silica and softens the rubber matrix due to increased temperature because of shear heating. In Figure 1, it is clear that further addition of the compounding ingredients in the third zone causes higher mixing torque as compared with the torque in the second zone. This is attributed to the incorporation of more solid particles on top of the ones added in the second zone. Also, it is seen that the oil loading significantly decreases the mixing torque and hence reduces the mixing energy. In the last zone, the torque progressively decreased due to plasticization and lubrication effects of oil molecules and other chemical ingredients added, such as stearic acid and diphenyl guanidine (DPG) [27]. In Figure 1, it is also seen that the silica-filled rubber compounds with aromatic oil and benzyl ester oils show lower mixing torques compared to the compound without oil. The decrease in mixing torque is due to plasticization and lubrication effects of oil molecules that cause decreasing torque and hence viscosity of the rubber compounds. This causes improvement of the distribution of silica and other chemical ingredients in the rubber matrix. In Figure 1, among the compounds with oil, it is seen that the silica-filled rubber compounds with aromatic oil have the highest mixing torque, while soybean benzyl ester shows the lowest mixing torque. It is probably due to the fact that the soybean benzyl ester oil contains longer hydrocarbon chains that might cause lowering of the frictional forces between the molecular chains during the mixing operation [28]. The mixing energy was calculated by Equation (1), as shown in Figure 2. It is clear that the silica-filled NR compounds show higher mixing energy than the silica-filled SBR compounds. It is noted that the physical adsorption and chemisorption interactions of silica and rubber are responsible for the filler-polymer interactions [27]. Also, the weak polar nature of SBR causes better affinity to the silica surface than the nonpolar NR

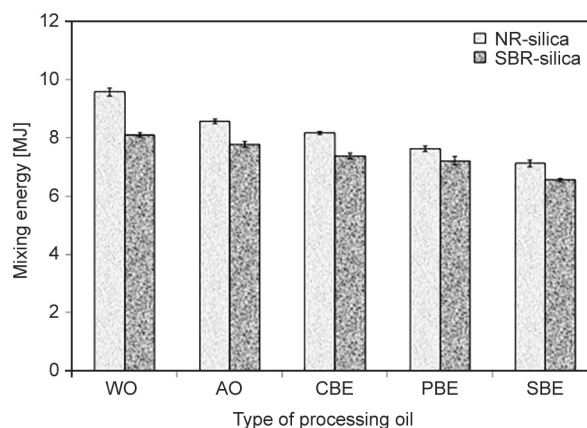


Figure 2. Mixing energy of silica filled NR and SBR compounds with various types of processing oil [*i.e.*, without oil (WO), aromatic oil (AO), coconut benzyl ester (CBE), palm benzyl ester (PBE) and soybean benzyl ester (SBE)] at a loading level of 10 phr.

molecules during the mixing [29]. This might be the reason for the lower energy required to disperse silica in the SBR matrix.

3.1.2. Mooney viscosity

The effect of oil types on the Mooney viscosity of the silica-filled NR, and SBR compounds is displayed in Figure 3. It is seen that the silica-filled compounds with processing oils have lower Mooney viscosities than the compound without oil. This is due to the plasticizing and lubrication effects of oil molecules so as to facilitate the molecular movement of rubber molecules to gain more chain flexibility. It is also seen that the silica-filled NR compounds show higher Mooney viscosities than the SBR compounds. This might be due to SBR having a lower molecular weight

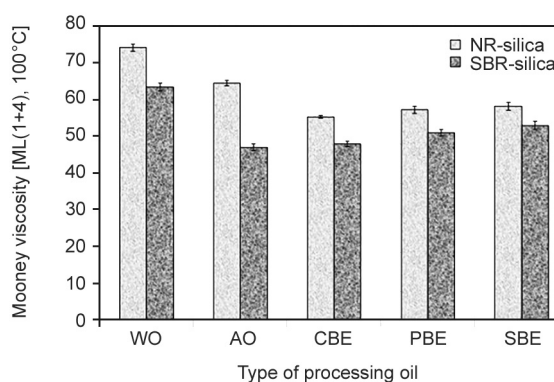


Figure 3. Mooney viscosity of silica filled NR and SBR compounds with various types of processing oil [*i.e.*, without oil (WO), aromatic oil (AO), coconut benzyl ester (CBE), palm benzyl ester (PBE) and soybean benzyl ester (SBE)] at a loading level of 10 phr.

and hence lower chain entanglement together with intermolecular forces than NR molecules. Figure 3 also reveals that the silica-filled NR compound with benzyl ester oils shows lower Mooney viscosity than the one with aromatic oil. Among the three different types of benzyl ester oils, the NR compound with coconut benzyl ester shows the lowest Mooney viscosity. This implies that the plasticizing and lubrication effects of coconut benzyl ester with the shortest hydrocarbon chains favor NR molecules than the other two types of benzyl ester oils, *i.e.*, palm benzyl ester and soybean benzyl ester. Furthermore, it is anticipated that the ester groups in benzyl ester oils might possibly interact with the silanol groups at the silica surface via hydrogen bonding, as possible chemical bonds formed between silanol groups on silica surfaces and polar functional groups in benzyl ester oil (BEO) shown in Figure 4. This might cause an improvement in the compatibility between rubber molecules and the silica surface. Thus, benzyl ester oils may be used as processing aids in natural rubber compounds. On the other hand, the silica-filled SBR compound with aromatic oil showed the lowest Mooney viscosity. This suggests that the aromatic oil has more plasticizing and lubrication effects in the silica-filled SBR compound than the benzyl ester oils and also favors the filler dispersion. It is noted that the SBR molecules contain aromatic rings along with the molecular structure so that they may be more compatible with the aromatic oil than the benzyl ester oils.

Figure 5 shows the Mooney stress-relaxation rate of silica-filled NR and SBR compounds with various

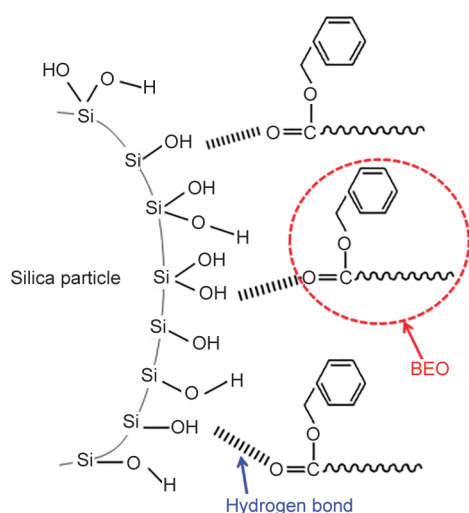


Figure 4. Possible chemical bonds between silanol groups on silica surfaces and benzyl ester oil (BEO).

processing oil types at a loading level of 10 phr. The Mooney stress relaxation rate is typically used to describe the elastic and viscous responses in the uncured rubber compounds. That is, a lower rate of Mooney stress relaxation indicates a higher elastic component, while a higher rate indicates a higher viscous component in the overall responses [28]. In Figure 5, it is seen that both NR and SBR compounds with oil have higher Mooney stress relaxation rates than the one without oil. This implies that the oil in rubber compounds causes a decrease of the elastic but increase of the viscous responses. This can be attributed to chain mobility and hence plastication and lubrication of the rubber molecules caused by the incorporation of the process oils. It is noted that a high viscous response of the uncured rubber compounds indicates better ease of processability [30, 31]. In Figure 5, it is also seen that the silica-filled NR compounds show lower Mooney stress relaxation rates which reflect higher elasticity than the silica-filled SBR compounds. This correlates well with the Mooney viscosity (Figure 4), as the silica-filled SBR had lower Mooney viscosity because of lower molecular weight, and hence a faster stress relaxation rate and hence higher viscous responses but lower elastic responses than the uncured filled NR compound.

3.1.3. Cure characteristics

The cure characteristics of the silica filled NR and SBR compounds with four different types of processing oils are displayed in Figure 6. Three different regions can be seen in the cure curves as a typical curve for accelerated sulfur vulcanization [32]. The

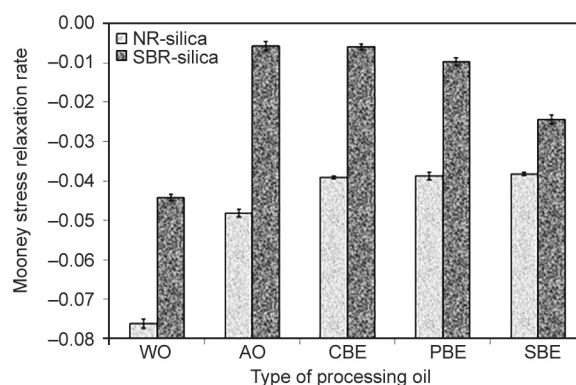


Figure 5. Mooney stress relaxation rate of silica filled NR and SBR compounds with various types of processing oil [*i.e.*, without oil (WO), aromatic oil (AO), coconut benzyl ester (CBE), palm benzyl ester (PBE) and soybean benzyl ester (SBE)] at a loading level of 10 phr.

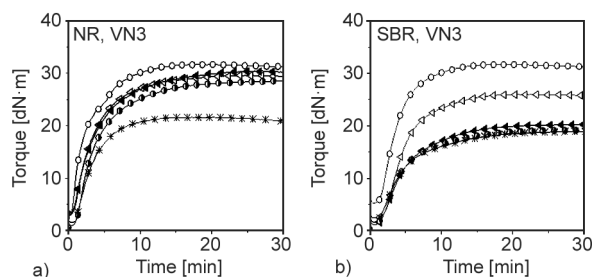


Figure 6. Cure curves of silica filled NR (a) and SBR (b) compounds with various types of processing oil [*i.e.*, without oil [without oil (WO, ○), aromatic oil (AO, ◁), coconut benzyl ester (CBE, ◀), palm benzyl ester (PBE, ●) and soybean benzyl ester (SBE, *)] at a loading level of 10 phr.

first region is the scorch or the induction period that provides safe processing time. The second region, where torques are abruptly rising as time increases, indicates the curing period. In this stage, the cross-linked networks of the rubber chains are formed, as observed by increasing torque and hence stiffness of the material. In the third region, the crosslinked rubbery networks are mature in the equilibrium state. Some rubber compounds may be over-cured to cause the reversion phenomenon, for instance, the NR compound with soybean benzyl ester (SBE). In Figure 6, it is also seen that the cure curves of silica-filled NR and SBR compounds without oil have the shortest induction period (*i.e.*, scorch time), indicating less process safety of these rubber compounds. In Figure 6, it is seen that the samples without oil showed the maximum torque values. This is attributed to the rubber compounds were not lubricated by oil, and also, the curing reaction did not disturb by the absorption of curing agents by oil. Furthermore, it is clear that mixing the same oil type in NR and SBR compound

caused different torque values. This may be due to differences in molecular characteristics, and hence Mooney viscosity of virgin NR and SBR together with NR contains higher unsaturation in molecules than SBR. This causes more reactivity of NR than SBR in curing reactions. The cure characteristics of the NR and SBR compounds with and without oil in terms of scorch time and cure rate index (*CRI*) are summarized in Figures 7a and 7b, respectively. It can be seen that the silica-filled NR compound shows shorter scorch times and higher cure rate indices than the silica filled SBR compounds. This may be due to the higher reactivity of the unsaturation (*i.e.*, $-C=C-$) in NR than the unsaturation of aromatic rings in SBR molecules [30]. Also, the chemical absorption between silica and curative in SBR and NR compounds with the same loading in both rubber compounds may be more or less the same but the difference in scorch time and cure rate index may come from differences in reactivity of rubber molecules. Furthermore, it is also clear that the NR and SBR compounds with benzyl ester oils exhibit shorter scorch times and lower cure rate indices than the rubber compounds with aromatic oil. It implies that the compounds with aromatic oil exhibit faster curing reactions and have slightly more process safely than the compounds with benzyl ester oils.

Figure 8a shows the minimum torques (M_L) of silica-filled NR and SBR compounds with various types of processing oils. It is noted that the minimum torque (M_L) is related to the compound viscosity and hence stiffness. Generally, the rubber chains have a certain probability of contacting the silica surface and entangling or get trapped in the voids of silica aggregates in uncured NR and SBR compounds. The

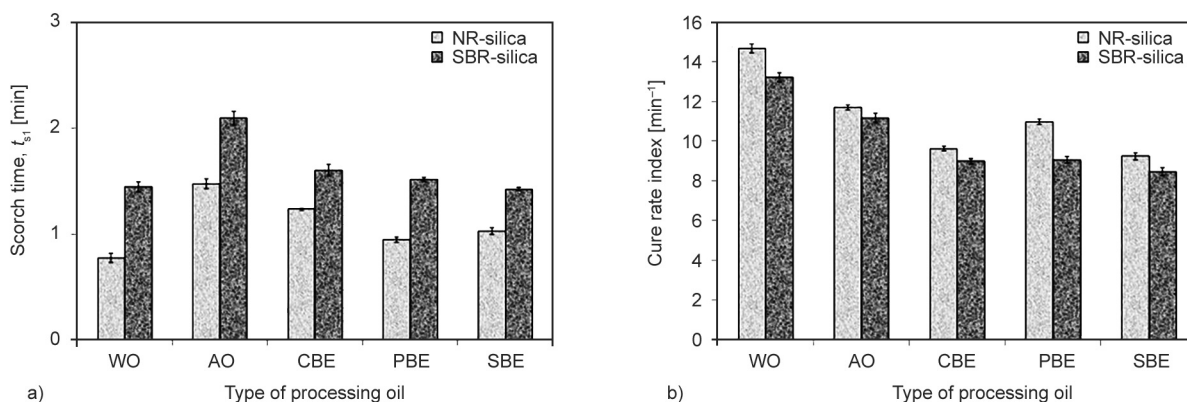


Figure 7. Scorch time (a) and cure rate index (*CRI*) (b) of silica filled NR and SBR compounds with various types of processing oil [*i.e.*, without oil (WO), aromatic oil (AO), coconut benzyl ester (CBE), palm benzyl ester (PBE) and soybean benzyl ester (SBE)] at a loading level of 10 phr.

rubber chains become highly immobilized and localized at the silica surface to form rubber shells surrounding the silica particles [33, 34]. Thus, the surfaces of the silica particles are covered by layers of entangled rubber chains which are considered as physical crosslinks [35]. These types of crosslinks hinder the mobility of the rubber chains and restrain their deformation. Also, the entangled rubber chains at the silica surfaces cause an increase in the minimum torque of the rubber compound. However, incorporation of process oil causes more chain flexibility and might be thicker layers of the rubber chains at the silica surface but less chain entanglement due to the oil. It is anticipated that the influence of plasticization and lubrication effects of the oil is more pronounced than the entanglement of rubber chains at the silica surface. Therefore, the M_L of silica-filled NR and SBR compounds without oil are higher than the ones with oil in the uncured state. It is also worth noting that the M_L of the uncured rubbers may be used as an indication of the degree of physical crosslinks. That is, the M_L increases correspondingly with an increase in specific surface areas of silica particles, as an increasing number of rubber chains is immobilized on the silica surface. In Figure 8a, it is clear that the silica-filled NR compounds show lower M_L than the SBR compounds. This may be related to the fact that SBR is not sensitive towards mastication like NR is [30], so the viscosities of the SBR compounds are not much changed. This contributes to the retention of the entangled SBR molecular layers at silica surfaces and hence increases of the minimum torque. Thereby, the silica filled SBR has more physical crosslinks in the uncured state than the silica filled NR. The silica-filled NR

compound with benzyl ester oil has a lower M_L than the one with aromatic oil. This can be attributed to a potential effect of the benzyl ester oil to cause decreasing of the chain entanglements of rubber molecules, in particular at the silica surface, and hence a decrease of the viscosity despite improving the filler dispersion and distribution. Thus, the benzyl ester oil could possibly be alternatively used as a processing aid or dispersing agent in silica filled NR compounds, where it shows superior performance and compound properties than the one with aromatic oil. In Figure 8a, it is also seen that similar values of M_L are observed in the compounds with coconut benzyl ester, palm benzyl ester, and soybean benzyl ester in silica-filled NR. Additionally, the silica-filled SBR compounds with aromatic oil show the lowest M_L . This is attributed to better compatibility of aromatic oil with SBR as compared to benzyl ester oils.

Figure 8b shows the torque differences or delta torque of silica-filled NR and SBR compounds with the various types of processing oil. It is noted that the torque difference ($M_H - M_L$) is related to the crosslink density of rubber vulcanizates when the agglomeration of filler is negligible. In Figure 8b, it is clear that the incorporation of oils into the silica-filled NR and SBR compounds causes a decrease in the torque difference. This indicates a decrease in the crosslink density of the rubber vulcanizates. It is also seen that the torque differences of NR vulcanizates are higher than those of the SBR vulcanizates. This is possibly due to more reactive carbon-carbon double bonds in NR molecules during sulfur vulcanization than the ones in the SBR molecules [36]. In Figure 8b, it is also seen that the torque differences of NR compounds

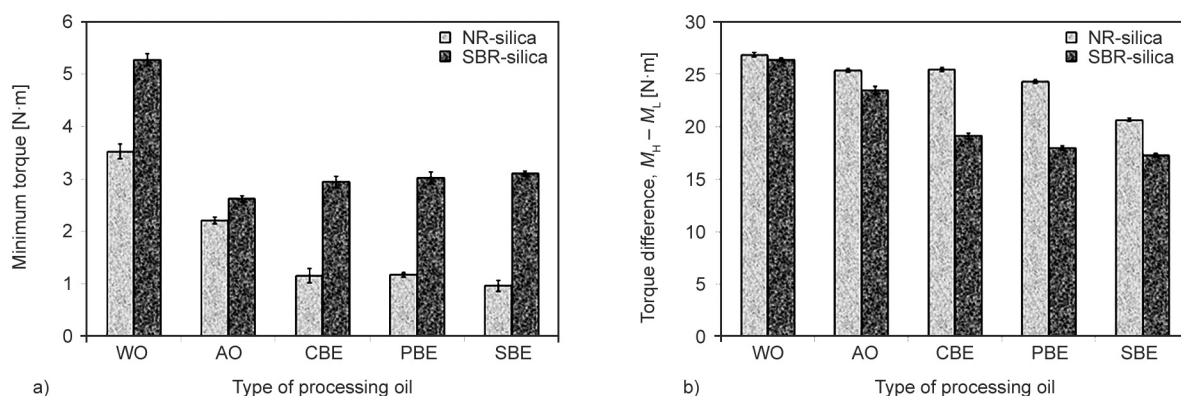


Figure 8. Minimum torque (a) and torque difference (b) of silica filled NR and SBR compounds with various types of processing oil [*i.e.*, without oil (WO), aromatic oil (AO), coconut benzyl ester (CBE), palm benzyl ester (PBE) and soybean benzyl ester (SBE)] at a loading level of 10 phr.

with the four different types of oil can be ordered as aromatic oil > coconut benzyl ester > palm benzyl ester > soybean benzyl ester. This is clear that the vulcanizate with aromatic oil exhibits the highest torque difference while the vulcanizate with soybean benzyl ester showed the lowest $M_H - M_L$ value. This is because soybean benzyl ester contains more unsaturation ($-C=C-$) than other types of oil. Therefore, a large amount of carbon-carbon double bonds in soybean benzyl ester may interfere with the vulcanization reaction by reacting with sulfur and/or sulfur donors during vulcanization. This leads to a decrease in crosslinking reaction and hence cross-linked structures in the rubber vulcanizates, as indicated by lower torque difference. It is noted that sulfur molecules have less capability to react with the stable carbon-carbon double bonds in aromatic oil molecules due to they are more stable than the double bonds in NR molecules [37]. In addition, among SBR vulcanizates, the highest torque difference was observed in the SBR vulcanizate with aromatic oil. This might be due to good dispersion of silica and the curing agent in the SBR compound with the aromatic oil.

3.1.4. Dynamic mechanical properties

Figure 9 shows the storage modulus (G') as a function of oscillating frequency for the silica-filled NR and SBR compounds containing different types of oil. It is clear that all compounds show an increase in G' with increasing oscillating frequency because higher frequency leaves less time for molecular relaxation. It is also seen that the incorporation of oil in the silica-filled NR and SBR compounds reduces G' due to the softening effects [30]. In Figure 9, it is seen that the silica-filled NR compounds with oil have higher G' than the SBR compounds. This is probably due to the higher crosslink density of the NR compounds. Also, the silica-filled NR compound with coconut benzyl ester oil gave the highest G' , followed by the ones with aromatic oil, palm benzyl ester, and soybean benzyl ester, respectively. This result is in good agreement with the torque differences (Figure 8b) and cure curves (Figure 6). It is also seen that the silica filled SBR compound with aromatic oil has the highest G' , indicating high compatibility between aromatic oil and SBR. However, the SBR compounds with the three types of benzyl ester oil (*i.e.*, coconut benzyl ester, palm benzyl ester and

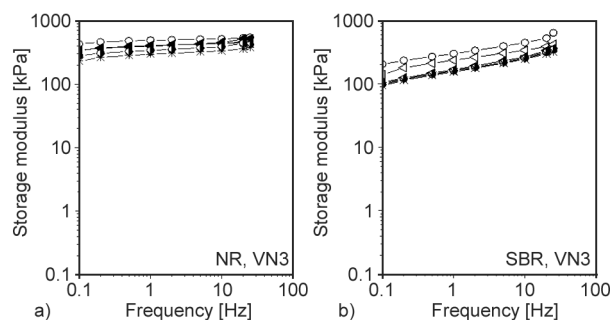


Figure 9. Storage modulus (G') as a function of frequency for silica filled NR (a) and SBR (b) vulcanizates with various types of processing oil [without oil (WO, \circ), aromatic oil (AO, \triangleleft), coconut benzyl ester (CBE, \blacktriangleleft), palm benzyl ester (PBE, \bullet) and soybean benzyl ester (SBE, $*$)] at a loading level of 10 phr.

soybean benzyl ester) do not show a significant difference in the G' values.

Figure 10 shows $\tan \delta$ curves as a function of oscillating frequency of the silica-filled NR and SBR compounds. It can be seen that the silica-filled NR compounds exhibited lower $\tan \delta$ at a given frequency than the SBR compounds. It is to be noted that $\tan \delta$ (or damping factor) indicates the ability of rubber networks to adsorb mechanical energy, *i.e.*, a low $\tan \delta$ means high rubber elasticity. Therefore, it is concluded that the NR compounds have a more elastic response than the SBR compounds. In Figure 10, it is also seen that the addition of oil in the NR and SBR compounds causes an increase of the $\tan \delta$, indicating loss of elasticity in the rubber compounds. This is because the oil causes a reduction in crosslink density of the filled rubber vulcanizates [38]. When the $\tan \delta$ at a given frequency is compared across the

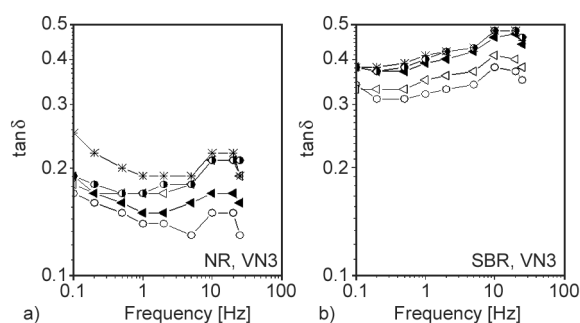


Figure 10. $\tan \delta$ as a function of frequency for silica filled NR (a) and SBR (b) vulcanizates with various types of processing oil [without oil (WO, \circ), aromatic oil (AO, \triangleleft), coconut benzyl ester (CBE, \blacktriangleleft), palm benzyl ester (PBE, \bullet) and soybean benzyl ester (SBE, $*$)] at a loading level of 10 phr.

silica filled NR and SBR compounds, it is seen that the compounds with soybean benzyl ester gave the highest $\tan \delta$ among the other types of oils used. This may be due to lower crosslink density due to the sulfur dilution effect [39].

3.2. Influence of oil types on mechanical properties of silica filled NR and SBR vulcanizates

Silica-filled NR and SBR vulcanizates were prepared using various types of benzyl ester oils and compared to the ones compounded with aromatic oil. Tensile properties, crosslink density, abrasion resistance, rebound resilience, heat build-up of the rubber vulcanizates were investigated.

3.2.1. Tensile properties

Figure 11 shows stress-strain curves of silica-filled NR and SBR vulcanizates with various types of processing oil at a loading level of 10 phr. It is seen that the initial slope (*i.e.*, Young's modulus), which indicates the stiffness and strength of the materials, decreases with addition of oil [40]. Furthermore, the tensile strength of the rubber vulcanizates decreases but elongation at break increases with the addition of oil. Additionally, the silica-filled NR vulcanizates show higher tensile strength than the SBR vulcanizates. This might be attributed to NR had higher crosslink density together with the capability of NR molecular chains to orient in the direction of stretching to cause strain-induced crystallization. This phenomenon contributes to the reinforcement of the rubber molecules when higher tensile strength and other strength properties are observed [41]. On the other

hand, the SBR molecular chains have no strain-induced crystallization, leading to poorer tensile and other related strength properties [42].

Figure 12 shows the tensile strength, elongation at break and 300% modulus of the silica-filled NR and SBR vulcanizates with various types of processing oil. It is confirmed in Figure 13a that the tensile strength of the rubber vulcanizates decreases with the incorporation of oil, which is attributed to a higher movement of the rubber molecular chains, or to provide more chain flexibility that causes an increase in free volume [40]. It is also seen that the aromatic oil gave higher tensile strength than the benzyl ester oils in the silica filled SBR vulcanizates. Additionally, different types of benzyl ester oil had little effect on the tensile strength of the silica-filled SBR vulcanizates. This might be because the SBR is more compatible with the aromatic oil than with the benzyl ester oils. Therefore, a better and finer dispersion of curing agents and filler in the SBR with aromatic oil was encountered [43]. In Figure 12b, it is seen the highest elongation at break is observed for the silica-filled NR vulcanizate with soybean benzyl ester, followed by the vulcanizates with palm benzyl ester, aromatic oil and coconut benzyl ester, respectively. This is probably due to soybean benzyl ester having long chain alkyl groups that could create more free volume in the rubber matrix that facilitate the extensibility of the rubber chains. On the other hand, the silica-filled SBR vulcanizates with benzyl ester oils exhibit less elongation at break than the one with aromatic oil. Moreover, the benzyl ester oils have a small effect on the elongation at break of the SBR vulcanizates, where the soybean benzyl

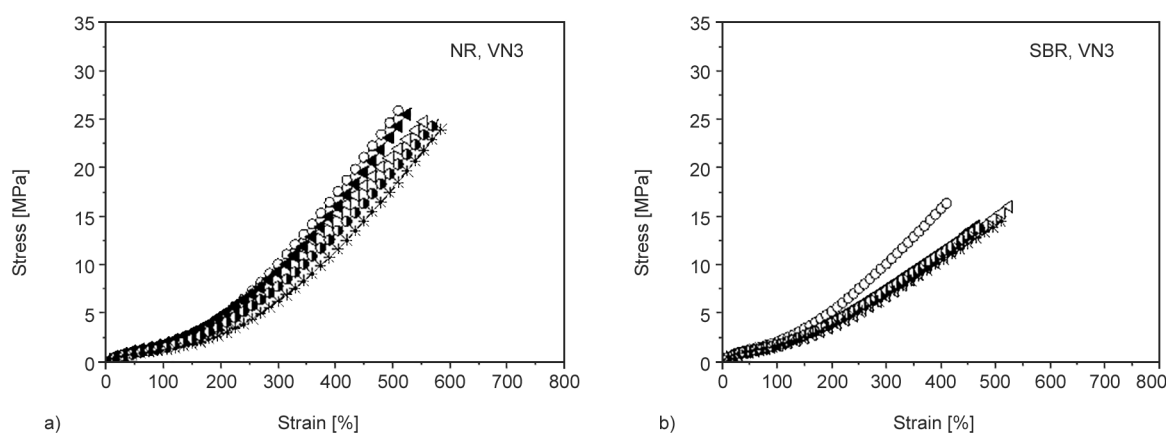


Figure 11. Stress-strain curves of silica filled NR and SBR vulcanizates with various types of processing oil [*i.e.*, without oil (WO, ○), aromatic oil (AO, △), coconut benzyl ester (CBE, ▲), palm benzyl ester (PBE, ●) and soybean benzyl ester (SBE, *)] at a loading level of 10 phr.

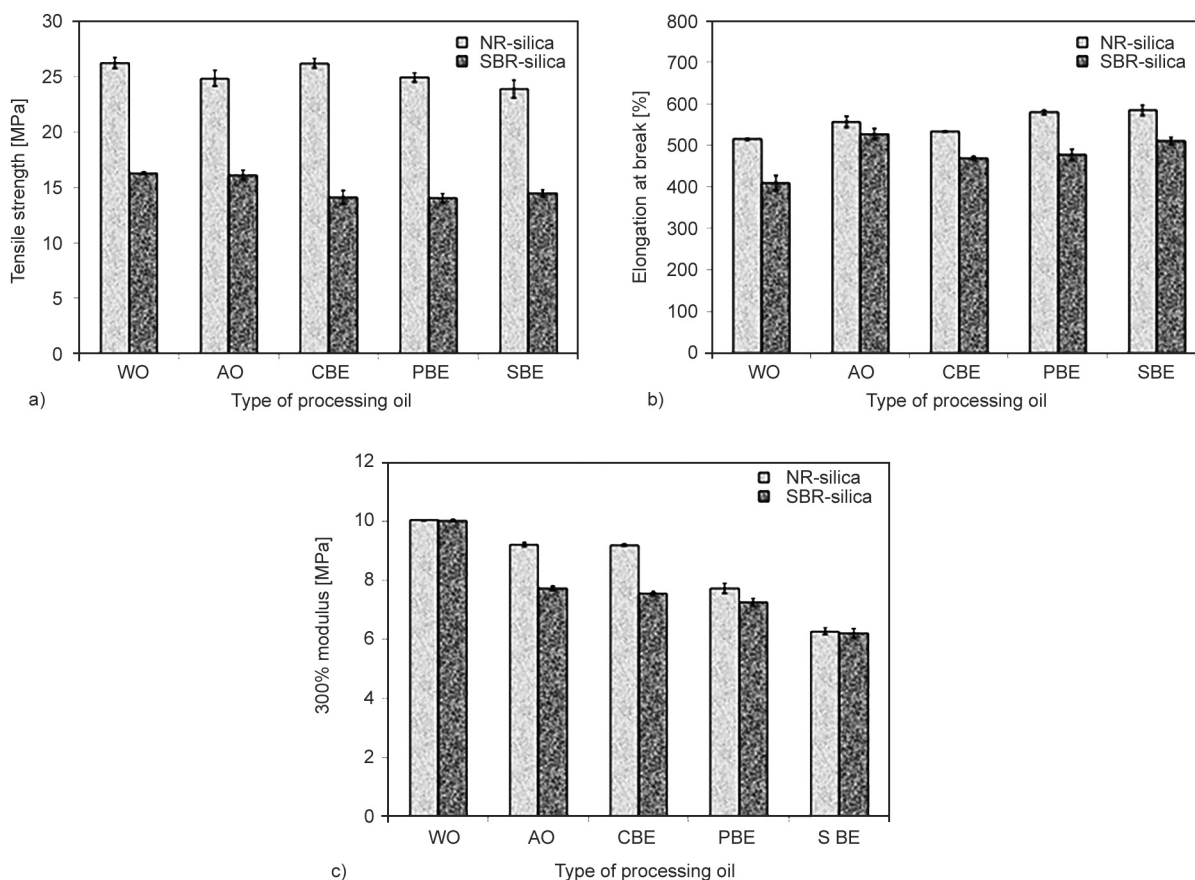


Figure 12. Tensile strength (a), elongation at break (b) and 300% modulus (c) of silica filled NR and SBR vulcanizates with various types of processing oil [*i.e.*, without oil (WO), aromatic oil (AO), coconut benzyl ester (CBE), palm benzyl ester (PBE) and soybean benzyl ester (SBE)] at a loading level of 10 phr.

ester gives the highest elongation at break as a result of the longest chain length of alkyl groups in the soybean benzyl ester molecules.

Figure 12c shows the moduli at 300% strain for silica filled NR and SBR vulcanizates with the various types of oil. It is seen that the silica-filled NR and SBR vulcanizates with aromatic oil have comparable magnitudes of 300% moduli to the one with coconut benzyl ester. In addition, the vulcanizates with soybean benzyl ester show the lowest 300% modulus. This is consistent with the lowest torque difference (Figure 8b), indicating the lowest level of crosslinked structures in the molecular network. This may be attributed to the soybean benzyl ester that contains more unsaturation than the other types of oil. The unsaturation may interfere with the vulcanization reaction by consuming or reacting with sulfur or sulfur donors during vulcanization which causes a lower crosslink density. This decreases the moduli and strength properties of the rubber vulcanizates.

3.2.2. Crosslink density

Figure 13 shows the apparent crosslink densities of the silica-filled NR and SBR vulcanizates with various types of processing oil. As may be expected, the

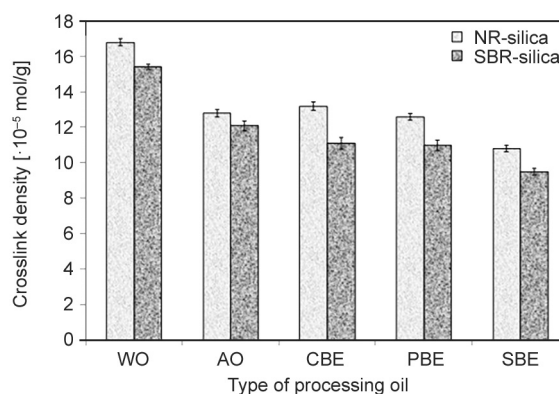


Figure 13. Crosslink density of silica filled NR and SBR vulcanizates with various types of processing oil [*i.e.*, without oil (WO), aromatic oil (AO), coconut benzyl ester (CBE), palm benzyl ester (PBE) and soybean benzyl ester (SBE)] at a loading level of 10 phr.

crosslink densities of the vulcanizates with oil are lower than the ones without oil. This is probably due to the adsorption of curatives by the unsaturation in oil molecules. Additionally, the silica-filled NR vulcanizates with the various types of oil had the following order of crosslink density: without oil > with coconut benzyl ester > with aromatic oil > with palm benzyl ester > with soybean benzyl ester. In the silica-filled SBR compounds, the aromatic oil gave higher crosslinking networks than the benzyl ester oils. This might be because the aromatic oil caused finer dispersion of the filler and curatives in the SBR matrix [44].

3.2.3. Tear strength

Figure 14 shows the tear strength of the silica-filled NR and SBR compounds with various types of processing oil. It is seen that a higher tear strength is

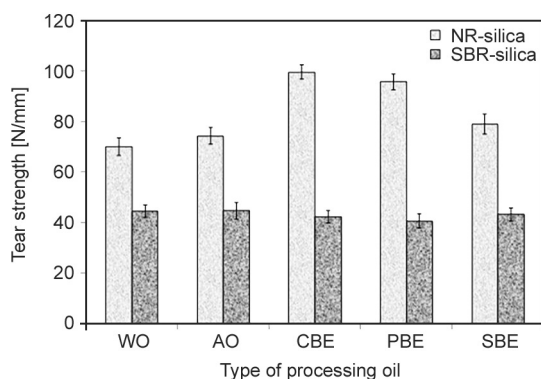


Figure 14. Tear strength of silica filled NR and SBR vulcanizates with various types of processing oil [*i.e.*, without oil (WO), aromatic oil (AO), coconut benzyl ester (CBE), palm benzyl ester (PBE) and soybean benzyl ester (SBE)] at a loading level of 10 phr.

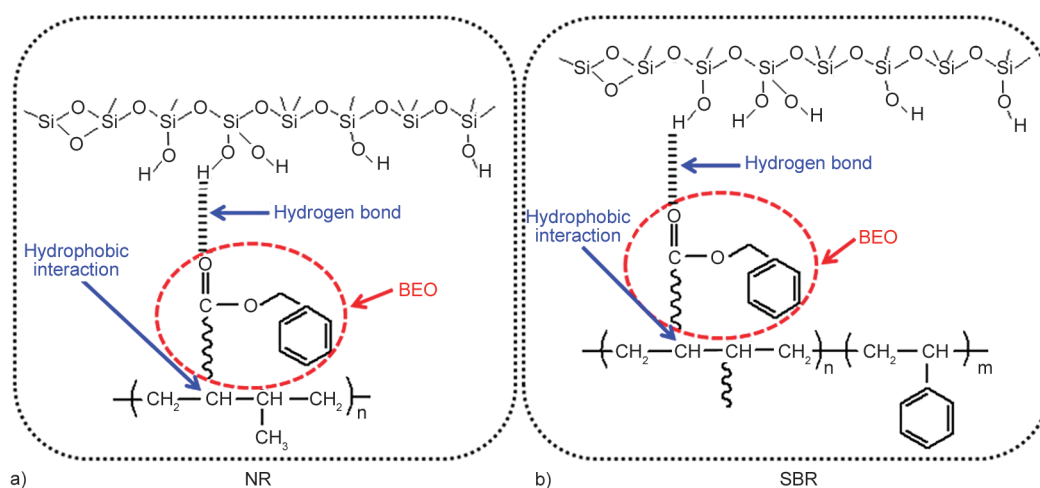


Figure 15. A proposed possible coupling reaction between silica and rubber molecules by physico-chemical bonding with benzyl ester oil molecules. (a) Natural rubber (NR), (b) styrene butadiene rubber (SBR).

observed for the silica-filled NR vulcanizates with oil as compared with the one without oil loading. Also, the benzyl ester oils (*i.e.*, coconut benzyl ester, palm benzyl ester and soybean benzyl ester) filled NR vulcanizates give higher tear strength than the one with aromatic oil. Also, it is clearly seen that the NR vulcanizate with coconut benzyl ester has the highest tear strength. This may be attributed to a higher filler-rubber interaction due to the fact that the oil could contribute to higher coverage layers at the silica surfaces. It is also anticipated that the oxygen atoms in the ester groups of the benzyl esters interact with the silanol groups at the silica surfaces and form hydrogen bonds (Figure 4). Also, a coupling reaction between silica and rubber molecules by physico-chemical bonding via the benzyl ester oil molecules might occur, as a proposed possible coupling reaction in Figure 15. It is noted that the hydrophobic interaction term is used to describe the tendency of nonpolar groups or molecules to interact and may aggregate in the medium. Thus, the benzyl ester oils could act as processing aids or as dispersing agents in the rubber compounds. As dispersing agents, they would contribute to filler dispersion in the rubber compounds [45]. Among the three types of benzyl ester oils, the coconut benzyl ester contains the shortest carbon chain length in its molecular chain. This leads to the highest probability to cover the silica surfaces, resulting in the higher compatibility with the finest filler dispersion [46]. In Figure 14, it is also seen that the incorporation of oils has no significant impact on the tear strengths of the silica-filled SBR vulcanizates. Also, the silica-filled SBR vulcanizates with oil show much lower tear strengths

than the NR vulcanizates due to lower crosslink density and no strain-induced crystallization in the SBR molecular networks [30].

3.2.4. Rebound resilience, heat build-up, and abrasion resistance index

The influence of the oils on rebound resilience and heat build-up of the silica-filled NR and SBR vulcanizates was investigated, as results show in Figure 16. As might have been expected, the rebound resilience of the vulcanizates slightly decreased with the addition of oils. It is noted that the rebound resilience represents the elastic part of the deformation energy, and this behavior is opposite to the energy dissipation caused by hysteresis [47]. In Figure 16, it is seen that the vulcanizates with oil reveal good damping behavior (*i.e.*, low heat build-up). This demonstrates that the rubber vulcanizates with oil have less energy dissipated as heat during deformation than the one without oil. This may be due to the oil molecules distributed into the free volume between the rubber molecular chains and dissipating the energy. Also, the filler-rubber interfaces or rubber layers may contribute to dissipation of heat and hence reduce the temperature rise in the rubber vulcanizates [30]. In Figures 16, it is also seen that the silica filled NR vulcanizates show higher rebound resilience and lower heat build-up than the silica filled SBR vulcanizates, indicating higher damping properties of the SBR vulcanizates [48]. Among the four different types of oil, the coconut benzyl ester shows the best elastic response in the silica filled NR vulcanizates, as reflected by the highest resilience (Figure 16a) and the least heat generated (Figure 16b). These two properties are related to the viscoelastic behavior of

the materials and may be affected by the reduced glass transition temperature (T_g) of the rubber vulcanizates with coconut benzyl ester, as reported in our previous work [17–21]. It was reported that rubber compounds with coconut benzyl ester showed lower T_g with superior elastic properties as compared to rubber compounds with other oil types. This was quoted to be due to the coconut benzyl ester molecules, which might be capable of reacting with functional groups on the silica surface and other functional groups in the rubber network, more so than the other oil types. In Figure 16, it is also seen that the silica-filled SBR vulcanizate with aromatic oil gave the highest rebound resilience and lowest heat build-up. This indicates the best compatibility between the aromatic oil and SBR, resulting in high resilience with low heat build-up of the silica-filled SBR vulcanizate.

Figure 17 shows the abrasion resistance index of the rubber vulcanizates determined by the Akron abrad-er. It is seen that the addition of oil in the silica-filled NR and SBR vulcanizates improves the abrasion resistance. The improved abrasion resistance of the rubber vulcanizates with oils may be attributed to the homogeneity of the materials and flexibility of the rubber chains [30]. In Figure 17, it is also seen that the silica filled NR vulcanizates show a lower abrasion resistance index than the filled SBR vulcanizates. This may be due to the SBR generally have a narrower molecular weight distribution than the NR, which makes the SBR more difficult to process than the NR and hence higher abrasion and wear resistance [49]. In Figure 17, it is also seen that the silica filled NR and SBR vulcanizates with benzyl ester oils showed higher abrasion resistance than

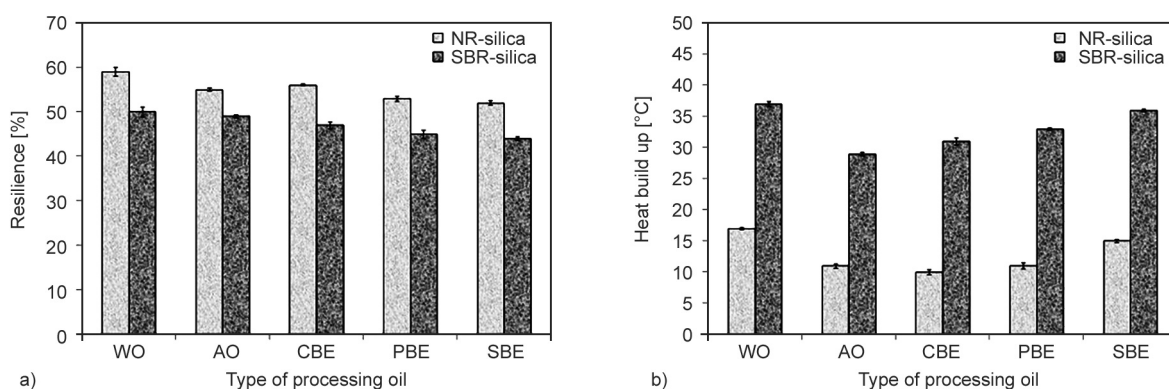


Figure 16. Rebound resilience (a) and heat build-up (b) of silica filled NR and SBR vulcanizates with various types of processing oil [*i.e.*, without oil (WO), aromatic oil (AO), coconut benzyl ester (CBE), palm benzyl ester (PBE) and soybean benzyl ester (SBE)] at a loading level of 10 phr.

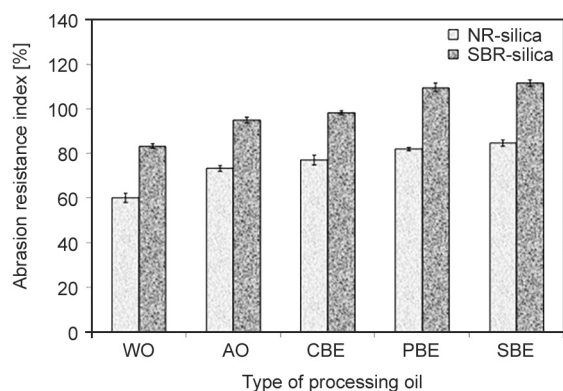


Figure 17. Abrasion resistance index of silica filled NR and SBR vulcanizates with various types of processing oil [*i.e.*, without oil (WO), aromatic oil (AO), coconut benzyl ester (CBE), palm benzyl ester (PBE) and soybean benzyl ester (SBE)] at a loading level of 10 phr.

the vulcanizates with aromatic oil. It is noted that abrasion resistance is normally a complex material behavior that is affected by several factors, although it is closely related to the viscoelastic properties. As the vulcanizates with benzyl ester oils have lower Tg than the one with aromatic oil, [17–21] the vulcanizates with benzyl ester oils are expected to have superior elastic properties, which leads to a higher resistance to wear when in contact with an abrasive surface [50]. In Figure 17, it is also seen that the silica-filled NR and SBR vulcanizates with soybean benzyl ester oil show the highest abrasion resistance.

4. Conclusions

The influence of benzyl ester oils (*i.e.*, coconut benzyl ester, palm benzyl ester, and soybean benzyl ester) and an aromatic oil on the properties of silica filled NR and SBR compounds, and vulcanizates was investigated. It was found that the NR and SBR compounds with benzyl ester oils showed lower mixing energies than the compounds with aromatic oil. Also, the Mooney viscosities of the NR compounds containing benzyl ester oils were lower than for their aromatic oil counterparts. In addition, the aromatic oil in the SBR compounds gave higher Mooney viscosities than the ones with benzyl ester oils. Furthermore, the cure rate indices (CRI) and torque differences of the NR and SBR compounds with benzyl ester oils were lower than for the compounds with aromatic oil. Also, the NR vulcanizates with coconut benzyl ester exhibited the best properties: tensile and tear strengths, crosslink density,

resilience, and heat build-up. However, the highest elongation at break was found for the NR vulcanizate with soybean benzyl ester. On the other hand, the SBR vulcanizate with superior mechanical properties was for the compound with aromatic oil. Moreover, the NR and SBR vulcanizates with soybean benzyl ester provided the highest abrasion resistance properties. It is therefore concluded that some types of the BEO could be possible as alternatives to be used instead of the typical aromatic oil in rubber compounds with some advantages.

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