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Surface Modification of Perlite by Using Silane for the Enhancement of Heat Aging Resistance of Natural Rubber Vulcanisates

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Abstract

The enhancement of mechanical properties of natural rubber vulcanisates was expected by surface modification of perlite particles. Thus, the objective of the present study was to investigate the cure properties and the heat aging resistance properties in terms of stress at 100% elongation, tensile strength, and percentage elongation at break after surface modification. Furthermore, the rebound resilience and abrasion resistance of perlite treated with silane filled in NR vulcanisates were investigated. In a comparison, the properties of clay-filled NR vulcanisates were determined. The results reveal that surface modification by using silane caused a reduction of scorch time and cure time but an increase in torque difference and swelling resistance. Also, surface modification gives better perlite-NR interactions before and after aging. The better heat resistance properties of perlite-filled NR vulcanisates than those of clay-filled vulcanisates is detected from relative property data. Nevertheless, a lower percentage of rebound resilience and abrasion resistance of perlite-filled vulcanisates before and after surface modification than those of clay-filled vulcanisates are observed. This is owing to the large particle size, low specific surface area, poor dispersion, and agglomeration of perlite in NR vulcanisates.

Keywords : Perlite; Surface Modification; Heat Resistance; Mechanical Properties; Natural Rubber Vulcanisates

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1. Introduction

Natural rubber (NR) has been known as a renewable natural polymer with numerous advantageous properties such as superior elasticity and resilience, low heat buildup, and high tensile and tear strength resulting from strain-induced crystallization. [1] Nevertheless, one of the major disadvantage of NR is an offensive odor or unbearable smell caused by incomplete degradation during storage, and thermal degradation during the processing of non-rubber components such as carbohydrates, proteins, and lipids. [2]

Using the gas chromatograph-mass spectrometer (GC-MS) technique, V. P. Hoven et al. [2] reported that the offensive odor was mainly caused by low-molecular-weight volatile fatty acids. To reduce the offensive odor, expensive odor-reducing substances such as chitosan, zeolite13x, and activated carbon black (to adsorb physically and/or chemically) were mixed in NR vulcanisates.

Our previous work [3–5] incorporated low-cost and porous materials such as perlite as odor-reducing fillers with a high content of SiO_2. Although NR vulcanisate with 30 phr perlite showed the potential of efficient odor reduction, it gave low tensile strength, rebound resilience, and heat resistance because of the low specific surface area of perlite and high level of silica-silica interaction due to silanol group (Si-OH) on surface, which caused a decrease in filler-rubber interaction. It has been known that a high degree of reinforcement effect can be governed by small particle size, high specific surface area, non polar group on surface, good filler dispersion, and high filler-rubber interaction. [6-8]

Surface modification by using silane coupling agent has long been recognized as an effective approach to increase filler-rubber interaction [6–13]. P. Sae-oui et al. [6] explained that silane coupling agent usually possesses two functionally active end groups: an alkoxy group that is able to react with the silanol group on the silica surface, and an organosilane group that usually has sulfur atoms in its molecule and is compatible with rubber. Thus, the modified fillers provide chemically active surfaces that can be involved in vulcanization, resulting in coupling bonds between the coupling agent and both the filler and the rubber phases. In other words, silane coupling agent can act as a bridge between silica and rubber, and promote the rubber-silica interaction.

This research was aimed to study the effect surface modification of perlite on cured characteristics and mechanical properties. Triethoxyvinylsilane was chosen because its short vinyl molecule could lead to low steric hindrance and good reactivity with silica in perlite [13]. Furthermore, to obtain aging resistance data required for long-term application that was subjected to a heat cycle, heat aging resistance tests in terms of stress at 100% elongation (M100), tensile strength, and percentage of elongation at the break

after being heated at 100ºC for 22 h were conducted. In addition, rebound resilience and abrasion resistance of perlite treated with silane filled in NR vulcanisates were studied. These properties of vulcanisates filled with perlite treated with silane were also compared with those filled with perlite and commercial filler. Clay was selected in this research since it is commercially used as low cost filler with semi-reinforcement effect.

2. Research Methodology

2.1 Materials

All materials used in the present study were used as received and were purchased from Lucky Four Co. Ltd. (Thailand), except for the expanded perlite, which was obtained from Thai Perlite Technology Co. Ltd. (Thailand). The control compound ingredients are listed in **Table 1**. Filler loading was fixed at 30 parts per hundred of rubber (phr) and added in control compound. Fillers included perlite, perlite treated with 2–8 wt% silane, and clay. Therefore, the filled-NR vulcanisates were denoted as perlite, psi2, psi4, psi6, psi8, and clay. Psi2 means NR vulcanisates filled with perlite modified with 2wt% silane. Thus, psi4, psi6, psi8, mean NR vulcanisates filled with perlite modified with 2, 4, 6 and 8% silane, respectively. Particle size was determined from the mean diameter of all fillers investigated by using a particle analyzer laser with 2 min of ultrasound (Mastersizer S, Malvern Instruments Limited., United Kingdom). The Brunauer-Emmett-Teller (BET) surface area of the fillers were obtained based on the BET theory using a nitrogen adsorption instrument (Quantachrome Autosorb-1, Quantachrome Corp., USA) according to ISO 9277. The mean particle size and specific surface area of perlite are 38.02 μm and 3.49 m^2/g, respectively. The mean particle size and specific surface area of clay are 6.08 μm and 5.35 m^2/g, respectively [5].

2.2 Surface Modification

Surface modification was similar to method mentioned by S. Thongsang, and N. Sombatsompop (2006) [9]. The surface of perlite powder was modified with triethoxyvinylsilane purchased from Lucky Four Co. Ltd. In this study, the silane loading was varied from 0–8 wt% of the perlite content. For example, for a silane content of 4.0 wt%, 4.0 g of silane was mixed with 100 ml of ethanol and stirred for 30 min. To obtain a uniform distribution of silane on the perlite surface, 100 g of perlite was then added to the solution and stirred for 15 min. Then, the modified perlite was dried in an oven at 100ºC for 12 h. Similarly, 2.0, 6.0, and 8.0 wt% of silane on the perlite surface were prepared by varying the initial silane content for 100 g of perlite.

Table 1 Control compound formulation used

Control ingredient	Amount (phr)
NR (STR20)	100
Sulphur	2.5
Stearic acid	2.0
Zinc Oxide (ZnO)	4.0
Tetramethyl thiuramdisulphide (TMTD)	0.5
Dibenzo thiozyldisulphide (MBTS)	1.0
Lowinox® (CPL)	1.0

2.3 Characterization of modified perlite

The Fourier Transform Infrared (FTIR) spectrum was attained using Thermo Scientific™ Nicolet™ 6700 FT-IR. The spectrum resolution was 4 cm^{-1} and the scanning range was from 2000-400 cm^{-1}.

2.4 Mixing and Vulcanisation Procedure.

The NR vulcanisate or cured NR preparation involved mastication, compounding, and molding processes. Firstly, NR was masticated in a laboratory-scale two-roll mill (model YFTR-8, Yong Fong Machinery Co. Ltd., Thailand). Secondly, stearic acid, ZnO, half of filler, MBTS, TMTD, CPL, the rest of filler and sulphur were added respectively. Notably, the mixing conditions were previously mentioned by T. Rattanaplome et al. [5], and D. Moonchai et al [14]. The mixing time for control compound was about 9 minutes, while the mixing time for compound with filler was about 13 minutes. Lastly, the vulcanisation of the compounds was done by using a hydraulic hot press (model HPC 100D, OOMN semi-automatic moulding press, Shanghai Zimmerli Weili Rubber and Plastic Machinery Co. Ltd., China) at 150ºC. The vulcanisation times were obtained by using a moving die rheometer (model UR-2010, U-CAN Dynatex, INC., Taiwan) which was operated at 150°C with 3° arc for 60 min in accordance with ASTM D5289 [5]. The cure characteristics, such as scorch time (ts_2), cure time (tc_{90}), and torque difference (M_H-M_L) were obtained from moving-die rheometer. The cure time was evaluated at the time at which the rheometer torque increases to 90% of the total torque change on the cure curve the The cure characteristics were evaluated in duplicate and the average values were used in data analysis.

2.5 Equilibrium swelling evaluation of the NR vulcanisates

The sample was immersed in 100 ml. toluene for 11 days (until the sample's weight was constant). The swollen vulcanised samples were taken out of the toluene and the excess toluene was blotted with a paper towel. Then, the swollen samples were placed in a clean weighing bottle and weighed precisely. The swelling ratio (Q) was calculated using equation (1). The value of swelling ratio of each vulcanizate was the average of three samples:

$$Q = (W_s - W_i)/W_i \quad (1)$$

W_s is the weight of swollen sample and W_i is the weight of dried sample before swelling [15].

2.6 Heat Aging Resistance Test

The specimens were placed in an oven equipped with an air circulating system at a test temperature of 100ºC for 22 h. [1]. The aged specimens were then measured for their tensile properties. According to our previous research [5], the dumbbell-shape specimens (about 2mm-thick) were tested at a crosshead speed at 500 mm/min and with a 500-N load cell using an Instron universal testing machine (model 5565, USA) according to ISO 37. The specimens were symmetrically placed at the grips of the testing machine to attain uniform tension distribution over the cross section. The tensile strength was assessed from the stress at the break. In addition, the elongation at break was examined. In this study, the relative tensile properties, i.e., M100, tensile strength, and percent of elongation at break, calculated from equation (2), were used to represent the aging resistance properties.

$$\text{Relative tensile properties} = \frac{\text{Paged}}{\text{Punaged}} \quad (2)$$

P_{unaged} and P_{aged} are the tensile properties of the samples before and after heat aging, respectively.

2.7 Mechanical Properties Measurements

To determine the rebound resilience, the cylindrical shaped samples (about 3-mm thick) were tested using a rebound tester (model Rebound Check-Pendolo Shob, Gibitre Instruments S.r.l., Italy) according to DIN53512. Rebound resilience was calculated from equation (3), where α is the maximum rebound angle.

$$\%\text{Rebound resilience} = (1-\cos\alpha) \times 100 \quad (3)$$

The abrasion resistance was evaluated according to ISO 4649 using an abrasion tester (Model AB 6252, Bareiss, Germany). The abrasion resistance of a sample was shown as volume loss when a cylindrically shaped specimen (about 6-mm thick) was abraded for an abrasion distance of 40 m with emery paper (60 grit) at a constant force of 10 N. Each mechanical property test was repeated five times.

2.8 Morphological Study

A morphological study was carried out on filler surface and the cryogenic fracture surfaces of NR vulcanisates using the JSM-5800LV scanning electron microscope (SEM). To remove the electrostatic charge buildup during the investigation, the surfaces of the samples were sputter coated with gold.

3. Results and Discussion

3.1 Characterizations of perlite and modified perlite.

The filler surface is shown in **Fig. 1**. It shows that perlite particles are irregular shape and big, whereas clay particles are small with relatively smooth surface. It also reveals surface openings with pores of perlite and perlite treated with 2 wt% silane showing no evidence effect due to surface treatment on surface morphology. A FTIR was employed for examining the functional groups on the perlite surface, perlite treated with 2-4 wt% silane and silica and then illustrated in **Fig. 2**. The results confirm that perlite, perlite treated with 2-4 wt% silane have the same functional groups (eg. physical-sorbed water and hydroxyl bonding at wave numbers of around 1624 cm^{-1}, Si-O vibration at wave numbers of around 1100cm^{-1} and Si-O-Al at wave numbers of around 783 cm^{-1}) [5, 16]. Especially, Si-O vibration at wave numbers of around 1100 cm^{-1} was reported as characteristics peak of siloxane groups of silica [9]. Thus, it was reasonable in this research to use perlite and perlite treated with silane as reinforcing filler in the NR

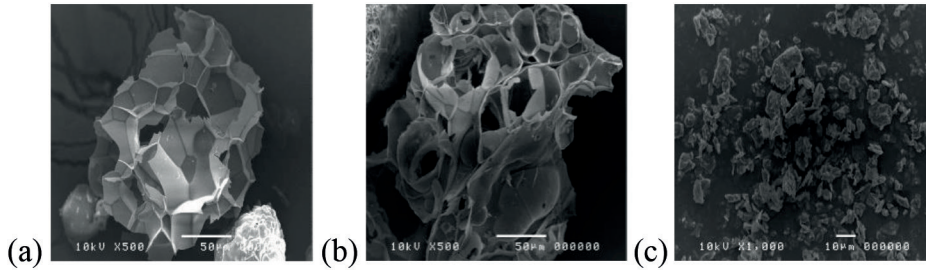


Fig. 1 SEM micrographs of filler surface of (a) perlite (b) perlite treated with 2wt% silane (c) clay

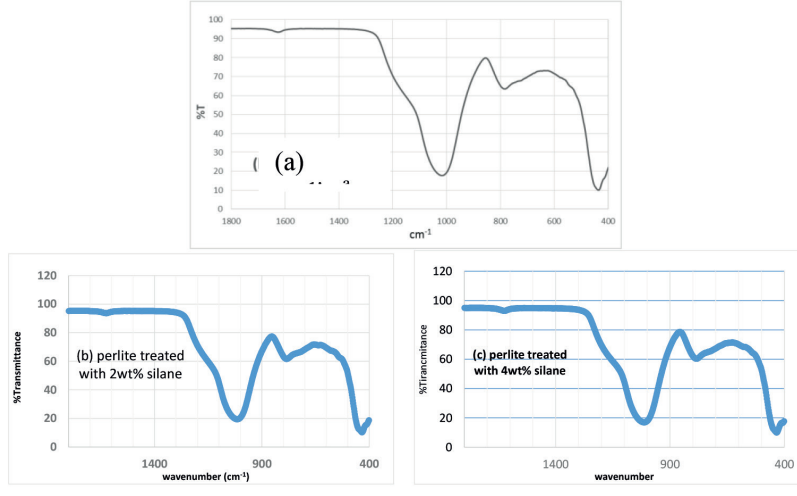


Fig. 2 FTIR spectra of filler particles (a) perlite particles (b) perlite treated with 2 wt% silane (c) perlite treated with 4 wt% silane

3.2 Cure characteristics

Cure properties of various NR vulcanisates are expressed in **Table 2**. Obviously, the addition of silane coupling agent reduces both scorch time and cure time. Similar observations were reported by Sae-oui et al. [6]. They explained that, without silane coupling agent, silanol groups on the silica surface could trap activator (Zn complex) and amine accelerator resulting in retard vulcanisation. Whereas, in the presence of silane, the alkoxy groups of silane coupling agent could react with the silanol groups and cause the silica surface less chemically reactive. Consequently, the amounts of trapped activator and accelerator were reduced giving rise to faster vulcanisation. Moreover, triethoxyvinylsilane is short chain structure resulting in the small amounts of trapped activator and accelerator providing faster cure rate. In contrast, clay-filled compounded give a slight increase in scorch time but a decrease in cure time. This could be due to the absorption of an activator by the hydroxyl surface group on clay [1, 4]. Similar observation in reduction of cure time in clay-filled compound was also reported by Moonchai et al. [14]. **Table 2** also presents the torque difference which is indirectly accociated with the total crosslink density. The total crosslink density is attributed by the sulphide crosslinks and physical crosslinks. As can be noticed from **Table 2**, the addition of fillers causes an increase in the torque difference. In addition, surface modification of silane causes an increase of the torque difference. However, the torque difference increases when treated with 2-4 wt% silane, and then starts to reduce at higher content of silane. The increase in torque difference at low content of silane is possible because the silane increases the crosslink density of the vulcanisate and it is not high enough to cause the steric hindrance effect. At high content of silane, the linkage formation between the rubber chain and the perlite particles may have been decreased due to the steric hindrance effect from silane [9]. It can also be observed from **Table 2** that torque difference of perlite-filled compound is in the same range of clay-filled compound. This could imply that the degree of crosslink in perlite-filled compound is the same level as in the clay-filled compound [5].

3.3 Swelling resistance

Fig. 3 illustrates swelling ratio of various NR vulcanisates. Swelling resistance of vulcanisates, which is conversely proportional to swelling ratio [15]. In accordance with torque difference, surface modification increases the swelling resistance of NR vulcanisates filled with perlite treated with silane. This could imply that total crosslink density tends to increase as silane content increases. Interestily, NR vulcanisates

filled with perlite treated with 4 wt% silane gave the highest torque difference (indicating highest crosslinking density) but not the lowest swelling ratio (meaning highest swelling resistance). It could be explained that the total crosslink density is resulted from both the sulphide crosslinks and physical crosslinks. Furthermore, the lowest swelling ratio (indicating highest swelling resistance) was noticed in clay-filled NR vulcanisates.

Table 2 Cure characteristics of various NR vulcanisates

Rubber vulcanisates	Torque difference, (dN.M)	Scorch time (min.)	Cure time (min.)
control[a]	12.67	2.26	9.27
perlite[a]	13.42	2.46	7.11
psi2	18.03	0.33	1.40
psi4	20.28	0.30	1.30
psi6	14.32	0.27	1.13
psi8	17.93	0.28	1.28
silica	14.21	2.00	3.75

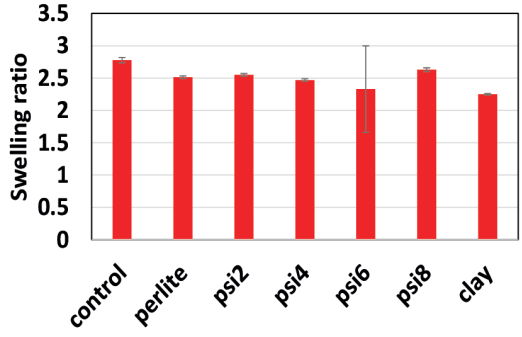


Fig. 3 Swelling resistance of various NR vulcanisates

3.4 Heat Aging Resistance Properties

The stress at 100% elongation or modulus at 100% elongation (M100) before and after aging, including their relative properties, are shown in **Fig. 4**. The M100 of different NR vulcanisates could reveal that the addition of filler with and without surface treatment into the rubber matrix causes an increase in rubber stiffness. [14] From **Fig. 4**, it appears that surface modifications could increase a reinforcement effect at silane loading of 2–4 wt%. Similar result was reported by S. Thongsang, and N. Sombatsompop, N. [9] in Si69 treatments on the properties of fly ash/natural rubber composites. Meanwhile, at high silane loading, an excess of silane coupling agent could act as a plasticizer, resulting in a decrease in M100 [6]. Also, there may be loss of ethoxy groups due to self condensation of triethoxyvinylsilane [13]. After heat aging, the M100 of perite-filled and modified perlite-filled vulcanisates tends to increase. This could be the result of a post-curing effect or the formation of additional networks for optimum cure samples [1, 17]. For clay-filled vulcanisates, a slight decrease in M100 after aging was observed [1]. This could be explained by the fact that the degree of crosslinking after thermal aging might exceed an optimum value and cause a dense network [1]. Also, the tensile properties shown in **Fig. 5** of perlite-filled vulcanisates (both treated and untreated surface) are lower than those of clay-

filled vulcanisates. This could be the result of the lower specific surface areas and larger particle sizes of perlite than those of clay [4]. The difference results between perlite clay-filled vulcanisates would be different in surface chemistry. The hydroxyl group on the perlite surface includes a silanol group (Si-OH) and hydrous oxides surface groups in alumina (Al-OH), whereas the hydroxyl group on the clay surface are only Al-OH [5, 16]. The higher polar group on silica surface not only leads to strong particle–particle interaction but also the weaker rubber–filler interaction [5,6].

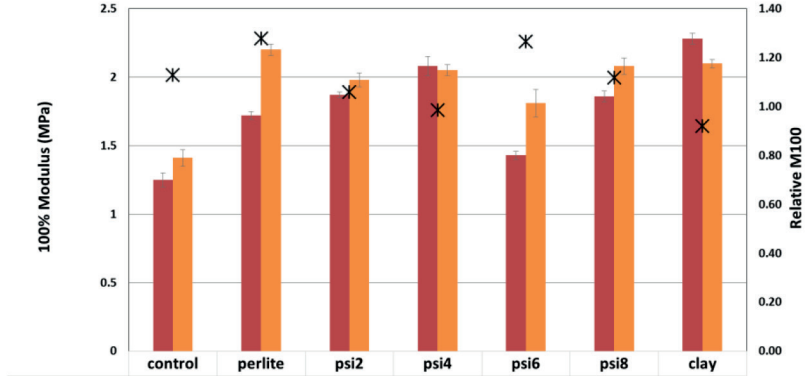
Fig. 6 depicts the percentage of elongation at the break of NR vulcanisates, and their relative properties. Again, surface modifications increase the elongation at the break of perlite-filled vulcanisation both before and after thermal aging. This suggests good interfacial adhesion between perlite particles and NR matrices by using silane as a coupling agent. As expected, the percentage of elongation at break tends to decrease after aging because of the post-curing effect decreasing the rubber molecular mobility. Considering the relative properties from **Fig. 4–6**, the higher relative tensile properties of perlite treated with silane filled in NR vulcanisates are found as caused by the stronger perlite-NR adhesion after thermal aging. This indicates that the surface modifications could enhance both degree of reinforcement and heat resistance more effectively than clay-filled vulcanisates.

3.2 Mechanical Properties

Fig. 7 illustrates the percentage of rebound resilence before aging.Obviously, the addition of filler causes an increase in stiffness and modulus, but a decrease in resilience because of the dilution effect [4, 5, 14]. Again, surface modifications of perlite give rise to increases in both stiffness and rebound resilience. Meanwhile, NR vulcanisates filled with perlite treated with 4 wt% silane exhibit the highest percentage of rebound resilience among perlite-filled NR vulcanisates. This could explain why optimum silane content might give better filler-NR adhesion, causing better filler incorporation in the NR matrix and leading to a high percentage of rebound resilience.

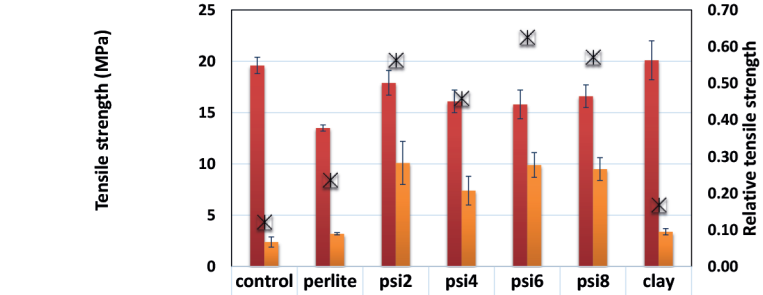
Moreover, the plasticizing effect at excessive silane loading (6–8 wt%) might be responsible for the high percentage of rebound resilience. However, clay-filled vulcanisates gives a higher rebound resilience even possess higher M100 than perlite-filled vulcanisates. This might be responsible by difference in filler bulk hardness and level of filler-NR matrix interaction [14]. Volume loss results, which is proportional to the abrasion resistance of various vulcanisates, are shown in **Fig. 8**. The results reveal that the increases in crosslinking density, hardness and modulus leads to an

enhancement of the abrasion resistance [15]. By contrast, it is clearly noticed from M100 and percentage rebound resilience data that modified perlite with a high modulus gives a higher volume loss, meaning a lower abrasion resistance. In particular, NR vulcanisates filled with perlite treated with 4 wt% and 8 wt% silane give the highest volume loss. A possible explanation is weak physical crosslinks. Similar explanation was stated by S. Thongsang, and N. Sombatsompop, N. [3]: the total crosslink density could arise from both the sulphidic crosslinks and physical crosslinks. As seen in **Fig. 5**, the volume loss of perlite treated with silane filled in NR vulcanisates is lower than that of clay-filled vulcanisates. This could be the result of weak physical crosslinks in perlite treated with silane filled in NR vulcanisates and poor filler dispersion. Another explanation would be more polar surface group on perlite than those on clay resulting in weaker filler-natural rubber interaction [5, 6].



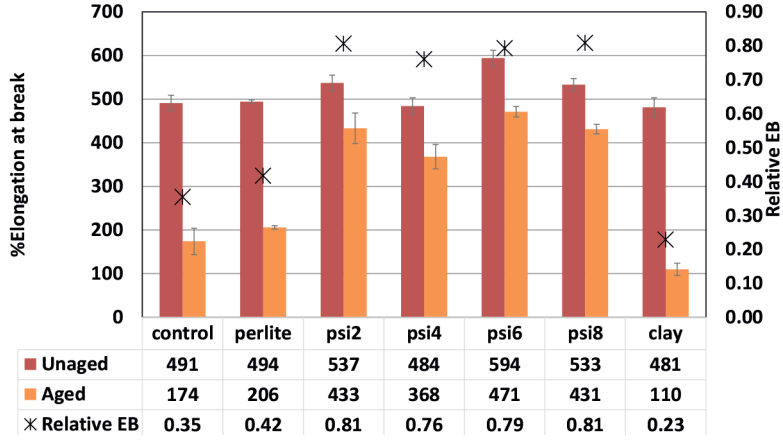
	control	perlite	psi2	psi4	psi6	psi8	clay
Unaged	1.25	1.72	1.87	2.08	1.43	1.86	2.28
Aged	1.41	2.20	1.98	2.05	1.81	2.08	2.10
RelativeM100	1.13	1.28	1.06	0.99	1.27	1.12	0.92

Fig. 4 100% modulus (M100) of various NR vulcanisates



	control	perlite	psi2	psi4	psi6	psi8	clay
Unaged	19.6	13.5	17.9	16.1	15.8	16.6	20.1
Aged	2.4	3.2	10.1	7.4	9.9	9.5	3.4
Relative tensile strength	0.12	0.24	0.56	0.46	0.63	0.57	0.17

Fig. 5 Tensile strength of NR vulcanisates



	control	perlite	psi2	psi4	psi6	psi8	clay
Unaged	491	494	537	484	594	533	481
Aged	174	206	433	368	471	431	110
Relative EB	0.35	0.42	0.81	0.76	0.79	0.81	0.23

Fig. 6 The percentage of elongation at break of NR vulcanisates

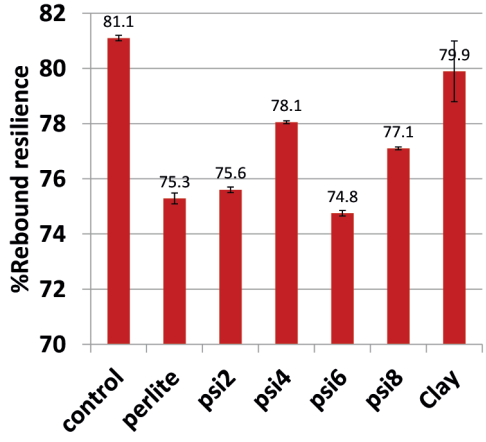


Fig. 7 The percentage of rebound resilience of NR vulcanisates before aging

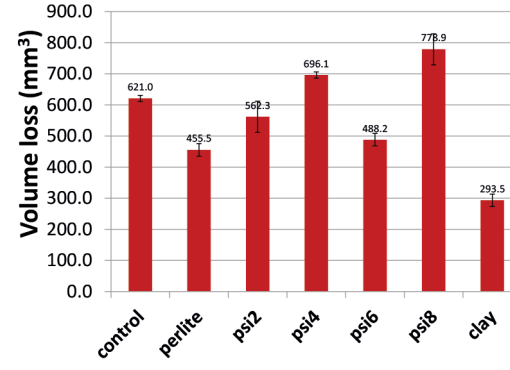


Fig. 8 Volume loss of NR vulcanisates before aging

3.3 Morphological Studies

SEM micrographs of various NR vulcanisates are presented in **Fig. 9**. From the micrographs, the agglomeration of perlite particles is more pronounced than that of perlite treated with 2 wt% silane. This could imply that surface modification using silane enhances the better perlite-rubber interactions but is not strong enough to exhibit drastic improvement in filler dispersion. The filler agglomeration in the rubber matrix could be due to strong filler–filler interaction resulting from the polar group from silanol on perlite surface. The SEM micrographs of clay-filled vulcanisates exhibit better filler dispersion resulting from smaller particle sizes, larger surface areas and less polar surface group, As a consequence, less polar surface group on clay leads to weaker filler-filler interaction, easier to deaggregate

during mixing and then generate a greater area to react with the NR matrix. These observations are more in accordance with a higher M100, tensile strength, percentage of rebound resilience, and abrasion resistance of clay-filled NR vulcanisates before aging than those of perite-filled vulcanisates (both treated and untreated surfaces).

4. Conclusion

Taken as a whole, surface modification by using silane promotes the cure rate and reduces scorch time and cure time but causes an increase in torque difference and swelling resistance. The key factors of the reinforcement effect in filled-NR vulcanisates include small particle size, high surface area, non-polar surface group, strong filler-NR interaction, and good filler dispersion.

From the tensile test results, the surface modifications using silane show improvement in perlite-NR interactions before and after aging. In addition, better heat resistance properties of perlite-filled NR vulcanisates than those of clay-filled NR vulcanisates is noticed from the relative property data. A silane content of 2-4 wt% gives optimal properties of natural rubber vulcanizates. However, it can be seen that a large particle size, low specific surface area, poor dispersion, and agglomeration of perlite treated with 2 wt% silane in NR vulcanisates leads to a lower percentage of rebound resilience and abrasion resistance than those of clay-filled vulcanisates.

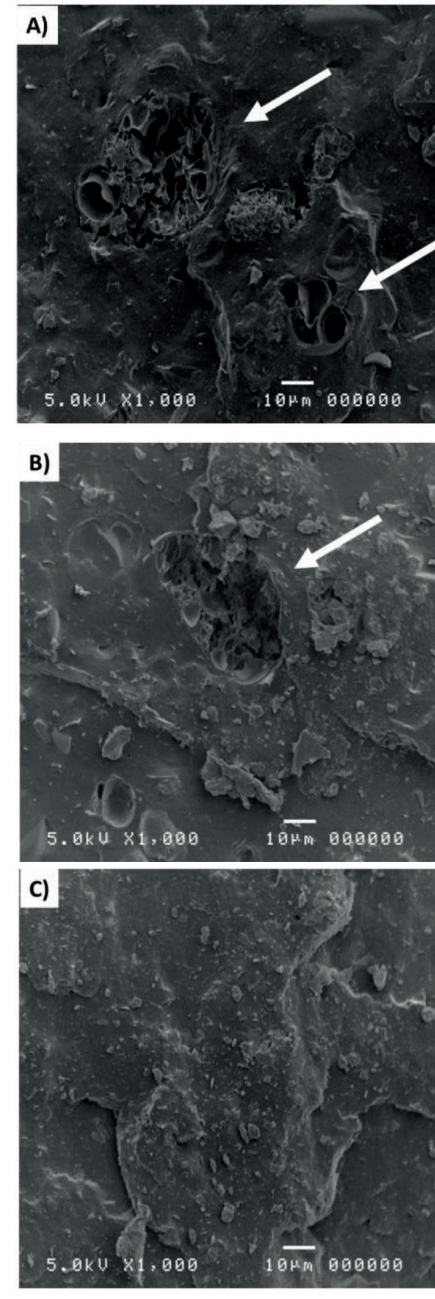


Fig. 9 SEM micrographs with magnification of 1000 of
A) perlite-filled NR vulcanisates
B) perlite treated with 2wt% silane filled in NR vulcanisates and
C) clay-filled NR vulcanisates

5. Acknowledgement

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