Material Properties

Effect of curing system on reinforcing efficiency of silane coupling agent

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Abstract

Silane coupling agent has long been used to enhance degree of reinforcement of silica. The mechanical properties of silica-filled vulcanizates are greatly improved in the presence of silane coupling agent, mainly due to an increase in rubber–filler interaction. Recently, various types of silane coupling agent have been developed and commercialized. In the present study, two types of silane coupling agent, i.e. bis-(3-triethoxysilylpropyl) tetrasulfane (Si-69) and 3-thiocyanatopropyl triethoxy silane (Si-264) were selected for comparison of their reinforcing action in various curing systems: conventional vulcanization (CV), semi-efficient vulcanization (semi-EV) and efficient vulcanization (EV). The results reveal that the addition of silane coupling agents not only improves compound processability, but also enhances the mechanical properties of the rubber vulcanizates. The effect of silane type on processability is found to be independent of the curing system. Compared with Si-69, Si-264 can react with the silanol groups on the silica surface more readily, due to its less bulky structure and lower viscosity. In other words, Si-264 can reduce the filler–filler interaction to a greater extent than Si-69, leading to better compound processability. The effect of silane type on the vulcanizate properties, on the other hand, depends greatly on the curing system. For CV and semi-EV systems, Si-264 imparts greater degree of reinforcement than Si-69. This might be attributed to the combined effects of better rubber–filler interaction, better filler dispersion and higher state of cure when Si-69 is replaced with Si-264. However, for the EV system, contrary results are obtained, i.e. Si-69 provides better reinforcement than Si-264. Explanation is given to the effect of sulfur contribution of Si-69 which is dominant only in the EV system.
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1. Introduction

In most applications, carbon black is widely used as reinforcing filler for rubber. However, in translucent or colored products, non-black fillers are preferred. Silica is the most important reinforcing filler in this category due to its fine particle size (high specific surface area). Apart from the particle size, the surface chemistry of sil-ica also greatly affects the degree of reinforcement. As silica contains a large number of silanol groups on its surface, it is considered as a highly polar filler and, thus, it is less compatible to non-polar rubbers such as natural rubber (NR), styrene butadiene rubber (SBR), etc. The poor rubber–filler interaction would lead to impaired mechanical properties of the rubber vulcanizates. Silica, therefore, provides less degree of reinforcement than carbon black when compared at the same specific surface area [1]. In addition, the silanol groups have the tendency to form hydrogen bonding between each other resulting in strong filler–filler interaction. Silica is, therefore, dif-

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ficult to distribute and disperse throughout the rubber matrix compared with carbon black. Also, when silica is added into rubber at high concentration, it tends to form a secondary network, alternatively called "filler–filler network". This would cause an increase in compound viscosity giving rise to difficulty in processing.

So far, the chemical treatment of silica surface has become the most successful method to improve rubber–filler interaction and reduce filler–filler interaction. Recently, much attention has been given to the use of silane coupling agents which serve, to some extent, to couple a filler to the rubber molecule on "like-to-like" basis. Generally, silane coupling agents possess two functionally active end groups, i.e. an alkoxy group which is capable of reacting with the silanol group on the silica surface whilst the organosilane group, generally having sulfur atoms in its molecule, is compatible with rubber and can participate in sulfur vulcanization leading to strong chemical linkage between the silane coupling agent and the rubber molecule. As a consequence, silane coupling agent functions as a bridge between silica and rubber and enhances the rubber–silica interaction. The degree of reinforcement is therefore greatly increased in the presence of silane coupling agent.

Nowadays, many types of silane coupling agents, which are different in their chemical structures, have been commercially developed. Even though extensive work has reported their function and their influences on processability and vulcanizate properties of the silica-filled vulcanizates [1–13], little attention is given to the reinforcing efficiency of silane coupling agent in various curing systems. It is therefore the aim of the present work to study the effect of curing system on reinforcing efficiency of the sulfur-containing silane coupling agents in silica-filled NR vulcanizates. Two types of silane coupling agent, i.e. bis-(3-triethoxysilylpropyl) tetrasulfane (Si-69) and 3-thiocyanatopropyl triethoxy silane (Si-264), were selected for comparison of their reinforcing action in various curing systems. The chemical structures of both Si-69 and Si-264 are given in Fig. 1.

2. Experimental

2.1. Materials

All mixing ingredients were used as received. Natural rubber (STR 5L) was supplied by Union Rubber Products Corp., Ltd. Silica (Ultrasil VN2 with specific surface area of 125 m^2/g) and the two types of silane coupling agent were supplied by JJ Degussa (Thailand) Co., Ltd. Tetramethyl thiuram monosulfide (Perkacit-TMTM) and *N-tert*-butyl-2-benzothiazyl sulfenamide (Santocure-TBBS) were obtained from Reliance Technochem (Flexsys) Co., Ltd. Stearic acid, zinc oxide (ZnO) and sulfur (S) were obtained from Chemmin Corporation Ltd. Polyethylene glycol (PEG) was supplied by Condea Chemica D.A.C.

2.2. Preparation and testing of rubber compounds

The rubber compounds were prepared using a laboratory-sized internal mixer (Haake Rheomix 3000p). The mixing conditions were as follows: fill factor = 0.7, chamber temperature = 40 °C, rotor speed = 40 rpm and mixing time = 12 min. The compound formulation is given in Table 1. In conventional vulcanization (CV)

Table 1
Compound formulation (unit: parts per hundred of rubber, phr)

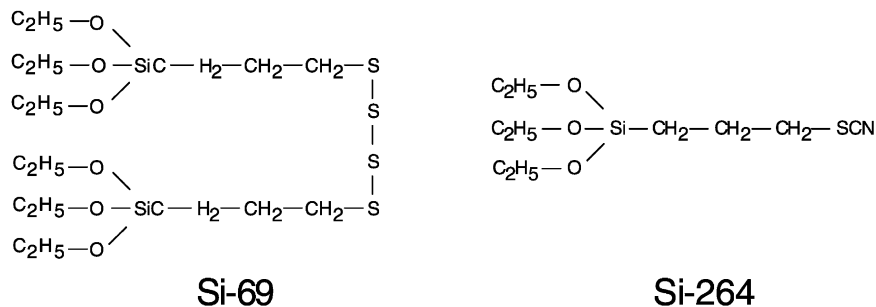| Ingredient	phr
Natural rubber (STR 5L)	100.0
Silica	40
ZnO	5.0
Stearic acid	2.0
TBBS	1.0
TMTM	Variable
Sulfur (S)	Variable
PEG	0.5
Silane coupling agent	0, 2.0

Fig. 1. The chemical structures of Si-69 and Si-264.

system, the amounts of TMTM and S were 0.1 and 2.5 phr, respectively. In semi-efficient vulcanization (semi-EV) system, the amounts of TMTM and S were 0.8 and 1.0 phr, respectively. For efficient vulcanization (EV) system, the amounts of TMTM and S were 4.0 and 0.2 phr, respectively. The mixing energy of every compound was recorded. After mixing, the Mooney viscosity (ML1 + 4 at 100 °C) of the compounds was measured by Mooney viscometer (TechPro viscTECH+). The degree of filler–filler interaction was evaluated by measuring the dynamic storage modulus (G') of the rubber compounds using a Rubber Process Analyzer (RPA 2000). The test was carried out at 100 °C with a frequency of 1.7 Hz and at variable strains, i.e. from 0.56% (the lower limit of the equipment) to 200.04%. The difference in G' at low and high strains, widely known as the "Payne effect" is used to represent the degree of filler–filler interaction [8].

2.3. Testing of rubber vulcanizates

After vulcanization, both tensile and tear properties were determined using an Instron 4500 series following ASTM D412 and ASTM D624 Die C, respectively. The Zwick abrasion tester 6102 was used for abrasion resistance determination (DIN 53516). The compression set was investigated according to ASTM D395 (method B) at 70 °C for 22 h. Crosslink density determination was carried out using an indirect method, namely a swelling test with hexane employed as the swelling liquid. The measurement of heat build up during dynamic deformation was carried out using a Goodrich flexometer Model II (ASTM D 623). The degree of filler dispersion was examined by scanning electron microscopy (SEM) (JEOL JSM-5410). The SEM micrographs were taken on the newly exposed surface of the rubber specimens fractured immediately after embrittling in liquid nitrogen. The specimens were then sputtered with gold to prevent charging on the surface.

3. Results and discussion

The effect of silane coupling agent on mixing energy of the rubber compounds with various curing systems is illustrated in Fig. 2. As can be seen, the mixing energy is significantly decreased in the presence of silane coupling agent. As the alkoxy groups of the silane coupling agent can react with the silanol groups on the silica surface, the addition of silane coupling agent significantly reduces the filler–filler interaction. Disagglomeration of silica can then take place easily. In addition, the other end group (organo-functional group) of the silane coupling agent has relatively low polarity and, therefore, silane coupling agent can improve rubber–filler compatibility. As a consequence, silane coupling agent can
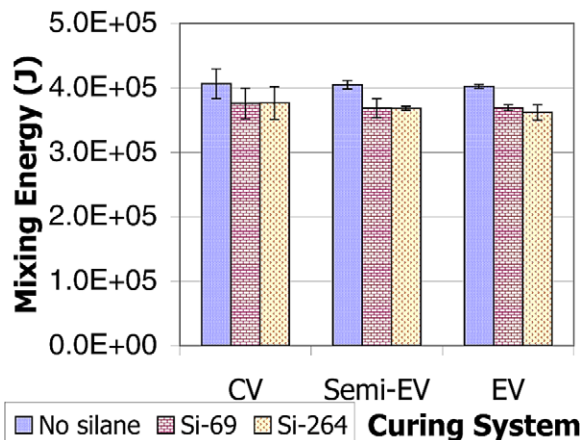
Fig. 2. The effect of silane type on mixing energy at various curing systems.

promote both wetting and dispersion processes giving rise to reduced viscosity (see also Fig. 3) and, hence, mixing energy. It can also be observed that, regardless of the curing system, the mixing energy of the Si-264 containing compound is slightly lower than that of the Si-69 containing compound. This is possibly due to the fact that Si-264 possesses less bulky structure and has lower molecular weight (lower viscosity), compared to Si-69. It is therefore easier for Si-264 to react with the silanol groups on the silica surface. Alternatively, it can be said that Si-264 can reduce the filler–filler interaction to a greater extent than Si-69. This is confirmed by the results of Payne effect obtained from the RPA as shown in Fig. 4. When sufficient amount of reinforcing filler is added into rubber, filler–filler interactions take place as a result of the decrease in the distances between the filler aggregates. As silica contains a large number of silanol groups on its surface, the strong filler–filler interaction exists through the hydrogen bonds. These interactions are particularly obvious when deformations are small. At low strain amplitudes, filler–filler interactions are
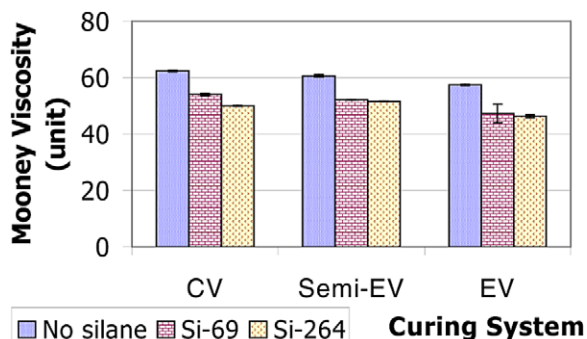
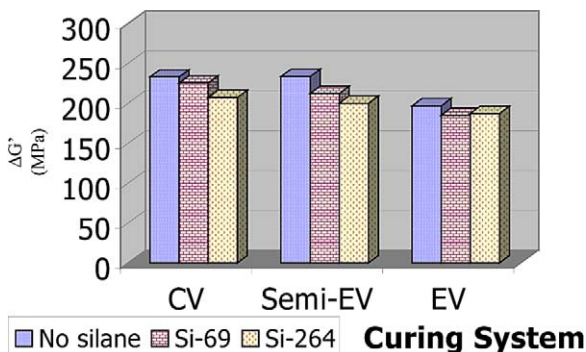Fig. 3. The effect of silane type on Mooney viscosity of the rubber compounds at various curing systems.

Fig. 4. The effect of silane type on the Payne effect at various curing systems.

thought to partially exist. At very high strain, the filler–filler interactions are fully destroyed and the rubber properties are fully dependent on the rubber network. The difference in dynamic shear modulus, G', at low strain and high strain amplitudes ($\Delta G'$) can thus be used to indicate the extent of filler–filler interaction. The results in Fig. 4 reveal that the filler–filler interaction is greatly reduced when the silane coupling agent is present. This is simply due to the fact that silane coupling agent could react with the silanol groups and make them less reactive. A higher degree of coupling leads to less filler–filler interaction and, therefore, a lower value of $\Delta G'$ [8]. The results also reveal that the Payne effect or filler–filler interaction is dependent on the curing system. The filler–filler interaction is found to decrease slightly when the curing system is changed from CV to semi-EV and EV, respectively. The EV system contains a large amount of TMTM which could react with the silanol groups on the silica surface and make it less reactive. The silica–silica interaction is therefore very low in this system. The silica–silica interaction in the CV system is, on the other hand, very strong because this system contains very little TMTM. This explains why both mixing energy and Mooney viscosity tend to decrease slightly in the following sequence: CV, semi-EV and EV.

Table 2 represents the effects of silane type on tensile properties and tear strength of the silica-filled vulcanizates with various curing systems. Obviously, the tensile strength (TS), 100% modulus (M_{100}) and tear strength increase significantly in all curing systems with the addition of silane coupling agent. This might be attributed to the combined effects of better rubber–filler interaction and improved filler dispersion. The addition of silane coupling agent noticeably improves the degree of filler dispersion as can be seen from the SEM micrographs (Fig. 5). This is simply due to the ability of silane coupling agent in reducing filler–filler interaction. In addition, the improvement in rubber–filler interaction also results in better filler dispersion [14].

Due to its greater ability to reduce filler–filler interaction, Si-264 imparts better filler dispersion than Si-69. This would explain why both tensile and tear strengths are found to improve when Si-69 is replaced by Si-264. This finding is particularly obvious in the CV and semi-EV systems. However, for the EV system, the improvement in such properties is not obvious in spite of the fact that Si-264 has better filler dispersion. A possible explanation is given to the ability of Si-69 to contribute sulfur atoms to the rubber matrix [1], a phenomenon called "sulfur contribution effect". Si-69 possesses four sulfur atoms in its molecule and these sulfurs could be pulled out into the rubber matrix by the active accelerators during the vulcanization reaction. As a consequence, this phenomenon is pronounced only in the system having large amounts of highly active accelerators with little free sulfur, i.e. the EV system. The contributed sulfur can participate in the vulcanization reaction and, thus, increase the state of cure.

Table 2
Tensile and tear properties of the rubber vulcanizates

| Curing system	Silane type	Tensile properties			Tear strength (N/mm)*
		TS (MPa)	M_{100} (MPa)	EB (%)	
CV	–	28.1 ± 0.9	2.32 ± 0.12	537.5 ± 26.1	78.4
	Si-69	32.1 ± 1.2	2.89 ± 0.18	445.3 ± 20.4	98.1
	Si-264	33.2 ± 0.8	2.94 ± 0.23	441.3 ± 17.3	116.7
Semi-EV	–	29.2 ± 0.8	1.43 ± 0.03	760.1 ± 20.3	73.7
	Si-69	30.3 ± 0.8	1.84 ± 0.06	673.8 ± 18.0	85.2
	Si-264	32.4 ± 0.6	1.88 ± 0.11	670.5 ± 18.6	90.6
EV	–	26.3 ± 0.8	1.03 ± 0.01	824.6 ± 27.8	65.5
	Si-69	29.8 ± 0.9	1.72 ± 0.02	646.2 ± 13.1	79.5
	Si-264	30.8 ± 0.6	1.40 ± 0.05	675.0 ± 24.0	77.5

* Median value.

(a)

(b)

(c)
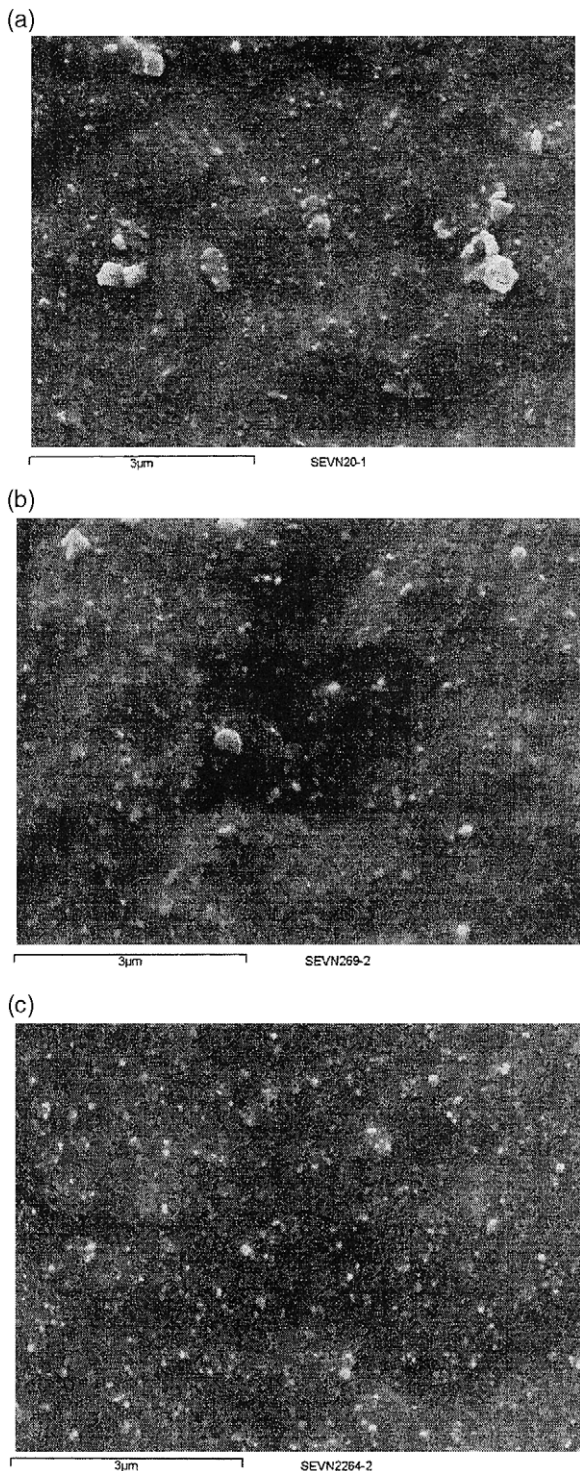
Fig. 5. SEM micrographs of the rubber vulcanizates in the semi-EV system: (a) without silane, (b) with 2 phr of Si-69 and (c) with 2 phr of Si-264.

The sulfur contribution effect is also supported by the elongation at break (EB) results. As can be seen from Table 2, the elongation at break of Si-69 containing vulcanizate is lower than that of Si-264 containing vulcanizate only in the EV system, whereas no significant difference is found in the other two curing systems. The results clearly indicate that in the EV system, Si-69 imparts vulcanizates with a higher state of cure than Si-264 due to the sulfur contribution effect. This is further confirmed by the swelling test results as shown in Fig. 6. It can be observed that the silane type has no significant effect on the swelling ratio of the rubber vulcanizates in the CV and semi-EV systems, even though a thorough look would reveal that Si-264 seems to give vulcanizates with slightly lower swelling ratio than Si-69 in these two curing systems. However, in the EV system, the effect of silane type on swelling ratio is more pronounced. In this particular curing system, Si-69 gives rubber vulcanizates with significantly lower swelling ratio than Si-264. As swelling ratio is inversely proportional to the degree of crosslinking, it is obvious that the sulfur contribution of Si-69 plays an important role on the state of cure only in the EV system. The results in Fig. 6 also reveal that the presence of silane coupling agent increases the crosslink density (reduces the swelling ratio) of the rubber vulcanizates, regardless of the curing system. This is attributed to the fact that (1) silane coupling agent can reduce the amount of accelerators trapped on silica surface and (2) silane coupling agent can participate in sulfur vulcanization reaction as it possesses sulfur in its molecule and it can actually act somehow like a sulfur-donor accelerator.

The effect of silane type on compression set of the rubber vulcanizates with various curing systems is illustrated in Fig. 7. As can be seen, the compression set is considerably reduced in the presence of silane coupling
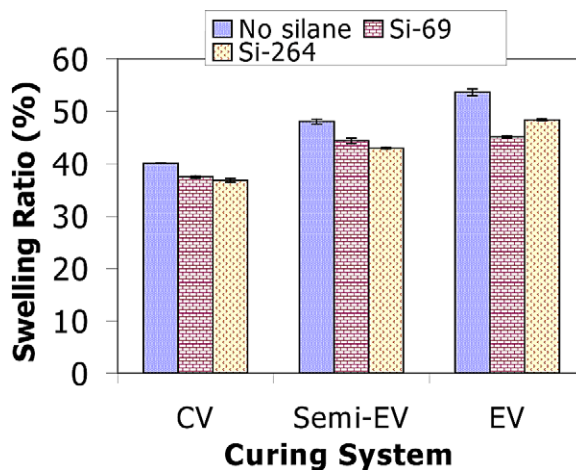

Fig. 6. Dependence of swelling ratio on the silane type at various curing systems.
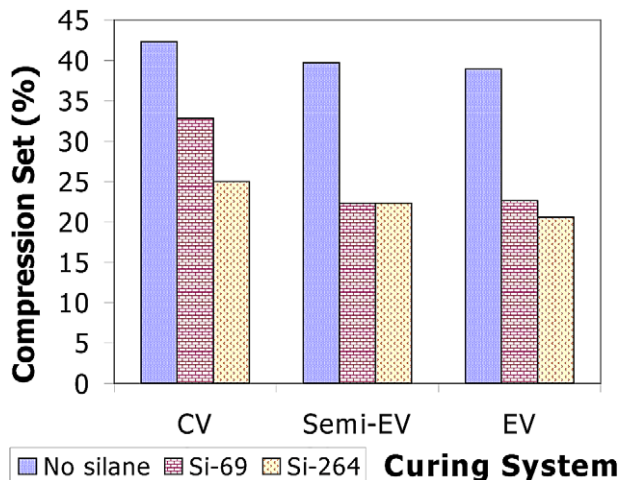
Fig. 7.   The effect of silane type on compression set of the rubber vulcanizates at various curing systems.

agent in all curing systems. This reduction is attributed to the combined effects of better filler dispersion and higher degree of crosslinking when the silane coupling agent is incorporated.

Since Si-264 can promote filler disagglomeration to a greater extent than Si-69 leading to better filler dispersion, Si-264 generally provides the rubber vulcanizates with slightly lower compression set than Si-69. In addition, Si-69 could contribute additional sulfur to the rubber matrix, particularly in the EV system, whereas Si-264 could not. It is therefore expected that the number of polysulfidic linkages in the system having Si-69 is higher than that in the system having Si-264. These longer sulfidic linkages could lead to poorer compression set at elevated temperature as they are not as thermally stable as the shorter sulfidic linkages.

The results also reveal the dependence of compression set on the curing system. As expected, the EV system imparts vulcanizates with lowest compression set value whereas the CV system imparts vulcanizates with the highest compression set value. This is simply due to the fact that the crosslink structure in the EV system is mainly mono-sulfidic crosslink which is stronger and more thermally stable than di-sulfidic and polysulfidic crosslinks which are mainly found in the semi-EV and CV systems, respectively. Interestingly, the results indicate that the effect of silane coupling agent is more pronounced in reducing the compression set than the effect of curing system.

Fig. 8 represents the effects of silane type and curing system on abrasion resistance of the rubber vulcanizates. The addition of silane coupling agent greatly improves the abrasion resistance as can be seen from the reduction of the abrasive volume loss. This improvement is caused by several factors, i.e. the enhanced rubber–filler interaction, better dispersion and higher degree of crosslinking.

Compared with Si-69, Si-264 can improve the abrasion resistance to a greater extent, particularly in the CV and semi-EV systems. This might be understandable from the combination of better filler dispersion and the stronger rubber–filler interaction (as Si-264 provides only mono-sulfidic linkage at the rubber–filler boundary whereas Si-69 provides the combination of mono-, di- and polysulfidic linkages). However, reverse results are found in the EV system where Si-69 enhances the abrasion resistance to a greater extent. Possible explanation is therefore given to the ability of Si-69 to contribute sulfur atoms to the rubber matrix as mentioned earlier.

Table 3 shows the effects of silane type and curing system on heat build up of the rubber vulcanizate. Obviously, heat build up is considerably reduced when silane coupling agent is added. This is simply due to improved filler dispersion and increased crosslink density in the presence of silane coupling agent. For CV and semi-EV systems, the silane type has no significant effect on heat build up. However, for the EV system, the silane type plays a major role in heat build up as Si-69 provides vulcanizates with substantially lower heat build up than Si-264. Again, the sulfur contribution of Si-69 could be used to explain the results. The contributed sulfurs from Si-69 not only cause an increase in crosslink density of the rubber matrix, but also change the crosslink structure from the short sulfur linkages into longer, more flexible sulfur linkages. The heat build up of the rubber vulcanizates in the EV system is therefore reduced when Si-264 is replaced by Si-69.

Considering the effect of curing system, the lowest heat build up is obtained in the CV system and followed by the semi-EV and EV systems, respectively. Possible explanation is given to the degree of crosslinking and the crosslink structure. As the rubber vulcanizates in the CV system have the highest degree of crosslinking and
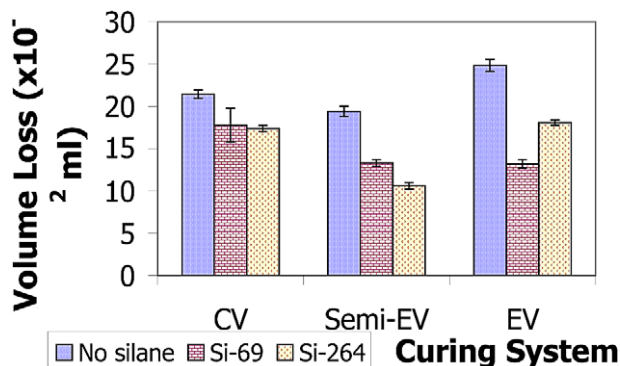
Fig. 8. The effect of silane type on the abrasion resistance of the rubber vulcanizates at various curing systems.

Table 3
Effect of silane type on heat build up of the rubber vulcanizates

Curing system	Temperature rise (°C)		
	No silane	Si-69	Si-264
CV	15.3 ± 0.6	11.3 ± 0.6	10.8 ± 1.0
Semi-EV	18.5 ± 1.0	11.8 ± 0.5	11.8 ± 0.5
EV	31.8 ± 1.0	10.7 ± 0.6	15.7 ± 0.6

they are also crosslinked through the longer, more flexible sulfur linkages, their dynamic properties, particularly the heat build up, are therefore better than those of the vulcanizates in the semi-EV and EV systems, respectively.

4. Conclusion

The addition of silane coupling agent is found to greatly improve compound processability by reducing both mixing energy and compound viscosity. Due to the less bulky structure and lower viscosity, Si-264 can reduce the filler–filler interaction to a greater extent than Si-69. As a consequence, regardless of the curing system, Si-264 imparts better processability than Si-69. The presence of silane coupling agent also significantly improves both mechanical and dynamic properties of the rubber vulcanizates, particularly the tensile strength, modulus, tear strength, compression set, abrasion resistance, as well as the heat build up. Explanation is given to the combined effects of improved rubber–filler interaction, higher state of cure and better filler dispersion. For CV and semi-EV systems, Si-264 generally provides stronger reinforcement than Si-69. This might be attributed to the combined effects of better filler dispersion and stronger rubber–filler interaction. However, for the EV system, Si-69 can enhance reinforcement to a greater degree than Si-264. This is simply due to the sulfur con-

tribution effect which is obviously dominant in this system where large amounts of active curatives are present.

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