CHAPTER 3 : RESULTS AND DISCUSSION

3.1 General

The objective of this study was to determine the degree of influence of varying levels of PEG on processing, cure and physical properties. The effect of PEG addition in the presence of silane-modified-silica compound (1 pphr Si-69) and unmodified silica compound (0 pphr Si-69) were studied. A summary of the compound properties obtained for the formulations were presented in Appendix 5 and 6 respectively.

Comments were based on results of processing and physical properties as well as on the results of regression analyses. Intercepts, correlation coefficients and coefficients of determination (r^2) were found in Appendix 7. Any r^2 correlation coefficient value > 98% is considered to be predictive; a value > 90% is considered to represent a significant relationship; while a value between 80% and 90% is considered indicative of a general trend. This guideline was used by Tultz et. al. [22]. Error analysis for typical test results were shown in Appendix 8.

3.2 Vulcanization Properties

Cure time, t_{95} at 150°C, reduces with increase in level of PEG incorporated in the compounds. The same trend is observed for both cases where 1 pphr and 0 pphr Si-69 is incorporated. This is similar to studies conducted by Byers [9] on the use of PEG in SBR compounds. Results are summarized in Table 10 and Figure 18.

The surface of silica is rough with pores. The incorporated PEG filled up the roughness of the silica surface and reduce adsorption of accelerator at the pores of

the surface. Thus, the amount of accelerator was not wasted when PEG was incorporated into the compounds. Therefore, the higher amount of accelerator eventually increases the acceleration process and the cure time reduces.

In his paper, Wang [11] explained that the more polar ingredients (eg. amine type of antioxidants and accelerators) which have poorer compatibility with less polar polymers will be driven to the filler surface where the polarity is relatively higher. Therefore, the amount of available surface area and the available number of filler active centers for polymer adsorption can be substantially reduced by the adsorption of these small molecules.

	Cure Time, mins				
Compounds	**0 PEG**	**0.5 PEG**	**1.5 PEG**	**3 PEG**	**5 PEG**
1 Si-69	11.15	8.63	8.02	7.72	7.95
0 Si-69	8.40	7.57	7.27	7.00	6.80

Table 10 : Comparison of cure time at different levels of PEG

The effect of PEG in reducing the compound cure time is more effective for compounds with 1 pphr Si-69 compared to that of 0 pphr Si-69. With the addition of 0.5 pphr PEG, cure time reduces from 11.15 mins to 8.63 mins. The effect of longer cure time caused by the incorporation of Si-69 is compensated by adding PEG.

There is a possibility that the active sites on the surface of silica that did not take part during the silica-coupling agent modification process will be filled by PEG, thus preventing the adsorption of accelerators. However, further increase in the level of PEG from 1.5 pphr to 5 pphr did not significantly reduce the cure time. It appears that 0.5 pphr PEG may be the optimum level required.

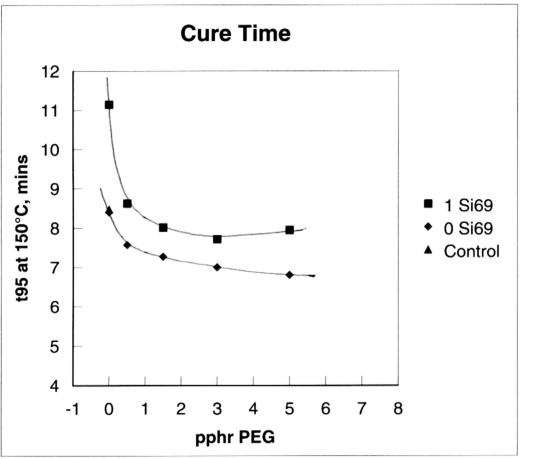

Figure 18 : Cure time versus pphr PEG for 0 and 1 pphr Si-69

3.3 Rheological Properties

3.3.1 Scorch Time

Scorch time, t_5 at 130°C measured from Mooney scorch gives an indication of the processing safety of the compound. Results are shown in Table 11 and Figure 19.

At 0 pphr PEG, partial replacement of carbon black with silica resulted in extended scorch time. When silane coupling agent was added to the compounds, Mooney scorch was decreased. This is in agreement to previous studies [22, 47, 48].

	Scorch Time, mins				
Compounds	**0 PEG**	**0.5 PEG**	**1.5 PEG**	**3 PEG**	**5 PEG**
1 Si-69	11.80	7.13	7.12	6.05	6.32
0 Si-69	13.02	9.05	7.12	6.68	6.72
Control	8.00				

Table 11 : Comparison of scorch time at different levels of PEG

The effect of PEG on the scorch time of compounds showed a similar trend as the cure time. Scorch time reduces with increasing level of PEG incorporated in the compounds. The same trend is observed for both cases where 1 pphr and 0 pphr Si-69 is incorporated.

Based on the same explanation in 3.2, there is less adsorption of accelerator on the surface of silica due to the presence of PEG. Therefore, a higher efficiency of acceleration will reduce the processing safety of the compound resulting in shorter scorch time.

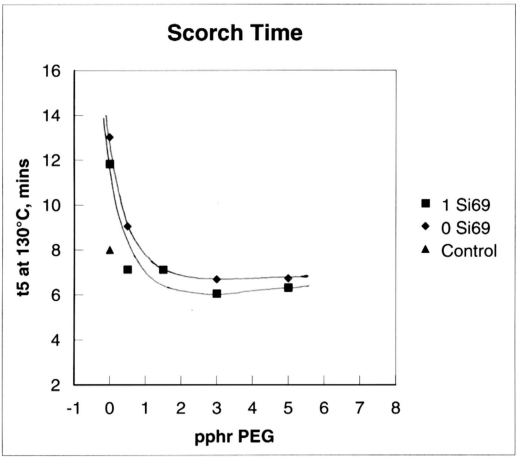

Figure 19 : Scorch time versus pphr PEG for 0 and 1 pphr Si-69

3.3.2 Cure Rate

Cure rate is a measure of the rate of curing of the compound after the processing safety period had lapsed i.e. (t_{35} - t_5) at 130°C from the Mooney Scorch. The shorter is the cure rate, the faster is the curing process. Results are depicted in Table 12 and Figure 20.

The addition of Si-69 contributed to a decrease in scorch time and cure time as well as a faster cure rate.

	Cure Rate, mins				
Compounds	**0 PEG**	**0.5 PEG**	**1.5 PEG**	**3 PEG**	**5 PEG**
1 Si-69	2.59	2.44	2.48	2.18	2.40
0 Si-69	3.18	3.03	2.85	2.74	2.61
Control	2.35				

Table 12 : Comparison of cure rate at different levels of PEG

With the addition of PEG, a faster cure rate is observed as shown in the table above. The explanation is similar to 3.2 and 3.3.1 regarding the prevention of molecule adsorption on the surface of silica.

Based on statistical analysis, compounds without Si-69 appears to show linear correlation with pphr PEG ($r^2 = 0.912$) compared to compounds with 1 pphr Si-69 ($r^2 = 0.327$).

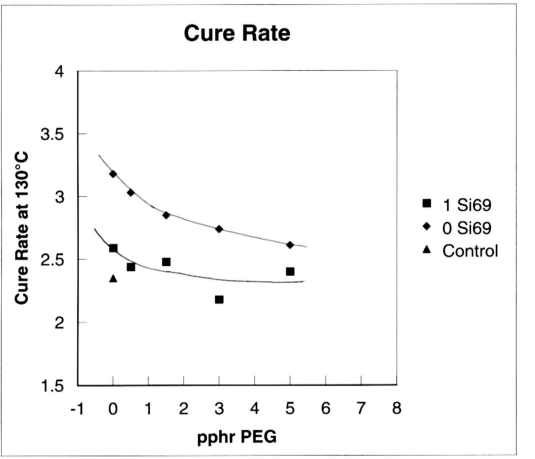

Figure 20 : Cure rate versus pphr PEG for 0 and 1 pphr Si-69

3.3.3 Mooney Viscosity

Mooney viscosity, ML(1+4) at 130°C, gives an indication of the processability of the compound. Results are presented in Table 13 and Figure 21.

	Mooney Viscosity				
Compounds	**0 PEG**	**0.5 PEG**	**1.5 PEG**	**3 PEG**	**5 PEG**
1 Si-69	59.5	62.9	60.3	61.1	60.8
0 Si-69	64.5	65.7	66.7	67.1	64.6
Control	63.5				

Table 13 : Comparison of Mooney viscosity at different levels of PEG

Generally, partial replacement of carbon black with silica results in increased viscosity [22, 47, 48]. Wolff et. al. showed that compound viscosity is decreased in the presence of silane coupling agent due to plasticizing effect [10, 47, 48].

From the table above, the addition of PEG had caused the viscosity to increase. This increase is higher in the compounds without Si-69 compared to that with 1 pphr Si-69. This could be due to the plasticizing effect of Si-69 which is able to prevent too much increase in viscosity. It is clear here that PEG does not contribute to any plasticizing effect such as that observed for Si-69 but instead caused an increase in viscosity.

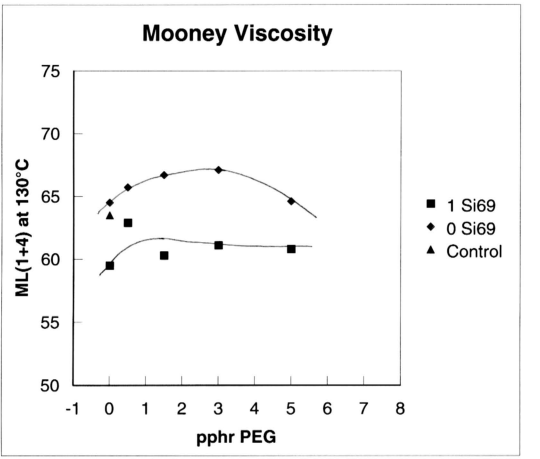

Figure 21 : Mooney viscosity versus pphr PEG for 0 and 1 pphr Si-69

3.4 State of Cure

3.4.1 Crosslink Density

Crosslink density (physical) which was calculated from the Flory Rehner equilibrium swelling measurement includes chemical crosslink density, filler stiffening effect and chain entanglement. Results are summarized in Table 14 and Figure 22.

	Crosslink Density, g/mol RH (x 10^{-4})				
Compounds	**0 PEG**	**0.5 PEG**	**1.5 PEG**	**3 PEG**	**5 PEG**
1 Si-69	2.549	2.531	2.477	2.451	2.490
0 Si-69	2.319	2.285	2.375	2.219	2.310
Control	2.133				

Table 14 : Comparison of crosslink density at different levels of PEG

Crosslink density appears to decrease with higher level of PEG. There are some uncertainties observed here. Results from cure characteristics (4.1 and 4.2) indicated that the effectiveness of acceleration had increased with the addition of PEG. This supports the fact that prevention of accelerator adsorption on silica surface by PEG had taken place. Therefore, one would expect that crosslink density of compounds with PEG should be higher than the compound without PEG as less accelerator would be adsorbed.

However, the addition of PEG had resulted in lower crosslink density measured. This could be due to the extraction of PEG by n-decane when the test was conducted.

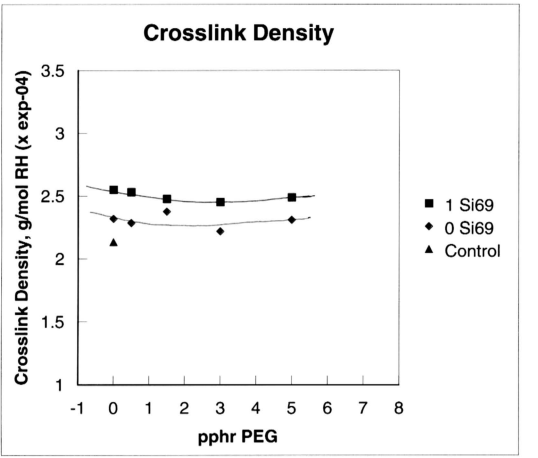

Figure 22 : Crosslink density versus pphr PEG for 0 and 1 pphr Si-69

3.4.2 Differences in Maximum and Minimum Torque, Δ(Torque)

Δ(torque) extracted from the rheometer curve gives an indication of the crosslinks inserted into the compound when vulcanization takes place. Results are shown in Table 15 and Figure 23.

At the minimum torque (ML), there is no crosslink formed yet. As soon as crosslinks started to form, the torque increases. Maximum state of crosslinks formation were attained at the maximum torque (MH). However, Δ(torque) is not equivalent to crosslink density but a combination of the effect of filler loading, viscosity and crosslink density.

Partial replacement of carbon black with silica results in reduction of Δ(torque). With addition of Si-69 and absence of PEG, Δ(torque) increases slightly. This is in agreement with studies conducted on crosslink density of silica-filled compounds [22].

	Δ(Torque), in lb				
Compounds	**0 PEG**	**0.5 PEG**	**1.5 PEG**	**3 PEG**	**5 PEG**
1 Si-69	13.23	12.96	12.82	12.34	12.25
0 Si-69	12.60	12.85	12.78	12.24	11.93
Control	16.08				

Table 15 : Comparison of Δ(torque) at different levels of PEG

For the compounds with 1 pphr Si-69, Δ(torque) reduces with the addition of PEG. However, in the absence of Si-69, Δ(torque) appears to increase slightly for 0.5 pphr PEG and 1.5 pphr PEG but reduces with further increase in PEG level.

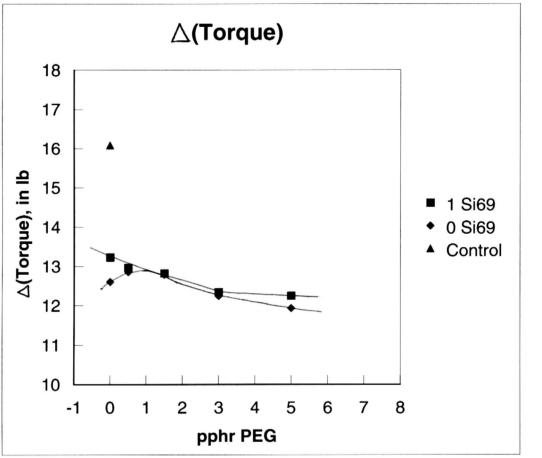

Figure 23 : Δ(Torque) versus pphr PEG for 0 and 1 pphr Si-69

Since PEG does not significantly increase Δ(torque) especially at higher levels of PEG, it may not have any contribution in increasing the strength properties of the compound. The effect of PEG is merely to fill up the pores on the silica surface and prevent adsorption of amine type of accelerator.

Statistical analysis had showed that both compounds with 1 pphr Si-69 (r^2 = 0.907) and without Si-69 (r^2 = 0.810) exhibit linear correlation with pphr PEG.

3.5 Tensile Stress-strain Properties

The stress-strain properties discussed here covers tensile strength (TS), elongation at break (EB) and modulus at 300% elongation (M300) and the results are tabulated in Table 16. Plot of tensile strength and modulus are shown in Figure 24 and Figure 25 respectively.

		0 PEG	0.5 PEG	1.5 PEG	3 PEG	5 PEG
1 Si-69	TS, MPa	29.0	29.3	29.3	27.2	27.4
	EB, %	540	540	560	540	540
	M300, MPa	13.9	14.9	13.3	12.6	12.9
0 Si-69	TS, MPa	29.2	30.3	27.5	29.0	28.3
	EB, %	550	560	540	560	570
	M300, MPa	13.5	13.3	12.7	12.7	11.8
Control	TS, MPa	30.7				
	EB, %	540				
	M300, MPa	14.9				

Table 16 : Comparison of stress-strain properties at different levels of PEG

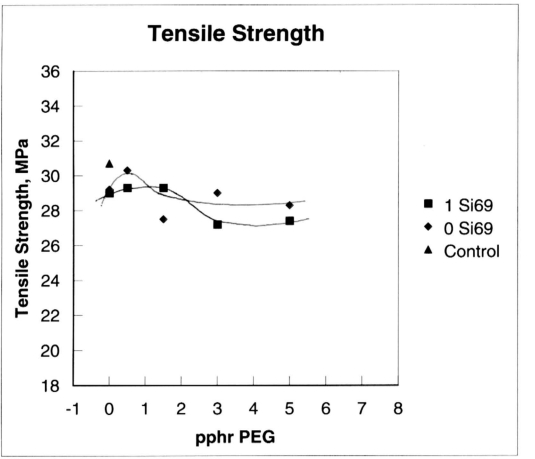

Figure 24 : Tensile strength versus pphr PEG for 0 and 1 pphr Si-69

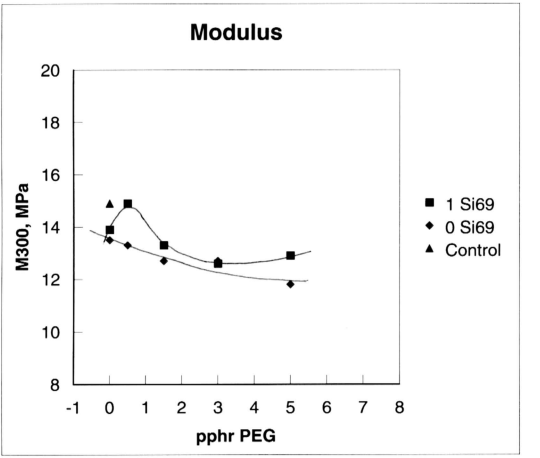

Figure 25 : M300 versus pphr PEG for 0 and 1 pphr Si-69

Tultz et. al. [22] showed that tensile strength and modulus decreased while elongation increased with partial replacement of carbon black with silica. The reverse effect on these properties were noted with addition of silane coupling agent.

In the absence of PEG, it was noted that tensile strength and modulus reduces with addition of silica as compared to the control compound properties. However, no improvement was observed in the stress-strain properties with the addition of Si-69. This appears to contradict the above statement.

In the presence of 1 pphr Si-69 and with the addition of PEG at 0.5 and 1.5 pphr, tensile strength remains the same but reduced with further increase in the level of PEG at 3 and 5 pphr. There was no significant differences in the elongation at break with addition of PEG. M300 showed slightly higher modulus at 0.5 pphr PEG but reduced with further increase in the level of PEG at 3 and 5 pphr.

In the absence of Si-69, tensile strength improved slightly with the addition of PEG at 0.5 pphr but reduced with further increase in the level of PEG. This could be due to the slightly higher crosslink density of the compound with 0.5 pphr PEG as explained in 3.4. There was no significant differences in the elongation at break with addition of PEG. M300 remains the same at 0.5 pphr PEG but reduced with further increase in the level of PEG.

From statistical analysis, M300 for compounds without Si-69 ($r^2 = 0.931$) has a linear relation trend with pphr PEG.

In short, there was only slight improvement in tensile strength and modulus for compound with 0 pphr and 1 pphr Si-69 respectively when 0.5 pphr PEG is added while other properties remain unchanged. However, stress-strain properties appears to be slightly poorer with further increase in PEG especially at 3 and 5 pphr. There is a possibility that the optimum level of PEG for stress-strain improvement lies in the region of 0.5 pphr PEG.

Ageing at 70°C for 3 days

		0 PEG	0.5 PEG	1.5 PEG	3 PEG	5 PEG
1 Si-69	TS, MPa	28.7	28.8	29.1	29.0	27.3
	EB, %	470	500	510	530	510
	M300	17.9	15.7	15.7	14.7	14.7
0 Si-69	TS, MPa	28.1	29.0	27.5	28.5	27.8
	EB, %	530	530	530	520	540
	M300	14.6	14.4	14.5	14.0	12.9
Control	TS, MPa	30.1				
	EB, %	490				
	M300	17.3				

Table 17 : Comparison of aged stress-strain properties at different levels of PEG

Results of tensile stress-strain propertis after ageing are summarized in Table 17. There is no significant trend that can be derived due to the effect of ageing on stress-strain properties. The addition of PEG did not show any improvement in stress-strain properties upon ageing.

3.6 Hardness

Results are shown in Table 18 and Figure 26. In the presence of Si-69, there are not much changes in the hardness at different levels of PEG. In the absence of Si-69, hardness appears to reduce slightly at 3 and 5 pphr PEG. Generally, hardness of the compounds with Si-69 is slightly higher than that without Si-69.

	Hardness, IRHD				
Compounds	**0 PEG**	**0.5 PEG**	**1.5 PEG**	**3 PEG**	**5 PEG**
1 Si-69	65	65	64	65	63
0 Si-69	64	63	64	62	62
Control	70				

Table 18 : Comparison of hardness at different levels of PEG

3.7 Resilience

Results are found in Table 19 and Figure 27. In the presence of Si-69, there are not much changes in the resilience at different levels of PEG. In the absence of Si-69, resilience appears to increase with addition of PEG. Generally, resilience of the compounds with Si-69 is slightly higher than the compounds without Si-69.

	Resilience, %				
Compounds	**0 PEG**	**0.5 PEG**	**1.5 PEG**	**3 PEG**	**5 PEG**
1 Si-69	66	66	65	66	65
0 Si-69	62	63	65	66	65
Control	59				

Table 19 : Comparison of resilience at different levels of PEG

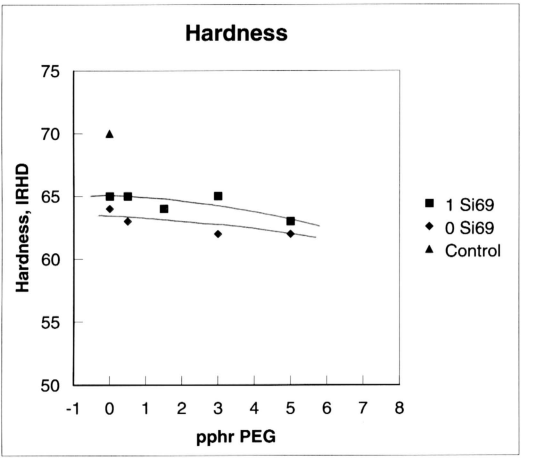

Figure 26 : Hardness versus pphr PEG for 0 and 1 pphr Si-69

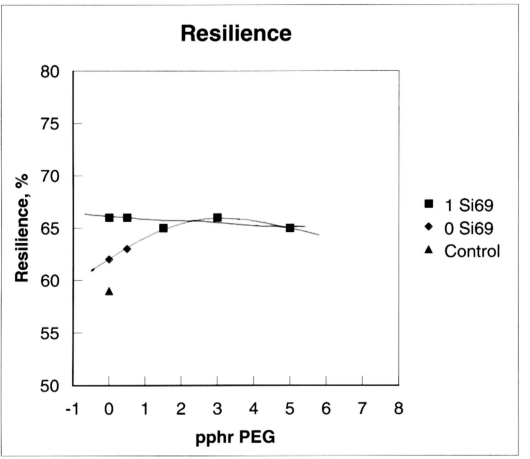

Figure 27 : Resilience versus pphr PEG for 0 and 1 pphr Si-69

The incorporation of PEG does not appear to improve the resilience of the compounds with Si-69. However, resilience is slightly higher with addition of PEG for compounds without Si-69.

3.8 Tear Strength

Tear strength indicates the resistance of the compound to tear. Results are presented in Table 20 and Figure 28.

	Tear Strength, N/mm				
Compounds	**0 PEG**	**0.5 PEG**	**1.5 PEG**	**3 PEG**	**5 PEG**
1 Si-69	29	31	37	43	44
0 Si-69	35	30	39	35	40
Control	24				

Table 20 : Comparison of tear strength at different levels of PEG

For compounds without any addition of PEG, there is an improvement in the tear strength with addition of silica but a negative effect in the presence of silane coupling agent. This was shown in the work carried out by Tultz et. al. [22]. Results obtained is in good agreement with their studies.

With the addition of PEG, tear strength increases for compounds with 1 pphr Si-69. However, this trend is not observed for the compounds with 0 pphr Si-69 whereby the tear strength appears to be similar to the compound without PEG regardless of the level of PEG used. The addition of PEG appears to improve the tear strength of the compounds with 1 pphr Si-69 to levels better than that of the compounds without Si69.

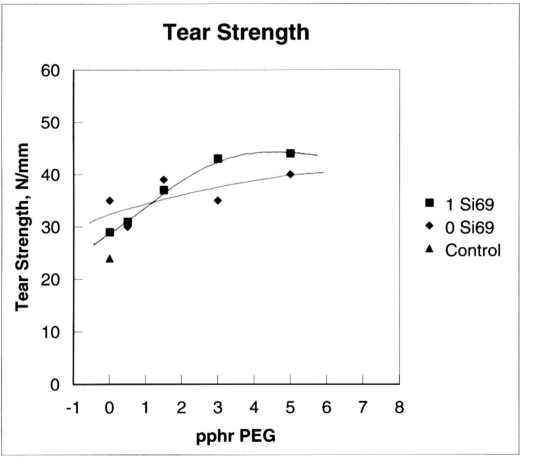

Figure 28 : Tear strength versus pphr PEG for 0 and 1 pphr Si-69

3.9 Heat Build-up

Table 21 and Figure 29 shows the test results obtained.

		0 PEG	0.5 PEG	1.5 PEG	3 PEG	5 PEG
1 Si-69	ΔT, °C	16	15	15	15	13
	Set, %	2.0	2.0	2.0	2.6	2.5
0 Si-69	ΔT, °C	16	16	15	15	15
	Set, %	4.0	4.0	3.5	3.5	4.5
Control	ΔT, °C	18				
	Set, %	3.0				

Table 21 : Comparison of heat build-up at different levels of PEG

Tultz [22] showed that partial incorporation of carbon black with silica was associated with lower heat build-up and higher permanent set, while incorporation of silane coupling agent further reduces the heat build-up. The results of heat build-up and permanent set for the compounds without PEG is in good agreement with the findings by Tultz.

Heat build-up of the compounds with and without Si-69 appear to be the same regardless of the level of PEG incorporated. The addition of PEG does not appear to have any effect on the heat build-up of both the compounds with and without Si-69.

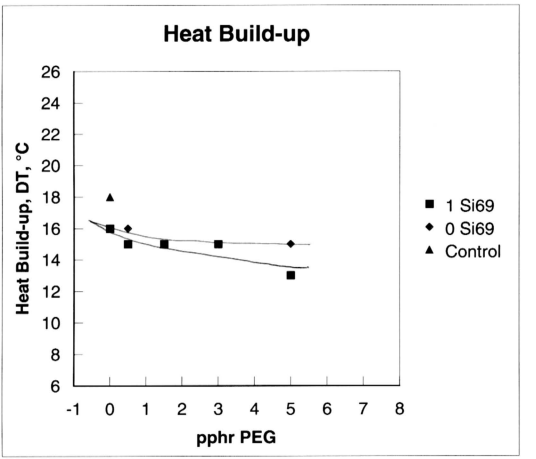

Figure 29 : Heat build-up versus pphr PEG for 0 and 1 pphr Si-69

3.10 Dynamic Mechanical Properties

Tan δ at 60°C relates to rolling resistance which is the loss properties of a tyre compound [49]. Results are shown in Table 22 and Figure 30.

	Tan δ at 60°C				
Compounds	**0 PEG**	**0.5 PEG**	**1.5 PEG**	**3 PEG**	**5 PEG**
1 Si-69	0.07	0.07	0.07	0.07	0.06
0 Si-69	0.08	0.08	0.08	0.08	0.07
Control	0.11				

Table 22 : Comparison of tan δ at different levels of PEG

Wolff et. al. [50] had shown that the strength of the filler network is much greater for the silica than for the carbon black. The greater strength of the filler network implies less breakdown and faster reformation of this network, a lower tan δ can be expected for the silica. They also confirmed that the differences in tan δ has to be attributed to differences in surface activity of the filler. Carbon black of similar surface area as the silica will impart a significantly higher tan δ than the silica.

The incorporation of PEG into the compounds did not have much effect on the tan δ for both 0 pphr and 1 pphr PEG. This may indicate that the addition of PEG does not contribute to any differences in surface activity of the silica. The effect of PEG is merely to fill up the roughness of the surface of silica and prevent adsoprtion of amine type of molecules.

Compounds with 0 pphr Si-69 showed slightly higher tan δ compared to that of the compounds with 1 pphr Si69. Both these compounds have lower tan δ than the control compound of same total filer loading due to lower tyre energy losses [22].

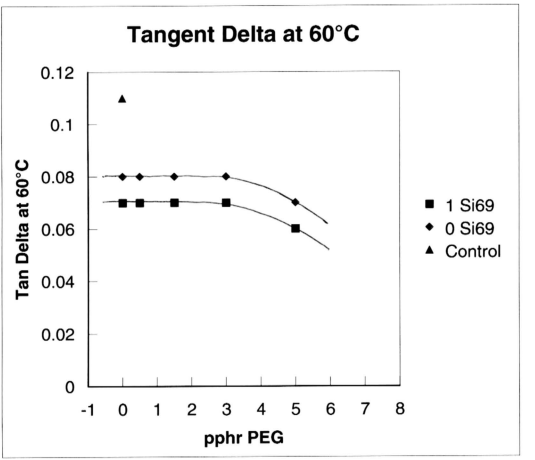

Figure 30 : Tangent delta versus pphr PEG for 0 and 1 pphr Si-69

Storage modulus, E', relates to the stability of the silica network. Results are summarized in Table 23 and Figure 31.

	E' x 10^7, dyn/cm^2				
Compounds	**0 PEG**	**0.5 PEG**	**1.5 PEG**	**3 PEG**	**5 PEG**
1 Si-69	11.3	10.5	9.67	9.34	9.73
0 Si-69	0.91	0.98	0.93	0.98	0.88

Table 23 : Comparison of storage modulus, E' at different levels of PEG

Overall, the compounds with both Si-69 and PEG showed much higher E' compared to the compounds with PEG alone. This indicates that the existence of a much stable filler network of the silica as contributed by the silane coupling agent through chemical reaction compared to that of PEG through physical adsorption.

The addition of PEG to the compounds with 1 pphr Si-69 had resulted in lower E'. The decrease in E' with addition of PEG was also observed in Wang's work [11] on the use of DEG in a natural rubber with peroxide cure system.

For the compounds without Si-69, the addition of PEG had resulted in slightly higher E'. The contribution of PEG towards stable filler network is not as significant as that of the silane coupling agent.

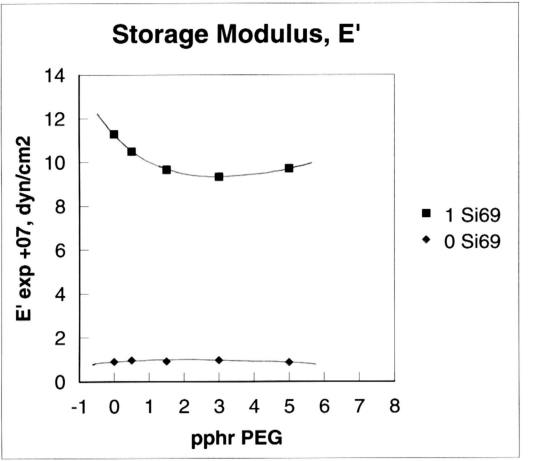

Figure 31 : Storage modulus, E' versus pphr PEG for 0 and 1 pphr Si-69

3.11 Cut Growth Resistance

Results are shown in Table 24. Rough roads cause repetitive, localized high pressure pounding of the tread surface, resulting in a fatigue fracture mechanism that causes small chip or chunks of tread material to come off the tyre. Improvement in chip/chunk performance is contributed by higher surface area fillers [51].

Silica is often used in on/off highway treads because of its ability to deflect and suppress cut propagation. The silica normally used have typical nitrogen surface area ranging from 140 to 175 m2/g [51].

Engelhardt et. al. [51] mentioned that the purpose of silane coupling agent is to minimize the polymer dewetting hysteresis mechanism and thereby reducing heat build-up. Another advantage of silane bonding is an improvement in road abrasion resistance because the silica particles have less tendency to come out of the polymer matrix when chemically bonded to it.

	No of cycles for the cut to extend from L to (L+10)mm, kc				
Compounds	**0 PEG**	**0.5 PEG**	**1.5 PEG**	**3 PEG**	**5 PEG**
1 Si-69	150.0	77.0	119.0	96.9	102.4
0 Si-69	14.3	19.2	17.2	29.1	12.7
Control	80.0				

Table 24 : Comparison of De Mattia cut growth resistance at different levels of PEG

Comparing the compounds with 0 pphr and 1 pphr Si-69, the latter showed much better cut growth resistance. This is in agreement to studies conducted on the effect of silane coupling agent in improving cut growth resistance in the paper by

Martin L. Engelhardt et. al. [51]. This improvement is observed with the use of silica with surface area of 120 m^2/g coupled with silane coupling agent.

However, with the addition of PEG, the compounds showed inferior cut growth resistance. The extent of inferior cut growth resistance is more significant in the compounds with 1 pphr Si-69 compared to the compounds without Si-69. As explained earlier, chemical bonding of silica reduces its tendency to detach from the polymer. The physical bonding contributed by PEG has no effect on the chemical bonding but instead caused poorer cut growth resistance.

3.12 Abrasion Resistance

Results can be found in Table 25 and Figure 32. The incorporation of Si-69 and silica improves the abrasion resistance as quoted by Wolff et. al. [10]. With the addition of PEG, improvement is observed in both the compounds with and without Si-69. A higher improvement in abrasion resistance is observed in the compounds with 1 pphr Si-69 compared to that without Si-69.

	Abrasion Resistance, ARI, %				
Compounds	**0 PEG**	**0.5 PEG**	**1.5 PEG**	**3 PEG**	**5 PEG**
1 Si-69	104	115	98	122	134
0 Si-69	90	88	96	89	109
Control	92				

Table 25 : Comparison of abrasion resistance at different levels of PEG

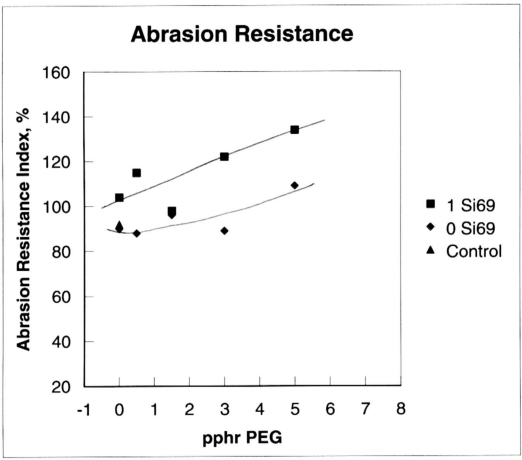

Figure 32 : Abrasion resistance index versus pphr PEG for 0 and 1 pphr Si-69