RESULTS AND DISCUSSION

1. Influence of vulcanization system

Besides the composition in the blend, crosslink network types and crosslink density are known to significantly influence on the mechanical properties of the vulcanizates. In general, the vulcanizates cured with EV and CV systems contain predominantly mono-, di-sulfidic networks, and polysulfidic networks, respectively. In addition, CV vulcanizates normally have higher crosslink density than EV vulcanizates (Pal *et al.*, 1982). It is thus of interest in this thesis to study the effect of vulcanization system (both CV and EV) on the cure characteristics and mechanical properties including thermal and fluid resistance of the natural rubber materials in order to receive the proper rubber compound formulation for rubber mat industry especially in livestock.

1.1 Cure Characteristics

The vulcanization characteristics of the prepared rubber compounds were determined by using the Moving Die Rheometer (MDR). Cure characteristics were reported for all vulcanization systems and from the cure characteristics, parameters; namely, minimum torque, maximum torque, ΔT (M_H-M_L), cure time, and scorch time were evaluated.

Data showing the variation of cure characteristics with various cure systems (CV and EV) compared to the control rubber formulation are represented in Table 5.

Table 5 Curing characteristics of rubber compounds with different vulcanization systems

Curing characteristics	Vulcanization system		
	Control	CV	EV
Minimum torque, M_L (lb-in)	2.35	2.41	1.46
Maximum torque, M_H (lb-in)	8.71	8.01	4.19
ΔT (M_H-M_L)	6.36	6.60	3.73
Scorch time, t_{s2} (min)	3.41	3.59	4.93
Cure time, t_{c90} (min)	6.03	5.82	5.91

It is seen that the compound vulcanized with CV system gives higher minimum torque than the compound vulcanized with EV system. Minimum torque is an indirect measure of the viscosity of the compound (Blow and Hepburn, 1985; Shah, 1998), or it can be generally treated as the measure of the stiffness of the unvulcanized test specimen taken at the lowest point of the curve. It is to say the processability of the compound vulcanized with CV system becomes more difficult than EV system. From the table, it is also seen that the maximum torque similarly trends like minimum torque. The compound vulcanized with CV system gives approximately twofold maximum torque than the compound vulcanized with EV system. This is because rubber compound vulcanized with CV system yields polysulfidic crosslinks, resulting in higher the number of crosslink that makes compound with higher viscosity. Maximum torque and torque difference gives an idea about the shear modulus, which indirectly related to the crosslink density of the compounds, of the fully vulcanized compound at the vulcanization temperature (Blow and Hepburn, 1985; Ismail *et al.*, 1995; Shah, 1998). Hence, it can be concluded that CV system has contributed to better crosslink.

Cure time is defined as the time required for optimum vulcanization of the samples. This is an important parameter as far as the vulcanization is concerned. Evaluation of cure time is a prerequisite for molding the compounds. The variations in cure time for different vulcanization systems were studied as shown in Table 5. It is noticed that the vulcanization system does not have significant effect on the cure time as a result of no significant changes in the cure time for different vulcanization systems.

1.2 Mechanical properties

The influence of vulcanization system on the mechanical properties, i.e., hardness, abrasion, compression set, and tear strength of the vulcanizates was investigated. The mentioned mechanical properties of CV and EV vulcanizates were compared with the control rubber formulation as shown in Table 6.

Table 6 Mechanical properties of vulcanizates with different vulcanization systems

Mechanical Properties	Vulcanization system		
	Control	CV	EV
Hardness (Shore A)	61±1	54±1	53±1
Abrasion (mm^3)	391±9	588±45	681±20
Compression set (%)	30.7±1	30.9±1	24.5
Tear strength (N/mm)	32.9±1	31.0±1	31.9±2

As can be seen from Table 6 and Figure 21, the hardness of the CV vulcanizate is slightly greater than those of the EV vulcanizate. The results indicate higher crosslink density of the vulcanizates in the CV system because there is more sulfur available for crosslink formation, compared to those in the EV system. The higher crosslink density and modulus of NR vulcanizates cured with the CV system relative to those in the EV system have also been investigated previously (Pal *et al.*, 1982).

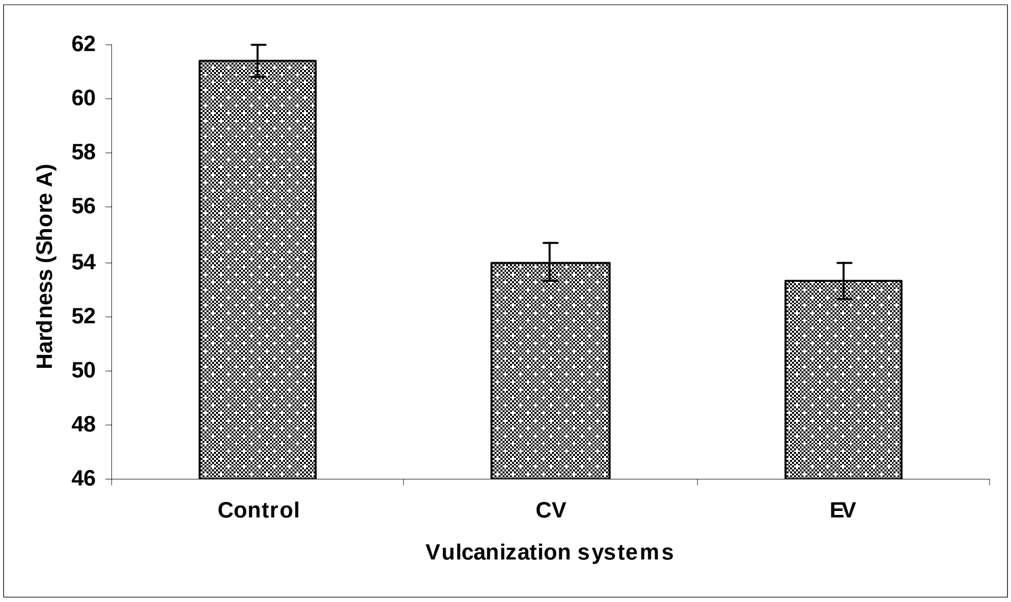

Figure 21 Hardness of vulcanizates with different vulcanization systems

Volume loss of CV and EV vulcanizates, which is inversely proportional to the abrasion resistance, is also given in Table 6 and Figure 22. The results reveal that the CV vulcanizate gives clearly higher abrasion resistance than EV vulcanizate. It has been reported that crosslink density, hardness, modulus, and friction coefficient of the vulcanizate are important factors controlling the abrasion resistance (Thavamani and Bhowmick,1993; Cho and Lee, 2001; Fukahori and Yamazaki, 1994a, 1994b; Fukahori and Yamazaki, 1995). The greater crosslink density and, hence, the hardness and modulus give rise to the enhancement of abrasion resistance. On the contrary, the lower the friction coefficient, the higher the abrasion resistance (Rattanasom *et al.*, 2005). From the results obtained in this experiment, the greater abrasion resistance of CV vulcanizate should be due to their higher hardness, relative to higher crosslink density than EV vulcanizate.

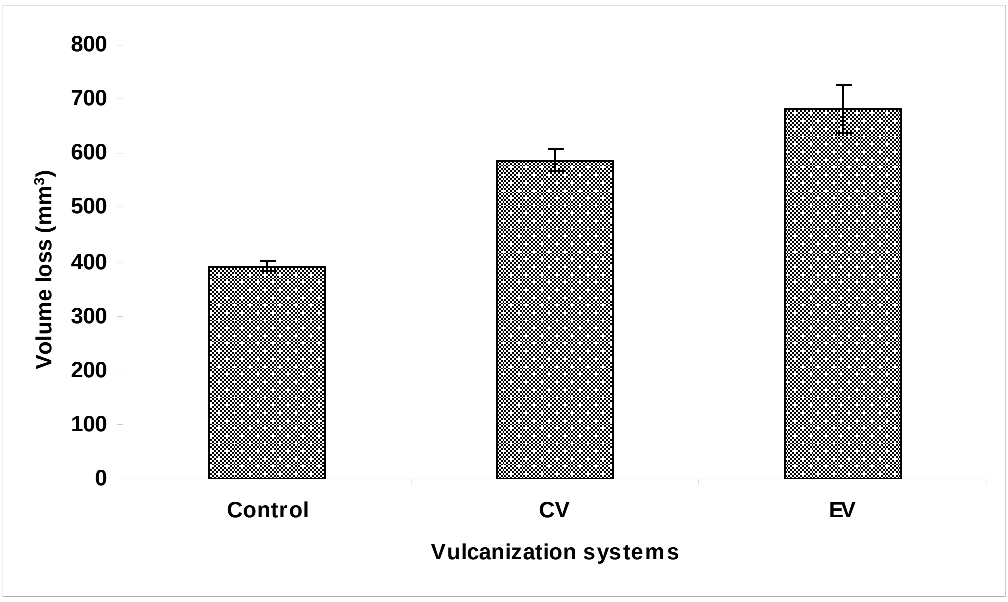

Figure 22 Volume loss of vulcanizates with different vulcanization systems

The results also reveal the dependence of compression set on the vulcanization system. As expected, the EV system imparts compound with lowest compression set value whereas the CV system imparts compound with the highest compression set value (Figure 23). 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 CV systems (Sae-oui *et al.,* 2004).

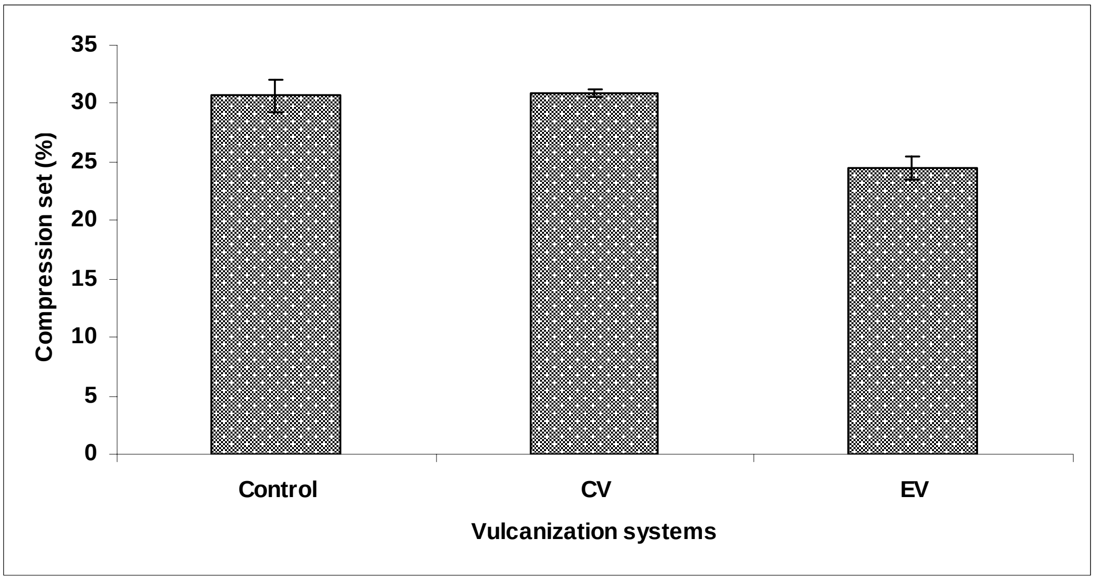

Figure 23 Compression set of vulcanizates with different vulcanization systems

The influence of crosslink structure and crosslink density in increasing tensile strength of NR compound cured with the CV system is also presented elsewhere (Pal *et al.*, 1982). However, it appears that tensile strength of the rubber compound in both systems becomes comparable (Rattanasom *et al.*, 2005). As for tensile strength, tear strength of CV and EV systems are comparable as seen in Figure 24. This result infers that tear strength of the vulcanizates is not dependent on the curing system.

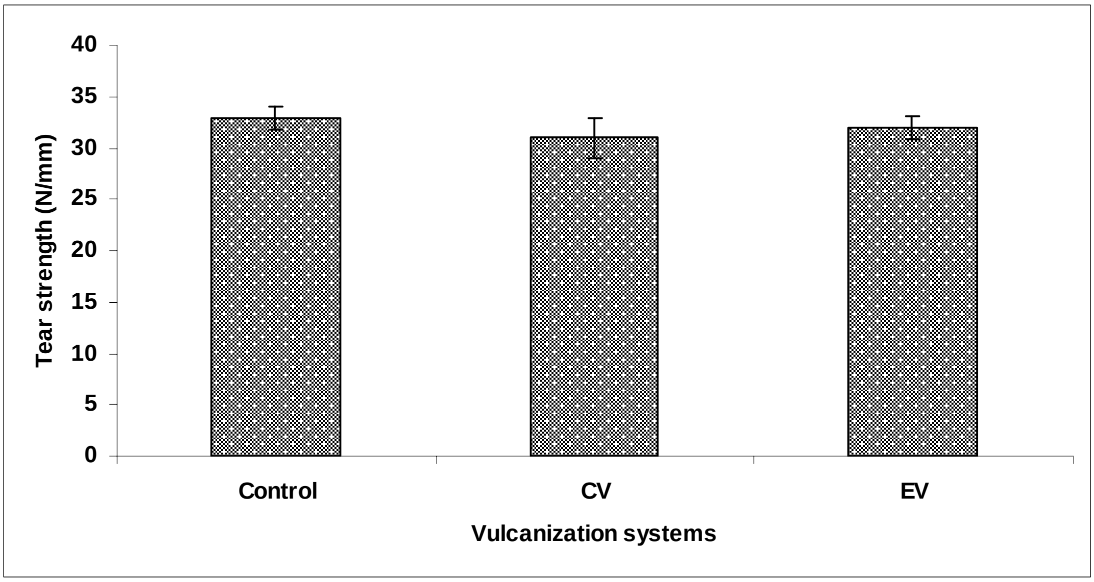

Figure 24 Tear strength of vulcanizates with different vulcanization systems

1.3 Thermal Aging

In this experiment, the effect of thermal aging on the mechanical properties, i.e., hardness, abrasion, compression set, and tear strength of the vulcanizates prepared from different vulcanization systems was also carried out. The results are shown as percentage change of the specimens after thermal aging in an oven at temperature of 70°C for 10 days as pictured in Figures 25-28.

Table 7 Mechanical properties of vulcanizates with different vulcanization systems after thermal exposure

Mechanical Properties	Vulcanization system		
	Control	CV	EV
Hardness (Shore A)	64±1	58±1	55±1
Abrasion (mm^3)	424±8	458±5	516±10
Compression set (%)	18.1±2	20.1±1	18.3±1
Tear strength (N/mm)	34.0±1	29.0±1	32.4±1

As presented in all Figures 25-28, the EV vulcanizates exhibit smaller percentage change in mechanical properties, including hardness, abrasion, compression set and tear strength, than the CV vulcanizates. This is attributed to the better heat stability of mono- and di-sulfidic networks in EV vulcanizates than the polysulfidic ones in the CV vulcanizates (Rattanasom *et al.*, 2005).

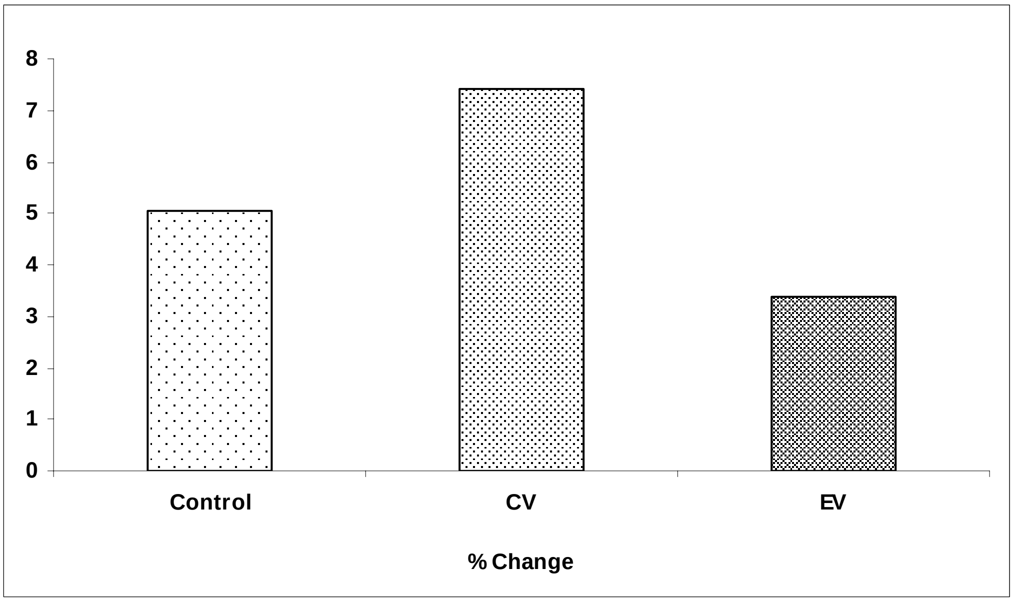

Figure 25 Percentage change in hardness of vulcanizates with different vulcanization systems after thermal exposure

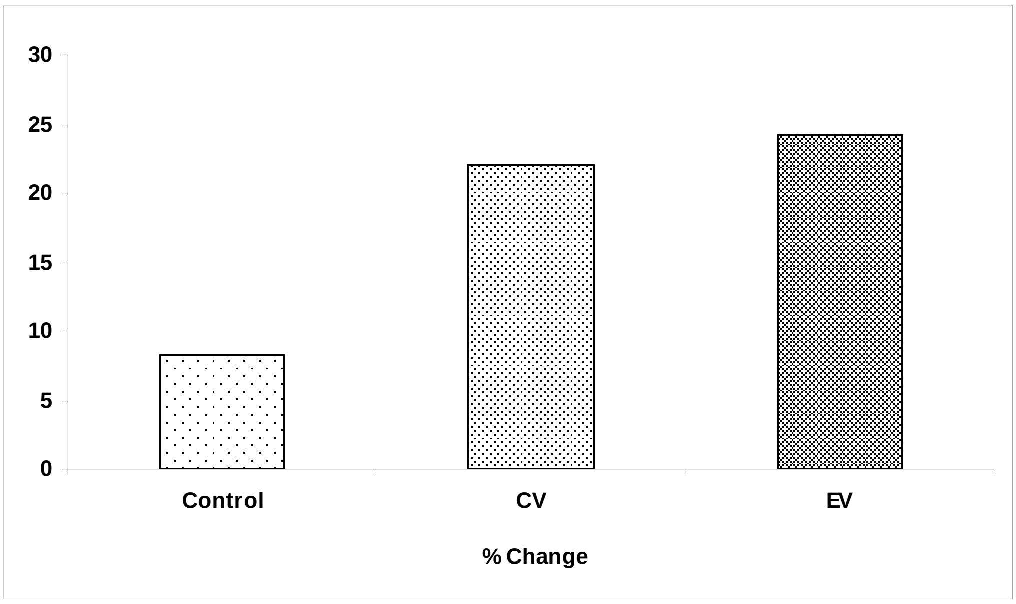

Figure 26 Percentage change in abrasion loss of vulcanizates with different vulcanization systems after thermal exposure

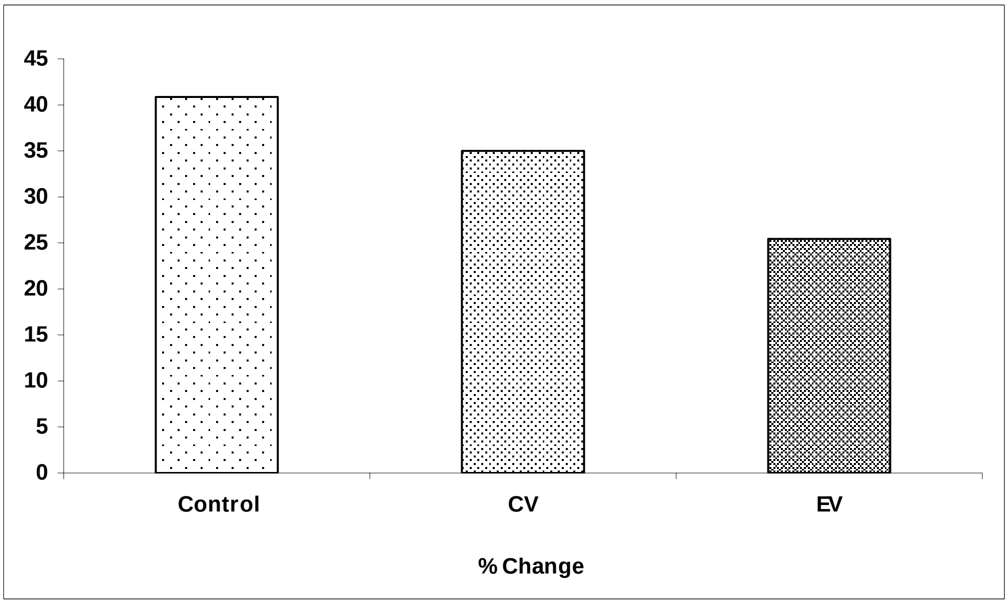

Figure 27 Percentage change in compression set of vulcanizates with different vulcanization systems after thermal exposure

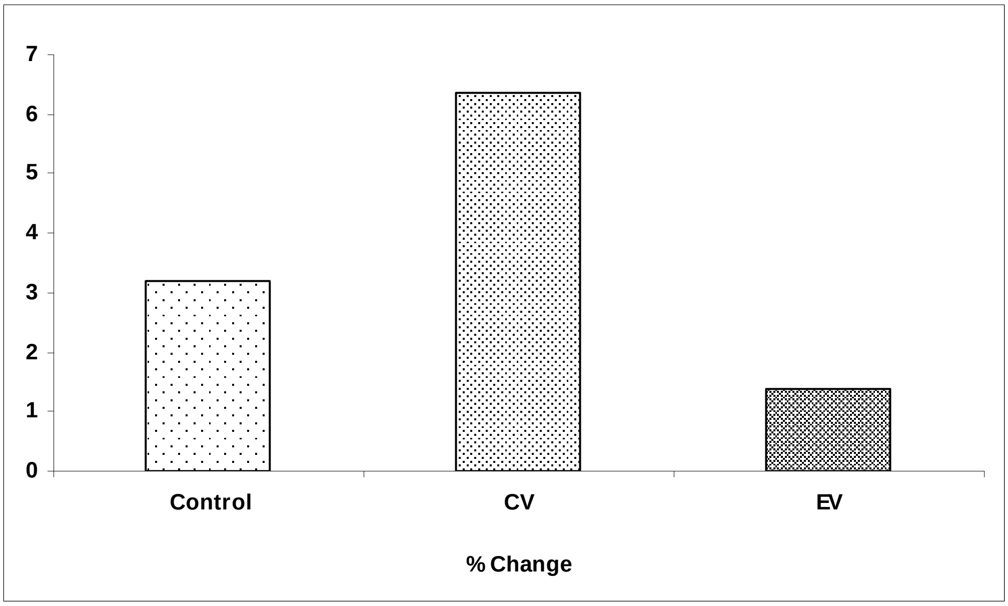

Figure 28 Percentage change in tear strength of vulcanizates with different vulcanization systems after thermal exposure

1.4 Fluid Resistance

The rubber materials of interest, in this study, are rubber mats for using in livestock, especially in cow (cattle), in which they can not be avoided of contact with water and cow's urine. It is thus essential to study the effect of fluid resistance (both water and cow's urine) on the mechanical properties of the vulcanizates cured with various vulcanization systems as represented in Table 8. The results are shown as percentage change of the specimens after immersion in fluid at room temperature for 70 hrs (Figures 29-32).

The mechanical properties of vulcanizates considerably decrease after immersion in fluid (both of water and cow's urine) compared with that before immersion in fluid (Table 8). The results obtained in all Figures 29-32 show that the CV vulcanizate exhibits better fluid resistance than the EV vulcanizate as a result of smaller percentage change in the mechanical properties, i.e., hardness, abrasion, compression set, and tear strength after fluid immersion (water and cow's urine) for

70 hrs. It can be possibly explained that vulcanizate cured with CV system has greater crosslink density than that cured with EV system, leading to the lower rubber swelling. Since rubber swelling is influenced by various factors, such as crosslink type and density, amount and type of filler and type of elastomer. It is well known that swelling ratio is inversely proportional to the degree of crosslinking, therefore, the CV vulcanizates with higher degree of crosslinking exhibit the lower percentage change after fluid (water and cow’s urine) immersion than the EV vulcanizates.

Table 8 Mechanical properties of vulcanizates with different vulcanization systems before and after immersion in water and cow's urine

Vulcanization system	Mechanical Properties							
	After immersion in water				After immersion in cow's urine			
	Hardness (shore A)	Abrasion (mm^3)	Compression Set (%)	Tear Strength (N/mm)	Hardness (shore A)	Abrasion (mm^3)	Compression Set (%)	Tear Strength (N/mm)
Control	61 (61)	391 (490)	30.7 (32.3)	32.9 (34.6)	61 (63)	391 (309)	30.7 (28.3)	32.9 (34.2)
CV	54 (54)	588 (483)	30.9 (45.7)	31.0 (30.4)	54 (56)	588 (320)	30.9 (27.5)	31.0 (29.6)
EV	53 (54)	681 (-)	24.5 (33.5)	31.9 (31.2)	53 (55)	681 (531)	24.5 (28.1)	31.9 (30.6)

Note: ( ) represents the values of mechanical properties after immersion in fluid

(-) can not be measured

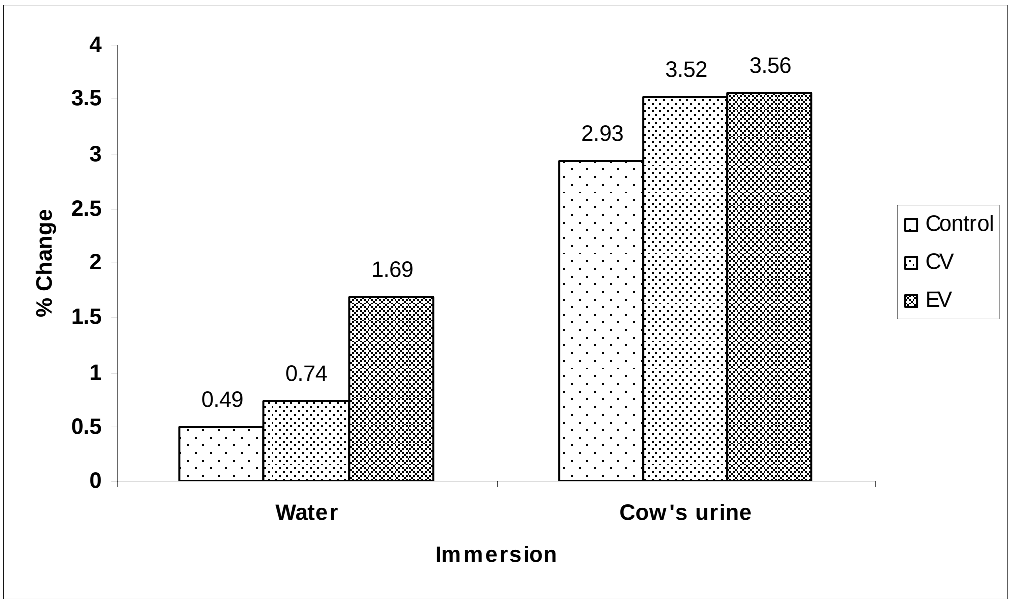

Figure 29 Percentage change in hardness of vulcanizates with different vulcanization systems after immersion in fluid

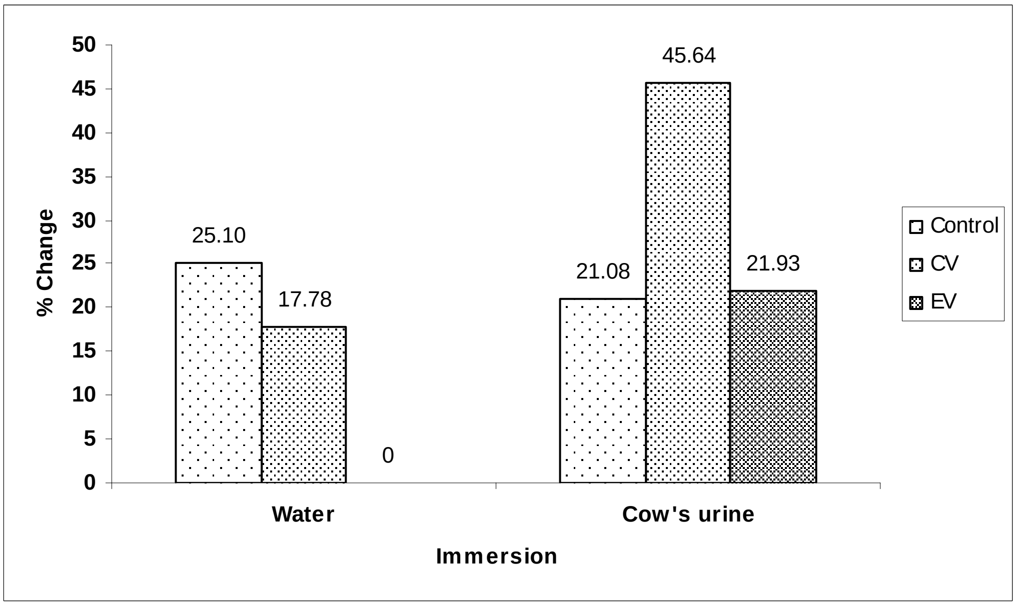

Figure 30 Percentage change in abrasion loss of vulcanizates with different vulcanization systems after immersion in fluid

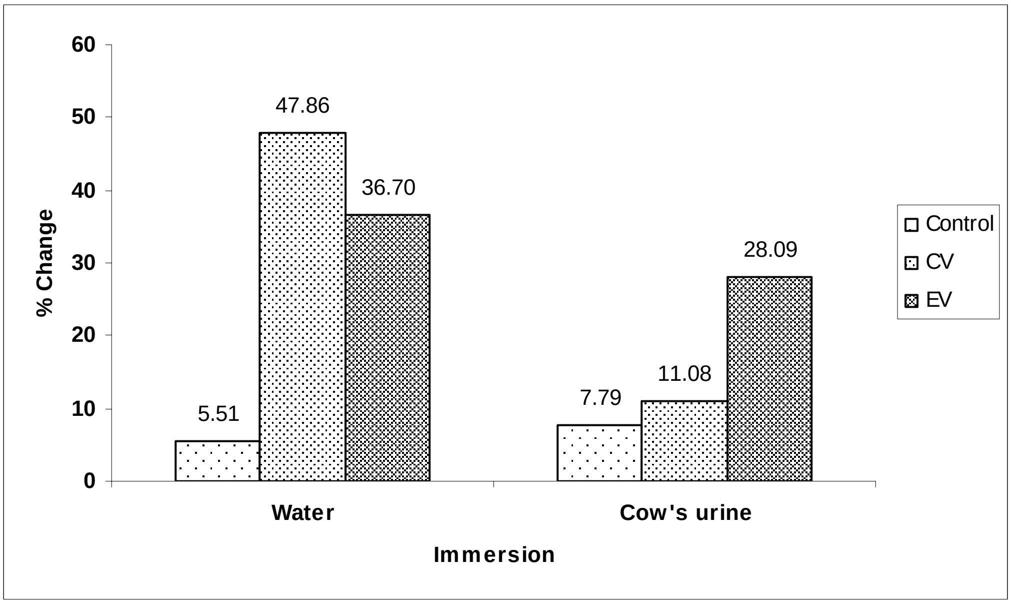

Figure 31 Percentage change in compression set of vulcanizates with different vulcanization systems after immersion in fluid

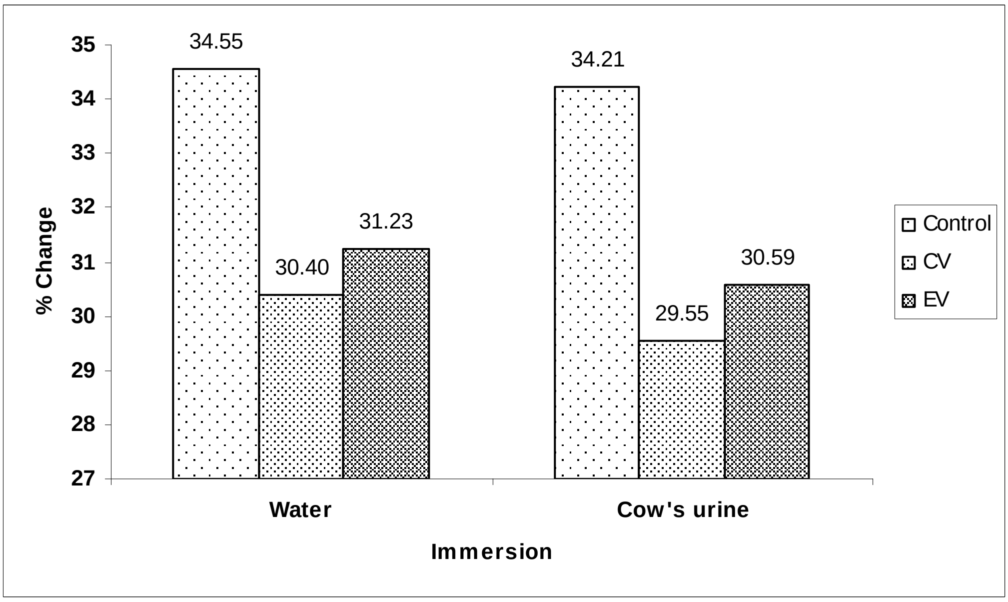

Figure 32 Percentage change in tear strength of vulcanizates with different vulcanization systems after immersion in fluid

From overall results, it can possibly be concluded that the vulcanizates cured with CV system shows better mechanical properties and fluid resistance than those cured with the EV system. However, the EV vulcanizate exhibits greater thermal resistance than the CV vulcanizate. Hence, vulcanizate cured with EV system will be used in the next study on the influence of types and amount of fillers on the mechanical properties of the vulcanizate because it provides moderate mechanical properties and fluid resistance but good thermal resistance of the vulcanizates.

2. Influence of types and amount of fillers

2.1 Filler Characterization

In this thesis the characteristics of natural zeolite are discussed. Its properties in rubber compounding and curing are described. Comparative data with conventional fillers (calcium carbonate; $CaCO_3$, Rice Hush Ask; RHA) is presented to illustrate the unique advantages that can be achieved when such fillers are replaced by natural zeolite.

The physical properties (determined by BET and particle sizeanalyzer) and chemical composition (measured by XRD) of fillers used in this study (natural zeolite, $CaCO_3$, and RHA) are given in Table 9 and 10, respectively.

Table 9 Physical properties of natural zeolite and other fillers

Filler	Mean Particle Size (µm)	Specific Surface Area (m^2/g)	Pore volume (cc/g)	Density (g/cm^3)
Natural	45	14.59	0.0003	2.66
$CaCO_3$	45	3.07	0.0002	2.71
RHA	150	79.22	0.0068	2.19

It is found in Table 9 that the mean agglomerate particles sizes of natural zeolite and calcium carbonate are not significantly different; however RHA filler shows the largest size. The BET surface area of natural zeolite is considerably lower than that of RHA, but slightly higher than $CaCO_3$. However, its pore volume is comparable to $CaCO_3$, while RHA is found to have the highest pore volume.

Table 10 Chemical composition of natural zeolite and other fillers

Chemical composition (%)	Natural zeolite	$CaCO_3$	RHA
Silica (SiO_2)	69.88	7.06	91.36
Alumina (Al_2O_3)	24.87	1.39	0.14
Sodium oxide (Na_2O)	2.20	-	4.17
Magnesium oxide (MgO)	0.46	-	0.35
Potassium oxide (K_2O)	0.42	-	2.97
Calcium oxide (CaO)	0.07	91.46	0.63
Titanium oxide (TiO_2)	1.20	-	0.02
Manganese dioxide (MnO_2)	-	-	0.21
Iron oxide (Fe_2O_3)	0.90	0.09	0.15

Table 10 represents the chemical composition of fillers that composed of metal oxides (e.g., silicon, aluminium, potassium, and sodium). Silica (SiO_2) is found to be mainly part of the component in RHA, and natural zeolite is mainly composed of silica (SiO_2) and alumina (Al_2O_3), while $CaCO_3$ is mainly composed of calcium oxide (CaO).

2.2 Cure Characteristics

Table 11 represents the value of maximum torque (M_H), minimum torque (M_L), scorch time (t_{s2}) and optimum curing time (t_{c90}) of the rubber compounds filled with various fillers at various filler loading. For all types of fillers, the results show that increasing the filler loading in natural rubber compounds increases both of maximum torque and minimum torque. From the minimum torque, this indicates that the processability of the compounds becomes a little more difficult with the increase in filler loading. The increment of both maximum torque and minimum torque could be due to the agglomeration of filler in the natural rubber matrix (Ismail *et al.*, 2002). It can also be seen that the addition of RHA increases not only scorch time, but also optimum curing time. This is possibly due to the reduction of accelerator in the rubber matrix, as it is trapped on the filler's surface as pictured in Figure 33 (Costa *et al.*, 2003).

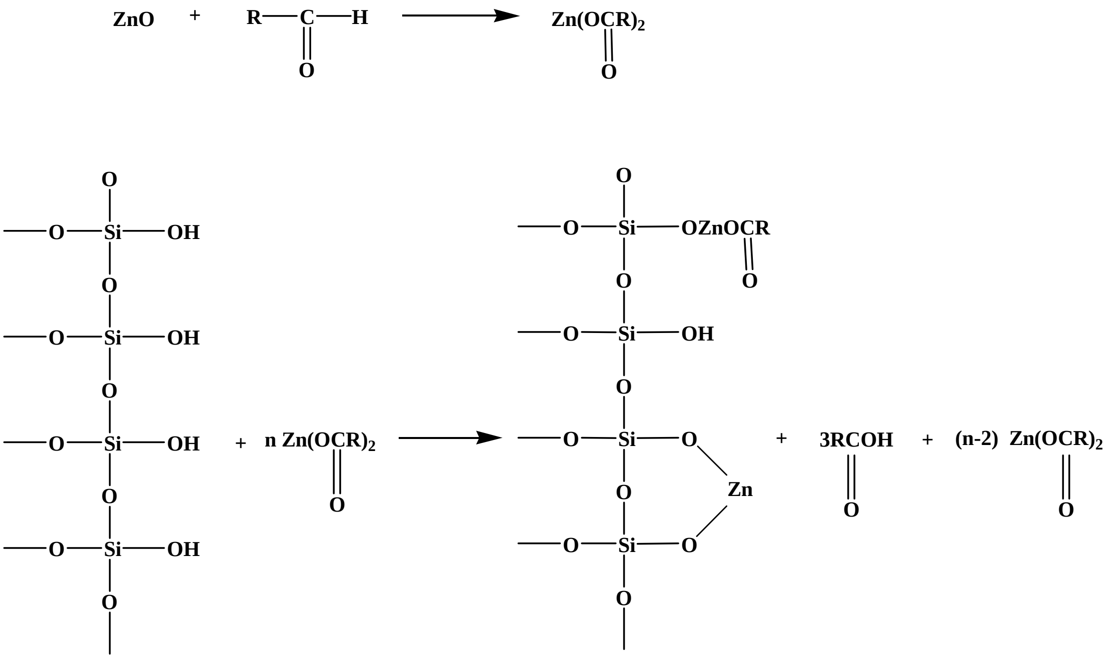

Figure 33 Ion exchange between silanol groups and zinc stearate on sililca surface.

Unlike RHA, scorch time and optimum curing time of natural zeolite and $CaCO_3$-filled rubber compounds decrease with increasing filler loading up to 200 phr. For $CaCO_3$, a possible explanation of this observation is given by the lack of silica in its composition. This is commonly explained by the surface silica (SiO_2) groups, which has hydrolyzed to silanols (-SiOH). These silanol groups behave as acid and are chemically active. The higher surface area fillers have more silanols available and are thus more reactive. In the case of rubber compound filled with natural zeolite, though there is silica in its composition similar to RHA, the optimum cure time in natural zeolite-filled rubber compound is lower than that in RHA-filled rubber compound. This is possibly due to natural zeolite has lower surface area and pore volume than RHA as presented in Table 9. It is to say although both natural zeolite and RHA are mainly composed of silica, natural zeolite has smaller surface area than RHA resulting in the poorer accelerator absorption. In RHA-filled rubber compound, the greater the surface area, the greater accelerator absorption leading to the higher optimum cure time as presented in Table 11.

Table 11 Cure characteristics of the rubber compounds

Filler loading (phr)		Cure characteristics			
		Max Torque, M_H, lb-in	Min Torque, M_L, lb-in	Scorch time (t_{s2}), min	Cure time (t_{c90}), min
gum		4.10	2.05	8.83	7.21
$CaCO_3$	100	4.37	1.61	5.16	6.38
	159	4.19	1.46	4.93	5.91
	200	4.90	1.70	4.61	6.06
	250	5.25	1.80	5.36	7.22
RHA	100	5.21	2.02	6.16	8.24
	159	5.91	2.53	5.17	7.00
	200	5.83	2.38	7.98	11.37
	250	6.09	2.85	9.73	13.90
Zeolite	100	4.07	1.61	5.42	6.19
	159	5.41	2.48	4.90	6.24
	200	4.74	2.00	3.86	4.71
	250	5.97	2.91	4.17	5.58

2.3 Mechanical Properties

The mechanical properties, namely the hardness, abrasion, tear strength, and compression set of the vulcanizates are determined and their variation with various filler loadings is also studied as shown in Figure 34-37 and Table 12-13.

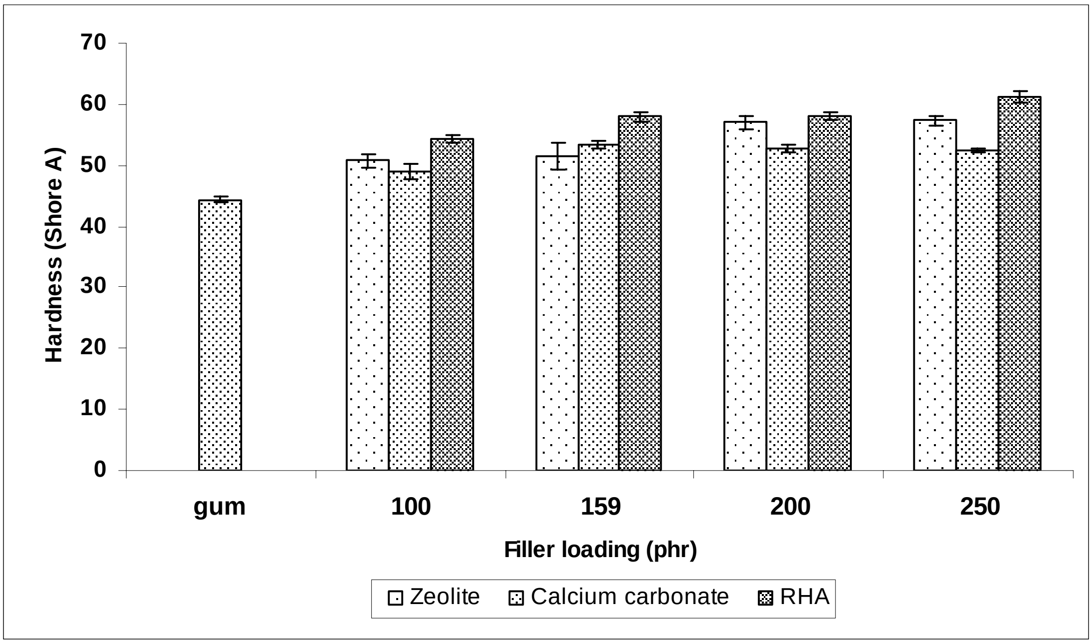

Figure 34 Effect of filler loading on hardness of natural zeolite-, $CaCO_3$- and RHA-filled vulcanizates

The effect of filler loading on hardness of vulcanizates filled with various types and amount of fillers is shown in Figure 34. It is discovered that the hardness of vulcanizates filled with all types of fillers increases with filler loading. This is simply explained by the fact that the incorporation of more rigid filler particles into rubber reduces elasticity of the rubber chains, leading to more rigid rubber vulcanizates. It can be also seen at the same filler loading that most of the rubber filled with RHA show the highest value of hardness, followed by natural zeolite and $CaCO_3$. This could be because of more specific surface area in RHA and natural zeolite. The more surface area, the more surface interaction, the greater hardness can be observed.

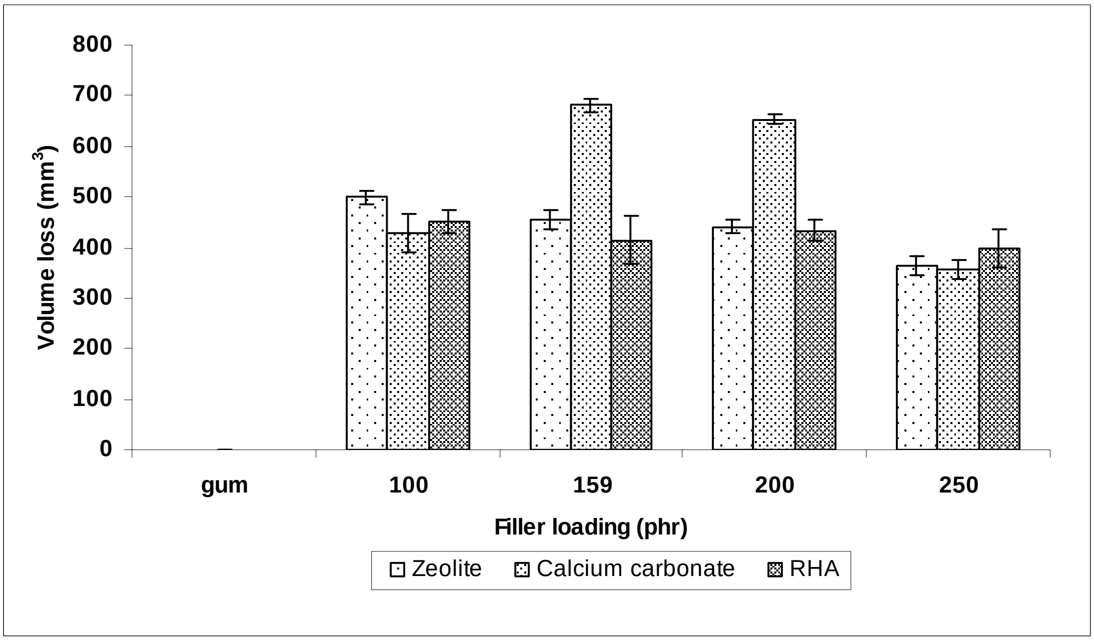

Figure 35 Effect of filler loading on abrasion resistance of natural zeolite-, $CaCO_3$- and RHA-filled vulcanizates

The abrasion resistance of the vulcanizates filled with natural zeolite can be slightly improved with filler loading as seen in Figure 35. The similar trend can be observed in the RHA-filled vulcanizates. In contrast, the abrasion resistance of the vulcanizates filled with $CaCO_3$ decreases with the increase in $CaCO_3$ loading. In general, abrasion resistance could be affected by the interaction between rubber and filler. That is to say that RHA has better interaction with natural rubber than natural zeolite and $CaCO_3$, respectively. Moreover, the abrasion resistance has the similar trend like the hardness, so it can be said that the greater hardness, the greater abrasion resistance.

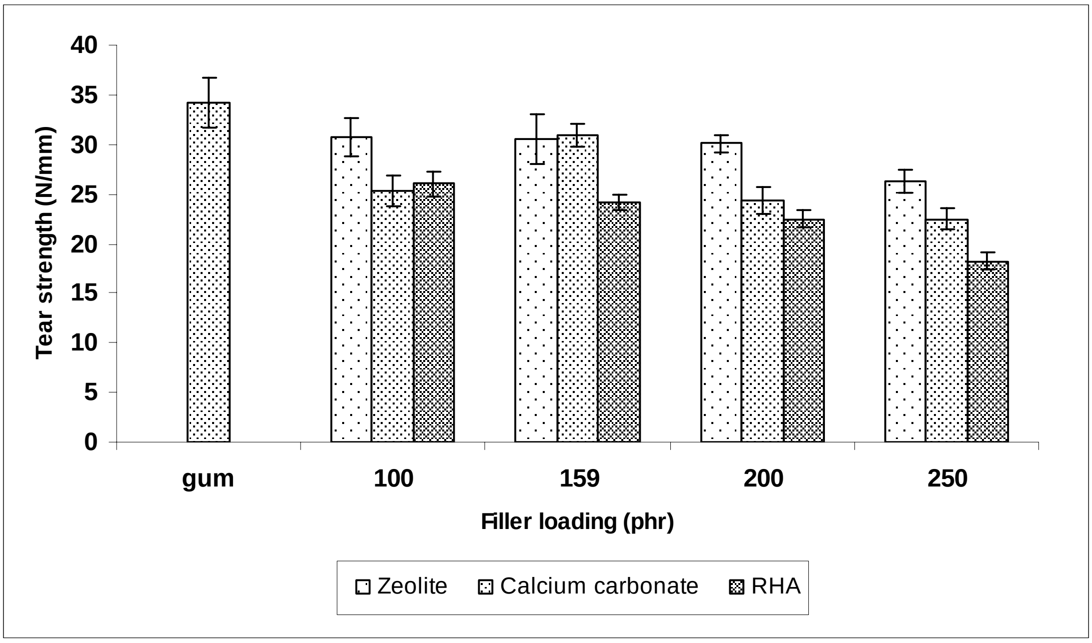

Figure 36 Effect of filler loading on tear strength of natural zeolite-, $CaCO_3$- and RHA-filled vulcanizates

Figure 36 shows the tear strength of the filled vulcanizates. In general, tear strength could be affected by the particle size and surface area of the filler. As can be seen, the addition of filler decreases somewhat the tear strength of vulcanizates. As more filler particles are introduced into the rubber, the elasticity of the rubber chains is reduced. Natural zeolite, at the particular loading, gives better tear strength than $CaCO_3$ because of its larger surface area. The addition of the RHA fillers slightly reduces the tear strength of the rubber materials. This may be attributed to their large particle size.

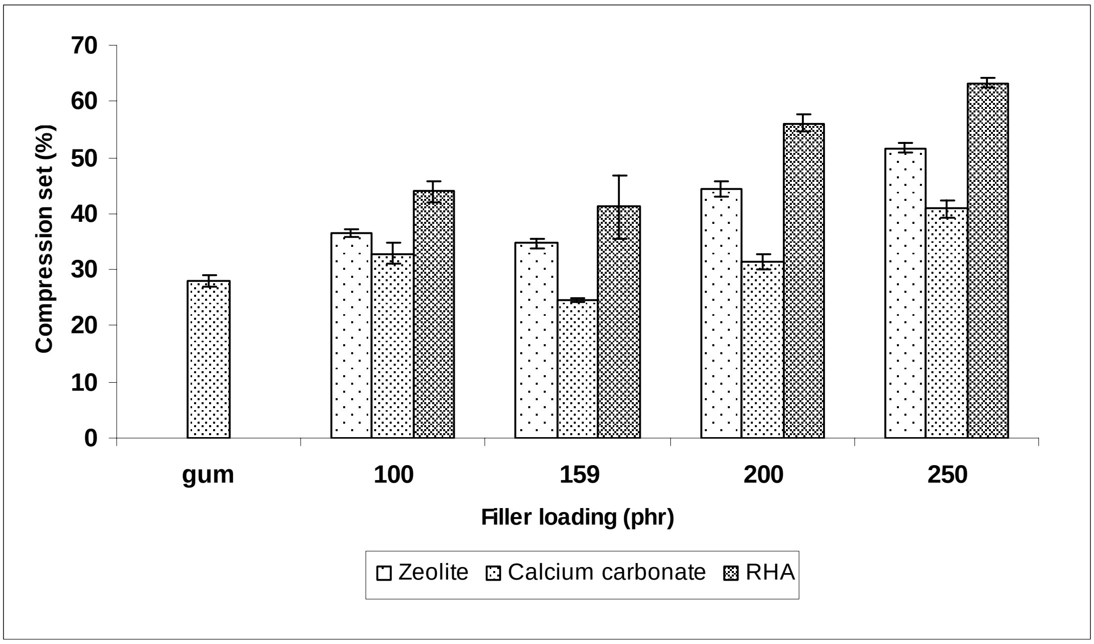

Figure 37 Effect of filler loading on compression set of natural zeolite-, $CaCO_3$- and RHA-filled vulcanizates

The effect of various filler loadings on compression set of the natural rubber materials is shown in Figure 37. It can be seen that for all types of filler, the vulcanizates filled with 159 phr filler show the optimum elasticity and the compression set of vulcanizates seem to impair with increasing filler loading. It can be explained that the more filler particles are introduced into the rubber; the elasticity of the rubber chains is reduced and the interaction of rubber-filler is increased, resulting in higher compression set properties.

2.4 Thermal Aging

As mentioned earlier, the products of interest are for rubber mat in livestock which is outdoor applications, therefore prolonged exposure (air, sunlight, rain, etc.), resulting in the change in elastomer molecule, can not be avoided. These changes are accelerated by oxidation from ozone and oxygen in the atmosphere, ultraviolet rays, temperature variations, and other environmental factors. Nevertheless, the effect of thermo-oxidative degradation on mechanical properties was determined in this study at the specific temperature and time (70^{o}C for 10 days).

In this experiment, the effect of thermal aging on mechanical properties of the vulcanizates with various types of fillers (natural zeolite, $CaCO_3$ and RHA) at 100, 159, 200 and 250 phr filler loading was investigated. The results are shown as percentage change of the specimens after thermal aging at 70 ^{o}C for 10 days.

Introduction of fillers into polymers leads to a wide range of interaction arising at the polymer-filler interface. These dispersed fillers considerably influence the properties of the polymer composites, including their degradation and stability. The major factors that control these properties are the surface chemistry of the filler, nature, shape and size of particle, size distribution and specific surface area etc. (Byrk, 1991). It was found that aluminum powder filled natural rubber composites showed better retention of mechanical properties after thermal ageing compared to other fillers like HAF, GPF, silica and acetylene black (Vinod *et al.*, 2002).

It is found (as seen in Table 12), in this thesis, that the hardness of the vulcanizate with all kinds of filler used in this study ($CaCO_3$, RHA and natural zeolite) increases after thermal ageing in comparison with that of unaged ones. In rubber compounds, temperature causes two competing reactions namely crosslink formation and scission of chains. The slight increase in hardness values of these vulcanizates after thermal ageing can be explained on the basis of these processes in which the effect of crosslinking predominates. However, it was confirmed by the increase of rebounding value after thermal ageing.

As can be seen from the results showing the percentage change in the mechanical properties of vulcanizates (Figures 38-41), it is discovered that the natural zeolite-filled vulcanizate exhibits lower percentage change in mechanical properties, in other word, the greater heat stability, than $CaCO_3$- and RHA-filled vulcanizates. This is possibly due to the fact that natural zeolite has larger amount of alumina than others filler (RHA and $CaCO_3$), leading to the smaller percentage change (the larger percentage retention) in the mechanical properties, including hardness, abrasion loss, compression set, and tear strength of the natural zeolite-filled vulcanizated. Similar trend has been observed in the aluminium powder-filled natural rubber composite in which it showed better retention of mechanical properties after thermal ageing compared to other fillers like carbon black and silica (Vinod *et al.*, 2002).

Table 12 Mechanical properties of vulcanizates with various filler loading before after thermal exposure

Filler loading (phr)		Mechanical properties			
		Hardness (Shore A)	Abrasion (mm^3)	Compression set (%)	Tear Strength (N/mm)
Gum		44±1 (50±1)	- (-)	28.0±1.1 (19.1±1.0)	34.2±2.6 (42.0±5.0)
Zeolite	100	51±1 (53±1)	500±37 (521±35)	36.6±0.6 (27.3±1.0)	30.7±1.9 (32.2±3.5)
	159	52±1 (56±2)	455±13 (331±14)	34.7±0.9 (21.6±1.8)	30.5±2.5 (30.0±2.0)
	200	57±1 (61)	441±9 (527±27)	44.5±1.4 (33.1±0.8)	31.1±0.9 (35.4±3.8)
	250	57±1 (64±2)	364±18 (459±6)	51.7±1.0 (27.2±1.5)	26.3±1.2 (31.6±1.3)
$CaCO_3$	100	49±1 (53±1)	428±13 (560±33)	32.8±1.9 (15.8±0.8)	25.3±1.6 (37.8±3.5)
	159	53±1 (55±1)	681±20 (516±10)	24.5±0.3 (18.3±1.2)	31.0±1.1 (29.0±0.8)
	200	53±1 (56±1)	652±13 (562±34)	31.4±1.2 (14.5±0.6)	24.3±1.4 (32.9±2.1)
	250	52 (57±1)	357±20 (462±14)	40.8±1.6 (16.4±0.8)	22.5±1.1 (26.4±1.3)
RHA	100	54±1 (57±2)	451±23 (436±10)	44.0±1.8 (31.5±0.3)	26.0±1.2 (27.8±1.4)
	159	58±1 (63±2)	415±47 (509±66)	41.2±5.5 (35.6±1.7)	24.1±0.8 (25.0±2.0)
	200	58±1 (61±1)	434±22 (561±18)	56.9±1.6 (31.1±1.2)	22.5±0.9 (16.0±1.6)
	250	61±1 (55±2)	397±38 (575±24)	63.3±0.8 (51.6±1.4)	18.2±0.8 (14.5±0.7)

Note: ( ) represents the values of mechanical properties after immersion in fluid

(-) can not be measured

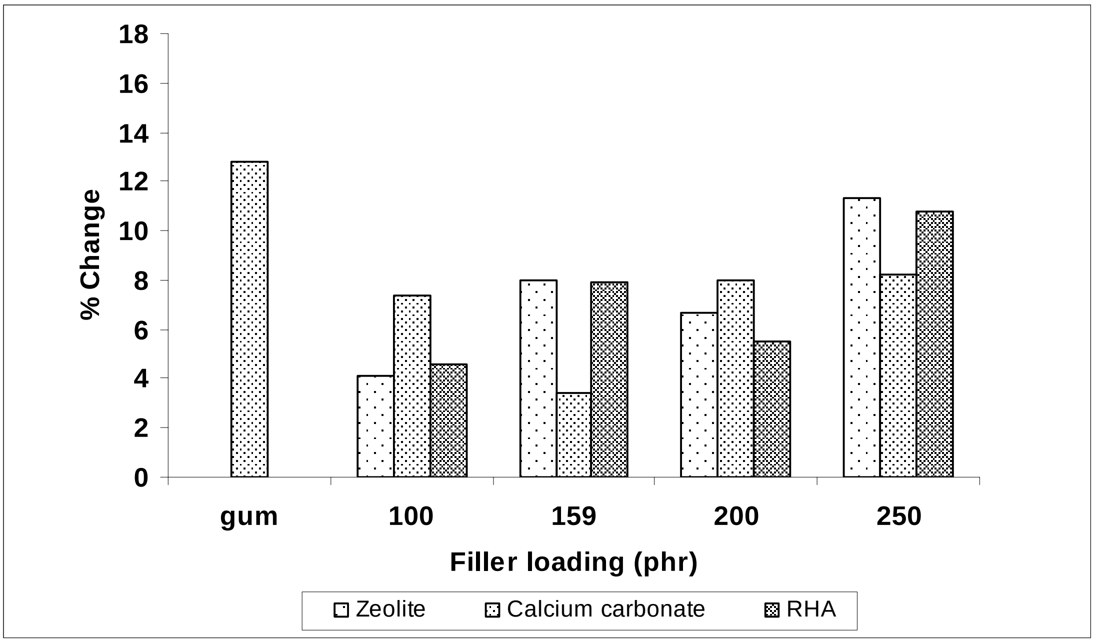

Figure 38 Percentage change in hardness of natural zeolite-, $CaCO_3$- and RHA-filled vulcanizates after thermal exposure

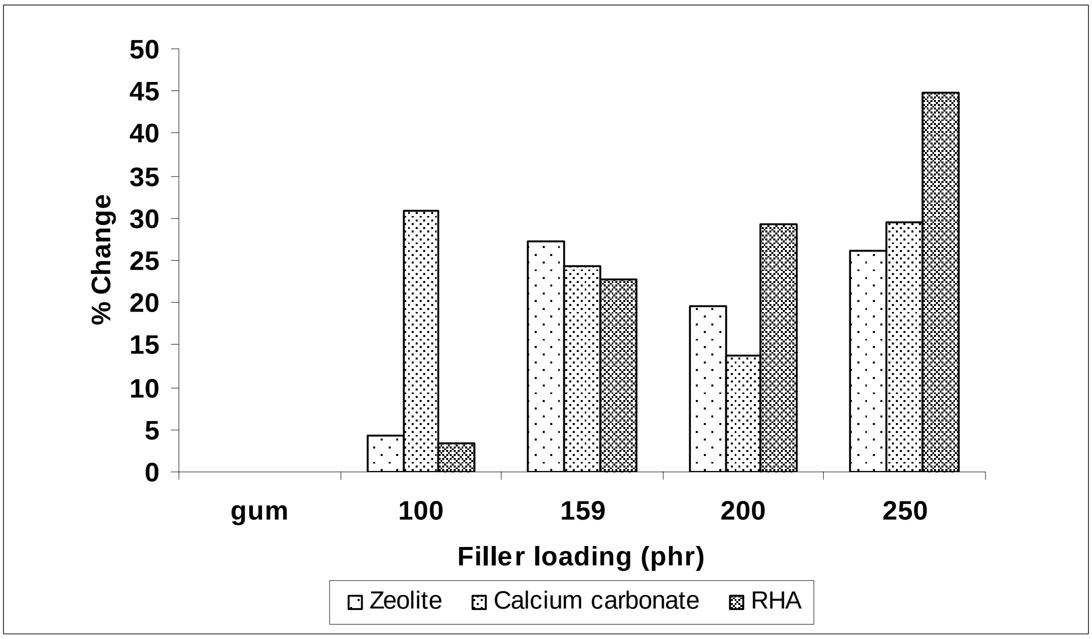

Figure 39 Percentage change in abrasion of natural zeolite-, $CaCO_3$- and RHA-filled vulcanizates after thermal exposure

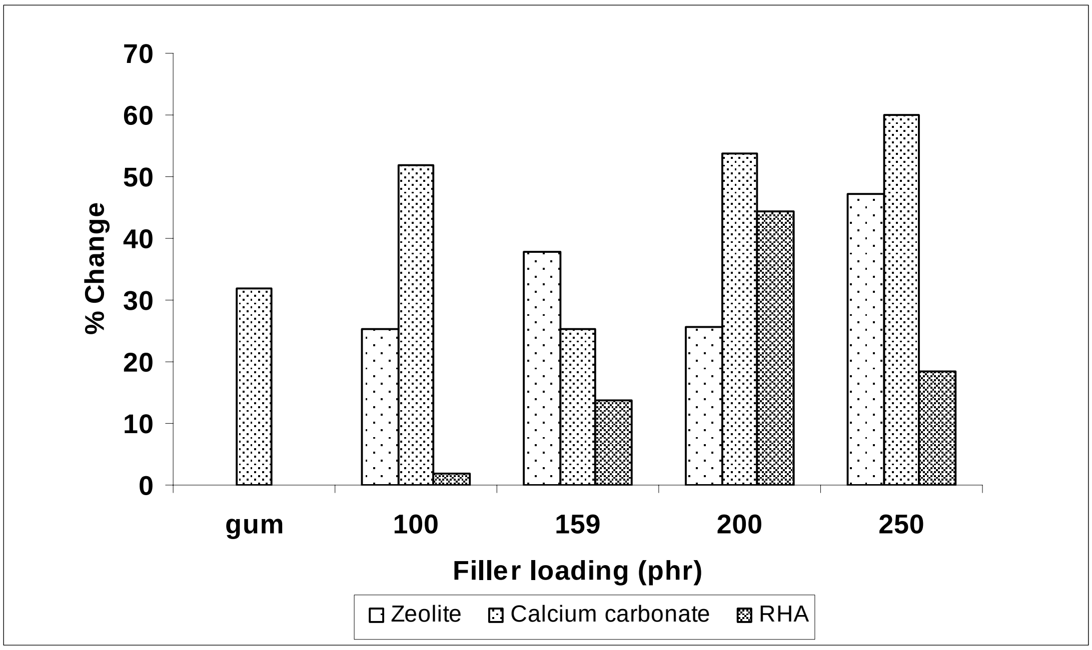

Figure 40 Percentage change in compression set of natural zeolite-, $CaCO_3$- and RHA-filled vulcanizates after thermal exposure

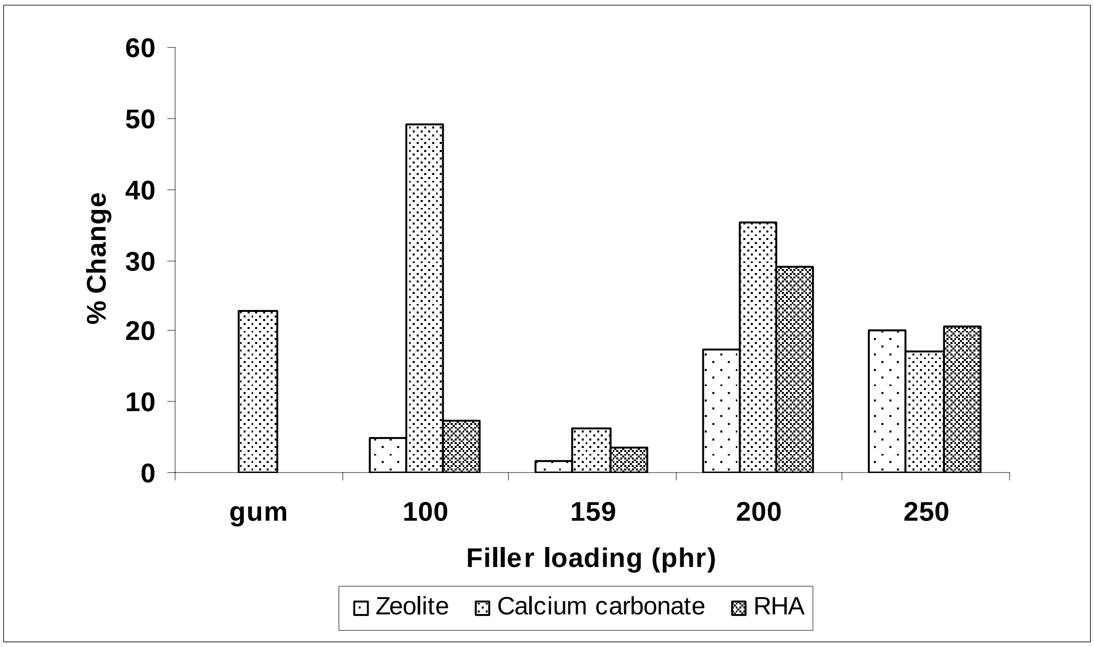

Figure 41 Percentage change in tear strength of natural zeolite-, $CaCO_3$- and RHA-filled vulcanizates after thermal exposure

2.5 Fluid Resistance

The effect of fluid resistance (both water and cow's urine) on mechanical properties of vulcanizates with various types of filler (natural zeolite, $CaCO_3$ and RHA) at 100, 159, 200 and 250 phr filler loading is presented in Table 13. The results are shown as percentage change of the specimens after immersion in fluid at room temperature for 70 hrs.

It can be observed from Table 13 that the mechanical properties of the vulcanizates filled with all fillers (natural zeolite, $CaCO_3$, and RHA) at particular loading significantly decrease after immersion with fluid both in water and cow's urine compared with that before immersion with fluid. In addition, the increase in filler loading in natural rubber compounds, and hence reduction of total natural rubber content, gives greater swelling-resistance (Ismail *et al.*, 2002). In contrast, in this experiment, it is found that the fluid resistance of the vulcanizates impaired with increasing filler loading as a result of greater percentage change in mechanical properties after fluid immersion (Figures 42-49). This is maybe due to aggregation of filler and their impaired dispersion. At the particular filler loading at 200 phr, it is found that natural zeolite-filled and RHA-filled vulcanizates have smaller percentage change in mechanical properties, i.e., hardness, abrasion, compression set and tear strength, than $CaCO_3$-filled vulcanizates. It can probably explained by the fact that both natural zeolite and RHA have more surface area than $CaCO_3$ (as seen in Table 9). As well known, the more surface area, the more filler-rubber interaction is. Therefore, the natural zeolite and RHA can have more interaction with natural rubber surface than $CaCO_3$, leading to the greater fluid resistance.

Table 13 Mechanical properties of vulcanizates with various filler loading before and after immersion in water and cow’s urine

Filler loading (phr)		Mechanical Properties							
		After immersion in water				After immersion in cow’s urine			
		Hardness (shore A)	Abrasion (mm^3)	Compression Set (%)	Tear Strength (N/mm)	Hardness (shore A)	Abrasion (mm^3)	Compression Set (%)	Tear Strength (N/mm)
Gum		44±1 (46±1)	- (265±10)	28.0±1.1 (34.5±1.2)	34.2±2.6 (36.0±4.0)	44±1 (47±1)	- (-)	28.0±1.1 (32.7±1.8)	34.2±2.6 (37.0±1.0)
Zeolite	100	51±1 (57)	500±37 (610±17)	36.6±0.6 (38.0±1.6)	30.7±1.9 (29.7±3.5)	51±1 (51±1)	500±37 (500±12)	36.6±0.6 (43.2±1.2)	30.7±1.9 (28.6±3.4)
	159	52±2 (52±1)	455±13 (438±27)	34.7±0.9 (38.2±0.8)	30.5±2.5 (28.0±4.0)	52±2 (53±1)	455±13 (438±62)	34.7±0.9 (40.0±1.7)	30.5±2.5 (27.0±1.0)
	200	57±1 (52)	441±9 (452±15)	44.5±1.4 (45.3±1.2)	31.1±0.9 (28.3±1.6)	57±1 (58)	441±9 (452±17)	44.5±1.4 (50.4±2.0)	31.1±0.9 (28.0±1.8)
	250	57±1 (60±1)	364±18 (430±31)	51.7±1.0 (49.4±0.9)	26.3±1.2 (26.0±1.9)	57±1 (60±1)	364±18 (396±25)	51.7±1.0 (54.5±2.6)	26.3±1.2 (25.8±0.7)
$CaCO_3$	100	49±1 (51±1)	428±13 (629±43)	32.8±1.9 (33.7±1.3)	25.3±1.6 (29.4±1.5)	49±1 (51±1)	428±13 (512±13)	32.8±1.9 (38.4±1.2)	25.3±1.6 (32.0±2.8)
	159	53±1 (54±1)	681±20 (-)	24.5±0.3 (33.5±1.2)	31.0±1.1 (30.4±1.2)	53±1 (55±1)	681±20 (531±55)	24.5±0.3 (28.1±0.9)	31.0±1.1 (29.6±0.6)
	200	53±1 (55±1)	652±13 (555±110)	31.4±1.2 (34.8±1.0)	24.3±1.4 (26.0±1.4)	53±1 (55±1)	652±13 (495±33)	31.4±1.2 (42.5±0.6)	24.3±1.4 (31.8±1.2)
	250	52 (52±1)	357±20 (477±54)	40.8±1.6 (38.3±1.2)	22.5±1.1 (22.5±1.2)	52 (55±2)	357±20 (436±33)	40.8±1.6 (22.6±1.6)	22.5±1.1 (21.9±0.8)

Table 13 (Continued)

Filler loading (phr)		Mechanical Properties							
		After immersion in water				After immersion in cow’s urine			
		Hardness (shore A)	Abrasion (mm^3)	Compression Set (%)	Tear Strength (N/mm)	Hardness (shore A)	Abrasion (mm^3)	Compression Set (%)	Tear Strength (N/mm)
RHA	100	54±1 (54)	451±23 (532±22)	44.0±1.8 (43.0±1.3)	26.0±1.2 (27.6±1.4)	54±1 (57±2)	451±23 (404±28)	44.0±1.8 (39.7±1.5)	26.0±1.2 (26.2±1.4)
	159	58±1 (61±2)	415±47 (520±70)	41.2±5.5 (39.7±2.0)	24.1±0.8 (25.0±2.0)	58±1 (61±1)	415±47 (488±52)	41.2±5.5 (42.4±2.3)	24.1±0.8 (25.0±3.0)
	200	58±1 (58±1)	434±22 (445±50)	56.1±1.6 (49.1±1.7)	22.5±0.9 (22.4±1.0)	58±1 (58±1)	434±22 (394±10)	56.1±1.6 (41.4±1.2)	22.5±0.9 (18.4±2.1)
	250	61±1 (53±2)	397±38 (498±43)	63.3±0.8 (58.0±1.7)	18.2±0.8 (16.8±1.0)	61±1 (55±2)	397±38 (410±11)	63.3±0.8 (58.2±1.6)	18.2±0.8 (21.4±2.3)

Note: ( ) represents the values of mechanical properties after immersion in fluid

(-) can not be measured

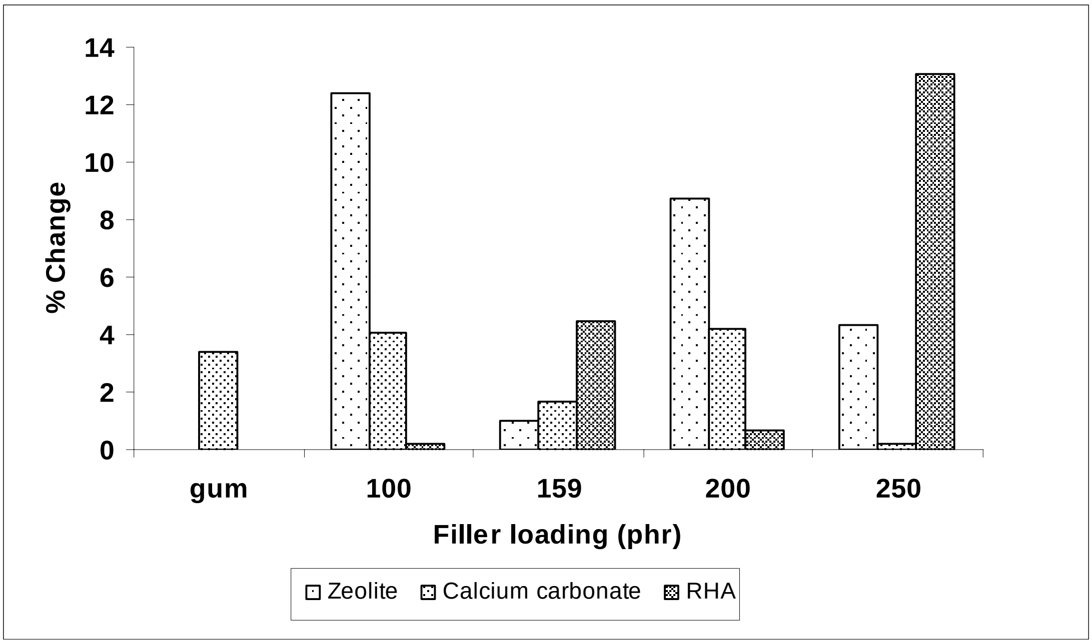

Figure 42 Percentage change in hardness of natural zeolite-, $CaCO_3$- and RHA-filled vulcanizates after immersion in water

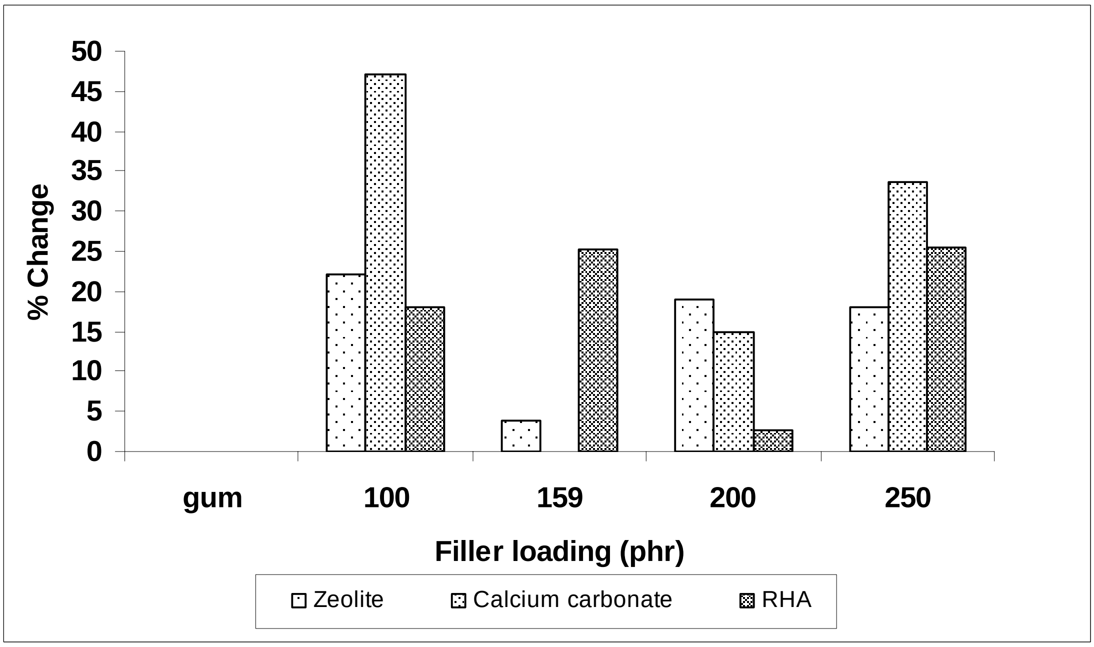

Figure 43 Percentage change in abrasion of natural zeolite-, $CaCO_3$- and RHA-filled vulcanizates after immersion in water

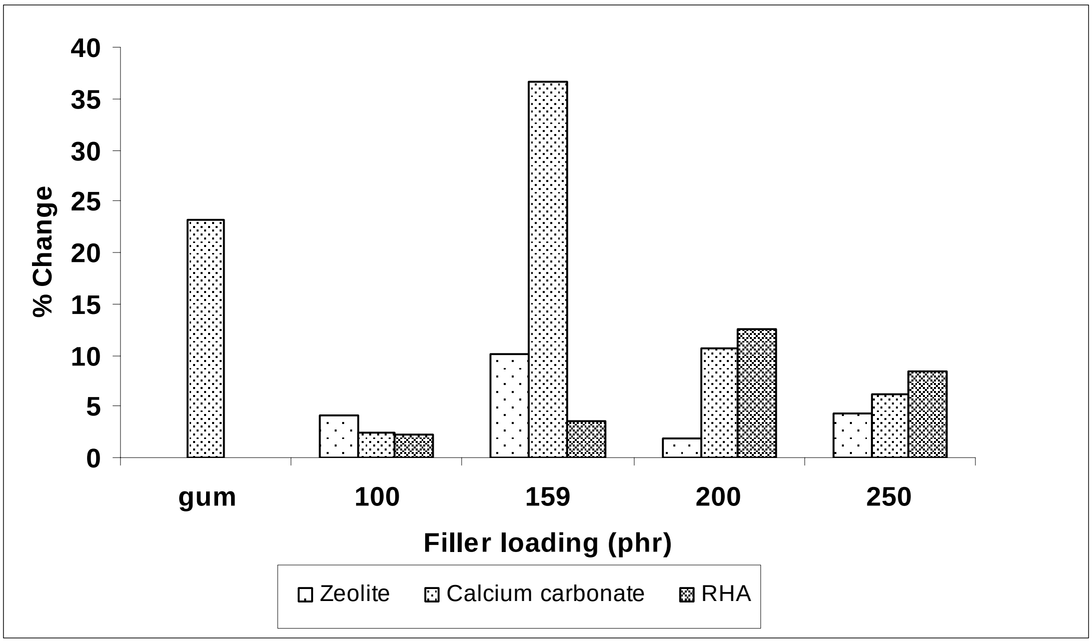

Figure 44 Percentage change in compression set of natural zeolite-, $CaCO_3$- and RHA-filled vulcanizates after immersion in water

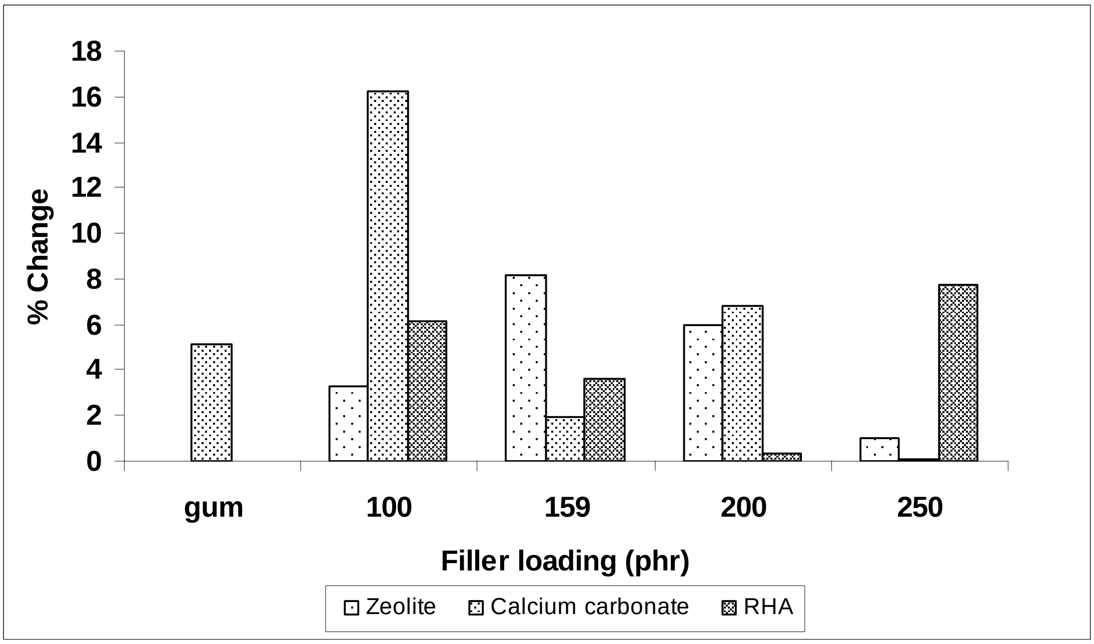

Figure 45 Percentage change in tear strength of natural zeolite-, $CaCO_3$- and RHA-filled vulcanizates after immersion in water

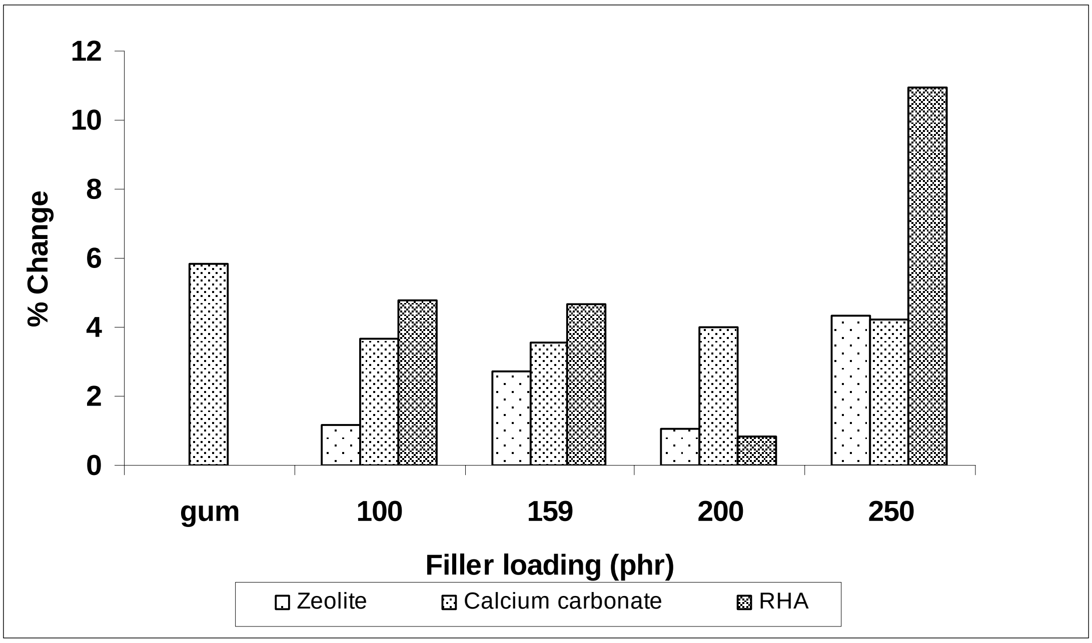

Figure 46 Percentage change in hardness of natural zeolite-, $CaCO_3$- and RHA-filled vulcanizates after immersion in cow's urine

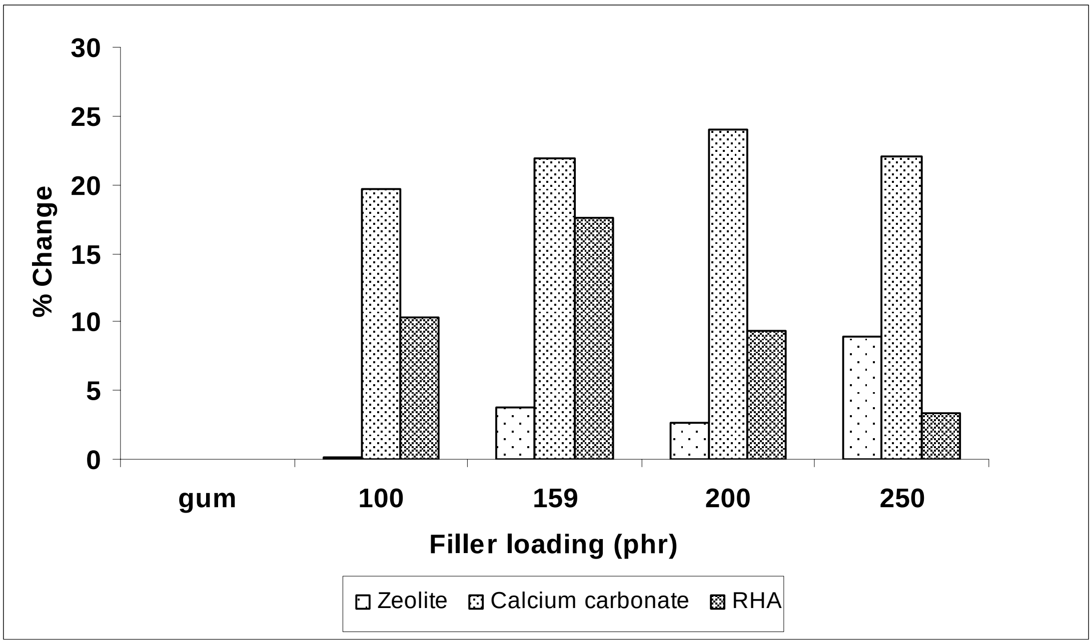

Figure 47 Percentage change in abrasion of natural zeolite-, $CaCO_3$- and RHA-filled vulcanizates after immersion in cow's urine

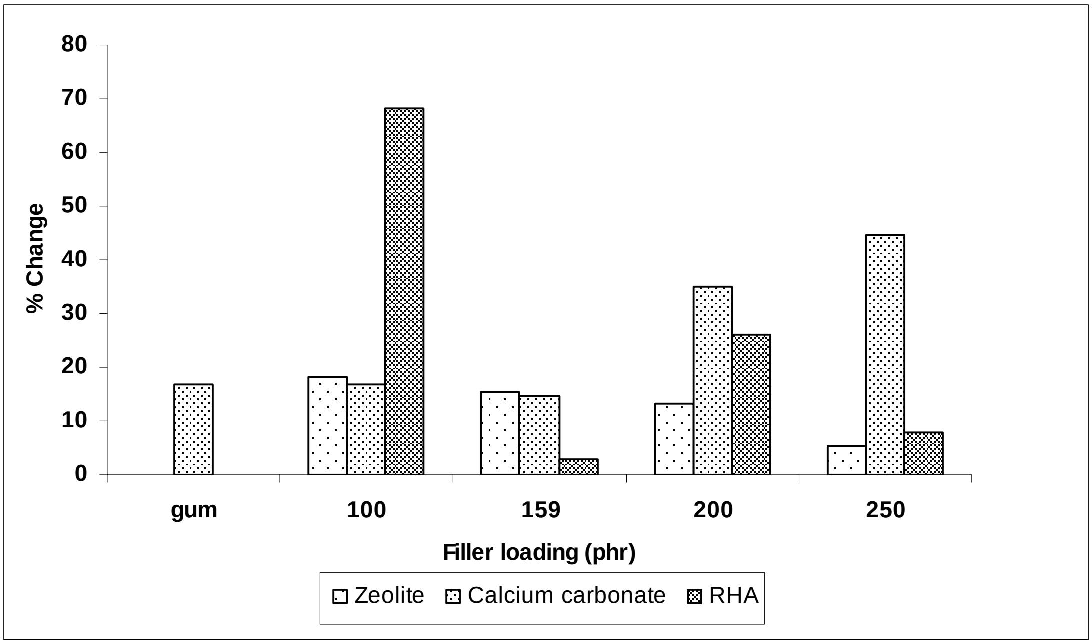

Figure 48 Percentage change in compression set of natural zeolite-, $CaCO_3$- and RHA-filled vulcanizates after immersion in cow's urine

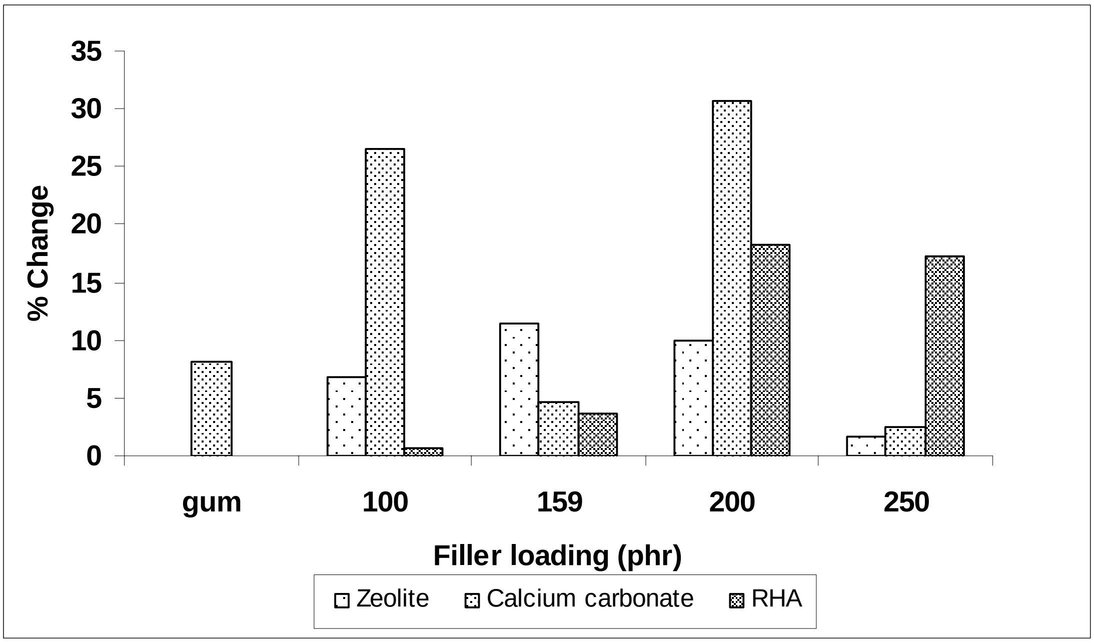

Figure 49 Percentage change in tear strength of natural zeolite-, $CaCO_3$- and RHA-filled vulcanizates after immersion in cow's urine

2.6 Mechanical properties of rubber mat after installation in Cow's Corral

From overall results, the laboratory tested mechanical properties of five rubber compound formulations, such as vulcanizates with 159 phr $CaCO_3$, 250 phr $CaCO_3$, 159 phr natural zeolite, 200 phr natural zeolite and 200 phr RHA, were considered to be the acceptable values for employing in rubber mat application. In this section, all five rubber compound formulations were thus manufactured as rubber mat with 30 mm thickness by the factory. The manufactured rubber mats were then installed in cow's corral. After 2 months, hardness and thickness of the rubber mats for all 5 formulations were measured at 2 different regions (i.e. irregular and regular contact by cows). Table 14 shows percentage change in hardness and thickness of the rubber mats after installation in cow's corral for 2 months

Table 14 Percentage change in hardness and thickness of the rubber mats after installation in cow's corral for 2 months

Filler loading (phr)	% Hardness change		% Thickness change	
	Regular	Irregular	Regular	Irregular
Zeolite 159	15.9	17.6	-2.51	-2.75
Zeolite 200	13.5	16.1	0.40	2.54
$CaCO_3$ 159	15.9	6.6	3.50	2.02
$CaCO_3$ 250	10.6	6.3	0.20	1.19
RHA 200	14.7	12.1	5.27	2.95

From the obtained result, the percentage change in hardness show no significant difference in the regular contact region in which the natural zeolite 159- and $CaCO_3$ 159 phr filled vulcanizates give the highest percentage change in hardness, followed by the RHA 200- , natural zeolite 200- and $CaCO_3$ 200 phr filled vulcanizates, respectively. For irregular contact region, the $CaCO_3$ filled vulcanizates give a smaller percentage change in hardness than the RHA-, natural zeolite-filled vulcanizates. In the case of thickness measurement, the RHA 200 phr filled vulcanizates give the highest percentage change in the regular contact region, followed by the $CaCO_3$ 159-, natural zeolite 159- and 200-, $CaCO_3$ 250 phr filled vulcanizates, respectively. In irregular contact region consideration, the $CaCO_3$ filled vulcanizates give a smaller percentage change in both thickness and hardness than the RHA-, and natural zeolite filled vulcanizates. As seen from the mechanical properties before and after installation in cow's corral, it should be noted that the vulcanizate filled with $CaCO_3$ 250 phr could be the appropriate formulation for using as rubber mat in cow's corral.