

## CHAPTER IV

### RESULTS AND DISCUSSION

The natural rubber STR 5L composites were prepared by two roll-mills and compression molding. The use of nanocalcium carbonates as fillers in natural rubber compounds, calcium carbonate, carbon black and silica were studied. The variables, which were expected to have an effect on rheology and mechanical properties were particle size, filler surface modification, filler loading and filler type. Rubber filled with 10, 20, 30,40 and 50 parts per hundred resin (phr) of nanocalcium carbonate were compared with that filled with uncoated nanocalcium carbonate and 2 $\mu$ -calcium carbonate. The mechanical properties of the rubber/nanocalcium carbonate composites were compared with the rubber composite filled with the commercial reinforcement such as carbon black (N330) and silica.

#### 4.1 Properties of Natural Rubber STR 5L

The Natural Rubber STR 5L has the properties as shown in Table 4.1.

**Table 4.1** The Properties of Natural Rubber STR 5L

Properties	Test results
Dirt, %	0.015
Ash, %	0.32
Volatile matter, %	0.21
Nitrogen, %	0.37

## 4.2 Properties of Nanocalcium Carbonate

High Gravity Reactive Precipitation (HGRP) production technology [20] can be utilized to produce crystalline nano-materials with a narrow particle distribution, specific crystal shape and morphology. The HGRP production technology is derived from and based on fundamental mass transfer principles as micro mixing of the reaction phase is achieved in microseconds. The reaction phase are brought together under a high gravity environment created by a rotation packed bed assembly allowing for ease of control to produce nano sized particles. The nanocalcium carbonate coated with stearic acid was obtained from BRS Intertrade Ltd., Part. and has the properties as shown in Table 4.2.

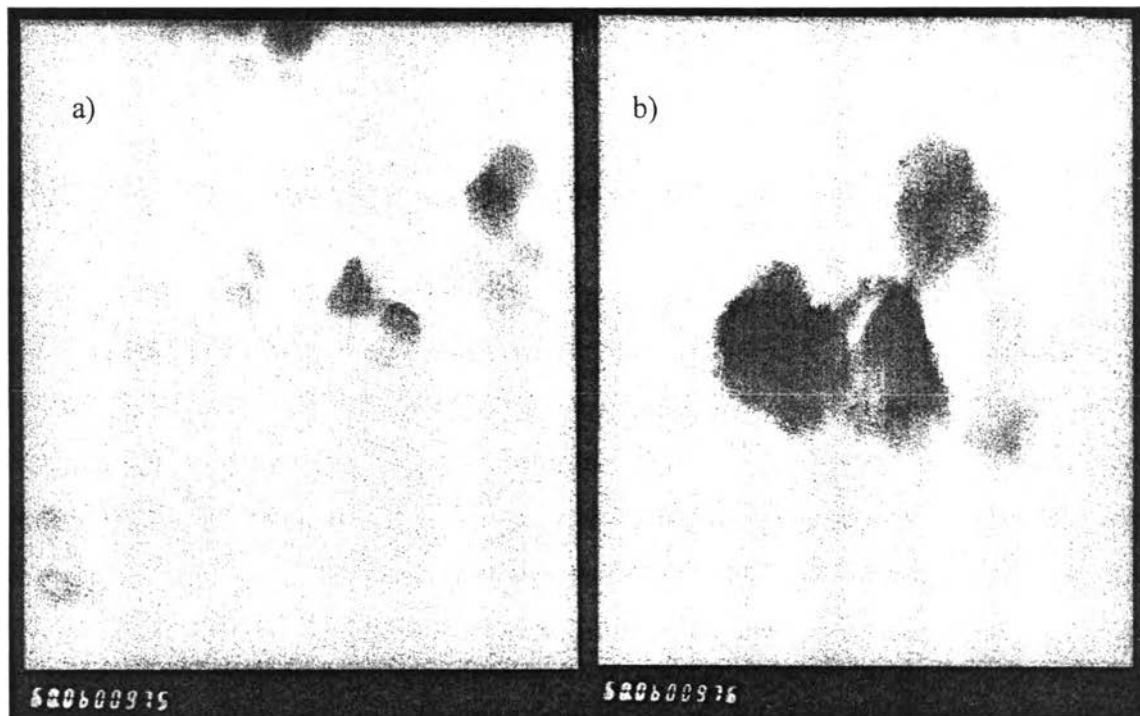
**Table 4.2** The Properties of Nanocalcium Carbonate

Properties	Test results
Appearance	White powder
Specific gravity	2.5-2.6
Particle size (avg), nm	40
Surface Area (BET), m <sup>2</sup> /g	> 45
Whiteness, %	> 95
Particle shape	Cubic
pH	8.5-9.5
Water content, %wt	< 0.5
CaCO <sub>3</sub> , %wt	94.5
MgO, %wt	< 0.5
Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> , %wt	< 0.3
SiO <sub>2</sub> , % wt	< 0.3
Activity, %	> 95
Surface modification	Stearic acid

### 4.3 Characteristic of Fillers

#### 4.3.1 Morphology of Nanocalcium Carbonate and Calcium Carbonate.

Figure 4.1 a) and 4.1 b) show transmission electron micrographs of nanocalcium carbonate compared to 2 $\mu$ -calcium carbonate. The particle size of nanocalcium carbonate calculated from micrograph is around 50 nm while particle size of 2 $\mu$ -calcium carbonate is around 3 micron. The aggregate of particle causes an error of particle size measurement.



**Figure 4.1** Transmission Electron Micrographs of Calcium Carbonate;  
a) Nanocalcium Carbonate, and b) 2 $\mu$ -Calcium Carbonate ( $\times 60000$ ).

### 4.3.2 Characterization of Nanocalcium Carbonate

The surface of nanocalcium carbonate were coated by chemicals to improve the dispersion in rubber compound. The function groups in coating chemicals on nanocalcium carbonate surface were analyzed by IR spectroscopy. Figures 4.2 a and 4.2 b show the infrared spectra in the region of 4000-400  $\text{cm}^{-1}$  for uncoated nanocalcium carbonate and coated nanocalcium carbonate, respectively. The infrared spectra of uncoated nanocalcium carbonate exhibited the dominant characteristic absorption bands of C=O at 1456  $\text{cm}^{-1}$ . The coated nanocalcium carbonate presents new peaks in the IR spectrum. Bands at 2935 and 2875  $\text{cm}^{-1}$  are attributed to the C-H asymmetric and symmetric stretching vibrations of stearic acid, respectively.

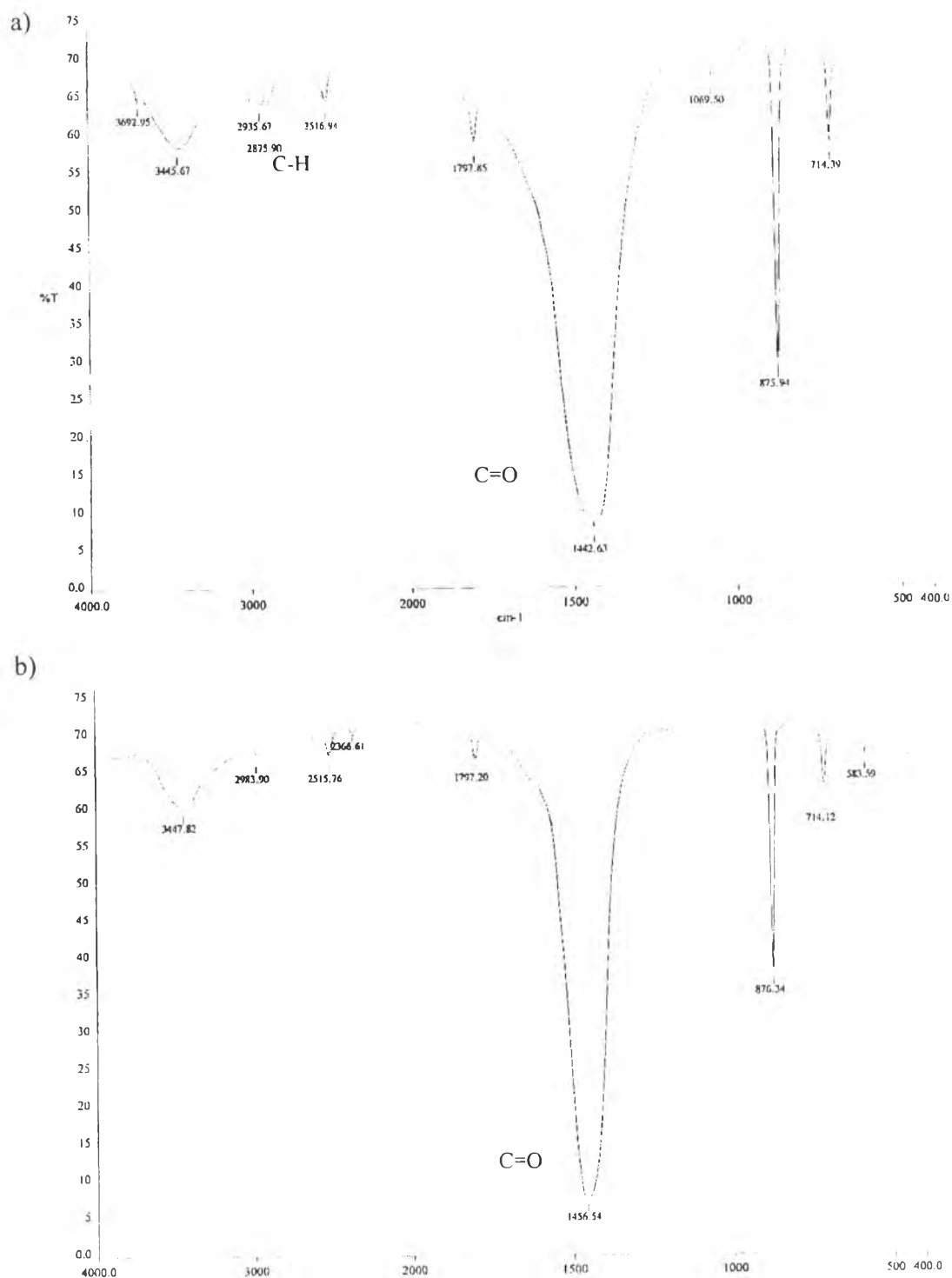
## 4.4 Effect of Particle Size and Surface modification.

### 4.4.1 Mooney Viscosity.

Table 4.3 shows that the viscosity of compounds is affected by factors such as filler loading. Figure 4.3 shows viscosities of rubber compounds at various filler loading for 3 types of calcium carbonate. It has been found that the Mooney viscosities of the compounds increased with increasing calcium carbonate loading. A filled system has high viscosity ,because the filler particles did not deform and thus the rubber continued to move at a higher velocity between particles for a given shear rate. This effect was reported by Guth and Gold empirically modified equation: [21]

$$\eta = \eta_0 (1 + 2.5c + 14.1c^2),$$

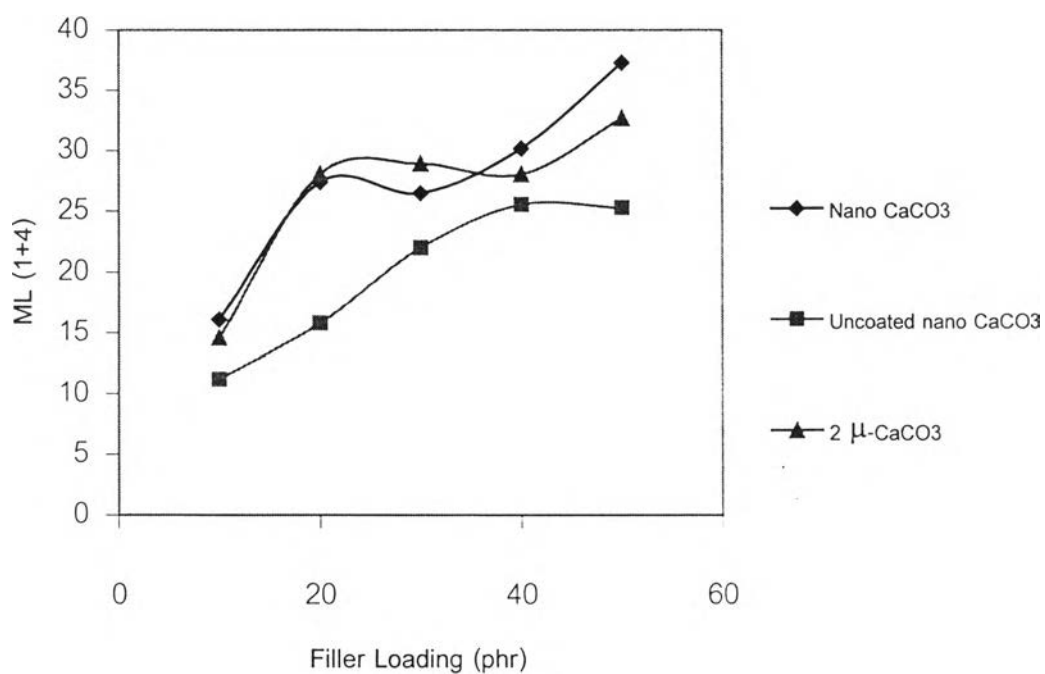
where  $\eta$  is the viscosity of the filled fluid;  $\eta_0$  is the viscosity of the pure fluid and  $c$  is the volume fraction of filler.



**Figure 4.2** IR Spectra of Nanocalcium Carbonate; a) Coated Nanocalcium Carbonate, and b) Uncoated Nanocalcium Carbonate.

**Table 4.3** Effect of Filler Content and Particle Size of Filler on Mooney Viscosity of Rubber Compound.

Filler Loading (phr)	Mooney viscosity		
	Nano CaCO <sub>3</sub>	Uncoated nano CaCO <sub>3</sub>	2 $\mu$ -CaCO <sub>3</sub>
10	16.1	11.2	14.6
20	27.4	15.8	28.1
30	26.5	22.0	29.0
40	30.2	25.6	28.1
50	37.3	25.3	32.7



**Figure 4.3** Effect of Filler Loading on Mooney Viscosity of Rubber Compounds.

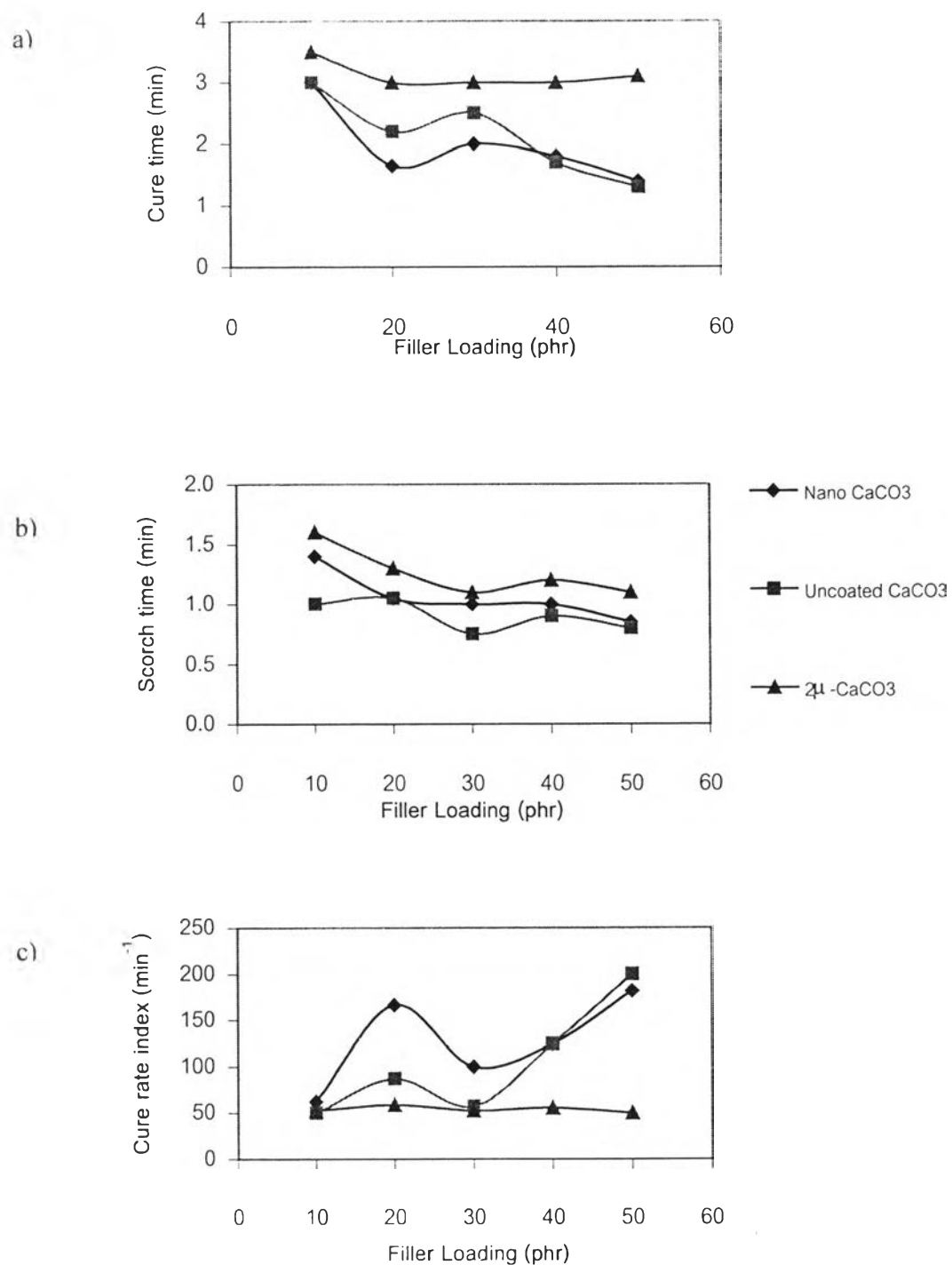
#### 4.4.2 Cure Characteristics.

The curing behavior of the composites at 150°C such as scorch time,  $t_{90}$  (time for 90% cure), torque value, and  $\Delta S$  (measured as the difference between maximum and minimum torque) are presented in Table 4.4, Figures 4.4 a, 4.4 b and 4.4 c. The results indicated that the cure time, scorch time, and cure rate index of nanocalcium carbonate filled compounds decreased with increasing of filler loading. Also the nanocalcium carbonate was coated by stearic acid that behaved as an effective accelerant agent for natural rubber vulcanization. Uncoated nanocalcium carbonate and 2 $\mu$ -calcium carbonate had less effect on the cure characteristics of the rubber, probably due to a poor compatibility between the fillers and hydrophobic polymer. Because this thesis used two accelerators in cure system, in short cure time, it was difficult to comparing the effect of filler type on cure properties. The torque value ( $\Delta S = S_{\max} - S_{\min}$ ) increased for the presence of nanocalcium carbonate and uncoated nanocalcium carbonate in rubber compounds, but did not change for 2 $\mu$ -calcium carbonate. Assuming that the torque value derived from Curemeter is related to the crosslinking density, the composites filled with nanocalcium carbonate have a higher number of crosslinks than that filled with 2 $\mu$ -calcium carbonate [15].

**Table 4.4** Effect of Filler Content, Filler Type, Particle Size of Filler and Surface Modification on Cure Properties of Rubber Compound.

Compound	Filler loading (phr)	Scorch time (min)	T <sub>90</sub> (min)	S <sub>max</sub> (dNm)	S <sub>min</sub> (dNm)	ΔS (dNm)	Cure rate index
Nano CaCO <sub>3</sub>	10	1.40	3.00	3.60	0.15	3.45	62.5
	20	1.05	1.65	3.60	0.15	3.45	166.7
	30	1.00	2.00	3.75	0.15	3.60	100.0
	40	1.00	1.70	3.90	0.15	3.75	142.9
	50	0.85	1.40	4.00	0.25	3.75	181.8
Uncoated nano CaCO <sub>3</sub>	10	1.00	3.00	3.60	0.05	4.15	50.0
	20	1.05	2.20	4.00	0.10	3.90	87.0
	30	0.75	2.50	3.60	0.10	3.58	57.1
	40	0.90	1.70	4.25	0.15	4.10	125.0
	50	0.80	1.30	4.15	0.20	3.95	200.0
2μ- CaCO <sub>3</sub>	10	1.60	3.50	3.40	0.10	3.30	52.6
	20	1.30	3.00	3.45	0.15	3.30	58.8
	30	1.10	2.15	3.50	0.15	3.35	95.2
	40	1.20	3.00	3.50	0.15	3.35	55.6
	50	1.10	3.10	3.60	0.15	3.45	50.0





**Figure 4.4** Effect of Filler Loading on; a) Cure Time, b) Scorch Time, and c) Cure Rate Index of Rubber Compounds.

#### 4.4.3 Mechanical Properties of Composite.

The rubber composites with different filler types (coated nanocalcium carbonate, uncoated nanocalcium carbonate and  $2\mu$ -calcium carbonate) at various filler loading (0,10, 20,30, 40 and 50 phr) were prepared by two-roll mill. The properties of nanocalcium carbonate, uncoated nanocalcium carbonate and  $2\mu$ -calcium carbonate filled rubber composites were compared. The tensile properties, tear strength and hardness of rubber composites are also presented in Table 4.5 and Figures 4.5 a to 4.6 c.

From Figures 4.5 a, 4.5 b, 4.5 c and 4.6 a, the tensile strength, ultimate elongation, modulus 100 and modulus 300 of coated nanocalcium carbonate / filled rubber composite increased with increasing filler loading and reached a maximum value at loading of 30 phr and then, decreased at loading of 40 phr. This was not expected since at low filler loading, the matrix material was in large quantity, so that all filler particles were capable of being completely wetted by the matrix material while at higher filler loading, the matrix (elastomer) was incapable of wetting the filler. This resulted in heterogeneity in the composites leading to deterioration of properties.

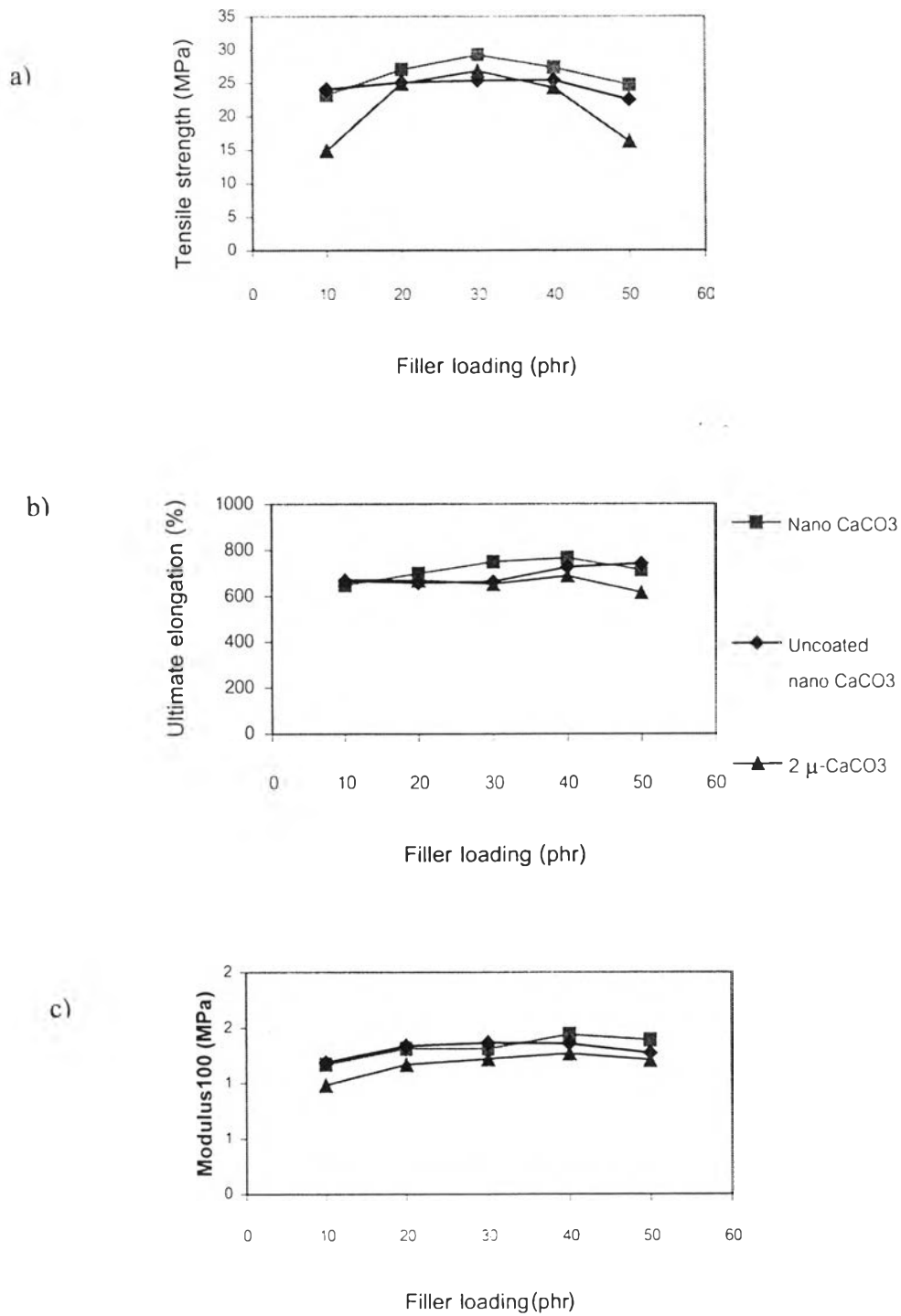
For  $2\mu$ -calcium carbonate / natural rubber composites, the results are similar to coated nanocalcium carbonate filled composite. The increase in tensile properties of coated nanocalcium carbonate was much higher than that of  $2\mu$ -calcium carbonate filled composite. The higher tensile property of coated nanocalcium carbonate filled composite may be due to smaller particle size of filler. Thus, tensile properties vary inversely with particle size for a given loading. As specific surface area increased, the strength of calcium carbonate filled vulcanisate generally increase. For finer particle, it was also difficult to disperse as the result of uncoated nanocalcium carbonate, however still higher than  $2\mu$ -calcium carbonate. Coated calcium carbonate is currently available in several fineness and almost all the commercially available products are coated with stearic acid. In many resins, the coating leads to improvement of the filler dispersion and exhibit the superior rheological and physical properties. Coating levels are nearly always directly related to filler surface area [22]. From Figure 4.6 b, tear strength was in similar manner as the tensile strength.

From Figure 4.6 c the hardness of nanocalcium carbonate/natural rubber composite and 2 $\mu$ -calcium carbonate/natural rubber composites was increased with increasing filler loading. This is due to the rigid nature of inorganic filler.

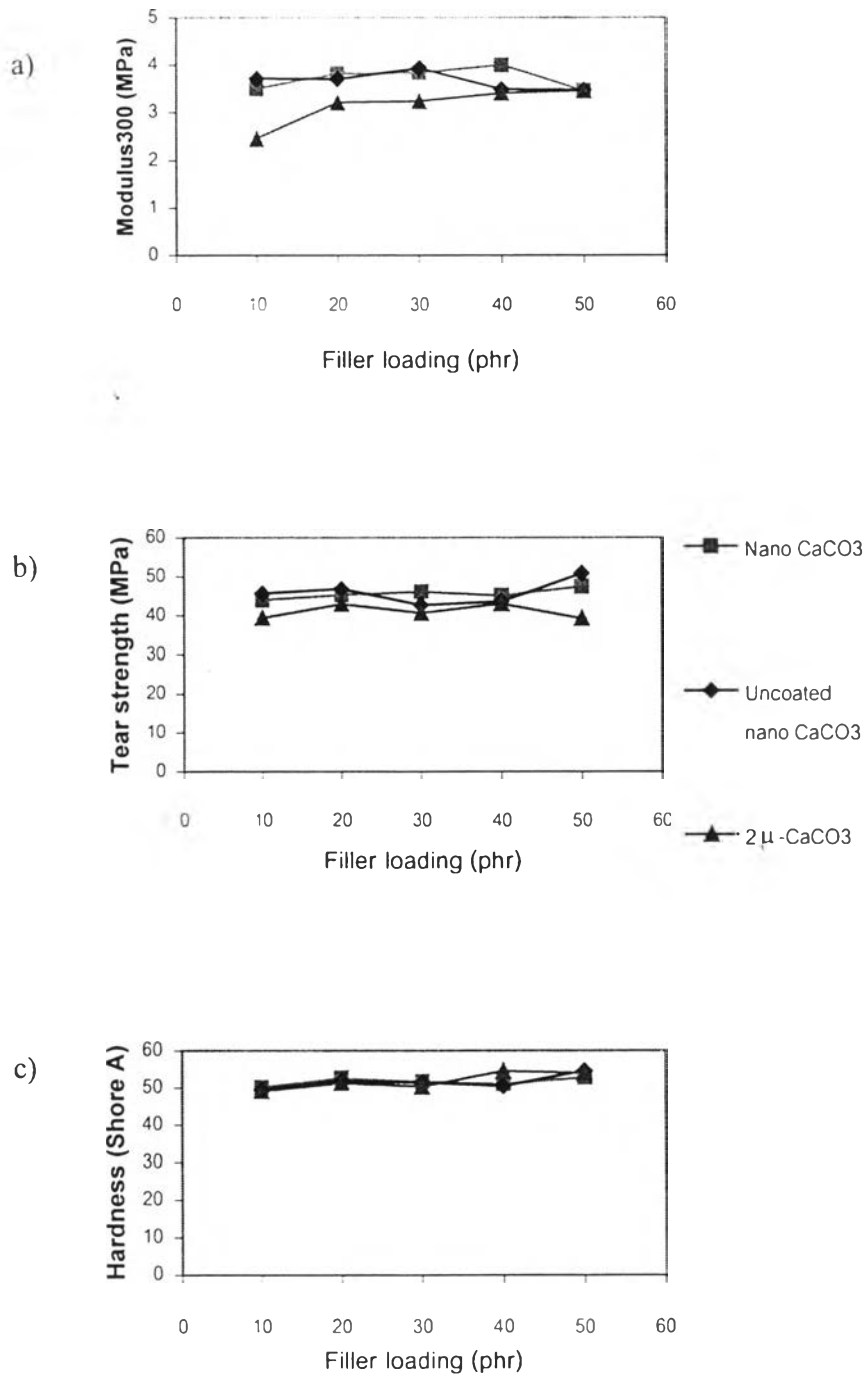
When compared the 2 $\mu$ -calcium carbonate with both coated and uncoated nanocalcium carbonate as fillers for natural rubber, at the same filler loading, the reinforcing effect of the nanocalcium carbonate is more noticeable.

**Table 4.5** Effect of Filler Content, Particle Size of Filler and Surface Modification on Mechanical Properties of Rubber Composites.

Compound	Filler loading (phr)	Tensile strength (MPa)	Ultimate elongation (%)	Modulus 100% (MPa)	Modulus 300% (MPa)	Tear strength (MPa)	Hardness (Shore A)
Nano CaCO <sub>3</sub>	10	23.1 ± 1.3	647 ± 45	1.33 ± 0.08	3.63 ± 0.36	44.0 ± 1.4	50.2 ± 0.3
	20	27.1 ± 0.7	698 ± 29	1.31 ± 0.03	3.83 ± 0.01	45.4 ± 2.0	52.7 ± 0.8
	30	29.2 ± 2.6	749 ± 22	1.31 ± 0.06	3.84 ± 0.17	46.2 ± 0.8	51.7 ± 0.6
	40	27.4 ± 2.5	766 ± 52	1.25 ± 0.04	4.00 ± 0.61	45.1 ± 1.0	51.0 ± 0.0
	50	24.7 ± 0.3	712 ± 62	1.39 ± 0.10	3.46 ± 0.40	47.4 ± 1.9	52.8 ± 0.3
Uncoated nano CaCO <sub>3</sub>	10	24.1 ± 0.5	668 ± 25	1.19 ± 0.12	3.72 ± 0.24	45.7 ± 1.2	49.5 ± 0.5
	20	25.1 ± 2.0	658 ± 40	1.34 ± 0.05	3.71 ± 0.24	46.9 ± 0.6	51.8 ± 0.8
	30	25.4 ± 1.8	662 ± 36	1.37 ± 0.08	3.94 ± 0.21	42.7 ± 0.3	51.5 ± 0.5
	40	24.3 ± 0.2	726 ± 65	1.35 ± 0.11	3.49 ± 0.49	43.6 ± 1.2	50.5 ± 0.5
	50	22.5 ± 0.3	741 ± 23	1.27 ± 0.04	3.48 ± 0.12	50.9 ± 1.5	54.7 ± 0.6
2 $\mu$ - CaCO <sub>3</sub>	10	14.9 ± 1.8	670 ± 72	0.98 ± 0.09	2.46 ± 0.26	39.4 ± 0.7	49.2 ± 0.3
	20	24.9 ± 1.2	669 ± 30	1.17 ± 0.11	3.21 ± 0.40	42.9 ± 0.6	51.3 ± 0.3
	30	26.8 ± 1.8	652 ± 86	1.22 ± 0.06	3.24 ± 0.23	41.6 ± 1.2	50.3 ± 0.6
	40	25.5 ± 2.5	688 ± 29	1.50 ± 0.02	4.07 ± 0.41	43.1 ± 1.7	54.5 ± 0.5
	50	16.3 ± 3.8	614 ± 35	1.21 ± 0.07	3.46 ± 0.28	39.3 ± 0.3	54.0 ± 0.0



**Figure 4.5** Effect of Filler Loading on; a) Tensile Strength, b) Ultimate Elongation, and c) Modulus 100% of Rubber Composites.



**Figure 4.6** Effect of Filler Loading on; a) Modulus 300%, b) Tear Strength, and c) Hardness of Rubber Composites.

#### 4.4.4 Crosslinking Density

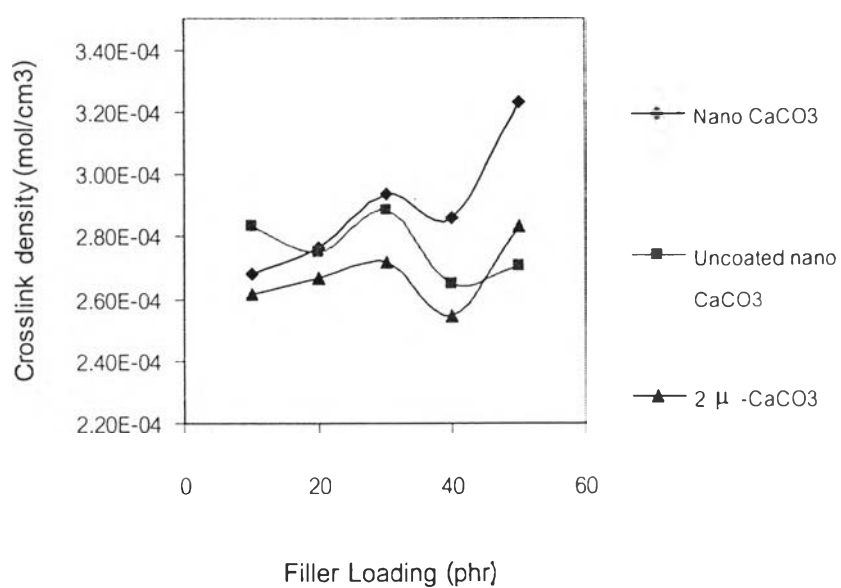
The crosslinking density was determined by Flory-Rhener equation. The result was reported in Table 4.6 and Figure 4.7, the crosslinking density of coated and uncoated nanocalcium carbonate/natural rubber composites were higher than that of  $2\mu$ -calcium carbonate/natural rubber composites due to the compatibility between nanocalcium carbonate and natural rubber phase. These results agree well with the rheology measurements indicating the good dispersion of the nanocalcium carbonate in the the elastomer phase.

Figures 4.8 a, 4.8 b and 4.8 c show the relation between tensile strength and tear strength, modulus and elongation with crosslinking density of coated nanocalcium carbonate/rubber composite. As crosslinking was increased, the gel point was further eventually reached, and a three dimensional network was formed. Some chains may not be attached to the network (soluble sol phase), but the whole composition no longer dissolved in a solvent, a gel cannot be fractured without breaking chemical bonds. Thus, strength is higher at the gel point, since chemical bond must be ruptured to create fracture surface. However, strength does not increase indefinitely with more crosslinking. When an external force deforms an elastomer, part of the energy is stored elastically in the chains and is available as a driving force for fracture. The remainder of the energy is dissipated through molecular motions into heat and, in this manner, is made unavailable to break chains. At high crosslink level, chain motions become restricted, and the “tight” network is incapable of dissipating much energy [23].

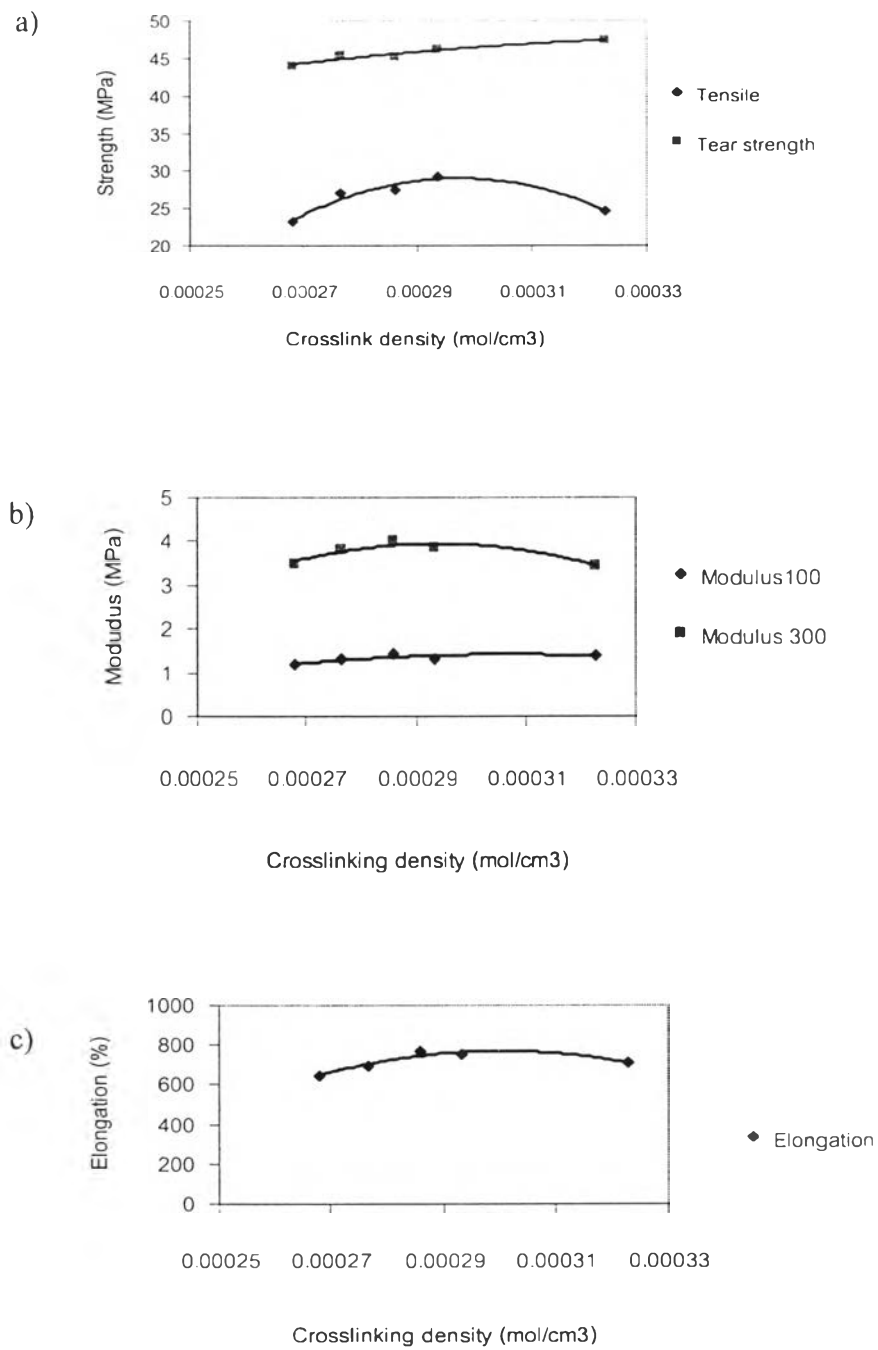
Tear strength also increased with increasing crosslink density. Hamed et al. [24] reported that the mechanical behavior such as, tear and tensile strength of an elastomer depended strongly on crosslink density and reached a maximum value as crosslink was increased.

**Table 4.6** Effect of Filler Content, Filler Type . Particle Size of Filler and Surface Modification on Crosslinking Density of Rubber Composites.

Filler Loading (phr)	Crosslinking density (mol/cm <sup>3</sup> )		
	Nano CaCO <sub>3</sub>	Uncoated nano CaCO <sub>3</sub>	2 $\mu$ -CaCO <sub>3</sub>
10	2.68E-04	2.83E-04	2.61E-04
20	2.77E-04	2.75E-04	2.67E-04
30	2.93E-04	2.89E-04	2.72E-04
40	2.86E-04	2.65E-04	2.54E-04
50	3.23E-04	2.71E-04	2.83E-04



**Figure 4.7** Effect of Filler Loading on Crosslinking Density of Rubber Composites.

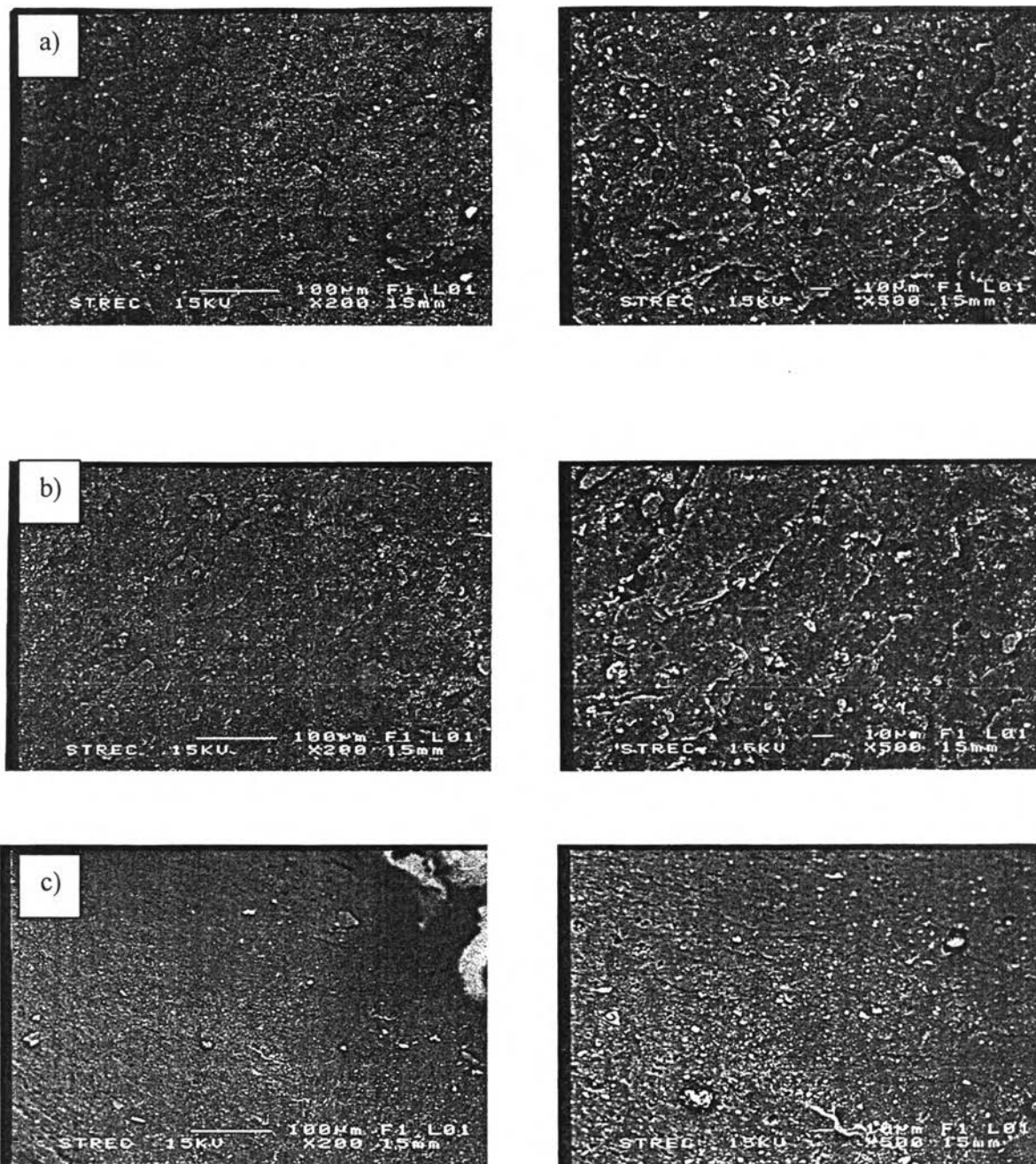


**Figure 4.8** Relationship between Crosslinking Density with; a) Strength, b) Modulus, and c) Elongation of Coated Nanocalcium Carbonate.



#### 4.4.5 Morphology

The SEM micrographs of fracture surface of coated nanocalcium carbonate, uncoated nanocalcium carbonate and 2 $\mu$ -calcium carbonate / rubber composites at loading 40 phr are shown in Figure 4.9 a, b and c, respectively. For the coated nanocalcium carbonate (Fig 4.9 a), some formation of agglomerates was observed because the filler was very fine in nanosize. These agglomerates caused the lower values of modulus. Figures 4.9 a, 4.9 b and 4.9 c show the coated nanocalcium carbonate exhibited the better dispersion than the uncoated and 2 $\mu$ -calcium carbonate in rubber matrix (the bright spots are calcium carbonate). Thus, higher values of mechanical properties are justified [17].



**Figure 4.9** SEM Micrographs of Fracture Surface; a) Coated Nanocalcium Carbonate b) Uncoated Nanocalcium Carbonate c) 2 $\mu$ -Calcium Carbonate. (x 200 and x 500 Magnification).

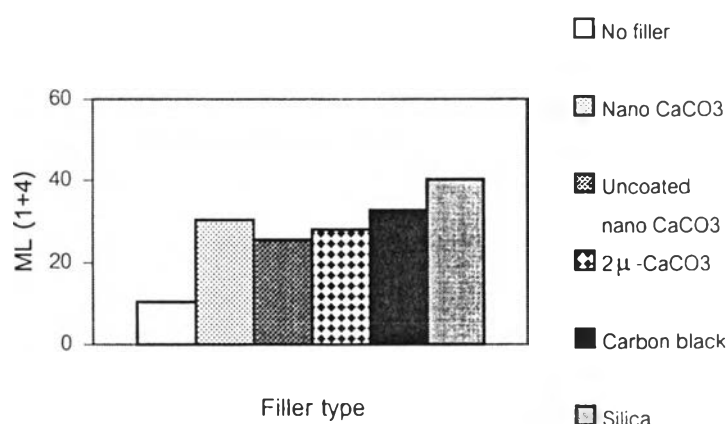
## 4.5 Comparison of Nanocalcium Carbonate with Conventional Reinforcement Fillers.

### 4.5.1 Mooney Viscosity.

From Table 4.7, the Mooney viscosity of rubber compounds filled with various fillers (40 phr) were compared. The viscosity of carbon black and silica filled rubber compound was higher than that of calcium carbonate filled rubber compound, this is probably attributed to the primary aggregation of fillers. The viscosity increase substantially at high silica loading [25]. For carbon black filled rubber compound, in general, the aggregation also leads to higher viscosity [8].

**Table 4.7** Effect of Filler Type on Mooney Viscosity of Rubber Compounds.

Compound	Filler Loading (phr)	Mooney viscosity
No filler	0	10.3
Carbon black	40	32.6
Silica	40	40.3



**Figure 4.10** Effect of Filler Types (40 phr loading) on Mooney Viscosity of Rubber Compounds.

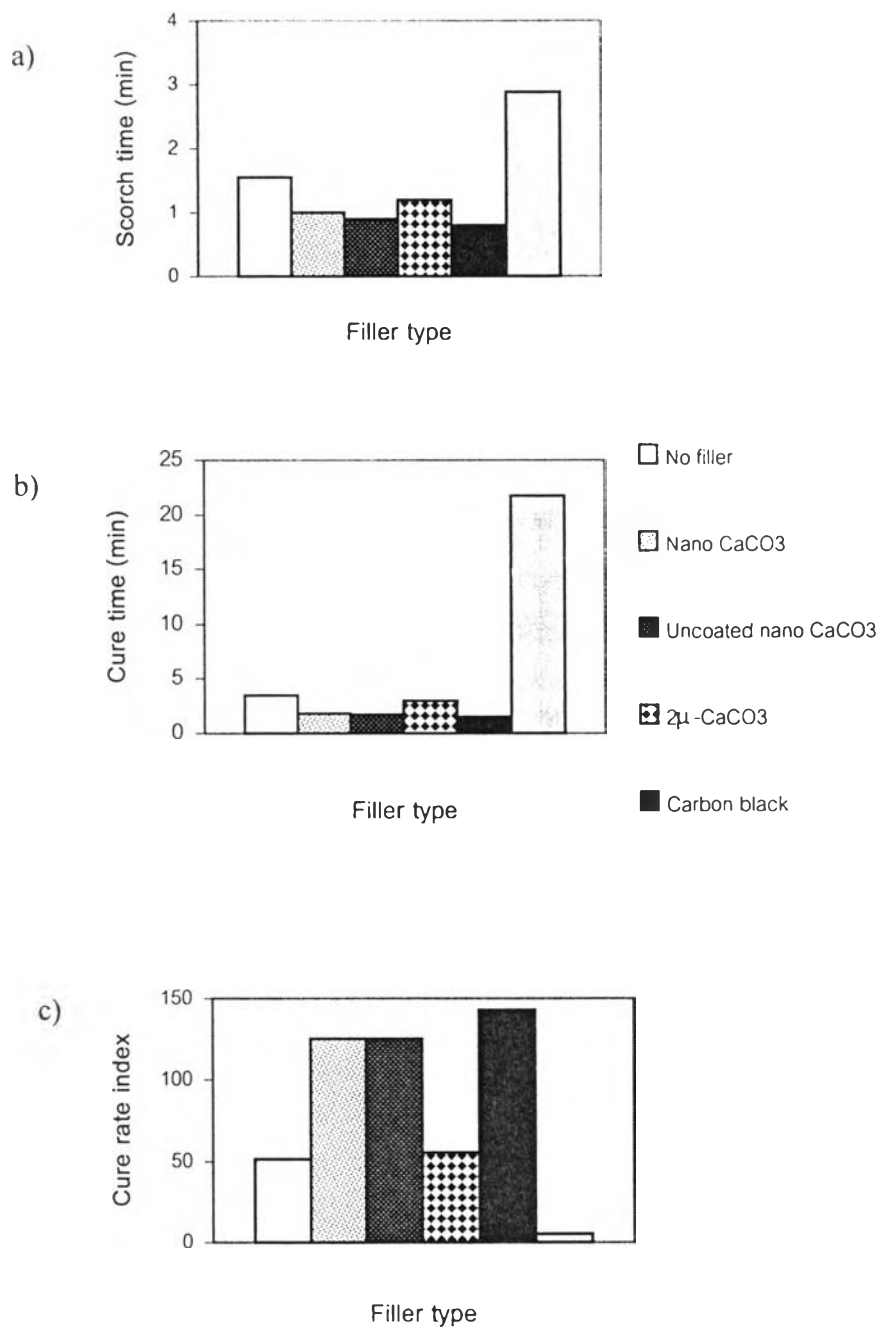
#### 4.5.2 Cure Characteristics.

The cure properties of carbon black and silica filled rubber compound are presented in Table 4.8 and Figures 4.11 a to 4.11 c. The scorch time and optimum cure time of carbon black filled compound were lower compared to that of calcium carbonate and silica filled compound. Various types of carbon black can be placed in an order of increasing activity which will hold for most accelerated sulfur cure. Because carbon black increases the viscosity of the batch, while carbon black improved dispersion, they also give the rise mixing and processing temperatures, and thus earlier scorching was observed [26]. It should be reiterated that there is an activating effect of carbon black, in that the carbon black actually assists in the curing of the rubber, reducing the needs for curative and cure time.

On the other hand, the scorch time and optimum cure time of silica filled rubber compound were very long. The surfaces of silica possess siloxane and silanol groups, and the silanol (or hydroxyl) groups are acidic. They interact with basic accelerators, causing detrimental effects such as slow cure rate and unacceptably long cure time, and also loss of crosslink density in sulfur-cured system. Moreover, because the surface of silica is polar and hydrophilic, there is a strong tendency to adsorb moisture which adversely influenced the curing reaction and hence the properties of the cured rubbers. The amount of water adsorbed on the surface controls the ionization of the silanol groups, which cause detrimental effects on the cure-process of rubber compounds [27]. Hydrated silicas retard cure and require the increased dosage of accelerator or the addition of materials such as glycols or amines to promote curing.

**Table 4.8** Effect of Filler Type on Cure Properties of Rubber Compounds.

Compound	Filler loading (phr)	Scorch time (min)	T <sub>90</sub> (min)	S <sub>max</sub> (dNm)	S <sub>min</sub> (dNm)	ΔS (dNm)	Cure rate index
No filler	0	1.55	3.50	3.40	0.10	3.30	51.3
Carbon black	40	1.20	3.10	4.70	0.15	4.55	30.3
Silica	40	2.88	21.75	5.10	0.30	4.80	5.3



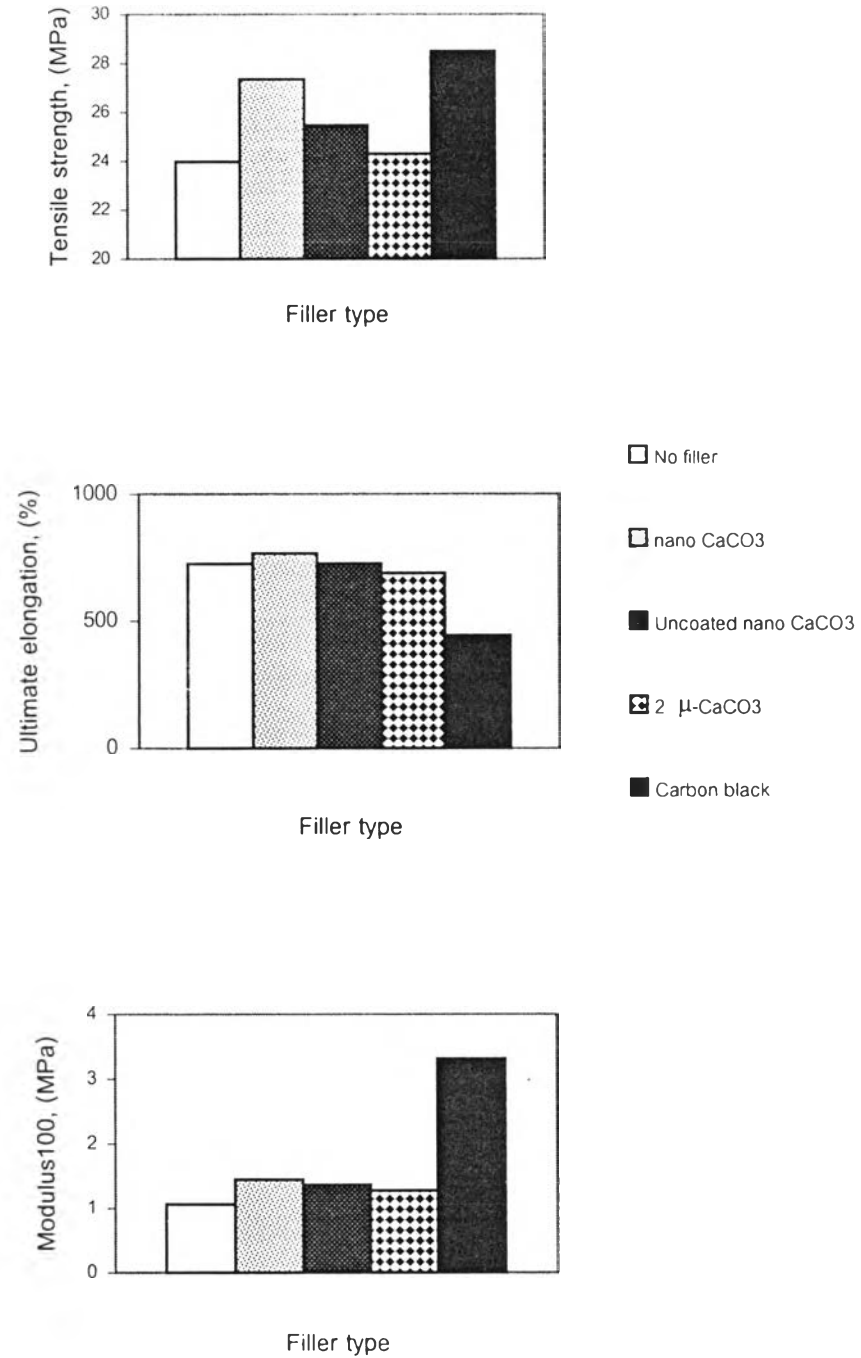
**Figure 4.11** Effect of Filler Type on; a) Scorch Time, b) Cure Time, and c) Cure Rate Index on Rubber Compounds at 40 phr Loading.

### 4.5.3 Mechanical Properties of Rubber Composite.

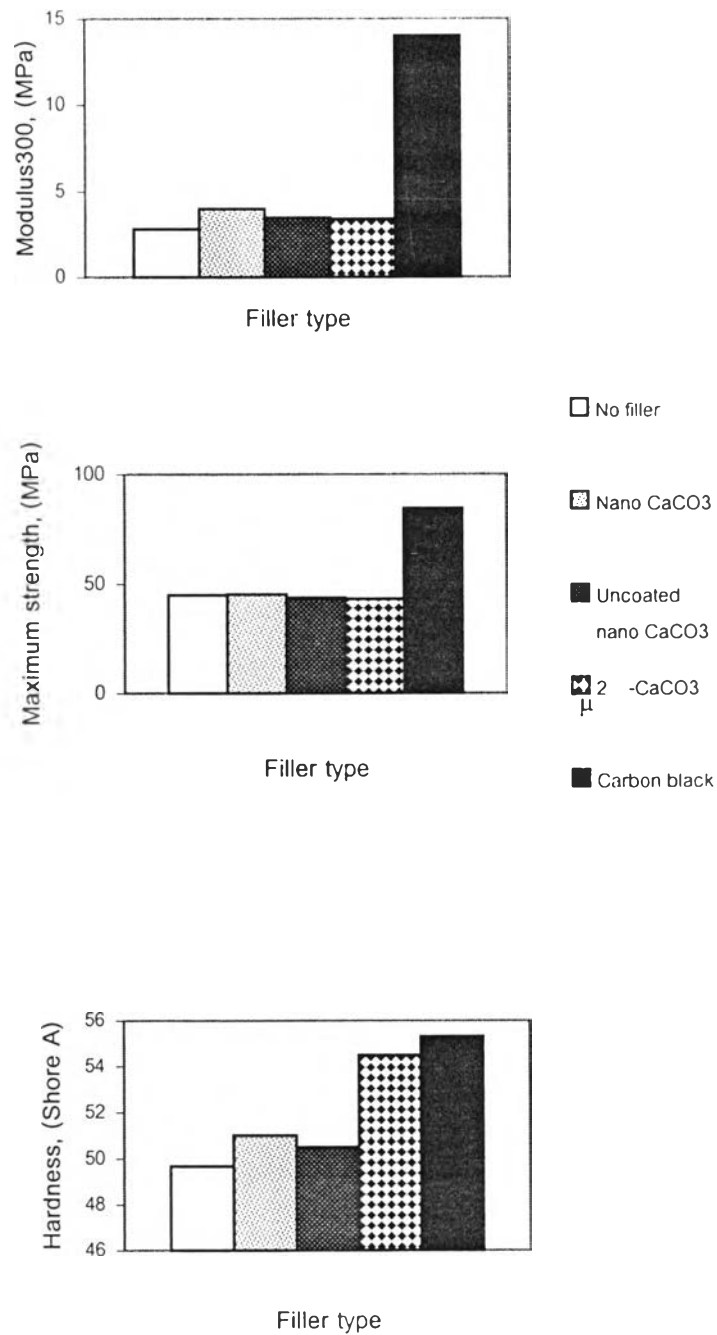
A comparison of mechanical properties between unfilled and carbon black filled rubber are presented in Table 4.9. Figure 4.12 a, shows that the tensile strength of carbon black /natural rubber composite exhibited the highest value. The carbon black surface contains the functional groups (phenolic and carboxylic group) capable of reacting with polymer molecules to form grafts during processing and vulcanisation [28]. Thus shear-generated polymeric free radicals have been shown to graft to the carbon black surface during mixing. Carbon black inhibits the free radical reactions through quinolic surface groups; these reactions also result in formation of polymer grafts. However, high content of carbon black gives rise to a marked loss in the elastic behavior of the natural rubber composite. From Figure 4.12 b, carbon black / natural rubber composite exhibits the lowest value of ultimate elongation. From Figure 4.12 c, 4.13 a and 4.13 b, the results of modulus 100, modulus 300 and tear strength also show the similar behavior as the tensile strength.

**Table 4.9** Effect of Carbon Black on Mechanical Properties.

Compound	Filler loading (phr)	Tensile strength (MPa)	Ultimate elongation (%)	Modulus 100% (MPa)	Modulus 300% (MPa)	Maximum strength (MPa)	Hardness (Shore A)
No filler	0	23.97 ± 0.40	725 ± 48	1.05 ± 0.03	2.82 ± 0.21	44.8 ± 1.3	49.7 ± 0.3
Carbon black	40	28.49 ± 1.08	444 ± 29	3.31 ± 0.31	14.03 ± 0.80	84.4 ± 12.7	55.3 ± 0.3



**Figure 4.12** Effect of Filler Type on; a) Tensile Strength, b) Ultimate Elongation, and c) Modulus 100% of Rubber Composites at 40 phr Loading.



**Figure 4.13** Effect of Filler Type on; a) Modulus 300%, b) Tear Strength, and c) Hardness of Rubber Composites at 40 phr Loading.

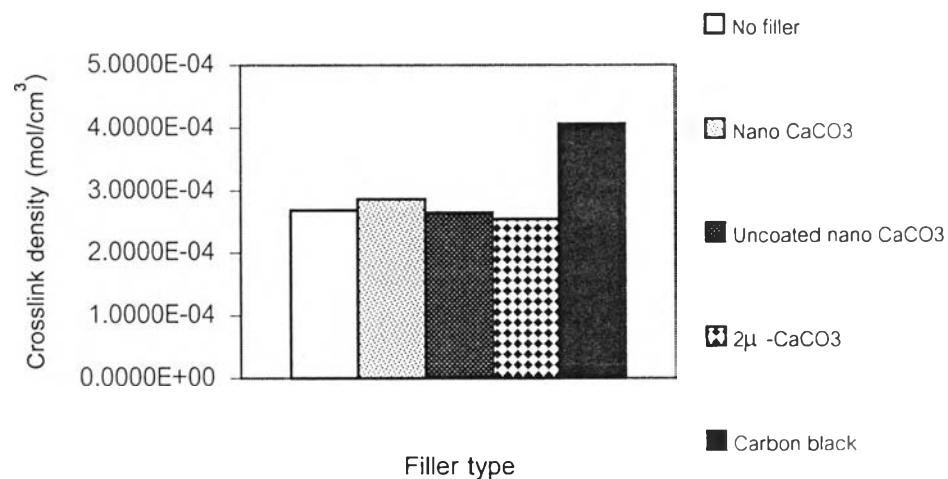


#### 4.5.4 Crosslinking Density

Crosslinking density of unfilled and carbon black rubber composites are presented in Table 4.10. It can be seen that the carbon black/rubber composite is significantly higher than that of calcium carbonate rubber composites and unfilled rubber. It can be explained that the uncrosslinked raw elastomers was entangled high molecular weight viscoelastic liquid, which was weak, inelastic, and could dissolve completely in solvent. The rubber/filler network was stiffer and stronger than the gum, but had the large-strain elasticity, attachments to the carbon black were primary irreversible, covalent chemical bonds. [29]

**Table 4.10** Effect of Carbon Black on Crosslinking Density.

Compound	Filler Loading (phr)	Crosslinking Density (mol/cm <sup>3</sup> )
No filler	0	2.69E-04
Carbon black	40	4.06E-04



**Figure 4.14** Effect of Filler Type on Crosslinking Density of Rubber Composites at 40 phr Loading.