CHAPTER IV

RESULTS AND DISCUSSION

In this study, the premixed natural rubber product containing carbon black was prepared by direct mixing the concentrated latex with the additives. The method for preparing the additives before mixing was used ball mill. The vulcanized sheet products were assessed the dispersion of carbon black. Finally, the mechanical properties were investigated.

4.1 Properties of Raw Materials

4.1.1 Natural Rubber Latex

The concentrated natural rubber latex was used in this study. The concentrated natural rubber latex consists of particles of rubber hydrocarbon and non-rubber constituents suspended in an aqueous serum phase. The average dry rubber content of latex may range between 60.0% and 61.0%.

The concentrated natural rubber latex was determined total solids and dry rubber content follows by ASTM D 1076 and the results were 61.85% and 60.26%. respectively. The percentage of total solids and dry rubber content were calculated in

Appendix A. The particle size distribution of rubber particle was determined by mastersizer as shown in Appendix B. The average diameter was 0.71 μm.

4.1.2 Carbon Black

The carbon black type N220 and N330 were used in this study and the properties are shown in Table 4.1 and Table 4.2.

Table 4.1 Analytical data of carbon black type N220

Test	Method	Typical Values	Results
	ASTM		
Iodine Adsorption Number,mg/g	D1510	121	118
DBP Absorption Number,ml/100g	D2414	114	115
Sieve Residue:Screen Size 500μm(No.35),%	D1514	0.001max	0.0000
Sieve Residue:Screen Size 45 μm(No.325),%	D1514	0.1max	0.0012
Heating Loss,%	D1509	2.5max	0.7

Table 4.2 Analytical data of carbon black type N330

Test	Method	Typical Values	Results
	ASTM		
Iodine Adsorption Number,mg/g	D1510	82	82
DBP Absorption Number,ml/100g	D2414	102	101
Sieve Residue:Screen Size 500μm(No.35),%	D1514	0.001max	0.0000
Sieve Residue:Screen Size 45 μm(No.325),%	D1514	0.1max	0.0010
Heating Loss,%	D1509	2.5max	0.5

4.2 Preparation of Premixed Natural Rubber Product Containing Carbon Black and Vulcanizing Agents

In sulfur vulcanization system, the additives were used in several formulations, a typical recipe being 0.5-4 parts sulfur, 0.5-2 parts accelerator, 2-10 parts accelerator activator, and 1-4 parts fatty acid per 100 parts rubber. The amount of filler was used until the optimum loading for this composition. In this experiment, compounded sheets contained 2-mercaptobenzothiazole(MBT), zinc oxide(ZnO), stearic acid and carbon black. They acted as accelerator, accelerator activator, fatty acid and filler, respectively.

4.2.1 Effect of Surfactant Concentration

Because the concentrated natural rubber latex was coagulated after direct mixing of carbon black and the chemicals into the concentrated latex. As the result, the aqueous dispersions of carbon black, sulfur, ZnO, stearic acid and MBT were prepared before mixing. The surfactants were used to stabilize the additives. Nonionic surfactant (Tergitol NP 10) was used in this experiment. Tergitol NP10 was used by varying the amount of 1, 2, 3 and 4 phr. The aqueous dispersions were prepared by ball mill at rate 130 rpm for 2 hr. The formulations of compounded sheets were obtained as follows:

- Concentrated natural rubber latex	100	parts by dry weight
- Carbon black type N330	25	phr
- Sulfur	2	phr
- ZnO	5	phr
- Stearic acid	2	phr
- MBT	1	phr

When Tergitol NP10 was used in the amount of 1 and 2 phr, the rubber latex coagulated after mixing with the additives. Therefore, the carbon black and other chemicals were not dispersed homogeneously in the compounded sheets. At using Tergitol NP10 of 3 and 4 phr, the rubber latex was coagulated by 5% formic acid by volume after the rubber latex mixed with the additives for 0.5 hr. The formic acid that used to coagulate the rubber latex when using Tergitol NP10 4 phr took more quantity than using Tergitol NP10 3 phr.

The appropriate amount of Tergitol NP10 of 3 phr was used because it could save cost in industry.

4.2.2 Effect of Mixing Time

The time of rubber production is very important. In this work, the time for preparing aqueous dispersion of the additives were studied. The formulations of compounded sheets were the same as the formulations of compounded sheets which were used to determine the appropriate amount of surfactant. Tergitol NP10 3 phr was used.

The compounded sheets that obtained from the coagulation procedure were prepared the vulcanized sheets. The properties of vulcanized sheets were studied. The temperature and the cure time of this compounded sheet were determined by rheometer. The cure curve is shown in Appendix B..

From Figure B.3 and rheometer data, the temperature used to cure was 150 °C. 90% of cure required time was 6.42 min. In this compounded sheet, the approximate cure time was 10 min because after 90% of cure required time, the cure curve was nearly constant at 77 dNm. This means the mechanical properties were slightly changed after 90% of required cure time. This compounded sheet was slow curing because the slope was not steep.

The dispersions of carbon black of vulcanized sheets were determined by optical microscope. The dispersion rating (DR.) values were assessed by comparison with the standard photographs and the results are shown in Table 4.3. The optical micrographs of carbon black dispersion are shown in Appendix C.

Table 4.3 Dispersion rating of vulcanized sheets at varying time for preparing aqueous dispersion

Time for preparing aqueous dispersion (hr)	Dispersion rating (DR)
1	4.5
2	4.5
3	5.0
4	5.0
5	5.0

The mechanical properties of the vulcanized sheets were studied to obtain the appropriate time for preparing aqueous dispersion or mixing time. The mechanical properties which determined in this study were the tensile strength, the elongation, the stress at a given elongation (modulus) and the hardness. Table 4.4 illustrate the effect of mixing time on the mechanical properties of the vulcanized sheets.

Table 4.4 Effect of mixing time on the mechanical properties of the vulcanized sheets

Properties	Mixing time (hr)				
	1	2	3	4	5
Tensile strength (MPa)	9.50	12.05	16.49	13.78	15.49
Elongation(%)	1148	1358	1538	1459	1473
Modulus 500% (MPa)	4.88	5.69	8.23	6.42	6.89
Hardness (shore A)	59.0	59.2	60.4	60.2	60.9

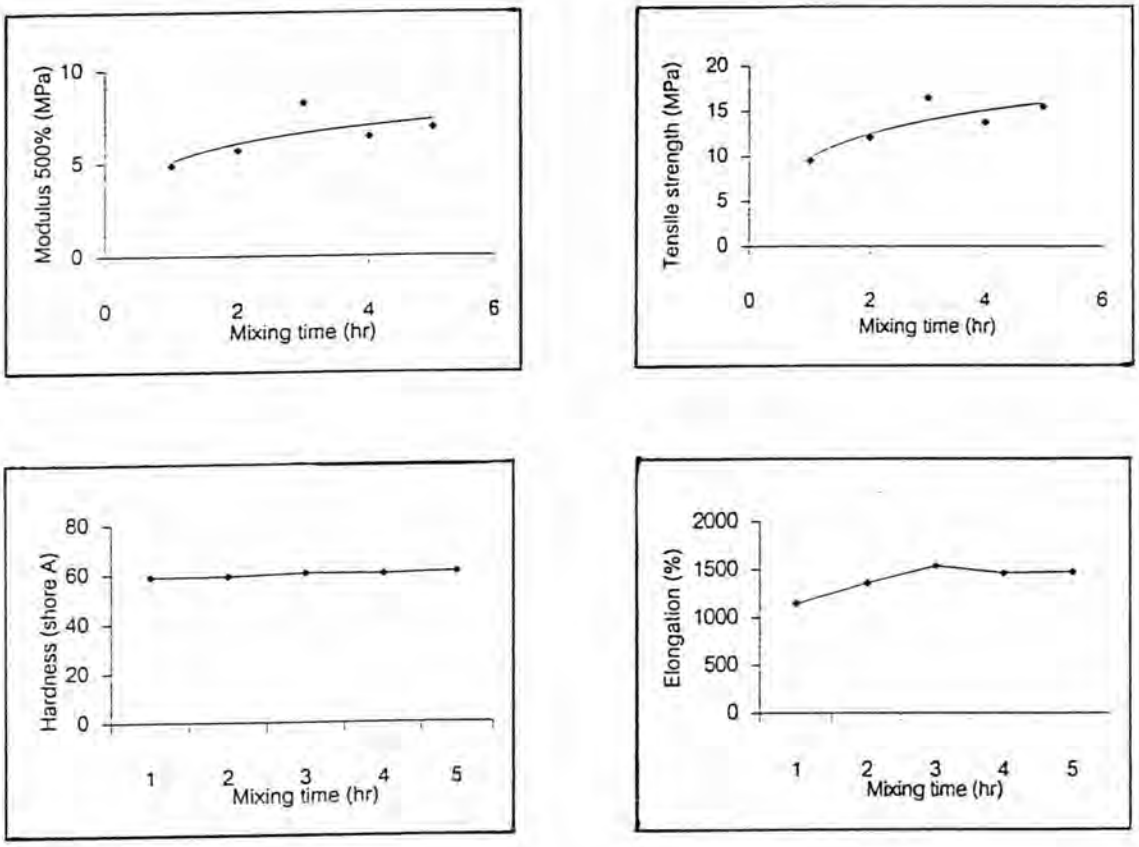


Figure 4.1 Effect of mixing time on the mechanical properties

From Table 4.4 and Figure 4.1, the tensile strength and modulus 500% of the vulcanized sheets after mixing time of 3 hours were nearly constant. The elongation and the hardness were slightly changed. Therefore, the mixing time of 3 hours was used to prepare aqueous dispersion of the additives.

4.2.3 Particle Size of the Aqueous Dispersions of the Additives

The aqueous dispersions of the additives after mixing time of 3 hours were analyzed by mastersizer to determine the particle size of the additives. The particle size distribution of the additives is shown in Appendix B.

The average diameter was 0.24 μm. The diameter was smaller than the diameter of rubber particles. According to prior assumption, the aqueous dispersions of the additives could be mixed homogeneously with the rubber latex because the particle size of the additives was smaller than the particle size of rubber latex.

4.3 Effect of the Amount of Sulfur

Sulfur was a curing agent that used in rubber industry. The effect of the amount of sulfur on the properties of vulcanized rubber was studied by varying the amount of 1, 2, 3 and 4 phr. The other additives were kept constant because the only use of sulfur could be crosslinked in vulcanized network. The time for preparing aqueous dispersions of the additives was 3 hours. The formulations of compounded sheets were the same as the formulations of compounded sheets which were used to determine the appropriate time of mixing except the amount of sulfur. The cure time

of 10 min at 150 °C was used to prepare the vulcanized sheets. The dispersion ratings of vulcanized sheets are shown in Table 4.5. The optical micrographs of carbon black dispersion of vulcanized sheets are shown in Appendix C. The properties of the vulcanized sheets were studied and the results are shown in Table 4.5.

Table 4.5 Effect of the amount of sulfur on the properties of vulcanized sheets

Properties	Amount of sulfur (phr)			
	1	2	3	4
Tensile strength (MPa)	10.81	16.49	12.46	9.25
Elongation (%)	1247	1538	1422	1037
Modulus 500%	5.94	8.23	6.06	4.92
Hardness (shore A)	55.6	60.4	59.4	61.2
Tear strength (kN/m)	36.47	57.15	42.37	33.38
Solvent swelling (%)	293	250	241	214
Dispersion Rating	4.5	5.0	4.5	4.5

From Table 4.5, the mechanical properties of vulcanized sheets containing sulfur 2 phr were the highest. Tensile strenght, elongation, modulus 500% and tear strength decreased when the sulfur content increased. The hardness of vulcanized sheets was changed a little. These properties of vulcanized sheets decreased when the amounts of sulfur increased because the sulfur could bloom onto the surface of compounded sheets. Then it could not crosslink in vulcanized network when the

compound sheets were prepared to the vulcanized sheets. The other reason was the sulfur might be present as pendent sulfides or cyclic sulfides as shown in Figure 2.1. This reduced the properties and the dispersion of carbon black. The solvent swelling of vulcanized sheet also decreased because the effect of blooming and the occurrence of cyclic sulfides. The amount of sulfur 2 phr was used to study the other effect. A scanning electron microscope was also used to study the carbon black dispersion of vulcanized sheets containing sulfur 2 phr and scanning electron micrograph is shown in Appendix C.

4.4 Effect of the Amount of Accelerator and Accelerator Activator

In this experiment, 2-mercaptobenzothiazole (MBT) was used as an accelerator. Zinc oxide (ZnO) and stearic acid were used as accelerator activators. The amounts of accelerator and accelerator activators were promptly changed because in the mechanisms of sulfur vulcanization, they reacted together to form active accelerator complex. The amount of MBT, ZnO and stearic acid were used at lowest, medium and highest quantity of industrial range use. The other additives were kept constant. The time for preparing aqueous dispersion of the additives was 3 hours. The formulations of compounded sheets were obtained as follows:

- Concentrated natural rubber latex	100	parts by dry weight
- Carbon black type N330	25	phr
- Sulfur	2	phr
- ZnO	2, 5, 10	phr
- Stearic acid	1, 2, 4	phr

- MBT	0.5, 1, 2	phr
- Tergitol NP10	3	phr

The cure time of 10 min at 150 °C was used to prepare the vulcanized sheets because this compounded sheets had the same ingredients as the compounded sheets, which were used to determine the appropriate time of mixing. The compounded sheets differed in the amount of accelerator and accelerator activator. The dispersion ratings of vulcanized sheets are shown in Table 4.6. The optical micrographs of carbon black dispersion of vulcanized sheets are shown in Appendix C. The properties of the vulcanized sheets were studied and the results are shown in Table 4.6.

Table 4.6 Effect of the amount of accelerator and accelerator activator on the properties of vulcanized sheets

Properties	Amount of accelerator and accelerator activator		
	low	medium	high
Tensile strength (MPa)	10.54	16.49	9.12
Elongation (%)	1256	1538	999
Modulus 500%	5.28	8.23	3.84
Hardness (shore A)	51.1	60.4	65.4
Tear strength (kN/m)	35.66	57.15	33.95
Solvent swelling (%)	265	250	208
Dispersion Rating	4.5	5.0	4.5

From Table 4.6, the best properties for the vulcanized sheets occurred when medium quantities of accelerator and accelerator activators were used at a industrial range. At low quantities of accelerator and accelerator activator, the properties were not good because the vulcanized sheets had little crosslinking. The solvent swelling had higher values when medium and high quantities of accelerator and accelerator activator were used. This is because the solvent swelling could be shown about the degree of crosslink. The solvent swelling of vulcanized sheets with high quantities of accelerator and accelerator activator had low values, but the properties were not good because of the greater effect of blooming. The hardness of vulcanized sheets had high values when high quantities of accelerator and accelerator activator were used because the chemicals could deteriorate the rubber properties. The use of medium quantities of accelerator and accelerator activators resulted in the best properties. Low quantities of accelerator and accelerator activator resulted in the slow sulfur curing and little crosslink. And the use of high quantities of accelerator and accelerator activators resulted in the blooming effect.

4.5 Effect of Types of Carbon Black[24,25,26]

Carbon black acts as the filler in the rubber compound. Carbon black type N 220 and N 330 were used in this study. The other additives were kept constant when the best properties resulted. The time for preparing aqueous dispersions of the additives was 3 hours. The formulations of compounded sheets were obtained as follows:

- Concentrated natural rubber latex	100	parts by dry weight
- Carbon black	25	phr
- Sulfur	2	phr
- ZnO	5	phr
- Stearic acid	2	phr
- MBT	1	phr
- Tergitol NP10	3	phr

The temperature and cure time of compounded sheets containing carbon black type N220 were determined. The cure curve of this compounded sheet is shown in Appendix B.

From Figure B.4 and rheometer data, the temperature used to cure was 150 °C. 90% of required cure time was 8.43 min. In this compound, the approximate cure time was also 10 min because after 90% of required cure time, the cure curve was nearly constant at 64 dNm. This mean the mechanical properties were a little change after 90% of required cure time. The dispersion ratings of vulcanized sheets are shown in Table 4.7 and the optical micrographs of carbon black dispersion are shown in Appendix C. A scanning electron microscope was also used to study the carbon black dispersion of vulcanized sheets containing carbon black type N220 and scanning electron micrograph is shown in Appendix C. The properties of the vulcanized sheets were studied and the results are shown in Table 4.7.

Table 4.7 Effect of types of carbon black on the properties of vulcanized sheets

Properties	Types of carbon black	
	N220	N330
Tensile strength (MPa)	11.74	16.49
Elongation (%)	1267	1538
Modulus 500%	6.23	8.23
Hardness (shore A)	60.3	60.4
Tear strength (kN/m)	40.42	57.15
Solvent swelling (%)	252	250
Dispersion Rating	5.0	5.0

From Table 4.7, the properties of vulcanized sheets containing carbon black type N330 were better than the vulcanized sheets containing carbon black type N220. Carbon black type N330 has the iodine adsorption number of 82 mg/g and DBP absorption number of 101 ml/100g. These properties indicate the surface area and the level of aggregation of carbon black. Carbon black type N220 has the iodine adsorption number of 118 mg/g and DBP absorption number of 115 ml/100g. Carbon black type N220 has more surface area than carbon black type N330. Therefore, the vulcanized sheets containing carbon black type N220 should has more tensile strength than the vulcanized sheets containing carbon black type N330. This may be due to the fact that the vulcanized sheets containing carbon black type N330 has more surface area to interact with the rubber when mixing with rubber latex for 0.5 hours. But the

results were opposite because the effect of level of aggregation of carbon black was greater that the effect of surface area of carbon black. Carbon black type N330 has more spherical particles than carbon black type N220 because it has lower DBP absorption values. The rubber particle mixed with carbon black type N330 were better than that of the carbon black type N220. The tensile strength, elongation, modulus 500% and tear strength of vulcanized sheets were also higher than that of the vulcanized sheets containing carbon black type N220.

4.6 Effect of Types of Surfactant

The surfactant was used to stabilize the aqueous dispersions of the additives before the rubber latex was added. Tergitol NP9 and Tergitol NP10, which are nonionic surfactants, were used in this experiment. The anionic surfactant –sodium dodecyl sulfate (SDS)– was also used. The amount of Tergitol NP9 and Tergitol NP10 were used at 3 phr, but the amount of SDS was used at 1.5 phr. If SDS was used at 3 phr, the rubber latex would not coagulate when adding formic acid. The time for preparing aqueous dispersions of the additives was also 3 hours. The formulations of compounded sheets were the same as the formulations of compounded sheets which were used to study effect of types of carbon black. The carbon black type N330 was used.

The temperature and cure times of compounded sheets containing Tergitol NP9 and SDS were determined. The cure curve of these compounded sheets are shown in Appendix B.

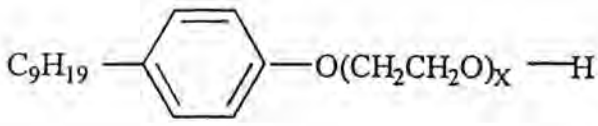
From Figure B.5 and rheometer data, the temperature used to cure was 150 °C. 90% of required cure time was 9.36 min. The approximate cure time of compounded sheets containing Tergitol NP9 was 12 min because the curve was constant at about 56 dNm after 90% of required cure time.

From Figure B.6 and rheometer data, the temperature used to cure was 150 °C. 90% of required cure time was 13.36 min. The approximate cure time of compounded sheets containing SDS was 15 min. The cure curve was constant at about 48 dNm after 90% of required cure time. The cure time of compounded sheets containing Tergitol NP10 is shown in Figure B.3 because it has the same ingredients. The dispersion ratings of vulcanized sheets are shown in Table 4.8. The optical micrographs of carbon black dispersion are shown in Appendix C. A scanning electron microscope was used to study the carbon black dispersion of vulcanized sheets containing Tergitol NP9 and SDS. Scanning electron micrographs are also shown in Appendix C. The properties of the vulcanized sheets were studied and the results are shown in Table 4.8.

Table 4.8 Effect of types of surfactant on the properties of vulcanized sheets

Properties	Types of surfactant		
	Tergitol NP9	Tergitol NP10	SDS
Tensile strength (MPa)	13.08	16.49	10.41
Elongation (%)	1331	1538	1191
Modulus 500%	5.52	8.23	4.93
Hardness (shore A)	60.1	60.4	62.2
Tear strength (kN/m)	45.39	57.15	33.89
Solvent swelling (%)	238	250	249
Dispersion Rating	5.0	5.0	4.5

From Table 4.8, the properties of vulcanized sheets containing SDS was not good. SDS is the anionic surfactant when it was used to prepare the aqueous dispersions of the additives. The dispersions were full of foam. This caused the rubber latex to not mix well with the additives. Tergitol NP9 and Tergitol NP10 are the same group of surfactants(nonionic surfactant). The NP surfactant are manufactured by reacting nonylphenol with ehtylene oxide. The reaction resulted in a very low level of unethoxylated hydrophobe and a narrow distribution of ethylene oxide adducts The general structure of NP surfactants are show below.



The properties of vulcanized sheets containing Tergitol NP10 were the best.

4.7 Effect of the Amount of Carbon Black

The effect of the amount of carbon black on the properties of vulcanized sheets was studied by varying the amount of carbon black at 25, 35 and 45 phr. The carbon black type N330 was used. The time for preparing aqueous dispersions of the additives was 3 hours. The formulations of compounded sheets were the same as the formulation of compounded sheets which were used to study the effect of the types of carbon black. But these formulations differed when the amount of Tergitol NP10 was changed to 4 and 5 phr when using carbon black 35 and 45 phr, respectively. The reason for changing the amount of Tergitol NP10 was because the rubber latex coagulated after mixing with the additives containing Tergitol NP10 3 phr.

The vulcanized sheets were prepared by using a cure time of 10 min at 150 °C. This is because the compounded sheets had the same ingredients as the compounded sheets which were used to determine the appropriate time of mixing, except the amounts of carbon black. The dispersion ratings are shown in Table 4.9 and the optical micrographs of carbon black dispersion are shown in Appendix C. The properties of the vulcanized sheets were studied and the results are shown in Table 4.9.

Table 4.9 Effect of the amount of carbon black on the properties of vulcanized sheets

Properties	Amount of carbon black		
	25	35	45
Tensile strength (MPa)	16.49	12.47	11.10
Elongation (%)	1538	1287	1106
Modulus 500%	8.23	6.28	5.41
Hardness (shore A)	60.4	61.6	65.2
Tear strength (kN/m)	57.15	45.15	36.76
Solvent swelling (%)	250	214	201
Dispersion Rating	5.0	5.0	4.5

From Table 4.9, the hardness increased when the amount of carbon black increased. Tensile strength, elongation, modulus 500% and tear strength decreased when the amount of carbon black increased. The solvent swelling of vulcanized sheets also decreased, but the properties were not good. According to prior assumptions, when solvent swelling decreases, the tensile strength and tear strength will increase. This is because the sulfur was a little crosslinked in vulcanized network caused by the large amount of carbon black.

4.8 Comparison the Properties of Vulcanized Sheets that Obtained from this Method with Common Method

The rubber could be softened either by mechanical work, termed mastication, by heat, or by chemicals known as peptisers. The increase of plasticity or decrease of viscosity brought about by mastication and peptisers was permanent ; by heat it might be permanent or temporary, depending on the nature of the rubber. The common method that was used to masticate and mixed the rubber with the additives was published in 1963. When the processing of rubber was first being commercially, two-roll mills were used. Later the internal mixer, rapid mixing and large through-put, was tending to replace the mill as a batch mixer because of its versatility.

4.8.1 Comparison some Properties with the Work of S.Bhoumick and S.Banerjee[17]

The work of S.Bhoumick and S.Banerjee was summarized in Literature Reviews(Chapter II). The formulations of compounded sheet using this method were the same as their work. But surfactants were used to stabilize the additives before the rubber latex was added. The time for preparing aqueous dispersions of the additives was 3 hours. The formulations of compounded sheets were obtained as follows:

- Concentrated natural rubber latex	100	parts by dry weight
- Carbon black	10	phr
- Sulfur	1	phr

- ZnO	5	phr
- Stearic acid	3	phr
- MBT	1	phr
- Tergitol NP10	3	phr

The cure time of 10 min at 150 °C was used to prepare the vulcanized sheets. Some mechanical properties were studied and compared with the work of S.Bhoumick and S.Banerjee as shown in Table 4.10. The dispersion rating of vulcanized sheets was also studied and the DR. was 5.5. The optical micrograph of carbon black dispersion is shown in Appendix C.

Table 4.10 Comparison the properties with the work of S.Bhoumick and S.Banerjee

Properties	S.Bhoumick and S.Banerjee	This method
Tensile strength (MPa)	5.68	8.11
Elongation (%)	810	1372
Modulus 200%	0.47	2.60
Hardness (shore A)	19.0	43.0
Resilience (%)	47.55	-*
Tear strength (kN/m)	-*	27.51
Solvent swelling (%)	-*	333

* the properties were not studied

From Table 4.10, the tensile strength, elongation, modulus 200% and hardness of vulcanized sheets that were obtained by this method had more value than the work of S.Bhoumick and S.Banerjee, especially the values of the elongation and the hardness.

4.8.2 Comparison the Properties with the Method that Used Two-roll Mills.

Natural rubber was mixed with the additives by two-roll mills and the formulations of compounded sheets were obtained as follows:

- Natural rubber	100	parts
- Carbon black type N330	25	phr
- Sulfur	2	phr
- ZnO	5	phr
- Stearic acid	2	phr
- MBT	1	phr

In this study, the smoked sheets rubber were used as raw rubber. The dried rubber that was obtained from acid coagulation of concentrated latex was also used as raw rubber. Preparing the vulcanized sheets used the same procedure as this method. The mechanical properties and the dispersion rating were studied and compared with this method as shown in Table 4.11. The optical micrographs of carbon black dispersion are shown in Appendix C. A scanning electron microscope was also used to study the carbon black dispersion of vulcanized sheets and scanning electron micrographs are shown in Appendix C.

Table 4.11 Comparison the properties with the method that used two-roll mills

Properties	Raw rubber		This method
	Smoked sheets	Coagulate from conc. latex	
Tensile strength (MPa)	12.43	8.10	16.49
Elongation (%)	1179	914	1538
Modulus 500%	7.40	6.46	8.23
Hardness (shore A)	54.9	54.4	60.4
Tear strength (kN/m)	39.73	30.75	57.15
Solvent swelling (%)	394	384	250
Dispersion Rating	6.5	6.5	5.0

The vulcanized sheets that obtained by this method had the best properties. The dispersion of carbon black of vulcanized sheets, which was obtained from two-roll mills, was better than the vulcanized sheets obtained from this method. According to prior assumptions, if the rubber has good dispersion of carbon black it will have good properties. This is because mixing the rubber with the additives by two-roll mills caused the level of aggregation of carbon black to increase. The aggregation of carbon black occurred by the shear stress and the effect of temperature. The temperature of 60°C was used. But when mixing occurred at a long time (about 10 min), the temperature reached 80 °C. The tensile strength, elongation and modulus 500% of vulcanized sheets containing raw rubber from acid coagulation of

concentrated natural rubber latex were the lowest. The solvent swelling of vulcanized sheets which was obtained from two-roll mills had higher values. This resulted in little of less occurrence of crosslinking in vulcanized network.