

CHAPTER IV

RESULTS AND DISCUSSION

The shear-induced coagulation of concentrated NR latex mixed with CB was studied. The effects of types and contents of CB on particle distribution, Mooney viscosity, cure characteristic and mechanical properties of the composite were investigated. Detailed investigations are presented below.

4.1 Shear-induced coagulation process

In this section, four grades of CB; N200, N330, 550 and N660, were the parameters to be investigated for their processibility by shear-induced coagulation of NR/CB mixed latex by high speed intensive mixer at 2,800 rpm. Each grade of CBs possessed different particle sizes and structures as the details shown in Table 2.4. The results of coagulation after shear applying are shown in Table 4.1.

Table 4.1 Coagulation results of latex mixed with different grades and quantities of carbon black

Grade of CB	Quantities of CB (phr)			
	20	30	40	50
N220	X	X	X	X
N330	O	O	O	O
N550	X	O	O	O
N660	O	O	O	O

Note: O = completed coagulation

X = no or not completed coagulation

From Table 4.1, it was clearly seen that most CBs resulted in successful coagulation of the CB/latex mixture. Only some types of CBs did not induce the coagulation. Complete shear-induced coagulation was obtained from NR latex mixed with N330 and N660 at 20, 30, 40, and 50 phr by the lab high speed intensive mixer at 2,800 rpm for 3 minutes. The coagulation of the NR latex mixed with N220 was not achieved. In case of 20 phr of N550, the remaining of latex was found at the end of shearing process. It was probably because the shear force was not high enough to induce the coagulation. It should be noted here that the coagulation of unfilled-CB NR latex could not be achieved by this machine parameters (2,800 rpm for 3 minutes) because the shearing time was under Mechanical Stability Time of this lot of latex (MST of this lot of latex is 1,076 second as in Appendix A). Therefore filling the latex with certain CB in fact helped induce the latex coagulation by shear.

Therefore only N330 and N550 CB grades were targeted for further experiments. The mechanical testing of NR/N660 was not carried out due to non-homogeneous of NR/CB vulcanized compound. The finished product therefore contained many defect points that were caused by poorly dispersed N660.

4.1.1 Distribution of CB in NR matrix

The NR/CB compounds from the shear-induced coagulation step were passed through a two-roll mill in order to pack the puffy solid to dense flat sheets for further analysis. The fracture surface of NR/CB compounds were analyzed by SEM (Figure 4.1). White spots representing the CB particles were dispersed in the rubber matrix (black-toned color). Some area are undispersed, showing as agglomerates in Figure 4.1a and aggregates in b and c. Similar results were observed for N550, the CB particles were poorly dispersed with some aggregate in rubber matrix as shown in Figure 4.2a-c. Shear-induced coagulation process could coagulate NR latex with CB slurry but CB was not well dispersed in the NR matrix in this step.

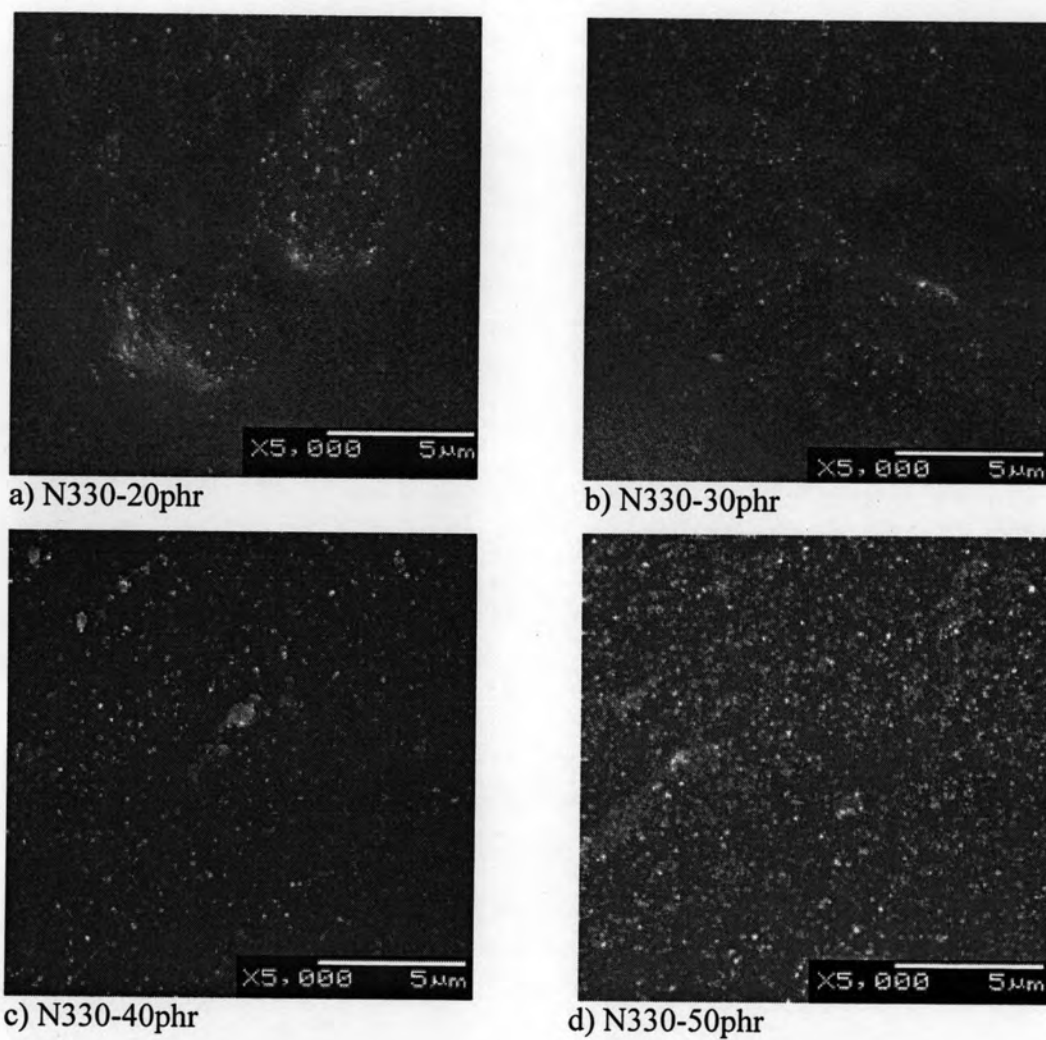


Figure 4.1 SEM micrographs of NR/N330 compound obtained from shear-induced coagulation after passing through the two-roll mill 10 times

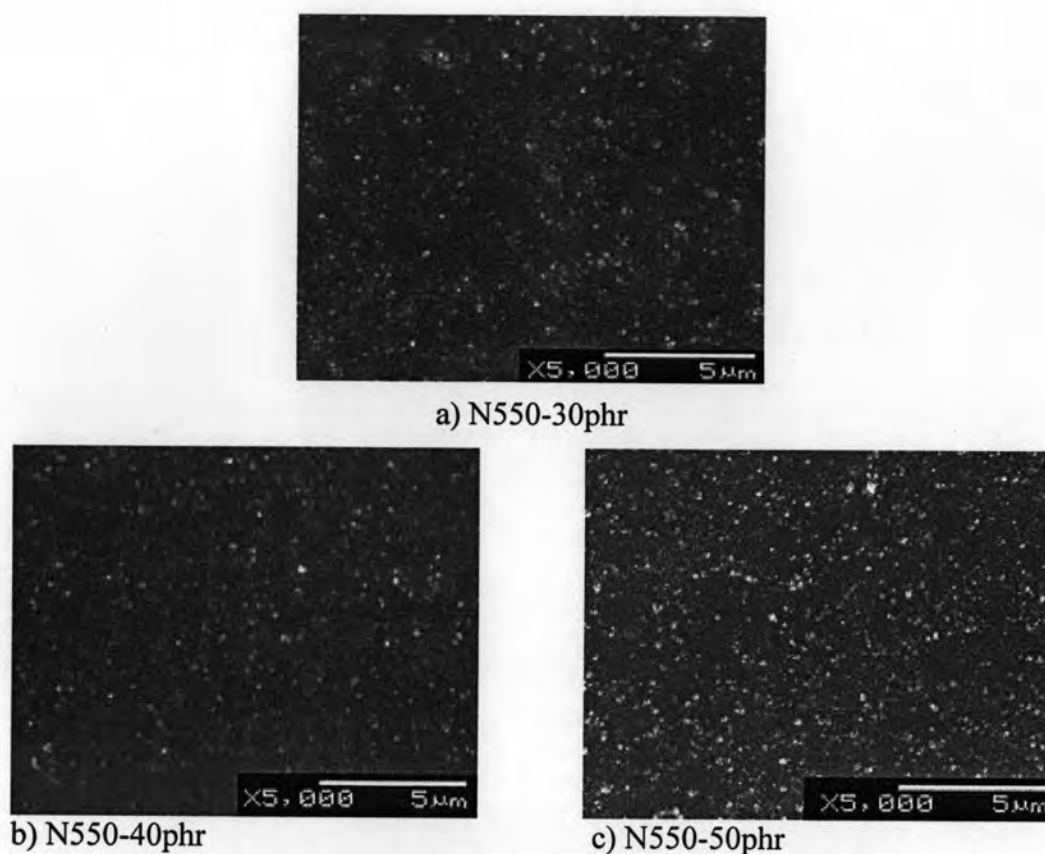


Figure 4.2 SEM micrographs of NR/N550 compound obtained from shear-induced coagulation after passing through the two-roll mill 10 times

4.1.2 Mooney Viscosity

The data in Figure 4.3 showed the viscosity increasing when CB content increased for both CB grades; N330 and N550, and both preparation methods; shear-induced coagulation and conventional mixing from solid rubber. Considering the same content of CB, the viscosity of the composite was not significantly different using the same method. These implied that the structure and particle size of CB did not affect directly the viscosity of the composites. Comparing between NR/CB from the latex and solid sheet having the same CB grade and content, the composite from solid NR possessed higher viscosity than the one from latex. It was possible that the latex slightly degraded by the shear force applied during the coagulation process, leading the reduction of viscosity. Analysis of the latex molecular weight was however not performed. It should be emphasized here that the Mooney viscosity of NR/CB composite from shear-

induced coagulation was quite low. This therefore can benefit the fabrication process.

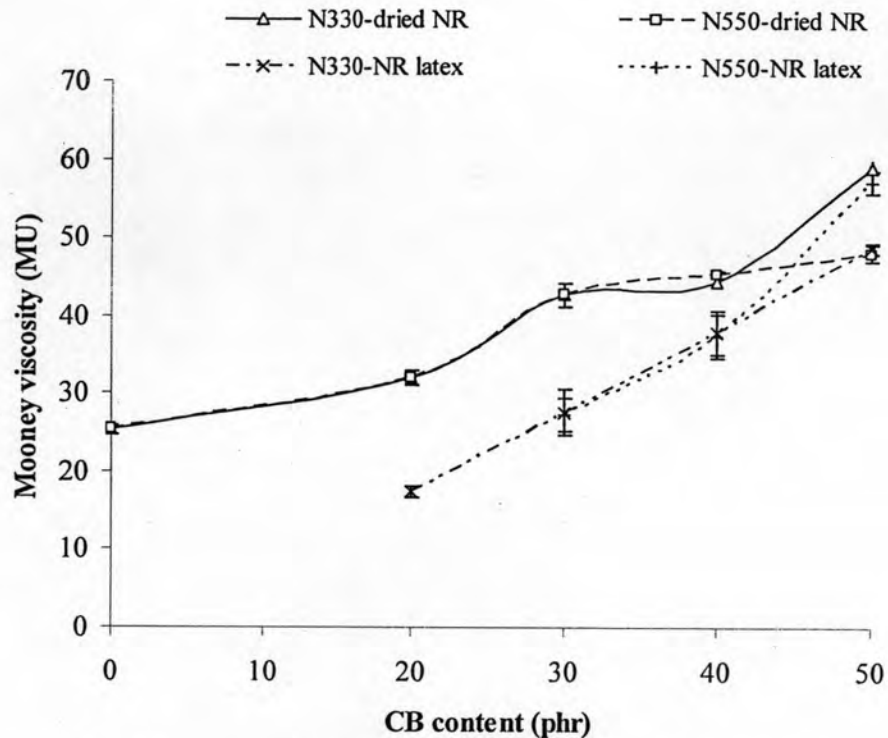


Figure 4.3 Mooney Viscosity; ML1+4(100°C) of NR/CB composites before vulcanization

4.2 Effect of mill-mixed shear on CB distribution in NR matrix

As mentioned earlier, CB particles in the NR/N330 compound from shear-induced coagulation were poorly dispersed in the rubber matrix (Figure 4.1). It was found that after this compound was mixed with curing chemicals by the two-roll mill, better dispersion of the CB was obtained (Figure 4.4). This observation suggested that the shear force alone from high speed mixer process was not able to increase the dispersion of CB in the N330 composite. Passing the composites through the two-roll mill 10 times only packed the puffy NR/CB composites closely but did not improve the CB dispersion. Comparing CB-N330 dispersion in the composites between the composites from solid NR and shear-induced coagulation in Figure 4.4 (a to d) and (e to h), both composites had the same CB distribution and no significant difference was observed among them.

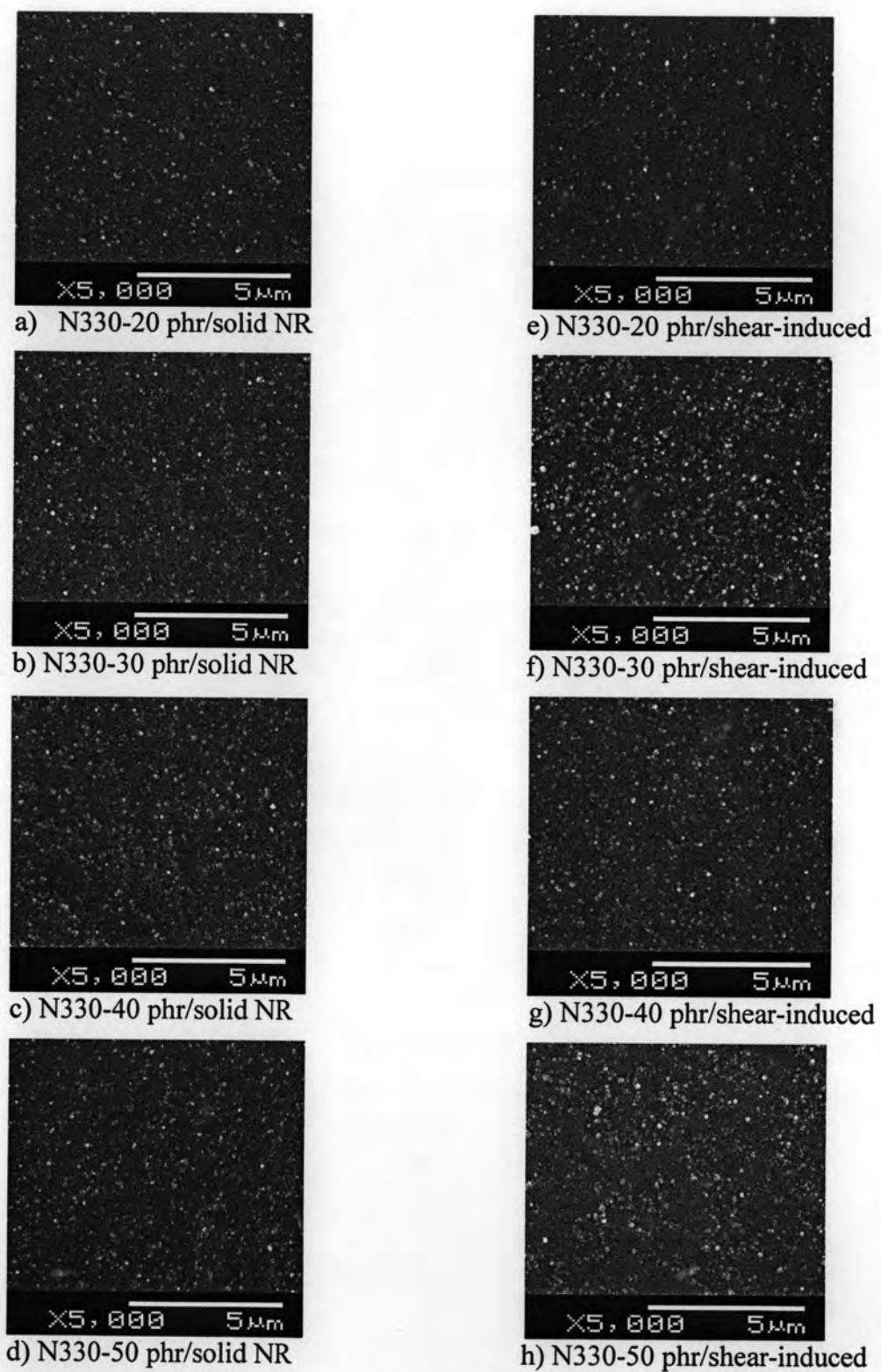
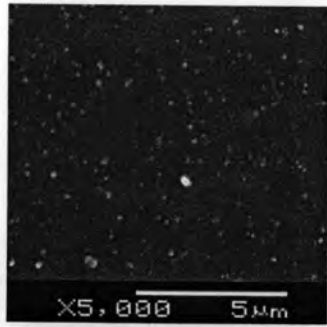


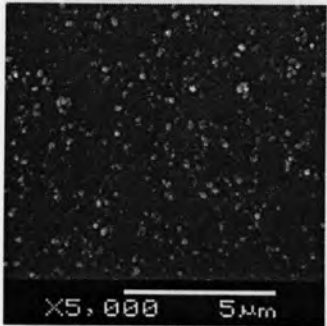
Figure 4.4 SEM micrographs of vulcanized NR/N330 composites from solid NR (a-d), and from shear-induced coagulation (e-h)

Similar situation was also found for the NR/CB-N550 vulcanizates (Figure 4.5 a-g). In the case of NR/CB-N550 compound from shear-induced coagulation CB-N550 was poorly dispersed in the NR matrix as shown in Figure 4.2 a-c and better dispersed was obtained after mixing with chemicals by the two-roll mill as shown in Figure 4.5 e-g. Comparing CB-N550 dispersion in the composites between the composites from solid NR (Figure 4.5 a-d) and shear-induced coagulation (Figure 4.5 e-g), both composites had the same CB distribution and no significant difference was observed among them. All data in Figure 4.1 and 4.2 show very poor CB dispersion but Figure 4.4 and 4.5 show good CB dispersion. Because the influence of shear force from passing through two-roll mill only help packing puffy NR/CB closely, but was not strong enough to disperse the carbon black. Therefore, large aggregate was still found. On the other hand, the influence of shear force during mixing with chemicals was high enough to improve filler dispersion in the rubber matrix. The high shear force can loosen the secondary structure (agglomerate) or large aggregate to primary structure as small aggregate of CB. The applied shear force could reduce the size of CB agglomerate by breaking down into aggregates and improve the CB dispersion in matrix, hence, the surface area of CB increased. In addition, the extent of chemical interaction between functional groups on carbon black surface and free radicals on NR molecules increased with increase in mixing time [17].

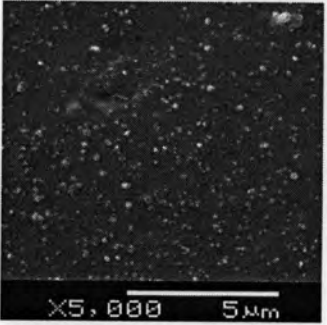
Moreover, the time period of mixing with chemicals of NR/CB compound from shear-induced coagulation was shorter than that from the solid NR. In the first step, NR/CB compound from shear-induced coagulation spent 2 minutes to get homogeneous NR/CB compound on the roll, but the solid NR required 2 minutes for mastication and 3-5 minutes to fill and disperse the carbon black in the rubber. This indicated that the incorporation of CB in NR matrix of the shear-induced coagulated NR/CB compound was rather easier than that of solid NR. The mixing time was reduced from 11-13 minutes to 8 minutes in mixing step.



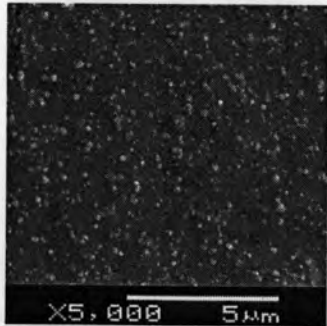
a) N550-20 phr/solid NR



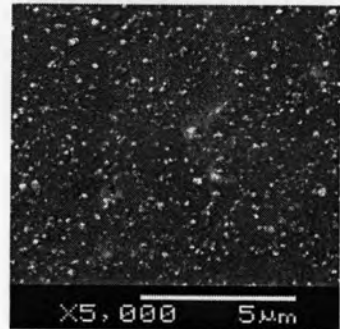
b) N550-30 phr/solid NR



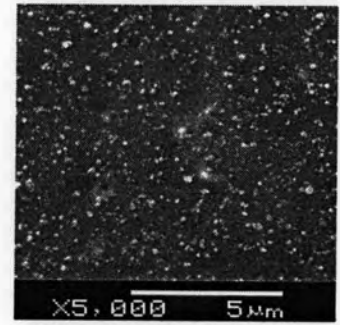
c) N550-40 phr/solid NR



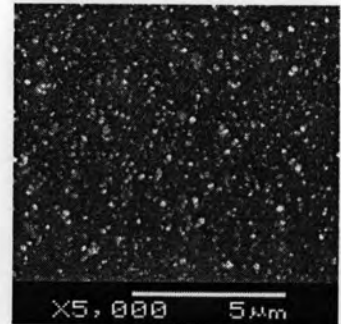
d) N550-50 phr/solid NR



e) N550-30 phr/shear-induced



f) N550-40 phr/shear-induced



g) N550-50 phr/shear-induced

Figure 4.5-1 SEM micrographs of NR/N550 composites from solid NR (a-d), and from shear-induced coagulation (e-g) at 5,000x

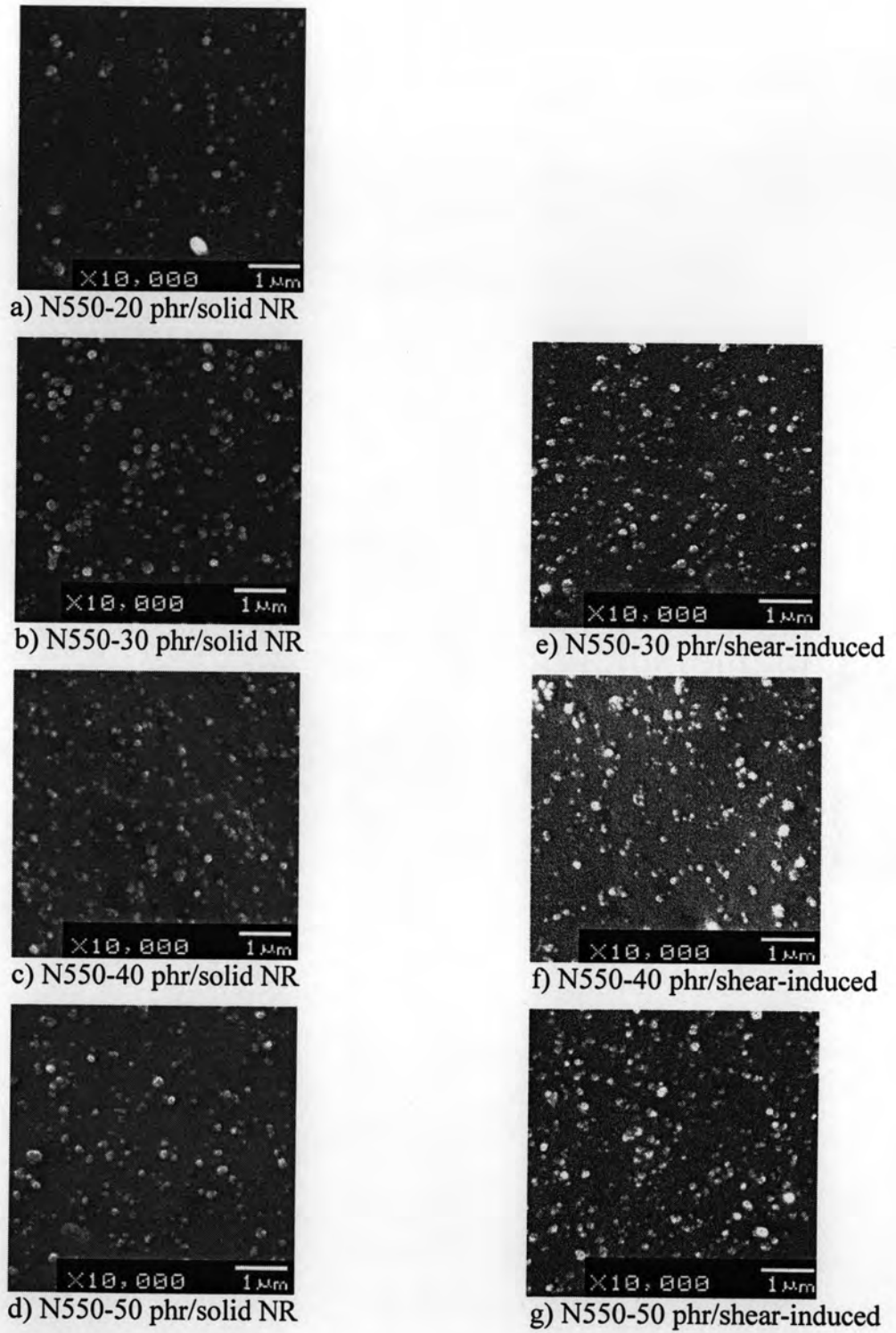


Figure 4.5-2 SEM micrographs of NR/N550 composites from solid NR (a-d), and from shear-induced coagulation (e-g) at 10,000x

4.3 Curing of NR/CB composites

Cure time (TS) and scorch time (TC₉₀) were investigated as major cure characteristics which were obtained from the cure curves of each composite. The influence of grade and quantity of CB on cure characteristics of NR/CB composites performed at 155°C are shown in Table 4.2.

Table 4.2 Curing characteristic of NR/CB compound before vulcanization

Entry	Sample	phr	ML (kgf-cm)	MH (kgf-cm)	TS2 (min)	TC90 (min)
0	Unfilled-solid NR	0	2.25	9.20	4:05	5:15
1	N330-solid NR	20	3.69	11.52	3:19	4:44
2		30	4.17	13.11	2:58	4:26
3		40	4.79	15.47	2:36	4:26
4		50	5.54	17.72	2:26	4:11
5	N330-NR latex	20	2.85	10.33	2:39	3:58
6		30	3.23	12.12	2:18	3:47
7		40	4.23	13.20	2:13	3:35
8		50	4.23	15.25	1:54	3:40
9	N550-solid NR	20	4.00	10.77	3:42	4:46
10		30	4.57	12.10	3:15	4:28
11		40	5.18	14.87	2:57	4:22
12		50	5.15	16.63	2:39	4:15
13	N550-NR latex	20	-	-	-	-
14		30	3.43	11.17	2:25	3:38
15		40	3.54	12.29	2:05	3:16
16		50	4.48	14.79	1:55	3:16

ML : Minimum torque

MH : Maximum torque

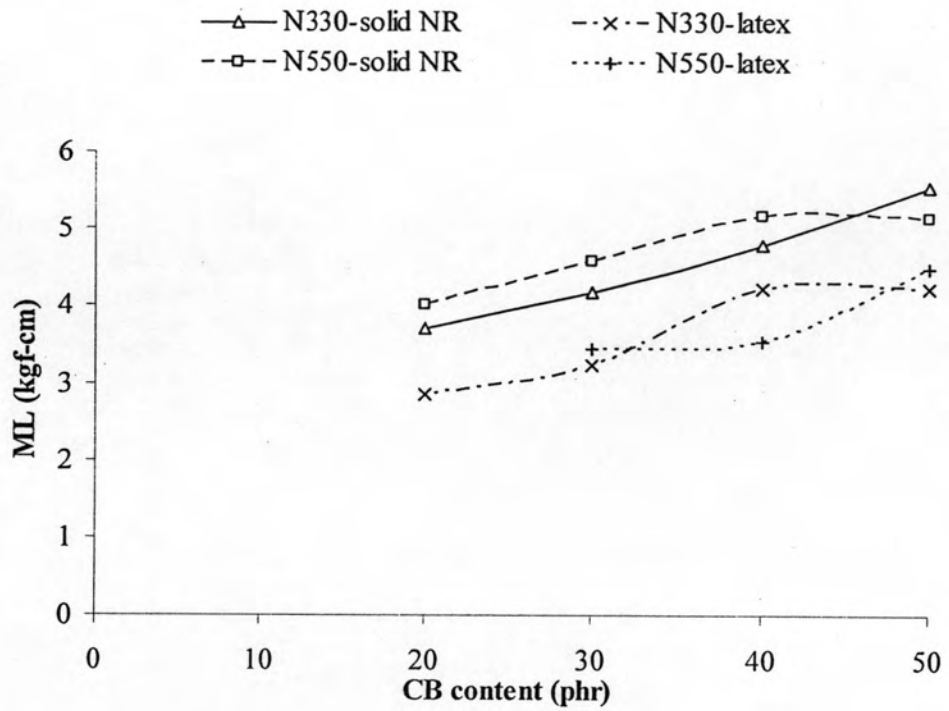


Figure 4.6-a Changes in ML as a function of CB content in NR/CB

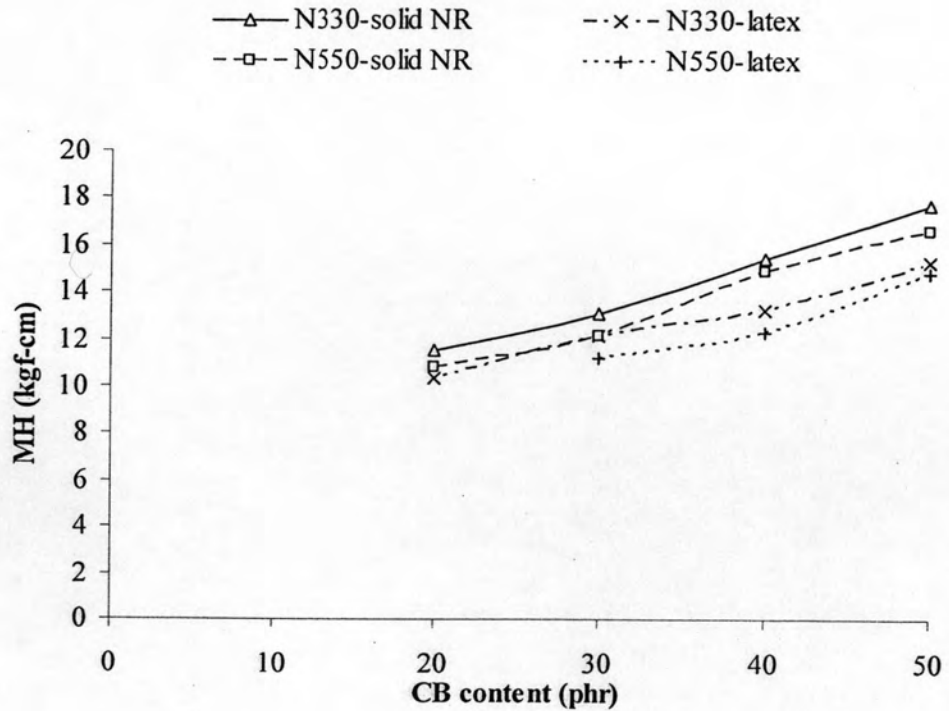


Figure 4.6-b Changes in MH as a function of CB content in NR/CB

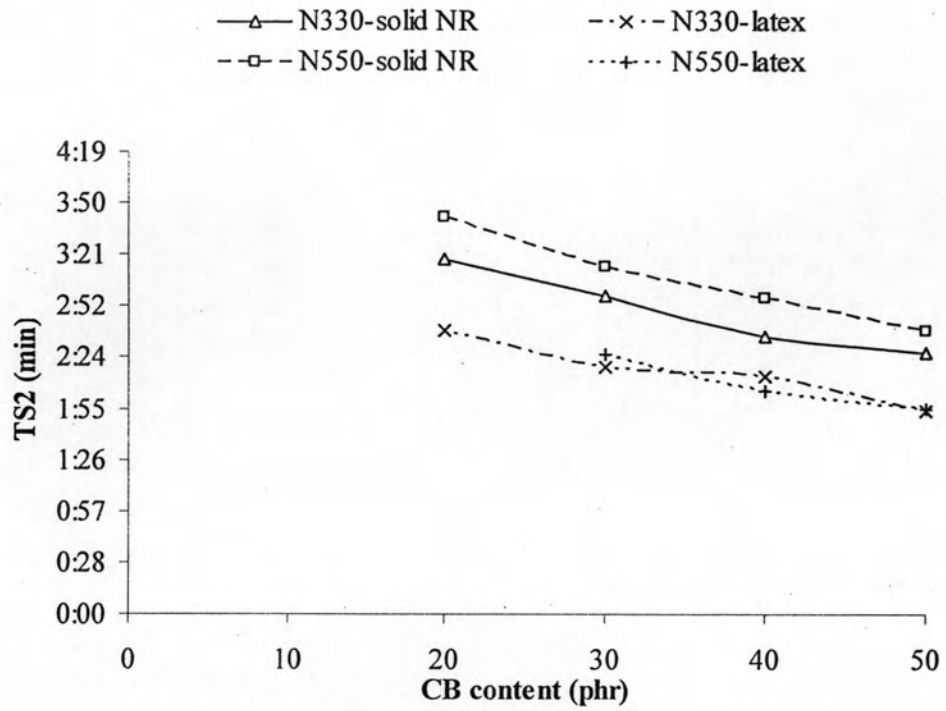


Figure 4.6-c Changes in TS2 as a function of CB content in NR/CB

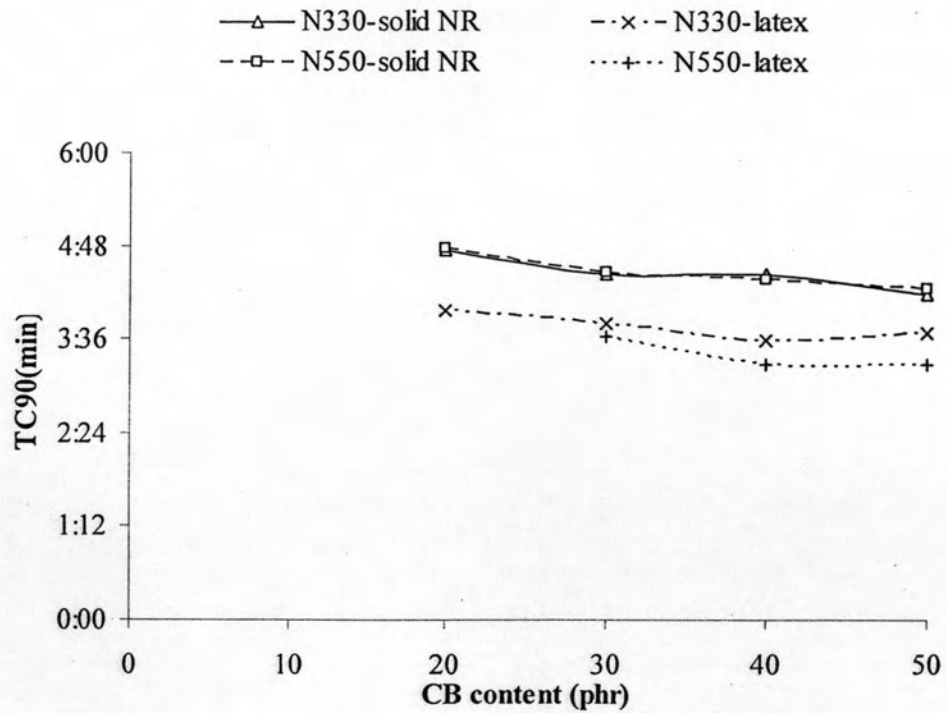


Figure 4.6-d Changes in TC90 as a function of CB content in NR/CB

When comparing the scorch and cure times of the composites within the same sample group (*entry 1-4, 5-8, 9-12 and 14-16*) in Table 4.2, it was found that increasing CB content from 20 to 50 phr led to a reduction of the scorch and cure time. The maximum torque was however increased with increasing the CB content. Comparing between NR/CB compound from solid NR and NR latex (*entry 1-4 and 9-12 VS 5-8 and 14-16*), the compound from NR latex had shorter scorch and cure time than those of the one from solid sheet. The unfilled compound (*entry 0*) got the longest scorch and cure time among all composites. Increasing CB content in the compounds led to an increase in the maximum torque (MH) but a reduction in scorch and cure time. The high torque was caused by higher friction occurring between CB particles and plate.

4.4 Specific gravity of compound

Specific gravity (SG) of each compound can be determined experimentally and calculated based on the formulation of compound so called 'SG from theory' (see appendix C, Table c-1). The two values can represent the percentage of components in the compound in formulation, both in materials and quantities. All SGs of the NR/CB vulcanizates are showed in Table 4.3. From the result, SGs from the experiment were lower than the theory. The quantities of CB in the vulcanizates were calculated from SG (experiment) as shown in Table 4.4.

Table 4.3 Specific gravity from the experiment VS theory

Entry	phr	SG (Theory)	SG (Experiment)			
			N330-solid	N330-latex	N550-solid	N550-latex
0	0	0.9533	0.9530	-	0.9529	-
1	20	1.0296	1.0261	1.0045	1.0215	-
2	30	1.0628	1.0532	1.0432	1.0533	1.0411
3	40	1.0932	1.0814	1.0722	1.0810	1.0735
4	50	1.1213	1.1105	1.1047	1.1095	1.1032

Table 4.4 The CB content in the composite

Entry	CB content Theory (phr)	CB content from experiment (phr)			
		N330-solid	N330-latex	N550-solid	N550-latex
1	20	20	13	18	-
2	30	27	24	27	24
3	40	36	33	36	33
4	50	46	44	46	44

The CB contents of NR/CB composite obtained from mixing the solid NR with CB were lower than the feed amount probably because some CB was lost into the air during the mixing process. In case of the shear-induced composite, the CB contents were also lower than the feed amount, and also slightly lower than the conventional composites. Loss of CB might occur during the shearing step where some CB could fall off or stick to the mixer during the high speed mixing. The reduced CB content would probably affect reinforce efficiency.

4.5 Mechanical testing of NR/CB vulcanizates

The mechanical properties of NR/CB vulcanizates such as hardness, tensile strength, modulus at 300% elongation (M300), elongation at break and tear strength, are shown in Figure 4.7-a to 4.6-e. The CB content of 0 phr meant the gum vulcanizate.

All mechanical properties of NR/CB vulcanizates were higher than those of gum vulcanizes (without CB) except the elongation which is reversed from other properties. Increasing the quantity of CB raised mechanical properties to higher value such as hardness, tensile strength, tensile modulus 300% elongation and tear strength, but the tensile strength and tear resistant showed highest values at 30 and 40 phr of CB content, respectively. The hardness of NR/CB vulcanizates having the same CB quantities from shear-induced coagulation was lower than that obtained from the solid NR. It was possibly due to the fact that the CB content in shear-induced vulcanizates was lower than the others as shown in the Table 4.4.

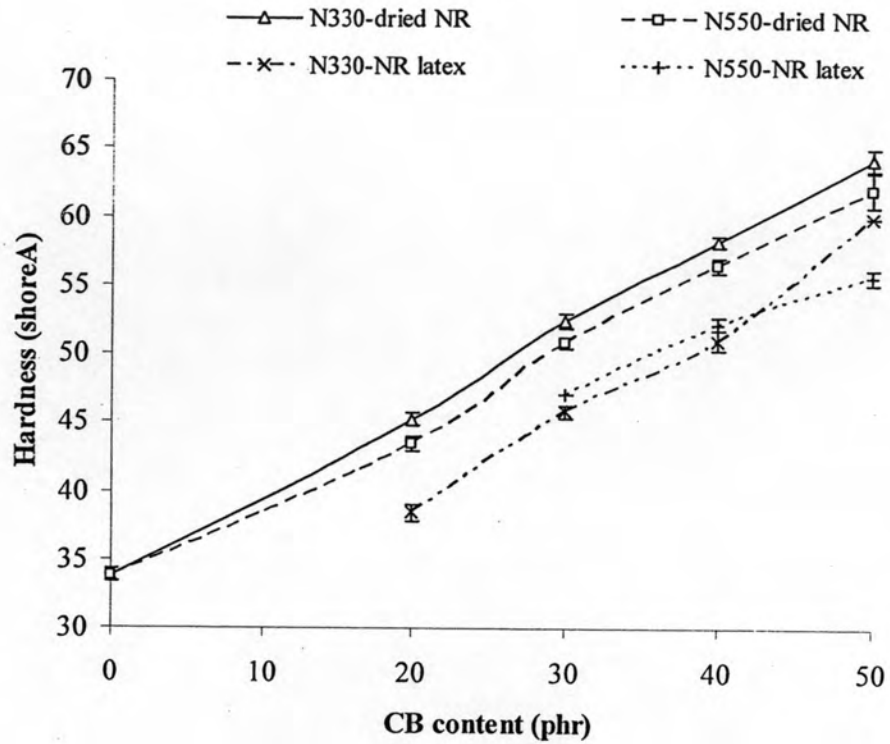


Figure 4.7-a Changes in hardness as a function of CB content in NR/CB vulcanizates.

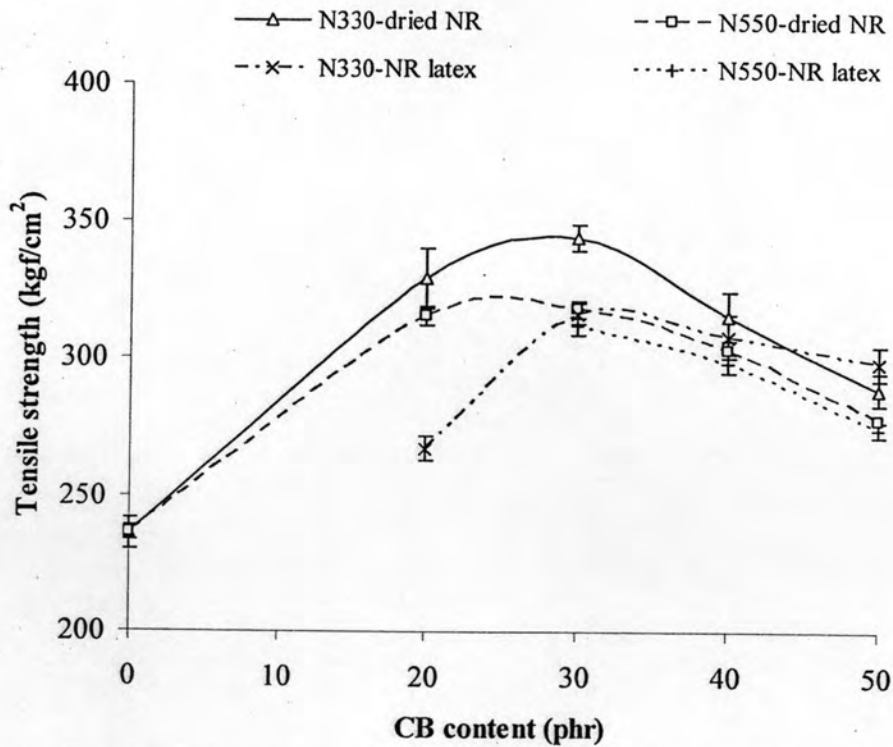


Figure 4.7-b Changes in tensile strength as a function of CB content in NR/CB vulcanizates.

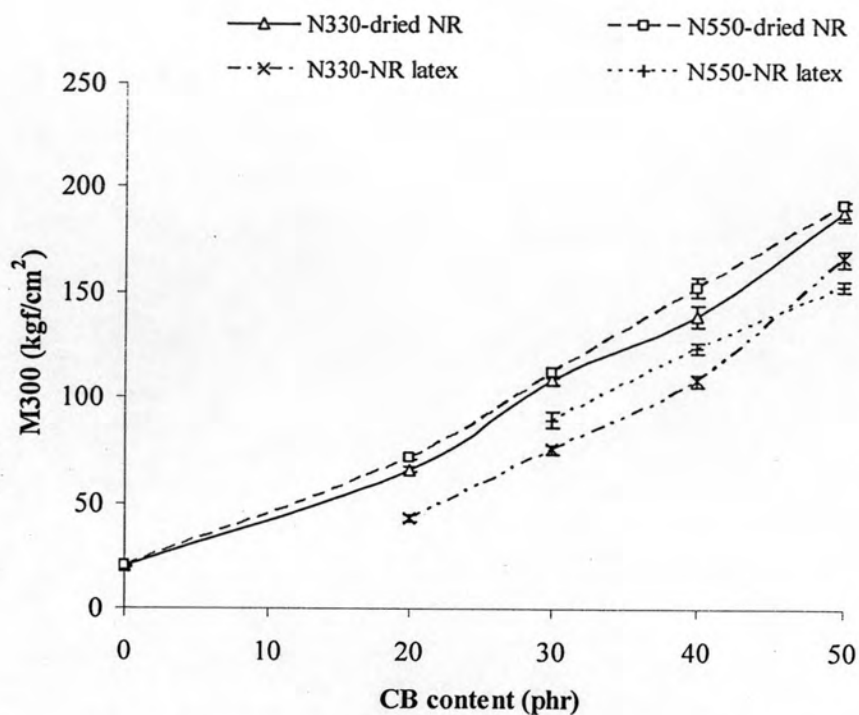


Figure 4.7-c Changes in M300 as a function of CB content in NR/CB vulcanizates.

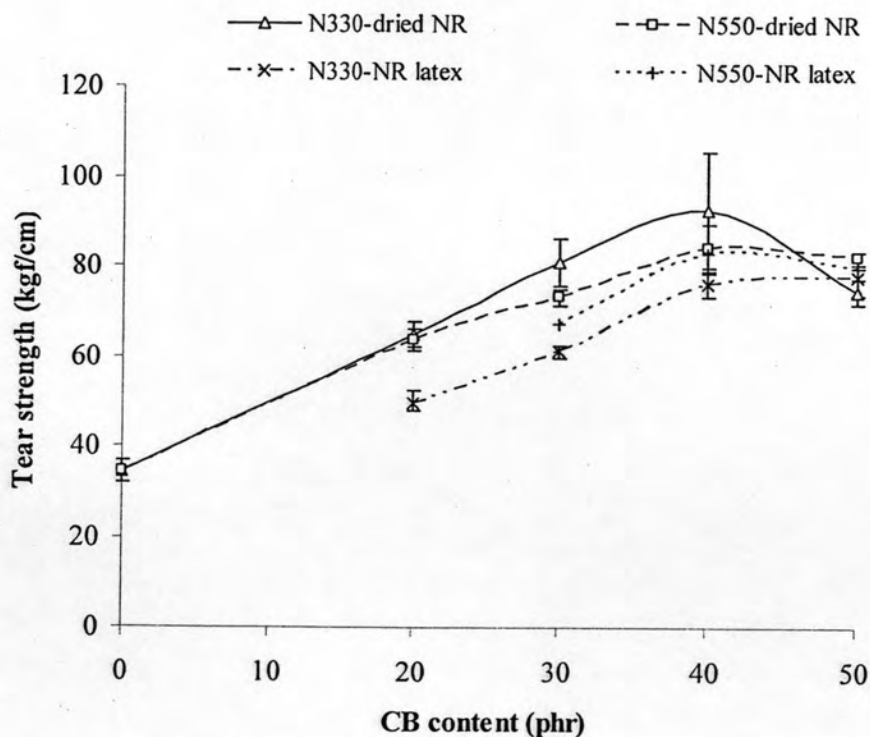


Figure 4.7-d Changes in tear strength as a function of CB content in NR/CB vulcanizates.

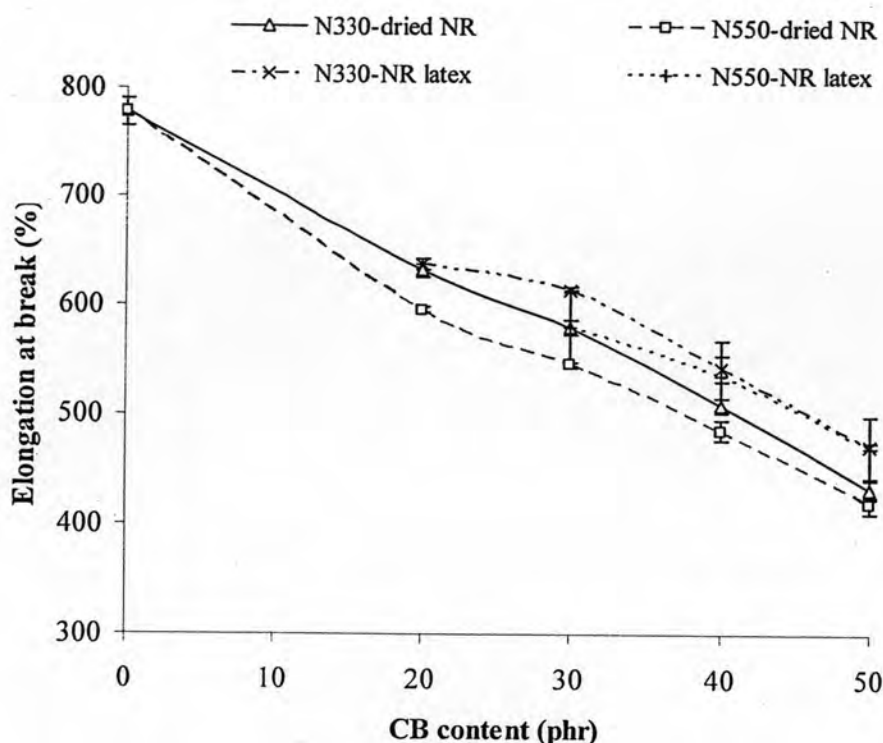


Figure 4.7-e Changes in elongation at break as a function of CB content in NR/CB vulcanizates.

NR/CB-N550 vulcanizates had slightly higher hardness than NR/CB-N330 did, due to the higher structure of N550. The highest tensile strength of all composite is obtained from the vulcanizate having 30 phr of CB. NR/CB-N330 vulcanizates had slightly higher value than NR/CB-N550 due to the lower structure of N330. Tensile strength of NR/CB-N330 and N550 vulcanizates from shear-induced coagulation were close to those from the solid NR, although their CB contents were somewhat lower.

The modulus at 300% elongation increased when the CB content was increased. The modulus of the NR/CB vulcanizates obtained from solid NR was higher than the shear-induced samples for both type of carbon black; N330 and N550. This was probably due to the higher CB content in the samples from solid NR. Increase CB quantities in the vulcanizates caused the elongation at break to decrease. The elongations at break of the shear-induced NR/CB vulcanizates were slightly higher than those of the ones obtained from solid rubber. It can be simply explained by the lower CB content in the shear-induced vulcanizates.